An investigation into the temporal and spatial trends of contaminants in Mangrove Lagoon, St. Thomas East End Reserves (STEER), U.S. Virgin Islands

P. Owen Clower

t-test was used to analyze the concentrations of contaminants between mangrove and lagoon sediment. A Wilcoxon's-signed rank test was used if assumptions of a t-test were not met. Concentrations at potentially toxic levels in Mangrove Lagoon were assessed by comparing contaminant concentrations to stated National Oceanic & Atmospheric Administration Sediment Quality Guidelines Effects Range-low (ERL) and Effects Range-Median (ERM) values for each contaminant. Contaminants in Mangrove Lagoon currently exceed toxic concentrations for most samples. Across the 38 samples taken in 2018, 31 of them exceeded at least one ERL threshold and 16 samples exceeded at least two ERL thresholds. ERL thresholds were exceeded for copper (29/38), arsenic (14/38), zinc (6/38), mercury (2/38), and silver (2/38); zinc recorded one sample above the ERM (M15). Most contaminant levels did not significantly differ between mangrove and lagoon samples. Only, aluminum ($p=0.0072$), cadmium ($p=0.0014$), silver ($p=0.0288$), nickel ($p=0.0012$), and iron ($p=0.0160$) had greater concentrations in lagoon sediment, while antimony ($p=0.0002$) had a greater concentration in mangrove sediments. Hurricanes Irma and Maria did not seem to impact contaminants levels in Mangrove Lagoon. Only selenium ($p=0.016$), mercury ($p=0.0416$), chromium ($p=0.0312$), silicon ($p=0.0063$), and TBT ($p=0.0430$) had significantly higher concentrations in 2010-2011, compared to 2018. Together, these results show sustained contamination of Mangrove Lagoon, but that conditions are improving as contaminant concentrations that exceeded ERL thresholds were less than historical values for re-sampled sites. Further, mangroves in this system may not be intercepting pollutants which may be for a variety of reasons including, the long history of historical pollution, and the increase in dead and damaged mangroves after Hurricanes Irma and Maria. Action, such as following the 2013 STEER Management Plan, needs to be taken to curb continued contaminant input into this important marine protected area.

An investigation into the temporal and spatial trends of contaminants in Mangrove Lagoon, St. Thomas East End Reserves (STEER), U.S. Virgin Islands

by
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CONTRIBUTION OF AUTHORS

Dr. Kristin Wilson Grimes acquired funding, conceived the project, and assisted in field work and editing.

Dr. Ian Hartwell assisted in shaping the project, provided background knowledge and editing.

Dr. Marilyn Brandt assisted in editing and statistics.

Sydney Nick assisted in developing the project as well as field work and editing.

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Chapter 1: Introduction:

Mangrove Importance:

Mangrove ecosystems are important as they provide many ecosystem services including: (1) protection to coastal communities against natural disasters such as tropical storms and tsunamis by dampening wind and wave energy (Kathiresan & Rajendran 2005; Alongi 2008; Das and Vincent 2009), (2) prevention of erosion by stabilizing sediments and the shoreline (Goforth 1980, Addo et al. 2011), (3) nursery habitats for coral reef fish (Nagelkerken et al. 2001, Nagelkerken et al. 2000; Mumby et al. 2004), and habitat for other organisms (Nagelkerken et al. 2008), (4) sinks for large amounts of carbon, particularly below ground (Donato et al. 2011; Jardine and Siikama¨ki 2014), and (5) interception of land-based sources of contaminants before they move into nearshore waters (Machado et al. 2002, Clark et al. 1997). The role mangroves play in the interception of contaminants is especially relevant to this study which examines contaminant levels in Mangrove Lagoon which is located in the western-most portion of the St. Thomas East End Reserves (STEER), a marine protected area (Figure 1).

Contaminant Overview:

This study measured a variety of potential contaminants in Mangrove Lagoon and the adjacent mangrove system. Specifically, this study measured five different contaminant classes. *Polycyclic aromatic hydrocarbons* (PAHs), are toxic chemicals that are shown to bioaccumulate within organisms (Pait et al. 2016, Nudi et al. 2006) causing detrimental effects including cancer and have the potential to limit growth of mangroves (Pi et al. 2016). They have also been shown to cause an iron plaque to form on roots with long-term exposure to waterlogged soil containing PAHs which can lead to root damage or mortality (Pi et al. 2016). PAHs are associated with the use and burning of fossil fuels such as oil, gas, and other organic materials (Pait et al. 2016). Some *trace and heavy elements* are essential micronutrients; however, many can be toxic at low concentrations (Pait et al. 2016) and have been shown to negatively affect the community structure of organisms such as gastropods (Amin et al. 2009). Concentrations of metals such as chromium, nickel, copper and arsenic over the National Oceanic & Atmospheric Administration's (NOAA's) Effects Range Low (ERL) threshold can cause potentially negative biological effects to organisms living in mangrove sediments (Islam et al. 2017). Metals can also cause long-term damage to plants because they can't be

degraded biologically, so when they are taken up directly into plant tissues the interaction between the plant tissue and metals causes toxic effects (Defew et al. 2005). Another pollutant, *dichlorodiphenyltrichloroethane (DDT)*, has been shown to interfere with the endocrine system of organisms (Pait et al. 2016) and may be most infamous for the harm it caused the American Eagle (*Haliaeetus leucocephalus*) and other piscivorous bird populations in the 1960s. Next, *tributyltin (TBT)* has been found to have toxic effects in some species at as little as 1 ng per liter of water (Bray and Langston 2006). TBT is unique as it degrades to dibutyltin, then monobutyltin, and then inorganic tin (Pait et al. 2016). The half-life of TBT to dibutyltin has been shown in experiments to be days and it takes another month to degrade to monobutyltin (Batley 1996); however, in anoxic sediments TBT degradation can take years (Batley 1996). Any levels of TBT found in Mangrove Lagoon could reflect current or historical contamination pathways. Lastly, *polychlorinated biphenyls (PCBs)* are toxic in concentrations above 22.7 ng/g and can bioaccumulate in mangroves (Alegria et al. 2016). Understanding how mangroves can prevent contaminant transport into Mangrove Lagoon habitat is important for continued management of STEER and its associated watersheds.

Mangroves Buffer Contaminants:

As mentioned previously, mangroves have been shown to intercept a wide variety of contaminants, including those that were measured in this study. One reason that mangroves are known to intercept contaminants is because they trap and accumulate fine sediments (clay and silt). Fine sediments are known to absorb contaminants and attract metals because of their high surface area and the charge structure on the surface of clay particles (Tam and Wong 2000). For example, Saenger and McConchie (2004) found that fine-grained mangrove sediments were highly efficient sinks of zinc, copper, and lead. They showed that concentrations of these metals, originating from a nearby landfill, dropped dramatically in a seaward direction due to the presence of mangroves. Similarly, mangrove sediments in Punta Mala Bay, Panama contained high levels of iron, manganese, zinc, lead, copper, nickel, chromium and cadmium, which were linked to sewage water, storm water runoff, and diffuse inputs from shipping activities (Defew et al. 2005). Working in Guanabara Bay, Brazil, Machado et al. (2002) found similar results. They evaluated the levels of mercury, zinc, and copper in mangrove sediments located adjacent to a 20-year-old landfill. Their research showed that over the past several decades, mangrove sediments in this area retained a large amount of the metal contaminants that originated from the landfill and surrounding urban sources. Machado et al. (2002) further hypothesized that this retention of contaminants led to a reduced amount of metal being transported to

Guanabara Bay waters, providing evidence that mangrove ecosystems can act as physical barriers to metal transport. This landfill receives most of the solid waste from Rio de Janeiro in Brazil, which suggests that even in high-pollutant environments, mangrove sediments can reduce contamination of adjacent nearshore, coastal waters. Finally, work by Keller et al. (2017) showed that mangrove stands between Bovoni Landfill and Mangrove Lagoon in St. Thomas, U.S. Virgin Islands, may act as a buffer and serve to slow or prevent metals and other contaminants from entering the lagoon based on measurements of contaminants in sediments and groundwater.

Contaminants in Mangrove Lagoon:

The results of Keller et al. (2017) are especially relevant because Mangrove Lagoon has several potential pollutant inputs. The Bovoni Landfill (Figure 1) is located near the western edge of Mangrove Lagoon. It serves the entire island of St. Thomas and the island of St. John and is unlined (Virgin Islands Waste Management Authority (VIWMA 2018). During its thirty years of operation, this landfill has been potentially seeping contaminated leachate into the adjacent Mangrove Lagoon (Ferguson 2013). Leachate can be a source of heavy metals that can become trapped in mangrove sediments (Clark 1998). This landfill has failed to follow U.S. Environmental Protection Agency (EPA) regulations in the past and as a result, is currently under an EPA consent decree requiring leachate interception, stormwater management, and other cleanup activities (United States of America v. Government of the U.S. Virgin Islands 2016). The extent and the exact characterization of contaminants from Bovoni is mostly unknown (Ferguson 2013); but surrounding mangroves have experienced die-offs (Ferguson 2013), presumably due, in part, to the leachate from the landfill. A second potential pathway for contaminants is Turpentine Run (Figure 1), an ephemeral waterway that drains over 60% of the Jersey Bay Watershed and discharges untreated stormwater and sewage overflows directly into Mangrove Lagoon (Ferguson 2013). Mangrove Lagoon potentially receives metals, like copper, from Turpentine Run, that drains commercial and residential waste into the east side of the lagoon (Pait et al 2014). Elevated levels of sedimentation, nutrients and bacteria have been detected in Mangrove Lagoon, especially after rain events, possibly due to an increase in water input from Turpentine Run (STEER 2011) or other overland flow, particularly in the northwestern portion of Mangrove Lagoon closest to Bovoni Road. A now abandoned area, once the location of the Nadir Wastewater Treatment Plant, located west of the horse racetrack (Figure 1) has been shown to be a historical pathway of contaminants (Nichols and Towle 1977; USEPA 1984). Decommissioned in the 1990's it was known to be overloaded, obsolete and constantly malfunctioning (Nichols and

Towle 1977). The current status of contaminant input at this location is unknown. Benner Bay (adjacent to Mangrove Lagoon; Figure 1) may be another pathway of contaminants. Pait et al. (2014) found high concentrations of TBT, including a site with a level of 298 ng Sn/g, in Benner Bay. This level was the third highest TBT level ever recorded by the NOAA National Status and Trends (NOAA NS&T) Program which is a national program that measures contaminants in coastal sediments. An additional study by Hartwell et al. (2016) found that site 16P, located close to Mangrove Lagoon in the channel between Mangrove Lagoon and Benner Bay, had new inputs of TBT (as revealed by dated geologic cores), and that the highest levels were found less than 5 cm from the surface, suggesting recent deposition (66.4 Sn/g dry weight).

A second ephemeral ghut, or stream, (Figure 1), located in the northwest portion of Mangrove Lagoon, and a dirt horse track (Figure 1) are two other potential pathways of contaminants in Mangrove Lagoon (Pait et al. 2014). The horse track is in close proximity to Turpentine Run and upon observation during field work in the summer of 2018 there was evidence of public dumping. The proximity of these potential pollution sources to Mangrove Lagoon may account for the higher concentrations of containments measured in Mangrove Lagoon, and Benner Bay, when compared to other areas of STEER (Pait et al. 2014). Moreover, other non-point source pollution such as illegal dumping, possible oil spills and debris from Bovoni Road and Highway 32 (Figure 1) may also contribute to contaminants in Mangrove Lagoon (Pait et al 2014).

Unfortunately, high pollutant levels have already been reported in Mangrove Lagoon. Pait et al. (2014), found that copper, zinc, and arsenic levels in Mangrove Lagoon were higher than the NOAA Effects Range-Low (ERL) sediment quality guidelines at several locations in Mangrove Lagoon. The ERL is meant to represent concentrations below which adverse effects rarely occur (Long 1999). ERL and Effects Range Median (ERM) thresholds express statistically-derived levels of contamination, in which toxic effects would be expected to be observed with at least a 10% (ERL) and 50% frequency (ERM). Over forty years ago, Nichols and Towle (1977) found levels of copper, zinc, and lead that exceeded present-day NOAA ERL thresholds in both mangrove and lagoon sediments, though these thresholds did not exist then. One sample, located inland from site 15 in this study (Figure 1), was actually above the ERL for three metals: copper (140 µg/g), zinc (150 µg/g), and lead (54 µg/g). This reveals that pollution within Mangrove Lagoon has been problematic and sustained for at least the last forty years.

Hurricane Effects on Mangroves and Contaminants:

The understanding of contaminants in Mangrove Lagoon was further complicated in September 2017, when two Category 5 storms, Hurricane Irma and Hurricane Maria, struck the U.S. Virgin Islands, heavily impacting the territory. The storms left St. Thomas almost completely defoliated and in a state of disrepair. Hurricanes can have a variety of negative effects on mangroves, including mortality, major physical damage, and decreases in the complexity of mangrove vegetation (Roth 1992). Roth (1992) analyzed regeneration of mangroves after Hurricane Joan, a Category 3 storm that impacted the Caribbean coast of Nicaragua in 1988. Half of the red mangroves (*Rhizophora mangle*) in the 0.15 hectare (ha) study area experienced mortality, and just over a third of all the mangroves in the study experienced mortality (Roth 1992). A study after Hurricane Wilma, a Category 3 storm that impacted the southern coast of Florida in 2005, showed that almost 1,250 ha of mangroves were destroyed in South Florida (Smith et al. 2009). Baldwin et al. (2001) showed that Hurricane Andrew changed the composition of entire mangrove stands around Cutler Canal and Mowry Canal in fringe mangrove forests adjacent to Biscayne Bay in South Florida. Cuter Canal changed from a *Rhizophora mangle*-dominated site, to a site with a mixture of three different species over a period of six years. Another Florida study showed that *R. mangle* impacted by Hurricanes Frances, a Category 2 storm, and Jeanne, a Category 3 storm, which impacted Florida in 2004, still showed reduced growth almost three years later (Feller et al. 2015). Hurricanes also have the potential to cause delayed mortality in *Rhizophora* trees; from delayed mortality of *R. mangle* twigs and small stems (Feller et al. 2005) to entire trees (Baldwin et al. 2001). *R. mangle* in Mangrove Lagoon may have long-term damage due to Hurricanes Irma and Maria that could last for many years. During sampling for this study, vast amounts of dead *R. mangle* were observed as well as numerous new seedlings.

In addition to changing tree species composition and structure, hurricanes also have the ability to mobilize large amounts of sediment (Reible et al. 2006; Mitra et al. 2009, Smith et al. 2009). In Florida, sediment deposits from Hurricane Wilma were found at a thickness of 2-8 cm and showed evidence of deposition as far as 16 km inland from the Gulf of Mexico, and in total covered an estimated 400 km^2 (Smith et al. 2009). Another study only recorded an average sediment disposition depth of 2.5 cm within 250 m inland from the Gulf of Mexico after Hurricane Wilma, which decreased to 1 cm from 450-700 m (Castañeda-Moya et al. 2010). Both studies show that

hurricanes can move large amounts of sediment. These results suggest that Hurricanes Irma and Maria could have caused large movements of sediment in Mangrove Lagoon and as a result potentially affected the distribution of contaminants due to the relationship of fine sediment to metal concentrations (Tam and Wong 2000; Pait et al. 2016).

While studies show that hurricanes can deposit large amounts of sediment and cause significant damage to mangroves, studies have been less clear on the role of hurricanes in contaminant distribution or re-distribution. Mitra et al. (2009) looked at the effects of Hurricanes Katrina and Rita, major storms that impacted Louisiana in 2005, on sedimentary contaminant dynamics in the Gulf of Mexico. Three sites, an inner shelf, mid-shelf, and a marsh site, were sampled for PAH concentrations. The marsh site was shown to have PAH concentrations that were derived from combustion sources but not from petroleum-derived PAHs that came from offshore. This was despite the site experiencing up to 3-4 meters of water inundation from Hurricane Katrina (Mitra et al. 2009). Similarly, Cobb et al. (2006), focused on lead and arsenic distributions in New Orleans, LA following Hurricane Katrina and Hurricane Rita. Their work suggested that flooding in the aftermath of Hurricane Rita neither redistributed toxic metals in some areas nor removed them. However, lead concentrations exceeded United States Environmental Protection Agency (US EPA) criteria throughout the city, but in some areas that did not experience flooding the levels of lead measured were lower than areas that did experience flooding (Cobb et al. 2006). The conflicting nature of these findings suggest that the relationship between hurricanes and contaminant concentrations is complex.

Summation:

Mangroves have the capacity to trap contaminants in their sediments (Machado et al. 2002, Clark et al. 1997). The contaminants they trap are dangerous to organisms and environments; some, are dangerous even in low concentrations. Mangroves are also damaged by hurricanes and hurricanes are known to mobilize sediment and can increase and decrease contaminant concentrations. Mangrove Lagoon currently contains elevated levels of contaminants and has several large potential sources of contaminants contributing to it. Therefore, the aim of this study was threefold: (1) to understand how Hurricanes Irma and Maria affected the concentrations of contaminants in Mangrove Lagoon in comparison to 2010-2011 levels, (2) to understand how current levels of metals and butyltins in Mangrove Lagoon and the adjacent mangrove differ, and (3) to determine potential pathways of

contaminants. This study will provide the clearest spatial distribution of contaminants in Mangrove Lagoon to-date, the only work describing how hurricanes impact sediment contaminants in the U.S. Virgin Islands, and document potential new sources of contaminants and pathways, which will assist in improved management of this marine protected area and NOAA Priority Watershed.

Hypotheses:

We hypothesized that the concentrations of contaminants measured in 2010-2011 would not differ from those measured in 2018. This was expected because of the conflicting nature of studies that show that hurricanes can increase, decrease, or cause no apparent change in concentrations of contaminants in coastal sediments. For the 2018 mangrove versus lagoon comparisons, we hypothesized that metal concentrations would be greater in mangrove sediment than lagoon sediments based on historical studies showing that mangrove prop roots hold fine sediment thereby intercepting pollutants, and also because we predicted most pollution was coming from land-based sources.

Chapter 2: Methods

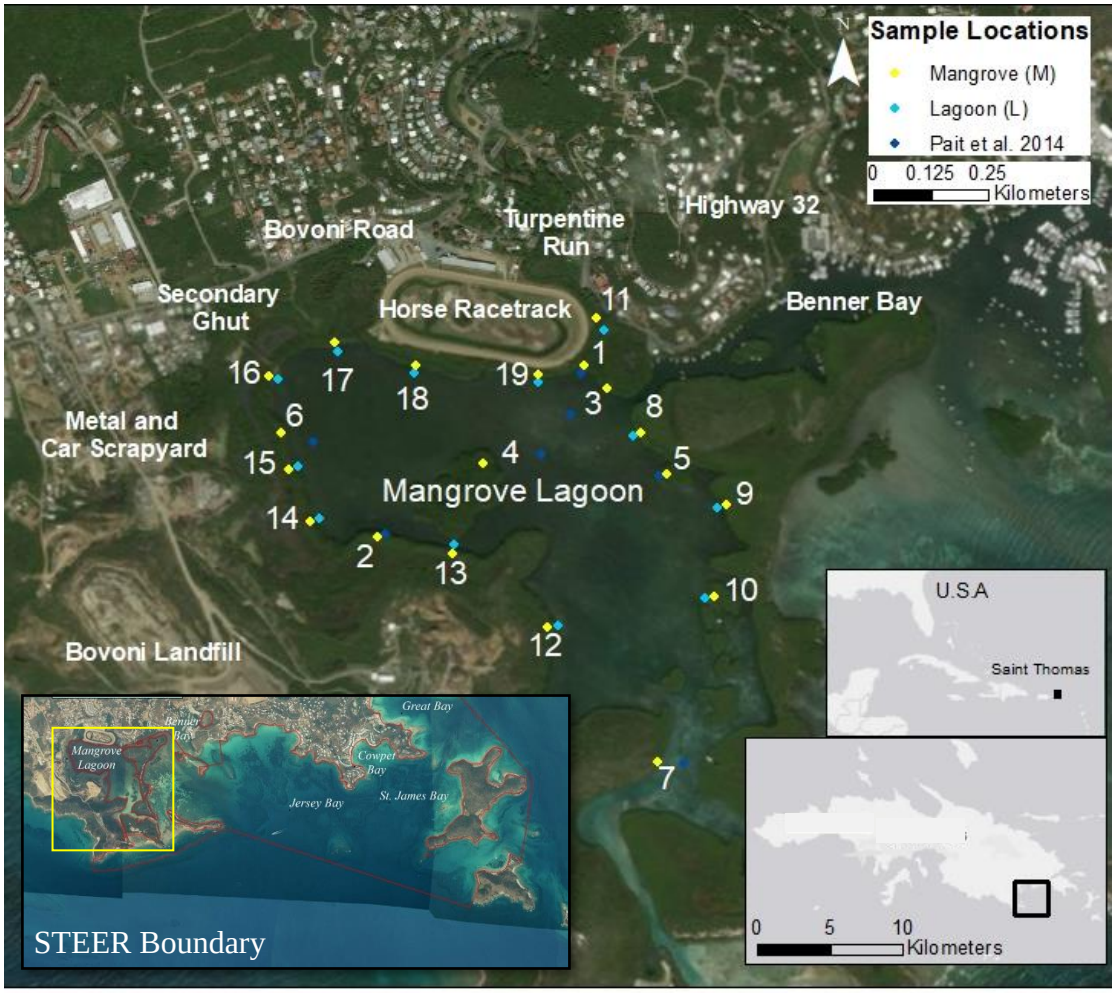

Figure 1: NOAA Coral Reef Conservation Program 2018 Mangrove Lagoon site locations. Potential sources of contaminants are shown. Dark blue points represent the seven samples that were re-sampled from Pait et al. 2014. Yellow represents mangrove samples and aqua represent lagoon samples. The inset map (reefconnect.org) to the bottom left represents the STEER boundary, with the yellow box highlighting the location of Mangrove Lagoon.

Experimental Design:

A total of thirty-eight samples were collected in Mangrove Lagoon and adjacent mangrove wetlands in July 2018 (Figure 1). Seven of the lagoon samples were re-sampled from the same locations as those in Pait et al. (2014; Figure 1). Five of those sites were chosen using a stratified random design in 2011. Two other samples were selected through targeted sampling in 2010. Pait et al. (2014) only sampled in the lagoon and did not include mangrove

locations. Thirty-one additional samples were strategically chosen to increase the understanding of the distribution of contaminants throughout Mangrove Lagoon and adjacent wetland habitats. Each lagoon sample was paired with a mangrove sample, creating 19 paired sites to allow for a comparison of mangrove and lagoon sediments. The minimum distance between mangrove sites was 50 meters and the minimum distance between lagoon sites was also 50 meters. This was to account for GIS variance and to follow National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Bioeffects Program Field Methods (Apeti et al. 2012). The minimum distance between lagoon and mangrove samples was 15 meters to create paired sites that could be compared.

Sample Collection:

Samples were collected under a permit **DFWCZM17004T** obtained from the U.S. Virgin Islands Department of Planning and Natural Resources, Division of Fish and Wildlife. Sample collection protocols followed the NOAA NS&T program with modification of the sediment collection device used.

To collect lagoon sediments, a kayak was used to reach each sample location with assistance from a handheld Global Positioning System (GPS) unit. Upon reaching the location of each lagoon sample, a YSI (Yellow Springs Instrument) ProDSS was used to collect surface temperature, dissolved oxygen (DO), salinity, and pH. Turbidity was determined using a secchi disk and depth was collected using a meter-long ruler. After collecting these data, a sediment corer was then used to collect sediment. Each core had the top 0-5 cm of sediment collected from it; this was repeated until enough sediment was collected to fill 1, certified clean (I-Chem®) 250-mL jar with 150mL of sediment and 1 Whirl-Pack® bag with at least 60 mL of sediment. If more than one sample was taken, all samples were combined into a stainless-steel bowl, homogenized using a stainless-steel mixer, and composite samples were subdivided into the I-Chem® jar and Whirl-Pack® bag. For each sediment sample, observations of texture, color, odor, and any visible benthos were recorded. An overhead photo of the undisturbed sediment and a north facing sample location photo were also taken.

Mangrove samples were collected on land at a distance of at least 15 meters away from the corresponding lagoon sample and in or adjacent to an area of live *R. mangle*. To collect each sample, a stainless-steel scoop was used to remove the top 2-3 cm of surface sediment after siphoning off any overlying water using a syringe. Like lagoon

samples, enough sediment was collected to fill 1, certified clean (I-Chem®) 250-mL jar with 150mL of sediment and 1 Whirl-Pack® bag with at least 60 mL of sediment. If more than one scoop was taken, all samples were combined into a stainless-steel bowl, homogenized using a stainless-steel mixer, and composite samples subdivided into the I-Chem® jar and Whirl-Pack® bag. For each sediment sample, observations of texture, color, odor, and any visible benthos were recorded. A photo of undisturbed sediment and a north-facing location photo were also taken.

All samples were stored on ice in the field. Upon return to the University of the Virgin Islands (UVI), jars were placed in bubble bags, laid on their sides and frozen, for storage. The Whirl-Pack® bags (used for grain size analyses) were stored in the refrigerator until shipping. Between samples all tools were rinsed with site water, followed by acetone, then distilled water. Acetone waste was placed in a separate waste bucket that was properly disposed of upon return to UVI.

Storage and Shipping Methods:

Jars were packed, in their bubble bags, into a box surrounded by insulation and extra bubble wrap to prevent shifting. Whirl-Pack® bags were placed into a Ziplock bag and then placed into a small Styrofoam cooler. Blue ice packs were used during transit to keep samples cold. Samples were sent to TDI-Brooks International, Inc. lab to be analyzed for the following contaminants: (PAHs), (PCBs), TBT, (DDT) and metals (aluminum, antimony, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silicon, silver, tin, and zinc). The full set of contaminants analyzed can be found in Supplemental Table 1. TBI-Brooks International is routinely used by NOAA's NST Program and was selected to ensure methodological consistency, reduce potential inter-lab errors, and to permit greater comparability of our study results to past data produced by the NST Program in STEER and elsewhere across the United States. Use of this lab allowed for reliable comparison between the data from 2010-2011 and 2018. For this study, trace metals and butyltins were measured across all samples. In addition, total PAH's, total PCB's, and total DDT were measured for only L1-L7 (Figure 1) to understand changes in contaminant levels from Pait et al. (2014).

Sediment Analyses:

The sixteen major and trace metals were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). A total of 55 PAHs were analyzed using gas chromatography/mass spectrometry (selected ion monitoring mode). Tributyltin (TBT) was analyzed using hexylation. A total of 59 PCBs and DDT were analyzed using SOP 1078, an internal method of TBI-Brooks International developed out of EPA SW846 & NOAA NS&T Mussel Watch (USEPA 2007a, USEPA 2007b). DDT is defined as the sum of the parent isomers (4,4´-DDT and 2,4´DDT), and the sum of the degradation products (DDMU, 2,4'-DDD, 4,4'-DDD, 2,4'-DDE, 4,4'-DDE).

Data Analysis*:*

Detection Limits

Some TBT and DDT concentrations were detected but were below the method detection limit. Due to the unreliability of these values they were treated as zeros for the purpose of data analysis. These values are represented by "<" in tables 4, 5, and 9.

Normalization of Metals

Metals that were recorded over the ERL limit for spatial comparisons were normalized to aluminum. This was done to assess samples where unusually high concentrations may indicate anthropogenic inputs (Pait et al. 2014; Hartwell et al. 2018).

NOAA Sediment Quality Guidelines

To provide context to the results of this study, data collected in Mangrove Lagoon in July 2018 were compared to data from the NST database and as previously mentioned with NOAA sediment quality guidelines. Metals that were over the ERL threshold and TBT concentrations were compared to national NST data and with Puerto Rico data. The NST median, average, and 85th % percentile were used to provide national and local context for copper, arsenic, zinc, mercury, silver, and TBT. The 85th% percentile is commonly used with NST data, as contaminants are log-normally distributed, and this percentile roughly represents the 95% confidence interval.

Grain Size and Water Quality

A paired t-test was used to compare the mean concentrations of all grain sizes (clay, silt, sand, and gravel), both temporally (2010-2011 vs. 2018) and spatially (mangrove vs. lagoon). If grain sizes did not meet assumptions of parametric tests even with transformation, a Wilcoxen's signed ranks test was used to test the median difference. For water quality the maximum, minimum, and average values for water depth, salinity, and temperature were calculated using the 19 lagoon samples.

Temporal Comparisons of Contaminants

For the purpose of this paper, contaminants that were measured from the two samples collected in 2010 with targeted sampling and the five samples collected in 2011 with statified random sampling (Pait et al. 2014) were compared as one unit to contaminants measured in 2018. The minimum, maximum, median, mean, and the number of samples over ERL values were determined based on the seven samples from Pait et al. (2014) and the re-sampled values from 2018. Paired t-tests were used to compare the mean concentrations of each contaminant between 2010-2011 and 2018. If data did not not meet assumptions of parametric tests even with transformation, a Wilcoxen's signed ranks test was used to test the median difference between 2010-2011 and 2018 sediments. This test was applied to silver, seleinum, and DDT concentrations. Lastly, a non-metric multidimensional scaling (NMDS) ordination of all contaminant concentrations was created using a Bray-Curtis dissimilarity matrix, and an analysis of similarity (ANOSIM) was applied to test for differences between time points for the entire suite of contaminants.

Spatial Comparisons of Contaminants

The minimum, maximum, median, mean, and the number of samples over ERL values were determined for mangrove and lagoon contaminants seperately. To test the ability of mangroves to intercept pollutants, paired t-tests were used to test the difference between mangrove and lagoon site pairs for each contaminant. If data did not meet assumptions for parametric tests, a one-sample Wilcoxen's signed ranks test was used to test the median difference between mangrove and lagoon sediments for each pair of samples. Except for chromium, copper, lead, aluminum and silicon, all other contaminants were analyzed with a one-sample Wilcoxen's signed ranks test. A Spearman Rho correlation test was performed to determine whether relationships existed between aluminum, fine sediment, and sand, with any metal that crossed an ERL threshold. Lastly, a NMDS ordination of the full suite of contaminants for each sample was created using a Bray-Curtis dissimilarity matrix, and an analysis of similarity (ANOSIM) test was

applied to test for differences in the suite of contaminants between mangrove and lagoon samples. All statistical analyses were performed in R-Studio (R.Core Team 3.4.3).

Chapter 3: Results

Water Quality

The average water depth at lagoon samples was 0.95 meters (m). The deepest water depth was 1.4 m at L7, while the shallowest water depth was 0.23 m at L16. The average salinity of lagoon samples was 35.92 PSU. The greatest salinity was 36.60 PSU at L15, while the lowest salinity was 28.19 PSU at L11. L11 is located in Turpentine Run. The average water temperature at lagoon samples was 30.14 ˚C. The highest water temperature was 32.30 ˚C at L11, while the lowest was 28.80 ˚C at L13. Additional, site-specific water quality data from this study can be found in the Supplemental Table 3.

2010-2011 vs. 2018: Temporal Comparisons

Grain size:

In 2010-2011, sand made up 39 ± 9% (mean ± SE) of the total sediment composition and by 2018 that percentage increased to 49.8 ± 8.96% (Table 1). The average composition of clay in 2010-2011 was 23 ± 6% and 24 ± 4% in 2018. In 2010-2011 fine sediment (clay + silt) made up an average of 52 ± 9%, while in 2018 it was 50 ± 9%. Gravel was not found in 2018, despite making up 8.52 ± 2.76% of the sediment in 2010-2011.

There was no significant difference in the mean percentage of fine sediment ($df = 6$, $t = 0.193$, $p = 0.853$), silt ($df = 6$, $t = 0.550$, $p = 0.602$), clay ($df = 6$, $t = -0.162$, $p = 0.877$), or sand ($df = 6$, $t = -0.964$, $p = 0.372$) between 2010-2011 and 2018. There were no significant differences between the median percentage of gravel between 2010-2011 and 2018 ($V = 15$, $p = 0.059$), either.

Though there were no significant changes in mean grain size composition between years, several locations had large individual, site-specific changes (Table 1). L1 increased from 36% fine sediment in 2010, to 82% in 2018 and during that same period L1 large grain sized sediment fell from 50% sand and 15% gravel in 2010 to only 18% sand in 2018. In 2011, fine sediment made up 55% of L4, but at this sample location in 2018, fine sediment declined to 13% . During that same period, L4 increased in sand composition from 26% in 2011 to 87% in 2018. L2 was composed of 82% fine sediment in 2010-2011, but had lost 27% of that fine sediment by 2018; this sediment was

replaced by an increased percentage of sand to 39%. Sand at site L7, was reduced by 10% in 2018 compared to 2010-2011, while fine sediment increased by 15% over the same time period. Only L3, located between L1 and L4 (Figure 1), did not experience total sediment composition changes greater than 10%. L3 only experienced a 2% increase in fine sediment and a 7% increase in sand. Overall, sand composition increased at sites L2-L6 from 2010-2011 to 2018, while it decreased in L1 and L7 during that time period. Fine sediment composition increased at sites L1, L3, L5, and L17, while it decreases in L2, L4, and L6, from 2010-2011 to 2018 (Table 1).

Table 1: The percent sediment composition of L1-L7 in 2010-2011 and 2018. Total gravel (p=0.059), sand (p=0.602), clay (p=0.877), and silt (p=0.372) were not significantly different between years. The average percentage is shown across years.

Mangrove Lagoon Sediment Composition (%)								
Years	2010-2011				2018			
Samples	Clay	Silt	Sand	Gravel	Clay	Silt	Sand	Gravel
L1	9	27	50	15	35	47	18	0
L2	51	37	12	0	33	28	39	0
L3	24	39	29	9	30	35	35	0
L4	24	31	26	19	7	6	87	0
L5	19	29	39	12	27	24	49	0
L6	30	36	35	0	27	26	47	0
L7	5	6	84	5	9	17	74	0
Average ± SE	23 ± 6	29 ± 4	39 ± 9	9 ± 3	24 ± 4	26 ± 5	50 ± 9	0

Overall:

Table 2 shows a summary of contaminants with NOAA NST standards. An ANOSIM and NMDS orientation (Supplemental Figure 4) showed that there was no significant difference in contaminants within and between 2010-2011 and 2018 ($R = -0.003$, $p = 0.434$).

Table 2: Basic statistics of the contaminant concentrations with known NS&T ERL and ERM limits from Mangrove Lagoon for site L1-L7 in 2010-2011 and 2018.

2010-2011 Sediments								
Metals (µg/g)	Minimum	Maximum	Median	Mean±SE	ERL	ERM	No. > ERL	No. > ERM
Ag	0	0	0	0	1	3.7	0	0
As	2	12	7	8±1	8.2	70	3	0
Cd	0	0.37	0.21	0.16±.06	1.2	9.6	0	0
Cr	11	36	31	28±3	81	370	0	0
Cu	6	79	61	55±10	34	270	6	0
Hg	0	0.12	0.08	0.07±.02	0.15	0.71	0	0
Ni	4	15	11	11±1	20.9	51.6	0	0
Pb	1	31	21	20±4	46.7	218	0	0
Zn	13	162	139	121±21	150	410	3	0
TBT (ng Sn/g)	0	3	1	1±.45	-	-	-	-
Total PAH (ng/g)	4	1152	298	494±200	4,022	44,792	0	0
Total PCB (ng/g)	0.20	22	3	6±3	22.7	180	0	0
Total DDT (ng/g)	0.00	0.87	0.09	0.20±0.12	1.58	46.1	0	0
2018 Sediments								
Metals (µg/g)	Minimum	Maximum	Median	Mean±SE	ERL	ERM	No. > ERL	No. > ERM
Ag	0	0	0	0.13±0.04	1	3.7	0	0
As	2	8	7	6±0.8	8.2	70	2	0
Cd	0	0.28	0.19	0.14±0.04	1.2	9.6	0	0
Cr	7	33	18	20±3	81	370	0	0
Cu	7	92	46	49±11	34	270	5	0
Hg	0	0.08	0.06	0.05±0.01	0.15	0.71	0	0
Ni	10	14	12	12±0.6	20.9	51.6	0	0
Pb	2	26	16	16±3	46.7	218	0	0
Zn	10	176	87	97±20	150	410	1	0
TBT (ng Sn/g)	0.10	1	0.28	0.19±0.19	-	-	-	-
Total PAH (ng/g)	10	1207	205	442±186	4,022	44,792	0	0
Total PCB(ng/g)	0	6	1	2±0.81	22.7	180	0	0
Total DDT (ng/g)	0	23	0	5±3	1.58	46.1	3	0

Metals:

In 2010-2011 and 2018, only concentrations of copper, arsenic, and zinc were found to exceed ERL thresholds (Table 2). In 2010-2011, copper exceeded the ERL for six samples (L1-L6), arsenic for three samples (L2, L4, L6), and zinc for three samples (L2-L4) (Table 3). In 2018, copper exceeded the ERL for five samples (L1-L4, L6), arsenic for two samples (L4,L6), and zinc for only one sample (L1). There was a reduction in the total number of samples above the NOAA ERL limits for these metals from 12 in 2010-2011, to 8 in 2018. The number of samples with copper concentrations that exceeded the ERL declined from 6 in 2010-2011, to 5 in 2018. L5 contained a copper concentration of 36.9 µg/g in 2011 which declined to 30.20 µg/g in 2018. Three of the five copper

concentrations over the ERL threshold in 2018 also decreased from 2010-2011 levels. The number of samples with arsenic concentrations over the ERL declined by one from 2010-2011 to 2018. For arsenic, the concentration at L2 declined from 12.00 µg/g in 2010 to 6.26 µg/g in 2018. The two samples that exceeded the ERL for arsenic in 2018 (L4 and L6) were at lower concentrations compared to those recorded in 2010-11 (Table 3). The locations that exceeded the ERL threshold for zinc in 2010-2011, did not do so in 2018. In 2018, L1 was the only sample above the ERL for zinc, and this sample also had a higher concentration (176 µg/g) than any sample measured in 2010-2011 and 2018 (Table 3), though this was the one zinc site that increased from 2010-2011.

Table 3: Metal concentrations across L1-L7 in 2010-2011 and 2018. The yellow highlighted values represent sites where the metal concentration was above the ERL limit for that metal. The number of sites with metals above the ERL declined from 2010-2011 to 2018.

	Metal Concentrations (µg/g)															
2018	Cu	As	Zn	Ag	Hg	Cd	Cr	Ni	Pb	Al	Fe	Mn	Sb	Se	Si	Sn
L1	92	6	176	0.24	0.08	0.28	33	14	26	65700	41200	378	1	0	154000	3
L2	46	6	87	0.16	0.07	0.19	17	12	15	36500	22700	176	1	0	78800	2
L3	73	7	146	0.14	0.06	0.24	28	14	22	60400	38100	360	1	0	153000	2
L4	42	8	87	0.12	0.05	0.11	18	12	16	40800	24800	212	1	0	99400	1
L5	30	7	68	0.00	0.03	0.00	16	12	13	34100	20200	159	0	0	75400	1
L6	59	8	108	0.23	0.08	0.19	25	13	18	50300	30700	239	1	0	114000	3
L7	7	2	10	0.00	0.00	0.00	7	10	2	5250	3290	59	0	0	22200	0
2010-2011	Cu	As	Zn	Ag	Hg	Cd	Cr	Ni	Pb	Al	Fe	Mn	Sb	Se	Si	Sn
L1	61	7	139	0.00	0.08	0.30	29	9	20	45100	29900	379	0.67	0.58	191000	3
L2	79	12	162	0.00	0.12	0.37	35	14	28	53200	36400	270	0.74	1	120000	5
L3	69	7	154	0.00	0.08	0.26	32	11	25	54300	35400	338	0.82	0.63	174000	3
L4	61	9	159	0.00	0.07	0.00	31	12	31	50000	32300	299	0.63	0.59	147000	2
L5	37	7	83	0.00	0.04	0.00	23	10	15	37400	23800	190	0.43	0.53	106000	2
L6	70	12	136	0.00	0.11	0.21	36	15	21	63800	40900	317	0.49	0.93	181000	4
L7	6	2	13	0.00	0.00	0.00	11	4	1	3520	2420	45	0.00	0.13	18400	0

L7 was the only sample that had no metal concentrations above the ERL in either 2010-2011 or 2018 (Table 3). L5 did not have any metals over the ERL in 2018. In 2010-2011 copper, arsenic, and zinc were above the ERL threshold at L2 and L4, but no sample contained all three metals over the ERL in 2018. Though mercury and silver were found over the ERL threshold during wider sampling in 2018 (at Site 17, and L8 respectively), at L1-L7 they were not above the ERL. Silver was below the detection limit in 2010-2011, but in 2018 silver was detected at L1-L6 but was still not found at L7 in 2018. Mercury was present in L1-L6 in 2010-2011 and decreased across L2-L6 in 2018.

Copper was above the ERL threshold at L1-L6 in 2010-2011 and at L1-L4 and L6 in 2018 (Table 3). The average copper concentration for Mangrove Lagoon was 55 ± 10 µg/g in 2010-2011 and decreased slightly in 2018 to 50 ± 11 µg/g. Both years contained an average concentration above the ERL threshold. The highest concentration in 2010-2011 was 78 µg/g at L2, but in 2018 the highest concentration was 92 µg/g at L1. L1 increased from 61 µg/g to 92 µg/g, while L2 declined from 79 µg/g to 46 µg/g from 2010-2011 to 2018. L4 experienced a steep decline in copper concentration from 61 µg/g in 2010-2011 to 42 µg/g in 2018. L6 also declined by 11 µg/g during that time period. L3, L5, and L7 were the only samples that did not change more than 10 µg/g. L7 was not above the copper ERL across both years and contained the lowest copper concentrations over both years, while L5 was not above the ERL limit for copper in 2018. Overall L1, L3, and L7 all increased in copper concentrations from 2010-2011 to 2018, while L2 and L4-L6 declined from 2010-2011 to 2018.

Arsenic was above the NOAA ERL concentration of 8.2 µg/g at L2, L4, and L6 in 2010-2011 and at L4 and L6 in 2018 (Table 2). L2, which was above the ERL threshold in 2010-2011, was not above it in 2018. This sample declined from 12 µg/g to 6 µg/g (Table 3). Unlike copper, the average arsenic concentrations each year were not above the ERL. In 2010-2011, the average was 8 ± 1 µg/g and in 2018 it was 6 ± 0.82 µg/g. L1, L2-L4, and L7 all changed less than 1 µg/g. Only L2 and L6 changed more than 1 µg/g between 2010-2011 and 2018. The highest concentration in 2010-2011 was 12 µg/g at L6 and despite declining by 4.01 µg/g this sample also had the highest concentration in 2018, at 8.39 µg/g. L2 declined by 6 µg/g, which was the largest change in arsenic among all samples. L7 contained the lowest concentrations in both study years. Overall L1, L2, and L4-L6 declined from 2010-2011 to 2018, while L3 and L7 slightly increased during that period.

Zinc was above the ERL concentration of 150 µg/g at L2-L4 in 2010-2011 but only at L1 in 2018 (Table 2). None of the samples over the ERL in 2010-2011 were over the ERL limit in 2018. The average zinc concentration in 2010-2011 was 121 ± 21 µg/g and by 2018, it had declined to 97 ± 20 µg/g. The average concentrations for each year were well under the ERL. L1 was the only sample that had a greater zinc concentration in 2018 than in 2010-2011. L1 had the greatest concentration in 2018 at 176 µg/g (Table 3). L2 experienced the greatest decline from 162 µg/g to 87 µg/g, and L4 declined from 159 µg/g to 87 µg/g; these samples declined in zinc concentrations by almost half

from 2010-2011 to 2018. L6 also experienced a large decline from 136 µg/g to 108 µg/g. The rest of the sites experienced changes that were less than 15 µg/g. L7 had the lowest zinc concentrations in both 2010-2011 and 2018. L2-L7 all had lower zinc concentrations in 2018 compared to 2010-2011.

Copper, arsenic, and zinc were the most toxic contaminants in both years; however, the concentrations of these contaminants were not significantly different between years. Only four metals showed significant differences between years, though none of these metals exceeded their respective ERL limits. Selenium had a significantly greater median concentration in 2010-2011 compared to 2018, when it was not detected ($V = 28$, $p = 0.016$). Mercury ($df = 6$, $t = 2.582$, $p = 0.042$), chromium ($df = 6$, $t = 2.798$, $p = 0.031$), and silicon ($df = 6$, $t = 4.106$, $p = 0.006$) had significantly greater mean concentrations in 2010-2011, compared to 2018. The other eleven metals showed no significant difference in mean concentrations between years.

TBT:

The average TBT level in Mangrove Lagoon during 2010-2011 was 1.31 ± 0.45 ng Sn/g (Figure 2). The highest concentration was L3 at 3.27 ng Sn/g, while L6 and L7 did not have any TBT present (Table 4). In 2018, the average TBT concentration declined to 0.19 ± 0.19 ng Sn/g. The highest concentration was at L1 with 1 ng Sn/g. All other samples did not contain any TBT over the detection limit. In 2010-2011, L1-L3 all had TBT concentrations higher than L1 in 2018. L1-L5 decreased in TBT concentrations from 2010-2011 to 2018. In 2010-2011, L6 and L7 did not contain any TBT and by 2018, L2-L7 all had concentrations that were below the detection limit for TBT. Though L3 did not contain TBT above the detection limit in 2018, it did have the highest di- and mono- butyltin concentrations at 9 ng Sn/g and 8 ng Sn/g, respectively. In 2010-2011, TBT made up 32 ± 13% of the butyltins in Mangrove Lagoon. Dibutyltin and monobutyltin made up 43 ± 14% and 10 ± 7%, respectively. In 2018, TBT only made up 3 ± 3% while dibutyltin and monobutyltin made up 15 ± 8% and 82 ± 9%, respectively. TBT and dibutyltin decreased between the two years while monobutyltin increased dramatically. L2-L5 decreased in TBT concentration from 2010-2011 to 2018. The mean TBT concentration in 2010-2011 was significantly greater than the mean TBT concentration in 2018 ($df = 6$, $t = 2.559$, $p = 0.043$).

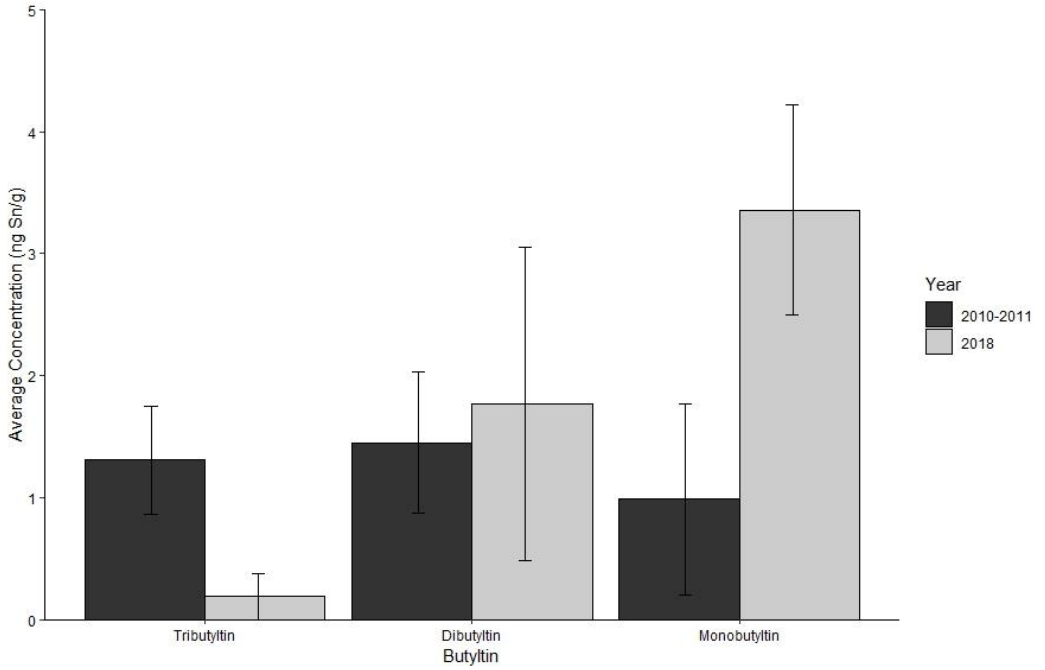

Figure 2: A side-by-side comparison of butyltin concentrations averaged (±SE) across sites L1-L7 in 2010-2011 and 2018. A paired t-test indicated a significant difference in the means of Tributyltin between 2010-2011 and 2018 (p=0.043).

Table 4: Butyltin, total PAH, and total PCB concentrations across L1-L7 in 2010-2011 and 2018. No site was above the ERL for total PAHs or total PCBs. "<" represents values below the method detection limit and as a result were treated as zeros. PAH and PCB results are discussed in the sections that follow.

	Butyltin Concentrations (ng Sn/g)			**PAHs and PCBs**	
Year	2018				
Samples	Tributyltin	Dibutyltin	Monobutyltin	Total PAHs (ng/g)	Total PCBs (ng/g)
L1	1	2	5	1207	6
L2	< 0.36	< 0.63	2	205	2
L3	< 0.61	9.30	8	1093	4
L4	< 0.26	1.34	3	315	1
L5	< 0.21	< 0.62	2	126	0
L6	< 0.28	< 0.70	2	144	1
L7	< 0.10	< 0.25	2	10	0
Year	2010/2011				
Samples	Tributyltin	Dibutyltin	Monobutyltin	Total PAHs (ng/g)	Total PCBs (ng/g)
L1	2	4	6	967	22
L2	2	3	1	298	9
L3	3	0	0	1152	1
L4	1	2	0	723	2
L5	0.90	2	0	161	3
L6	0	0	0	151	3
L7	0	0	0	4	0

Total DDTs:

In 2010-2011, no sample was above the NOAA ERL limit of 1.58 ng/g. However, in 2018, sites L1, L2, and L5 all exceeded the ERL (Figure 3). The average total DDT in 2010-2011 was 0.2 ± 0.12 ng/g while the average total DDT in 2018 was 5 ± 3ng/g. L1 had a concentration of 22 ng/g, L2 had a concentration of 11 ng/g, and L5 had a concentration of 3 ng/g. The DDT concentration at L1 increased by a factor of 25. And the DDT concentrations at L2 and L5 increased by a factor of 28, in comparison to the 2010-2011 values. Overall, only L6 declined slightly from 2010-2011 to 2018, while sites L3 and L7 did not change (Table 5). Despite these differences there was no significant difference between the median DDT concentrations between years (V = 1, p = 0.106).

Table 5: Total DDT concentrations for L1-L7 in 2010-2011 and 2018. The yellow highlighted values represent sites where the Total DDT concentration was above the ERL limit. The average total DDT in 2010-2011 was 0.23±0.12 ng/g while the average total DDT in 2018 was 5.45±3.31ng/g. Despite these differences a Wilcoxon's signed rank test showed no significant difference between years (p=0.106). "<" represents values below the method detection limit and as a result were treated as zeros.

DDT Concentrations (ng/g)								
2018	DDMU	2,4'-DDD	4,4'-DDD	2,4'-DDE	4,4'-DDE	2,4'-DDT	4,4'-DDT	Total DDT
L1	<0.11	<0.02	22	<0.07	<0.04	<0.04	1.	23
L2	<0.11	<0.02	11	<0.07	0.47	<0.04	0.62	12
L3	<0.11	<0.02	<0.02	<0.07	<0.04	<0.04	<0.03	0
L4	<0.11	<0.02	0.48	<0.07	<0.04	<0.04	<0.03	0.48
L5	<0.11	<0.02	3	<0.07	<0.04	<0.04	<0.03	3
L6	<0.11	<0.02	<0.02	<0.07	<0.04	<0.04	<0.03	0
L7	<0.11	<0.02	<0.02	<0.07	<0.04	<0.04	<0.03	0
2010-2011	DDMU	2,4'-DDD	4,4'-DDD	2,4'-DDE	4,4'-DDE	2,4'-DDT	4,4'-DDT	Total DDT
L1	0.42	0	0.12	0	0.26	0.00	0.07	0.87
L2	<0.06	0	<0.05	0	0.12	0.16	0.10	0.38
L3	0	0	0	0	0	0	0	0
L4	0	0	0	<0.04	0	0	0	0
L5	<0.04	0	0	0.06	0	0	0	0.06
L6	0	0.09	0	0	0	0	0	0.09
L7	0	0	0	0	0	0	0	0

Figure 3: Spatial distribution of DDT between 2010-2011 and 2018

Total PAHs:

No sample between the two sampling periods were above the PAH NOAA ERL limit of 4,022 ng/g (Table 2). In 2010-2011, the average was 494 ± 170 ng/g and by 2018 that average had declined to 443 ± 186 ng/g (Figure 4). The highest PAH concentrations were found at L1 and L3 for both years, though these concentrations were still far

below the ERL limit (Table 4). L1 and L7 were the only samples that had an increase in PAH concentration from 2010-2011 to 2018. L2-L6 declined in PAH concentration during that time (Table 4). L4 had the largest individual decline of 407 ng/g while L1 had the largest increase of 239 ng/g. The mean total PAH between 2010-2011 and 2018 was not significantly different (df = 6, t = 0.705, p = 0.507).

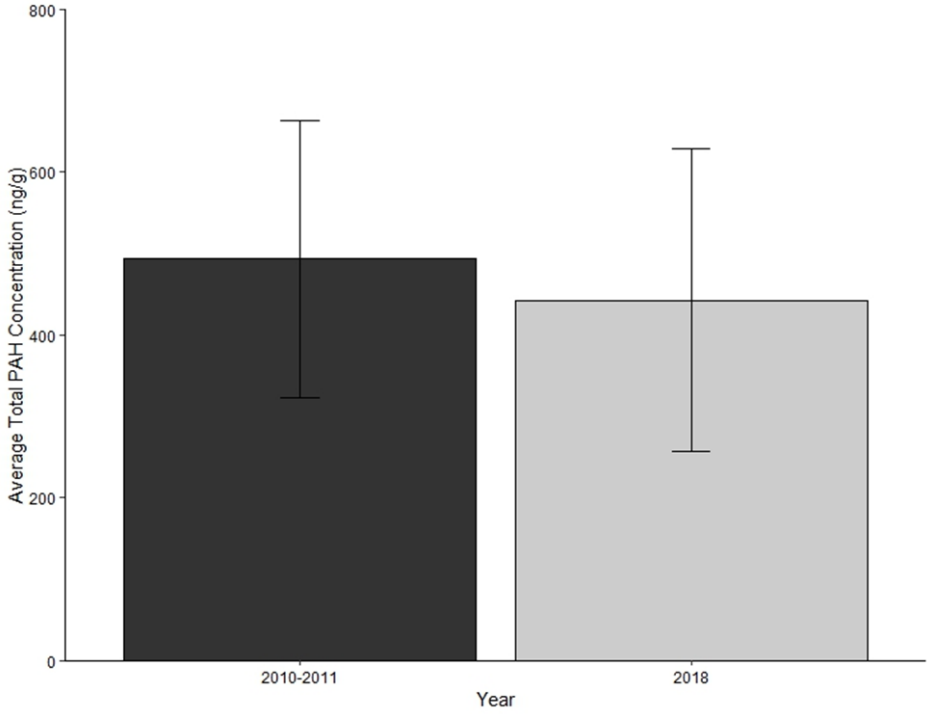

Figure 4: A side-by-side comparison of total PAH concentrations averaged (±SE) L1-L7 in 2010-2011 and 2018. There was no significance difference of total PAH between years (p=0.5072).

Total PCBs:

No sample in 2010-2011 and 2018 was above the NOAA ERL limit of 22.7 ng/g for PCBs (Table 2). The average total PCB in 2010-2011 was 6 ± 3 ng/g while the average total PCB in 2018 was 2 ± 0.81 ng/g (Figure 5). L1 had the highest PCB concentration in both 2010-2011 at 22 ng/g and 2018 at 6 ng/g. All samples, except L3, declined in PCBs between years and L3 only increased by 2 ng/g (Table 4). PCB concentrations were the lowest at L7 and the greatest at L1 for both years. There was no significant difference in means between the two years (df = 6, t = 2.037, p = 0.089).

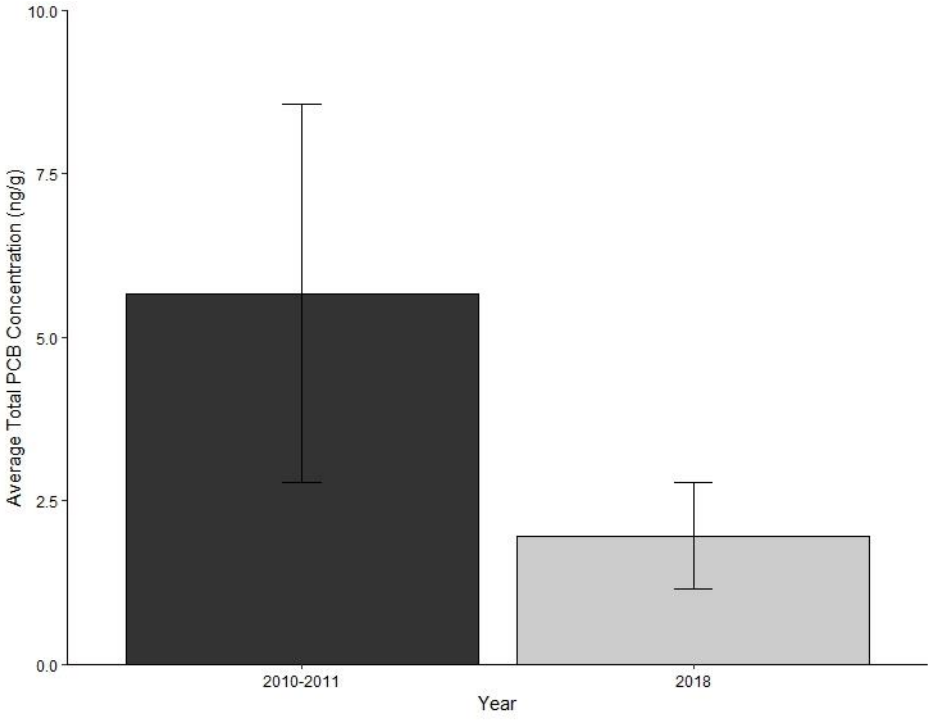

Figure 5: A side-by-side comparison of total PCB concentrations averaged (±SE) across L1-L7 in 2010-2011 and 2018. The average total PCB in 2010-2011 was 5.67±2.89 ng/g while the average total PCB in 2018 was 1.96±0.81 ng/g. A paired t-test showed no significant difference between the two years (p=0.089).

Mangrove vs. Lagoon: Spatial Comparisons

Grain Size:

There were no significant differences in sediment composition between mangrove and lagoon sediments. A paired t-test showed no significant difference in the mean percentages of sand, silt, or clay between mangrove and lagoon sites; sand ($df = 18$, $t = 0.057$, $p=0.955$), silt ($df = 18$, $t = 0.362$, $p = 0.7216$), and clay ($df = 18$, $t = -0.409$, $p = 0.6873$). Gravel was not found in Mangrove Lagoon in 2018 (Table 6). Sand made up the largest portion of both mangrove and lagoon sediment at 48 ± 3% and 48 ± 4%, respectively. The composition of clay and silt was similar between mangrove and lagoon sediment. Mangrove sediment contained an average clay percentage of 26 ± 3% and an average silt percentage of 26 ± 2% , while lagoon sediments contained averages of 25 ± 2% and 27 ± 2, respectively for those size fractions. The average percentage of fine sediment (clay + silt) was 52 ± 4% in mangrove sediments while lagoon sediments averaged 52 ± 3%. Fine sediment made up a greater percentage then sand in both mangrove and lagoon sediments. Table 6 shows the average ± SE comparison between grain sizes.

Several sites exhibited wide variation in sediment grain size, however (Table 6). Site L4 only had a fine sediment percentage of 13% while M4 had a fine sediment percentage of 60%. L1 and L2 both contained more than 30% fine sediment than corresponding, paired mangrove samples. L14 contained 20% more fine sediment then M14. M13 and M16 both contained 20% more fine sediment then L13 and M16.

Table 6: The percent grain size composition of the 19 mangrove sites and the 19 lagoon sites. Sand (p=0.9553), silt (p=0.7216), and clay (p=0.6873) were not significantly different from one another. There was no gravel found in Mangrove Lagoon sediment. Samples names are mnemonics indicating sediment type (Lagoon or Mangrove) and site number. There was no gravel found in 2018.

Mangrove Lagoon Sediment Composition (%)						
Sediment	Mangrove			Lagoon		
Sites	Clay	Silt	Sand	Clay	Silt	Sand
1	11	35	53	35	47	18
2	6	20	74	33	28	39
3	57	1	42	30	35	35
4	19	41	40	7	6	87
5	18	22	60	27	24	49
6	30	27	43	27	26	47
7	9	29	62	9	17	74
8	16	42	42	26	26	48
9	26	28	45	32	32	36
10	16	26	58	26	20	54
11	13	30	57	28	29	43
12	43	16	40	27	19	54
13	34	22	44	19	10	70
14	35	20	45	40	35	25
15	43	26	32	42	29	29
16	45	32	22	23	34	43
17	31	28	41	19	37	44
18	24	25	51	15	30	55
19	26	23	51	10	32	58
Average ± SE	26±3	26±2	48±3	25±2	27±2	48±4

Overall:

Table 7 shows a summary of contaminants with NOAA NST standards between mangrove and lagoon sediments. An ANOSIM and NMDS (Supplemental Figure 5) showed that there was no significant difference in contaminants within and between mangrove and lagoon sediments ($R = 0.019$, $p = 0.232$).

Table 7:Basic statistics for contaminants with known NOAA ERL and ERM limits for Mangrove Lagoon across the 19 mangrove and 19 lagoon sites.

	Mangrove Sediments							
Metals (µg/g)	Minimum	Maximum	Median	Mean ± SE	ERL	ERM	No. > ERL	No. > ERM
Ag	0	0.50	0.12	0.13±0.03	1	3.7	0	0
As	3	23	5	8±1	8.2	70	8	0
Cd	0	0.25	0.12	0.10±0.02	1.2	9.6	0	0
Cr	8	29	18	18±2	81	370	0	0
Cu	25	88	41	48±4	34	270	15	0
Hg	0.04	0.20	0.05	0.06±0.01	0.15	0.71	1	0
Ni	5	19	9	10±0.9	20.9	51.6	0	0
Pb	6	28	13	15±2	46.7	218	0	0
Zn	32	684	72	112±33	150	410	3	1
TBT (ng Sn/g)	0	0	0	0	-	-	-	-
	Lagoon Sediments							
Metals (µg/g)	Minimum	Maximum	Median	Mean ± SE	ERL	ERM	No. > ERL	No. > ERM
Ag	0	3	0.14	0.34±0.16	1	3.7	2	0
As	2	16	7	7±0.7	8.2	70	6	0
Cd	0	0.54	0.19	0.18±0.03	1.2	9.6	0	0
Cr	2	33	18	19±2	81	370	0	0
Cu	7	125	46	50±7	34	270	14	0
Hg	0	0.37	0.06	0.07±0.02	0.15	0.71	1	0
Ni	10	18	12	13±0.5	20.9	51.6	0	0
Pb	2	36	15	16±2	46.7	218	0	0
Zn	10	247	87	97±13	150	410	3	0
TBT (ng Sn/g)	0	115	0	6±6	-	-	-	-

Metals:

Of the 38 samples collected in 2018, 31 of them contained at least one metal over its respective ERL limit and 16 samples contained at least two metals over respective ERL limits. Copper concentrations were over the ERL at 29 of 38 samples (Table 8). Fifteen of those samples were in mangrove sediment (M1-M4, M6-M9, M11, and M14-M19); and 14 were lagoon samples (L1-L4, L6, L8-9, L11, L14-L19). Arsenic concentrations were measured over the ERL in 8 mangrove samples (M3, M5, M7-M10, M15, and M17) and 6 lagoon samples (L4, L6, L14-L15, L17-L18). Samples M11 and M17 contained zinc concentrations that exceeded ERL thresholds, while site M15 had a zinc concentration that exceeded the ERM (the only site to exceed that threshold in this study). Samples L1, L11, and L17 all contained zinc concentrations over the ERL. M17 and L17 contained mercury at concentrations that exceeded the ERL while sites L8 and L17, contained silver concentrations over the ERL. Only two mangrove samples, M12 and M13, did not contain metals above the NOAA ERL limit (Table 8), while five lagoon samples did not contain metals above the NOAA ERL limit (Table 8); those five were, L5, L7, L10, L12, and L13.

Table 8: Metal concentrations across the 19 mangrove and 19 lagoon sites. The light-yellow highlighted values are above the National Oceanic & Atmospheric Administration (NOAA) sediment quality guidelines effects range low (ERL) limit for that metal. The dark-yellow highlighted value is above the NOAA sediment quality guidelines effects range median (ERM) limit for that metal. Bolded samples represent samples where no ERL values were crossed.

Metal Concentrations (µg/g)																
Samples	Cu	As	Zn	Ag	Hg	Cd	Cr	Ni	Pb	Al	Fe	Mn	Sb	Se	Si	Sn
L1	92	6	176	0.24	0.08	0.28	33	14	26	65700	41200	378	1	0	154000	3
M1	67	4	144	0.22	0.09	0.19	29	12	25	56800	31400	402	1	2.2	166000	3
L2	46	6	87	0.16	0.07	0.19	17	12	15	36500	22700	176	0.77	0	78800	2
M2	39	4	49	0	0.06	0.00	8	7	10	13400	8420	119	2	0	29900	1
L3	73	7	146	0.14	0.06	0.24	28	14	22	60400	38100	360	0.90	0	153000	2
M3	60	8	104	0.16	0.07	0.18	22	9	19	48500	25500	206	1	0	126000	2
L4	42	8	87	0.12	0.05	0.11	18	12	16	40800	24800	212	0.54	0	99400	1
M4	34	4	46	0	0.05	0.11	9	5	8	19300	10800	83	0.74	0	41600	1
L5	30	7	68	0	0.03	0	16	12	13	34100	20200	159	0.48	0	75400	1
M5	30	9	48	0	0.04	0	11	6	8	20400	11700	76.9	1	0	45300	1
L6	59	8	108	0.23	0.08	0.19	25	13	18	50300	30700	239	0.54	0	114000	3
M6	63	5	96	0.17	0.07	0	22	11	21	40100	23300	210	0.54	0	91800	2
L7	7	2	10	0	0.00	0	7	10	2	5250	3290	59	0.31	0	22200	0
M7	34	21	34	0.12	0.04	0	24	9	7	14700	8470	87.7	0.99	1	37900	0.90
L8	36	8	75	1	0.05	0.10	14	12	15	33900	21500	174	0.60	0	77400	1
M8	38	9	60	0.38	0.05	0	14	7	11	27200	15500	156	0.88	1	67600	1
L9	39	5	74	0.11	0.04	0.16	22	13	13	39700	22400	170	0.45	0	85000	0.83
M9	42	19	72	0	0.05	0.13	18	9	13	34800	19000	131	1	1	79200	1
L10	20	5	38	0	0.02	0	8	11	8	17700	10200	88.2	0.35	0	40600	0.31
M10	31	23	52	0	0.06	0	13	7	9	21400	12100	77.6	1	2	46500	0.85
L11	79	4	176	0.24	0.07	0.38	31	14	36	63900	39300	565	1	0	186000	2
M11	70	3	153	0.21	0.05	0.25	29	13	28	64500	38700	624	1	0	211000	10
L12	14	5	28	0	0.02	0	7	11	8	13800	8170	63.8	0.35	0	29500	0.31
M12	25	7	32	0	0.05	0	13	6	6	15300	9520	510	0.47	0	37700	0.56
L13	15	7	27	0	0.03	0	2	10	6	13000	10200	69.5	0.51	0	28500	0
M13	25	4	34	0	0.05	0	8	5	6	13800	7740	115	1	0	29200	1
L14	54	16	104	0.14	0.06	0.23	22	12	17	39800	24000	175	0.33	1	94600	1
M14	60	5	106	0.21	0.08	0.19	17	11	21	25600	15000	185	2	0	52300	2
L15	57	10	106	0.18	0.05	0.32	20	12	18	36200	21700	165	0.31	1	81700	1
M15	60	8	684	0.13	0.05	0.13	24	19	16	32500	61700	265	1	0	72200	6
L16	69	6	128	0.18	0.07	0.30	26	13	20	47100	28900	247	0.34	1	110000	2
M16	72	5	129	0.14	0.07	0.23	28	14	19	53200	31000	270	0.46	0	124000	2
L17	125	11	247	3	0.37	0.54	31	18	27	54500	34300	270	0.68	2	127000	15
M17	88	9	165	0.50	0.20	0.24	28	16	24	49000	26300	250	1	2	115000	9
L18	50	9	89	0.28	0.08	0.20	18	17	14	48100	25900	241	0.49	0	120000	3
M18	35	3	53	0.10	0.04	0.12	19	10	12	46200	23700	438	0.48	0	143000	1
L19	39	8	77	0.13	0.06	0.13	17	12	13	42900	25800	261	0.51	0	126000	1
M19	41	4	72	0.12	0.05	0.15	14	7	13	29500	18100	275	0.60	0	81500	1

In lagoon sediments, the lowest metal concentrations were all found at L7 (Table 8). Most of the highest metal concentrations in lagoon samples were found at L17 (copper, zinc, silver, mercury, cadmium, nickel, selenium, and tin) with L1 (chromium, aluminum, iron, and silicon), L11 (lead, antimony, and manganese), and L14 (arsenic) rounding out the rest of the highest concentrations. The five metals that exceeded ERL thresholds in the lagoon sediments were all present at L17. Mangrove sediments were more varied in which samples contained the highest concentration. M11 contained the highest concentration of cadmium, lead, tin, aluminum, manganese, and silicon, with M15 (zinc, nickel, and iron), M17 (copper, silver and mercury), M1 (chromium and selenium), M10 (arsenic), and M14 (antimony) rounding out the rest of the highest concentrations.

Copper was above the NOAA ERL concentration at 29 of the 38 samples (Figure 6). These included all samples located in the northwest portion of Mangrove Lagoon, the two samples in Turpentine Run, the three samples surrounding the entrance to Benner Bay, and the southernmost mangrove sample. Site 17 contained the highest concentrations of copper. The lagoon sample had a concentration of 125 µg/g and the mangrove sample had a concentration of 87.6 µg/g (Table 8). When copper was normalized with aluminum, 9 of the 38 samples were outliers, L15-L17, M2, M6, M7, M14, M15, and M17 (Figure 7). Both samples at site 15 and 17 were outliers. Both sediment types contained an average concentration of copper above the ERL, with the lagoon average being 50 ± 7 µg/g and the mangrove average being copper at 48 ± 4 µg/g. The nine samples that were not above the ERL were all located in the south and southeastern portion of Mangrove Lagoon. The lowest concentrations were contained in L7, L12, and L13. These samples make up the south and southwest portions of Mangrove Lagoon. Copper was positively correlated with fine sediment (Spearman Rho = 0.501, p = 0.001), negatively correlated with sand (rho = -0.501, p = 0.001.), and positively correlated with aluminum (rho = 0.856, $p = 7.055 \times 10^{-12}$).

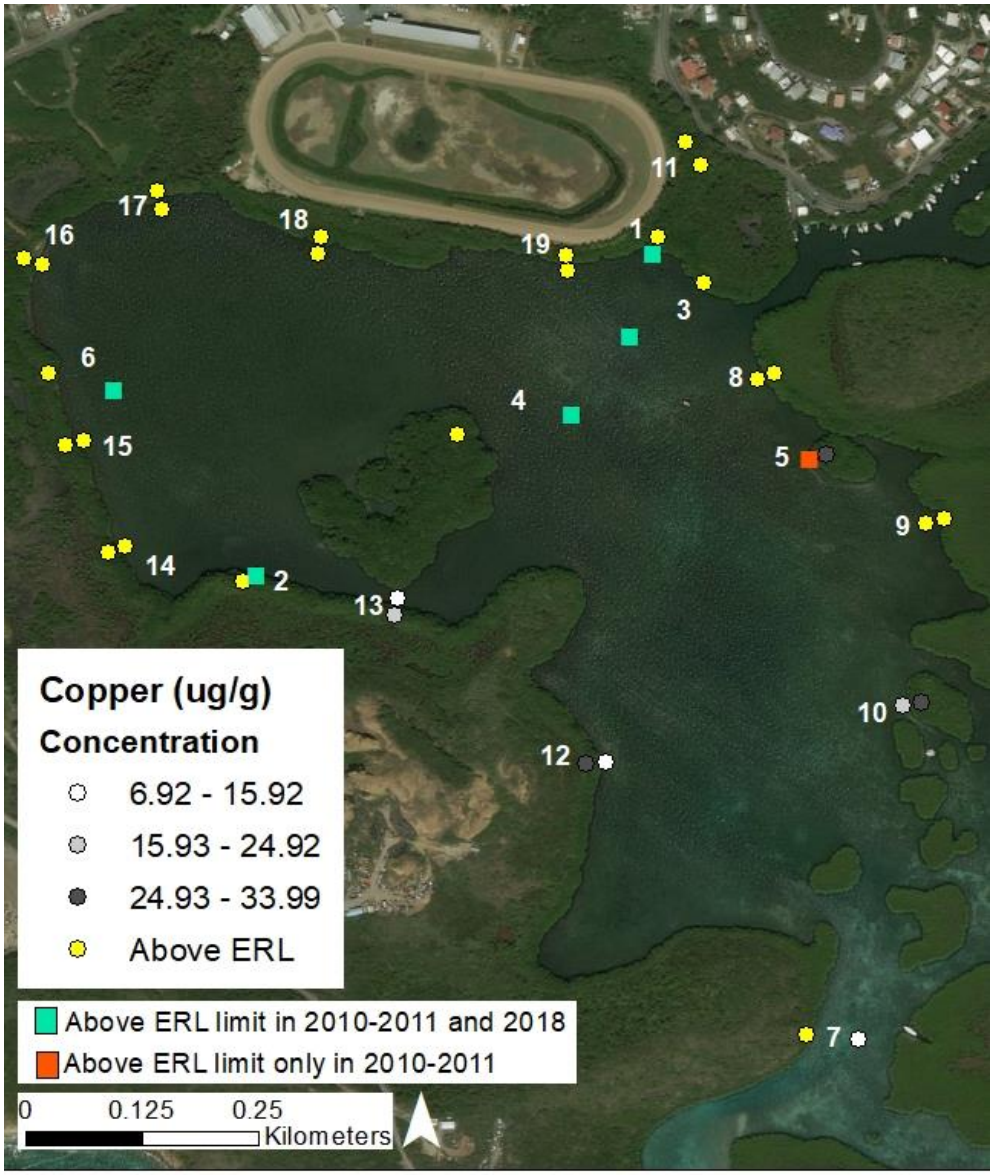

Figure 6: Copper concentrations for the 2018 sampling of Mangrove Lagoon and historical ERL samples. Twenty-nine sites were above the NOAA ERL concentration of 34 µg/g.

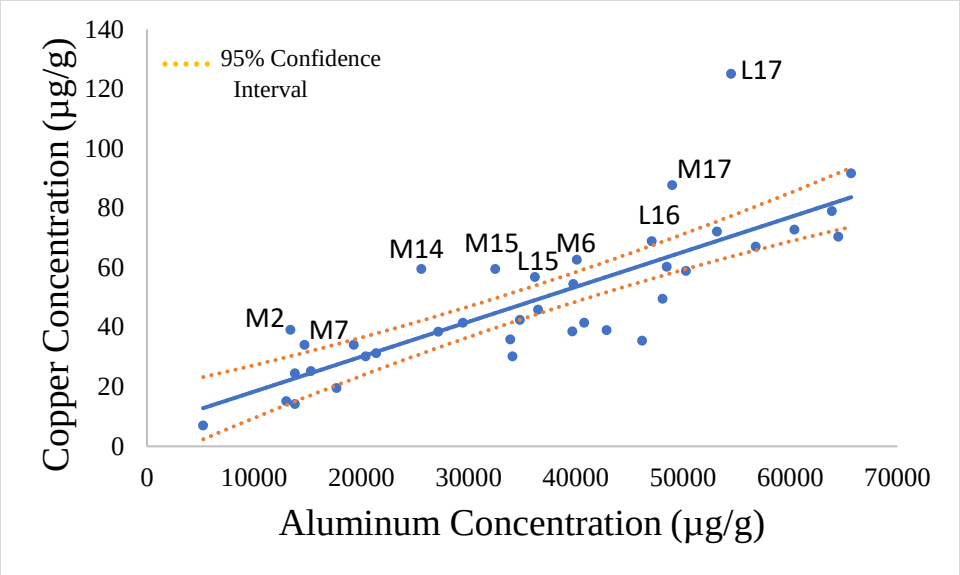

Figure 7: Relationship between sediment copper and aluminum in mangrove and lagoon sediment, including sample confidence intervals. Samples above the confidence intervals suggest evidence of anthropogenic inputs.

Arsenic was above the NOAA ERL concentration of 8.2 µg/g in 14 of the 38 samples (Figure 8). The six locations that exceeded the ERL threshold in lagoon sediments were generally located in the northwest portion of Mangrove Lagoon. Samples L14, L6, L15, L17, and L18 are all located along the western edge of Mangrove Lagoon; there, only L16 did not exceed the ERL concentration. The other sample, L4, is in the central portion of Mangrove Lagoon. The eight mangrove samples that exceeded the ERL threshold for arsenic occur generally in the eastern portion of Mangrove Lagoon. Samples M3, M5, M7-M10 are all located along the eastern edge of Mangrove Lagoon. The other two mangrove samples that contained high arsenic levels were M15 and M17. Paired mangrove and lagoon samples at sites 15 and 17, both exceeded the ERL limit. The average arsenic concentration in the mangrove sediments was above the ERL at 8 ± 1 µg/g. M10, M9, and M7 contained the highest arsenic levels at 23.1, 21.2, and 18.6 µg/g, respectively (Table 8). The average arsenic concentration for lagoon sediments was 7 ± 0.68 µg/g. L14, L17, and L15 contained the highest lagoon concentrations at 16 µg/g, 11 µg/g, and 10 µg/g. When arsenic was normalized with aluminum the six samples that showed evidence of anthropogenic inputs were the same samples that contained the highest arsenic concentrations (Figure 9). Arsenic was not correlated with fine sediment (Spearman Rho = 0.107, p = 0.524), sand (rho = -0.107, p = 0.524), or aluminum (rho = 0.051, p = 0.763).

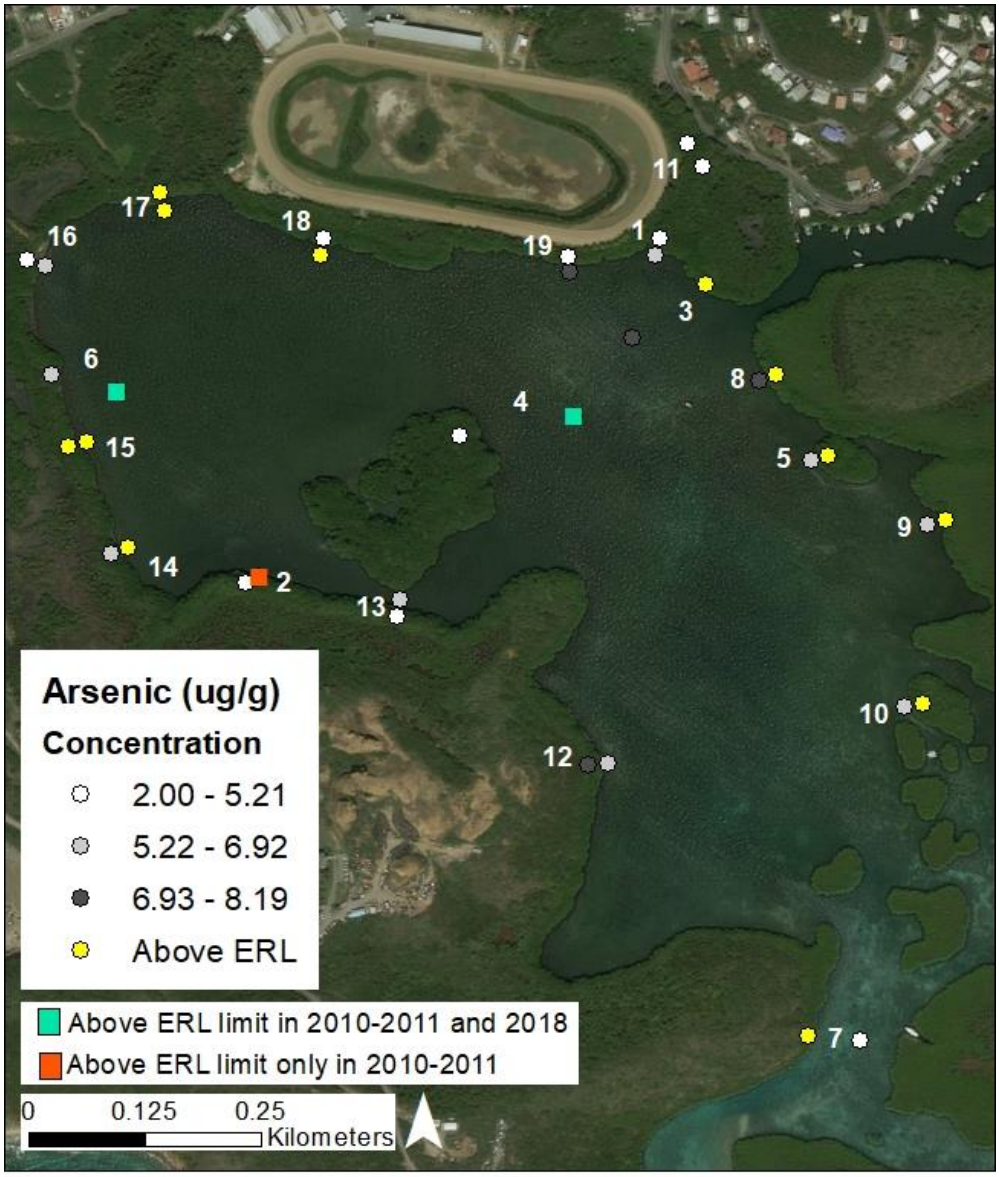

Figure 8: Arsenic concentrations for the 2018 sampling of Mangrove Lagoon and historical ERL samples. Fourteen sites were above the NOAA ERL concentration of 8.2 µg/g.

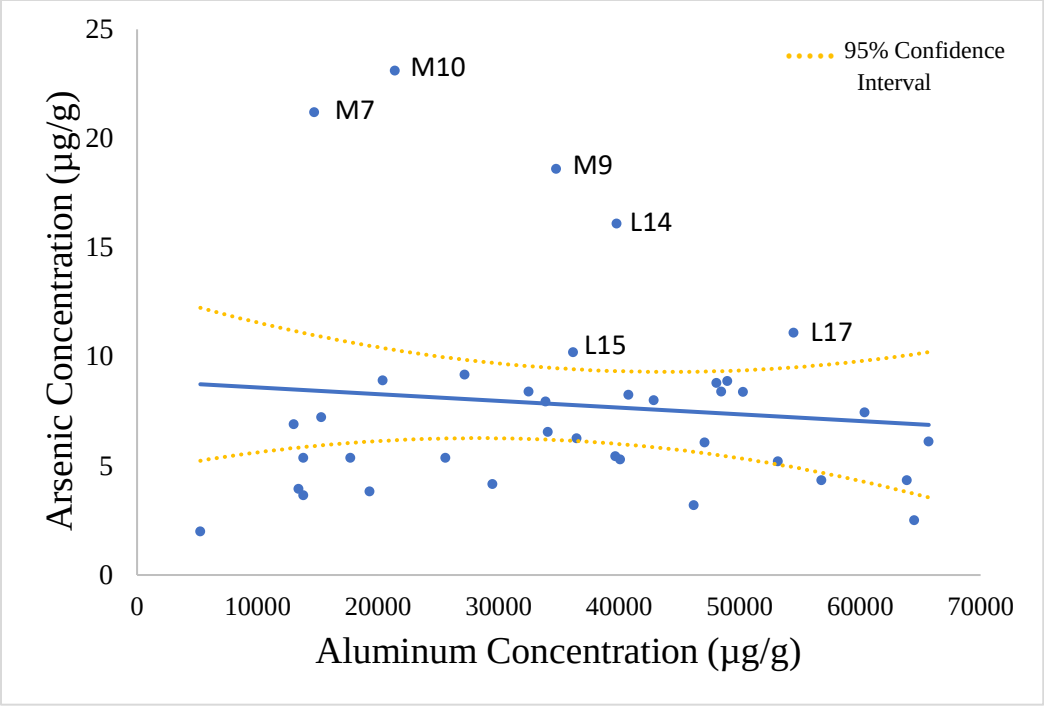

Figure 9: Relationship between sediment copper and aluminum in mangrove and lagoon sediment, including sample confidence intervals. Samples above the confidence intervals suggest evidence of anthropogenic inputs.

Zinc exceeded the ERL concentration of 150 µg/g at 6 of the 38 samples (Figure 10). L17 (247 µg/g), L1 (176 µg/g), and L11 (176 µg/g) were the three lagoon samples that were found to have zinc concentrations over the ERL threshold (Table 8). L11 and L1 were associated with Turpentine Run, and L17 was located in the northwest corner of Mangrove Lagoon. The average zinc concentration for lagoon sediments was 97 ± 13 µg/g. M15 (684 µg/g), M17 (165 µg/g), and M11 (153 µg/g) were the three mangrove samples found to exceed the ERL threshold (Table 8). M15 and M17 were located in the western portion of Mangrove Lagoon, while M11 was located in Turpentine Run. Both mangroves and lagoon samples at sites 11 and 17 contained concentrations of zinc that exceeded the ERL. The average zinc concentration for mangrove sediments was 112 ± 33 µg/g. Only the two greatest zinc concentrations, M15 and L17, showed direct evidence for anthropogenic inputs when normalized to aluminum (Figure 11). Zinc was positively correlated with fine sediment, (Spearman Rho = 0.506, p = 0.001), negatively correlated with sand (rho = -0.506, p = 0.001), and positively correlated with aluminum (rho = 0.858, p = 5.818e-12).

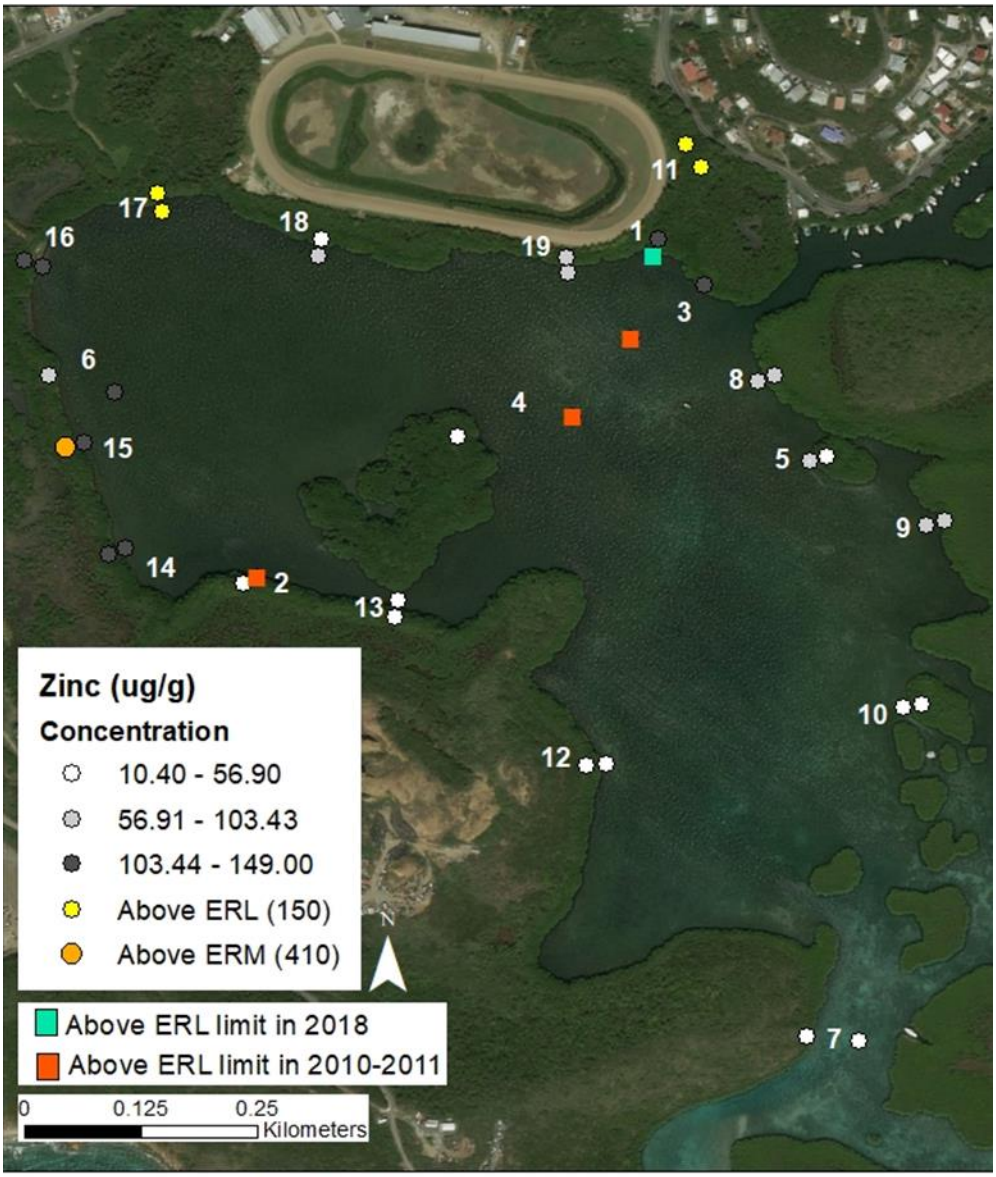

Figure 10: Zinc concentrations for the 2018 sampling of Mangrove Lagoon and historical ERL samples. Five sites were above the NOAA ERL concentration of 150 µg/g and one was above the ERM concentration of 410 µg/g. M15 had a zinc concentration of 684 µg/g.

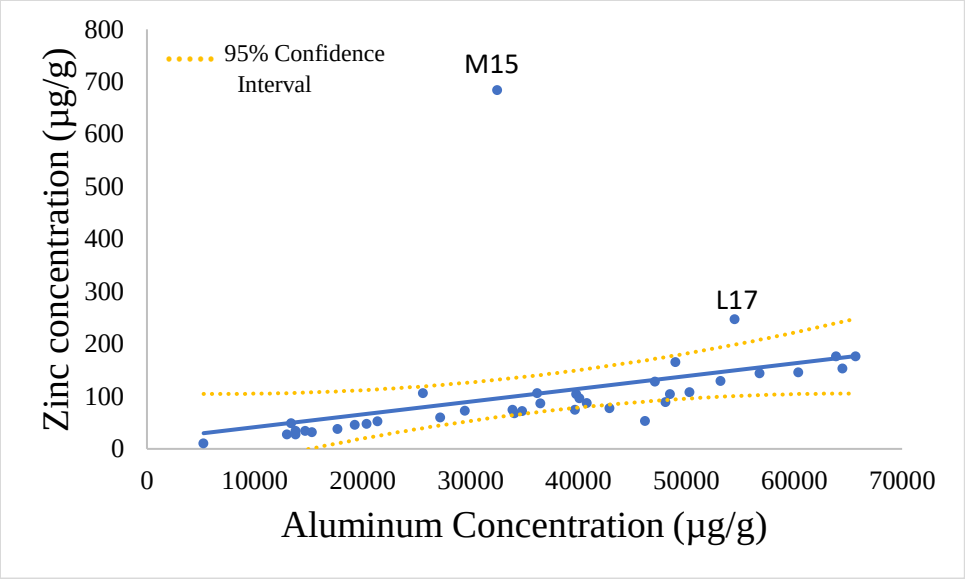

Figure 11: Relationship between sediment zinc and aluminum in mangrove and lagoon sediment, including sample confidence intervals. Samples above the confidence intervals suggest evidence of anthropogenic inputs.

Both of the mercury concentrations that crossed the ERL threshold of 0.15 µg/g were found at site 17 (Figure 12). M17 had a concentration of 0.2 µg/g, while L17 contained a concentration that was more than double the ERL limit at 0.369 µg/g (Table 8). No other sample contained a concentration close to the ERL threshold, as no other sample contained a mercury concentration above 0.1 µg/g. The average mercury concentration for lagoon sediments was 0.07 ± 0.02 µg/g compared with the average mercury concentration of 0.06 ± 0.01 µg/g in mangrove sediments. When mercury was normalized with aluminum, 7 of the 38 samples showed evidence of anthropogenic inputs, L17, M2, M10, M12-M14, and M17 (Figure 13). These were all samples located in western Mangrove Lagoon. The samples at site 17, like with copper, both showed evidence of anthropogenic inputs, as well as being the only samples with mercury concentrations that exceeded the ERL. Mercury was positively correlated with fine sediment (Spearman Rho = 0.364, p = 0.025), negatively correlated with sand (rho = -0.364, p = 0.025), and positively correlated with aluminum (rho = 655, p = 8.172e-06).

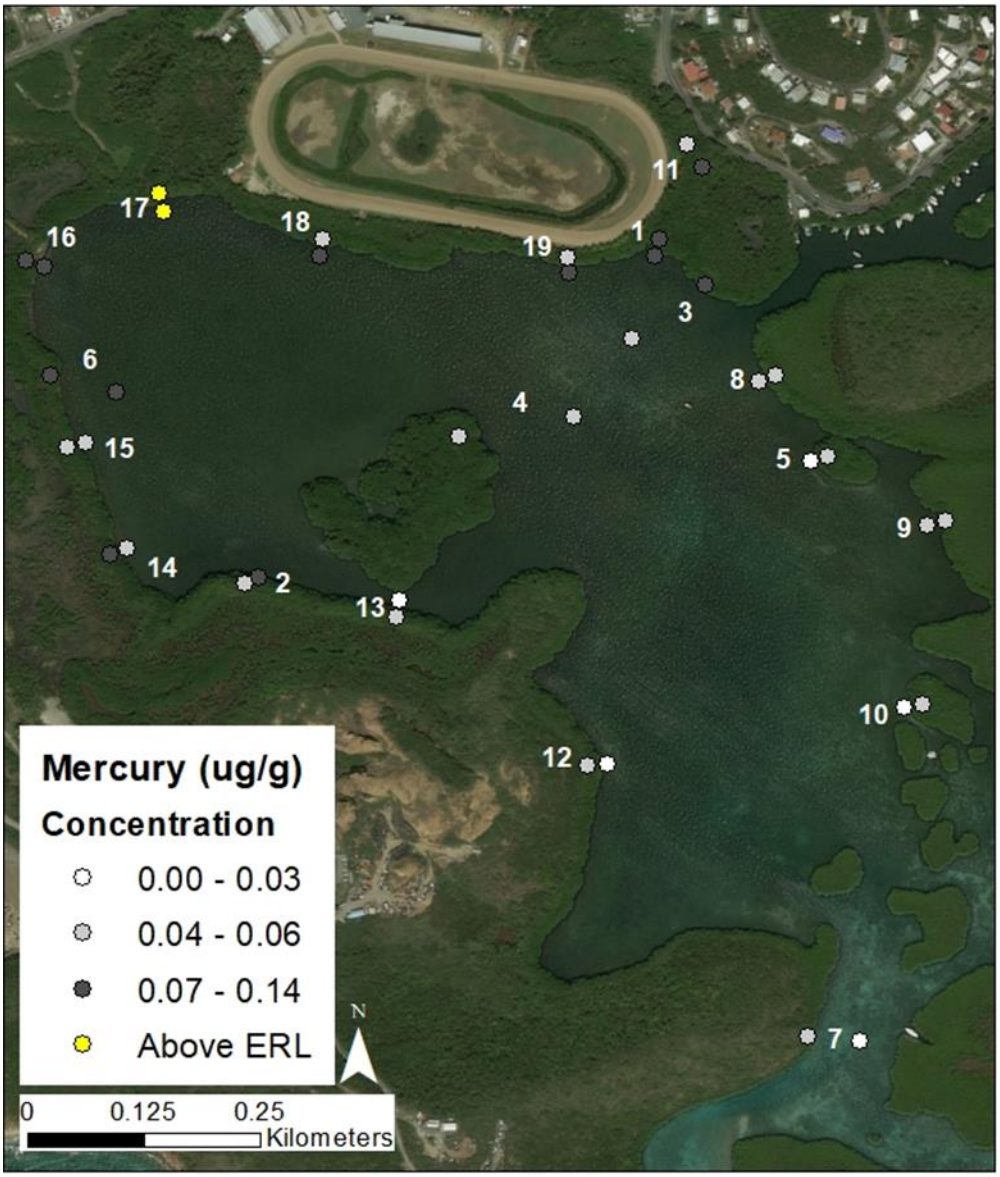

Figure 12: Mercury concentrations for the 2018 sampling of Mangrove Lagoon. Two sites were above the NOAA ERL concentration of 0.15 µg/g. Both of those were at site 17, the mangrove site had a mercury concentration of 0.202 µg/g and the lagoon site had a mercury concentration of 0.369 µg/g.

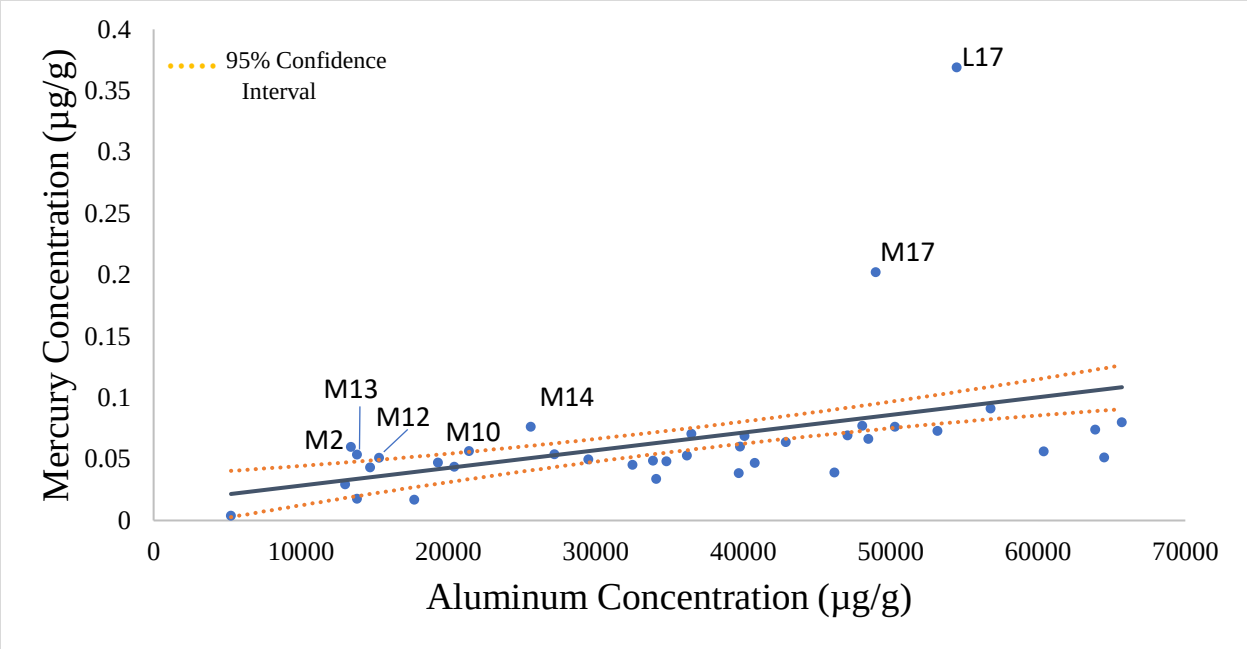

Figure 13: Relationship between sediment mercury and aluminum in mangrove and lagoon sediment, including sample confidence intervals. Samples above the confidence intervals suggest evidence of anthropogenic inputs.

L17 and L8 contained the two silver concentrations over the ERL concentration of 1 µg/g (Figure 14). L8 had a silver concentration of 1 µg/g, while L17 contained a concentration almost triple the ERL at 3 µg/g (Table 8). No mangrove site exceeded the ERL threshold for silver, though the two highest concentrations in the mangroves were also located at M17 and M8. These sites were located on opposite sides of Mangrove Lagoon. Site 8 on the eastern edge and site 17 on the northwestern edge. These were also the four samples that when normalized to aluminum were shown to have evidence of anthropogenic inputs (Figure 15). The average silver concentration for lagoon sediments was 0.34 ± 0.16 µg/g while mangrove sediments had an average concentration of 0.13 ± 0.03 µg/g. Silver was positively correlated with fine sediment (Spearman Rho = 0.357, p = 0.028), negatively correlated with sand (rho = -0.357, p = 0.028), and positively correlated with aluminum (rho = 0.703, p = 8.483e-07).

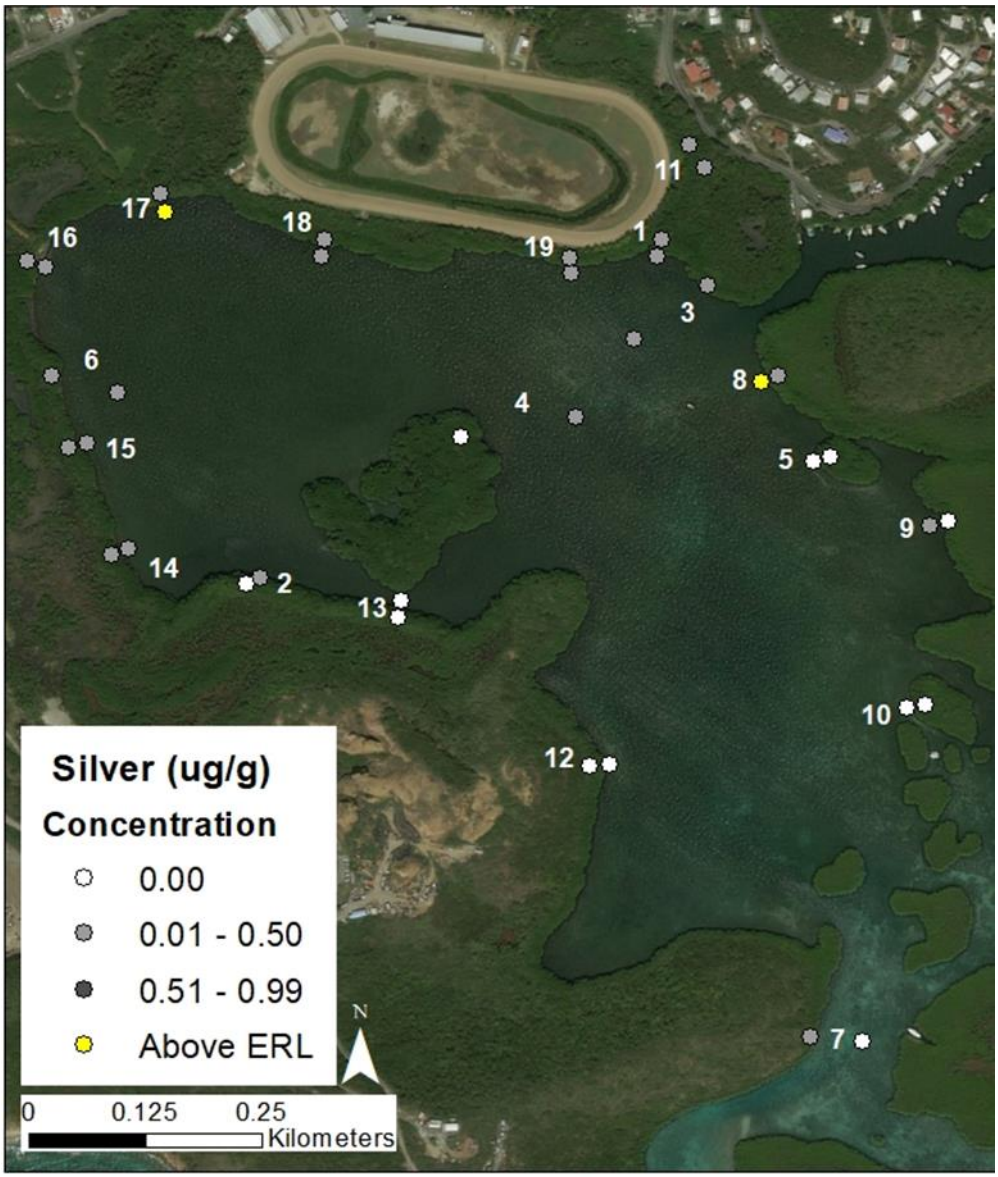

Figure 14: Silver concentrations for the 2018 sampling of Mangrove Lagoon. Two sites were above the NOAA ERL concentration of 1.0 µg/g. Both sites were in the lagoon. L17 had a silver concentration of 2.97 µg/g and L8 had a silver concentration of 1.31 µg/g.

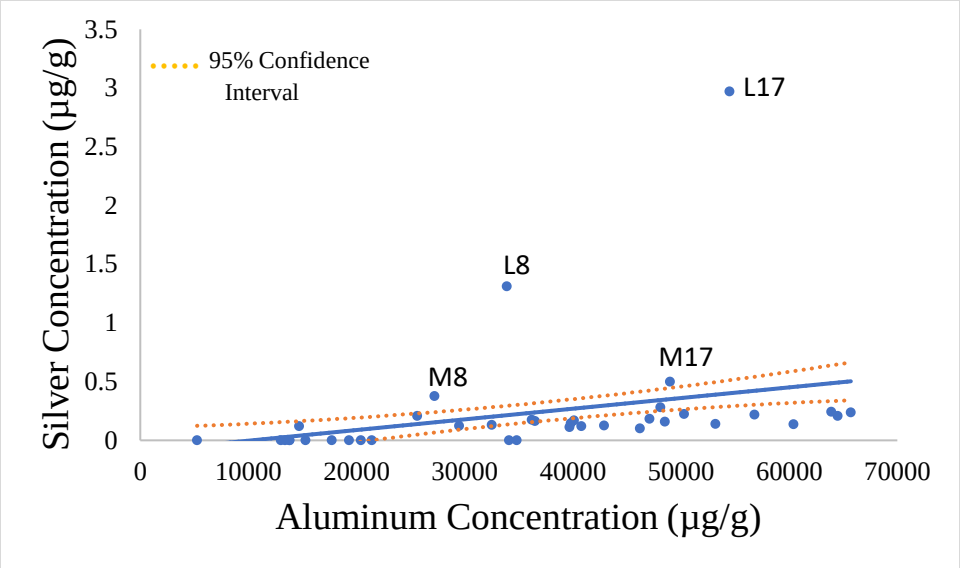

Figure 15: Relationship between sediment silver and aluminum in mangrove and lagoon sediment, including sample confidence intervals. Samples above the confidence intervals suggest evidence of anthropogenic inputs.

Site seventeen contained the most metals that measured above the ERL (Table 8). Copper, arsenic, zinc, silver, and mercury were all above the ERL at L17. No other lagoon site contained more than two metals above respective ERL thresholds. M17 contained four metals over the ERL limit: copper, arsenic, zinc, and mercury. M15, with three metals over the ERL limit, was the only other site to contain more than two metals over the ERL limit for mangrove sites. M15 was the only site across both lagoon and mangrove sediments to have a metal over the ERM (zinc, 684 µg/g, which is more than 1.5 times the ERM concentration). For both mangrove and lagoon samples combined, site 17 contained the most metals over the ERL with nine, followed by site 15 with five, and sites 8 and 11 with four each (Figure 16).

Only six metals showed significant differences in mean or median metal concentrations by sediment type, while the other ten showed no significant differences. Silver ($V = 21$, $p = 0.029$), cadmium ($V = 3$, $p = 0.002$), nickel ($V = 19$, $p = 0.001$), and iron ($V = 36$, $p = 0.016$), had significantly greater median concentrations in the lagoon sediments compared to mangrove sediments. Aluminum ($df = 18$, $t = -3.03$, $p = 0.007$) was shown to have a significantly greater mean concentration in lagoon sediments. Antimony ($V = 180$, $p = 0.0002$) was the only metal to have a significantly greater median in mangrove compared to lagoon sediment.

TBT:

Mangrove sediments did not contain any TBT concentrations above the detection limit. The average lagoon TBT concentration was 6±6 ng Sn/g (Figure 16). The median TBT concentration for mangrove and lagoon sediments were both 0 ng Sn/g. M1 contained the highest dibutyltin and monobutyltin concentration among mangrove sediments at 16 ng Sn/g and 30 ng Sn/g respectively, while L17 contained the greatest TBT, dibutyltin, and monobutyltin concentrations across all samples (Table 9). L17 contained the greatest TBT concentration at 115 ng Sn/g. The median TBT concentrations were not significantly different between mangrove and lagoon sediments (V = 0, p = 0.1003).

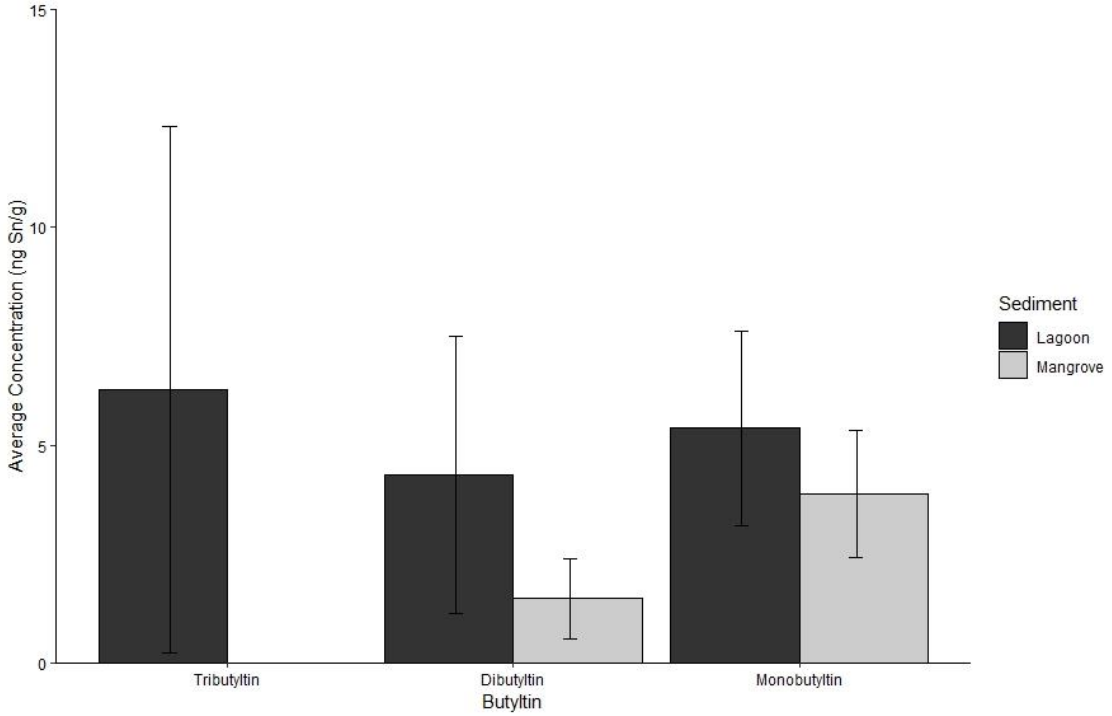

Figure 16: A side-by-side comparison of butyltin concentrations averaged across the 19 mangrove and 19 lagoon sites. There was a significant difference between the median TBT concentrations mangrove and lagoon sediments. A Wilcoxon's signed-ranks test showed that there was not significant difference in the median TBT concentration between the mangrove and lagoon sediments (p=0.1003)

Table 9: The butyltin concentrations across the 19 mangrove sites and the 19 lagoon sites. "<" represents values below the method detection limit.

Butyltin Concentrations (ng Sn/g)						
	Mangrove			Lagoon		
Sites	Tributyltin	Dibutyltin	Monobutyltin	Tributyltin	Dibutyltin	Monobutyltin
1	< 0.25	16	30	1	2	5
2	< 0.06	< 0.10	2	< 0.36	< 0.63	2
3	< 0.40	1	5	< 0.61	9	8
4	< 0.06	< 0.22	2	< 0.26	1	3
5	< 0.18	< 0.21	2	< 0.21	< 0.62	2
6	< 0.18	< 0.49	2	< 0.28	< 0.70	2
7	< 0.19	< 0.27	2	< 0.10	< 0.25	2
8	< 0.18	< 0.39	2	< 0.48	1	3
9	< 0.19	< 0.40	2	< 0.23	< 0.67	2
10	< 0.08	< 0.27	2	< 0.14	< 0.34	1
11	< 0.32	2	5	< 0.34	3	9
12	< 0.06	< 0.15	1	< 0.09	< 0.25	1
13	< 0.05	< 0.33	1	< 0.04	< 0.20	2
14	< 0.10	< 0.40	3	< 0.56	< 0.91	4
15	< 0.15	< 0.45	2	2	1	4
16	< 0.27	< 0.65	2	1	1	3
17	< 0.44	8	5	115	61	44
18	< 0.06	< 0.33	2	< 0.32	1	3
19	< 0.29	< 0.70	4	< 0.20	< 0.70	2

Chapter 4: Discussion

Contaminant State of Mangrove Lagoon

Copper, arsenic, and zinc were the only metals that were over their respective ERL limits in both 2010-2011 and 2018. No other metals were over the ERL in 2010-2011. In 2018, copper, arsenic, and zinc were also the metals with the most samples over the ERL threshold in 2018. These results show that these metals are historically and presently, the most problematic metals in Mangrove Lagoon, suggesting long-term and widespread contamination, with the potential to result in cumulative toxic impacts to the surrounding environment and organisms.

Though these metals are the most problematic, they are mostly concentrated in the western and northern portions of Mangrove Lagoon. The only samples that were never over the ERL limit in 2018 were samples, L5, L7, L10, and sites 12 and 13. This suggests that southern Mangrove Lagoon is less polluted then the northern portion of Mangrove Lagoon (Figure 17). This pattern was also followed in the historical and spatial comparisons. When comparing the metal concentrations at L1-L7 in 2010-2011 and 2018, L7 routinely contained the lowest contaminant concentrations and was the only sample that never crossed an ERL threshold in either 2010-2011 or 2018. This was the also the case for PCBs, PAHs, and DDT. L5, the sample located the furthest from the northern and western portions of Mangrove Lagoon after L7, was generally the sample with the second lowest contaminant concentrations. This was the case in the wider 2018 sampling as well, as the southern samples listed above tended to contain the lowest metal concentrations compared to other sites. Most samples that exceeded ERL thresholds in 2018, were located in the northern and western portions of Mangrove Lagoon. High levels of copper were found throughout the northern portion of Mangrove Lagoon. The only samples not containing copper concentrations over the ERL threshold for this metal, were sites 5, 10, 12, 13, and L7, which are all located in the southern portion of Mangrove Lagoon. Arsenic does not show this pattern, which may relate back to how the source and pathway for arsenic could be different than that of copper and other metals, perhaps aerial deposition. The five samples that were over the ERL threshold for zinc in 2018, were located in the northern and western portions of Mangrove Lagoon. The two samples that were over the ERL for mercury were also present at site 17 in this northwestern region. Continuing with the major pattern of the other metals discussed, the southern sites tended to be those with the smallest concentrations of mercury (e.g., L13, L12, L10, and L7). Lastly, the two samples for silver were present in

the northern portion of Mangrove Lagoon at L17 and L8. The sites in the southern portion of Mangrove Lagoon did not contain any silver concentration, including L7, but also sites 5, 13, 12, and 10. This pattern suggests that there is a strong north-south contaminant gradient. This could be explained due do the lack of any known potential sources of contaminants in the southern portion of Mangrove Lagoon. This would mean that any contaminants present in southern samples were either transported there from the north, through sediment transport, through possible aerial transport, or due to possible deposition from the 2017 hurricanes.

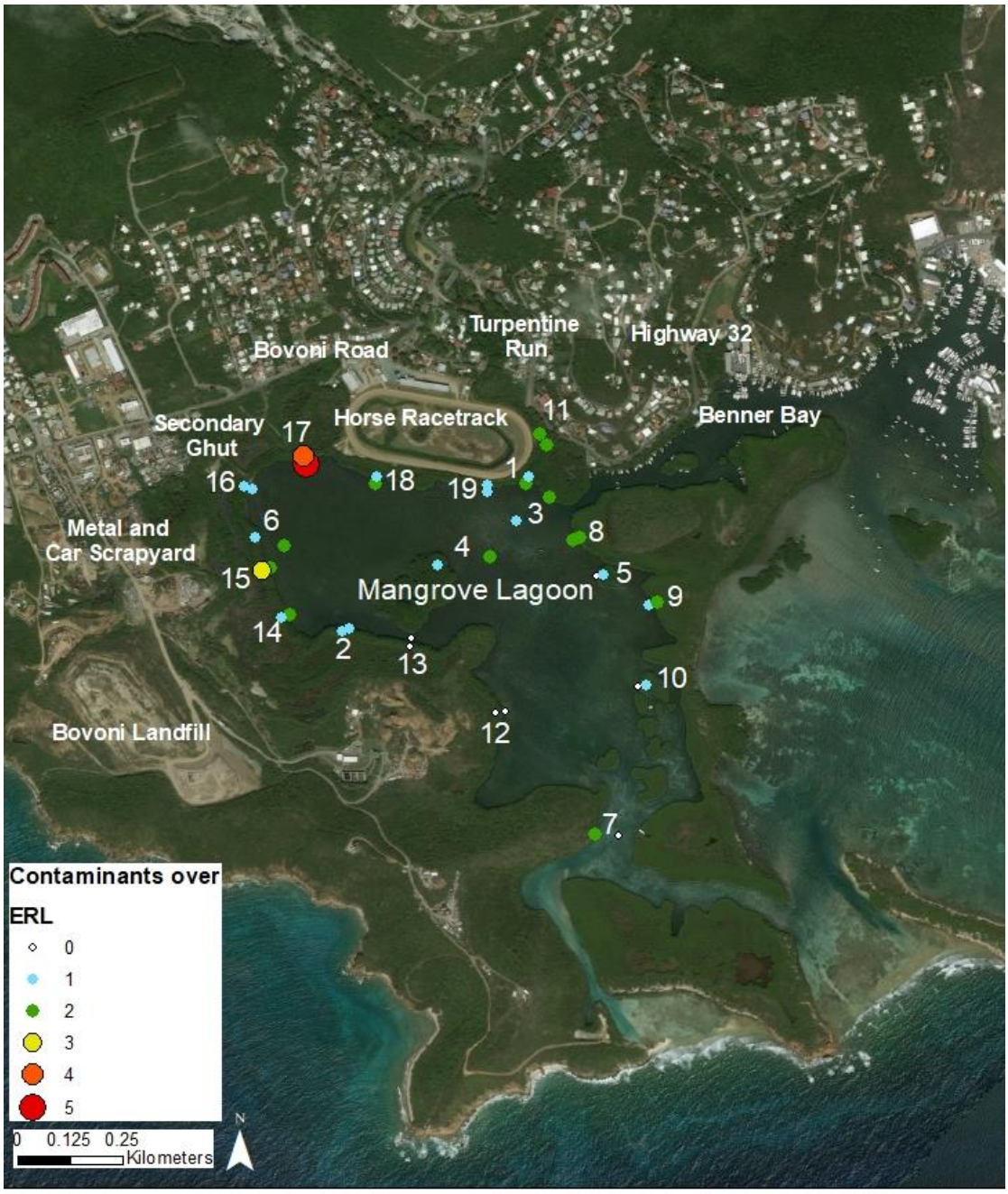

Figure 17: Map of 2018 samples showing the number of contaminants that were measured over the ERL limit.

Several potential pathways for copper were identified in this study. Turpentine Run, with run-off from residential areas throughout the Jersey Bay Watershed, is the most likely pathway for copper in samples L11 and M11, the two samples within Turpentine Run, as they both exceeded the ERL threshold (Figure 6). Inputs from Bovoni Landfill,

the car scrapyard located adjacent to site 15, the secondary ghut adjacent to site 16, and the re-discovered polluted site 17, are all also possible sources of copper, as all of the western sites in Mangrove Lagoon were above the ERL threshold for copper in 2018. Benner Bay may also be a source as suggested in Pait et al. (2016). Pait et al. (2016) noticed a possible positive gradient from Benner Bay toward Mangrove Lagoon for copper. Benner Bay has many marinas and copper is used as an antifoulant in bottom paint for boats. Site 16P from Hartwell et al. (2016) was located in the channel between Benner Bay and Mangrove Lagoon. This site recorded a copper concentration of 93 µg/g showing that sediment transport from Benner Bay could result in copper levels over the ERL at sites 8 and 9 from this study, though sediment transport pathways are unknown. M7 was also above the ERL with no clearly identifiable copper source.

Elevated levels of copper have been in found in Mangrove Lagoon, historically (Pait et al. 2014). L1-L6 were over the ERL limit for copper in 2010-2011 (Pait et al. 2014) and L1-L4 and L6 still exceeded the ERL in 2018. Based on the 2010 concentration of copper at L1 these data suggest that Turpentine Run has been a potential source for copper historically. The car scrapyard also seems to be an historical source of copper based on the concentration measured at L6. Benner Bay may also be an historical pollutant source as site 16P contained a copper concentration of 47 µg/g in 2011 (Pait et al. 2014) and increased to a concentration of 93 µg/g by 2013 (Hartwell et al. 2016). It is important to point out that some of the samples over the ERL limit in 2018 (L2, L4, and L6) all decreased in copper concentration since 2010-2011, showing that these sites may be slowly improving, though L1 and L3 increased in copper concentration during those same years. This increase at L1 and L3 may be due to inputs from Turpentine Run, maybe due to the hurricanes or continued input over the past 8-year period.

In comparison with national NOAA NST data (n = 4,549 samples), the average concentration for copper in mangrove and lagoon sediments in this study, were both above the NST copper median of 18.2 µg/g, though they were both below the NST average concentration of 63 µg/g and the NST 85th percentile of 70.15 µg/g. Overall, 35 of the 38 samples were over the NST median, 10 of the 38 were over the NST average, and 7 of the 38 were over the NST 85th percentile. This reveals that in comparison to national data, the copper concentrations in Mangrove Lagoon are greater; specifically, they are greater than the median of the recorded copper concentrations while most were below average.

Acevedo-Figueroa et al. (2006) measured metals in the sediments of the San José Lagoon in Puerto Rico, which is part of the San Juan Bay Estuary System, a US EPA-designated estuary system of national importance, established in 1992 (USEPA 2000). The average (± standard deviation) for copper (105±47 µg/g) was greater than the average concentrations contained in Mangrove Lagoon. In comparison to Puerto Rico NST data (n = 207 samples), the copper concentrations in Mangrove Lagoon were higher. The average concentration of copper in mangrove and lagoon sediments were both above the Puerto Rico NST median of 10.6 µg/g and the Puerto Rico NST average of 25.50 µg/g. They were both below the Puerto Rico NST 85th percentile of 57.86 µg/g. Overall, 37 of the 38 samples were over the Puerto Rico NST median, 32 of the 38 were at or above the Puerto Rico NST average, and 24 of the 38 were at or over the Puerto Rico NST 85th percentile.

In comparison to other studies in STEER, Hartwell et al. (2016) found site 16P, the sample located in the channel between Mangrove Lagoon and Benner Bay, had a greater copper concentration (93 µg/g) than 37 other samples in their study. Across the ten samples collected in Benner Bay, the copper average (± SE) was far greater than the copper averages for mangrove and lagoon sediments in Mangrove Lagoon from this study; 249 ± 137 µg/g vs. 48 ± 4 µg/g and 50 ± 7 µg/g, respectively. This reveals that if sediment and contaminant transport does occur from Benner Bay to Mangrove Lagoon, that concentrations are potentially high enough to result in samples reaching or exceeding the ERL threshold within Mangrove Lagoon.

Several potential pathways for arsenic were identified in this study. Samples above the ERL threshold in the eastern portion of the study area were mangrove samples. The elevated arsenic samples were located on Bovoni Cay, which is not connected to land, so there is no obvious pollutant source. A possible arsenic source for these samples could be the inlet from Benner Bay. Site 16P from Hartwell et al. (2016) contained an arsenic concentration of 11 µg/g, which was above the ERL of 8.2 µg/g. A combination of sediment transport and possible heavy wave action from the 2017 hurricanes, may account for ERL concentrations in mangrove sediments exceeding those of lagoon sediments, though the grain sizes did not differ between paired samples at these sites. Another possibility may arise from the amount of hurricane debris that was taken to Bovoni Landfill and other temporary areas after Hurricanes Irma and Maria. Much of this was wood debris which had various levels of sorting applied to it, before being

chipped for mulch. Pressure-treated wood contributed to these debris piles and pressure-treated wood is known to contain both arsenic and copper (Stilwell et al. 1997). It is possible that airborne arsenic settled at these sites from this source, though additional investigation would be needed to confirm this hypothesis. Chromated copper arsenate (CCA), which contains 34% inorganic arsenic, is a pesticide and preservative that has been used to pressure treat lumber beginning in the 1940s (Chen and Olsen 2016). It was banned from industrial use and construction by the EPA in 2003 though risk remains from products produced before 2003; it is possible that material that was mulched following Hurricanes Irma and Maria, released inorganic arsenic into the air, groundwater, or environment entering the lagoon via overland flow. Weather patterns move east to west across this part of STEER, which may explain the patterns observed. Another feasible option for the elevated levels of arsenic along the eastern edge of Mangrove Lagoon in mangrove sediments, is the breakdown of washed up hurricane debris from September 2017 to July 2018 when these samples were collected. The western sites contained more lagoon samples over the ERL then mangrove samples. L14, L15, and L6 were all over the ERL. Site 15 and site 17 were the only sites where both samples exceeded the ERL, showing that these locations specifically may be sources for arsenic. Site 15 and 17 were also sites in which both samples were over the copper ERL limit. Once again, M7 was above the ERL with no clear source of arsenic. Turpentine Run is most likely not a source for arsenic as site 11 had some of the lowest measured levels of arsenic and they were well below the ERL threshold (Figure 8). Sites 1, 16, 2, and 13 did not have elevated levels of arsenic.

Like copper, arsenic has been found at potentially toxic concentrations in Mangrove Lagoon, historically. L2, L4, and L6 were over the ERL limit for copper in 2010-2011 (Pait et al. 2014) and L4 and L6 were still over the ERL in 2018. L4 is in the middle of Mangrove Lagoon, and based on L11, Turpentine Run is probably not a source of arsenic for L4. This points to the main source being from Benner Bay sediment transport. Site 16P only recorded an arsenic concentration of 8 µg/g in 2011 (Pait et al. 2014), which was just below the ERL limit though the arsenic concentration at 16P increased to 11 µg/g by 2013 (Hartwell et al. 2016). Between 2010-2011 and 2018 L6 dropped below the ERL limit and L2 and L4, though they were still over the ERL limit in 2018, also declined during that period. Only L7 and L3 did not decline from 2010-2011. Overall, arsenic concentrations were lower in 2018 than in 2010-2011, showing that concentrations of arsenic in Mangrove Lagoon are declining and conditions, improving.

In comparison with national NOAA NST data (n = 4,377 samples), the average arsenic concentrations for mangrove and lagoon sediments were above the NST median of 7.02 µg/g, though they were both below the NST average of 8.34 µg/g and NST 85th percentile for arsenic at 13.6 µg/g. Overall, 35 of the 38 samples exceeded the NST median, 10 of the 38 were at or above the NST average, and 7 of the 38 were at or over the NST 85th percentile.

In comparison to other regional studies, Mangrove Lagoon does not have the highest arsenic concentrations recorded for this area. Acevedo-Figueroa et al. (2006) found an arsenic concentration of 13 ± 5 µg/g which was higher than the average arsenic concentrations for both mangrove and lagoon sediments in this study. In comparison with Puerto Rico NST data (n = 207 samples), the average arsenic concentration in mangrove and lagoon sediment were both above the median of 4.2 µg/g and the Puerto Rico NST average of 5.98 µg/g. They were both below the Puerto Rico NST 85th percentile of 12.06 µg/g. Overall, 31 of the 38 samples were over the Puerto Rico NST median, 23 of the 38 were above the Puerto Rico NST average, and only 4 of the 38 were over the Puerto Rico NST 85th percentile. This reveals that in comparison to regional data, most arsenic concentrations in Mangrove Lagoon are greater than the median and average reported for this region.

In Hartwell et al. (2016), site 16P had a concentration of 11 µg/g which was greater than 33 samples in this study. However, the average arsenic concentration in Benner Bay was 8 ± 1 µg/g, which was comparable with both mangrove and lagoon arsenic averages (Hartwell et al. 2016). This shows that the adjacent Benner Bay contained equal concentrations of arsenic based on the similar arsenic average values present in Benner Bay and Mangrove Lagoon.

Several potential pathways for zinc were identified in this study. One pathway for zinc seems to be Turpentine Run as site 11 and L1 were both above the ERL limit for zinc and site 3 and M1 also had elevated concentrations of zinc. Both samples at site 17 were also above the ERL, suggesting that this site might not only be near a source for zinc, but also copper and arsenic as that site is the only site throughout Mangrove Lagoon in which both mangrove and lagoon samples were above the ERL for all three metals. The highest concentration of zinc was found at M15. This concentration (684 µg/g) is the highest zinc concentration yet recorded in STEER. Pait et al. (2014) found one site at 392 µg/g and Hartwell et al. (2016) revealed another site at 574 µg/g; both sites were in Benner Bay. Zinc was also

the only metal to exceed the NST ERM (410 µg/g). Current or past activities at the car scrapyard, are likely sources for this high zinc concentration, as zinc is heavily used in the galvanization of steel and iron. Other possible sources include the breakdown of car tires, which, if improperly disposed of, could lead to elevated zinc concentrations. Interestingly, Bovoni Landfill's Consent Decree lists improper disposal of tires as one of the violations leading to the consent decree action.

Zinc, like copper and arsenic, has been shown historically, to be present in Mangrove Lagoon in toxic concentrations. In 2010-2011, L2-L4 exceeded the ERL limit in Mangrove Lagoon (Pait et al 2014). However, unlike copper and arsenic, no sample that was above the ERL in 2010-2011 was above the ERL in 2018. In 2018, L1 was the only sample that exceeded the ERL threshold and this concentration was greater than any concentration measured in Mangrove Lagoon in 2010-2011. This may provide evidence that Turpentine Run has only recently (since 2010-2011) become a pathway for zinc, as the increase at L1 is mostly likely due to inputs from Turpentine Run. Following a similar pattern as copper and arsenic concentrations, L2-L6 declined in zinc concentrations from 2010-2011 to 2018. L7 only increased marginally from 2010 to 2018.

In comparison with national NOAA NST data (n = 4,452 samples), the average zinc concentrations for mangrove and lagoon sediments were above the current NST median of 73 µg/g. The average zinc concentrations in lagoon sediments were below the NST average of 100.06 µg/g and the NST 85th percentile of 172 µg/g. The average zinc concentration in mangrove sediments was below the NST 85th percentile, but above the NST zinc average. Overall, 22/38 samples were over the national NS&T median, 15/38 samples were over the NST average, and only 4 samples were over the NST 85th percentile. Most samples were greater than the national NST median and many were greater than the average. On a national level, the zinc concentrations in Mangrove Lagoon can be considered high.

In comparison with the Puerto Rico NST data (n = 207 samples), the average zinc concentrations for mangrove and lagoon sediments were greater than the median (21 µg/g), average (38.28 µg/g), and 85th percentile (90.7 µg/g). Overall, 37/38 samples were greater than the Puerto Rico NST median, 32/38 samples were greater than the average, and 16/38 samples were greater than the 85th percentile.

In 2013, Hartwell et al. (2016) found that site 16P was comparable to metal concentrations measured in Mangrove Lagoon (Zn was measured at 118 µg/g, for example). However, the site closet to the marinas in Benner Bay, BB-2, contained concentrations far greater than all samples in Mangrove Lagoon except for M15, which contained the greatest zinc concentration in STEER (574 µg/g). At 143 ± 50 µg/g the average zinc concentration in Hartwell et al. (2016) was greater than the averages for Mangrove Lagoon in this study, though it was within the standard error. So, like arsenic, the zinc concentrations between Mangrove Lagoon and Benner Bay are comparable and both are very high when compared to the Puerto Rico NST data.

Two samples in 2018 contained mercury concentrations over the ERL of 0.15 µg/g (Figure 12). Both samples were at site 17, showing that this site is most likely located near a source for mercury. Both mercury concentrations are the highest yet found in Mangrove Lagoon and among the highest in STEER. Only site BB2 in Hartwell et al. (2016) is greater at 0.410 µg/g. Comparing data from 2010-11 to 2018, mercury levels have slightly declined suggesting site improvement (L2-L6 declined in mercury concentration from 2010-2011 to 2018, while L1 and L7 were the same for 2010-2011 and 2018). This shows that like copper, arsenic, and zinc, most of the sites measured in 2010-2011 contained slightly lower concentrations when measured again in 2018.

In comparison with national NST data (n = 4149 samples), the average mercury concentration for mangrove sediment in Mangrove Lagoon was equal to the current NST median of 0.06 µg/g, while the average concentration in lagoon sediments was above the median. The NST average (0.20 µg/g) and 85th percentile (0.33 µg/g) were both greater than the mercury average for mangrove and lagoon sediments. L17 at 0.37 µg/g was above the NST 85th percentile of 0.33 µg/g. Overall, 15/38 samples were over the NST median, while only two were over the average and one over the 85th percentile. So, on the national level, mercury levels in Mangrove Lagoon are not very high.

When compared to Puerto Rico NST data (n = 207 samples), the average mercury concentrations in Mangrove Lagoon are high, however. The lagoon and mangrove mercury concentration averages were above the Puerto Rico NST median (0.01 µg/g) and average (0.03 µg/g). In addition, the lagoon average was equal to the Puerto Rico NST 85th percentile concentration of (0.07 µg/g). Overall, 37/38 samples were over the median, 35/39 samples were over the average, and 10/38 samples were over the 85th percentile.

In Hartwell et al. (2016), site 16P was comparable to concentrations of mercury found in mangrove sediments from this study (16P = 0.061 µg/g). However, the site closest to the marinas in Benner Bay, BB-2, contained concentrations greater than those in Mangrove Lagoon at 0.410 µg/g. The mean mercury concentration in Hartwell et al. (2016) at 0.10 ± 0.03 µg/g was greater than the average concentrations in Mangrove Lagoon in this study, though they were all are within the standard error.

Two samples in 2018 contained silver concentrations over the ERL of 1 µg/g (Figure 14). Silver was unusual, compared to other contaminants, as the two samples over the ERL limit were located on opposite sides of Mangrove Lagoon. L17 contained a concentration of silver that was almost three times the silver ERL limit. On the eastern side of Mangrove Lagoon, L8 was also above the ERL threshold for silver. This is interesting as samples L1-L7 and site 16P did not contain a silver concentration at all in 2010-2011 (Pait et al. 2014). In 2018, L1-L4, and L6 did contain small amounts of silver, but all at levels below the ERL concentration. As recently as 2013, silver was not present at site 16P (Hartwell et al. 2016). This would point to Benner Bay not being a pathway for silver, and with only low concentrations of silver found at site 11, Turpentine Run is probably not a viable pathway either. There is no other clear source for silver.

When compared with the national NST values (n = 4,331 samples), the average silver concentrations for mangrove and lagoon sediments in this study, were greater than the median of 0.13 µg/g, though they were both below the average NST concentration of 0.42 µg/g and the NST 85th percentile concentration of 0.67 µg/g. The two samples that measured over the ERL limit for silver were over the NST 85th percentile concentration. Overall, 20/38 samples were over the median, three samples were over the average, and two samples were over the 85th percentile. So, on a national level, most silver concentrations in Mangrove Lagoon would not be considered very high. When compared to the Puerto Rico NST values (n = 207 samples) the average silver concentrations for mangrove and lagoon sediments were greater than the Puerto Rico median (0.07 µg/g), average (0.07 µg/g), and 85th percentile (0.12 µg/g). Overall, 26/38 were over the median and average, and 25/38 were over the Puerto Rico NST 85th percentile. This reveals that the silver concentrations in Mangrove Lagoon are high when compared to Puerto Rico NST data. Unlike the previous metals thus far discussed, the average silver concentrations in mangrove and lagoon sediments

were greater than the average silver concentration contained in Hartwell et al. (2016) at 0.04 ± 0.03 µg/g. This shows that the silver concentrations measured in Mangrove Lagoon are the highest ever recorded in STEER, unlike copper, arsenic, and zinc which were either comparable to Benner Bay concentrations or lower.

The TBT averages for lagoon sediments were over the current NST (n = 2,021 samples) median of 0.14 ng Sn/g, the NST average of 3.98 ng Sn/g and the NST 85th percentile of 2.80 ng Sn/g, though the average TBT concentration in lagoon sediment was driven by L17. Overall, only 4/38 samples were over the NST median. Only L17, with a TBT concentration of 114.87 ng Sn/g, was over the average and the 85th percentile. At 114.87 ng Sn/g, L17 is the highest concentration yet recorded in Mangrove Lagoon and is the 13th highest TBT detection of the NST program. Outside of L17 the TBT concentrations measured in Mangrove Lagoon would be considered low on a national level. When compared to the Puerto Rico NST values (n = 205 samples) the average TBT concentration for lagoon sediments were greater than the median of 0 ng Sn/g, the average concentration of 0.54 ng Sn/g, and the 85th percentile of 0.13 ng Sn/g. Only five TBT concentrations in STEER have been greater than the concentration measured at L17; site BB-2 had a TBT concentration of 248 ng Sn/g (Pait et al. 2014) and Hartwell et al. (2016) measured TBT concentrations of 1,102 ng Sn/g (re-sampled BB-2), 993 ng Sn/g, 217 ng Sn/g and 134 ng Sn/g at various locations in Benner Bay. The average TBT concentration found in Hartwell et al. (2016) was 236 ± 123 µg/g; this concentration was extremely high when compared to regional data. This shows that the marina dominated Benner Bay contains TBT concentrations well above 1 ng Sn/g. This area is connected to Mangrove Lagoon by a small channel thereby being a potential source of TBT contamination to Mangrove Lagoon. This is unlikely however due to sites 3, 4, and 8 all containing samples below 1 ng Sn/g. L17 is also located on the opposite side of Mangrove Lagoon from Benner Bay. The high level of TBT at L17 may be related to the elevated levels of metals located at this site or it may suggest point-source contamination at the site (e.g., a decomposing derelict boat, of which there is one near this site, pers. obs.). The relative proportion of TBT at L17 relative to mono- and di- butyltin suggests recent deposition at this site.

TBT was also measured in 2010-2011 and showed low concentrations then. There was a decline in TBT concentration from 2010-2011 to 2018 at L1-L5. In 2010-2011, there were four samples over 1 ng Sn/g and by 2018 only L1 was above that concentration. This follows the pattern set by the metals; most samples declined in

contaminant concentration from 2010-2011 to 2018. The pattern of TBT concentrations at L1-L7 in 2010-2011 suggested recent deposition due to TBT concentrations being relatively high in proportion to mono- and di- butyltin levels. However, the lack of TBT concentrations of L1-L7 suggest that TBT is not a problem to Mangrove Lagoon over most of the area sampled. Though TBT is illegal in the USVI, it is still legal in the BVI (Titley-O'Neal et al. 2011) and as a result of heavy boat traffic between the two nations, it is possible that TBT may be entering this system via that pathway.

Site 17 was the most polluted site in 2018. L17 was the only sample where all five metals that were measured in Mangrove Lagoon were over their ERL limit (Table 7). M17 contained four of the five metals that were measured in Mangrove Lagoon over the ERL. This reveals that this site is likely near a source of pollution to Mangrove Lagoon that was not known in Pait et al. (2014). L17 also contained the highest TBT concentration yet found in Mangrove Lagoon: it was just over 58 times greater than the next highest concentration of 2 ng Sn/g. Site 17 is adjacent to the now abandoned Nadir wastewater treatment station that was constructed in 1973 (US EPA 1984). In 1984, the U.S. Environmental Protection Agency released the Final Environmental Impact Statement (FEIS) of the impact of updating the wastewater facilities in the Turpentine Run area. This report revealed that the Nadir treatment station discharged poor quality effluent into Mangrove Lagoon during this time. This FEIS recommended that the plan be approved as it would close the Nadir treatment station and lead to the closure of four other stations that all led to contamination entering Mangrove Lagoon at that time. The contaminants levels at site 17 reveal that though now closed, this treatment station is still potentially impacting the health of Mangrove Lagoon. This site is also close to Bovoni Road and two secondary ghuts (Figure 1). These two potential pathways may explain the elevated contaminants into this location. The hurricanes may have also resuspended sediments in the lagoon and/or released sediments that were sedentary in the mangroves. These sediments may have already been contaminated before the hurricanes and were just disturbed and lead to the heightened levels of contaminants found at site 17. This site is not well understood and needs to be investigated further to further pinpoint where these high levels of contaminants originate. Site 17 needs to be investigated in the future to pinpoint where these high levels of contaminants originate from.

Overall several metals are present in potentially toxic concentrations in Mangrove Lagoon. Based on the historical sampling of L1-L7, however, concentrations of contaminants in Mangrove Lagoon may be on the decline, though not significantly, due to the decrease in average concentration and number of samples above the ERL limit for most metals (Table 9).

Total DDT, along with total PAHs and total PCBs, were only measured at L1-L7 in 2018. For total DDT, three samples (L1, L2, and L5) were all above the ERL limit at 23 ng/g, 12 ng/g and 3 ng/g respectively, in 2018. However, a large majority of the total DDT was made up of 4,4'-DDD which shows that parent compounds have degraded, and that this DDT is likely old. L3, L6, and L7 had total DDT concentrations of zero in 2018. No sample in 2010-2011, was above the ERL. However, L1-L2 and L4-L5 increased in their total DDT concentrations from 2010-2011 to 2018, much like silver. And, as no site in 2010-2011 was greater than 1 ng/g this increase of L1, L2, and L5 may reflect the release of DDT from the watershed. Hurricanes Irma and Maria may have released sediment containing DDT from past agricultural uses into Turpentine Run. L1 is in the direct line of the Turpentine Run outflow. Turpentine Run is likely not the source of DDT at L5 due to its distance from that potential pathway. Benner Bay may be an option, though this is unlikely, as site 16P only contained a total DDT concentration of 0.082 ng/g in 2011 (Pait et al. 2014). Another option is the resuspension and redistribution of DDT within Mangrove Lagoon, as a result of the hurricanes. This hypothesis is supported by the spatial distribution of samples above the DDT ERL threshold, With L1, L2, and L5 being over the ERL in different areas of Mangrove Lagoon.

For total PAH's, no samples in 2010-2011 and 2018 neared the PAH ERL of 4,022 ng/g. The highest PAH concentration found in 2018 was 1207 ng/g at L1. PAHs are associated with oils and other fossil fuels, as well as organic materials like decaying vegetation, wood, and trash. Low concentrations of PAH indicate low impacts of oil and fossil fuels on Mangrove Lagoon. Perylene is an indicator of residue from natural decaying vegetation (NRC 1985). In 2018 Perylene was 2% of the total PAHs, which shows that natural origins of PAHs, such as decayed vegetation, are not large sources of PAHs in Mangrove Lagoon. It should be noted that L1 had the highest total PAH concentration in 2018 and second highest in 2010. This site is directly adjacent to Turpentine Run which drains over half of the Jersey Bay Watershed (Ferguson 2013). So, oil from road runoff or natural sources are potentially channeled directly into this site. L3, which is the next closest to Turpentine Run had the highest PAH concentration

in 2010 and the second highest in 2018. Lastly, L4 which is third in distance from Turpentine Run contained the third highest total PAH concentration across both years. This all points to Turpentine Run being a potential source for the low concentration PAH's that do enter Mangrove Lagoon. L2-L6 declined in PAH concentrations from 2010-2011 to 2018. Only L1 and L7 increased in PAH concentration from 2010-2011 to 2018.

The ratios of phenanthrene-to-anthracene (P/A) and fluoranthene-to-pyrene (F/P) have been used to assess the contributions of pyrogenic (combustion) and petrogenic (uncombusted) sources of PAHs (Budzinski et al. 1997 as cited in Pait et al. 2016). A P/A ratio less than 10 and a F/P ratio greater than one, indicate more of a pyrogenic source. In Pait et al. (2014), all Mangrove Lagoon sites had P/A ratios less than ten. This same trend carried over to the 2018 sampling. In 2018, the P/A ratio for all of the sites decreased from those measured in 2010-2011, except for L7, which increased from 0 to 7 but still indicated more pyrogenic sources. The F/P ratio in Pait et al. (2014) was less clear as several samples were above or close to 1. This indicated pyrogenic sources as shown by the P/A ratio, but L3 (0.70), L4 (0.83) and L5 (0.94) had ratios indicating possible petrogenic contributions. This pattern seems to have continued to present. By 2018, samples L1-L6 all contained F/P ratios below 0.80. This points to Mangrove Lagoon likely receiving PAH contributions from both combusted fossil fuels and uncombusted fuels.

Lastly, for PCBs, no samples in 2010-2011 or 2018 neared the PCB ERL of 22.7 ng/g. L1 was close in 2010-2011, but by 2018 the concentration had declined dramatically. Only L3 increased in PCB concentration from 2010-2011 to 2018, L1-L2 and L4-L7 declined from 2010-2011 to 2018. This pattern follows most contaminants that were measured in Pait et al (2014). Most samples measured in Pait et al. (2014) declined in concentration from 2010-2011 to 2018.

This analysis shows that historically PAHs and PCBs have not been recorded at dangerous levels in Mangrove Lagoon according to NST guidelines. Despite a 7-8-year change and experiencing two hurricanes in 2017, PCBs and PAHs do not seem to be a threat to Mangrove Lagoon. DDT concentrations were recorded at concentrations that exceeded ERL thresholds in three samples in 2018, but those concentrations were made up of mostly degraded products, indicating the source of the DDT may be old. These findings justify more sampling effort to better document patterns of DDT within Mangrove Lagoon in the future.

2010-2011 – 2018: Hurricane Effects

The overall sediment composition did not change between 2010-2011 and 2018, though individual sample locations did change, suggesting that Mangrove Lagoon was massively re-worked as the result of Hurricanes Irma and Maria or other large disturbance events that could cause similar morphological changes. This lack of overall change in sediment composition may also suggest that the grain size may not have affected the overall concentrations of metals between years in Mangrove Lagoon, though they likely affected the concentrations at individual locations. Despite the lack of overall change, there were many individual site-specific changes in grain size which likely account for individual changes in copper, arsenic and zinc concentrations, since fine sediments and concentrations of copper and zinc were highly correlated. L1 had the largest increase in fine sediment among all samples and this increase corresponds to the largest increase in copper and zinc concentrations among samples (Table 1 & Table 2). Likewise, L2 and L4 were the samples that had the greatest decrease in fine sediment from 2010-2011 to 2018, which corresponds to the largest decreases in copper and zinc concentrations observed in this study. L6 experienced the third largest decrease in fine sediment and likewise the copper and zinc concentrations at L6 also experienced the third largest decline. L3 and L7 experienced the least amount of sediment change and seemed to have the least amount of changes among copper and zinc concentrations. These patterns point to a strong relationship between copper, zinc, and fine sediment, which was shown for the wider sampling in Mangrove Lagoon during 2018. The relationship between fine sediment and arsenic was less clear. Arsenic was not correlated with fine sediment, though the two samples that experienced the greatest declines in arsenic, L2 and L6, were also samples that lost a large amount of fine sediment.

The sediment composition, copper, and zinc concentration at L1 was likely influenced by Turpentine Run. Site 11 showed that Turpentine Run was indeed a source for copper and zinc, but not for arsenic, which accounts for the lower level of arsenic at L1. Rushing water from this stream may be partially responsible for the change in sediment composition at L4. It seems like these two samples flipped in terms of sediment composition, possibly due to the movement of sand from L1 caused partially by Turpentine Run and the deposition of that sand around L4. Also, with L4 being in the middle of Mangrove Lagoon it was fully exposed to wave action, which is likely another reason why this sample experienced the most sediment change.

Hurricanes Irma and Maria did not seem to have affected TBT, PAH, or PCB concentrations based on an evaluation of concentrations measured in 2010-2011 and 2018 at sites L1-L7. Besides the general decline from 2010-2011 to 2018 which was experienced across all contaminants except DDT, the hurricanes did not cause a significant change as there does not seem to be evidence of any recent addition of these contaminants. Several samples of DDT were shown to be over ERL limits, but this can likely be explained by the resuspension of old DDT buried in sediments as the DDT was made up of mostly degraded products.

Evidence suggests that in general there were not many statistically significant changes in the mean of most metals between years, especially among metals with NST guidelines. These results support the original hypothesis that there would be no significant difference between the levels of contaminants between 2010-2011 and 2018. The hurricanes did not seem to lead to a significant increase or decrease in contaminant levels across time. There was a general decline in contaminants which may relate to the effects of the hurricane though. However, the lack of clear outlets from Mangrove Lagoon and the presence of high levels of contaminants in mangrove samples from the 2018 sampling are probable reasons as to why the 2017 hurricanes did not significantly affect the levels of contaminants in Mangrove Lagoon.

There was probably not a flushing effect of sediment and contaminants into the southern portion of Mangrove Lagoon as evidenced by the lack of change in sediment grain size at L7 between the two time periods. L7 was routinely the less polluted sample across L1-L7. This suggests that contaminants did not move into southern lagoon sediments or they may have moved into southern sediment locations but were washed away quickly due to circulation. It has been shown that contaminants can be the same even after major storm events. Abel et al. (2007) showed that concentrations of lead were not different from concentrations before Katrina and Rita in Louisiana though many of the samples were still above the 400µg/g recommend by the EPA. Reible et al. (2006) further states that it is difficult to fully evaluate contaminants after a storm due to the possibility that both the frequency and distribution of contaminants may not differ. This is because the levels of containments before the storm may have already been at dangerous levels. This may be the case for Mangrove Lagoon as this area has already experienced an extensive amount of pollution, so the effects of the 2017 hurricane season may not be clearly seen.

This lack of historical data is a limitation of this study. The 2017 hurricanes could have changed the concentrations of contaminants significantly without any way of knowing, because there are no data for lagoon sediments over a vast portion of Mangrove Lagoon and there are no data for mangrove sediments immediately before the storm. Clark et al. (2017) acknowledges that mangroves and wetlands in general are not stable and a change in environmental conditions can change these areas from a sink of contaminants to a source of those same contaminants. Clark et al. (1997) in a study from Brisbane, Australia, remeasured levels of copper, cadmium, lead, and zinc from the same transects that were measured in (Saenger et al. 1991). Clark et al. (1997) found that mangroves lost their buffering capacity when comparing data sets from 1989 and 1991 because the metals had been remobilized and moved down a hydraulic gradient or were re-trapped in the water table due to a prolonged period of drought.

Another related limitation to this portion of the study is that these samples were collected 10 months after Hurricanes Irma and Maria. The results of this study suggest that Hurricanes Irma and Maria did not cause significant change in metal concentrations for these samples. However, many changes could have occurred at these locations in that ten-month period that could have affected the results from this study. Ten months of rain and storms after the hurricanes could have continued to input contaminants into Mangrove Lagoon, especially through Turpentine Run. The cleanup of derelict boats and other hurricane debris in the ten months after the storm could have left behind high levels of contaminants would not be known to this study. The addition of an enormous amount of hurricane debris to Bovoni Landfill in the ten-month period after the hurricanes could have led to an increase in leachate that reached Mangrove Lagoon. This may suggest that the contaminants measured in 2018, especially in lagoon sediments, are more elevated then they would have been immediately after Hurricanes Irma and Maria resulting in arsenic and copper being found in more concentrations over the ERL threshold then what would have been found without hurricane effects.

Mangrove vs. Lagoon: Spatial Comparisons

Four of the five metals that were over the ERL limit were positively correlated with fine sediment. Where copper, zinc, mercury, and silver concentrations were greater, fine sediment was also more prevalent. These metals all had an inverse relationship with sand. So, samples with low amounts of fine sediment, such as site 7, in general had the

lowest concentrations of contaminants. However, the amount of fine sediment was not significantly different between sediment types and evidence suggests that in general mangrove sediments did not contain greater metal or TBT concentrations then lagoon sediments.

Another gage for samples difference is the relationship between these metals and aluminum. Aluminum is a major element in Earth's crust (Turekian and Wedepohl 1961). This allows aluminum to be used to normalize elements to look for outliers from normal crust ratios that are indicative of anthropogenic contamination. From this analysis, copper, zinc, and mercury were positively correlated with aluminum and several revealed samples above predicted values based on aluminum. For copper, all samples which suggested anthropogenic inputs were over the ERL limit, all of which were located along the western side of Mangrove Lagoon. This shows that specifically the car scrapyard, Bovoni Landfill, and site 17 are likely inputs for these contaminants to mangrove and lagoon sediments. Though arsenic was not correlated with aluminum, the six samples that were over the predicted values were also the six highest arsenic concentrations. The mangrove and lagoon samples that contained the highest arsenic concentrations were separated on different sides of Mangrove Lagoon. This likely reveals at least two different pathways of anthropogenic sources for arsenic. For zinc, the two samples that were above the predicted values provide further evidence that site 17 and site 15 are near direct sources of anthropogenic pollutants.

There were only six metals that were significantly different between mangrove and lagoon sediments. Of those six, five were significantly greater in the lagoon sediments. These results do not support the original hypothesis which stated that contaminants would be significantly greater in mangrove sediments. However, it appears that mangroves are intercepting metals in a way that provides some protection to the adjacent lagoon as mangrove sediments were contaminated with potentially toxic levels of contaminants. Due to the lack of knowledge of historical contaminant concentrations in mangrove sediments in STEER, the role that mangroves were playing before the storms cannot be known. Clark et al. (1997) showed that a change in environmental conditions can alter how mangroves act as buffers between polluted sites and the environment. One limitation of this study in assessing the ability of mangroves to intercept pollutants was that only the top 2-3 cm of sediment was collected for analyses. Clark et al. (1997) found high concentrations of heavy metals in sediments as deep as 30 cm. Keller et al. (2017) found most heavy metals at depths of 12-22cm. Though the top 2-5 cm collected in this study may reflect the most recent metal deposits they do

not reflect a depth- and time-integrated picture of contamination in Mangrove Lagoon. Another reason for the mangrove sediments in this study not containing higher concentrations is likely due to the distance from the lagoon sediments. Clark et al. (1997) observed the highest levels of metals between 50-100 m from the water's edge, and sometimes as much as 300 m. The mangrove sediments in this study were 15 m from lagoon sediments. Keller et al. (2017) suggests this as well as sites located closet to Mangrove Lagoon did not test above the detection limits for metals, while those sites further away and located closest inland, did. So, it could be expected that the lowest metal concentrations in mangrove sediments would be found in sediments closest to the water's edge. Another possibility to account for the levels of metals found in mangrove sediments is the uptake of contaminants into mangrove tissue. Pinheiro et al. (2012) showed that *R. mangle* leaves are effective for monitoring metals and act as bioindicators of mangrove areas contaminated by various metals. The role that mangroves play in uptaking contaminants is not known because such a study has not taken place in Mangrove Lagoon. Lastly, as shown in Keller et al. (2017), groundwater movement occurs in different directions seasonally on the western edge of Mangrove Lagoon. So, groundwater may move higher concentrations of metals instead of overland flow, again pointing to the need to investigate contaminants at depth and in different constituents of the system (e.g., sediment, groundwater, surface water). This would provide clarity on contaminant movement as some contaminants get remobilized in anoxic sediment and diffuse to the surface where they appear to concentrate due to reoxidation (Saenger and McConchie 2004) .

Lagoon sediments had significantly higher TBT concentrations then mangrove sediments. This is expected because TBT is associated with marine activities that would occur more within the lagoon compared to the mangroves. The lagoon sediment also had a higher TBT average then the average TBT of mangrove sediment. This significant difference was not driven by L17. Though L17 recorded the highest TBT concentration, TBT for this sample probably did not come from land-based sources due to the low TBT concentration at M17. This provides evidence for some other source for this TBT concentration. This could be linked to a derelict boat that could be buried there or possibly illegal dumping of some waste, such as boat paint, that contained high amounts of TBT.

Management implications:

Mangrove Lagoon is a part of an MPA that only seems to be receiving limited benefits for its protection. This area serves as one of the largest remaining mangroves stands in St. Thomas and the U.S. Virgin Islands. Currently, the concentrations of metals are at levels that are known to cause toxic effects for organisms. This study provides evidence that action needs to be taken to protect Mangrove Lagoon. Management actions have already been weighed and recommended in the STEER watershed plan created in 2013 by the Horsley Written Group with stakeholder input (Ferguson 2013). This plan thoroughly assessed the potential sources of pollution in the entire STEER watershed and recommended ways to remedy the problems pollution causes. This would potentially help decrease the levels of copper and zinc coming from Turpentine Run. One thing is clear, these mangroves are currently holding dangerous levels of contaminants in their sediments. Any further modification of these mangrove stands is likely to release those contaminants into Mangrove Lagoon. Saenger and McConchie (2004) recommended that sediment disturbances in polluted mangroves be minimized. In this way, the contaminants in the sediments are not disturbed. Removing garbage dumps from the area, as recommended by Clark (1998), can help prevent runoff contamination into Mangrove Lagoon. Though it is unlikely that Bovoni Landfill will close in the near future, other garbage sites like dumpsters along roadsides around Mangrove Lagoon could be easily moved to other areas. Based on the zinc concentrations at M15 moving the car scrapyard could go a long way in decreasing zinc concentrations at that sample location.

Recently, the Army Core of Engineers presented the draft environmental assessment on the proposed plan to reduce flooding by rechanneling Turpentine Run (USACE 2019) to decrease flooding in the area. This plan would lead to the creation of a 1,300-foot long levee starting south of the new Bovoni Road Bridge and ending at the horse racetrack with the addition of an interior drainage conveyance from the existing small concrete channel by a 72-inch underground pipe (length of 1,745 feet) which would run under the levee and racetrack and ultimately discharge into Mangrove Lagoon (USACE 2019). This would move the current outlet from Turpentine Run further to the west where an underground, 6 ft pipe would empty into Mangrove Lagoon from under the horse racetrack, close to site 19. This study showed that Turpentine Run is a pathway for potentially toxic levels of copper and zinc so the addition of more impervious material could lead to an increase in copper and zinc concentrations into Mangrove Lagoon, as well as potentially other contaminants. Channelization would likely lead to increased water volumes

entering this portion of Mangrove Lagoon, potentially contributing new contaminants to this area or redistributing contamination that is already present in the lagoon. This new input could then increase the level of contamination in this area of Mangrove Lagoon, possibly leading to sediments containing more contaminants over ERL thresholds. This action would also likely decrease the current levels of contamination around site 11 as there would be less water transporting contaminants to site 11. However, the possible increase in contaminant concentrations into Mangrove Lagoon should be considered before any final plan is agreed upon.

Future Work:

To further pinpoint management needs, more research should be conducted to clarify and expand on the results of this study. This study identified three potential pathways of contaminants into Mangrove Lagoon: Bovoni Landfill, Turpentine Run and site 17. For Turpentine Run and site 17, additional studies could help determine contaminant sources and how to best mitigate their impact on Mangrove Lagoon. Benner Bay was mentioned as a possible pathway to explain the contaminants present at several samples in Mangrove Lagoon. However, due to the lack of knowledge of sediment transport and water flow in the channel connecting the two bodies of water, the impact of Benner Bay pollutant sources, marinas and other boat activities, on Mangrove Lagoon can not be fully explained. Future work should focus on the channel and the circulation of water in Mangrove Lagoon to better explain the distribution of contaminants and potential pathways of contamination. Nichols and Towle (1977) did some work on water flow in and out of Mangrove Lagoon, but this was over 40 years ago and has likely changed. In addition, collecting sediment mangroves samples further inland will help determine the fuller contaminant state of mangrove sediments instead of only sampling mangroves close to the water's edge. Another option could be to collect deeper cores to look at historical patterns and possibly patterns of contamination as they relate to groundwater flow. Previous surveys conducted in STEER assessed the level of contaminants in coral, conch, and fish, however these surveys were not conducted in the northern portion of Mangrove Lagoon (Pait et al. 2016). Future studies could measure levels of contaminants present in organisms in the northern Mangrove Lagoon to determine potential affects that these contaminants are having on the organisms in these areas. Lastly, mangroves have been known to uptake contaminants into their tissues, leaves, and bark (Saenger and McConchie 2004; Pinheiro et al. 2012). No such study has taken place in Mangrove Lagoon; such a study would allow mangrove health to be assessed in terms of the direct affect these contaminants are having on the mangrove trees themselves.

Chapter 5: Conclusion

Mangrove Lagoon is a polluted system. High concentrations of contaminants are found in both mangrove and lagoon sediments, are widespread throughout Mangrove Lagoon (but especially in the north and northwest portions) and have been impacting this system for at least 8 years, though gray literature reports suggest that contamination likely extends back decades to at least the 1970s. Many of the measured contaminant concentrations found in this study, are known to result in negative effects for organisms. The Bovoni Landfill and associated activities and Turpentine Run are the two most probable sources of contaminants to Mangrove Lagoon. In addition, this study documented high levels of contamination at site 17, a new, potential pathway of contaminants that warrants further investigation. This study also revealed how different contaminants likely have different pathways into Mangrove Lagoon. For example, the spatial distribution of contaminants suggest that Turpentine Run is a pathway for copper and zinc, but not arsenic. Measured concentrations at sample M15 suggest that the current car scrapyard or buried materials from past activities near that location, are a source for zinc into Mangrove Lagoon. Mitigation actions need to be taken immediately to prevent further contamination of Mangrove Lagoon. The 2013 STEER watershed management plan addresses many of the problems associated with the surrounding watershed and especially, Turpentine Run. Though this study provides the most detailed picture of contamination in Mangrove Lagoon to-date, additional studies that investigate the Turpentine Run and site 17 pathways, the levels of contaminants in trees and organisms, and mangrove sediments further from the water's edge, will increase our understanding of this system and will further pinpoint pollutant sources.

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Supplemental:

Supplemental Table 1: Contaminant List

PAHs (low MW)	PAHs (high MW)	Organochlorine Pesticides	PCBs
Naphthalene	Fluoranthene	2,4'-DDD	PCB101_90
1-Methylnaphthalene	Pyrene	4,4'-DDD	PCB105
2-Methylnaphthalene	C1-Fluoranthenes_Pyrenes	2,4'-DDE	PCB110_77
2,6-Dimethylnaphthalene	C2-Fluoranthenes_Pyrenes	4,4'-DDE	PCB118
1,6,7-Trimethylnaphthalene	C3-Fluoranthenes_Pyrenes	2,4'-DDT	PCB128
C1-Naphthalenes	Naphthobenzothiophene	4,4'-DDT	PCB138_160
C2-Naphthalenes	C1-Naphthobenzothiophene		PCB146
C3-Naphthalenes	C2-Naphthobenzothiophene	**Major and Trace Elements**	PCB149_123
C4-Naphthalenes	C3-Naphthobenzothiophene	Aluminum (Al)	PCB151
Benzothiophene	Benz[a]anthracene	Antimony (Sb)	PCB153_132
C1-Benzothiophene	Chrysene	Arsenic (As)	PCB156_171_202
C2-Benzothiophene	C1-Chrysenes	Cadmium (Cd)	PCB158
C3-Benzothiophene	C2-Chrysenes	Chromium (Cr)	PCB170_190
Biphenyl	C3-Chrysenes	Copper (Cu)	PCB174
Acenaphthylene	C4-Chrysenes	Iron (Fe)	PCB18
Acenaphthene	Benzo[b]fluoranthene	Lead (Pb)	PCB180
Dibenzofuran	Benzo[k]fluoranthene	Manganese (Mn)	PCB183
Fluorene	Benzo[e]pyrene	Mercury (Hg)	PCB187
C1-Fluorenes	Benzo[a]pyrene	Nickel (Ni)	PCB194
C2-Fluorenes	Perylene	Selenium (Se)	PCB195_208
C3-Fluorenes	Indeno[1,2,3-c,d]pyrene	Silicon (Si)	PCB199
Anthracene	Dibenzo[a,h]anthracene	Silver (Ag)	PCB201_173_157
Phenanthrene	Benzo[g,h,i]perylene	Tin (Sn)	PCB206
1-Methylphenanthrene		Zinc (Zn)	PCB209
C1-Phenanthrenes_Anthracenes	**Butyltins**		PCB28
C2-Phenanthrenes_Anthracenes	Monobutyltin		PCB29
C3-Phenanthrenes_Anthracenes	Dibutyltin		PCB31
C4-Phenanthrenes_Anthracenes	Tributyltin		PCB44
Dibenzothiophene	Tetrabutyltin		PCB45
C1-Dibenzothiophenes			PCB49
C2-Dibenzothiophenes			PCB52
C3-Dibenzothiophenes			PCB56_60
			PCB66
			PCB70
			PCB74_61
			PCB8_5
			PCB87_115
			PCB95
			PCB99

Supplemental Table 2: Field characteristics of each sediment sample

Samples	Texture	Color	Odor/Sheen	Benthos
L1	Mud	Black	Sulfur	Algae
L2	Shell/hash	Black	Sulfur	black algae mat
L3	Mud	Black	None	Halophila, algae
L4	Mud/Shell	Black/Gray	Sulfur	Algae
L5	Mud/Shell	Black/Gray	Sulfur	Cnidaria, Algae, Halophila
L6	Mud/Shell	Black/Gray	None	Algae
L7	Sand/Shell	Gray	None	Cnidaria, Algae, Halophila
L8	Shell	Black	Sulfur	Cnidaria, Algae, Halophila
L9	Mud/Sand	Gray	None	Cnidaria, SAV*
L10	Shell	Gray	None	Algae/Cnidaria
L11	Mud	Black/Gray	Sulfur	None
L12	Shell	Gray	Organic	Sav*/Cnidaria
L13	Shell	Gray	Oily	worms/algae/bioturbators
L14	Mud	Black/Gray	Sulfur	Algae/Amphapods
L15	Mud	Black	Sulfur	Algae/Amphapods
L16	Mud	Black	Sulfur	None
L17	Mud	Black/Gray	Sulfer	None
L18	Mud/Shell	Black	None	Molluscs, Halophila
L19	Mud/Shell	Black	None	None
M1	Peat	Brown	None	Crustacea
M2	Peat	Brown	None	Molluscs, Crustacea
M3	Peat	Brown	Oily / no odor	Molluscs, Crustacea
M4	Sticky/Peat	Brown	None	Molluscs, Crustacea
M5	Peat	Brown	None	Molluscs, Crustacea
M6	Peat	Brown	None	Molluscs, Crustacea
M7	Peat	Brown	None	Crustacea
M8	Peat	Brown	None	Crustacea
M9	Peat	Brown	Sulfer	Molluscs, Crustacea
M10	Peat	Brown	None	Molluscs/Crustacea
M11	Clay	Brown	Oily/Sewage	None
M12	Peat	Brown	None	Crustacea
M13	Sticky/Peat	Brown	None	Worms/Crustacea/Termites
M14	Peat	Black/Brown	None	Crustacea
M15	Mud/Peat	Brown	None	Molluscs/Crustacea
M16	Mud/Peat	Brown	Sulfur	Worms/Molluscs/Crustacea
M17	Sticky/Peat	Brown	None	Worms/Molluscs/Crustacea
M18	Sticky	Brown	None	Crustacea
M19	Peat	Brown	None	Worms/Molluscs

Supplemental Table 3: Water quality characteristics of each lagoon sample

Samples	DO %	DO mg/l	Salinity (PSU)	pH	Temperature (˚C)	Depth (m)	Secchi Depth (m)
L1	124.4	7.64	36.03	8.17	31.2	1	1
L2	112.8	7.05	36.5	8.17	29.6	1.15	1.15
L3	87.3	5.47	36.19	7.93	29.2	1.1	1.1
L4	95.2	5.95	36.24	8.03	29.4	1	1
L5	83.3	5.22	36.28	7.99	29.3	0.98	0.98
L6	123	7.52	36.48	8.23	30.9	1.2	1
L7	103.1	6.51	36.1	8.05	28.9	1.4	1.4
L8	83.4	5.24	36.26	7.94	29.1	0.88	0.88
L9	89.8	5.53	36.54	7.98	29.8	1.05	1.05
L10	94.5	5.88	36.37	8.05	29.6	0.89	0.89
L11	44.7	2.75	28.19	7.77	32.3	0.8	N/A
L12	99.1	6.17	36.31	8.08	29.7	0.85	0.85
L13	92	6	36.42	8.04	28.8	1.1	1.1
L14	155.3	9.55	36.56	8.31	30.8	0.65	0.65
L15	167.7	10.11	36.6	8.37	31.7	0.5	0.5
L16	46.5	2.75	36.53	7.94	31.2	0.23	0.23
L17	104.4	6.44	36.44	8.15	30.1	1.04	1.04
L18	101.7	6.26	36.44	8.13	30.3	1.1	1.1
L19	118.3	7.3	36	8.16	30.8	1.1	1.1

Supplemental Table 4: Latitude and longitude of samples along with the date and time the samples were collected

Samples	Latitude	Longitude	Date	Time
L1	18.31659698	-64.87622833	7/25/2018	1:21 PM
L2	18.31348801	-64.88005066	7/24/2018	11:43 AM
L3	18.31579781	-64.87644958	7/25/2018	9:02 AM
L4	18.31503677	-64.87701416	7/25/2018	9:25 AM
L5	18.31461906	-64.87471771	7/27/2018	9:23 AM
L6	18.3152771	-64.88143158	7/24/2018	2:44 PM
L7	18.30900764	-64.87424469	7/27/2018	12:07 PM
L8	18.31538963	-64.87521362	7/27/2018	8:45 AM
L9	18.31398964	-64.87358856	7/27/2018	10:08 AM
L10	18.31222916	-64.87381744	7/27/2018	10:51 AM
L11	18.31745	-64.87577	7/27/2018	2:05 PM
L12	18.31168556	-64.8766861	7/27/2018	11:27 AM
L13	18.31327057	-64.87869263	7/24/2018	10:32 AM
L14	18.31377029	-64.88132477	7/24/2018	12:55 PM
L15	18.31479073	-64.88172913	7/24/2018	1:53 PM
L16	18.31649399	-64.88212585	7/25/2018	10:26 AM
L17	18.31703186	-64.88096619	7/25/2018	11:15 AM
L18	18.3166008	-64.87947083	7/25/2018	11:49 AM
L19	18.31643295	-64.87705994	7/25/2018	12:44 AM
M1	18.3167572	-64.87617493	7/25/2018	1:43 PM
M2	18.31343651	-64.88019562	7/24/2018	12:12 PM
M3	18.31631851	-64.87573242	7/25/2018	2:03 PM
M4	18.31484795	-64.87812042	7/25/2018	9:55 AM
M5	18.3146534	-64.87454987	7/27/2018	9:50 AM
M6	18.31543922	-64.88207245	7/24/2018	3:15 PM
M7	18.3090477	-64.87474823	7/27/2018	12:28 PM
M8	18.31543732	-64.87506104	7/27/2018	9:13 AM
M9	18.31403542	-64.87341309	7/27/2018	10:27 AM
M10	18.31226158	-64.87363434	7/27/2018	11:10 AM
M11	18.31767	-64.87592	7/27/2018	1:56 PM
M12	18.31166649	-64.87687683	7/27/2018	11:41 AM
M13	18.31310272	-64.87872314	7/24/2018	11:25 AM
M14	18.31371689	-64.88149261	7/24/2018	1:30 PM
M15	18.31474495	-64.8819046	7/24/2018	2:23 PM
M16	18.3165493	-64.88230133	7/25/2018	10:51 AM
M17	18.31719589	-64.88101196	7/25/2018	11:34 AM
M18	18.31675339	-64.87944031	7/25/2018	12:08 PM
M19	18.31658554	-64.87706757	7/25/2018	1:08 PM


L1
NOAA CRCP
STEER
7/25/2018


M1


L2
NOAA-CRCP
STEER
7/24/2018


M2


L3
Metals


M3


L4
NOAA-CRCP
STEER
7/25/2018


M4


L5
NOAA-CRCP
STEER
7/27/2018


M5


L6
NOAA-CRCP
STEER
7/24/2018


M6


L7
NOAA-CRCP
STEER
7/27/2018


L8


M8

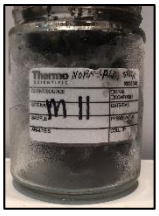

L9


M9


L10


M10


L11


M11


L12

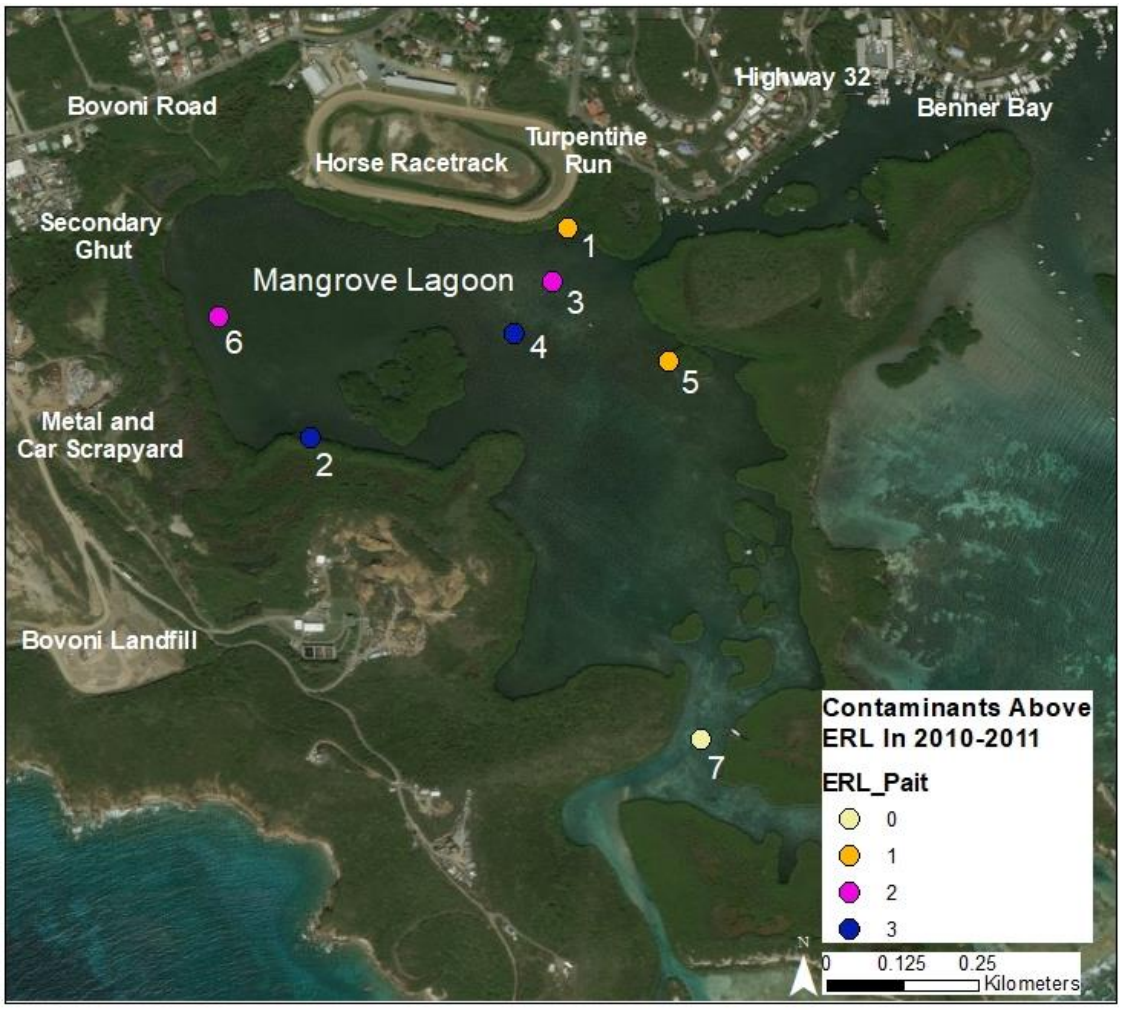

L13


M13


L14

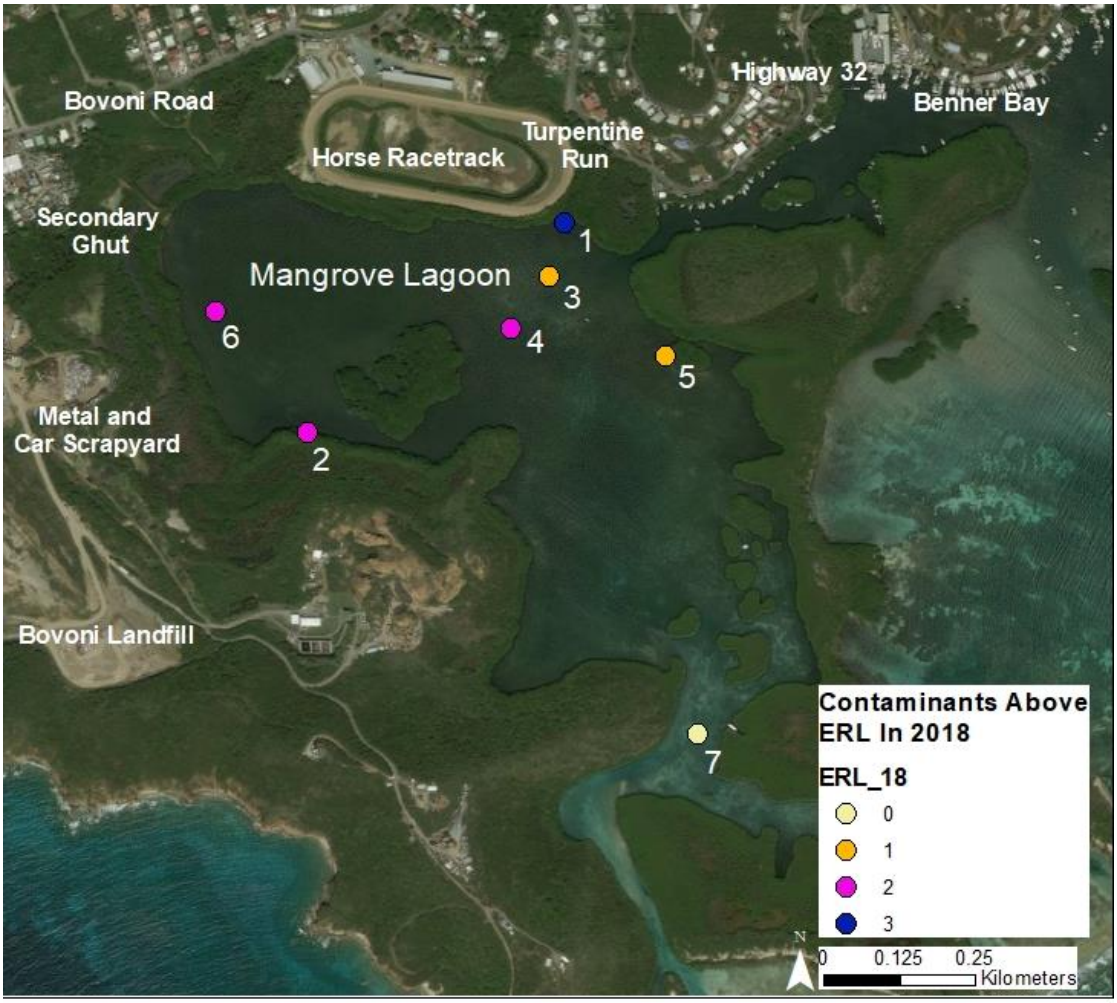

M14

Supplemental Figure 1: Photos of quadrat, northern view, and sediment sample for lagoon and mangrove sediments in order from left to right. Photo Credit: P. Owen Clower; Kristin Wilson Grimes

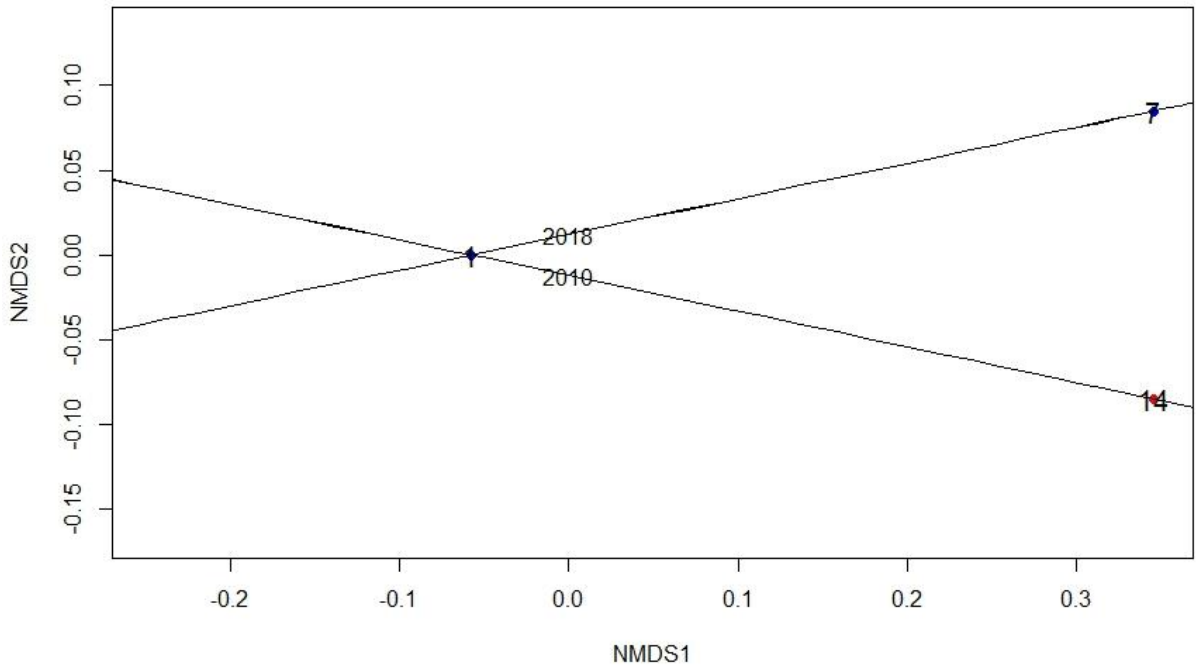


Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

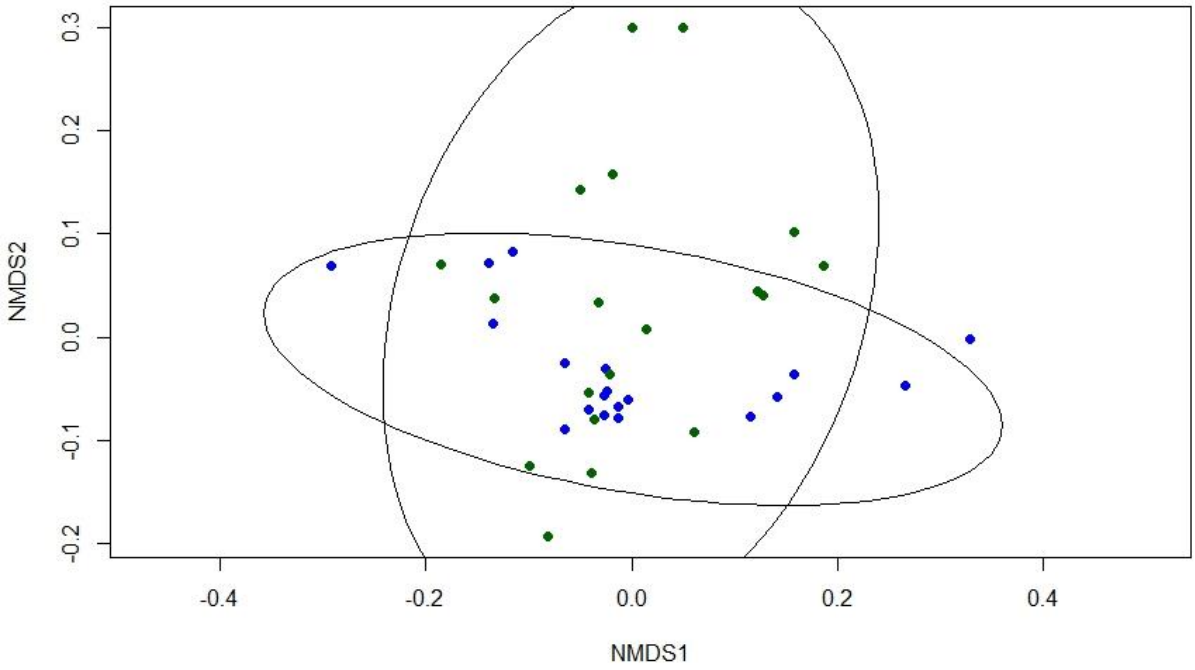
Supplemental Figure 2: Map of samples measured in 2010-2011 showing the number of contaminants measured over the ERL limit



Supplemental Figure 3: Map of samples re-measured from Pait et al. (2014) in the summer of 2018 showing number of contaminants over the ERL limit.



Supplemental Figure 4: Non-metric Multidimensional Scaling (NMDS) ordination of samples using a Bray-Curtis dissimilarity matrix. An analysis of similarity (ANOSIM) found no clustering of samples by year. Blue = 2018; Green = 2010-2011. Stress Value = 3.99193e-05. A subset of the NMDS without L7 (7 in 2018 and 14 in 2010-2011) was performed and the stress was so large it indicated no patterns.



Supplemental Figure 5: Non-metric Multidimensional Scaling (NMDS) ordination of samples using a Bray-Curtis dissimilarity matrix. An analysis of similarity (ANOSIM) found no clustering of samples by year. Blue = Lagoon; Green = Mangrove. Stress Value = 0.135.