Silting dynamics and metal contaminants in the Georgetown Inner Harbor

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Silting dynamics and metal contaminants in the Georgetown Inner Harbor

by Ezekiel W. Meyers

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Abstract

The Georgetown inner harbor is an abandoned oxbow-like river loop and a vital historic site with a wealth of traditional businesses and heavy local industry located within Winyah Bay. Since the modification of the Sampit River in 1949, chronic rapid silting has plagued the inner harbor. With these substantial amounts of fine-grained material accumulating inside the inner harbor, business operations along the waterfront, navigational and maritime operations, and contamination within the harbor are of major concern.

The goals of this study were to (a) understand the silting dynamics inside the inner harbor, (b) identify heavy metals which might be of environmental concern and their potential sources, and (c) decipher changes in metal content above and below the stratigraphic boundary indicating the past dredging depth to see if sources may have been different before and after dredging.

To accomplish these goals, four sediment cores were taken throughout the inner harbor. Physical and geochemical properties of each core were examined including grain size distribution, total organic content, dry bulk density, X-ray fluorescence core scanner element intensity distribution, X-ray images, and heavy metal concentrations. Supplemental samples were collected and measured for grain size distribution including three suspended sediment samples, 12 piston cores, and six grab samples. In-situ turbidity measurements from two sites within Winyah Bay were also examined.
The sediment within the inner harbor is composed of 52 ± 0.47% of cohesive material (finer than 10 μm) with at least 15 ± 0.12% of total organic matter. The mud that reaches the inner harbor settles in the form of flocculated suspension. This process causes 2.65% more coarser material (between 20 and 40 μm) to settle at the two harbor entrances, while 2.87% more finer material (less than 10 μm) is deposited in the backside of the harbor loop. Deposition occurs during periods of slack tide until the accommodation space available has been filled up to less than 4 m in the eastern channel and 0.6 m in the western. This study shows that silting of the inner harbor happens over a few lunar tidal cycles, i.e., within a few months.

Heavy metals, including arsenic (19.3 to 23.8 ppm), chromium (77.4 to 105.6 ppm), copper (26.8 to 40.2 ppm), nickel (28.8 to 36.6 ppm), and zinc (90.7 to 180.3 ppm), were found to be above Effects Range Low (ERL) concentrations (Long and Morgan 1990, Long et al. 1995, MacDonald et al. 1996). The lateral and vertical distribution of these metals was found to differ by specific metal. Vertically, in the eastern channel, lead and chromium were observed in higher concentrations below the dredge boundary. Above the dredge boundary, when compared to below, Br was higher in the eastern channel and Mn in at the eastern entrance to the inner harbor. Potential sources identified, based of lateral distribution of metal content, include industrial sources, shipyards and marinas, and local business and tourism along the waterfront.
**Table of Contents**

Copyright..................................................................................................................ii
Acknowledgments.........................................................................................................iii
Abstract......................................................................................................................iv
List of tables..............................................................................................................vii
List of figures...........................................................................................................viii
Introduction..............................................................................................................1
Methods....................................................................................................................17
Results.....................................................................................................................23
Discussion................................................................................................................51
Conclusion...............................................................................................................71
References...............................................................................................................73
List of Tables

Table 1. Grain size parameters of inner harbor mud and suspended sediment.

Table 2. Laminae counts between larger layers of X-ray images.

Table 3. Heavy metal concentrations of inner harbor mud and sediment quality guidelines.

Table 4: Correlations of metal content and inner harbor sediment parameters.

Table 5: Heavy metal concentrations in the inner harbor from various studies.
List of Figures

Figure 1. Overview map of study area, Winyah Bay.

Figure 2. Overview map of Georgetown inner Harbor.

Figure 3. Bathymetric maps of the Georgetown Harbor form 1879 and 2018.

Figure 4. Grain size distribution curves of sediment from Georgetown Harbor.

Figure 5. Average grain size distribution curves for harbor mud and suspended sediment.

Figure 6. Plot of sediment characteristics of sediment from within Winyah Bay.

Figure 7. Ternary plot of Winyah Bay and Georgetown Harbor sediment.

Figure 8. Summary image of physical and geochemical parameters of harbor sediment.

Figure 9. Turbidity measurements within Winyah Bay.

Figure 10. Total metal content of sediment throughout the inner harbor.

Figure 11. Metal concentrations above and below dredging depth in the eastern channel.

Figure 12. Metal concentrations above and below dredging depth in the eastern entrance.

Figure 13. XRF element ratio plots identifying dominance of Ca and K.

Figure 14. XRF heavy metal ratios from eastern channel of Georgetown Harbor.

Figure 15. XRF heavy metal ratios from eastern entrance of Georgetown Harbor.

Figure 16. XRF heavy metal ratios from western entrance of Georgetown Harbor.

Figure 17. XRF heavy metal ratios from western channel of Georgetown Harbor.

Figure 18. Box plots of metal concentrations measured across the Georgetown Harbor.
Introduction

Located at the interface between oceans and rivers, estuaries are some of the most productive ecosystems throughout the world (Chapman and Wang 2001, Patchineelam et al. 1999). Estuaries can be complex systems as they receive sediment input and water flow from both terrigenous and marine sources (Patchineelam et al. 1999). Dynamics in these systems can be constantly modified due to changing tidal strength, river discharge, wind direction, rainfall, and anthropogenic influence. Anthropogenic influences include development of industry and businesses, structural modification of the waterway, and usage of the body of water, all which can lead to undesired consequences. Heavy metal contamination, one of these consequences, is becoming not only an increasing problem around the world, due to its’ toxicity to humans and organisms, but also within these estuaries specifically (Chapman and Wang 2001, Davies et al. 2009).

Georgetown Harbor Situation. Winyah Bay is located approximately 70 km north of Charleston, South Carolina (US) and is the fourth largest estuary along the North American East Coast (Figure 1) (Voulgaris et al. 2002). This complex estuary has five river systems that discharge into it including the Pee Dee, Little Pee Dee, Waccamaw, Black, Sampit, and Lynches rivers. Altogether, these rivers form a drainage basin for Winyah Bay of 47,060 km². Covering an area of approximately 62 km² and averaging 4.2 m in water depth, the entire bay is influenced by mixed semidiurnal tides (Patchineelam et al. 1999).
Along the uppermost portion of Winyah Bay, where the Sampit River discharges into the estuary, stands Georgetown Harbor (Figure 2). Georgetown Harbor is where much of the economic and industrial activity within Winyah Bay occurs. These activities include steel mill and paper mill operations, and a historic waterfront, a hotspot for tourism in the area. The inner part of the harbor has seen dramatic changes in the past decades due to river modification. Originally, Georgetown Harbor was developed on a meander in the Sampit River, near where the river mouth discharged into Winyah Bay. As industrial businesses developed upstream and within the harbor, the necessity for larger watercraft to navigate the area became prominent. Due to the difficulty of navigation through the meander, in 1949, the U.S. Army Corps of Engineers (USACE) cut an artificial shortcut in the Sampit turning the harbor into an oxbow-lake like situation (Figure 3). As a result of the modification, current velocity, driven primarily by tides, has greatly decreased within the now harbor loop leading to chronic silting that has plagued the inner harbor. In turn, dredging has become a necessary, continuous process (Hanebuth et al. 2019). Due to the cost of the persistent dredging and its brief effectiveness, the dredging of the harbor has been terminated in 2006. As a result, the inner harbor has filled with silt leaving the harbor loop at a limited water depth.

Industrial and local surface runoff, upstream discharge of sediment and pollution, and other nonpoint sources have had a substantial impact on the sediment within the harbor loop (Long 1998). One of these factors is heavy metal content within the harbor mud deposit (Long 1998). The toxicity and persistent nature of these metals can pose a serious threat to the aquatic environment which is seen to be an increasing problem on a global scale (Zhang et al. 2014). Within the harbor, the heavy metal content in the
sediment is likely to change with the silting dynamics, changing industry, and alteration of land usage through time. Identifying these differences can help determine potential sources of metal contaminants and changes of the metal concentrations through time. This knowledge is useful to help better understanding the Georgetown Harbor system and how these contaminants have accumulated since the termination of dredging in 2006.
Figure 1: Overview map of Winyah Bay showing the Georgetown Inner Harbor (Red Circle), sites of turbidity data collected (blue stars), and one of the three sites where suspended sediment samples were collected (yellow star).
Figure 2: Current conditions of the inner harbor with the heavy industry in its western part and the local businesses along the historic working waterfront to the east (Google Earth). Red dots show locations where sediment gravity cores were collected. Yellow stars show where suspended sediment samples were collected.
Figure 3: (a.) Map generated from an 1879 bathymetric survey showing the natural river meander (Keyes 2019). (b.) Bathymetric map showing 2018 conditions of the Georgetown Harbor (Hanebuth et al. 2019).

The Georgetown Harbor Silting Feasibility Study, funded by both the city and county of Georgetown, is focused on identifying a more cost effective and sustainable solution to the silting issue within the inner harbor. This project began in fall of 2018 and Phase II concluded in August 2022 (Hanebuth et al. 2019, Hanebuth and Meyers 2022). Several distinct aspects of the inner harbor system including water level, current speeds, and turbidity levels have been monitored in the area over the four-year span. With this data, models have been created and manipulated to examine several potential solutions for the silting issue. This study takes a closer look at the specific silting dynamics of the system and heavy metal contamination within the harbor aiding the Harbor Silting Project. By examining heavy metal content, the study also helps to uncover how the surrounding area of this historic harbor has impacted the system and on what time frame these impacts have been seen.
Scientific Background

*Silting in the Georgetown Inner Harbor.* Since the modification of the Sampit River system in 1949, chronic silting has plagued the Georgetown inner harbor. Following this change, water currents, driven by the incoming and outgoing tides, dramatically decreased within the inner harbor loop. This change in water velocity allowed for fine sediment to be deposited. Water depth along the eastern portion of the channel ranges from 1.5 to 4.3 m while the western portion is much shallower at 0.3 to 0.6 m below Mean Low Water (MLW) (Hanebuth et al. 2019). Bathymetric maps of the natural conditions collected in 1879 and again in 2018 show shallowing of the water depth within the inner harbor (Figure 3) (Hanebuth et al. 2019, Keyes 2019). Dredging in the inner harbor became necessary almost immediately after the modification of the Sampit River. In order to eliminate the cost of repetitive dredging, the harbor was last dredged in 2006 which quickly silted up to its current water depths, with some of these depths being anthropogenically controlled due to large vessel traffic within the harbor loop.

Studies of the inner harbor have attempted to calculate sedimentation rates at which the harbor is being filled using historic bathymetric maps (GEL Engineering LCC 2022). The study by GEL Engineering LCC found deposition rates in the western channel to be over 1.2 m/yr (4 ft/yr) while in the eastern channel these rates were projected to be less than 0.5 m/yr (1.5 ft/yr) (2022). Numerical models of the area have been examined as part of the Georgetown Harbor Silting Study to see how modifications to this system will impact the sediment flow and deposition in the area. The main idea is that increasing water velocity in the harbor would result in fine sediment being unable to settle, thus,
greatly reducing the silting along the inner harbor. These modifications must be carefully considered to avoid unintended consequences such as erosion and or accumulation of coarser sediment. The GEL model found that introducing a deflection wall would not produce enough current to reduce dredging needs, and that completely closing the shortcut would completely restore current flow, but further studies would need to be conducted to determine if this method is a viable solution (GEL Engineering LCC 2022). Other potential engineering solutions such as a partial deflection wall and did not show the desired results with this model and the proposed solution was dredging followed by repetitive agitation dredging, when necessary, likely every other year (GEL Engineering LCC 2022). Another study using a different model, produced in Phase I of the Georgetown Harbor Silting Study by Hanebuth et al. (2019), revealed that several engineering solutions such as partial closure of the entrances and curved deflection walls would not produce enough current flow to prevent silting in the inner harbor. A complete closure of the shortcut was also examined in the model and while stronger current speeds were produced, new silting and erosion would occur in unwanted areas along the western entrance and working waterfront, respectively (Hanebuth et al. 2019). While these models are useful; knowing the specific silting dynamics including distribution of sediment grain size and when silting is occurring, i.e. constant sedimentation, during storm events, or over a single tidal cycle, would improve these models and aid in making suggestions on what the most cost effective and sustainable solution is the silting issue.

*Heavy Metals in the Environment.* Heavy metal contamination is becoming an increasing problem around the world with many areas of high vessel traffic seeing some of the largest impacts (OSPAR 2009). The term heavy metal often refers to metals which
can be toxic at low concentrations such as arsenic, cadmium, chromium, lead, and mercury. There are several routes for these metals to infiltrate marine environments including industrial sources, stormwater runoff, wastewater discharge, agricultural activities, and atmospheric fallout (Long 1998, Pohl 2020). Several of these potential sources can be found around Winyah Bay and Georgetown Harbor. Not only can these local sources bring pollutants in, but the multitude of rivers which drain into this basin can transport metals and other toxins into the bay as well (Turner and Burt 1985). As of 1998, an assessment by Department of Health and Environmental Control (DHEC) claimed there were 13 undisclosed point source discharges - though not further specified in that report – into Winyah Bay (likely larger today due to further development) (Long 1998).

Heavy metals are often examined based on Sediment Quality Guidelines (SQG) by comparing their concentrations to standardized environmentally relevant limits such as Effects Range Low (ERL), Effects Range Median (ERM), Threshold Effect Level (TEL), and Probable Effect Level (PEL) (Cotti-Rausch et al. 2012, Long & Morgan 1990, MacDonald et al. 1996, Long et al. 1995). These limits define the concentration levels for each of these metals in sediment which are known to be associated with measurable negative biological effects (Long & Morgan 1990, Long et al. 1995, MacDonald et al. 1996). TEL represents the upper limit of contaminant concentrations which no effects are expected (> 75% no-effects) while the PEL represents contaminant concentrations which are normally associated with biological effects on growth or survival (>75% effects) (Birch G.F. 2011, Cotti-Rausch et al. 2012). ERL describes the concentrations among the lower 10th percentile that cause biological effects on organisms, and ERM describes the
50th percentile at which concentrations were seen to cause biological effects (Birch G.F. 2011, Long and Morgan 1990, Long et al. 1995).

Previous studies and assessments have examined metal content in sediment in and around Winyah Bay and found metal concentrations varying based on which part of the bay was examined (Chen and Torres 2012, Long 1998, Ward 1993). A 1993 study examining dredge material from the Sampit River, inner harbor, and harbor entrance channel found arsenic (2.4 – 25.0 μg/g), nickel (0.75 – 36.4 μg/g), and chromium (4.18 – 103.0 μg/g) to be above the ERL concentrations but only in Sampit River locations (Ward 1993). A National Oceanic and Atmospheric (NOAA) study from 1998 found prominent levels of aluminum (7-10.3 μg/g dry weight), cadmium (.2-.52 μg/g), and arsenic (16.4 - 21.3 μg/g) within the harbor, however, the only concentration exceeding the ERL level at the time was arsenic (ERL = 8.2 μg/g dry weight) (Long 1998).

**Metal Transfer to Seabed.** The transportation of metals to the seabed can happen in a variety of ways depending on the type of metal and its individual chemical and physical preferences. Sedimentary characteristics play a key role in this enrichment process. Three of the main ways that this process is known to occur is a) precipitation of the metals out of the water column, b) coagulation and flocculation with finer grained material such as clay minerals, and c) absorption into organic material (Long 1998, Pradit et al. 2013, Tansel and Radiuddin 2016, Zhang et al. 2014). While each of these processes impacts the metals in different ways, all aid in the transfer of metals from the water column to the seabed.
The process of precipitation occurs when metal ions react with sulfide or hydroxide ions to produce a precipitate (Ansari et al. 2000, Zhang et al 2014). This process, while also occurring naturally, is one of the most common ways used to treat wastewater as this process removes heavy metals, reducing pollution (Pohl 2020). Two of the most essential elements of this chemical precipitation and co-precipitation of trace elements are iron and manganese, but several other metals such as arsenic, zinc and copper are also known to precipitate out of solution (Ansari et al. 2000, Nath et al. 2005, Zhang et al. 2014).

Entrapment in fine sediment is another pathway for the transportation of metals to the seabed (Tansel and Rafiuddin 2016, Zhang et al. 2014). Sediment less than 63 μm in size (silt and clay), especially those below the cohesive boundary, around 10 μm, are often recognized as the most effective method for the entrapment of metals (Zhang et al. 2014). Coagulation, the chemical process which neutralizes the particle’s surface charge, and flocculation, the physical process which enables them to bind together, are the most common processes involved in grain size influence in metal transfer. Studies have shown that finer sediment below the cohesion boundary can contain up to 10 times the amount of metal concentrations than that of coarse, non-cohesive sediment (Tansel and Rafiuddin 2016). Metals such as iron, chromium, manganese, nickel, lead, and zinc have been observed in studies to be transferred to the sediment by this process (Zhang et al. 2014).

Examining grain size influence on metal content in Winyah Bay, a NOAA study performed in 1998 examining sediment toxicity, found that aluminum, arsenic, cadmium, chromium, copper, and lead concentrations coincided in quantity with the proportion of fine sediment compared to sand throughout the estuary (Long 1998).
Dissolved organic matter is the final accumulation pathway for metals to the seabed (Singh et al. 2017, Zhang et al. 2014). Metals such as copper and chromium are known to be bound by this pathway (Zhang et al. 2014). Organic content within the water can vary due to several factors both within and surrounding the body of water being examined. Land use and land cover of wetlands, developed areas such as towns and cities, and farmland in the surrounding area can influence the extent/abundance of organic matter in the surrounding waterbodies. (Singh et al. 2017, Tiefenbacher et al. 2020). Local wetlands are known to produce copious amounts of organic matter, but in more developed or in agricultural areas, the introduction of nutrients such as nitrogen and phosphorus, which can be used by microbes and planktonic organisms in the water, can lead to an increase in organic matter (Singh et al. 2017, Tiefenbacher et al. 2020, Zhang et al. 2014). The dissolved organic matter in the water column is known to trap metal ions through coordinate bonding which then settle to the seabed (Du Laing et al. 2009). Finer particles of organic matter are also known to have effects like that of cohesive silt and clay fractions by coagulation and flocculation and can also reduce the bioavailability and thus toxicity and solubility of many metals (Kungolos et al. 2005, Zhang et al. 2014).

Potential metal sources in the Georgetown inner harbor. There are several potential sources of metals in and around Georgetown Harbor. Some of these sources include industries such as the steel mill and paper mill, city out-spill pipes, marinas and shipyards, local buried sources, and other upstream sources. Each of these potential sources are expected to release a specific metal signature which they are producers of. An example for the steel mill would be iron and manganese, as these elements are commonly used metals for this specific industry. City out-spill pipes could reveal a variety of metals
which may be transported from land into the harbor as surface runoff. For marinas and shipyards, zinc or Aluminum may be seen as it is used to aid in the prevention of corrosion for some vessels. Local buried sources could include silver, zinc, and mercury as there had been speculation of old submarine batteries being dumped in the harbor in the early to mid-1900s. Finally, upstream sources, like out-spill pipes, could include a diverse group of metals which have been brought into the area through both the Sampit, Pee Dee, and Waccamaw River systems including copper, nickel, and arsenic which are often found in pesticides (Shrivastava 2009). While a variety of metals are expected to be seen, examining metals of higher concentrations and proximity to each potential source can help determine where these metals are coming from.
Research Motivation, Research Question, and Hypothesis.

With minimal flow velocity within the inner harbor loop of the historical waterfront, substantial amounts of fine, organic rich sediment have been able to accumulate within the inner harbor over a brief period of time. Along the waterfront and in the surrounding area, several potential sources of metal pollutants can be identified. Numerous metal sources, in combination with the very fine-grained characteristics of the sediment and slowed-down flow dynamics in this area produce an ideal location for the accumulation of metals in the seabed. Comprehension of the silting dynamics and variations of this through time is an important first step in understanding how this system has developed into what it is today and how metal concentrations have changed. This information will be beneficial for the Georgetown community and provide further insight to the Harbor Silting Feasibility Study. This study will primarily focus on answering following three major questions:

1. *What mechanisms control the silting dynamics in the study area and how have they changed over time?*

2. *Which specific heavy metals are present within the inner harbor mud and how have the metal concentrations which are present changed through time and why?*

3. *What might the specific potential sources of these metals be?*
Hypothesis

1. It is hypothesized that since the termination of dredging, the harbor had a period of rapid silting which then slowed once the current water depths had been reached (reaching zero accommodation space). Previous studies suggested that sediment in the harbor is composed of very fine, organic-rich material, and that within the harbor there are low water flow velocities, solely driven by local tidal currents. Water depth is believed to be maintained by currents and mixing produced by larger fishing vessels within the harbor. Mechanisms expected to lead to this rapid silting include sediment and water discharge from the multitude of rivers and tidal pumping of sediment into the system.

2. It is expected to find a high level of heavy metal concentrations within the study area due to several potential sources and favorable sediment properties which are known to aid in the transfer of metals to the seabed. Differences in overall metal concentrations over time is also expected to be observed as the silting occurs, especially within sediment which have accumulated prior to the previous dredging pursuits. This variability in contamination levels is likely due to changes within the surrounding Georgetown community, such as closures of industries, land use changes and development, and modifications of harbor uses, and potential efforts to reduce contamination.

3. It is also expected that a limited number of potential sources which may have the highest impact on heavy metal concentrations will be identifiable based on metal type and proximity to the site where samples were collected. Likely sources
include stormwater runoff, out-spill pipes, steel mills and other large industries, marinas and shipyards, but maybe also buried sources.
Methods

*Inner Harbor Material Collection*. Four sites were selected around the inner harbor loop. These sites include the center of the entrances and channels within both the east and west portions of the inner harbor (Figure 2). Water depth in the eastern channel, eastern entrance, western channel and western entrance was 2.25 m, 3.41 m, 1.98 m, and 4.18 m (MLW) respectively. At each of these four sites, a gravity sediment core, ranging in length from 170 to 323 cm, was collected using a 15 m long research vessel equipped with a hydraulic A-frame. Sediment samples were taken from the cores at 20 cm increments unless distinct sedimentary changes of mineral composition or grain size were identified. Various laboratory analyses, as detailed below, were performed to identify the physical and geochemical properties of each core.

*Sediment Sample Analyses*. Physical parameters measured include dry bulk density and grain size distribution. Dry bulk density (DBD) was collected by removing all moisture by heating, using a sediment oven, from a determined sediment volume and known sample weight. Following the removal of all moisture, samples were weighed to see how much of the original weight was porewater, which allows for the calculation of the DBD. DBD helps examine the degree of compaction of the deposit varying with sediment depth. Grain size distribution (GSD) was measured using a CILAS 1190 Laser Particle Size Analyzer at Coastal Carolina University. This instrument determines grain size by measuring reflected and refracted light beams. Not only will GSD show what size...
of particles are settling within the harbor loop but also how the GSD of the accumulated sediment has changed over time for each location and in-between locations.

Three geochemical parameters have been examined. Following the collection of the samples from each core, one set of samples was immediately dried to suppress chemical reactions while the second set was used for all other analyses. Dried samples, taken at 40 cm increments down-core (in more frequent increments when distinct changes in stratigraphy were observed), were used to measure heavy metal concentrations at the USCS chem lab in Santa Cruz, California (collaboration with Dr. Ferdinand Oberle). For this process, each sample was digested using hydrochloric, nitric, perchloric, and hydrofluoric acids at a low temperature and then analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). ICP-OES measures the excited atoms and ions in a sample at the wavelength characteristics of certain elements while ICP-MS identifies elements by an atom's mass using mass spectrometry and can detect lower concentrations but is less cost efficient. Both methods combined will be used to examine samples for 49 different major, minor, and trace elements.

Total organic content (TOC) was measured through the loss on ignition method (Dean 1974). Following the removal of all moisture in each sample for DBD analysis, the sediment samples were placed in a furnace at 550 degrees Celsius for four hours. This process burns off all the organic material and, once weighed after being in the furnace, allows for a mass of organic matter to be converted into a TOC percentage for each sample.
X-ray fluorescence (XRF) element distribution intensities and X-ray imaging of each sediment core was scanned at 1 cm and 0.2 mm resolution, respectively. This measurement was done using a non-destructive ITRAX sediment core scanner at the Lamont-Doherty Earth Observatory (LDEO) Core Repository at Columbia University. Two successive runs were performed first with a Cr and then Mo tube to examine light and heavy elements, respectively. It is important to note that the XRF element intensities are useful to identify relative changes throughout the core but do not provide absolute concentration values; therefore, they are a semi-quantitative approach. Element ratios need to be built when comparing one element intensity value to another measured at the same core depth since the values are only semi-quantitate. The XRF core scanner detects heavier (larger) elements preferentially, thus, a natural log (used to determine proportional differences) ratio value of 2, for instance, does not mean that one element does effectively occur twice as often as the other; but does mean that by looking at how that ratio has changed with sediment accumulation, one can identify how overall sediment and contamination dynamics in this system have changed over the past decades. The XRF element ratios allow for the correlation of sediment across the harbor and potential prediction of sedimentation rates and dredging depths by looking for variations in the ratios through each sediment core. Also, the XRF element intensities provide a connection between the sediment cores collected for this study and cores analyzed in 2017 which have been dated via the $^{210}\text{Pb}$ excess and $^{137}\text{Cs}$ methods (Clark 2018). Thus, cross correlating the sediment cores was assumed to help projecting the age models towards the new cores.
Scanned X-ray images taken of these sediment cores reflect changes in sediment density, but also provide information regarding sediment composition, grain size, water content, compaction degree, and abundance of biogenic components (Grobe et al. 2017). The X-ray images revealed various sediment composition and structures which could not be seen with the XRF data and were used to develop estimations regarding sedimentation rates.

*Additional Material Collected.* In addition to the four sediment cores taken within the inner harbor, additional data was collected to provide a comprehensive, framing picture. In the areas surrounding the harbor, including the Sampit River, Pee Dee River, and upper portions of Winyah Bay, 12 piston cores and six grab samples were collected to examine what sediment is available to the system. Sediment cores were sampled with one sample being taken from every stratum throughout each core. Individual stratum were determined by changes in mineral composition and grain size. At the entrance to the eastern portion of the inner harbor and the mouth of the Pee Dee and Sampit Rivers, suspended sediment samples were collected 0.5 m off the seabed (Figures 1 and 2). 15 gallons of water were collected for each sample 0.5 m from the seabed using a pump. Water was methodically removed over several days, allowing all sediment to settle and slowly removing water with a siphon, using caution to prevent the removal of any of the sediment. Once consolidated, these samples along with the piston cores and grab samples were then processed and GSD was measured using a CILAS 1190 Laser Particle Size Analyzer.

Turbidity levels within the upper parts of the harbor were examined by *in-situ* turbidity sensors to see if the amount of sediment in suspension in the upper portion of
Winyah Bay varied over time. Turbidity measurements collected at the USGS navigation mark near the entrance to Georgetown Harbor from Phase I of the Georgetown Harbor Silting Study were collected using a Campbell CR300 turbidity sensor, while measurements collected from the middle of Winyah Bay by NOAA were collected using YSI EXO2 sondes (Hanebuth et al. 2019, NOAA National Estuarine Research Reserve System) (Figure 1). These measurements were examined over a month-long period for the USGS navigation mark at a 12-hour average, and a four-year period at a five-day average for the NOAA station.

_Literature integration._ Current industrial and land use conditions of the Georgetown Harbor are also an important aspect of this study. Looking through historical reports, previous data, dredging history, and local operations of the harbor reveals much information about land use changes, sources of heavy metals, and modifications of the surrounding area which may influence the inner harbor sediment dynamics and heavy metal pollution. These parameters, including estimate of sedimentation timing, sediment physical and geochemical properties, and the others studies done in the inner harbor (including the results of the two numerical modeling approaches), all work together to help uncover and further the understanding of the dynamics of the rapid silting in this system. This integration leads to insight as to what heavy metals are present in this area, including how and why these heavy metal concentrations have changed over time.

_Data Analysis._ Physical and geochemical parameter data were used to examine sedimentation rates and specific silting dynamics within the harbor and how these dynamics changed over time. To examine contrasts between the pre- and post-dredged status, the dredge depth needed to be identified. To do this identification, pre- and post-
dredging water depths were examined using high resolution bathymetric maps surveyed by USACE in 2005, 2006, and 2008, along with more recent bathymetric maps from 2017 and 2020 produced by the Coastal Geosystems Research Lab (Hanebuth et al. 2019, Hanebuth and Meyers 2022). XRF element intensity ratios were also used to aid in the identification of stratigraphic dredging boundaries within the cores. A log of visual description was collected immediately following the opening of the cores documenting changes seen within the vertical accretion of the sediment. Combining these data sets and verifying between each set, allowed for identification of dredge depths and provided information about sedimentation rates in the harbor.

When examining the heavy metals, the data collected was analyzed to examine differences between locations throughout the harbor, and identify vertical changes seen throughout the cores. All heavy metals along with some trace metals were examined in greater detail. Correlation coefficients were calculated and used to compare different physical and geochemical parameters to the metals which allowed for the determination of if the silting dynamics are influencing metal content or if these concentrations are controlled by other sources such as local industry, land use, and harbor usage. Heavy metal concentrations were compared to the standardized limits including effects range low (ERL) and effects range medium (ERM), as well as Threshold Effect Limit (TEL) and Probable Effect Limit (PEL) to see if the levels of metal pollution within the harbor are of environmental concern (Cotti-Rausch et al. 2012, Long and Morgan 1990, MacDonald et al. 1996, Long et al. 1995).
Results

*Grain Size Distribution (GSD).* Of the four gravity cores which were collected from the harbor, ranging from 170 to 323 cm, all were composed of fine silts and clays, with the only core to reach bedrock being core CGS 1018-1 located within the Eastern Channel. One anomaly was seen where a 3 cm thick layer comprised of 55% sand was observed in core CGS1018-2 at 234-237 cm. This sand layer was determined to be an event layer and was excluded from the data since it does not represent the typical sediment dynamics seen within the system. Excluding the anomaly, sediment throughout the entire harbor system were found to be composed primarily of the same sized material averaging $99.6 \pm 0.31\%$ being silt and clay, with over $52 \pm 0.47\%$ falling below the $10 \mu m$ cohesive boundary (Table 1).

*Table 1:* Grain size parameters and total organic content of sediments collected from the Georgetown inner harbor and suspended sediments from surrounding area.

<table>
<thead>
<tr>
<th></th>
<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
<th>&lt; 10 μm (%)</th>
<th>D50 (μm)</th>
<th>TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGS 1018-1</td>
<td>30.46</td>
<td>69.39</td>
<td>0.15</td>
<td>52.42</td>
<td>5.82</td>
<td>15.81</td>
</tr>
<tr>
<td>CGS 1018-2</td>
<td>30.86</td>
<td>68.55</td>
<td>0.59</td>
<td>49.92</td>
<td>5.87</td>
<td>15.60</td>
</tr>
<tr>
<td>CGS 1018-3</td>
<td>31.03</td>
<td>68.21</td>
<td>0.76</td>
<td>50.30</td>
<td>5.78</td>
<td>15.58</td>
</tr>
<tr>
<td>CGS 1018-4</td>
<td>31.17</td>
<td>68.75</td>
<td>0.08</td>
<td>53.54</td>
<td>5.59</td>
<td>16.55</td>
</tr>
<tr>
<td>Sampit River Suspended</td>
<td>20.20</td>
<td>79.80</td>
<td>0.00</td>
<td>52.88</td>
<td>8.23</td>
<td>N/A</td>
</tr>
<tr>
<td>Pee Dee River Suspended</td>
<td>20.56</td>
<td>79.44</td>
<td>0.00</td>
<td>52.70</td>
<td>8.17</td>
<td>N/A</td>
</tr>
<tr>
<td>East Entrance Suspended</td>
<td>21.30</td>
<td>78.70</td>
<td>0.00</td>
<td>57.86</td>
<td>7.54</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Grain size in the harbor shows every location has a similar distribution of grain size throughout the entire depth of the cores obtained showing that there is no temporal changes (Figure 4). By averaging these individual histogram values for each location, a trend is seen in both cores CGS1018-1 and CGS1018-4 (cores within the inner harbor) and also between cores CGS1018-2 and CGS1018-3 (cores at channel entrances) (Figure 5). Sediment from deeper within the inner harbor was shown to contain 5.8% more of sediment finer than 20 μm, while the opposite is true for the harbor entrance cores which had 5.6% more sediment coarser than 25 μm.

Suspended sediment grain size was measured at the eastern entrance to the inner harbor and near the mouth of the Sampit and Pee Dee Rivers. Grain size at all three sites revealed a composition of 20.2-21.3% clay and 78.7-79.8% silt with all showing very similar distributional trends. 52.9% of sediment was below the cohesive boundary at both river mouths, while 57.9% of sediment fell below this boundary at the eastern entrance to the inner harbor (Table 1). GSD for the suspended sediment samples showed a bimodal distribution with two peaks, one at 10 μm and the other around 35 μm (Figure 5). Sediment sampled at the river mouths of the Sampit (near western entrance) and the Pee Dee Rivers showed almost identical distributions while suspended sediment sampled at the entrance of the eastern channel of the inner harbor was found to be composed of finer material with, 5.1% more sediment falling below 10 μm.

In addition to the harbor samples and the suspended sediment samples, the 12 piston cores and six grab samples collected within the upper portion of Winyah Bay were analyzed. Grain size for the sediment found within the bay revealed three distinct groups with no special or temporal trends identified. One composed of more than 85% sand with
Figure 4: Grain size distribution of samples collected in the Georgetown Harbor.
the average sand grain size between 400 and 700 μm, the second, composed of between 45 and 85% sand with an average sand grain size of 93 to 200 μm, and the final group comprises of less than 25% sand where, if sand is present, averages 63 μm, right at the sand/silt border (Figure 6). All samples taken from the four harbor cores as well as suspended sediment grain size was found to fit within the parameters of the third group of sediment found within Winyah Bay, composed of mostly silt and clay sized sediment (Figure 7).
Figure 6: (a.) Scatter plot of samples taken from piston cores and grab samples within upper portions and Winyah Bay showing % of sand from each sample compared to the most common sand grain size overserved. (b.) Ternary plot showing grain size characteristics samples from piston cores and grab samples.
Figure 7: Ternary plot showing grain size characteristics of samples taken within Upper portions of Winyah Bay and samples taken within Georgetown Harbor.
Dry Bulk Density (DBD) and Total Organic Consentient (TOC). DBD of all the sediment from the harbor fell below 0.6 g/cc with an average of 0.34 ± 0.01% g/cc and shows an overall increasing trend with increasing depth. Some variation in this pattern is seen in all cores, primarily in cores CGS1018-1 and CGS1018-2, where slight decreases of DBD are seen around 145 cm in core CGS1018-1 and 120 cm in core CGS1018-2. Below this depth a slight decrease is seen followed by continuation of the increasing tendency. For TOC, the average throughout the harbor samples was found to be 15.99 ± 0.12% with all values measured ranging from 14 to 18% of total organic content. This highly cohesive and highly organic sediment was found constantly across the inner harbor (Figure 8).

X-ray Fluorescence (XRF) Element Distribution. XRF scans of the harbor cores revealed that samples were influenced by the content of Ca and Al, of which, Ca reduced the amount of noise seen throughout the ratios and thus were used for the analysis. The XRF ratio, Ti/Ca proved most useful in the identification of the dredge depths by examining for large changes in the ratio throughout the core. Once depth was dredge depth was identified using the XRF ratios, historic bathymetric maps and dredging reports from the USACE (2005, 2006, and 2008) were examined to verify the identified depth. 2006 dredge depth in core CGS1018-1 was identified to be around 160 cm below the seabed while in core CGS1018-2 it was found to be approximately 95 cm below the seabed (Figure 8). XRF ratios show that following the 2006 dredge boundary, changes in deposition occur which modify the system. In core CGS1018-1, following dredging, the ratio between Ti and Ca is altered, shifting towards a more negative ratio, and as new silting occurs and conditions stabilize, a shift towards a more positive XRF ratio is
**Figure 8:** Summary plots of cores taken from Georgetown Harbor including (a.) X-ray and associated brightness plot, (b.) XRF element intensity ratio of ln(Ti/Ca), (c.) dry bulk density, (d.) total organic content, and (e.) XRF total count sum. Orange Bands represent dredge depth. Dredge depth was not reached in core CGS 1018-3 and CGS 1018-4.
seen. Within the western portion of the channel (CGS 1018-1 and CGS 1018-2), USACE bathymetric maps reveal that the dredge depth was deeper than the depth reached by the cores obtained, thus, were unable to be identified (USACE 2005, 2006, and 2008).

The correlation of these cores across the four locations using the XRF data was unsuccessful due to dredge depths not being reached with the cores located within the western channel, the varying sedimentation rates between the sites, and anthropogenic mixing of the upper layers. The inability to correlate the cores reveals that each location has its own deposition and sedimentary characteristics. Cores taken from a past study of the harbor also had similar XRF scans done along with the Pb/Cs dating (Clark, 2018). These cores were collected within a location that was not dredged which had filled in rapidly following the modification of the Sampit River. Thus, were composed of much older sediment, which were also not able to be correlated to any of the current cores by the XRF data. Due to correlation not being possible, using the Pb/Cs dating collected for the older cores to aid in determination of age of the new cores collected during this study proved unsuccessful.

*X-Ray Images.* X-rays of all four cores were taken and revealed cyclical patterns of light and dark bands. Throughout the cores, where darker bands appear, the material is denser, and the opposite is true for the lighter bands. These larger cyclical patterns were identified at the peaks between the maximum brightness to the next peak of maximum brightness. This pattern is best observed in core CGS1018-4 but can be seen throughout all samples (Figure 8). Plots of brightness intensity are shown over the original X-ray images to better identify smaller changes in brightness and identify finer changes of individual laminae (Figure 8). Core CGS 1018-4 revealed, approximately 30.5 ± 0.81
**Table 2:** Count of lamina between each lighter lamination seen within X-ray for core CGS 1018-4.

<table>
<thead>
<tr>
<th>Depth in Core (cm)</th>
<th>Layer Thickness (cm)</th>
<th>Lamina Number</th>
<th>Lamina/Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>41 – 56</td>
<td>15</td>
<td>1 – 31</td>
<td>31</td>
</tr>
<tr>
<td>56 – 90</td>
<td>34</td>
<td>32 – 63</td>
<td>32</td>
</tr>
<tr>
<td>90 – 115</td>
<td>25</td>
<td>64 – 91</td>
<td>28</td>
</tr>
<tr>
<td>115 – 136</td>
<td>21</td>
<td>92 – 119</td>
<td>28</td>
</tr>
<tr>
<td>136 – 170</td>
<td>34</td>
<td>120 – 148</td>
<td>29</td>
</tr>
<tr>
<td>170 – 191</td>
<td>21</td>
<td>149 – 180</td>
<td>32</td>
</tr>
<tr>
<td>201 – 226</td>
<td>35</td>
<td>181 – 213</td>
<td>33</td>
</tr>
<tr>
<td>226 – 248</td>
<td>22</td>
<td>214 – 244</td>
<td>31</td>
</tr>
<tr>
<td>248 – 268</td>
<td>20</td>
<td>245 – 275</td>
<td>31</td>
</tr>
<tr>
<td>268 – 288</td>
<td>20</td>
<td>276 – 309</td>
<td>33</td>
</tr>
<tr>
<td>288 – 312</td>
<td>24</td>
<td>310 – 342</td>
<td>33</td>
</tr>
<tr>
<td>312 - 325</td>
<td>13</td>
<td>343 - 355</td>
<td>24</td>
</tr>
</tbody>
</table>

smaller laminae between each larger cycle. The counting of the lamina was done multiple times for each larger cycle and revealed similar results throughout (Table 2).

*Turbidity Measurements.* Along with the data collected from the cores, turbidity levels within the surrounding Winyah Bay area were obtained. A five-day average of four years’ worth of turbidity data was examined from the NERR station NIWBBWQ (Figure 9) (NOAA National Estuarine Research Reserve System). These turbidity measurements show large amounts of variation with some of the largest peaks seen around 240 NTU while other periods average around 20 NTU. Large amounts of variability, up to a 200 NTU shift, was seen throughout the four year period that was examined with largest peaks occurring once a once a month followed by a smaller peak. Turbidity levels collected as part of the Harbor Silting Project, at the USGS navigation mark near the
Figure 9: (a.) 5-day moving average of turbidity from Winyah Bay NERR Station NIWBBWQ over a 4-year period (NOAA National Estuarine Research Reserve System). 

(b.) 12-hour moving average of turbidity from USGS Navigation mark collected by Coastal Geosystems during phase 1 of Harbor Silting Project (Hanebuth et al. 2019).
eastern entrance to the inner harbor, show a similar trend where there are some periods of elevated turbidity over 200 NTU (Figure 9). One month’s worth of data, analyzed using a 12-hour average, shows that over this time, there are two periods of overall elevated turbidity approximately two weeks apart at times when spring tide is occurring. This pattern is seen regularly over the multi-year data set.

*Metal Concentrations.* In all cores, 60 different metals were measured at incremental depths. Sediment in each core was found to contain an average of between 13.4 and 15.5% Fe and Al together. When excluding Fe and Al, since they represent 99 ± 0.0001% of metals found in the inner harbor mud, along with all concentrations of metals which are often found naturally in terrigenous sediment, including Ti, Mn, Mg, Ca, and K, the composition of the mud in the inner harbor contained 0.15% ± 0.002% of additional metals (Figure 10). Toxicity levels were examined for seven heavy metals, including arsenic, cadmium, chromium, copper, lead, nickel, and zinc, several of which were found to be above the standardized toxicity limits of TEL, PEL, and ERL, but none were found to be above ERM (Long and Morgan 1990, Long et al. 1995, MacDonald et al. 1996). Out of the seven heavy metals examined, five metals were observed over the ERL for at least one or more sites across the inner harbor. Arsenic concentrations in the inner harbor ranged from 19.3 to 23.8 ppm. These concentrations are over double the ERL concentration level for Arsenic (8.2 ppm), over three times the TEL (5.9 ppm), and 11 times the PEL (1.7 ppm) concentration. Heavy metals including chromium (77.4 to 105.6 ppm), copper (26.8 to 40.2 ppm), nickel (28.8 to 36.6 ppm), and zinc (90.7 to 180.3 ppm) were also found to have concentrations above the ERL concentrations of 81.0 ppm, 34.0 ppm, 20.9 ppm, and 150 ppm, respectively (Table 3, Figure 10).
Figure 10: Total metal content in the Georgetown inner harbor sediment excluding which are often found naturally occurring in sediment (Fe, Al, Ti, Mn, Mg, Ca, and K). For single-core datasets that consist of more than four metal concentration values, boxes illustrate first to third quartile with its median value represented by a bar horizontally across the box. Whiskers show maximum and minimum values for each dataset. For datasets with less than four metal concentration values, top and bottom of the boxes represent maximum and minimum values and no whiskers are shown. The mean is represented in all boxes with an “x”, and the measured concentration data points are shown on the plots with an “o” marker. Markers (“o”) outside of the box represents outlier values. Outlier values are determined as values which fall more than 1.5 times the range of the box outside the first and third quartile values. When metal concentrations are referenced in the text, average values (“x”) of metal concentrations are used since these values best represent the overall concentrations.
Table 3: TEL, PEL, ERL and ERM heavy metal concentrations (Long et al. 1995) and average concentration of heavy metals in each core taken throughout the Georgetown inner harbor. Underlined values represent concentrations above ERL concentrations.

<table>
<thead>
<tr>
<th>Metal</th>
<th>TEL</th>
<th>PEL</th>
<th>ERL</th>
<th>ERM</th>
<th>CGS 1018-1</th>
<th>CGS 1018-2</th>
<th>CGS 1018-3</th>
<th>CGS 1018-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>5.9</td>
<td>1.7</td>
<td>8.2</td>
<td>70.0</td>
<td>19.5</td>
<td>19.3</td>
<td>22.9</td>
<td>23.8</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.6</td>
<td>3.5</td>
<td>1.2</td>
<td>9.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>37.3</td>
<td>90.0</td>
<td>81.0</td>
<td>370.0</td>
<td>105.6</td>
<td>77.4</td>
<td>82.8</td>
<td>83.4</td>
</tr>
<tr>
<td>Copper</td>
<td>35.7</td>
<td>197.0</td>
<td>34.0</td>
<td>270.0</td>
<td>40.2</td>
<td>26.8</td>
<td>37.0</td>
<td>27.7</td>
</tr>
<tr>
<td>Lead</td>
<td>35.0</td>
<td>197.0</td>
<td>46.7</td>
<td>218.0</td>
<td>40.1</td>
<td>27.3</td>
<td>28.1</td>
<td>30.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>18.0</td>
<td>36.0</td>
<td>20.9</td>
<td>51.6</td>
<td>36.6</td>
<td>28.8</td>
<td>28.8</td>
<td>32.6</td>
</tr>
<tr>
<td>Zinc</td>
<td>123.0</td>
<td>315.0</td>
<td>150.0</td>
<td>410.0</td>
<td>180.3</td>
<td>90.7</td>
<td>104.1</td>
<td>152.6</td>
</tr>
</tbody>
</table>

Metal Correlation with Sediment Properties. Correlation coefficients ranging from -1 to 1 and the associated p-values were calculated for total metal content compared to TOC, DBD, and grain size parameters including clay, silt, and sand content, content of sediment below the cohesive boundary, skewness of the GSD, and D10, D50, and D90 parameters, which show the grain size at which 10, 50, and 90% of sediment size fall below. The coefficients showed that a significant negative correlation (-0.69) was seen between total metals and TOC in core CGS 1018-4, and another negative correlation (-0.84) between total metal content and DBD was seen in core CGS 1018-2 (p < 0.05). These two trends were the only correlations found to be significant throughout all cores.
Table 4: Correlation Coefficient values between total metal content compared to DBD, TOC, and GSD parameters. White values represent significant correlations (< 0.05), red cells represent a negative correlation, and blue cells represent positive correlations.

<table>
<thead>
<tr>
<th></th>
<th>Total Metals (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CGS 1018-1</td>
</tr>
<tr>
<td>Dry Bulk Density (g/cc)</td>
<td>-0.35</td>
</tr>
<tr>
<td>TOC %</td>
<td>0.47</td>
</tr>
<tr>
<td>Clay (&lt;4 μm)</td>
<td>0.07</td>
</tr>
<tr>
<td>Silt (4&lt;x&lt;63 μm)</td>
<td>-0.06</td>
</tr>
<tr>
<td>Sand (&gt;63 μm)</td>
<td>-0.36</td>
</tr>
<tr>
<td>&lt;10 μm</td>
<td>0.17</td>
</tr>
<tr>
<td>Skewness</td>
<td>-0.01</td>
</tr>
<tr>
<td>D10</td>
<td>-0.07</td>
</tr>
<tr>
<td>D50</td>
<td>-0.15</td>
</tr>
<tr>
<td>D90</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

No significant trend was seen between metal content and any of the grain size parameters examined, and no cores showed any overlapping trends (p > 0.05) (Table 4). While GSD and TOC are often seen to correspond with metal content due to the varying pathways of accumulation, both these parameters were homogeneous throughout the inner harbor making it difficult to identify any trends.

Changes in Metal Deposition. The dredge depth of the last dredging effort in 2006 was only reached in the two sediment cores within the eastern channel (Cores CGS 1018-1 and CGS 1018-2). Concentrations for 12 metals, including several of the heavy metals found to be above harmful levels, were examined using box plots (Figures 11 & 12).
In core CGS 1018-1, Pb and Cr were found at higher concentrations below than above the stratigraphic dredge boundary, identified at 160 cm below the seabed (Figure 11). Pb and Cr concentrations above the dredge boundary were found to average 32.76 ± 0.36 and 90.80 ± 2.15 ppm, respectively, while below the average concentrations were 52.37 ± 7.22 and 130.33 ± 18.41 ppm, respectively. All other metal concentrations revealed overlapping ranges in the box plots, i.e., no statistically significant difference. Particularly, Al, Ni, Zn, Ba, and Mn concentrations were relative the same above and below this stratigraphic depth. While the metal concentrations of Cu and Fe do statistically overlap prior and after the last dredge time, these concentrations reveal tendencies of higher concentrations below the 2006 dredge depth like Pb and Cr. Unlike Pb and Cr, Br had a tendency towards higher concentrations above the dredge depth (above: 110.16 ± 8.08 ppm, below: 66.50 ± 14.64 ppm).

Within core CGS 1018-2, less variations were seen than in the previous core when comparing concentrations below and above the 2006 dredge boundary, identified at 95 cm below the seabed (Figure 12). Often, concentrations above the dredge depth fell statistically within the range of concentrations seen below. This observation includes the metals Al, Cu, Pb, Ni, Zn, Ba, Fe, and Cr. The other four metals examined, As, Br, Mn, and Mg, show a tendency of higher concentrations above the dredge depth, with 23.94 ± 0.98, 1107.19 ± 8.83, 1584.46 ± 246.27 ppm, and 0.84 ± 0.03%, respectively, when compared to 17.62 ± 2.40, 48.53 ± 13.50, 963.21 ± 248.05 ppm, and 0.59 ± 0.02%, respectively; but the value still showed some statistical overlap in concentration range prior and post dredging. Dredge depths in the two cores collected in the western channel, were not reached by the gravity cores obtained.
Figure 11: Box plots of metal concentrations above and below the dredge boundary 160 cm below seabed from core CGS 1018-1 taken within the eastern channel of the Georgetown inner harbor.
Figure 12: Box plots of metal concentrations above and below the dredge boundary 90 cm below seabed from core CGS 1018-2 taken at the eastern entrance of the Georgetown inner harbor.
Differences in the heavy metal concentrations of arsenic, chromium, copper, lead, nickel, and zinc, both above and below dredge depth, were also examined using the XRF element ratio with a base of potassium. Potassium was used as the base for the ratio for these analyses since it is a common terrigenous element and was shown to have less of an overall influence on the ratio trends than calcium. Using K as the base of the ratios allowed for changes in the heavy metal intensities to be the controlling factor seen in the XRF ratio plots. This was observed when comparing the natural log of the element ratios Cr/Ca, K/Ca, and Cr/K. Using Ca and K as the base for each ratio and then comparing the two together demonstrated which element had a larger overall influence by examining which trend the K/Ca curve was more similar to. Knowing which element is more dominant is important in regards to ensuring the base element has a minimal influence on the ratio curve that is observed for the metals. A similar trend was seen in both graphs when calcium is used as the base element of the ratio where higher counts of Ca can be seen below 125 cm, but a more unique trend which allows for Cr to be the primary factor driving variation in the ratio plot was seen when K was used as the base (Figure 13). Similar results were observed when using other metals in the element ratios with Ca and K as the base. These plots suggested that potassium has less overall influence on the ratio and is more useful for this study in examining vertical changes in metal accumulation. Therefore, metals examined using XRF ratios were normalized to K.
XRF element ratios for core CGS 1018-1, revealed varying accumulation patterns with depth with when comparing vertical changes between the XFR ratios and the measured metal concentrations throughout the core. This difference was observed primarily with Co and Ni where below the 2006 dredge boundary, the XRF ratios showed lower Co and Ni levels, but the concentrations revealed increasing concentrations of these metals (Figure 14). For core CGS 1018-2, the XRF ratios more closely resembled what was observed with the metal concentrations but showed less overall variation with depth. XRF ratios in core CGS 1018-2 measured above the dredge boundary were constricted within the range of the ratios found below this boundary (Figure 15).
Throughout all cores, variation in the XRF ratios of heavy metals were changing with depth revealing lots of noise within the data. For all cores, every heavy metal XRF ratio showed a high variability. This variability over a small depth range represented changes in metal concentrations with peak ratios of more positive values representing increased content of the heavy metal or less K content. Peaks that are not seen across all ratios for an individual core suggest changes in heavy metal content and not variability in K.

Such variability and overall changes were not only observed for cores CGS 1018-1 and CGS 1018-2 but also within the western channel in cores CGS 1018-3 and CGS 1018-4 (Figures 16 & 17). While cores in the eastern channel show some slight variability in heavy metal content, with large decreasing changes in Co and Ni ratios only being seen associated with the dredge boundary, the overall ratio levels remain the same with depth. Cores in the western channel revealed larger ranges in XRF element ratios closer to the modern seabed while smaller ranges are seen with increasing depth. In core CGS 1018-3, several element ratios, including that of Cr, Cu, and Ni show a slight increase moving upwards through the core at 85 cm in depth. Core CGS 1018-4 shows a similar trend for Cr and Cu, but for Ni a more linear increasing trend ascending upwards through the core trend is seen. All other heavy metals in cores CGS 1018-3 and CGS 1018-4 show more stability in average XRF element ratios and trends throughout the entire core.
Figure 14: XRF element ratios for six heavy metals from core CGS 1018-1 taken within the eastern channel of the Georgetown inner harbor. Orange bar represents 2006 dredge depth identified using USACE (2005, 2006) bathymetric maps and ln(Ti/Ca) XRF ratios.
Figure 15: XRF element ratios for six heavy metals from core CGS 1018-2 taken at the entrance to the eastern channel of the Georgetown inner harbor. Orange bar represents 2006 dredge depth identified using USACE (2005, 2006) bathymetric maps and ln(Ti/Ca) XRF ratios.
Figure 16: XRF element ratios for six heavy metals from core CGS 1018-3 taken at the western entrance to the Georgetown inner harbor.
Figure 17: XRF element ratios for six heavy metals from core CGS 1018-4 taken within the western channel of the Georgetown inner harbor.
Variations in Metal Content Across the Inner Harbor Mud. When comparing metal concentrations to identify potential sources for these metals, it was discovered that several of these concentrations were seen to have lateral variability across the inner harbor (Figure 18). For cores in the eastern portion of the inner harbor (CGS 1018-1 and CGS 1018-2) only concentrations found above the dredge depth were considered, since cores in the western portion (CGS 1018-3 and CGS 1018-4) did not reach below dredge depth.

Arsenic concentrations were found to be lower only in core CGS 1018-1 averaging 18.74 ± 1.17 ppm while all other cores averaged between 22.88 ± 1.46 to 23.94 ± 0.98 ppm. Metals including Cr, Cu, Pb, Ni, Zn, and Al were found at the highest concentrations in core CGS 1018-1 when compared to all other cores. Core CGS 1018-2 revealed higher concentrations of Mn than any of the other three cores. Metals including Pb, Ni, Zn, and Al revealed a tendency of elevated levels at the sites further within the inner harbor (CGS 1018-1 and CGS 1018-3) and lower concentrations at the entrances with each of these metals having the highest concentrations in core CGS 1018-1. In the eastern portion of the inner harbor, cores CGS 1018-1 and CGS 1018-2 revealed elevated levels of Fe and lower concentrations of Br when compared to the western channel cores. Similar concentrations of both Ba and Mg were found throughout the inner harbor with some sites having a larger range of concentrations than others.
Figure 18: Box plots of metal concentrations throughout Georgetown inner harbor.

Colored lines represent sediment quality guidelines produced by Long et al. (1995). For legend see Figure 18 continued.
Figure 18 continued: Legend of boxplots including sample size (n), what box and whiskers represent, and which core is represented by each box. Samples where boxes fell completely within the range of whiskers of another plot were considered statistically indistinguishable, samples where only a portion of the box fell within the range of another plots whiskers were determined to have a potential statistical difference, and if no overlap was seen between plots it was determined to be significantly different.
Discussion

Silting Dynamics of the Inner Harbor Mud

*Silting in the harbor.* Sediment sampled within Winyah Bay was found to be a part of one of three groups determined by grain size distribution, of which, the material found within the inner harbor mud fits into the third group, composed of the finest material with sand content less than 25%. Sediment fitting into this group were found throughout much of the upper portion of Winyah Bay where there is low flow velocity. The suspended sediment samples taken were also found to fit within this group of fine sediment corresponding to what was observed within the harbor. Since there are multiple sources of this fine sediment found throughout the bay, it suggests that there is plenty of this material which can be supplied to the harbor leading to a continuation of silting until no more sediment can accumulate due to lack of accumulation space.

Flocculation is a very common process that occurs within estuaries where particles are tightly held together by organic matter and fine grained material and are continually changing sizes by accumulating more material or breaking apart (Eisma 1986). With sediment in the inner harbor falling within the third group of identified sediment, 52 ± 0.47% of the sediment composition being finer than 10 µm, and 16 ± 0.12% of total organic matter in the inner harbor mud, as well as in suspension, it is likely that the settling occurring in the inner harbor is done through flocculation. The small
particles aggregate together and behave, hydrodynamically, as a larger particle while in the water column which allows for faster deposition.

The suspended sediment at the eastern entrance and both the Sampit and Pee Dee river mouths, shows a much higher composition of finer grained material than the sediment which had been deposited within the inner harbor. Although the sediment and organic matter form flocs and settle as larger particles, flocs that are composed of larger grains would be larger than those composed of smaller grains and thus settle faster. In the inner harbor, this process, suggests that while there is plenty of material around 10 μm that is suspended within the water column, a larger portion of the sediment 20 μm and greater are the ones that settle within the inner harbor. The flocs composed of the finer material are likely to stay in suspension even with the limited water current that moves through the inner harbor.

The association between larger sediment and the settling of flocs, is also seen when looking at the material at the entrances compared to deeper within the inner harbor. A study found that flocs that contain silt have an overall larger size and thus settle out of suspension at least twice as fast as flocs containing only clay sized particles (Tran and Strom 2017). This process is seen in the grain size distribution where a slightly more coarse composition is seen at the entrances. More flocs composed of relatively coarser grained material (20 - 40 μm) settle at the entrances due to the larger sizes while flocs composed of finer material are less dense and travel further within the inner harbor before settling. The bathymetric maps taken before and after dredging by the USACE in 2006 and 2008 show that sediment deposition occurs at higher rates near the entrances of the inner harbor compared to deeper within. These maps further support what is observed
with grain size as flocs containing coarser sediment settle faster, but flocs composed of finer material are able to be transported deeper within the inner harbor, settle at slower rates, and are more likely to be re-suspended resulting in slower deposition rates when compared to the inner harbor entrances. The higher rate of deposition occurring at the entrances is also supported by the XRF data being unable to be correlated.

Following dredging, the harbor would silt up to its current depths within months to a few years, depending on location within the inner harbor, which is why dredging was a constant requirement (GEL Engineering LCC 2022). X-ray images of the cores suggest that sediment is moved into the harbor by the tides and settles at periods of slack tide. This is seen with in this data when looking at the cyclical lighter colored bands in the x-rays, approximately 30 smaller lamina were seen per larger cycle (Figure 8, Table 2). The 30 smaller cycles per larger cycle is similar to what would be expected for tides in the area. The Georgetown harbor is influenced by semi-diurnal mixed tides, thus, you would expect around 28 tidal cycles to occur between two spring tide periods (Patchineelam et al. 1999). The number of lamina observed per larger cycle in the X-ray images differing from theoretical values expected could be due to variability of tidal strength, suspended sediment available, erosion, and resuspension of sediment as these signals are inconsistent and often poorly preserved (Liu et al. 2022). Due to the number of smaller laminae between each larger cycle, smaller variations seen in the x-ray images are expected to coincide with individual tidal cycles, while larger cycles show the differences between spring and neap tides. Spring tides and the associated stronger current would lead to more sediment in suspension allowing deposition to occur in the harbor at higher rates while during neap tide conditions there is less sediment in suspension and thus
lower sedimentation rates. Repetitive filling, occurring during every tidal cycle, explains the rapid silting rates which have been observed within the harbor.

The Turbidity Maximum Zone (TMZ) within Winyah Bay has been documented as far up as the entrance to the Pee Dee River (Patchineelam and Kjerfve 2004). The location of the TMZ can also be seen in the turbidity levels collected from the NERR station and USGS navigation mark. The large peaks seen in Figure 9 show that there are periods of time where the TMZ was able to reach each of these sites during periods of spring tides, approximately twice a month. While turbidity is not a direct measurement of the suspended sediment the two are closely related (Davies-Colley and Smith 2001). Since large variability is seen in the turbidity levels of upper Winyah Bay one can expect the suspended sediment levels to also be highly variable. The deposition of fine material within the inner harbor during a single tidal cycle, along with highly variable suspended sediment rates, show that deposition in the harbor is not a continuous rate but likely has large amounts of variability. Times of low discharge from the Pee Dee River are associated with the TMZ reaching the deepest within Winyah Bay (Patchineelam and Kjerfve 2004). This is due to the location of the TMZ being near the location of maximum saltwater intrusion and the large amounts of freshwater discharged from the rivers prevents the saltwater brought in by the tides to penetrate as deeply into the estuary (Patchineelam and Kjerfve 2004). Therefore, we would likely see the largest sedimentation rates in the harbor during spring tides and periods of low river freshwater discharge.

While some models predict constant silting rates within the inner harbor based on differences of bathymetric maps, this study shows that the rates silting is occurring are
not constant and change depending on tides, but similar to other reports, following dredging, the silting continues as long as there is accommodation space (GEL Engineering LCC 2022). Following this period of rapid filling, once depth is maintained by natural causes such as the wave base, as seen in the western portion of the channel, or anthropogenic sources, such as currents and mixing produced by vessel traffic seen primarily in the eastern channel, the sedimentation rate slows dramatically. Without having sufficient bathymetry of the inner harbor to show exactly when the current depth were reached, it is difficult to identify an overall sedimentation rate as it appears to be somewhat variable due to changes within tidal strength but also influences of storms, wind direction, and river discharge. With the X-ray images presented in this study, it shows that sedimentation occurred at different rates depending on the tides, but following dredging, very rapid accumulation occurs over a matter of months until no more sediment could be accommodated.

The silting dynamics seen with the current system make the models used for the overall Georgetown Harbor Silting Project much more complex. Sedimentation rate predictions based off of the bathymetric maps may be less useful for the inner harbor since they project a constant rate of deposition over time while this report suggests that these rates are constantly changing due to factors such as tidal strength and river discharge. Also, these rates alter since flocculants are constantly changing size as they continuously break apart and reform into varying sizes (Eisma 1986). The continuous changes make it much harder to look at sedimentation in the harbor. Large silting events could also occur during storms as more sediment is suspended and pumped into the harbor, or when wind is moving into Winyah Bay raising the overall water level
increasing flow in the harbor. Due to these factors, uniform shoaling rates, calculated in these models, may not be the best representation of what is occurring in the system.

Overall, silting dynamics in the area appear to be driven by flocculation of the sediment and organic material and also tidal conditions and river discharge. Flocs containing slightly larger grained material tend to fall out near the entrances leading to a higher sedimentation rate, while the flocs with more fine grained material settle further within the inner harbor. The filling of the harbor occurs throughout a tidal cycle as new sediment is pumped in and is able to settle at periods of slack water. While there is variation of the sedimentation rate depending on the strength of the tides and river discharge, there is plenty of material available in the system coming from the surrounding areas suggesting that without natural or anthropogenic forces maintaining the current depths, the harbor would completely silt up.

*Sediment Dynamics Outlook.* In order to develop a better overall understanding of this system, get a better idea on the sedimentation rates, and gather further evidence of the filling occurring over a single tidal cycle, *in-situ* sediment traps installed flush with the seabed could be used to measure the accumulation of the fine grained material could be deployed in the harbor. While current deposition in the harbor is very low and the effectiveness of this method would be minimal, if dredging does occur in the harbor in the near future, an opportunity presents itself to examine exactly how silting in this unique system occurs. Age dating the sediment within the cores would not only help provide information about sedimentation rates, but also could help strengthen the argument for the dredge depth locations, verifying that the changes in sediment record are due to changes following dredging. This would allow for much more accurate
sedimentation rates of each part of the harbor as well as evidence to show how river discharge, tides, and amount of suspended sediment in the system affects these rates.

Metals in the Inner Harbor Mud

*Environmental Concern of Metals in the Inner Harbor Mud.* Throughout the inner harbor, several heavy metals are observed at potentially hazardous levels when compared to TEL, PEL, ERL, and ERM concentrations (Long and Morgan 1990, MacDonald et al. 1996, Long et al. 1995). Concentrations above their respective ERL were found for heavy metals including arsenic, chromium, copper, nickel, and zinc. These concentrations can be harmful to marine organisms as well as people who use the inner harbor for business and recreation. While being trapped within the sediment, the overall bioavailability and toxicity of these heavy metals is minimized, however, when found within the water column, these heavy metals pose a much larger threat (Zhang et al. 2014). The physical and geochemical properties of the sediment, such as high organic content and fine-grained material, and physical-chemical properties of the overlying and pore water, such as low oxygen, as observed in the inner harbor, aid in the minimization of the impact these heavy metals have on the surrounding environment (Zhang et al. 2014). If the sediment were to be dredged and moved into an area where oxygen is more readily available, not only would the extreme amounts of organic material use up large sums of the available oxygen, but the bioavailability and toxicity of the metals would likely be increased due to the oxidation process.
Table 5: Heavy metal concentrations (ppm) measured throughout the Georgetown inner harbor from studies dating back to 1993 (GEL Engineering LCC 2022, Long 1998, Ward 1993).

<table>
<thead>
<tr>
<th>Metals</th>
<th>Coastal Geosystems 2021 (This Study)</th>
<th>GEL 2021</th>
<th>Long 1998</th>
<th>Ward 1993</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CGS 1018-1</td>
<td>CGS 1018-2</td>
<td>CGS 1018-3</td>
<td>CGS 1018-4</td>
</tr>
<tr>
<td>Arsenic</td>
<td>19.5</td>
<td>19.3</td>
<td>22.9</td>
<td>23.8</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>105.6</td>
<td>77.4</td>
<td>82.8</td>
<td>83.4</td>
</tr>
<tr>
<td>Copper</td>
<td>40.2</td>
<td>26.8</td>
<td>37.0</td>
<td>27.7</td>
</tr>
<tr>
<td>Lead</td>
<td>40.1</td>
<td>27.3</td>
<td>28.1</td>
<td>30.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>36.6</td>
<td>28.8</td>
<td>28.8</td>
<td>32.6</td>
</tr>
<tr>
<td>Zinc</td>
<td>180.3</td>
<td>90.7</td>
<td>104.1</td>
<td>152.6</td>
</tr>
</tbody>
</table>

The overall concentrations of heavy metals varied between studies (Table 5). Out of four studies measuring metals around the inner harbor (GEL Engineering LCC 2022, Long 1998, Ward 1993), dating back to 1993, all found arsenic concentrations well above the ERL concentration of 8.2 ppm. Both chromium and nickel concentrations were above ERL levels of 81.0 and 20.9 ppm respectively, for at least 75% of sites in all but one study (GEL Engineering LCC 2022, Long 1998, Ward 1993). The GEL study shows major differences not only to the concentrations presented for this study, but also the other two studies, despite samples being taken only five months prior to the samples collected and presented above (GEL Engineering LCC 2022). This variability in metal concentrations by the GEL study could be due to the method of which samples were collected. Samples of the inner harbor mud collected by GEL were analyzed as bulk samples, where sediment from the entire core was combined into one mixed sample, as opposed to taking measurements at a specified interval. The consistency, apart from the
GEL study, between the heavy metal concentrations suggest that while there is always some variability, overall metal concentrations have not seen significant changes since the 1990s for heavy metals including arsenic, cadmium, chromium, and nickel, and that there is has always been some variation in metal content laterally across the inner harbor. With these similarities in concentrations between the data presented above and other previous studies in the area, lack of variation in heavy metal concentrations seen throughout the inner harbor is likely due to input sources which have not drastically changed between the 1990s and when the inner harbor filled to its current depths.

**Metals and Sediment Property Correlation.** No overall trends were seen when examining metal concentrations compared to grain size parameters, DBD, or TOC in contrast to what was expected (Table 4). Higher metal concentrations are expected to be associated with finer grained material, especially material smaller than the cohesive boundary of 10 μm, and material containing high amounts of organic matter (Long 1998, Pradit et al. 2013, Tansel and Radiuddin 2016, Zhang et al. 2014). Throughout the samples, minor variation in sediment composition were observed vertically throughout the core and laterally across the inner harbor. Without large variation in sediment composition, the difficulty in determining correlation between metals and sediment GSD, TOC, and DBD increases. One would expect, if more disparity between GSD, TOC, and DBD was observed and samples contained coarser and larger distributions of sand, as seen in the first and second group of what was found in Winyah Bay, then correlations and trends would be more apparent. A significant correlation between metal content and grain size was seen in Winyah Bay when samples were examined within the inner harbor and throughout the entire estuary allowing for a wide variety of sediment to be sampled.
(NOAA 1998). While no correlations between metals and sediment parameters were seen in this study, the similarities in the sediment across the inner harbor proved beneficial. Without differences in the sediment GSD, TOC, and DBD, differences between heavy metal concentrations laterally across the inner harbor are more likely due to differences in metal sources and not differences in sediment characteristics that these metals interact with.

**Metal Variation Through Time.** For Core CGS 1018-1 metals such as Pb, Br, and Cr revealed different concentrations above and below the dredge depth (Figure 11). Other metals that were examined, often showed concentrations both above and below the dredge depth that either completely or dominantly fell within the range of opposing (above/below) concentrations which were interpreted as statistically indistinguishable. Metals showing this overlapping range include Al, Cu, Ni, Zn, As, Ba, Fe, and Mn. Both Pb and Cr had lower concentrations above the dredge boundary compared to those below. These differences in concentrations could be due to the changes in the potential source of both metals along with the opening and closing of industry and the usage of the working waterfront. Pb and Cr are both common pollutants produced by the steel industry and may show higher concentrations below the dredge boundary since the Georgetown steel mill was shut down beginning in 2003 (DoE 1995). The closure of the steel mill likely lead to a reduction of the pollution coming from this potential source, thus lower concentrations of these metals were observed after dredging in 2006.

Br is the only metal examined in core CGS1018-1 which did not have an overlapping range and had higher concentrations above than below the dredge depth. These higher concentrations could also have to do with the source of where the Br is
coming from. One potential source of Br for the entire Georgetown harbor is the paper industry (Vainikka and Hupa 2011). Assuming that the source for the Br measured in this area is from the paper mill, it is possible that higher production of paper products or less preventative measures to prevent the contamination, could lead to the increase in Br concentrations that is seen above the dredge depth.

For the eastern entrance, core CGS1018-2, concentrations of metals revealed that above the dredge boundary, metals concentrations typically fall between the ranges of samples for the metal concentrations below the dredge boundary. This tendency is seen for all metals examined except for Br, Mn, and Mg (Figure 12). While Mn and Br concentrations are slightly higher above the dredge depth, a majority of both samples fell within the range of concentrations measured below. Mg concentrations had higher concentrations above the dredge depth and could be due to a potential local source much closer to the eastern entrance. Overall, in this core, metal concentrations above and below the dredge depth were much more similar than the metal concentrations above and below in core CGS 1018-1.

For the cores in the western portion of the channel, CGS 1018-3 and CGS 1018-4, changes in metal content was observed for Cr, Cu, and Ni in the XRF data (Figures 16 & 17). Without reaching the dredging depth with these cores, comparing changes above and below the dredge boundary is not feasible, but the changes seen with the XRF ratio curves reveal that there are changes occurring on a smaller timescale. With the inner harbor filling within a matter of months identifying the reasoning for these changes is difficult as it could be due to a very short lived event.
Examining the metal variation through time proved difficult due to only half of the cores collected reaching below the dredge depth in the respected area, and only eight and seven samples from cores CGS 1018-1 and CGS 1018-2, respectively, which were measured for metal concentrations. In core CGS 1018-1, five samples were from above the dredge boundary and three taken below, while in core CGS 1018-2, only three samples were collected above and four below. With the differing numbers of samples above and below the dredge boundary for both cores, all statistical analyses were unsuccessful. Box plots used to show the differences above and below in Figures 11 and 12 may also not be the best representation due to the few number of samples along with the large amounts of variability seen with the accumulation of the metals which is shown in the XRF ratio plots (Figures 14 and 15). Metal concentrations examined may only represent a small time period since the deposition of sediment in this area occurs at very rapid rates throughout most of the inner harbor (GEL Engineering LCC 2021). Although results may be influenced by factors such as accumulation rates and small and differing sample sizes, examining metal concentrations which do not tend to overlap in range and those which have the largest differences such as Mg in core CGS 1018-2 may prove more crucial in understanding this system since the variation of other metals may not be significant.

Variations of Metals Across the Inner Harbor and Potential Sources. When examining potential sources, the lateral variability of concentrations across the inner harbor was examined for all samples above the dredge depth. Several metals, including Pb, Ni, Zn, and Al, were all found at greater concentrations within the inner harbor (CGS 1018-1 and CGS 1018-4), with the largest concentrations observed in core CGS 1018-1,
when compared to the concentrations at the entrances (Figure 18). This trend could be due to the 3% greater amount of cohesive material (> 10 μm) being observed at sites further within the inner harbor which are able to entrap and contain these metals at higher rates than sediments above 10 μm (Tansel and Rafiuddin 2016). The rate at which each of these sites accumulate sediment also could influence the metal concentrations by dilution. The two sites at the entrances are known to have much higher deposition rates, and the eastern portion of the inner harbor has the slowest (GEL Engineering LCC 2021). Due to the differences in deposition, metals at the entrances may be found in more diluted concentrations when compared to those within the inner harbor. Slower deposition could allow for more metals to accumulate which get trapped in flocs and deposited while faster deposition does not reveal as long of a time signature for the metals due to the dilution of the concentrations.

Another possibility of why this tendency of higher concentrations further within the inner harbor is seen with Pb, Ni, Zn, and Al could be due to the sources where these metals are introduced into the inner harbor. The steel mill located along the northwestern bank of the inner harbor is one possible source of metal pollutants in the area. Steel production is known to produce several contaminants including each of these four metals. With the Georgetown steel mill temporarily ceasing operations in 2003 it is possible that these heavy metals were input into the water column by surface runoff after the mill closed (DoE 1995). Larger concentrations found within the inner harbor, closer in proximity to the steel mill, and in areas of lower sedimentation rates, explains why higher concentrations of Pb, Ni, Zn, and Al are seen further within the inner harbor when compared to the entrances.
Metals which did not have increasing concentrations further within the inner harbor, but are also commonly found to be contaminants produced by the steel industry include Fe, As, and Mn (Figure 18) (DoE 1995). Contrary to what was expected, Fe concentrations were found to be slightly higher in the eastern portions of the inner harbor than in the west suggesting that there is another potential source other than the steel mill. The eastern portion of the channel is bordered by a working waterfront with several businesses and tourism along with increased vessel traffic, both recreational and industrial. With iron concentrations only elevated on this side of the inner harbor, potential sources, other than the steel mill, for this iron could be the shipyards and marinas, docks, and sources stemming from development along the waterfront.

Manganese concentrations were expected to be highest closest to the steel mill, but in turn were actually found in greater concentration at the eastern entrance in core CGS 1018-2 and lowest concentration in core CGS 1018-1 (Figure 18). Common Mn sources include mining, metal smelting, agricultural products such as pesticides, fossil fuel burning, and can also occur naturally as it is often leached from rocks (Li et al. 2013). With concentrations only elevated at the eastern entrance and not the western entrance as well, it is not likely that this source came in from Winyah Bay. While Mn concentrations above the dredge boundary are higher, concentrations found below the dredge depth are more uniform with what is seen across other locations, leading to the conclusion that this elevated concentration of Mn came from a closer potentially buried source located near the entrance and only had influence in this area after dredging in 2006.
Arsenic concentrations were found to be the lowest in core CGS 1018-1 within the eastern channel and highest concentrations in core CGS 1018-2 (Figure 18). Potential sources that were hypothesized to be major contributors of As to the inner harbor were out-spill pipes and the steel mill. The lateral distribution pattern of As reveals these potential sources may not be the main influencers on As concentrations across the inner harbor. Instead of looking for sources, examining the pathway of As to the seabed may help explain the variation. Co-precipitation of As with Mn-oxyhydroxides is a common pathway which transports As in the water column to the seabed (Nath et al. 2005). When comparing the variation of As and Mn across all locations, a similar pattern is seen with core CGS 1018-1 having the lowest concentrations, CGS1018-2 having the highest, and CGS 1018-3 and CGS 1018-4 both falling in between. Similar tendencies in both As and Mn concentrations suggest that the pathway that As is transported to the seabed has a greater influence on its distribution than potential sources.

Metals such as Cr and Cu both had elevated concentrations in core CGS 1018-1 compared to the other cores which all showed similar concentrations. The range of Cr and Cu concentrations shown in the box plots for core CSG 1018-4 were slightly above those for the cores at the entrance but not as much as what is seen for Pb, Ni, Zn, and Al (Figure 18). The slight variation of Cr and Cu concentrations seen within western channel compared to the two entrances, could be due to the 3% difference in amount of cohesive material or the faster rate of deposition while the main source of these metals is located closer to core CGS 1018-1. Potential sources for chromium include the steel mill as it is a common byproduct produced in this industry, recreational and industrial vessels, located in the shipyards and marinas, as several of the parts and ornamentation of these vessels
contain chromium, and surface runoff from the harbor front businesses (DoE 1995). A potential source of copper could be surface runoff from the businesses and tourists along the working waterfront. Metal pipes, electrical wires, and automobile parts such as brake pads on cars all have high concentrations of copper composition which degrade over time allowing them to be transported into the harbor by surface runoff (Srivastava 2009). Another possible source of Cu which is located nearest the location of core CGS 1018-1 could be the shipyards and marinas. A study identified antifouling agents used on marine vessels to be a potentially significant source of copper pollution off the coast of California (Young et al. 1979). With several potential sources and uses of Cu it is difficult to determine exactly which source a majority of these heavy metal contaminants come from.

Bromine was observed in elevated levels only in the western portion of the channel when compared to the eastern (Figure 18). Br is commonly used in agriculture, the paper industry, and industrial cooling for water treatment (Vainikka and Hupa 2011). Potential sources including both the paper industry and agricultural sources could produce contaminants, such as bromine, which travel down the Sampit River and in turn get pumped into the inner harbor by the tides leading to higher concentrations within the western portion of the harbor. Elevated Br levels due to the paper mill is also what was observed for core CGS 1018-2 temporally, as these elevated levels were seen to occur after the 2006 dredging occurred.

Other metals examined including both magnesium and barium revealed similar concentrations throughout the entire inner harbor. This uniformity across the inner harbor makes it difficult to determine a potential source of both metals (Figure 18).
Both the box plots and the XRF ratios examined show that the concentrations of these metals in the sediment are constantly varying as they accumulate and no metals accumulate at constant concentrations. The broad range of concentrations, seen in many of the box plots, suggest that there are a lot of variances between samples and that each metal accumulates at different rates over time (Figure 18). The XRF ratios reveal a similar pattern of varying deposition of metals throughout the inner harbor both vertically and laterally (Figures 14, 15, 16, and 17). The changing concentrations of these metals could represent the changing deposition in the inner harbor that is seen to occur due to tidal strength, river discharge, and storm events. The larger amounts of fine sediment brought into the inner harbor allows for more contaminants to be trapped through absorption increasing the overall concentration observed. With accumulation of the sediment in the inner harbor happening at such large rates, it is likely that the metal concentrations examined only represent a brief period of what is happening in the inner harbor. Another reason for variance in the metal concentration accumulating vertically, is the overall amount of these contaminants coming from the potential sources. At times, more metals may be introduced into the inner harbor due to higher production from the industry increasing certain metal pollution, increased utilization of the inner harbor and working waterfront, and more frequent storm events which could increase metals input into the inner harbor by surface runoff resulting in higher concentrations being observed in the sediment.

*Inner Harbor Mud Metals Outlook*. While these potential sources of heavy metal contaminants are based on proximity, further analysis could be done examining what heavy metals are found directly at these hypothesized sources. Examining contaminants
at these sources, would allow for cross examination of the lateral variation of heavy metals found in the harbor compared to what actual heavy metals are being put off by each potential source. Studies have been done examining metal concentrations in relation to proximity to various industries and sources, but in all cases, the study area was more densely sampled which allowed for the use of modeling approaches to identify these sources (Khorshidi et al. 2021, Niu et al. 2021). With denser sampling covering all parts of the inner harbor and some of the surrounding area, along with identifying exactly what metals are associated most with each source, a modeling approach would prove useful in more accurately identifying these potential sources.

A correlation between metal concentrations and XRF measurements to expand the opportunities presented with statistical approaches proved unsuccessful for this study. A similar approach, successfully completed by Rodriguez-Germade et al. (2014), was used to take the semi-quantitative XRF values and correlate these measurements to metal concentrations to show metal pollution levels changes over time. This method allowed for the identification of when metal concentrations were above the ERL concentration levels for individual metals using the XRF data. The study also explained that exposure time for the analyzed elements impacts the measurements and accuracy of the values produced from the Itrax Core Scanners. For Rodriguez-Germade et al. (2014) samples, data obtained from 100 second exposure time proved to be of the highest quality. While optimum exposure time can vary depending on material, it is often accepted that longer exposure times produce more accurate results (Huang 2016). Frequency of measurements also produce better overall datasets for XRF scans and can give more accuracy of variability observed (Rodriguez-Germade et al. 2014). The XRF element intensities for
this Georgetown study were done at 1 cm increments with 15 second exposure times. Similar to what was seen in the Rodriguez-Germade et al. (2014) study, a longer exposure time and more frequent measurements could increase the accuracy of the XRF data and potentially allow for a correlation to be done between the measured metal concentrations and the semi-quantitative XRF values. With this improved dataset, a more detailed analysis of the inner harbor could be done.

Along with higher frequency measurements of metal concentrations and longer exposure times for the XRF analysis, measuring metal concentrations for the samples that were collected within Winyah Bay could prove beneficial. Metal concentration measurements for the additional locations, sampled with piston cores and grab samples, could help identify the more natural conditions occurring in Winyah Bay. This background data would likely reveal a significant correlation between GSD and metal concentrations since there was more variability in GSD outside of the inner harbor. Obtaining deeper cores within the western portion of the channel and securing sediment below the dredge depth, would reveal more about changes in metal concentrations over time and if concentrations laterally across the inner harbor were different in previous times.

Statistical approaches comparing differences seen both laterally and vertically were unsuccessful due to the limited sample size and the mismatching number of samples in each core. To further and better understand the changes seen and determine significance of the contrast observed, more metal concentration samples measured with higher frequency would be needed. This would allow for larger datasets and increase
possibilities for statistical approaches allowing for further support of the conclusions found in this study.
Conclusions

Sediment Dynamics. Sediment dynamics across the inner harbor reveal that deposition has occurred at faster rates at the entrances and slower rates deeper within the Georgetown inner harbor. Not only do these differences occur laterally but also vertically as deposition occurs over an individual tidal cycle and is likely to be variable due to variation in the amount of suspended sediment available in area, tidal strength, and river discharge. Sediment in the inner harbor settles through flocculation as flocs containing sediment of larger grain size settle at the entrance and finer material settles further within the inner harbor. Within Winyah Bay, GSD of seabed and suspended sediment samples revealed fine-grained material in the surrounding area which match that of the inner harbor, suggesting that there is plenty of material available which can be supplied to the inner harbor. Dredge depths were only reached in the eastern part of the inner harbor, but no substantial differences were seen in sediment dynamics above and below the dredge depth.

Metals in the Inner Harbor Mud. Several metal concentrations including arsenic, chromium, copper, nickel, and zinc were found to be above the ERL concentration at multiple sites throughout the inner harbor. No significant correlation was seen between metal concentrations and GSD, DBD, or TOC suggesting that lateral differences across the harbor are due to potential sources. Core CGS 1018-1 revealed higher Pb and Cr concentrations and lower Br concentrations below the dredge boundary of 160 cm below
the seabed. Core CGS 1018-2 showed concentrations of only Mn having very different concentrations above and below the dredge depth of 95 cm with concentrations above the dredge depth averaging more. These differences could be due to changing land use and industrial changes in the area. Potential sources identified include the steel mill, paper mill, the working waterfront, and shipyards and marinas. Further studies examining the inner harbor could be done using more statistical and modeling approaches along with analysis of containments located directly at the potential sources to better solidify the findings discussed in this study.
References


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