## RAPID SURVEY OF ANTHROPOGENIC CONTAMINANTS IN SURFICIAL SEDIMENTS OF THE ASHLEY RIVER, CHARLESTON, SOUTH CAROLINA

by

#### SCOTT EDWARD NOAKES

#### (Under the Direction of John E. Noakes)

#### ABSTRACT

The Continuous Sediment Sampling System (CS<sup>3</sup>), a unique, rapid seafloor sediment sampling system developed at The University of Georgia's Center for Applied Isotope Studies, has been routinely utilized in the offshore dredged material disposal sites, but recently has been applied in riverine and estuarine environments. The CS<sup>3</sup> is capable of rapidly collecting surficial sediment samples over a large estuarine or riverine environment in a relatively short time period enabling a cost-effective method for completing large scale regional environmental surveys. The Ashley River, located in Charleston, South Carolina, served as an excellent test site for such a survey because of contamination problems resulting from extensive, long-term regional industrial and urban development.

The sediment mapping results for the Ashley River clearly demonstrated the usefulness for the CS<sup>3</sup> in the riverine or estuarine environment. The CS<sup>3</sup> was effectively deployed without event and was able to collect numerous samples within a short period of time. Many of the contoured survey analytes showed trends of elevated concentrations that appeared to be directly associated with known industrial and urban contamination sources. The Ashley River has a high concentration of silt and clay, which due to their high surface area and ionic attraction tend to adsorb trace metals. This affiliation is commonly referred to the grain-size effect. One method for normalizing the data to offset the grain-size effect is to ratio the metals to aluminum, a common geochemical normalizing factor. However, after normalizing the data, many of the contoured trends still showed correlation to these potential contaminant sources.

As a result of this study, it has been demonstrated that the technology now exists to rapidly survey large estuarine and riverine environments in a cost-effective manner. Large databases of elemental, organic, chemical, and physical data can be compiled to aid in the prediction and assessment of the environmental fate of contaminant chemicals in the aquatic environment.

INDEX WORDS: Marine pollution, Sediment mapping, Seafloor survey, Environmental monitoring, Baseline, Estuary, Ashley River

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#### CHAPTER 1

#### INTRODUCTION

Urban and industrial development in the United States is consuming valuable coastal land at an alarming rate destroying wildlife habitat and degrading water quality. Approximately 20,000 acres of coastal marshes are disappearing per year (NRI, 2000). Coastal marshes are essential for filtering suspended sediment and pollutants prior to flowing into the estuaries and oceans. It has been estimated that more than one-fourth of the coastal land converted from rural to suburban and urban uses since the beginning of European influence has occurred during 1982 to 1997 and upon completion of further studies, it is anticipated that this rate will continue to increase (NRI, 2000).

The volume of contaminated sediment entering the marine environment through point and non-point sources has become an enormous problem facing scientists today. The delineation of priority areas at risk for contaminant mobility challenges scientists and resource managers, who are increasingly prevailed upon to provide a predictive understanding of the processes and relative dangers associated with the degrading of the aquatic environment. A primary problem associated with the continuous, rapid coastal development is how to monitor and evaluate such vast regions for environmental impact. Within the developing framework of accepted sediment assessment techniques, there are no methods or tools designed to respond to the broad scope and wide areal distribution of existing contaminated aquatic habitats. Given current methods and instrumentation, it is difficult to assess contaminant impacts over large geographic areas, particularly where funding resources are limited or time constraints are imposed. There is a clear need for advanced survey systems that will enable the delineation and characterization of contaminant loads in a regional framework. Such information is required for the realistic evaluation of the extent of pollution, the bioavailability of hazardous compounds, and the potential for mobility of the contaminants in terms of the need for long-term monitoring and site remediation. There also continues to be a need for rapid, reliable techniques for determining the environmental impact of new chemicals and proposed changes to effluent discharges in order to provide guidance and control measures for industry and regulatory agencies.

Previous studies have clearly demonstrated that many, if not most, of the contaminants of greatest concern are only sparingly soluble in water. These contaminants include many trace and heavy metals and organic compounds such as polychlorinated biphenyls (PCBs), organochlorine pesticides, and polyaromatic hydrocarbons (PAHs) (Karickhoff, 1981; Hites and Eisenreich, 1987). These compounds are highly concentrated onto particulate substrate, either suspended in the water column or present in bottom sediments. A number of sedimentary processes control the speciation, partitioning, and mobility of the individual contaminants in bottom sediments, and therefore are ultimately responsible for their toxicity and environmental impact (Karickhoff *et al*, 1979; Eadie *et al*, 1992; Fredrickson *et al*, 2003). Unfortunately detailed regional studies of these processes are expensive, time consuming, and cannot be conducted with sufficient frequency and spatial resolution to fully assess contaminant impacts for extended sites.

An accurate assessment of the environmental impact of sediment-associated contaminants requires a detailed understanding of their transport and reactivity within the sedimentary system, and thus should include two components: a reconnaissance survey-based measurement program to assess regional contaminant distributions, followed by sediment characteristic and specific process-oriented studies of the reactivity and mobility of the contaminants in order to assess their actual impact. Scientific approaches based on real time, broad-scale, comprehensive assessments of the extent and severity of metal and organic contaminants in aquatic ecosystems can respond directly to immediate needs for site prioritization and provide a scientifically valid basis for delineating site-specific target study areas.

This dissertation will present a reconnaissance survey method that is capable of determining the distribution of multiple metal and organic sediment contaminants. The focus will not be on the analytical methodology used to obtain the sample results, but more on the methodology of rapidly and cost effectively collecting large numbers of samples and presenting them in a manner that is readily utilized by state and federal government agencies.

#### CHAPTER 2

#### STUDY AREA

#### Background

The Ashley River, which is part of the Santee River Basin, is located in the Lower Coastal Plain and Coastal Zone of South Carolina. It converges with the Cooper and Wando Rivers to form the Charleston Harbor. The Ashley River Basin incorporates 894 square miles, which primarily consists of forested land and forested wetland (SCDHEC, 1993). Only about 10% of the Ashley River is bordered by urban land, which is mostly the greater City of Charleston. It was this region of the Ashley River, adjacent to the city of Charleston that served as the test site for this project because of contamination problems resulting from extensive, long-term regional industrial development (Figure 1).

The study area included approximately 11 km (6 nautical miles) of the Ashley River beginning at the mouth of the river and traveling upstream to the Memorial Bridge (Highway 7) (Figure 2). This section of the river is strongly affected by tidal surges, which can effectively disperse contaminants in sediment both upstream and downstream of the initial input into the river. There were a total of 149 sediment samples collected within the study area in a two and a half day time period. Each of these samples was analyzed for elemental concentration (20 analytes) and organic compounds (8 analytes). Sample spacing was approximately 260 m (~850 ft) with 6 transects in the mouth of the river and 3 transects following the length of the study area. The CS<sup>3</sup> sediment sampling was completed in early May utilizing a 23 foot Environmental Protection Agency (EPA)



Figure 1. Ashley River, South Carolina project area.



Figure 2. Ashley River study area and sampling stations.

survey vessel. The survey operations were based out of the South Carolina Department of Natural Resources (SCDNR) facility located on James Island in the Charleston Harbor.

#### Potential Pollution Sources on the Ashley River

There are many potential sources of pollution along the Ashley River ranging from natural to anthropogenic, and point and non-point sources (Figure 3, Table 1). The Ashley River transects a relatively shallow deposit of phosphatic rock, which is highly erodible, and relatively high in trace elements (Slansky, 1986). The erosion process is continuous and adds to the trace element content in the surficial sediment in the riverbed. However, much of the phosphate deposits occur as nodule or boulders distributed in a layer of sand and clay (Collings, 1947). Since most of the associated trace elements are bound in nodules and boulders, they should remain out of the water column unless commercially mined and processed into a finer fraction.

The Ashley River also has seven permitted municipal dischargers in the basin with a combined discharge of approximately 53 million gallons per day (SCDHEC, 2000). One such municipal facility is the Plum Island Wastewater Treatment facility, which is permitted for processing a maximum of 18 million gallons of sewage per day, and is located immediately downstream of Wappoo Creek near the mouth of the Ashley River (NPDES, 2003). There are also several large marinas located along the Ashley River, which could potentially contribute to the trace metal, sewage, and polyaromatic hydrocarbon input to the river.

Industrial activity has also been present along the Ashley River since the mid 1800's with the introduction of a phosphate production facility in 1867 (Collings, 1947).



Figure 3. Potential pollution sources along the Ashley River.

Source	Contaminant
Phosphate and Fertilizer Production	phosphorus, sulfate trace metals (phosphate ore is high in most trace metals)
Wood Treatment Facility	chromium, copper, arsenic pentachlorophenol, naphthalene, anthracene, carbazole, pyrene
Marina and Docks	tin pentachlorophenol, naphthalene, anthracene, carbazole, pyrene
Wastewater Treatment Facility	iron, nickel, lead, chromium, zinc, copper titanium phthalate
Urban population	trace metals pentachlorophenol, naphthalene, anthracene, carbazole, pyrene, 4- methlyphenol ( <i>p</i> -cresol), DDE
Bridges	trace metals (from paint) organic compounds related to automotive uses

Table 1. Potential Pollution Sources on the Ashley River.

At its peak, there were seven phosphate production facilities located on the Ashley River. Even after the decline of the phosphate mining operations, several of the facilities continued importing and processing the phosphate ore into fertilizer. The flow of wastewater from the phosphate production facilities impacted the Ashley River with phosphorus, fluorides, sulfates, and gypsum (Zeller, 1997). In addition to the phosphate production facilities, the Koppers Company site along the Ashley River was used for wood-treating operations. This site was in operation for approximately 38 years treating utility poles and raw lumber. Wastewater from the site flowed into the Ashley River and adjoining tidal marshes. The tidal marshes along the Ashley River may have actually helped to protect the river by filtering the fine-grained sediment and immobilize the heavy metals and organic compounds (Odum, 2000).

Approximately 10% of the Ashley River is bordered by urban development. Runoff from urbanization readily flows from city streets into the tidal creeks and then into the Ashley River carrying with it many types of pollutants. These can include pesticides, insecticides, metals, plasticizers, and polyaromatic hydrocarbons. Much of the toxic waste from these potential pollution sources are bound to sediments and transported in this manner to the river sediment and coastal ocean seafloor. In coastal areas all over the world, the discharge of these toxic wastes causes readily identifiable environmental degradation in localized regions (Abel, 1989).

#### CHAPTER 3

#### TECHNICAL APPROACH

Continuous Sediment Sampling System (CS<sup>3</sup>)

The Center for Applied Isotope Studies (CAIS) has been involved in the development of a rapid seafloor survey system, the Continuous Sediment Sampling System ( $CS^3$ ) (Noakes and Harding, 1982). It has been routinely utilized in monitoring plans for the Ocean Dredged Material Disposal Sites, but recently the focus has been shifted to riverine and estuarine environments. The  $CS^3$  is capable of rapidly collecting surficial sediment samples over a large marine environment while moving at 3 knots enabling a cost-effective method for completing large-scale regional environmental surveys (Noakes *et al*, 1999, Noakes and Noakes, 2003). With the  $CS^3$ , a six-mile portion of the Ashley River was sampled utilizing a close sampling grid to determine elemental, organic, and physical site characterization maps. The technical specifications for the  $CS^3$  are listed in Table 2.

The  $CS^3$  used a positive displacement pump mounted aboard a stainless steel sled (Figure 4) to deliver a continuous slurry of surficial sediment and water to a shipboard sample processor (Figure 5). Umbilicals including a power cable and a slurry transport hose connected the towed sled to shipboard data acquisition and sample collection systems. For data acquisition, the  $CS^3$  used a differential Global Positioning System (DGPS) and depth sounder to mark the sample location and water depth.

Analytical method	X-Ray Fluorescence Gas Chromatograph Mass Spectromete Multi-parameter Sensor Package
Data results	Parts per million (ppm) Weight percent (wt%)
Format	Hard-copy printout
Sampling interval	260 m (variable)
Calibration test	NIST Standards
Navigational method	DGPS
Operating range	
Penetration (sled)	~2-5 cm
Ship speed	2.5 to 3 knots
Sample	Sediment wafer on quartz fiber filter
Sample size	38 mm
Sample woight	80-120 mg

Table 2. CS<sup>3</sup> Technical Specifications



Figure 4.  $CS^3$  sled.



Figure 5. CS<sup>3</sup> sample processor.

The CS<sup>3</sup> sled was towed along the river bottom while the sediments in its path were perturbated to a depth of approximately 2 to 5 cm under normal operating conditions and formed a plume from which the surficial sediments were sampled. The CS<sup>3</sup> submersible pump delivered a continuous stream of these sediments to the survey vessel via a rubber transport hose. The sediment slurry passed unobstructed through the sample processor consisting entirely of plastic and rubber parts, first flowing through a centrifugal cone where the fine sediment fraction (<200  $\mu$ m) was selectively separated for sample analysis. The CS<sup>3</sup> was designed specifically for preferential sampling of the clay-sized fraction to provide an amplified signal for reconnaissance-level determinations of sediment elemental and organic constituents. The fine-grained sediments were of primary interest as they are the ultimate sink for most aquatic contaminants and the primary site of the sorption reactions that govern the fate and persistence of these contaminants (Spacie, 1994; Lee and Jones, 1987; Noakes and Harding, 1982).

The CS<sup>3</sup> samples were collected by diverting a portion of the slurry that was flowing through the sample processor into a collection chamber (Figure 6). The slurry in the collection chamber was dewatered by suction and the remaining sediment was deposited on a quartz fiber filter. A total of 149 sediment samples were collected within the study area in a two and a half day time period. Each of these samples was analyzed for elemental concentration (20 analytes) and organic compounds (8 analytes). Sample spacing was approximately 260 m (~850 ft) with 6 transects in the mouth of the river and 3 transects following the length of the study area.

The sediment samples collected were later analyzed at the CAIS laboratory using elemental x-ray fluorescence spectroscopy (XRF). Duplicate samples were also analyzed



Figure 6.  $CS^3$  sample and collection chamber.

for organic compounds at the Agricultural and Environmental Services Laboratory using a 5890 Hewlett Packard gas chromatograph mass spectrometer (GCMS).

#### Physical and Chemical Measurements

In addition to the surficial sediment samples collected from the river bottom, water quality measurements were made at the sediment-water interface. A commercially available, multi-parameter sensor package monitored the sediment slurry prior to flowing through the CS<sup>3</sup> sample processor (Figure 7). A flow cell was mounted on the sensor body allowing a diverted portion of the sediment slurry to flow past the sensors and then discharged overboard. Measurements for pH, salinity, conductivity, dissolved oxygen, redox, and temperature were logged at each CS<sup>3</sup> sample collection station. The sensors were connected to the system computer by a RS-232 cable allowing electronic transfer of the data directly to the computer file for storage. The data from these measurements were used in generating physical and chemical parameter maps for the Ashley River.



Figure 7. Multi-parameter sensor measuring the sediment-water interface.

#### Sediment-Grab Sampling

Sediment-grab samples were collected from the river bottom to provide ground truth information for the CS<sup>3</sup> data and samples. The South Carolina Department of Natural Resources (SCDNR) supplied a 23 ft Privateer survey vessel for the sample collection. A stainless steel, sediment-grab device was deployed off the port side of the Privateer using a davit powered by an electric cathead. The sediment-grab device was a clamshell dredge mounted in a weighted stainless steel frame designed for added stability and penetration when sampling sediment in the riverine environment. It had been found previously that a stand-alone clamshell dredge did not perform well in strong river currents and tidal surge.

The approximate sample locations were determined prior to collection by evaluation of the CS<sup>3</sup> river data. Ten sampling stations were visited along the river with a duplicate sample collected at one of the stations (Figure 8). The actual sampling locations were determined by DGPS and only varied slightly from the pre-selected stations due to obstructions such as shallow water depth, bridges, marinas, and moored vessels. The sample coordinates were recorded in a survey logbook along with the time, water depth and field observations.

The sediment-grab device was cleaned and inspected prior to each deployment. In order to mimic the sampling depth of the  $CS^3$  sled, no more than the top 7.5 cm of sediment were collected from the sediment-grab sample. The  $CS^3$  sled typically penetrates the bottom sediment by approximately 2 to 5 cm with the surficial sediment being the main component that was resuspended and pumped to the surface for sampling. The samples were stored in plastic bags for elemental analysis or glass containers for



Figure 8. Sediment-grab stations on the Ashley River.

organic analysis, labeled according to site number, and immediately stored in an ice filled cooler. Following completion of the sample collection, the samples were transported in an ice-filled cooler to the CAIS laboratory for analysis.

#### CHAPTER 4

#### ANALYTICAL METHODOLOGY

Surficial sediment samples were collected at 133 of the 149 sampling stations within the study area during the two and a half day time period. The sediment samples were collected on pre-weighed quartz-fiber wafers with typical sediment weights ranging from 60 to 120 mg. The samples were stored in stainless steel bins and allowed to air dry until shipped to the CAIS laboratory for analyses. Dual sample chambers were installed on the CS<sup>3</sup> to allow for collection of duplicate samples at each of the sampling stations. One sample was for elemental concentration (20 analytes) and the other for organic compounds (8 analytes). Table 3 outlines the elemental, organic, chemical, and physical analytes for the survey.

#### **Elemental Analyses**

## <u>CS<sup>3</sup> Samples</u>

The CS<sup>3</sup> wafer samples and the sediment-grab samples collected were analyzed for elemental content using XRF. The CS<sup>3</sup> wafer samples were analyzed "as is," *i.e.*, they were not subjected to any treatment other than air-drying prior to analysis. The samples were, however, weighed prior to analyses to ensure that each sample did at least meet or exceed the 50 mg sample weight required for accurate elemental analysis. A Philips MagiX wavelength dispersive, XRF instrument, was used to analyze the wafer samples.

Element	Reporting Unit	Element	Reporting Unit
Aluminum Silicon Phosphorus Sulfur Titanium Potassium Calcium Chlorine Iron	weight percent (wt%)	Manganese Chromium Copper Nickel Zinc Strontium Zirconium Arsenic Tin Barium Lead	parts per million (ppm)
Organic Compound	Reporting Unit	Organic Compound	Reporting Unit
Phthalate Pyrene Naphthalene DDE	ppm	Carbazole Anthracene 4-Methylphenol Pentachlorophenol	ppm
Physical and Chemical	Reporting Unit	Physical and Chemical	Reporting Unit
Water temperature pH Salinity	°C parts per thousand (ppt)	Dissolved oxygen Conductivity Oxygen reduction potential	mg/l mmhos/cm mV

## Table 3. Survey Analytes for the Ashley River.

The XRF was equipped with a PW2540 VRC Multi-Sample Changer capable of handling up to 168 samples per load. The samples were placed in clear acrylic sample holders and loaded into the holding trays mounted inside the sample chamber. The XRF has a robotic arm that picks up each individual sample one at a time and places it into the sample chamber where it is subjected to x-rays. The x-rays excite the particles in the sediment sample, which in turn emit x-rays that are particular to each element present in the sample.

The major elements were determined in their oxide state and then converted using an Excel spreadsheet to elemental concentration and listed as weight percent (wt%). The trace elements were determined in their individual state and listed in parts per million (ppm). A National Institute of Standard Testing (NIST) standard, 8704, was prepared on a wafer and analyzed along with the Ashley River samples to ensure quality control during the analyses (Appendix A). The results of the CS<sup>3</sup> sample analyses were compiled in a computer file according to station numbers (Appendix B), and twodimensional maps were generated from the data. The minimum detection limits for the XRF are shown in Table 4.

#### Sediment-Grab Samples

The sediment-grab samples collected for elemental analyses were returned to the CAIS laboratory where they were oven-dried at approximately 60° C to drive off any moisture present in the sample. The sediment from the grab sample was then ground with an acid-washed ceramic ball mill until the sample would pass through a 230-mesh sieve. A plasticizer solution made of 100 gm of Eluacite and 500 mL acetone was mixed

Element	Symbol	Detection Limit	Average Concentration (wf%)	Element	Symbol	Detection Limit	Average Concentration (nnm)	
Aluminum	AI	0.02	4.46 <sup>1</sup>	Manganese	Mn	5	271 <sup>1</sup>	
Silicon	Si	0.03	$21.90^{2}$	Chromium	Cr	9	$48^{1}$	
Phosphorus	Р	0.001	$0.14^{2}$	Copper	Cu	7	$22^{1}$	
Sulfur	$\mathbf{S}$	0.001	$1.48^{2}$	Nickel	.N	С	$17^1$	
Titanium	Ti	<0.01	$0.21^{2}$	Zinc	Zn	8	$84^{1}$	
Potassium	К	0.002	$1.17^{2}$	Strontium	$\mathbf{Sr}$	С	$120^{3}$	
Calcium	Ca	0.004	$2.80^{2}$	Zirconium	Zr	9	$80^2$	
Chlorine	CI	0.001		Arsenic	$\mathbf{As}$	6	$13^{1}$	
Iron	Fe	<0.01	$2.97^{1}$	Barium	Ba	8	$440^{3}$	
				Lead	Pb	10	$18^{1}$	
				Tin	Sn	5	5 <sup>3</sup>	
<sup>1</sup> Average c	concentra	tions derived f	rom South Caro	lina estuarin	e and coa	stal clav-ric	h sediment	

Concentrations.
e Sediment
and Average
Analyses a
Elemental
its for XRF
<b>Detection</b> lim
Table 4. I

samples (Van Dolah *et al*, 2002).

Sites in the southeastern United States. <sup>3</sup>Average concentrations for metals in sediment from NOAA Screening Quick Reference Tables,

Buchman, 1999.

with the sample. The ground sediment sample was then thoroughly mixed with the plasticizer solution at a rate of 10 gm of sediment to 2 mL of plasticizer. At this time, the sediment-plasticizer mix was placed in a 39 mm by 10 mm round sample container. The sample was placed in a pellet press and subjected to 30,000 pounds per square inch (psi) for 5 minutes. The resulting sample was a neatly pressed 40 mm by 3 mm round pellet ready for analyses in the XRF. The pellet sample was analyzed for elemental content in the same manner as the CS<sup>3</sup> samples. An NIST 8704 pellet was prepared in the same manner as the Ashley River pellets to ensure the quality control during the analyses (Appendix A).

#### Organic Analyses

### CS<sup>3</sup> Samples

Unlike the  $CS^3$  samples collected for elemental analyses, the samples collected for organic analyses required sample prep prior to analyses. Upon return to the laboratory, each wafer sample was air-dried, weighed, and inserted into a glass culture tube that had been pre-rinsed with methylene chloride ( $Ch_2Cl_2$ ) and methanol. Approximately 10 mL of  $Ch_2Cl_2$  was added to each tube completely immersing the  $CS^3$  sample. The samples were then sonicated for 15 minutes. Immediately following sonication, the solute was transferred to a pre-rinsed and labeled Turbovap vessel and concentrated to a volume of 1 mL. The Turbovap vessels were rinsed with a small quantity of methylene chloride and the contents transferred by a glass Pasteur pipette into a 2 mL glass vial. For each sample, 1  $\mu$ L of a semi-volatile internal standard concentrated at 100  $\mu$ g/mL was added. Each sample was then concentrated by air injection to manually evaporate the final volume to 0.1 mL. The 0.1 mL volume was determined by using a reference vial for

comparison. The prepared sample was then transferred to a 0.15 mL glass vial insert for analyses.

For chromatographic separation of the sample, a HP 5890 GC equipped with a 30 meter, 0.25 ID, Phenomenex ZB-5 column was used. Additionally, the HP 5890 was equipped with a HP 7873A autosampler. The GC was connected to a HP5970 mass spectrometer operating in the selected ion-monitoring (SIM) mode. The HP RTE-A data system was used for mass spectrometer control and data acquisition. The organic analytes and the reporting units for this part of the study are shown in Table 3. The retention times, detection limits and percent recovery are shown in Table 5. The results of the CS<sup>3</sup> sample analyses were compiled in a computer file according to station numbers (Appendix C), and two-dimensional maps were generated from the data.

#### Sediment-Grab Samples

The sediment-grab samples collected in the Ashley River contained considerably more volume and weight of marine sediment than the  $CS^3$  wafer samples. Therefore, these samples required different sample preparation than the  $CS^3$  samples. A 35 mg subsample was collected from each blended sediment-grab sample and 40 to 50 mL of  $Ch_2Cl_2$  was added. The sample was placed in a container and loaded into a shaker for 30 to 40 minutes. After shaken, the samples were filtered using a Buchner funnel and vacuum pump. The filtered sample was dried down to a final volume of 2 mL. The samples were then analyzed on an HP 5890 GC against a known standard list.
Component	Retention Time	Detection Limit <sup>1</sup>	Recovery $(\%)^2$	
4-Methyphenol	11.56	<0.1 µg/sample	97.6	
Naphthalene	13.83	<0.1 µg/sample	92.8	
Pentachlorophenol	21.95	<0.1 µg/sample	NR <sup>3</sup>	
Anthracene	22.44	<0.1 µg/sample	96.4	
Carbazole	22.87	<0.1 µg/sample	76.8	
Pyrene	26.08	<0.1 µg/sample	100.4	
p,pDDE	26.38	<0.1 µg/sample	111.6	
Phthalate	29.23	<0.1 µg/sample	184	

Table 5. HP 5890 GCMS Operational Parameters.

<sup>1</sup>Average sample weight of 100 mg sediment <sup>2</sup>Spiking level range from 0.1 to 1.0 μg/sample. <sup>3</sup>Not Recovered.

#### System Calibration

The system was initially calibrated utilizing a 10-ppm standard with the mass spectrometer in linear scan mode. This was used to determine the retention times and major ion characteristics for each target. A SIM method and ID file were set up using the characterized parameters for target recognition and integration. The ID file was fine tuned by running repeated analysis of low-level standards. This process resulted in a bias toward false positive hits. However, the bias was determined to be necessary to identify all possible low level hits in the samples.

Prior to running the actual Ashley River samples, a four-point calibration using standards ranging from 0.05 to 1 ppm was performed. It was determined that values ranging from low to high levels were linear for the calibration. While the Ashley River samples were being analyzed; the system was monitored using repeated calibration standards at 0.1 and 0.5 ppm.

#### Chemical and Physical Measurements

A question of relevancy can be raised about the sensors being placed on the survey vessel as compared to lowered to the river bottom for site measurements. This is a valid concern and was addressed in a previous CAIS study (Noakes *et al*, 1991). Two similar multi-parameter sensor instruments were used to simultaneously compare the results of a unit mounted onboard a survey vessel and the other mounted in a submersible sled towed on the seafloor. A fourteen gallon per minute submersible pump was mounted parallel to the submerged sensor package to allow the same sediment-water slurry in contact with the submerged sensor package to be pumped to a flow cell mounted

on the surface sensor package. This procedure allowed the same sediment-water slurry to flow over the two sensors within approximately the same data sampling time period.

Both surface and submerged probes performed well in the field-testing and were shown to have comparable measurements and maintained calibration at the end of the experiment. As a result of the tests, the surface probe showed to have a higher conductivity (+14 mmhos/cm) and salinity (+10 ppt) than the submerged probe. It was determined that the increase was related to the higher quantity of sediment being pumped over the surface probe as compared to the submerged probe. The pH was essentially the same from one unit to the other. The dissolved oxygen was slightly lower (-1.8 % saturation) in the surface probe as compared to the submerged probe. Air bubbles trapped on the dissolved oxygen probe upon deployment may have caused the slight increase in dissolved oxygen reading from the submerged probe as compared to the surface probe. In either case, surface or submerged, the multi-parameter probes did perform well and proved to have potential use for sediment mapping deployment in the Ashley River survey.

# System Calibration

To monitor the performance of the sensor package, calibration of the unit was checked prior to and immediately after use each day. The pH glass electrode was visually checked each day for abrasions and gently cleaned with a soft cloth to remove any buildup of sediment. The pH was calibrated using a buffer solution of pH 4 and then a slope buffer with a pH of 7.

The dissolved oxygen sensor was calibrated daily using the Winkler Titration method (Greenberg *et al*, 1992). Using the Winkler Titration method, the dissolved

oxygen in water was determined through a series of chemical reactions where  $Mn^{+2}$  was converted to  $Mn^{+4}$ . The  $Mn^{+4}$  and iodine (I<sub>2</sub>) were then acidified to form a reaction, which released free I<sub>2</sub>. The I<sub>2</sub> was quantitatively the same as the dissolved oxygen in the water sample. The sample was then titrated with sodium thiosulfate resulting in a direct readout of mL on the titration burette. During the titration process, the precipitate changed from white to brown and then to yellow. At this point, starch was added, which turned the solution blue. When all the free I<sub>2</sub> in solution had turned to clear, then the titration was complete.

The conductivity was calibrated by using a 0.5 KCl Molar standard solution. Prior to calibration, the conductivity sensor was cleaned. The white cell block was removed from the sensor housing to reveal the six nickel electrodes and each of these electrodes were polished with fine sand paper and wiped with a clean cloth. The cellblock was then replaced and the unit was ready for calibration. The conductivity solution was placed in the calibration cup and the unit allowed time to stabilize. If needed, the correct value of the solution was input into the software. The salinity was calculated using the conductivity readings.

The oxygen reduction (redox) potential was measured using a platinum electrode. The redox sensor calibration was verified using a solution of quinhydrone mixed with pH 4 buffer to read 500 mV. Additionally, the sensor was checked daily to ensure that it was clean and clear from sediment buildup. The temperature calibration was factory set for the sensor package and was not recommended for individual calibration. In addition to cleaning of the specific sensors, the sensor body and flow cell was cleaned and readied

for the next days use. No system battery maintenance was required since an external 12volt battery source was used to power the sensors.

### Mapping Software

Plotting of the data was an important part of this dissertation. Golden Software's Surfer, Version 6.0 mapping software was used to generate the survey contour maps. The software utilized kriging, a geostatistical gridding method used to interpolate irregularly spaced three-dimensional data (xyz) onto an evenly spaced grid. Spline smoothing to eliminate angular contours was then used to further refine the data. Matrix smoothing was also used to refine data spikes and reduce background noise between nodes (Keckler, 1997).

The data range from low to high determined the contour frequency. Each contour was color coded and filled, based on an even distribution of the available colors ranging from blue to red, to aid in displaying the resulting trends in the analytes. A red color on the contour map does not necessarily represent unusually high concentrations, but rather the highest in the data range. Additional boundary lines were overlayed to define surface features such as rivers, creeks, or islands and appropriate text was assigned to each landmark.

By utilizing Surfer, the  $CS^3$  data was plotted in such a way as to identify trends in the analyte concentrations. These trends can be used to identify potential sources of contamination input into the Ashley River.

## CHAPTER 5

#### ELEMENTAL AND ORGANIC ANALYSES

As stated in Chapter 2, there are many potential sources of point and non-point pollution sources flowing into the Ashley River. Wastewater treatment facilities or other National Pollutant Discharge Elimination System (NPDES) permit holders, a total of seven along the Ashley River, would be considered potential sources of point-source pollution since the source can be traced to a discrete location (Libes, 1992). Non-point-source pollution is considerably more difficult to determine. Examples of non-point-source pollution along the Ashley River would include the storm water runoff and ground water seeps from the industrial area adjacent to the eastern shore. Additional non-point-source pollution would include the high-density population associated with the city of Charleston. Storm water runoff from city streets, parking lots, lawns, and golf courses tend to add considerable amounts of metals and organic compounds to the environment.

The following pages present data in a two-dimensional format and discuss the results from the Ashley River study. Results for the CS<sup>3</sup> sample analyses are presented in Appendices B (elemental) and C (organic). Since there are many potential pollution sources associated with the Ashley River, a clear and concise conclusion as to their origin may not readily be determined. However, as a result of this study, there were many areas of defined contaminant deposition shown on the Ashley River. The probable sources of some of these contaminants can be implicated to sites along the river.

#### Bathymetry

At each sampling station, bathymetric readings were recorded along with the station coordinates. The depth was corrected to mean low tide by using the tidal charts for the day of sampling as well the nearest time available (NOAA, 2002). The bathymetric data is important because it indicates potential scouring, shoaling, or dredged channels that would tend to alter the particle size distribution of the surficial sediment on the river bottom (Figure 9). Dredging or scouring would typically remove the fine-grained sediment fraction, which generally contains the higher concentrations of trace metals and organic matter.

The deeper water of the Ashley River channel was clearly shown from the mouth of the river and heading upstream to the Highway 17 bridges. No CS<sup>3</sup> samples could be collected within this part of the channel due to the absence of fine-grained sediment on the river bottom which was most likely a result from channel maintenance dredging. Upstream of the Highway 17 Bridges, where the channel was not routinely dredged, the water depth decreased by several feet and the surficial sediment became siltier. Scouring due to river currents was evident along the eastern bank of the Ashley River in the bend just prior to the Memorial Bridge (Highway 7) while shoaling was evident along the western shore. A deposition zone was noticed on the Ashley River just downstream of the junction of Orangegrove and Oldtown Creeks where the river was less than 8 feet deep. Shoaling was also present along the western shore of the Ashley River near the mouth of the river where water depths were approximately 2 feet deep.



Figure 9. Bathymetric contours (ft) corrected to mean low tide for the Ashley River.

# **Elemental Analyses**

# CS<sup>3</sup> Samples

Aluminum (Figure 10), due to the dominant role it plays in the aluminosilicate clays, makes an excellent indicator of the fine-grained sediment distribution in estuarine and coastal marine sediments. Due to the high surface area and ionic attraction, these clays tend to attract and bind trace metals (Krumbein and Sloss, 1963). The association of fine-grained sediment (clays) with trace metal concentrations has been commonly referred to as the grain-size effect. Past studies have shown that using aluminum as a geochemical normalizer can aid in offsetting the grain size effect (Goldberg *et al*, 1979; Windom *et al*, 1989).

Overall, the aluminum concentrations only varied by approximately 20% indicating that there would be a minimal grain-size effect on the analytes within the study area. The highest aluminum concentrations were found adjacent to the industrial area and the large marina located along the eastern riverbank. Since aluminum is generally not considered an anthropogenic contaminant, its presence at these two areas would be considered coincidental, most likely representing depositional zones along the river. However, significant shoaling or sediment deposition was not shown in the bathymetric plot (Figure 9).

A sediment distribution study completed in 1988 by the Marine Resources Research Institute (MRRI) at SCDNR presented data that showed the clay/silt distribution in the Ashley River (Figure 11) (Levisen and Van Dolah, 1997). The 1988 MRRI data showed an overlap of sediment containing greater than 50% clay and silt with the 2002 CS<sup>3</sup> aluminum data further demonstrating the link between aluminum



Figure 10. Aluminum concentrations (wt%) in the surficial sediment of the Ashley River.



Figure 11. Clay and silt distribution (1988) in the Ashley River surficial sediments.

concentrations and the aluminosilicate clays. Since fourteen years had elapsed between the MRRI data and the  $CS^3$  data, it also demonstrates that these areas are typical riverine depositional zones and generally would be expected to be high in trace metals.

As discussed in Chapter 2, the Ashley River traverses a deposit of phosphatic rock. This deposit was first exploited in the 1860s and the mining and processing of the ore continued until the late 1970s. During the many years of phosphate production, waste products, containing high concentrations of phosphates and sulfates, were introduced into the environment through non-point and permitted industrial discharges. One of the components released during refining the phosphate ore is phosphorus (Zeller, 1997). The distribution of phosphorus in the surficial sediments of the Ashley River is shown in Figure 12.

The phosphorus concentrations in the upper reach of the survey area were approximately double that of the lower section. Phosphorus concentrations were found to be 0.25 wt% in the surficial river sediment adjacent to where the former phosphate processing facilities were once located. The phosphorus concentrations continued to decrease further downstream as the phosphorus-laden sediment became mixed with sediment not affected by the phosphate mining operations. The phosphorus concentration near the mouth of the Ashley River was found to be approximately 0.12 wt%.

The area shown to contain higher phosphorus concentration has had a long history of problems related to phosphorus contamination. A "no wake" zone currently protects this area in an attempt to keep shoreline erosion to a minimum. Several reports of "flaming marsh" or "mud fires" have been reported adjacent to the industrial area of the Ashley River (Fanning, 2002). During times of low tides or drought, the shoreline



Figure 12. Phosphorus concentrations (wt%) in the surficial sediments of the Ashley River.

containing high concentration of phosphorus can dry out, spontaneously igniting. There have also been past occurrences of "flaming shrimp" on the Ashley River (Wenner, 2002). Fishermen trawling for shrimp on the Ashley River have reported that some shrimp have spontaneously ignited upon retrieval of their nets. The shrimp contained high concentrations of phosphorus and when they dried onboard ship, the shrimp would ignite.

Adjacent to the phosphate production facilities located on the east side of the Ashley River is a former wood-treatment operation that primarily treated raw lumber and utilities poles with creosote (Zeller, 1997). In addition to the creosote, pentachlorophenol and copper chromium arsenate (CCA) were also used at the site for treatment purposes. The surface drainage for the facility is directed towards the Ashley River either directly or through the adjacent marsh. Very few of the CS<sup>3</sup> samples had detectable levels of pentachlorophenol. However, there were two samples directly adjacent to the former wood-treatment facility, the highest of which had approximately 0.36-ppm pentachlorophenol. The majority of the samples with detectable pentachlorophenol were located on the Ashley River between Orangegrove Creek and the Highway 17 bridges. The highest reaching approximately 1.4 ppm near the mouth of Orangegrove Creek. Pentachlorophenol is discussed in further detail in the organic analyses section of this report.

Since CCA was also used for wood treatment, it would be understandable that chromium and copper, being components of the compound, might be present in the river sediments. Figure 13 shows the chromium concentrations in the surficial sediments in the river bottom. The highest chromium concentration (170 ppm, shown in red) detected



Figure 13. Chromium concentrations (ppm) in the surficial sediments of the Ashley River.

on the Ashley River was directly adjacent to the wood-treatment facility. Lower chromium concentrations were observed upstream and downstream of the site where the former wood treatment facility was located. Further downstream on the Ashley River there were slightly elevated concentrations (100 ppm) detected near the mouth of Orangegrove Creek. Once again, the concentrations were lower immediately upstream and downstream of the mouth of the creek indicating an input of chromium from the Orangegrove creek. The concentrations increased again to approximately 150 ppm about 1 mile further downstream near the Highway 17 Bridge. Bridges have typically been sources of contamination, largely due to construction, cleaning and painting, and surface runoff (Noakes, 1993).

The copper concentrations in the Ashley River surficial sediments are shown in Figure 14. It was anticipated that the copper concentrations would coincide with chromium due to the relationship with the wood treatment operation. However, this was not the case. Concentrations did, however, start increasing just below the industrial area to reach a maximum (169 ppm) adjacent to where Diesel Creek enters the Ashley River suggesting a possible source for copper unrelated to the wood treatment source. The copper concentrations showed a decrease immediately downstream of the Highway 17 Bridge. An area of elevated copper concentration was also indicated adjacent to the Charleston seawall near Battery Point Park. The high copper concentrations located along the seawall may be related to an outfall pipe that the CS<sup>3</sup> sled snagged while collecting samples during the survey.

Orangegrove Creek joins Oldtown Creek to form a drainage system for approximately 1.5 square miles of salt marsh. Salt marshes have a high concentration of



Figure 14. Copper concentrations (ppm) in the surficial sediments of the Ashley River.

organic matter, which is continually degrading. One product of the organic matter degradation is sulfur (Bates *et al*, 1999). Sulfur concentrations (Figure 15) reached a maximum (~2 wt%, shown in red) in the river near the mouth of Orangegrove Creek. In addition to the sulfur contribution from the salt marsh, there is also a wild animal farm adjoining the western bank of Orangegrove Creek. Until recently, drainage from the animal pens was allowed to flow directly into the creek. The drainage has since been diverted into the municipal wastewater system.

Modern wastewater treatment plants often produce effluents that are cleaner than the waters into which they discharge (Peirce *et al*, 1998). Through a series of primary, secondary, and tertiary treatments, the wastewater is cleaned of contaminants including solids, metals, and organic compounds. The Plum Island Wastewater Treatment Plant outflow is located near the mouth of the Ashley River and would appear to validate this principle. In contrast to the high sulfur concentration previously discussed near the mouth of Orangegrove Creek, the sulfur concentrations immediately adjacent to the Plum Island Wastewater Treatment Plant were actually lower than the sulfur concentrations detected within the surficial sediments of the surrounding river. A low sulfur plume from the treatment plant is shown in light blue (Figure 15).

In addition to the primary, secondary, and tertiary treatments that the wastewater is subjected to during processing, the effluent is also disinfected with chlorine. Generally, a 30-minute exposure to chlorine is sufficient to kill most bacteria with residual chlorine remaining in the water. This residual chlorine can be harmful to the natural ecosystem if released so most wastewater treatment plants dechlorinate the effluent prior to discharge by adding sulfur dioxide or activated carbon (Gray, 1989).



Figure 15. Sulfur concentrations (wt%) in the surficial sediments of the Ashley River.

The chlorine concentrations for the surficial sediment in the Ashley River (Figure 16) showed a plume of lower chlorine concentrations in conjunction with the wastewater treatment plant outfall pipe indicating that the freshwater effluent released by the Plum Island Wastewater Treatment Plant had lower chlorine concentration than the brackish Ashley River water that it flowed into.

Many major and trace metals are present in wastewater outfalls including iron, nickel, lead, chromium, cadmium, zinc, and copper (Gray, 1989). Iron is a readily abundant element in the earth's crust and generally not considered a contaminant (Goldberg *et al*, 1979). Wastewater treatment facilities typically remove excess iron from the effluent by converting ferrous iron to the ferric state and precipitation of ferric hydroxide (Patterson, 1977). However, iron was present in the wastewater effluent from the Plum Island Treatment Plant and acted as an effective tracer for the effluent (Figure 17). Increased iron concentrations in the surficial sediment in the Ashley River showed the footprint for the effluent dispersion from the wastewater treatment plant.

Titanium also proved to be an excellent tracer for the wastewater effluent flowing into the Ashley River. Titanium, in the form of titanium dioxide, is used in many household products as a brilliant white pigment. It is widely used in paper, paint, printing ink, plastics, enamel, and textiles (American, 1956). These products, especially the dyes and pigments, are readily input into the domestic sewage system and are transported to the wastewater treatment plant. Since titanium is not generally considered an environmental hazard, the wastewater treatment process does not remove it from the effluent. The titanium concentrations related to the wastewater treatment effluent can be clearly seen near the mouth of the Ashley River (Figure 18). The remaining areas of



Figure 16. Chlorine concentrations (wt%) in the surficial sediments of the Ashley River.



Figure 17. Iron concentrations (wt%) in the surficial sediments of the Ashley River.



Figure 18. Titanium concentrations (wt%) in the surficial sediments of the Ashley River.

elevated titanium concentrations that were located near the industrial section and the large marina appeared to covary with that of the elevated aluminum concentrations.

Tin, in the form of tributyltin, has been routinely used in the antifouling paint on marine vessels for many years. The paint has been used to stop the growth of barnacles and algae below the water line of commercial and recreational marine vessels (U. S. Government, 1987). The metals, such as tin, found in the bottom paint leach from the coatings and prevent marine organisms from attaching to the ship hulls. It has been found that paint containing tributyltin has been very effective, perhaps too effective, in killing marine organisms. Mussels, dolphins, whales, and sea otters are among the many casualties linked to paints with tributyltin (BBC News, 1998). The metals from the paint disperse into the seawater and settle into the marine surficial sediment near harbors and shipping channels. The metals enter the food chain through the marine invertebrates and then are passed along through the higher trophic levels.

Elevated tin levels were found in the surficial sediments along the eastern shore of the Ashley River immediately corresponding to the expansive marinas located on the river (Figure 19). The marinas cover approximately two-thirds of a nautical mile along the river and extend into the river by approximately 1000 feet. The southern-most dockage in this area is a Coast Guard Facility, which can support relatively large vessels. The tin concentrations drop rapidly beyond the area where the boats are docked. There were also some vessels moored across the channel from the marinas. These vessels did not appear to adversely affect the tin concentrations in the surficial sediments, most likely due to the wider spacing between vessels.



Figure 19. Tin concentrations (ppm) in the surficial sediments of the Ashley River. (Photo by Ashley Marina)

Tin, or the absence of tin, also had a correlation with the Plum Island Wastewater Treatment Plant. A distinctly lower tin concentration was present where the treatment effluent empties into the Ashley River. Tin is not typically a problem with municipal wastewater, but more commonly related to marine and industrial activity. The industrial section of the river, especially the eastern shore immediately adjacent to the industrial facilities, also had relatively low tin concentrations. Tributyltin is often used as a wood preservative; however, there were no known reports of it being used at the wood treatment facility along the Ashley River.

The remainder of the elemental analytes targeted in the surficial sediment of the Ashley River did not reveal any definitive patterns relating to potential point or non-point sources of pollution, as did the examples discussed previously in this chapter. These analytes have in many instances been used to track potential sources within a surveyed area and so were included in the target list. Results were obtained for each of the analytes and contour maps were generated. However, these maps were not included in the main text, but for simplicity presented in Appendix D.

Lead, nickel, zinc, and zirconium (Appendix D) all reached maximum concentrations along the marshy shoreline opposite the industrial area. This area was very shallow (<3 ft) and located on the inside of the river bend with considerably slower river currents. The sediment primarily consisted of clay and silty sediment, which commonly adsorbs trace metals due to the high surface area and ionic attraction. However, trace metals other than lead, nickel, zinc, and zirconium such as chromium and copper that would typically coincide with the clay concentration did not covary with aluminum as expected.

#### Sediment-Grab Samples

The CS<sup>3</sup> sediment-mapping concept is based on the ability to rapidly cover a region of concern and to determine the elemental distribution of that area. In order to achieve this goal, the CS<sup>3</sup> survey methodology is employed for rapidly collecting a considerable number of closely spaced surficial sediment samples over a relatively large region. The results for each point are then averaged with several of the surrounding points using the mapping software and displayed in two-dimensional contour maps. This principle generates a good representation of the elemental concentration of the surficial sediment for the surveyed region and aids in locating areas of potential environmental concern.

A previous ground-truth study had been completed to successfully show the correlation of the  $CS^3$  sampling methodology as compared to standard sediment-grab samples (Noakes *et al*, 1985). However, a select number of sediment-grab samples still needed to be collected for site-specific validation "ground truth" purposes. As discussed in Chapter 3, Technical Approach, ten sediment-grab samples (Figure 8) were collected from the Ashley River and analyzed for elemental content (Table 6). The sediment-grab sample locations were chosen based on the  $CS^3$  elemental concentrations maps generated for the river. Care was taken to collect only the surficial sediment from the river, but due to the silty, semi-consolidated consistency of the river bottom, the actual sediment surface was difficult to determine in some of the samples.

As expected, the phosphorus concentration in the sediment-grab samples reached a peak adjacent to the industrial area on the Ashley River. The phosphorus concentrations started out moderately high near the Memorial Bridge (Highway 7) and

Grab	1	2	3a	3b	4	5	6	7	8	9	10
Sample											
Latitude	32° 50.178'N	32° 49.735'N	32° 49.528'N	32° 49.528'N	32° 49.332'N	32° 48.672'N	32° 47.916'N	32° 46.879'N	32° 46.607'N	32° 46.344'N	32° 45.538'N
Longitude	79° 58.950'W	79° 58.048'W	79° 57.991'W	79° 57.991'W	79° 57.954'W	79° 58.086'W	79° 58.452'W	79° 57.635'W	79° 56.997'W	79° 57.096'W	79° 56.278'W
<b>F1</b>											
Element		0		0.40		Wt%o	0.40				- 10
Al	7.42	4.78	7.66	8.49	6.06	6.62	8.10	7.03	7.90	7.35	5.40
Si	24.40	35.73	21.88	24.00	26.59	24.37	24.57	23.83	23.97	26.28	26.21
K	0.99	0.55	1.03	1.09	0.99	1.01	1.03	1.03	1.12	1.24	1.21
Р	0.39	0.17	0.38	0.31	0.68	0.62	0.30	0.38	0.22	0.10	0.14
Ca	2.02	0.66	2.50	2.04	4.85	5.00	2.97	3.63	3.13	1.94	3.43
Ti	0.46	0.35	0.50	0.52	0.96	0.63	0.56	1.29	0.50	0.91	1.67
Fe	3.40	1.48	4.13	4.13	2.51	2.82	3.68	3.32	3.97	3.47	2.83
						ppm					
Mn	387	155	465	465	387	387	465	465	465	465	697
Cr	85	62	101	106	187	152	113	115	109	93	105
Ni	23	9	27	29	17	20	24	21	27	20	15
Cu	32	10	40	38	20	23	26	34	36	12	10
Zn	114	38	148	140	81	89	100	135	125	64	60
Sr	172	71	201	178	258	269	216	236	217	174	248
Zr	254	1060	335	271	1990	1050	713	4620	308	2170	3460
Ва	192	81	184	209	279	237	183	277	233	235	342
Sn	<2	<2	<2	<2	3	2	2	2	4	<2	3
As	19	11	25	23	12	16	20	22	22	13	13
Pb	38	12	46	44	29	30	38	33	43	20	20

 Table 6. Ashley River Sediment-grab XRF Elemental Analyses.

then peaked near the former phosphate production facility. The phosphorus concentrations, as represented by the sediment-grab samples were higher in the industrial section of the river than that shown by the CS<sup>3</sup> phosphorus maps. The difference in the results can be readily explained by the difference in penetration of the CS<sup>3</sup> sled, which samples primarily surficial sediment versus the deeper penetrating sediment-grab sampler. The phosphorus concentrations would be higher at depth since the phosphate production facility has not been in operation for many years and the levels of phosphorus entering the river has decreased considerably as a result. Additionally, as part of the Resource Conservation and Recovery Act (RCRA) cleanup at the site, a geotextile mat has been installed along the riverbank to reduce erosion of the phosphorus-laden sediment and encourage deposition of an overlying layer of clean sediment (Fanning, 2002). The phosphorus concentrations in the river had decreased further downstream near Orangegrove Creek and appeared to remain constant until the Highway 17 Bridges.

Beyond the Highway 17 Bridges, the phosphorus concentrations continued to decrease further downstream towards the confluence of the Ashley River and the Charleston Harbor. The phosphorus concentrations in the lower section of the Ashley River were very similar to that shown in the CS<sup>3</sup> distribution maps. This would be expected since much of the phosphorus from the many years of phosphate production was deposited in the river sediment near the production facility and was not transported downstream towards the Charleston Harbor. Therefore, the phosphorus concentrations in the river sediment near the confluence of the Ashley River and the Charleston Harbor was uniform in distribution relative to sediment depth.

Chromium concentrations detected in the sediment-grab samples closely compared to the CS<sup>3</sup> chromium concentration map (Figure 20). Many of the sedimentgrab samples showed an exact duplication of the chromium concentrations represented in the CS<sup>3</sup> chromium concentration map while other sediment-grab samples were either slightly higher or lower. The maximum chromium concentration detected adjacent to the industrial section of the Ashley River was 187 ppm in the sediment-grab sample as compared to 170 ppm in the CS<sup>3</sup> samples. The only chromium concentration from a sediment-grab sample that appeared to be considerably different from the CS<sup>3</sup> results was located near the confluence of the Ashley River and Charleston Harbor. Chromium was detected at 105 ppm as compared to approximately 75 ppm as represented in the CS<sup>3</sup> chromium concentration map.

Most of the remaining elemental results from the sediment-grab samples were similar to the corresponding  $CS^3$  elemental concentration maps. However, the copper concentrations were considerably lower in the sediment-grab samples as compared to the  $CS^3$  copper concentrations. Some variability in results is expected due to the differences in sample methodology. That is, collecting a whole sample from the river bottom as compared to pumping a slurry of surficial sediment and water to the surface for sampling. Also, the averaging effect utilized in the mapping software will lower the value of a single high number as well as increase the value of a low number.

As part of EPA's Environmental Monitoring and Assessment Program (EMAP), sediment samples were collected in the Ashley River in 1995 (EMAP, 1995)(Table 8, Figure 21). Only three of the EMAP samples were collected directly in the Ashley River and one was collected in Diesel Creek, located on the eastern shore of the Ashley River.



Figure 20. CS; chromium concentration map with overlay of the sediment-grab chromium concentrations.

Station	CP95151	CP95152	CP95ASM	CP95DIE
Latitude	32° 47.08'N	32° 47.05'N	32° 46.81'N	32° 48.26'N
Longitude	79° 57.91'W	79° 57.72'W	79° 57.82'W	79° 57.96'W
Element		wt%		
Al	2.79	4.35	3.52	8.44
Fe	1.57	2.26	0.92	4.31
Si	4.19	3.78	3.98	2.54
		ppm		
Mn	309	363	342	352
Cr	44	65	112	120
Cu	11	15	33	34
Ni	9	14	13	27
As	8	11	10	20
Zn	51	69	84	151
Sn	1.2	1.4	1.6	2.7
Pb	16	25	42	51

Table 7. EMAP (1995) Elemental Data from the Ashley River.



Figure 21. EMAP sample locations on the Ashley River.

Generally, the EMAP elemental concentrations agreed with both the CS<sup>3</sup> elemental distribution maps and the sediment-grab samples from the Ashley River. Considering that there was approximately seven years between the EMAP sampling and CS<sup>3</sup> sediment mapping survey and that the sampling stations were different than the sampling stations from this project, any correlation with the data would be considered successful.

The copper concentrations, which were higher in the CS<sup>3</sup> elemental distribution map, but considerably lower in the sediment-grab samples, were also lower in the EMAP samples. It is not readily known why the copper concentrations were so much higher in the CS<sup>3</sup> samples as compared to the EMAP and sediment-grab samples. However, due to the fact that the CS<sup>3</sup> samples the surficial sediment, it is most likely that the high copper concentrations were present in the very surficial sediment and not at depth as generally sampled by the sediment-grab sampling device.

# Organic Analyses

# CS<sup>3</sup> Samples

Polycyclic aromatic hydrocarbons (PAH) are another form of industrial waste that typically enters the marine environment from non-point sources and also industrial and municipal discharges (EPA, 1987). One common PAH found in the environment is anthracene. It is derived from coal tar and used in the production of dyes, pigments, plastics, insecticides, wood preservatives and coating materials. Figure 22 shows the anthracene distribution in the surficial sediments of the Ashley River. The most pronounced feature shown in the anthracene distribution is near the mouth of Orangegrove Creek, which enters the Ashley River on the western bank. The upper reach of Orangegrove Creek borders a residential area, which would potentially produce storm



Figure 22. Anthracene concentrations (ppm) in the surficial sediments of the Ashley River.

water runoff that is high in PAH. Additionally, the use of pressure treated wood in docks and embankments would also add to the anthracene concentrations in the water. Anthracene reached a maximum of 1.3 ppm in the surficial sediment at the confluence of the Ashley River and Orangegrove Creek. The strategic location of the increased anthracene concentrations at the mouth of the creek indicate that higher concentrations of anthracene were coming from Orangegrove Creek, although no samples were collected directly in the creek to confirm the actual source.

Another area of slightly elevated anthracene levels was present upstream of Orangegrove Creek on the Ashley River. This area (shown in yellow) is adjacent to the main industrial section, which included a wood treatment facility, marina, and the phosphate processing facilities. Creosote was the primary preservative utilized in the treatment of raw lumber and utility poles at the site. Creosote contains approximately 2% anthracene as one of the major components in the compound (Table 8; Lorenz and Gjovik, 1972).

The anthracene levels adjacent to the wood treatment facility were above ambient for the river, but only reaching levels of approximately 0.2 ppm. Low levels of anthracene in this section of the river were expected since the wood-treatment facility had been out of operation since 1978. It is doubtful that the phosphate industry contributed any anthracene to the river, as it was not used in any part of their fertilizer processing operation. Most likely, the marina docks present in this section of the river were the primary contributor to anthracene detected in the surficial sediment. The remaining sections of the Ashley River (shown in blue) had anthracene levels either at or below the system detection levels of 0.1 ppm.

Component	Approximate Percentage
Naphthalene	3.0
Anthracene	2.0
Carbazole	2.0
Pyrene	8.5

# Table 8. Major Organic Compounds in Creosote.

Compiled from Lorenz, 1972.
An industrially generated, organic compound commonly found in the environment is Bis (2-Ethylhexyl) phthalate. Phthalate is used as a plasticizer for industrial applications as well as every day household products (Colborn *et al*, 1997). It has been found to enter the environment through non-point sources, industrial discharges, and municipal wastewater.

Immediately adjacent to the industrial area of the Ashley River, there was a noticeable increase in the phthalate concentration. Both immediately upstream and downstream of the industrial area, phthalate was non-detectable. Phthalate concentrations reached a maximum of 500 ppm approximately ½ nautical mile downstream from the industrial area on the Ashley River (Figure 23). There is no known reason for the high concentration of phthalate in this part of the river except for the rapid decrease of water depth. This may be a settling area for fine-grained sediment allowing the phthalate-rich sediment to accumulate.

The phthalate concentrations drop off quickly beyond the peak in concentration until a more gradual increase near the mouth of Orangegrove Creek. As stated earlier, Orangegrove Creek borders a residential area, which can contribute phthalate into the environment through storm water runoff into the creeks and rivers. The effect of the phthalate in the storm water runoff can be seen as a plume flowing downstream from the mouth of Orangegrove Creek. Detectable levels of phthalate continued downstream towards the Highway 17 Bridges after which phthalate was mostly non-detectable until the confluence of Wappoo Creek where phthalate concentrations were found again. An increase in the phthalate concentrations was also noted at the mouth of the Ashley River where it flows into the Charleston Harbor.



Figure 23. Phthalate concentrations (ppm) in the surficial sediments of the Ashley River.

Pyrene is another anthropogenic compound that is commonly found in marine sediment (Figure 24). It is not commercially produced or used but rather a product of incomplete combustion of organic materials such as gasoline, diesel, coal, and wood. It is often found in smoke from industrial, municipal, and domestic origin. Pyrene is a major component of creosote (8.5%) and has also been detected in leachate from coal tar and creosote (EPA, 2002).

Pyrene readily binds to suspended sediment in the environment and resists degradation by microbes or reactive chemicals. Depending on the particulate size and settling distribution, some of the pyrene-rich sediment would be expected to settle in the vicinity of where it enters the river. Pyrene was detected in two locations along the Ashley River. One such area was located adjacent to the industrial area on the river. Two possible sources for pyrene exist in this area: the wood treatment facility and a marina.

The wood treatment facility used creosote in their wood preservative operations. Since pyrene comprises approximately 8.5% of the creosote, it would be understandable that runoff from the facility would contain pyrene. Another contributor to the pyrene found in the surficial sediment was the marina located amongst the facilities. Most marine vessels port their engine exhaust directly into the water. The pyrene in the exhaust would be directly introduced into the water column where it could adhere to the suspended particles in the water. Even though there was significant current in the river at this point, some of the suspended particles would tend to settle near the marina.

Pyrene was also detected further downstream from the confluence of Orangegrove Creek and the Ashley River. Unlike the first area discussed, the second pyrene-rich



Figure 24. Pyrene concentrations (ppm) in the surficial sediments of the Ashley River.

sediment did not directly correspond with a potential source. However, it did correlate with elevated levels of phthalate and a shallower section in the river, which could indicate a sediment deposition zone within the river. Further downstream, there were no detectable levels of pyrene in the marine sediment. There were also no indications of pyrene in association with the large marina located on the eastern shore of the Ashley River from the Highway 17 Bridges to the Coast Guard facility.

One of the most commonly used pesticides in the United States is pentachlorophenol. It is widely used as an industrial preservative in pressure treated lumber. As initially discussed in the elemental analyses section of this report, pentachlorophenol was used at the former wood treatment facility located on the Ashley River. Pentachlorophenol is also used in insecticide, fungicide, herbicide, molluscide, algaecide, disinfectants, and in antifouling paint (NSC, 2003).

Not found naturally in the environment, pentachlorophenol is produced through the chlorination of phenol. It degrades rapidly in water so unless there is a steady supply of the compound, it should not persist in the environment in high concentrations. This was the case in the Ashley River. Detectable levels of pentachlorophenol were found immediately adjacent to the industrial area along the Ashley River (Figure 25). No detectable levels of pentachlorophenol were found either immediately upstream or downstream of this area.

Detectable levels of pentachlorophenol appeared near the confluence of Orangegrove Creek and the Ashley River. The concentrations continued to increase to a point approximately one-quarter mile downstream along the eastern shore of the Ashley



Figure 25. Pentachlorophenol concentrations (ppm) in the surficial sediments of the Ashley River.

River. This is the same general area where both phthalate and pyrene were detected in the river. At this time, no contaminant sources are known to be present along this section of the Ashley River.

Carbazole, with approximately 2 weight percent, is a major component of creosote and is generated during coal gasification (EPA, 1984). In addition to the major uses of creosote, thousands of tons of carbazole are also used annually in the production of dyes, pharmaceuticals, and plastics (Ellis *et al*, 2003). In the Ashley River, carbazole was detected in several locations (Figure 26). As would be expected, carbazole was detected near the former wood treatment facility that used creosote to treat utility poles and raw lumber. Additionally, there are also several large docks located in this area, which generally use creosote as a preservative in the submerged pilings supporting the docks.

Both Orangegrove and Wappoo Creeks appeared to have a plume of carbazolerich sediment coming from their confluence with the Ashley River. The presence of carbazole from the creeks could be from creosote coated dock pilings or possibly from urban runoff containing household dyes, pharmaceuticals, and plastics. This concept is further validated by the presence of phthalate, a plasticizer often found in urban runoff and also detected in the Ashley River surficial sediment near the mouths of both creeks. The area containing the highest concentrations of carbazole was located at the mouth of the Ashley River near the shore and out of the main river current. At the time of sampling, it was noted that there were some old pilings in the water near where the samples were collected. These pilings were most likely coated with creosote, which had leached the carbazole into the surrounding sediment.



Figure 26. Carbazole concentrations (ppm) in the surficial sediments of the Ashley River.

Naphthalene, 4-methylphenol, and DDE were not present in sufficient quantity to produce concentration maps. However, some of the CS<sup>3</sup> samples did show detectable concentrations of these organic compounds. The samples that detected naphthalene, 4-methylphenol, and DDE were plotted with the highest concentrations labeled. By plotting these points, it gave a good representation of where the organic compounds were present on the river and aided in comparing the location of the compounds relative to the other more prominent organic compounds found in the surficial river sediment.

Naphthalene was one of the compounds not detected in the majority of the CS<sup>3</sup> samples collected in the Ashley River (Figure 27). Naphthalene is a major component of creosote, which contains approximately 3 weight percent of the compound (Lorenz and Gjovik, 1972). It is also used widely in the production of dyes, resins, leather tanning agents and insecticide, but most prominently known for its use in mothballs. Naphthalene can also enter the environment through the burning of wood and fossil fuels. It readily dissolves in water and only becomes weakly attached to soils. The dissolved naphthalene in water readily evaporates or is destroyed by bacteria within a couple of weeks from the initial introduction to the environment (ATSDR, 1995).

The wide use of naphthalene in both industrial and residential use most likely explains the presence of the compound in the surficial sediments of the Ashley River. Additionally, the rapid destruction and dissipation of the compound would also explain why it was not detectable in most parts of the river. Given that the majority of naphthalene is gone approximately two weeks after introduction into the environment, it would take a steady input for the compound to be readily detectable. For residual creosote from the former wood treatment facility to input any naphthalene into the river



Figure 27. Detectable concentrations of naphthalene (ppm) in the surficial sediment of the Ashley River.

would be relatively unlikely, as the facility has been closed for many years. However, it would be possible for the creosote used to preserve the pilings in the docks along this part of the river to leach some naphthalene into the surrounding water and surficial sediment.

The most likely source of naphthalene in the surficial sediment would be from industrial and urban storm water runoff and outfall pipes. Residue from burning fossil fuels in the operation of onsite generators and other industrial engines can be concentrated on industrial sites and later transported to the river through storm water runoff. Additionally, naphthalene found in dyes and insecticides from residential usage can also enter the river through storm water effluent outfall pipes terminating in the river.

Naphthalene concentrations as high as 1.9 ppm were detected in the Ashley River channel starting near the confluence of Orangegrove Creek and continued for approximately one mile downstream. This was approximately the same general area where there were elevated concentrations of phthalate, pyrene, pentachlorophenol, and carbazole, which would indicate a potential deposition zone or unknown effluent inputting organic compounds into the river.

4-Methylphenol, or more commonly known as *p*-cresol, was another organic compound that was targeted for analyses in the Ashley River surficial sediment. *p*-Cresol biodegrades rapidly in the environment and does not readily adsorb to sediment (Pelish, 2003). It is commonly found in the natural oils of conifers, oaks and sandalwood trees and is a by-product of the pulpwood processing operation (IPCS, 1995). *p*-Cresol is also found in fossil fuels and is generally produced through the distillation of coal tar. It can enter the environment through combustion of fossil fuels, storm water runoff and industrial effluent. *p*-Cresol is used in the production of lubricating oils and automotive

fuels, rubber, polymers, elastomers, food products, and dyes which make their way into the municipal wastewater treatment facilities and storm water runoff.

The rapid biodegradation is the most likely reason why *p*-cresol was not readily detected in the  $CS^3$  surficial sediments samples collected in the Ashley River. Similar to naphthalene, *p*-cresol was mostly detected in the  $CS^3$  samples collected within the main river channel (Figure 28). Detectable concentrations of *p*-cresol were found adjacent to the industrial area on the Ashley River and continued downstream for approximately one mile. After approximately one half mile further downstream and near the confluence of Orangegrove Creek, the detectable concentrations of *p*-cresol reappeared. The highest concentrations, reaching upwards of 6.2 ppm, were found from the confluence of the Orangegrove Creek to approximately one and a half mile downstream where the concentrations were once again below detection. Beyond that point, only a few of the  $CS^3$  samples contained detectable levels further downstream to the mouth of the Ashley River.

There was no indication that any p-cresol concentrations were associated with the Plum Island Wastewater Treatment facility or any of the other organic compounds investigated in this study. The absence of p-cresol in the wastewater effluent may be due to the high volatility of the compound in the turbulent water as it passes through the treatment facility.

Analysis of dichlorodiphenyldichloroethylene (DDE), a breakdown product of dichlorodiphenyltrichloroethane (DDT), was only detected in four of the CS<sup>3</sup> samples collected in the Ashley River (Figure 29). The DDE concentrations in the four samples were actually very low, near the minimum detection limit for the analyses.



Figure 28. Detectable concentrations of 4-methylphenol (*p*-cresol) (ppm) in the surficial sediment of the Ashley River.



Figure 29. Detectable concentrations of DDE (ppm) in the surficial sediment of the Ashley River.

DDT was a widely used pesticide in the United States until it was banned in 1972 due to harmful effects to wildlife. DDT forms a strong bond with sediment, but will still breakdown to DDE within two to fifteen years in the environment (ATSDR, 2002). DDT and DDE tend to build up in plants as well as the fatty tissues in animals, birds, and fish making it an environmentally sensitive anthropogenic compound. DDE has no commercial value but has been listed by EPA as a probable human carcinogen making it an important survey analyte for the Ashley River.

#### Sediment-Grab Samples

Many of the organic compounds analyzed in the CS<sup>3</sup> samples were below the instrumentation detection limits. This was true for the sediment-grab samples collected in the Ashley River as well. Of the eight organic compounds analyzed in the sediment-grab samples, only three were determined to have detectable concentrations present (Table 9). Very low organic contaminant concentrations were expected since the EMAP program had previously analyzed several of the same survey analytes in 1995 (Table 10).

Naphthalene, anthracene, and DDE, three of the EMAP analytes collected in 1995 were below the anticipated detection limit for the analytical method used during the Ashley River sediment mapping survey so it was expected that concentrations would be below detection limits for the CS<sup>3</sup> and sediment-grab samples. However, pyrene was above the anticipated minimum detection limit with EMAP concentrations ranging from 0.28 to 3.86 ppm. Pyrene detected in the CS<sup>3</sup> samples ranged up to 5.35 ppm and the sediment-grab samples ranged up to 3.3 ppm.

Phthalate concentrations were among the most abundant of the organic compounds detected in the Ashley River sediments. The sediment-grab phthalate

Grab Sample	1	2	3a	3b	4	5	6	L	∞	6	10
Latitude Longitude	32° 50.178'N 79° 58.950'W	32° 49.735'N 79° 58.048'W	I 32° 49.528'Y V 79° 57.991'V	V 32° 49.528'Ì V 79° 57.991'V	N 32° 49.332'  W 79° 57.954"	N 32° 48.672' W 79° 58.086'	N 32° 47.916' W 79° 58.452'	N 32º 46.879'] W 79º 57.635''	N 32º 46.607' W 79º 56.997'	N 32° 46.344'N W 79° 57.096'M	32° 45.538'N   79° 56.278'W
Compound					dd	Ш					
4-Methylphenol	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Naphthalene	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Pentachlorophenol	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Anthracene	0.85	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Carbazole	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Pyrene	3.30	<0.25	1.1	0.52	<0.25	0.61	0.35	<0.25	1.20	<0.25	<0.25
DDE	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Phthalate	35.80	5.20	4.70	2.40	<0.25	3.90	2.80	4.70	7.70	11.20	1.20

Table 9. Ashley River Sediment-grab Organic Analyses.

Table 10. EMAP (1995) Organic Data from the Ashley River.

Station	CP95151	CP95152	CP95ASM	CP95DIE	
Latitude	32° 47.08'N	32° 47.05'N	32° 46.81'N	32° 48.26'N	
Longitude	79° 57.91'W	79° 57.72'W	79° 57.82'W	79° 57.96'W	
Compound		ıdd	в		
Napthalene	0.02	0.04	0.01	0.03	
Anthracene	0.05	0.14	0.04	0.12	
Pyrene	0.48	3.86	0.28	0.72	
DDE	0.0002	0.0006	0.001	0.003	

concentrations were posted on the  $CS^3$  phthalate concentration map for a comparison of the data (Figure 30). With the exception of two sediment-grab samples, the phthalate concentrations were in very close correlation with the  $CS^3$  phthalate distribution map.

The CS<sup>3</sup> phthalate concentration map did not show any detectable concentrations near the Memorial Bridge (Highway 7) as compared to a phthalate concentration of 35.80 ppm in sediment-grab Sample 1. Sediment-grab Sample 5 was collected in the area that had been identified by the CS<sup>3</sup> phthalate distribution map as having up to 500 ppm phthalate in a very consolidated area in the river. However, the phthalate concentration detected in Sample 5 was only 3.9 ppm. The difference in concentrations could be either from a variation in sample location or potentially from sample contamination anywhere in the procedure from collection to analyses. It was noted in Table 5 that the phthalate standard spike had a recovery rate of 184% during the CS<sup>3</sup> sample analyses, which would indicate an analytical error.



Figure 30. CS<sup>3</sup> phthalate concentration map with overlay of the sediment-grab phthalate concentrations.

# CHAPTER 6

# CHEMICAL AND PHYSICAL MEASUREMENTS

Estuaries are very dynamic and are influenced by tidal fluxes as well as unique chemical and physical parameters. These continual changes in the estuarine environment are a major factor in determining the biological population and diversity as well as in determining the dissolved trace metal and organic concentrations in the water column. Interactions with the metals in the water column and changes in salinity, pH, and dissolved oxygen (DO) can either cause the metals to precipitate or go into solution. The chemical and physical parameters measured at the sediment-water interface (Appendix E) can be useful in interpreting these interactions. Typical measurements for these parameters are normally collected from bottom water, sediment pore water or sediment. Since these measurements were collected from the sediment-water interface and represented a combination of bottom water, sediment pore water, and sediment, the value of the results are still under discussion.

The salinity in an estuary changes slowly from 0 ppt in freshwater to approximately 35 ppt in seawater. The higher saline water is denser than the freshwater and commonly forms a salt wedge at the bottom. That is, the freshwater rides over the salt water resulting in the surface water to be less saline than the bottom water. By measuring the salinity at the sediment-water interface, a good indication of the salinity at the bottom can be determined. A drawback to using the CS<sup>3</sup> to measure salinity is that a higher salinity reading will most likely be measured in the sediment-water slurry due to

the salt ions in the bottom sediment. However, lowering a salinity probe in a high-energy environment can be difficult, while towing the  $CS^3$  sled on the estuarine bottom is a relatively simple task.

The salinity in the Ashley River study area started at 18 ppt near the Memorial Bridge (Highway 7) and reached a maximum of 29 ppt at the confluence of the Ashley River and the Charleston Harbor (Figure 31). Effects of the fresher water from Orangegrove and Wappoo Creeks can be seen as the water mixed with the more saline water of the Ashley River. Evidence of the salt wedge effect was shown immediately adjacent to the industrial area where the denser saline water migrated into the deeper channel of the river. The effect of the river current was also evident at the confluence of the Ashley River and the Charleston Harbor where the faster moving water along the City of Charleston side of the river kept the denser saline water from moving upstream into the Ashley River or possibly the result of an outfall pipe with a freshwater effluent.

The dissolved trace metal concentrations are generally associated with the salinity gradient (Windom *et al*, 1999). For example, as salinity increases, the dissolved iron concentration in the water column decreases. Manganese also has a similar relation to the increasing salinity. The iron and manganese decrease is related to the formation of hydrated oxides, which precipitates and accumulates in the bottom sediment (Windom, 1976). Additionally, as salinity increases, the pH in the water column also typically increases. By mapping the salinity at the sediment-water interface, even with the tidal flux, an estimation of the salinity gradient can be made and used to interpret the metal precipitation rates.



Figure 31. Salinity (ppt) measurements taken at the sediment-water interface in the Ashley River.

The pH of a solution is the measure of the concentration of the hydrogen ion based on a negative logarithmic scale from 0 to 14 with 7 being neutral (Harrison *et al*, 1991). The lower the pH, the more acidic the solution and the more hydrogen ion concentration in solution. Fresh water pH in the South Carolina Coastal Plains averages around 6.4 (Chestnut, 2002). The pH of most surface seawater in atmospheric equilibrium is 8.2 (Millero, 1996). In most estuaries, the pH increases as the water becomes more saline. The pH in the Ashley River started around 7.4 near the Memorial Bridge (Highway 7) and continued to increase downstream until the confluence of the Ashley River with the Charleston Harbor where the pH reached 7.8 (Figure 32). The increase in the pH was overall very gradual, but consistent with no noticeable effect of water flow from either Orangegrove or Wappoo Creeks as was the case with the salinity measurements.

The dissolved oxygen (DO), expressed in percent saturation, in an estuary is probably the most important factor affecting biological organisms. Fish are more sensitive to changes in the DO than are the benthic organisms such as worms or bacteria. However, the benthic organisms are generally not mobile enough to move to another area in the estuary if the DO concentration becomes too low or too high. The DO is measured in percent saturation of oxygen in the water column. For this study, the DO was measured at the sediment-water interface, or the primary home for the benthic organisms.

The DO in the Ashley River ranged from a low of 40% in the riverbend near the Memorial Bridge (Highway 7) to a high of 90% near the confluence of the Ashley River and the Charleston Harbor (Figure 33). There was no apparent effect from the water flow from Orangegrove and Wappoo Creeks on the DO in the Ashley River. The effluent



Figure 32. pH measurements taken at the sediment-water interface in the Ashley River.



Figure 33. Percent oxygen saturation at the sediment-water interface in the Ashley River.

from wastewater treatment facilities typically consumes DO. However, there was no apparent connection to the DO in the Ashley River and the effluent from the Plum Island Wastewater Treatment Plant located near the confluence of the Ashley River and the Charleston Harbor.

Higher DO was also present at the confluence of the Ashley River and the Charleston Harbor. It was in this same general area that the CS<sup>3</sup> sled was snagged during the survey. It was noted at the time that the sled was snagged, that the salinity was distinctly lower than the surrounding area suggesting freshwater input into the river. It is possible that the higher DO is a result of highly oxygenated freshwater coming from the storm water drain system.

Water temperature can be a major factor in determining the DO concentrations in an estuary. Warm water is not as efficient as cold water at dissolving oxygen and holding it in solution. The warmest water in the Ashley River was measured near the Memorial Bridge (Highway 7) and the coolest water located downstream (Figure 34). In all, there was only a difference of approximately 1 °C from the warmest to the coolest. However, there was a correlation in the temperature and DO measurements taken on the Ashley River. The sediment-water interface at Memorial Bridge was the warmest and also had the lowest DO. The coldest sediment-water measurements, located immediately upstream of Wappoo Creek, had the highest DO concentrations.



Figure 34. Temperature (°C) measurements taken at the sediment-water interface in the Ashley River.

# CHAPTER 7

## NORMALIZED DATA

Up until this point, the elemental values presented in this dissertation have been the actual values derived as part of the instrumental analytical process. While this method of analytical reporting is not wrong, it may not fully represent the whole meaning or relationship of that value in context to the environment. To properly assess anthropogenic inputs to estuarine and coastal sediments, the grain size effect needs to be addressed. Marine sediments, especially those found in estuaries and near coastal areas, contain a high quantity of fine-grained clay minerals. These clay minerals, mostly hydrous aluminum silicates, have considerable surface area and a high ionic adsorption that tends to attract and bind trace metals (Krumbein and Sloss, 1963).

Many methods to offset the grain size effect have been investigated with varying levels of success. The use of aluminum as a geochemical normalizer is probably the most effective method for studying marine sediment contamination (Goldberg *et al*, 1979). Aluminum, abundantly present in natural sediment and generally not associated with anthropogenic input, is ideally suited as a geochemical normalizer. Studies have determined that many trace metals covary with aluminum and that the normalized data can be a useful tool in determining the true extent of the anthropogenic contamination in marine sediment (Windom *et al*, 1989).

Aluminum, due to the dominant role it plays in the aluminosilicate clays, makes an excellent indicator of the fine-grained sediment distribution in the Ashley River. Due

to the geochemical binding of trace metals with the aluminosilicate clays, it would be expected to detect higher trace metals in the clay-rich sediments than in sandier sections of the river. However, the aluminum concentrations in the river sediment varied only by approximately 20% indicating that there would be a minimal grain size effect. In order to normalize the data to remove whatever effect the clay-rich sediment may have, the trace metal concentrations are divided by the aluminum concentrations. The sediments that continue to have a higher metal to aluminum ratio would then be considered impacted by anthropogenic input.

As discussed in Chapter 5, copper chromium arsenate was used at the former wood treatment facility to preserve raw lumber. Since chromium was part of the compound used in treating the lumber, it was essential to normalize the data to segregate areas of impact from the sediments merely containing high clay content. The chromium values were normalized to aluminum to reduce the grain size effect and determine potentially impacted areas on the river (Figure 35). As a result, the areas of concern have been reduced somewhat in size, but are still associated with the same landmarks as before normalizing. The shoreline immediately adjacent to the wood treatment facility still has higher chromium to aluminum ratios as compared to most of the river sediment. This means that the sediment at this location contains higher chromium than would normally be expected in the river sediment.

Chromium concentrations originally showed to be higher near the mouth of Orangegrove Creek prior to normalizing. After normalizing, there still seems to be higher than normal chromium, but nowhere near the chromium ratios adjacent to the wood treatment facility further upstream. The chromium ratios located near the



Figure 35. Chromium to aluminum ratios in the surficial sediment of the Ashley River.

Highway 17 Bridges where as high as those found near the wood treatment facility showing definite signs of anthropogenic input. Most likely the higher chromium concentrations came from the many years of paint residue from the bridges being deposited in the river with each cleaning and painting operation (Noakes, 1993). The chromium ratios also appear to be increasing at the confluence of the Ashley River and the Charleston Harbor. However, no CS<sup>3</sup> samples were collected beyond the confluence so it cannot be determined if the higher chromium ratios continue further into the Charleston Harbor.

Copper was also used in the wood treatment process and therefore of particular interest. The copper concentrations were normalized to aluminum (Figure 36) in the same manner as chromium. In contrast to chromium, the copper ratios were relatively low in the river sediments adjacent to the industrial section, which included the wood treatment facility. However, the copper ratios increased immediately downstream of the industrial section and reached a maximum where Diesel Creek enters the Ashley River. The elevated copper ratios continued downstream for approximately one mile and then decreased. Another area of elevated copper ratios was present along the Charleston seawall near the confluence of the Ashley River and the Charleston Harbor. It was at this location that the CS<sup>3</sup> sled was snagged on a possible storm water outfall during the survey. At the time the sled was snagged, the salinity measurements were considerable lower than the surrounding area indicating freshwater entering the river.

Arsenic (Appendix D) was also used in the wood treating process and was normalized to aluminum in the same manner as chromium and copper (Figure 37). Unlike either chromium or copper, the northern section of the Ashley River did not show



Figure 36. Copper to aluminum ratios in the surficial sediment of the Ashley River.



Figure 37. Arsenic to aluminum ratios in the surficial sediment of the Ashley River.

any unusual arsenic ratios. Elevated arsenic ratios did not appear until downstream of the Wappoo Creek and were only marginally present from that point to the confluence of the Ashley River and the Charleston Harbor. The overall uniformity of arsenic in the Ashley River may be related to the high occurrence of arsenic in the phosphate deposits intersecting the river near the Memorial Bridge (Highway 7) (Slansky, 1986). The long-term release of arsenic from the deposits from both erosion and through the phosphate ore processing would have input a continuous supply of arsenic into the river giving it a relatively uniform, but slightly increasing distribution downstream.

# CHAPTER 8

## CONCLUSION

As with many coastal estuaries, considerable industrial and residential development has occurred along the shores of the Ashley River. Because of this development, considerable quantities of anthropogenic contaminants are generated and make their way to the river through point and non-point sources. Permitted discharges such as industrial and wastewater treatment facilities as well as urban storm water runoff have input these contaminants into the river system. These contaminants have a high affinity for selective association with fine-grained river sediment. The CS<sup>3</sup> specifically designed to sample the surficial fine-grained sediment in a riverine, estuarine, or offshore marine environment, was implemented to survey and map the surficial fine-grained sediment in the Ashley River.

The CS<sup>3</sup> proved capable of mapping a large riverine environment with a highdensity sampling grid. A total of 149 sampling stations along a 6-mile section of the Ashley River were visited in two and a half days, which resulted in thirty-four analytes per sampling station. Approximately 5,000 data points enabled detailed distribution maps for elemental, organic, physical, and chemical analytes to be compiled for the surficial sediment in the Ashley River. The distribution maps clearly indicated above ambient anthropogenic contaminants associated with urban and industrial non-point sources along the river. The Plum Island Wastewater Treatment facility, which yields a

finite point source effluent flowing into the Ashley River, was positively identified through multiple analyte analysis.

To verify the  $CS^3$  sample results with more traditional sampling methods, ten sediment-grab samples were collected from the river based on the  $CS^3$  results. These samples were subjected to the same analytical methodology as the  $CS^3$  samples which resulted in good data correlation. Additionally, historical data on the Ashley River was retrieved from the EPA EMAP database. Even with sampling and location differences, the EMAP data correlated well with the  $CS^3$  data.

Since the CS<sup>3</sup> specifically samples the fine-grained sediment fraction, there was some concern that the data might be somewhat biased by that principle. Normalizing the data to a common element such as aluminum can readily test the bias potential. The distribution maps for the normalized data continued to show that contaminated sediment was present in areas of the river that were associated with urban and industrial non-point sources.

Contaminated sediment distribution maps of this magnitude are eagerly anticipated by state and federal agencies to delineate and characterize contaminant loads within a regional framework. With the CS<sup>3</sup> a realistic and economical evaluation of the extent of riverine or estuarine pollution and the capability to determine the mobility of anthropogenic contaminants is now a reality for long-term monitoring and site remediation.

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## APPENDIX A

## QUALITY ASSURANCE AND CONTROL

#### A.0 QUALITY ASSURANCE AND CONTROL

#### A.1 ELEMENTAL ANALYSIS

A replicate sample analysis was performed for both the NIST wafer and the standard NIST pellet. Table A-1 shows the results of the replicate analyses processed from the NIST Standard 8704 wafer. Repeating XRF analysis on the same wafer multiple times generated the precision and accuracy results. All analytes for the filter sample were within the expected range of precision and accuracy. Table A-2 shows the results of the replicate analysis on the standard NIST 8704 and PACS-2 marine sediment pellet.

System	Analyte	Precision <sup>a</sup>	Accuracy <sup>b</sup>	Precision <sup>c</sup>	Accuracy <sup>c</sup>
XRF	Al	±3.7%	±1.4%	±25%	±25%
wt%	Si	±2.2%	±6.3%	±25%	±25%
	Fe	±2.4%	±3.7%	±25%	±25%
	Ca	±2.0%	±1.2%	±25%	±25%
	Ti	$\pm 2.1\%$	$\pm 0.2\%$	±25%	±25%
	Р	±0.0%	±10.0%	±25%	±25%
ppm	Cr	±6.31%	±23.4%	±25%	±25%
	Mn	±1.3%	±11.4%	±25%	±25%
	Ni	±5.7%	±7.0%	±25%	±25%
	Cu	±7.6%	±17.4%	±25%	±25%
	Zn	±3.9%	±9.5%	±25%	±25%
	Sr	±1.7%	±4.5%	±25%	±25%
	Zr	±13.5%	±14.3%	±25%	±25%
	Sn	±12.6%	±28.2%	±40%	$\pm 40\%$
	Ba	$\pm 6.6\%$	$\pm 6.8\%$	±25%	±25%
	Pb	±15.6%	$\pm 8.5\%$	±25%	±25%
	As	$\pm 3.8\%$	±6.2%	±25%	±25%

Table A-1. XRF Data Quality Measurements for Filters.

<sup>a</sup>Relative standard deviation based on replicate analysis of NIST 8704 filter.

<sup>b</sup>Difference from true value based on replicate analysis of NIST 8704 filter.

<sup>c</sup>Acceptance/rejection values.

System	Analyte	Precision <sup>a</sup>	Accuracy <sup>b</sup>	Precision <sup>c</sup>	Accuracy <sup>c</sup>
XRF	Al	$\pm 0.4\%$	±3.2%	±25%	±25%
wt%	Si	±0.2%	±2.4%	±25%	±25%
	Fe	±0.1%	$\pm 0.8\%$	±25%	±25%
	Ca	±0.2%	$\pm 0.8\%$	±25%	±25%
	Ti	$\pm 6.8\%$	±1.4%	±25%	±25%
	Р	$\pm 0.0\%$	±10.0%	±25%	±25%
ppm	Cr	±1.21%	±6.4%	±25%	±25%
	Mn	±2.1%	±7.1%	±25%	±25%
	Ni	±5.0%	$\pm 0.0\%$	±25%	±25%
	Cu	±1.0%	±4.9%	±25%	±25%
	Zn	±0.2%	±12.7%	±25%	±25%
	Sr	±0.3%	±14.9%	±25%	±25%
	Zr	±0.3%	±0.1%	±25%	±25%
	Sn	±12.6%	±28.2%	±40%	$\pm 40\%$
	Ba	±1.2%	±3.6%	±25%	±25%
	Pb	$\pm 0.5\%$	$\pm 8.5\%$	±25%	±25%
	As	±3.8%	±6.2%	±25%	±25%

Table A-2. XRF Data Quality Measurements for Pellets.

<sup>a</sup>Relative standard deviation based on replicate analysis of NIST 8704 and PACS-2 pellets. <sup>b</sup>Difference from true value based on replicate analysis of NIST 8704 and PACS-2 pellets. <sup>c</sup>Acceptance/rejection values.

#### A.1 ORGANIC ANALYSIS

A combination of spiked samples and blanks were analyzed for both wafer and sediment-grab samples to monitor the system calibration during analyses. Table A-3 shows the averaged results for 5 wafer blank samples analyzed. Table A-4 shows the averaged results for 5 wafer samples spiked with 1  $\mu$ g/mL of the corresponding organic compounds. Table A-5 shows the results for the blank sample run with the sediment-grab samples. Table A-6 shows the results for the spiked sample (10  $\mu$ g/mL for corresponding compound) analyzed with the sediment-grab samples.

Organic Compound	Concentration $(\mu g/mL)^a$
Methylphenol	0
Naphthalene	0
Pentachlorophenol	0
Anthracene	0
Carbazole	0
Pyrene	0
DDE	0
Phthalate	0.33 <sup>b</sup>

Table A-3. HPGC/MS Data Quality Measurements for Wafer Blank Samples.

<sup>a</sup>Based on an average of 5 blank samples. <sup>b</sup>One phthalate blank sample detected 1.67 µg/mL.

Organic Compound	Concentration (µg/mL) <sup>a</sup>
Methylphenol	0.984
Naphthalene	0.904
Pentachlorophenol	0.464
Anthracene	0.790
Carbazole	1.198
Pyrene	0.970
DDE	1.060
Phthalate	1.132

Organic Compound	Concentration $(\mu g/mL)^a$
Methylphenol	0.03
Naphthalene	0.18
Pentachlorophenol	NR <sup>b</sup>
Anthracene	0.02
Carbazole	0.07
Pyrene	0.82
DDE	0.01
Phthalate	9.48

# Table A-5. HPGC/MS Data Quality Measurements for Sediment-Grab Blank Samples.

<sup>a</sup>Values based on 1 blank sample. <sup>b</sup>Not recovered.

#### Table A-6. HPGC/MS Data Quality Measurements for Sediment-Grab Samples.

Organic Compound	Concentration $(\mu g/mL)^a$
Methylphenol	14.74
Naphthalene	10.33
Pentachlorophenol	NR <sup>b</sup>
Anthracene	11.38
Carbazole	13.31
Pyrene	15.28
DDE	11.02
Phthalate	33.79

<sup>a</sup>Values based on 1 spiked sample. Sample spiked with 10  $\mu$ g/mL of the corresponding compound. <sup>b</sup>Not recovered.

### APPENDIX B

#### ASHLEY RIVER ELEMENTAL ANALYSES

Station	Lat	titude	Loi	ngitude	Depth	Al	Si	Р	S	Cl	Κ	Ca	Ti	Fe
	Deg	. Min.	De	eg. Min.	ft	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
1	32	45.965	79	55.603	9.7	5.97	25.77	0.13	1.65	7.10	1.00	1.75	0.01	1.21
2	32	45.965	79	55.603	12.1	5.26	24.90	0.12	1.97	8.59	1.03	1.80	0.01	1.14
3	32	45.965	79	55.603	20.8									
4	32	45.965	79	55.603	21.8									
5	32	45.965	79	55.603	22.1									
6	32	45.965	79	55.603	20.8									
7	32	45.965	79	55.603	22.2									
8	32	45.965	79	55.603	22.3									
9	32	45.965	79	55.603	25.2									
10	32	45.965	79	55.603	27.3									
11	32	45.965	79	55.603	24.5									
12	32	45.965	79	55.603	23.6									
13	32	45.965	79	55.603	29.1									
14	32	45.965	79	55.603	32.2									
15	32	45.965	79	55.603	25.3									
16	32	45.965	79	55.603	24.2	5.75	23.79	0.15	1.67	7.88	1.21	1.85	0.47	2.56
17	32	45.965	79	55.603	20.2	6.83	25.79	0.16	1.58	5.28	1.07	1.58	0.46	2.32
18	32	45.965	79	55.603	14.8	5.98	24.29	0.14	1.86	8.56	1.06	1.45	0.01	1.43
19	32	45.965	79	55.603	18.5	7.03	24.27	0.15	1.55	6.72	1.10	1.40	0.44	2.33
20	32	45.965	79	55.603	21.8	6.83	23.59	0.17	1.68	7.70	1.15	1.41	0.45	2.23
21	32	45.965	79	55.603	9.0	5.88	24.28	0.17	1.84	8.76	1.06	1.39	0.01	1.40
22	32	45.965	79	55.603	8.7	6.30	23.91	0.16	1.72	8.31	1.14	1.33	0.40	1.70
23	32	45.965	79	55.603	10.1	5.94	24.09	0.17	1.81	8.95	1.04	1.41	0.01	1.45
24	32	45.965	79	55.603	11.8	6.23	22.72	0.17	1.64	9.46	1.35	1.25	0.45	2.11
25	32	45.965	79	55.603	11.8	6.46	23.31	0.15	1.70	8.70	1.18	1.20	0.43	1.90
26	32	45.965	79	55.603	13.1	6.15	24.29	0.17	1.73	8.75	1.10	1.26	0.01	1.38
27	32	45.965	79	55.603	14.5	6.59	22.90	0.17	1.52	8.25	1.15	1.41	0.48	2.79
28	32	45.965	79	55.603	16.7	6.31	24.19	0.15	1.84	7.56	1.18	1.48	0.43	1.99
29	32	45.965	79	55.603	17.0	6.16	25.50	0.15	1.88	7.48	1.00	1.34	0.01	1.29
30	32	45.965	79	55.603	19.8	7.01	25.15	0.14	1.98	5.97	1.09	1.38	0.41	1.98
31	32	45.965	79	55.603	23.3	6.49	24.69	0.18	1.78	7.28	1.13	1.36	0.41	1.79
32	32	45.965	79	55.603	25.6	6.60	24.62	0.15	1.94	6.84	1.11	1.32	0.41	1.96
33	32	45.965	79	55.603	21.1	7.68	25.11	0.15	1.69	4.50	1.01	1.17	0.49	3.17
34	32	45.965	79	55.603	19.2	6.68	24.40	0.16	1.91	6.86	1.09	1.31	0.43	2.09
35	32	45.965	79	55.603	25.6									
36	32	45.965	79	55.603	25.7	6.63	24.07	0.19	1.82	7.52	1.14	1.39	0.41	1.81
37	32	45.965	79	55.603	17.7	6.11	24.33	0.17	1.78	8.91	1.00	1.21	0.01	1.16
38	32	45.965	79	55.603	13.8	6.77	24.41	0.18	1.67	7.42	1.10	1.13	0.43	1.94
39	32	45.965	79	55.603	9.6	6.71	26.46	0.20	1.56	5.52	1.05	1.06	0.42	1.85
40	32	45.965	79	55.603	9.3	7.34	27.05	0.18	1.44	3.41	0.94	1.01	0.48	2.91
41	32	45.965	79	55.603	10.8	7.65	26.97	0.19	1.17	2.87	0.86	1.13	0.50	3.52

Appendix B. Ashley River Elemental Analyses (wt% range).

Appendix B. Ashley River Elemental Analyses (wt% rat	nge).
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Station	Lat	itude	Lor	ngitude	Depth	Al	Si	Р	S	Cl	Κ	Ca	Ti	Fe
	Deg	. Min.	De	g. Min.	ft	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
42	32	45.965	79	55.603	9.5	7.10	27.31	0.24	1.01	3.59	0.80	1.31	0.47	2.77
43	32	45.965	79	55.603	19.5	6.78	25.40	0.22	1.35	5.41	0.99	1.36	0.49	3.05
44	32	45.965	79	55.603	4.0	6.19	23.92	0.19	1.62	8.48	1.13	1.24	0.40	1.84
45	32	45.965	79	55.603	3.0	7.75	26.39	0.20	0.95	3.02	0.87	1.47	0.51	3.93
46	32	45.965	79	55.603	3.0	7.25	25.23	0.19	1.31	4.78	0.93	1.44	0.52	3.59
47	32	45.965	79	55.603	3.0	7.67	26.23	0.19	1.29	2.27	0.83	1.89	0.53	4.36
48	32	45.965	79	55.603	2.9	7.48	26.23	0.20	1.40	3.18	0.92	1.57	0.50	3.69
49	32	45.965	79	55.603	5.0	7.66	26.05	0.20	1.36	3.06	0.92	1.59	0.52	3.89
50	32	45.965	79	55.603	4.0	7.57	26.52	0.20	1.05	2.63	0.84	1.46	0.51	4.33
51	32	45.965	79	55.603	4.0	5.73	24.96	0.21	1.47	7.17	1.08	1.59	0.44	1.99
52	32	45.965	79	55.603	4.0	7.45	26.21	0.17	1.18	3.06	0.89	1.32	0.53	4.30
53	32	45.965	79	55.603	8.0	6.52	26.00	0.22	1.23	3.64	0.86	1.99	0.51	4.08
54	32	45.965	79	55.603	9.0	7.25	26.15		1.11	3.37	0.88	1.74	0.53	4.21
55	32	45.965	79	55.603	10.0	6.04	25.07	0.20	1.47	5.54	1.04	2.68	0.47	2.59
56	32	45.965	79	55.603	9.0	6.91	25.97	0.21	1.33	4.57	0.96	1.45	0.49	3.13
57	32	45.965	79	55.603		7.19	26.50	0.17	1.27	3.46	0.91	1.51	0.52	3.47
58	32	45.965	79	55.603		6.95	26.39	0.17	1.13	3.13	0.84	1.99	0.56	3.82
59	32	45.965	79	55.603	8.0	6.86	26.72	0.16	1.27	3.82	0.96	1.58	0.51	3.13
60	32	45.965	79	55.603	10.0	6.71	26.09	0.18	1.39	5.34	1.07	1.37	0.47	2.42
61	32	45.965	79	55.603	12.0	6.24	25.17	0.18	1.81	6.86	1.07	1.60	0.41	1.89
62	32	45.965	79	55.603	15.0	6.42	24.93	0.17	1.78	6.69	1.10	1.67	0.43	1.95
63	32	45.965	79	55.603	18.0	6.97	25.92	0.15	1.46	4.92	1.12	1.50	0.50	2.66
64	32	45.965	79	55.603	15.0	5.85	23.64	0.12	1.93	8.60	1.07	1.54	0.41	1.50
65	32	45.965	79	55.603	11.0	7.27	25.92	0.15	1.38	3.79	1.03	1.28	0.52	3.81
66	32	45.965	79	55.603	16.0	6.59	25.44	0.16	1.47	5.77	1.14	1.51	0.47	2.68
67	32	45.965	79	55.603	7.0	7.13	25.65	0.13	1.45	4.53	1.09	1.38	0.52	3.25
68	32	45.965	79	55.603	13.0	6.10	26.15	0.13	1.54	5.89	1.13	1.31	0.44	2.14
69	32	45.965	79	55.603	10.0	6.77	25.96	0.13	1.45	5.35	1.12	1.39	0.49	2.47
70	32	45.965	79	55.603	16.0	6.31	26.49	0.13	1.44	5.91	1.07	1.30	0.44	1.99
71	32	45.965	79	55.603	14.0	6.83	25.62	0.15	1.46	5.84	1.14	1.41	0.45	2.25
72	32	45.965	79	55.603	20.0	6.63	24.44	0.14	1.61	7.32	1.11	1.41	0.42	1.91
73	32	45.965	79	55.603	18.0	7.17	22.82	0.12	1.47	8.05	1.27	1.38	0.50	3.01
74	32	45.965	79	55.603	19.2	7.15	23.99	0.13	1.37	7.48	1.14	1.37	0.43	1.96
75	32	45.965	79	55.603	9.1	6.47	24.50	0.13	1.48	7.52	1.10	1.33	0.41	1.70
76	32	45.965	79	55.603	15.3	7.27	25.57	0.14	1.24	4.86	1.07	1.51	0.48	2.67
77	32	45.965	79	55.603	28.0	6.37	24.27	0.13	1.50	8.00	1.13	1.47	0.40	1.63
78	32	45.965	79	55.603	28.2	6.61	24.86	0.12	1.42	7.16	1.16	1.37	0.42	1.86
79	32	45.965	79	55.603	26.0	5.28	25.70	0.11	1.45	8.31	0.72	1.26	0.01	1.02
80	32	45.965	79	55.603	20.0	6.53	23.90	0.12	1.51	8.76	0.93	1.32	0.01	1.36
81	32	45.965	79	55.603	19.1	5.70	26.19	0.10	1.42	7.35	0.89	1.27	0.01	1.28
82	32	45.965	79	55.603	18.2	6.08	22.87	0.13	1.47	8.21	1.08	1.46	2.30	1.61
83	32	45.965	79	55.603	19.8	7.24	25.15	0.15	1.25	5.97	1.07	1.68	0.44	2.07

Appendix B. Ashley River Elemental Analyses (wt% ran	ge).
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Station	La	titude	Loi	ngitude	Depth	Al	Si	Р	S	Cl	Κ	Ca	Ti	Fe
	Deg	. Min.	De	g. Min.	ft	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
84	32	45.965	79	55.603	19.7	6.72	25.27	0.13	1.35	6.14	1.11	1.77	0.45	2.12
85	32	45.965	79	55.603	18.8	6.78	24.89	0.13	1.33	6.36	1.18	1.92	0.44	2.28
86	32	45.965	79	55.603	17.5	7.06	23.48	0.13	1.44	7.79	1.08	1.37	0.42	1.95
87	32	45.965	79	55.603	16.7	6.97	25.05	0.12	1.32	5.45	1.18	2.04	0.49	2.82
88	32	45.965	79	55.603	6.3	6.99	26.73	0.13	1.12	3.40	0.98	1.82	0.53	3.41
89	32	45.965	79	55.603	8.3	7.68	26.07	0.15	1.03	3.43	0.95	1.62	0.52	3.82
90	32	45.965	79	55.603	6.6	6.81	25.77	0.17	1.47	5.31	1.07	1.47	0.48	2.54
91	32	45.965	79	55.603	9.4	6.59	24.63	0.14	1.63	6.96	1.13	1.22	0.42	2.02
92	32	45.965	79	55.603	3.8	6.63	25.59	0.17	1.60	5.77	1.13	1.37	0.44	2.46
93	32	45.965	79	55.603	6.4	6.72	25.80	0.18	1.43	4.82	1.07	1.54	0.50	3.22
94	32	45.965	79	55.603		6.82	25.50	0.13	1.72	5.30	1.10	1.51	0.47	2.47
95	32	45.965	79	55.603	10.2	6.46	25.40	0.17	1.53	6.69	1.03	1.33	0.43	1.91
96	32	45.965	79	55.603	10.9	7.57	24.37	0.20	1.27	5.63	1.00	1.22	0.50	3.39
97	32	45.965	79	55.603	7.9	6.73	25.45	0.18	1.42	6.09	1.04	1.27	0.45	2.20
98	32	45.965	79	55.603	13.8	6.80	25.41	0.21	1.32	5.39	1.04	1.39	0.49	3.04
99	32	45.965	79	55.603	14.6	5.52	25.15	0.17	1.64	8.41	0.96	1.18	0.01	1.10
100	32	45.965	79	55.603	14.8	6.57	24.67	0.19	1.42	6.54	1.04	1.32	0.47	2.52
101	32	45.965	79	55.603	21.8	7.33	25.70	0.19	1.37	4.47	1.04	1.30	0.50	3.32
102	32	45.965	79	55.603	15.5	7.31	25.93	0.18	1.30	4.76	1.00	1.15	0.48	2.93
103	32	45.965	79	55.603	22.2	6.31	24.10	0.17	1.53	8.47	1.08	1.17	0.42	1.54
104	32	45.965	79	55.603	26.6	6.65	25.62	0.19	1.41	6.48	0.96	1.14	0.42	2.05
105	32	45.965	79	55.603	28.5	6.97	25.51	0.19	1.54	5.21	1.06	1.46	0.46	2.70
106	32	45.965	79	55.603	22.2	7.20	25.79	0.20	1.39	4.55	1.01	1.41	0.50	3.11
107	32	45.965	79	55.603	21.6	7.47	25.39	0.21	1.35	4.11	1.00	1.42	0.52	3.82
108	32	45.965	79	55.603	23.2	7.30	25.17	0.20	1.63	5.13	1.01	1.18	0.48	3.01
109	32	45.965	79	55.603	26.2	7.36	25.81	0.18	1.63	4.94	1.00	1.20	0.44	2.38
110	32	45.965	79	55.603	15.1	6.76	25.47	0.18	1.56	6.17	1.03	1.30	0.44	2.04
111	32	45.965	79	55.603	10.3	7.46	26.89	0.19	1.19	3.26	0.94	1.33	0.51	3.21
112	32	45.965	79	55.603	8.9	6.71	25.07	0.18	1.55	6.45	1.07	1.49	0.43	2.00
113	32	45.965	79	55.603	12.1	6.83	25.26	0.22	1.42	5.90	1.09	1.46	0.46	2.34
114	32	45.965	79	55.603	18.7	6.11	23.46	0.23	1.65	7.36	1.06	3.45	0.43	1.74
115	32	45.965	79	55.603	17.8	6.44	23.77	0.17	1.66	8.23	1.06	1.50	0.59	1.51
116	32	45.965	79	55.603	14.1	7.13	25.67	0.19	1.63	5.39	1.03	1.32	0.45	2.20
117	32	45.965	79	55.603	14.1	6.58	25.05	0.12	1.24	5.57	1.15	2.10	0.49	3.08
118	32	45.965	79	55.603	16.1	6.08	24.09	0.12	1.48	7.99	1.14	1.81	0.41	1.87
119	32	45.965	79	55.603	10.8	7.63	24.89	0.13	1.35	5.18	1.15	1.93	0.47	2.66
120	32	45.965	79	55.603	5.2	6.23	24.07	0.12	1.45	7.96	1.13	1.80	0.41	1.80
121	32	45.965	79	55.603	24.1	6.28	24.45	0.13	1.48	7.22	1.15	1.80	0.43	2.15
122	32	45.965	79	55.603	24.2	6.56	25.74	0.13	1.26	4.87	1.08	2.14	0.49	2.91
123	32	45.965	79	55.603	24.1	7.07	25.55	0.11	1.32	4.87	1.10	1.79	0.49	2.87
124	32	45.965	79	55.603	24.0	6.49	25.01	0.11	1.49	5.96	1.09	2.05	0.51	2.56
125	32	45.965	79	55.603	11.1	6.03	24.87	0.12	1.34	7.01	1.14	2.13	0.45	2.00

Appendix B. Ashley River Elemental Analyses (wt% rat	nge).
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Station	Lat	titude	Long	gitude	Depth	Al	Si	Р	S	Cl	Κ	Ca	Ti	Fe
	Deg	. Min.	Deg	. Min.	ft	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
126	32	45.965	79	55.603	2.4	6.90	25.84	0.13	1.22	4.31	1.07	2.04	0.51	3.31
127	32	45.965	79	55.603	26.2	6.15	25.08	0.13	1.44	6.73	1.10	2.11	0.46	2.09
128	32	45.965	79	55.603	8.3	5.89	24.25	0.13	1.53	8.36	1.04	1.78	0.41	1.58
129	32	45.965	79	55.603	4.5									
130	32	45.965	79	55.603	26.2									
131	32	45.965	79	55.603	7.9	5.95	22.41	0.11	1.47	9.16	1.36	2.17	0.47	2.37
132	32	45.965	79	55.603	4.4	5.78	23.70	0.11	1.46	8.45	1.14	2.06	0.42	1.82
133	32	45.965	79	55.603	4.0	6.36	24.18	0.12	1.34	7.10	1.24	2.11	0.45	2.34
134	32	45.965	79	55.603	4.4	6.09	24.21	0.12	1.43	7.87	1.17	1.89	0.43	1.89
135	32	45.965	79	55.603	4.1	6.26	23.75	0.12	1.53	7.99	1.13	1.80	0.41	1.75
136	32	45.965	79	55.603	3.4	6.37	24.72	0.13	1.37	6.61	1.13	1.92	0.46	2.26
137	32	45.965	79	55.603	3.3	6.92	25.51	0.13	1.28	4.96	1.12	1.93	0.48	2.89
138	32	45.965	79	55.603	5.0	6.80	25.56	0.12	1.30	5.15	1.10	1.79	0.48	2.84
139	32	45.965	79	55.603	5.0	5.84	25.37	0.12	1.37	6.19	1.06	2.09	0.48	2.27
140	32	45.965	79	55.603	5.0	6.94	26.34	0.12	1.00	3.09	0.95	2.15	0.52	4.08
141	32	45.965	79	55.603	5.0	7.92	25.48	0.10	0.88	2.31	0.73	1.58	0.43	2.75
142	32	45.965	79	55.603	5.0	5.83	24.12	0.12	1.55	8.45	1.10	1.68	0.01	1.54
143	32	45.965	79	55.603	5.0	6.24	25.40	0.13	1.35	5.87	1.14	1.98	0.47	2.45
144	32	45.965	79	55.603	28.1	6.02	23.61	0.12	1.56	9.25	1.04	1.58	0.01	1.32
145	32	45.965	79	55.603	19.3									
146	32	45.965	79	55.603	23.2	6.70	25.27	0.14	1.34	5.86	1.13	1.78	0.44	2.53
147	32	45.965	79	55.603	21.2	7.01	25.81	0.15	1.19	4.41	1.08	1.83	0.51	3.25
148	32	45.965	79	55.603	5.0	6.60	26.27	0.15	1.31	4.86	1.06	1.94	0.47	2.53
149	32	45.965	79	55.603	5.0	7.30	26.03	0.16	1.08	3.53	1.01	1.99	0.53	3.72

Appendix B.	Ashlev	River	Elemental	Analyses	(ppm range).
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Station	Latitude	Lo	ngitude	Depth	Cr	Mn	Ni	Cu	Zn	As	Sr	Zr	Sn	Ba	Pb
	Deg. Min.	De	eg. Min.	ft	ppm										
1	32 45.965	79	55.603	9.7	77	309	22	72	170	21	38	4	9	420	4
2	32 45.965	79	55.603	12.1	70	349	19	66	98	18	69	5	ND	542	ND
3	32 45.965	79	55.603	20.8											
4	32 45.965	79	55.603	21.8											
5	32 45.965	79	55.603	22.1											
6	32 45.965	79	55.603	20.8											
7	32 45.965	79	55.603	22.2											
8	32 45.965	79	55.603	22.3											
9	32 45.965	79	55.603	25.2											
10	32 45.965	79	55.603	27.3											
11	32 45.965	79	55.603	24.5											
12	32 45.965	79	55.603	23.6											
13	32 45.965	79	55.603	29.1											
14	32 45.965	79	55.603	32.2											
15	32 45.965	79	55.603	25.3											
16	32 45.965	79	55.603	24.2	86	330	31	167	140	19	108	10	10	496	ND
17	32 45.965	79	55.603	20.2	75	439	30	185	159	17	69	8	10	440	ND
18	32 45.965	79	55.603	14.8	69	427	23	101	93	17	97	4	10	365	ND
19	32 45.965	79	55.603	18.5	64	448	31	159	99	20	97	10	10	450	ND
20	32 45.965	79	55.603	21.8	62	446	29	122	90	18	94	8	9	386	ND
21	32 45.965	79	55.603	9.0	72	389	20	93	102	19	96	0	10	462	ND
22	32 45.965	79	55.603	8.7	69	326	25	93	61	17	99	5	10	457	ND
23	32 45.965	79	55.603	10.1	69	468	23	79	53	20	98	6	10	348	ND
24	32 45.965	79	55.603	11.8	69	412	29	114	83	17	86	8	10	435	ND
25	32 45.965	79	55.603	11.8	54	338	30	116	78	18	103	8	10	372	ND
26	32 45.965	79	55.603	13.1	74	365	21	110	103	19	95	0	10	473	ND
27	32 45.965	79	55.603	14.5	59	339	36	152	147	16	88	15	10	411	7
28	32 45.965	79	55.603	16.7	63	265	26	155	125	16	101	7	ND	382	ND
29	32 45.965	79	55.603	17.0	73	346	21	77	55	20	48	6	7	536	ND
30	32 45.965	79	55.603	19.8	62	285	27	177	138	14	93	8	10	379	ND
31	32 45.965	79	55.603	23.3	61	355	24	140	124	17	98	8	ND	440	ND
32	32 45.965	79	55.603	25.6	60	320	28	118	76	18	45	0	9	470	ND
33	32 45.965	79	55.603	21.1	58	423	47	122	155	15	76	17	9	500	8
34	32 45.965	79	55.603	19.2	57	326	31	133	107	16	65	8	10	415	ND
35	32 45.965	79	55.603	25.6											
36	32 45.965	79	55.603	25.7	62	383	28	114	78	18	94	5	9	458	ND
37	32 45.965	79	55.603	17.7	64	330	22	68	53	18	92	4	10	427	ND
38	32 45.965	79	55.603	13.8	61	347	28	121	87	17	66	11	8	421	ND
39	32 45.965	79	55.603	9.6	64	369	30	134	85	18	74	8	10	421	ND
40	32 45.965	79	55.603	9.3	60	428	47	122	122	19	85	10	9	368	11

Appendix B. Ashley River Elemental Analyses (ppm 1	ange).
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Station	La	atitude	Lo	ngitude	Depth	Cr	Mn	Ni	Cu	Zn	As	Sr	Zr	Sn	Ва	Pb
	De	g. Min.	De	eg. Min.	ft	ppm										
41	32	45.965	79	55.603	10.8	55	487	57	54	150	16	116	14	8	447	17
42	32	45.965	79	55.603	9.5	64	456	41	107	109	17	128	16	10	444	14
43	32	45.965	79	55.603	19.5	58	473	41	154	163	17	94	15	9	431	9
44	32	45.965	79	55.603	4.0	59	366	28	106	64	19	80	7	10	459	ND
45	32	45.965	79	55.603	3.0	50	572	63	ND	184	16	86	24	10	440	24
46	32	45.965	79	55.603	3.0	49	461	50	97	166	14	134	23	8	504	ND
47	32	45.965	79	55.603	3.0	51	625	66	ND	174	15	201	33	ND	483	28
48	32	45.965	79	55.603	2.9	50	493	58	33	145	17	91	21	10	408	18
49	32	45.965	79	55.603	5.0	36	610	61	17	143	14	114	17	10	366	ND
50	32	45.965	79	55.603	4.0	47	550	62	ND	186	16	192	39	ND	429	25
51	32	45.965	79	55.603	4.0	61	319	29	99	75	19	85	18	9	423	ND
52	32	45.965	79	55.603	4.0	36	700	63	ND	178	14	91	34	9	474	ND
53	32	45.965	79	55.603	8.0	48	591	53	24	135	17	100	30	9	472	20
54	32	45.965	79	55.603	9.0	65	503	61	ND	151	16	202	37	8	386	22
55	32	45.965	79	55.603	10.0	56	421	33	135	137	19	104	12	9	473	7
56	32	45.965	79	55.603	9.0	51	590	41	142	168	15	95	19	ND	452	10
57	32	45.965	79	55.603		35	563	52	56	129	15	119	21	10	452	14
58	32	45.965	79	55.603		35	578	53	33	163	21	94	52	9	420	19
59	32	45.965	79	55.603	8.0	37	477	45	136	150	21	104	19	ND	429	8
60	32	45.965	79	55.603	10.0	55	348	32	130	100	16	77	11	10	394	3
61	32	45.965	79	55.603	12.0	64	411	27	108	66	16	57	8	8	494	ND
62	32	45.965	79	55.603	15.0	59	419	28	111	71	16	79	8	10	496	ND
63	32	45.965	79	55.603	18.0	66	394	33	169	144	14	76	15	9	339	ND
64	32	45.965	79	55.603	15.0	66	329	22	85	86	19	96	12	10	382	nd
65	32	45.965	79	55.603	11.0	42	617	52	95	178	11	92	24	ND	402	11
66	32	45.965	79	55.603	16.0	50	499	35	127	106	14	91	12	ND	403	ND
67	32	45.965	79	55.603	7.0	54	402	42	111	127	13	93	16	10	318	9
68	32	45.965	79	55.603	13.0	51	339	31	121	73	17	84	11	10	425	ND
69	32	45.965	79	55.603	10.0	45	433	32	166	136	18	72	11	10	419	ND
70	32	45.965	79	55.603	16.0	59	399	28	114	78	21	80	5	9	408	ND
71	32	45.965	79	55.603	14.0	60	446	32	128	72	19	84	8	10	332	ND
72	32	45.965	79	55.603	20.0	54	259	31	130	73	20	102	13	10	451	ND
73	32	45.965	79	55.603	18.0	76	172	39	107	108	17	100	9	9	461	ND
74	32	45.965	79	55.603	19.2	85	557	18	ND	ND	24	103	6	9	424	ND
75	32	45.965	79	55.603	9.1	86	563	17	ND	ND	22	63	6	10	423	ND
76	32	45.965	79	55.603	15.3	89	539	22	60	90	22	93	9	9	412	ND
77	32	45.965	79	55.603	28.0	89	569	16	ND	ND	21	67	7	10	413	ND
78	32	45.965	79	55.603	28.2	86	560	16	ND	81	18	72	8	9	452	ND
79	32	45.965	79	55.603	26.0	86	577	15	ND	ND	24	88	3	10	414	ND
80	32	45.965	79	55.603	20.0	86	519	15	ND	ND	24	50	4	9	410	ND
81	32	45.965	79	55.603	19.1	86	590	16	ND	ND	22	41	0	9	438	ND
82	32	45.965	79	55.603	18.2	57	362	25	94	62	17	71	6	8	375	ND

Appendix B. Ashley River Elemental Analyses (ppm range	:).
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Station	La	atitude	Lo	ngitude	Depth	Cr	Mn	Ni	Cu	Zn	As	Sr	Zr	Sn	Ва	Pb
	De	g. Min.	De	eg. Min.	ft	ppm										
83	32	45.965	79	55.603	19.8	61	428	31	143	92	15	71	8	9	438	ND
84	32	45.965	79	55.603	19.7	63	332	33	128	76	17	96	9	7	438	ND
85	32	45.965	79	55.603	18.8	55	341	31	124	71	19	85	8	9	454	ND
86	32	45.965	79	55.603	17.5	89	663	20	49	67	21	71	9	9	414	ND
87	32	45.965	79	55.603	16.7	103	533	21	53	101	19	112	10	9	432	ND
88	32	45.965	79	55.603	6.3	123	422	26	72	109	24	121	16	10	445	7
89	32	45.965	79	55.603	8.3	115	550	27	110	172	20	127	18	9	465	11
90	32	45.965	79	55.603	6.6	101	647	20	52	103	21	80	10	ND	409	ND
91	32	45.965	79	55.603	9.4	88	547	17	4	53	23	95	8	ND	398	ND
92	32	45.965	79	55.603	3.8	91	518	17	41	117	22	95	13	8	425	ND
93	32	45.965	79	55.603	6.4	106	589	20	61	125	20	109	16	9	436	7
94	32	45.965	79	55.603		69	294	31	170	150	19	95	11	10	442	ND
95	32	45.965	79	55.603	10.2	56	311	31	130	77	16	91	5	10	425	ND
96	32	45.965	79	55.603	10.9	39	614	42	163	195	19	96	15	ND	401	12
97	32	45.965	79	55.603	7.9	50	347	29	165	142	19	77	8	9	474	5
98	32	45.965	79	55.603	13.8	58	480	42	153	177	18	98	10	9	461	8
99	32	45.965	79	55.603	14.6	68	339	22	55	ND	17	87	4	9	450	ND
100	32	45.965	79	55.603	14.8	60	428	31	177	162	19	81	10	ND	423	ND
101	32	45.965	79	55.603	21.8	66	479	38	174	185	15	106	13	8	487	9
102	32	45.965	79	55.603	15.5	55	476	42	129	113	17	85	10	10	464	7
103	32	45.965	79	55.603	22.2	83	614	16	ND	ND	22	94	7	10	425	ND
104	32	45.965	79	55.603	26.6	89	604	19	19	55	21	56	13	7	321	ND
105	32	45.965	79	55.603	28.5	123	509	21	56	102	23	102	12	ND	466	9
106	32	45.965	79	55.603	22.2	117	646	22	74	115	19	84	9	8	322	5
107	32	45.965	79	55.603	21.6	112	619	24	103	185	19	122	17	ND	463	18
108	32	45.965	79	55.603	23.2	101	563	22	61	101	21	103	10	8	357	8
109	32	45.965	79	55.603	26.2	109	462	19	67	143	20	81	8	8	466	7
110	32	45.965	79	55.603	15.1	95	501	18	5	ND	23	75	8	9	432	ND
111	32	45.965	79	55.603	10.3	106	421	24	108	189	17	103	14	10	464	15
112	32	45.965	79	55.603	8.9	99	424	16	9	95	23	111	11	ND	381	ND
113	32	45.965	79	55.603	12.1	89	544	20	32	74	20	78	8	8	378	6
114	32	45.965	79	55.603	18.7	93	505	17	ND	ND	22	99	10	7	462	ND
115	32	45.965	79	55.603	17.8	88	513	17	ND	ND	22	82	0	10	431	ND
116	32	45.965	79	55.603	14.1	94	478	20	29	64	21	75	9	9	426	7
117	32	45.965	79	55.603	14.1	130	527	22	47	79	20	101	18	8	423	ND
118	32	45.965	79	55.603	16.1	88	559	16	ND	ND	21	75	6	9	449	ND
119	32	45.965	79	55.603	10.8	93	495	20	57	110	19	117	7	9	502	20
120	32	45.965	79	55.603	5.2	90	624	17	ND	ND	21	77	8	10	435	ND
121	32	45.965	79	55.603	24.1	90	618	18	4	ND	21	67	11	8	456	ND
122	32	45.965	79	55.603	24.2	100	563	22	45	65	20	122	17	10	478	ND
123	32	45.965	79	55.603	24.1	89	563	20	70	121	23	95	16	9	437	ND
124	32	45.965	79	55.603	24.0	92	574	20	42	67	23	105	11	8	381	ND

Appendix B. Ashley River Elen	nental Analyses (ppm range).
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Station	L	Latitude I		atitude Longitude		ngitude	Depth	Cr	Mn	Ni	Cu	Zn	As	Sr	Zr	Sn	Ba	Pb
	De	g. Min.	De	eg. Min.	ft	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm		
125	32	45.965	79	55.603	11.1							101	7			ND		
126	32	45.965	79	55.603	2.4	87	559	16	ND	76	19	122	16	9	417	ND		
127	32	45.965	79	55.603	26.2	102	640	22	91	142	21	106	7	ND	441	7		
128	32	45.965	79	55.603	8.3	95	581	18	ND	ND	21	78	8	9	433	ND		
129	32	45.965	79	55.603	4.5	87	553	16	ND	ND	21			10	384	ND		
130	32	45.965	79	55.603	26.2											ND		
131	32	45.965	79	55.603	7.9	103	421	20	7	ND	23	120	9	9	408	ND		
132	32	45.965	79	55.603	4.4	90	544	16	ND	55	23	102	11	10	476	ND		
133	32	45.965	79	55.603	4.0	94	579	18	18	81	22	105	11	ND	459	ND		
134	32	45.965	79	55.603	4.4	87	600	16	ND	64	22	122	9	10	421	ND		
135	32	45.965	79	55.603	4.1	86	586	16	ND	57	24	76	5	8	468	ND		
136	32	45.965	79	55.603	3.4	90	559	17	21	80	24	85	7	ND	449	ND		
137	32	45.965	79	55.603	3.3	90	515	21	54	76	22	115	14	ND	446	ND		
138	32	45.965	79	55.603	5.0	94	490	20	51	77	21	109	15	8	414	ND		
139	32	45.965	79	55.603	5.0	97	519	19	16	ND	24	83	14	ND	422	ND		
140	32	45.965	79	55.603	5.0	120	562	28	63	130	21	208	32	9	438	13		
141	32	45.965	79	55.603	5.0	97	577	26	75	126	23	102	15	ND	434	8		
142	32	45.965	79	55.603	5.0	84	555	15	ND	ND	22	73	8	9	379	ND		
143	32	45.965	79	55.603	5.0	93	521	17	30	91	24	96	13	ND	402	ND		
144	32	45.965	79	55.603	28.1	82	599	16	ND	ND	25	71	8	9	434	ND		
145	32	45.965	79	55.603	19.3													
146	32	45.965	79	55.603	23.2	96	557	19	32	59	22	103	10	ND	411	ND		
147	32	45.965	79	55.603	21.2	101	631	21	73	126	20	120	13	10	420	ND		
148	32	45.965	79	55.603	5.0	122	650	18	37	96	23	95	13	11	418	ND		
149	32	45.965	79	55.603	5.0	101	630	24	70	121	19	150	16	11	419	ND		

## APPENDIX C

#### ASHLEY RIVER ORGANIC ANALYSES

Appendix C.	Ashley River	Organic Analyses	(ppm).
		1	lot

Station	L	atitude	Lo	ngitude	Denth	4-Methylphenol	Naphthalene	Pentachlorophene	Anthracene	Carbazole	Pyrene	p,p'DDE	Phthalate
Station	De	g. Min.	D	eg. Min.	ft	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
		0.		0			· · · /	,	,				· · · ·
1	32	45.965	79	55.603	9.7	2.17	0.88			0.09	0.11		49.98
2	32	45.965	79	55.603	12.1	0.44			0.10	0.03	0.07		19.27
3	32	45.965	79	55.603	20.8								
4	32	45.965	79	55.603	21.8								
5	32	45.965	79	55.603	22.1								
6	32	45.965	79	55.603	20.8								
7	32	45.965	79	55.603	22.2								
8	32	45.965	79	55.603	22.3								
9	32	45.965	79	55.603	25.2								
10	32	45.965	79	55.603	27.3								
11	32	45.965	79	55.603	24.5								
12	32	45.965	79	55.603	23.6								
13	32	45.965	79	55.603	29.1								
14	32	45.965	79	55.603	32.2								
15	32	45.965	79	55.603	25.3	0.01	0.01	0.10	0.07	0.04	0		
16	32	45.965	79	55.603	24.2	0.01	0.01	0.12	0.06	0.04	0.55	0.03	42.18
17	32	45.965	79	55.603	20.2	0.16	0.07	0.50	0.15	0.05	0.61		36.42
18	32	45.965	79	55.603	14.8	4.96	1.46	0.52	0.07	0.04	0.39		61.69
19	32	45.965	79	55.603	18.5	0.15	116	0.06	0.09	0.04	2.22		33.89
20	32	45.965	79	55.603	21.8	6.30	1.16	0.81	0.94	0.08	4.70		95.66
21	32	45.965	79	55.603	9.0	0.04	0.02	1.37	0.25	0.13	0.61		73.27
22	32	45.965	79	55.603	8.7	2.15	0.54		0.10	0.05	0.98		52.34
23	32	45.965	79	55.603	10.1	0.51	1.00		1.27	0.06	0.85		39.26
24	32	45.965	79	55.603	11.8	4.59	1.90		0.83	0.05	0.94		52.37
25	32	45.965	79	55.603	11.8	0.36			0.04	0.06	0.45	0.01	51.93
26	32	45.965	79	55.603	13.1			0.00	0.02	0.04	0.10		52.60
27	32	45.965	79	55.603	14.5	0.02		0.08	0.02	0.05	0.11		33.20
28	32	45.965	79	55.603	16.7	0.02	0.01		0.05	0.05	0.57		28.17
29	32	45.965	79	55.603	17.0	0.01	0.01		0.02	0.04	0.46		531.53
30	32	45.965	79	55.603	19.8	0.02	0.02		0.02	0.03	0.31		329.42
31	32	45.965	79	55.603	23.3	0.02			0.02	0.02	0.15		110.68
32	32	45.965	79	55.603	25.6	0.02	0.02		0.02	0.03	0.17		45.89
33	32	45.965	79	55.603	21.1	0.02	0.02	0.10	0.02	0.02	0.12		74.28
34	32	45.965	79	55.603	19.2	0.02	0.02	0.12	0.02	0.02	0.18		55.86
35	32	45.965	79	55.603	25.6								

Appendix C.	Ashley	River	Organic An	nalyses	(ppm).	
				1		lol

Station	Lat	titude	Lor	ngitude	Depth	4-Methylphenol	Naphthalene	Pentachlorophen	Anthracene	Carbazole	Pyrene	p,p'DDE	Phthalate
	Deg	. Min.	De	g. Min.	ft	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
36	32	45.965	79	55.603	25.7	0.02	0.13		0.69	0.35	5.35		597.50
37	32	45.965	79	55.603	17.7					0.04	0.02		5.07
38	32	45.965	79	55.603	13.8					0.03	0.03		5.47
39	32	45.965	79	55.603	9.6	0.02		0.05		0.49	0.21		46.52
40	32	45.965	79	55.603	9.3					0.54	0.03		2.31
41	32	45.965	79	55.603	10.8					0.06	0.03		2.51
42	32	45.965	79	55.603	9.5	0.01		0.01	0.01	0.12	0.16		25.17
43	32	45.965	79	55.603	19.5					0.04	0.02		3.84
44	32	45.965	79	55.603	4.0					0.03	0.01		4.78
45	32	45.965	79	55.603	3.0					0.01	0.03		2.02
46	32	45.965	79	55.603	3.0					0.02	0.02		4.05
47	32	45.965	79	55.603	3.0				0.01	0.46	0.05		1.48
48	32	45.965	79	55.603	2.9					0.05	0.08		2.11
49	32	45.965	79	55.603	5.0					0.00	0.03		1.39
50	32	45.965	79	55.603	4.0					0.02	0.14		1.09
51	32	45.965	79	55.603	4.0					0.06	0.05		4.30
52	32	45.965	79	55.603	4.0				0.01	0.19	0.03		1.58
53	32	45.965	79	55.603	8.0					0.02	0.03		0.59
54	32	45.965	79	55.603	9.0				0.01	0.03	0.06		0.88
55	32	45.965	79	55.603	10.0					0.03	0.08		2.23
56	32	45.965	79	55.603	9.0					0.02	0.03		0.84
57	32	45.965	79	55.603					0.01	0.05	0.03		1.61
58	32	45.965	79	55.603					0.01	0.02	0.04		1.81
59	32	45.965	79	55.603	8.0					0.02	0.02		1.48
60	32	45.965	79	55.603	10.0					0.00	0.03		1.54
61	32	45.965	79	55.603	12.0					0.02	0.02		3.10
62	32	45.965	79	55.603	15.0					0.03	0.02		4.76
63	32	45.965	79	55.603	18.0					0.25	0.04		3.19
64	32	45.965	79	55.603	15.0					0.17	0.02		4.77
65	32	45.965	79	55.603	11.0				0.01	0.08	0.03		8.30
66	32	45.965	79	55.603	16.0		0.01	0.02	0.17	0.79	0.19		23.52
67	32	45.965	79	55.603	7.0			0.01		0.02	0.03		2.53
68	32	45.965	79	55.603	13.0				0.01				2.20
69	32	45.965	79	55.603	10.0			0.02	0.02	0.12	0.04		4.10
70	32	45.965	79	55.603	16.0					0.03	0.01		2.70
71	32	45.965	79	55.603	14.0			0.01		0.03	0.03		2.39
72	32	45.965	79	55.603	20.0			0.02		0.03	0.02		4.99

Appendix C.	Ashley River	Organic Analyses	(ppm).
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Station	La	atitude	Lo	ngitude	Depth	4-Methylphenol	Naphthalene	Pentachlorophenol	Anthracene	Carbazole	Pyrene	p,p'DDE	Phthalate
	Deg	g. Min.	De	eg. Min.	ft	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
70	22	45.065	70	55 (02	10.0					0.02	0.02		1.45
73	32	45.965	79	55.603	18.0					0.02	0.02		1.45
/4	32	45.965	79 70	55.603	19.2					0.04	0.02		3.69
75	32	45.965	79	55.603	9.1					0.03	0.01		2.56
76	32	45.965	79	55.603	15.3					0.09	0.02		1.42
77	32	45.965	79	55.603	28.0			0.10	0.10	0.06	0.02		3.11
78	32	45.965	79	55.603	28.2			0.18	0.12	0.83	0.13	0.02	43.35
79	32	45.965	79	55.603	26.0	0.00		0.02		0.05	0.02		4.63
80	32	45.965	79	55.603	20.0	0.02		0.02		0.09	0.02		12.08
81	32	45.965	79	55.603	19.1					0.19	0.19		3.74
82	32	45.965	79	55.603	18.2					0.04	0.02		3.43
83	32	45.965	79	55.603	19.8					0.03	0.02		2.82
84	32	45.965	79	55.603	19.7				0.03	0.19	0.03		5.37
85	32	45.965	79	55.603	18.8					0.03	0.02		3.92
86	32	45.965	79	55.603	17.5					0.05	0.01		3.52
87	32	45.965	79	55.603	16.7					0.78	0.01		2.33
88	32	45.965	79	55.603	6.3					0.07	0.04		1.84
89	32	45.965	79	55.603	8.3			0.01	0.01	0.03	0.07		1.04
90	32	45.965	79	55.603	6.6					0.02	0.04		1.84
91	32	45 965	79	55 603	94					0.03	0.05		4 99
92	32	45 965	79	55 603	3.8				0.03	0.03	0.04		5 43
93	32	45 965	79	55 603	6.4			0.01	0.01	0.04	0.08		1 78
94	32	45 965	79	55 603	0.1			0.01		0.03	0.09		2.07
94	32	45 065	70	55 603	10.2			0.01		0.02	0.22		2.07
95	22	45.905	70	55.602	10.2					0.01	0.07		7.05 7.69
90	32 22	45.905	79	55.602	10.9				0.02	0.03	0.08		2.08
97	32 22	45.905	79	55.005	12.9				0.02	0.03	0.00		5.42 2.51
98	32 22	45.905	79	55.005	13.8					0.01	0.04		2.51
99	32	45.965	79	55.603	14.0					0.02	0.04		0.07
100	32	45.965	79	55.603	14.8				0.01	0.20	0.03		3.91
101	32	45.965	79	55.603	21.8				0.01	0.07	0.09		1.91
102	32	45.965	79	55.603	15.5				0.01	0.01	0.07		2.01
103	32	45.965	79	55.603	22.2			0.04	0.01	0.03	0.07		0.10
104	32	45.965	79	55.603	26.6			0.01	0.09	0.10	0.43		0.59
105	32	45.965	79	55.603	28.5				0.19	0.12	0.10		0.10
106	32	45.965	79	55.603	22.2					0.02	0.04		0.05
107	32	45.965	79	55.603	21.6			0.01	0.01	0.02	0.06		0.06
108	32	45.965	79	55.603	23.2	0.07	0.12	0.36	0.13	0.99	0.91	0.01	3.38
109	32	45.965	79	55.603	26.2					0.03	0.03		0.15

Pentachloropheno 4-Methylphenol Naphthalene Anthracene Carbazole p,p'DDE Phthalate Pyrene Station Latitude Longitude Depth (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) Deg. Min. Deg. Min. ft 0.03 0.05 110 32 45.965 79 55.603 15.1 0.07 0.03 0.06 111 32 45.965 79 55.603 10.3 0.09 0.72 0.07 112 32 45.965 79 55.603 8.9 0.13 0.23 0.03 113 32 45.965 79 55.603 12.1 0.07 114 32 45.965 79 55.603 18.7 0.15 0.02 0.09 0.08 0.02 115 32 45.965 79 55.603 17.8 0.10 0.01 0.01 0.42 0.19 0.01 116 32 45.965 79 55.603 14.1 1.12 0.03 0.01 117 32 45.965 79 0.09 55.603 14.1 0.79 118 32 45.965 79 55.603 16.1 0.57 0.07 0.01 119 32 45.965 79 55.603 10.8 0.06 0.05 120 32 45.965 79 55.603 5.2 0.12 0.02 0.03 55.603 121 32 45.965 79 24.1 0.13 0.02 0.01 122 32 45.965 79 55.603 24.2 0.08 0.03 0.02 123 32 45.965 79 55.603 24.1 0.08 0.03 0.01 124 32 45.965 79 55.603 24.0 0.08 0.02 0.01 125 32 45.965 79 55.603 11.1 0.04 126 32 45.965 79 55.603 2.4 0.05 0.02 127 32 45.965 79 55.603 26.2 0.17 0.02 0.02 128 32 45.965 79 55.603 8.3 0.12 0.00 0.02 129 32 45.965 79 55.603 4.5 0.18 0.06 130 32 45.965 79 55.603 26.2 0.02 0.14 0.69 0.01 131 32 45.965 79 55.603 7.9 0.28 4.4 0.03 0.02 2.03 132 32 45.965 79 55.603 0.66 0.58 133 32 45.965 79 4.055.603 0.21 0.02 0.10 134 32 45.965 79 55.603 0.12 4.4 0.04 0.01 135 32 45.965 79 55.603 4.1 0.09 136 32 45.965 79 55.603 3.4 0.03 0.01 0.10 0.02 0.01 137 32 45.965 79 55.603 3.3 0.09 0.02 0.01 138 32 45.965 79 55.603 5.0 0.10 0.01 0.01 139 32 45.965 79 55.603 5.0 0.10 0.04 0.11 0.01 140 32 45.965 79 5.0 0.13 55.603 0.02 0.01 141 32 45.965 79 55.603 5.0 0.07 0.03 142 32 45.965 79 55.603 5.0 0.08 0.02 143 32 45.965 79 55.603 5.0 0.25 0.04 144 32 45.965 79 0.19 55.603 28.1 145 32 45.965 79 19.3 55.603 0.01 0.09 0.02 146 32 45.965 79 55.603 23.2 0.09

Appendix C. Ashley River Organic Analyses (ppm).

Appendix C. Ashley River Organic Analyses (ppm).

Station	T	atitude	Lor	ngitude	Depth	4-Methylphenol	Naphthalene	Pentachloropheno	Anthracene	Carbazole	Pyrene	p,p'DDE	Phthalate
Station	De	eg. Min.	De	g. Min.	ft	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
147	32	45.965	79	55.603	21.2				0.01	0.03	0.03		0.11
148	32	45.965	79	55.603	5.0					0.03	0.01		0.08
149	32	45.965	79	55.603	5.0				0.01	0.03	0.03		0.09

### APPENDIX D

#### ASHLEY RIVER ELEMENTAL CONCENTRATION MAPS



Figure D-1. Silicon concentrations (wt%) for the Ashley River.



Figure D-2. Calcium concentrations (wt%) for the Ashley River.



Figure D-3. Potassium concentrations (wt%) for the Ashley River.



Figure D-4. Nickel concentrations (ppm) for the Ashley River.



Figure D-5. Zinc concentrations (ppm) for the Ashley River.



Figure D-6. Strontium concentrations (ppm) for the Ashley River



Figure D-7. Zirconium concentrations (ppm) for the Ashley River



Figure D-7. Barium concentrations (ppm) for the Ashley River.



Figure D-8. Lead concentrations (ppm) for the Ashley River.



Figure D-9. Arsenic concentrations (ppm) for the Ashley River.

### APPENDIX E

## CHEMICAL AND PHYSICAL PARAMETERS

#### IN THE SEDIMENT-WATER INTERFACE
Station	Lati	tude	Long	itude	Depth	Depth	Temp	pН	Salinity	DO	Redox
	Deg.	Min.	Deg.	Min.	(ft)	(Tidal)	°C		(ppt)	mg/l	mV
1	32	45.965	79	55.603	9.7	7.0	23.9	7.7	28.5	79.7	5.7
2	32	45.965	79	55.603	12.1	9.5	24.8	7.7	28.5	36.9	2.6
3	32	45.965	79	55.603	20.8	18.3	24.1	7.8	28.5	79.6	5.6
4	32	45.965	79	55.603	21.8	19.3		7.8	27.9	79.0	5.6
5	32	45.965	79	55.603	22.1	20.2	24.1	7.8	26.8	82.5	5.9
6	32	45.965	79	55.603	20.8	19.3	24.3	7.7	26.0	81.9	5.9
7	32	45.965	79	55.603	22.2	20.8	24.4	7.7	26.2	81.3	5.8
8	32	45.965	79	55.603	22.3	20.9	24.3	7.7	26.2	82.5	5.9
9	32	45.965	79	55.603	25.2	23.9	24.4	7.6	27.3	79.5	5.6
10	32	45.965	79	55.603	27.3	26.1	24.5	7.6	27.6	79.4	5.6
11	32	45.965	79	55.603	24.5	23.3	24.3	7.6	26.1	82.2	5.9
12	32	45.965	79	55.603	23.6	22.5	24.3	7.6	26.1	81.6	5.8
13	32	45.965	79	55.603	29.1	28.1	24.3	7.6	26.1	80.1	5.7
14	32	45.965	79	55.603	32.2	31.2	24.4	7.6	26.2	78.7	5.6
15	32	45.965	79	55.603	25.3	24.4	24.4	7.6	26.2	77.0	5.5
16	32	45.965	79	55.603	24.2	23.4	24.4	7.6	25.7	90.5	6.5
17	32	45.965	79	55.603	20.2	19.4	24.5	7.5	25.8	40.6	2.9
18	32	45.965	79	55.603	14.8	14.1	24.3	7.5	25.9	74.5	5.3
19	32	45.965	79	55.603	18.5	17.8	24.4	7.5	26.1	76.1	5.4
20	32	45.965	79	55.603	21.8	21.1	24.4	7.5	26.0	76.0	5.4
21	32	45.965	79	55.603	9.0	8.3	24.6	7.5	25.9	76.7	5.5
22	32	45.965	79	55.603	8.7	8.0	24.6	7.5	26.3	79.5	5.7
23	32	45.965	79	55.603	10.1	9.4	24.5	7.5	25.9	78.6	5.6
24	32	45.965	79	55.603	11.8	11.2	24.5	7.5	25.3	78.5	5.6
25	32	45.965	79	55.603	11.8	11.2	24.5	7.5	14.1	78.1	6.0
26	32	45.965	79	55.603	13.1	12.5	24.5	7.5	25.2	78.8	5.6
27	32	45.965	79	55.603	14.5	13.9	24.5	7.5	25.4	80.1	5.7
28	32	45.965	79	55.603	16.7	16.1	24.5	7.5	25.3	79.8	5.7
29	32	45.965	79	55.603	17.0	16.4	24.6	7.5	25.6	72.0	5.1
30	32	45.965	79	55.603	19.8	19.2	24.6	7.5	25.5	76.6	5.5
31	32	45.965	79	55.603	23.3	22.7	24.6	7.5	25.8	79.2	5.6
32	32	45.965	79	55.603	25.6	25.0	24.5	7.5	25.5	78.1	5.6
33	32	45.965	79	55.603	21.1	20.5	24.5	7.5	25.3	77.2	5.5
34	32	45.965	79	55.603	19.2	18.6	24.6	7.5	25.0	77.3	5.5
35	32	45.965	79	55.603	25.6	25.0	24.5	7.5	25.1	78.2	5.6
36	32	45.965	79	55.603	25.7	25.1	24.6	7.5	24.7	76.5	5.5
37	32	45.965	79	55.603	17.7	17.1	24.6	7.5	24.4	78.4	5.6
38	32	45.965	79	55.603	13.8	13.2	24.5	7.5	20.6	76.4	5.6
39	32	45.965	79	55.603	9.6	8.9	24.6	7.4	23.9	72.0	5.2
40	32	45.965	79	55.603	9.3	8.6	24.8	7.4	22.5	3.7	

Appendix E. Chemical and physical parameters in the sediment-water interface.

Station	Lati	tude	Long	itude	Depth	Depth	Temp	pН	Salinity	DO	Redox
	Deg.	Min.	Deg.	Min.	(ft)	(Tidal)	°C		(ppt)	mg/l	mV
41	32	45.965	79	55.603	10.8	10.0	25.0	7.4	11.9	31.6	2.4
42	32	45.965	79	55.603	9.5	8.6	25.0	7.4	10.8	49.5	3.8
43	32	45.965	79	55.603	19.5	18.6	24.8	7.4	8.0	60.4	4.8
44	32	45.965	79	55.603	4.0	3.1	25.6	7.5	24.5	88.8	6.3
45	32	45.965	79	55.603	3.0	2.1	26.2	7.2	20.6	1.7	0.1
46	32	45.965	79	55.603	3.0	0.9	25.4	7.5	22.9	35.3	2.5
47	32	45.965	79	55.603	3.0	-0.2	25.6	7.4	16.7	33.5	2.5
48	32	45.965	79	55.603	2.9	0.8	25.5	7.4	8.8	48.0	3.7
49	32	45.965	79	55.603	5.0	2.9	25.8	7.3	8.7	2.0	0.2
50	32	45.965	79	55.603	4.0	1.7	25.8	7.3	8.6	45.3	3.5
51	32	45.965	79	55.603	4.0	1.3	29.2	7.3	8.1	1.3	0.1
52	32	45.965	79	55.603	4.0	1.0	25.7	7.3	24.2	5.0	0.4
53	32	45.965	79	55.603	8.0	4.8	25.7	7.4	24.9	7.2	0.5
54	32	45.965	79	55.603	9.0	5.8	24.9	7.3	25.3	21.5	1.5
55	32	45.965	79	55.603	10.0	6.7	24.7	7.5	25.8	75.0	5.3
56	32	45.965	79	55.603	9.0	5.6	24.8	7.5	25.9	74.5	5.3
57	32	45.965	79	55.603			25.1	7.4	25.4	61.3	4.3
58	32	45.965	79	55.603			24.9	7.5	25.8	67.3	4.8
59	32	45.965	79	55.603	8.0	4.4	24.7	7.5	25.9	75.7	5.4
60	32	45.965	79	55.603	10.0	6.3	24.7	7.5	25.7	73.5	5.2
61	32	45.965	79	55.603	12.0	8.3	24.7	7.6	25.7	76.3	5.4
62	32	45.965	79	55.603	15.0	11.3	24.8	7.6	26.2	76.7	5.4
63	32	45.965	79	55.603	18.0	14.2	24.8	7.6	26.0	79.1	5.6
64	32	45.965	79	55.603	15.0	11.1	25.0	7.6	17.5	74.6	5.5
65	32	45.965	79	55.603	11.0	6.8	24.9	7.6	26.6	89.4	6.3
66	32	45.965	79	55.603	16.0	11.6	24.8	7.7	26.6	88.0	6.2
67	32	45.965	79	55.603	7.0	2.6	24.9	7.7	26.6	86.9	6.1
68	32	45.965	79	55.603	13.0	8.5	24.8	7.7	26.4	86.3	6.1
69	32	45.965	79	55.603	10.0	5.5	25.0	7.7	26.3	81.2	5.7
70	32	45.965	79	55.603	16.0	11.5	24.9	7.8	26.4	85.4	6.0
71	32	45.965	79	55.603	14.0	9.4	24.7	7.8	26.6	86.4	6.1
72	32	45.965	79	55.603	20.0	15.4	24.7	7.8	26.5	82.8	5.9
73	32	45.965	79	55.603	18.0	14.3	24.7	7.7	27.4	92.9	6.4
74	32	45.965	79	55.603	19.2	15.6	24.9	7.7	25.3	73.9	5.2
75	32	45.965	79	55.603	9.1	5.8	24.6	7.7	26.7	90.4	6.4
76	32	45.965	79	55.603	15.3	12.0	24.5	7.7	26.2	92.0	6.5
77	32	45.965	79	55.603	28.0	24.8	24.5	7.7	17.1	89.6	6.7
78	32	45.965	79	55.603	28.2	25.0	24.5	7.8	27.2	42.4	3.0
79	32	45.965	79	55.603	26.0	22.8	24.5	7.8	26.9	92.2	6.5
80	32	45.965	79	55.603	20.0	16.8	24.5	7.8	26.2	78.3	5.6
81	32	45.965	79	55.603	19.1	16.0	24.4	7.8	26.8	93.1	6.6
82	32	45.965	79	55.603	18.2	15.2	24.4	7.8	27.2	92.3	6.5

Appendix E. Chemical and physical parameters in the sediment-water interface	ce.
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Station	Lati	tude	Long	itude	Depth	Depth	Temp	pН	Salinity	DO	Redox
	Deg.	Min.	Deg.	Min.	(ft)	(Tidal)	°C		(ppt)	mg/l	mV
83	32	45.965	79	55.603	19.8	17.1	24.4	7.8	26.8	104.8	7.4
84	32	45.965	79	55.603	19.7	17.0	24.4	7.8	26.8	89.0	6.3
85	32	45.965	79	55.603	18.8	16.2	24.4	7.8	27.5	87.9	6.2
86	32	45.965	79	55.603	17.5	15.0	24.3	7.8	27.4	91.0	6.5
87	32	45.965	79	55.603	16.7	14.3	24.3	7.8	27.7	93.0	6.6
88	32	45.965	79	55.603	6.3	4.5	25.3	7.8	27.4	92.0	6.4
89	32	45.965	79	55.603	8.3	6.6	24.9	7.6	26.5	71.5	5.0
90	32	45.965	79	55.603	6.6	5.0	25.0	7.7	27.2	90.1	6.3
91	32	45.965	79	55.603	9.4	7.9	24.9	7.6	27.1	85.1	6.0
92	32	45.965	79	55.603	3.8	2.3	25.1	7.6	25.1	25.1	2.1
93	32	45.965	79	55.603	6.4	4.9	25.2	7.6	25.9	64.0	3.0
94	32	45.965	79	55.603			25.2	7.6	25.9	64.0	4.5
95	32	45.965	79	55.603	10.2	8.9					
96	32	45.965	79	55.603	10.9	9.6	25.2	7.6	26.3	88.2	6.2
97	32	45.965	79	55.603	7.9	6.7	25.3	7.6	25.8	84.1	5.9
98	32	45.965	79	55.603	13.8	12.6	25.1	7.6	26.2	90.4	6.4
99	32	45.965	79	55.603	14.6	13.5	25.2	7.6	25.8	88.7	6.2
100	32	45.965	79	55.603	14.8	13.7	25.3	7.6	25.5	85.4	6.0
101	32	45.965	79	55.603	21.8	20.7	25.1	7.6	26.0	86.4	6.1
102	32	45.965	79	55.603	15.5	14.3	25.1	7.6	25.6	92.6	6.5
103	32	45.965	79	55.603	22.2	21.1	25.1	7.6	25.5	91.9	6.5
104	32	45.965	79	55.603	26.6	25.5	25.2	7.6	25.6	94.1	6.6
105	32	45.965	79	55.603	28.5	27.5	25.1	7.6	25.4	94.2	6.7
106	32	45.965	79	55.603	22.2	21.3	25.2	7.6	25.3	94.6	6.7
107	32	45.965	79	55.603	21.6	20.7	25.3	7.6	25.2	93.3	6.6
108	32	45.965	79	55.603	23.2	22.3	25.3	7.5	24.9	83.4	5.9
109	32	45.965	79	55.603	26.2	25.4	25.2	7.6	25.1	92.7	6.5
110	32	45.965	79	55.603	15.1	14.4	25.6	7.6	25.0	91.0	6.4
111	32	45.965	79	55.603	10.3	9.6	25.5	7.5	25.0	84.4	5.9
112	32	45.965	79	55.603	8.9	8.2	25.6	7.5	24.6	71.7	5.1
113	32	45.965	79	55.603	12.1	11.4	25.4	7.6	24.5	83.6	5.9
114	32	45.965	79	55.603	18.7	18.1	25.4	7.6	24.6	89.8	6.4
115	32	45.965	79	55.603	17.8	17.2	25.5	7.6	24.0	86.2	6.1
116	32	45.965	79	55.603	14.1	13.5	25.9	7.5	24.0	86.5	6.1
117	32	45.965	79	55.603	14.1	13.4	25.1	7.6	27.2	87.3	6.1
118	32	45.965	79	55.603	16.1	15.4	25.1	7.6	27.1	91.5	6.4
119	32	45.965	79	55.603	10.8	10.1	26.2	7.7	26.8	57.1	3.9
120	32	45.965	79	55.603	5.2	4.4	25.7	7.8	26.7	105.3	7.3
121	32	45.965	79	55.603	24.1	23.2	25.5	7.7	26.1	96.3	0.7
122	32	45.965	79	55.603	24.2	23.3	25.3	7.7	27.0	89.6	6.2
123	32	45.965	79	55.603	24.1	23.2	25.2	7.6	27.0	81.8	5.7
124	32	45.965	79	55.603	24.0	23.1	26.0	7.7	26.4	99.6	6.9

Appendix E. Chemical and physical parameters in the sediment-water interfac	ce.
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Station	Lati	tude	Long	itude	Depth	Depth	Temp	рН	Salinity	DO	Redox
	Deg.	Min.	Deg.	Min.	(ft)	(Tidal)	°C		(ppt)	mg/l	mV
125	32	45.965	79	55.603	11.1	9.7	25.4	7.6	26.5	46.5	3.3
126	32	45.965	79	55.603	2.4	1.0	25.6	7.7	26.4	101.5	7.1
127	32	45.965	79	55.603	26.2	24.7	25.7	7.7	23.8	100.0	7.1
128	32	45.965	79	55.603	8.3	6.3	25.2	7.8	26.1	90.6	6.4
129	32	45.965	79	55.603	4.5	2.2	25.5	7.8	24.6	101.4	7.2
130	32	45.965	79	55.603	26.2	23.9	26.1	7.8	25.0	104.5	7.3
131	32	45.965	79	55.603	7.9	3.0	24.8	7.8	30.2	71.7	5.0
132	32	45.965	79	55.603	4.4	-0.4	24.7	7.8	28.9	71.1	5.0
133	32	45.965	79	55.603	4.0	-0.8	24.7	7.8	28.8	76.2	5.3
134	32	45.965	79	55.603	4.4	-0.4	24.8	7.8	28.6	73.8	5.2
135	32	45.965	79	55.603	4.1	-0.6	24.9	7.8	28.0	72.5	5.1
136	32	45.965	79	55.603	3.4	-1.3	24.7	7.8	27.6	76.4	5.4
137	32	45.965	79	55.603	3.3	-1.4	24.8	7.8	26.9	73.5	5.2
138	32	45.965	79	55.603	5.0	0.3	25.0	7.8	27.3	65.6	4.6
139	32	45.965	79	55.603	5.0	0.4	25.0	7.8	27.2	73.6	5.2
140	32	45.965	79	55.603	5.0	0.5	25.0	7.7	26.8	62.7	4.4
141	32	45.965	79	55.603	5.0	0.5	24.9	7.7	27.3	66.9	4.7
142	32	45.965	79	55.603	5.0	0.5	24.8	7.7	27.3	73.4	5.2
143	32	45.965	79	55.603	5.0	0.6	24.9	7.8	26.9	77.4	5.4
144	32	45.965	79	55.603	28.1	23.9	25.9	7.8	25.9	66.7	4.6
145	32	45.965	79	55.603	19.3	15.2	24.8	7.8	28.5	79.4	5.5
146	32	45.965	79	55.603	23.2	19.2	24.8	7.8	27.9	49.7	3.5
147	32	45.965	79	55.603	21.2	17.3	25.0	7.8	27.6	71.7	5.0
148	32	45.965	79	55.603	5.0	1.2	26.0	7.8	16.5	95.8	7.0
149	32	45.965	79	55.603	5.0	1.3	25.1	7.7	26.3	47.3	3.3

Appendix E. Chemical and physica	l parameters in the sediment-water in	nterface.
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