

## **4. BULK SEDIMENT TESTING PROGRAM**

### **4.1 MATERIALS AND METHODS**

#### **4.1.1 Sample Receipt and Homogenization**

The sediment samples were transported from Charleston, South Carolina to EA's laboratory facilities in Sparks, Maryland via refrigeration truck at 4°C, and arrived at EA on 15 July 1998. Upon receipt, the cores were visually inspected, and the labeled core sleeves were compared against the COC record.

The sediments from each station were extracted from the core sleeves and were composited and homogenized in pre-cleaned 55-gallon fiberglass containers. For each station, the core section containing the surficial sediments was composited and homogenized first. Following the surficial sediments, successive core sections from a given station were composited in the 55-gallon container. Each sample was homogenized until the sediment was thoroughly mixed (including dense clay portions) and was of uniform consistency. When not actively being processed, the samples were stored in a secured walk-in cooler, in the dark at 4°C. Upon completion of compositing and homogenization of each station, subsamples of sediment were removed for bulk chemistry analyses, were placed into pre-cleaned glass jars using stainless steel spoons, and were labeled. The remainder of the sediment was used for biological testing.

A second COC form was completed for the homogenized sediment, with the sample homogenization time recorded as the initiation of the sample holding time. The bulk sediment samples were hand-delivered to the analytical laboratory, where the samples were compared against the COC form. The samples were logged into the analytical chemistry laboratory and given a unique accession number. Samples were stored in walk-in coolers (cooled to 4°C) following receipt and prior to analysis. A copy of the bulk sediment COC is provided in Attachment 4-1.

Rinsate samples that were collected in the field were sent directly to EA's analytical laboratory via overnight express. Upon receipt at the laboratory, the samples were checked against the COC, were logged, and were given a unique accession number. Samples were stored in walk-in coolers (cooled to 4°C) following receipt and prior to analysis. Copies of the COC forms for the rinsate samples are provided in Attachment 4-2.

#### **4.1.2 Analytical Methods and Detection Limits**

Bulk sediments and rinsate samples were analyzed for the suite of analytes approved by U.S. EPA Region IV and the USACE—Charleston District and presented in the SAPP (1998) and approved EA Work Plan (EA 1998). The project-specific analytical methods for sediment and rinsate analyses are provided in Table 4-1. Detection limits for sediment and rinsate analyses are provided in Tables 4-2 and 4-3, respectively. EA's analytical laboratory conducted all tests with the exception of tributyltin and dioxins/furans. Data/Analysis Technologies, Inc. (DAT), located in Dublin, Ohio, conducted the tributyltin analyses, and Ionics International, Inc., located in

Houston, Texas, conducted the dioxin and furan testing. EA's ecotoxicology laboratory performed the grain size analysis (see Table 3-12).

### **4.1.3 Data Analysis**

Concentrations of analytes detected in project sediments were compared to concentrations in reference sediment, and percent difference was calculated for cases where sediment concentrations at individual stations exceeded the reference values. If an analyte was not detected in the reference sediment but was detected in the project sediment, the detection limit was used as the reference concentration for the percent difference calculations. For trace metals and total organic carbon (TOC), mean concentrations ( $\pm$  SE) of detected analytes were calculated for each project reach (Charleston Naval Base, Cooper River Berthing, Wando River Berthing, and Wando River Realignment) and were presented graphically against the reference value. In cases where trace metals were not detected, the detection limit was used as the concentration for calculating the mean.

## **4.2 BULK SEDIMENT RESULTS**

Results of the bulk sediment chemistry analysis are presented in the following sub-sections. Sample weights were adjusted for percent moisture prior to extraction in order to achieve the required detection limits. Analytical results are reported on a dry weight basis. Data qualifiers for the organic data are provided in Table 4-4. Inorganic data qualifiers are provided in Table 4-5. Copies of the final raw data sheets are provided in Attachment 4-1. Analytical narratives, which include a synopsis of laboratory QA/QC results for Laboratory Control Samples and Matrix Spike/Matrix Spike Duplicate Recoveries, are provided in Attachment 4-1. Certificates of Analysis for glassware are provided in Attachment 4-3. EA's analytical laboratory will retain and archive the results of these analyses for seven years from the date of issuance of the final results.

### **4.2.1 Metals/Others**

Results of the trace metals analyses are provided in Table 4-6. Seven of the 13 metals exceeded the reference concentration at all 11 project stations. Percent difference for metals concentrations exceeding the reference value are provided in Table 4-7. Silver and tributyltin were not detected in any sample. Cadmium was detected only in the reference sample, and mercury was detected in sediment from two stations in the Charleston Naval Base berths, with only CNB-02 exceeding the reference value. Mean concentrations ( $\pm$  SE) at each sampling reach for nine of the trace metals are provided in Figure 4-1. The mean concentrations of antimony, arsenic, chromium, copper, lead, nickel, selenium, and zinc were highest in sediments from the Charleston Naval Base berths (see Figure 4-1).

Analytical narratives (Attachment 4-1) indicate that fluoride determinations were influenced by matrix interferences. Fluoride was not detected in the Charleston Naval Base sediments, and fluoride ion spiked into samples CNB-01 and CNB-02 was not recovered. Fluoride was detected at concentrations substantially higher than the reference concentration in sediments from the

other three project reaches (Table 4-7). The reported results for the samples may be false positives due to matrix interference.

In the 11 project stations, the average concentration of Total Organic Carbon (TOC) was 2.8 percent. Overall, TOC was highest in samples from the Charleston Naval Base, ranging from 3.34 percent to 6.75 percent. TOC in the reference sediment was 0.56 percent. Graphical comparisons of mean TOC concentrations for the four project reaches and the reference site are provided in Figure 4-2.

Results of the grain size analysis are provided in Table 3-12. Graphical comparisons of the mean grain size distribution for the project reaches and the reference site are provided in Figure 4-3. The composition of sediments from the Charleston Naval Base berths and the Wando River Berthing area were similar to each other, with higher proportions of silt/clay than sand. The composition of sediments from the Cooper River Berthing Area and the Wando River Realignment Area were similar to each other, with higher proportions of sand than silt/clay. The physical characteristics of the reference sediment were dissimilar to the project reach sediments. The reference sediment was primarily comprised of sand (97 percent).

#### **4.2.2 Pesticides**

Results of the pesticide analyses are provided in Table 4-8. In the 11 project samples, pesticides were detected in 4 of 121 cases. Only two of the 11 target pesticides were detected in project sediments (DDT and heptachlor), and no pesticides were detected in the reference sediment. In the Charleston Naval Base berths, DDT and heptachlor exceeded the detection limit by 170 percent (CNB-02) and 144 percent (CNB-01), respectively (Table 4-9). Low concentrations of heptachlor were also detected at both Wando River Berthing Area stations.

#### **4.2.3 PCBs**

Results of the PCB analysis are provided in Table 4-10. In the 11 project samples, PCBs were detected in 7 of 231 cases. Only two of the twenty-one congeners tested were detected in the samples. Only one congener (IUPAC-18) exceeded the reference value in one sample (WDR-02), and the detected concentration was only 4.8 percent higher than the reference value (Table 4-11). In addition, congener IUPAC-8 was reported in two of the Wando Reach Realignment stations (WDR-01 and WDR-02), but neither sample exceeded the concentration in the reference sediment. Analytical narratives (Attachment 4-1) indicated that due to the nature of the sample matrix, the chromatographic patterns, and the low reporting limits (MDLs), there is the possibility of false positive results in samples with reported concentrations of congeners.

#### **4.2.4 Polynuclear Aromatic Hydrocarbons (PAHs)**

Results of the PAHs analyses are provided in Table 4-12. In the 11 project samples, PAHs exceeded the reference value in 39 of 198 cases. PAHs were not detected in the reference sediment. Percent difference for PAH concentrations exceeding the reference values are provided in Table 4-13. Twelve of the 18 target PAHs were detected in the sediment samples. The highest incidence of detected PAHs was reported in the Charleston Naval Base samples. Ten of the 18 target PAHs were detected in the CNB samples, eight of the target PAHs were

detected in the Cooper River Berthing Area, two of the target PAHs were detected in the Wando River Berthing Area, and four of the target PAHs were detected in the Wando Reach Realignment sediments. Benzo(b)fluoranthene was the most commonly detected PAH (8 locations), followed by benzo(a)anthracene (5 locations).

#### **4.2.5 Dioxins and Furans**

Results of the dioxin and furan analyses and associated TEF and TEQ values are provided in Table 4-14. In the 11 project samples, dioxin congeners were detected in 23 of 77 cases. Two dioxin congeners, 1,2,3,4,6,7,8-HpCDD and OCDD, were detected in all project samples, including the reference site sediment. All detected concentrations in the project reaches, with the exception of station CPB-03, exceeded concentrations reported for the reference site. Percent difference for dioxin concentrations exceeding the reference values are provided in Table 4-15. Concentrations of both congeners were highest at stations in the Wando River Berthing Area. The detected dioxin congeners have low TEF potency, and TEQ values were <1 part per trillion in all but one sample (WDB-02). Furan congeners were not detected in any of the samples.

### **4.3 RINSATE BLANK RESULTS**

Rinsate blanks were collected to ensure that sampling equipment (the coring unit) and sample holding containers (the polypropylene buckets for the reference sediment) did not contaminate the samples. Results of the rinsate analysis are presented in the following sub-sections. Analytical results are reported as ug/L or ng/L. Copies of the final raw data sheets are provided in Attachment 4-2. Analytical narratives, which include a synopsis of laboratory QA/QC results for Laboratory Control Samples and Matrix Spike/Matrix Spike Duplicate Recoveries, are provided in Attachment 4-2. Certificates of Analysis for glassware are provided in Attachment 4-3. EA's analytical laboratory will retain and archive the results of these analyses for seven years from the date of issuance of the final results.

#### **4.3.1 Metals/Others**

Results of trace metals in the equipment rinsates are provided in Table 4-16. Seven of the 15 analytes were detected in the rinsate samples, but the majority was detected at concentrations below the contract required detection limit.

#### **4.3.2 Pesticides**

Results of the pesticide analyses for the equipment rinsates are provided in Table 4-17. None of the target pesticides were detected in the rinsate samples.

#### **4.3.3 PCBs**

Results of the PCB analyses for the equipment rinsates are provided in Table 4-18. Low concentrations of three congeners, IUPAC-28, IUPAC-44 and IUPAC-52, were detected in the rinsate samples. IUPAC-28 was detected in the method blank at a concentration of 0.049 ug/L. This laboratory contamination may have caused false positive results for IUPAC-28 in three of

the four rinsate samples. None of the congeners detected in the rinsate samples were detected in the sediment samples.

#### **4.3.4 Polynuclear Aromatic Hydrocarbons (PAHs)**

Results of the PAH analyses for the equipment rinsates are provided in Table 4-19. None of the target PAHs was detected in the rinsate samples.

#### **4.3.5 Dioxins and Furans**

Results of the dioxin and furan analyses for the equipment rinsates are provided in Table 4-20. The dioxin congener OCDD was detected in the rinsates from the three project reaches, but the concentration was between the calibrated range and the contract required detection limit. None of the furan congeners were detected in the rinsate blanks.

### **4.4 DISCUSSION**

A summary of the analytes exceeding the reference sediment concentrations is provided in Table 4-21. Overall, 18.3 percent of the sample/contaminant possibilities exceeded the reference sediment concentrations. The majority of exceedences were for metals (59 percent of total), followed by PAHs (24 percent of total) and dioxins (13.7 percent of total). The greatest number of exceedences occurred in the Charleston Naval Base sediments, totaling 59 of 240 cases (24.6 percent). Percent exceedence for the other three reaches was similar: 16.3 percent, 16.9 percent, and 15.0 percent for the Cooper River Berthing, Wando River Berthing, and Wando River Realignment areas, respectively.

Grain size analysis revealed that the physical characteristics of the reference sediment were different than physical characteristics of the project reach sediments (Figure 4-3). General trends for trace metal concentrations (Figure 4-1) and TOC (Figure 4-2) among the project reaches parallel the distribution of silt in the project reach sediments. Exceedences for both metals and PAHs may be attributed to the differences in the physical characteristics of the project sediments compared to the reference sediments. Metals and PAHs tend to bind to silt and organic particulates. Because the reference sediment was primarily sand, low concentrations of trace metals and PAHs would be expected and were observed in this study.

Metals and PAHs had the highest number of total exceedences in the Charleston Naval Base berths. Concentrations of metals and PAHs in the Charleston Naval Base berths may be directly related to the high TOC concentrations reported for the samples. The average concentration of TOC in the Charleston Naval Base reach was approximately 870 percent higher than the concentration at the reference site and was at least 200 percent greater than average TOC concentrations reported in the other three project reaches (refer to Figure 4-2).