



## Bench Testing Report – Analytical Variability as a Function of Sediment Sample Extraction Mass

*by Damarys A. Acevedo and Trudy J. Estes*

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**PURPOSE:** The purpose of this research was to evaluate the reduction in analytical variability that could be achieved by increasing the subsample mass of sediment samples extracted for chemical or physical analysis. The hypothesis was that for particulate associated contaminants the probability of capturing a contaminated particle increases as subsample mass increases. A bench scale testing plan was designed to evaluate the variability associated with different extraction subsample masses as reflected by the variance and the resulting confidence interval (CI) around the mean. If successful, the CI of the mean would be reduced with a smaller number of subsamples than would otherwise be required. This could potentially result in significant cost savings while also providing higher confidence in the characterization of the material and beneficial use suitability determinations based on characterization results.

**BACKGROUND:** Sediment characterization is a challenging problem, given the heterogeneous nature of the solid constituents in sediments and the varying degree of affinity each has for anthropogenic contaminants. Furthermore, the properties of a large volume of sediment are extrapolated from small samples, which are further sub-sampled for chemical analysis using as little as 0.5 g for metals and 15.0 g for organics. As the heterogeneity of the sediment and of the contaminant distribution within the sediment increases, so does the potential for error arising from the sub-sampling procedure.

Typically, navigation dredged material contains a variety of anthropogenic contaminants from multiple sources, including navigation vessels, industrial and sewer outfalls, non-point source runoff and atmospheric deposition. Polychlorinated biphenyls (PCBs), poly-nuclear aromatic hydrocarbons (PAHs), herbicides, pesticides, and heavy metals are commonly found at varying concentrations. Some sediments may contain dioxins, organometallics such as tri-butyl tin and methyl-mercury, or other “non-conventional” contaminants such as pharmaceuticals and seeds of invasive vegetative species. Each contaminant is likely to distribute through the sediment differently as a function of the means of contamination, the affinity for the sediment solids, the mechanism of sorption and the size of the particles to which the contaminant is sorbed. In the case of vegetative species, distribution may be a function of the particle size of the constituent itself.

A preliminary analysis was conducted to test the general hypothesis of the study. Figure 1 illustrates the main concept of the hypothesis; Scenario 1 and Scenario 2 represent sample groups for which large and small subsample areas (analogous to large and small subsample masses), respectively, were taken. A random number generator was used to determine which subsamples would be withdrawn if 2, 3, 4, 5, 6, or 7 subsamples were extracted for analysis. For each sample set, the subsamples were withdrawn 15 times. The number of dots in each subsample, which represent contaminated particles (and which are the same in both groups), were counted and the

mean number of dots and coefficient of variation were estimated for each scenario and each subsample set (see Table 1). The mean number of dots was always larger for the sample group with large subsample area, and is analogous to taking larger subsample masses for extraction. The coefficient of variation was very consistent for the sample group with large subsample area (ranging from 0.36 to 0.47) and quite variable and of higher magnitude (with two exceptions) for the sample group with small subsample area (ranging from 0 to 2.4). These results suggest that uncertainty will generally be higher for a sample group with smaller subsample area (or smaller subsample mass). These results also suggest that there is likely an optimum sub-sampling size for each matrix that will assure more consistency in analytical results.

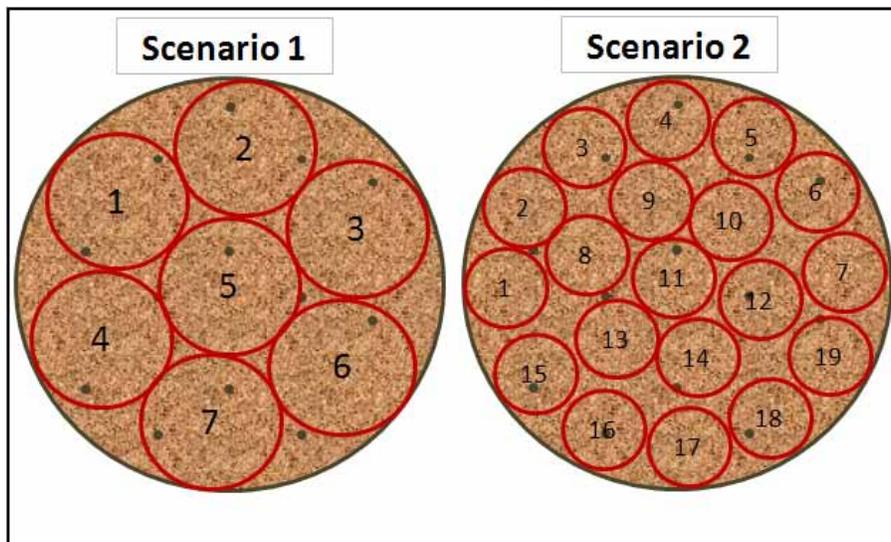


Figure 1. Illustration of the hypothesis concept.

| <b>Table 1. Results of the exercise performed to illustrate the hypothesis concept.</b> |                                  |  |  |
|---|----------------------------------|--|--|
| <b>Scenario</b>   | <b># of subsamples extracted</b> | <b>Mean number of dots in the subsamples</b> | <b>CV for number of dots in the subsamples</b> |
| 1   | 2                                | 1.5  | 0.47   |
|   | 3                                | 1.3  | 0.43   |
|   | 4                                | 1.3  | 0.40   |
|   | 5                                | 1.4  | 0.39   |
|   | 6                                | 1.5  | 0.36   |
|   | 7                                | 1.4  | 0.37   |
|   | 2                                | 2  | 0.7  |
| 3   |                                  | 0.2  | 2.4  |
| 4   |                                  | 0.2  | 2.2  |
| 5   |                                  | 1.0  | 0  |
| 6   |                                  | 0.3  | 1.7  |
| 7   |                                  | 1.0  | 0  |

## MATERIALS AND METHODS:

**Materials.** The study focused on two different groups of contaminants, known to be commonly found in sediments and to have different sorption characteristics: heavy metals (excluding mercury) and PAHs. A Calumet River freshwater dredged material sample that was collected and archived as part of the Chicago Confined Disposal Facility (CDF) characterization effort (U.S. Army Corps of Engineers (USACE) 2006) was used in this study. The archived samples had been refrigerated at a temperature of 4 °C since collection. Based on the previous characterization, this sample was thought to have measurable concentrations of both PAHs and heavy metals.

### Methods.

**Equipment decontamination.** To prevent cross-contamination of the samples, equipment used to homogenize and pack the Calumet River sediment sample was decontaminated according to the requirements for metals and organics analyses. Equipment was washed with a clean brush and Liqui-nox®, and then rinsed with tap water, acetone (histological grade), three times with distilled de-ionized (DDI) water, nitric acid (10%), and three times with DDI water.

**Testing matrix.** A matrix of subsample masses was developed for each contaminant sample group for comparative analysis. Multiple replicates of each subsample mass were taken for analysis from the homogenized sediment sample (Table 2) in order to evaluate the effect of subsample mass on variability of the replicate results. Table 2 provides the subsample mass and the number of replicates for each sample group. Typically, extraction subsample masses are determined based on different factors, such as the expected levels of contaminant present in the sample and equipment limitations. A thorough literature review was used to ascertain the range of reported extraction subsample masses for the sample preparation methods used in this study (e.g. American Society for Testing and Materials (ASTM) D5369, U.S. Environmental Protection Agency (USEPA) methods 3050B and 3540C). For metals extractions, subsample masses reported in the literature ranged from 0.5 g to 20.0 g; 0.5 g to 1.0 g is typically used by the Engineer Research and Development Center (ERDC) analytical laboratory.<sup>1</sup> For organic contaminant extractions, subsample masses reported in the literature ranged from 15.0 to 30.0 g; 15.0 g is typically used by the ERDC analytical laboratory.<sup>2</sup>

| <b>Table 2. Metals and PAH Sample Matrix.</b> |     |    |    |    |    |    |
|---|-----|----|----|----|----|----|
| <b>Metals Sample Groups</b>                   |     |    |    |    |    |    |
| <i>Subsample Mass (g)</i>                     | 0.5 | 1  | 5  | 10 | 20 | 30 |
| <i>Number of Subsamples (Replicates)</i>      | 15  | 15 | 15 | 15 | 15 | 15 |
| <b>PAHs Sample Groups</b>                     |     |    |    |    |    |    |
| <i>Subsample Mass (g)</i>                     | 15  | 30 | 45 | 60 | 75 |    |
| <i>Number of Subsamples (Replicates)</i>      | 15  | 15 | 15 | 15 | 15 |    |

<sup>1</sup> Personal Communication. 2009. Dr. Anthony Bednar, Research Chemist, ERDC-EL, Vicksburg, MS.

<sup>2</sup> Personal Communication. 2009. Allyson Harrison, Biologist/Chemistry Analyst, ERDC-EL, Vicksburg, MS.

**Homogenization and subsampling.** The sediment selected for this study was wet, with 72 % solids content. The sediment (31.2 kg) was homogenized using a Hobart® mixer for 30 minutes, until visually homogenous. Homogenized sediment for both metals and organics analysis was packaged separately in glass jars with Teflon® lids. Samples were stored at 4 ° until processed; all samples were analyzed at the same time with the objective of minimizing variability originating with the extraction and analysis steps. Each individual jar of sediment was re-homogenized by the analytical lab, each jar was emptied into a stainless steel pan and the sample was mixed thoroughly with a spatula. Individual subsamples (replicates) were taken from each jar according to the matrix outline in Table 2.

**Analytical and quality assurance methods.** Sediment subsamples were analyzed for grain size distribution, water content, total organic carbon (TOC), metals concentration (excluding mercury), and individual PAHs concentration. The analyzed metals include: antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, nickel, selenium, silver, thallium, tin, and zinc. The analyzed PAHs include: naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, indeno (1,2,3-cd) pyrene, dibenz (a,h) anthracene, and benzo (g,h,i) perylene.

A single sample was taken for measurement of grain size distribution for each sample group; given that the sediment aliquots for each sample group were relatively small, and the sediment had been well homogenized such that the physical properties could be assumed to be relatively consistent, sample replicates were not considered necessary to support a qualitative comparison of sample groups.

The grain size distribution was measured using an LS™ 100Q Laser Diffraction Particle Size Analyzer. Particle sizes ranging from 0.4 µm to 948 µm are measurable with this instrument, which provides a distribution of particles through a laser technology based on Mie scattering and Fraunhofer diffraction. A small quantity<sup>1</sup> (approximately 0.5-1.0 g) of sediment from each sample group was added to approximately 100-150 mL of water and sonicated using an Ultrasonic Processor. The samples were sonicated for 2 minutes using amplitude of 14% to disperse the sediment particles. Sonication time and amplitude were limited in order to avoid breakdown of the particulates and alteration of the grain size distribution of the sample. After sonication, the slurry was added to the fluid module of the particle size analyzer; the instrument measures and reports the percent particle size by volume, along with statistical measures of the particle size distribution.

For each PAH sample group, water content was measured gravimetrically on one subsample taken specifically for determination of water content (metals subsamples were dried prior to extraction). Given that the sediment aliquots for each sample group were relatively small and had been twice homogenized, replicate samples were not considered necessary for water content analysis. This is also consistent with the customary handling of sediment samples for organics analysis.

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<sup>1</sup> Determined based on the LS™ 100Q Laser Diffraction Particle Size Analyzer reference manual.

The TOC was measured with a Texmar DC 180 (183 boat sampler) on each individual replicate subsample in order to facilitate interpretation of the influence of TOC on the analytical variability. The TOC was measured according to EPA Method 9060A (USEPA 2004).

All of the sediment mass in each replicate subsample was extracted/digested in a single extraction/digestion vessel, regardless of the mass used. Many of the subsample masses were larger than typical, requiring the use of oversize extraction/digestion vessels. The metals samples were dried, ground, and sieved prior to digestion and analysis. The metals digestions were done in a borosilicate glass digestion vessel based on USEPA Method 3050B (USEPA 1996). Sample digestion followed the solid:liquid ratios described in Method 3050B. Metals samples were analyzed by ICP-MS following USEPA Method 6020A (USEPA 2007). A Perkin Elmer Elan DRC II ICP-MS was used along with Scandium, Yttrium, Rhodium, Terbium, and Holmium as internal standards to correct for matrix effects and instrumental drift.

For the PAHs, the wet sediment samples were mixed with Hydromatrix (diatomaceous earth used as a drying agent/dispersant) in a glass flask, then placed in a cellulose thimble and extracted overnight by soxhlet based on SW 846-Method 3540C (USEPA 1996). PAH extracts were concentrated and cleaned up using silica gel following SW 846-Method 3630C modified (USEPA 1996). The PAH samples were analyzed by GC/MS, following SW 846 Method 8270C (USEPA 1996) selected ion monitoring mode using a HP5 MS column.

Quality assurance measures were employed as part of the analysis of the metals and PAHs samples. Digestion blanks and lab control samples (LCS's) were prepared with each metals digestion batch of 20 samples. Analytical blanks, LCS's and quality control check standards (produced by Environmental Resource Associates) were analyzed with each instrument batch for the metals. For the PAHs, blanks and LCS's were run approximately every 20 samples. Duplicates were not included in the batches corresponding to the metals and PAHs because 15 replicates were performed for each sample group. Matrix spikes were not included in the batches because the Calumet River samples had been previously characterized and were known to have high concentrations of both PAHs and heavy metals; the influence of matrix effects would be comparatively small relative to the contaminant concentrations. Further, matrix effects would not be expected to greatly affect relative contaminant measurements in subsamples taken from the same homogenized sediment sample, as was the case in this study.

**Data analysis.** The mean, variance, standard deviation, standard error, coefficient of variation and confidence interval were calculated for each contaminant and sample group using SAS (SAS Institute, Inc. 2003). Also, SAS was used for detection of outliers, normality tests, correlation analysis, and tests for the comparison of means, medians, and variances. Correlation of TOC to concentration of each replicate and percentage of fines to mean concentration of each sample group was also evaluated in SAS.

## **RESULTS:**

**Physical and chemical characterization.** Sediment physical and chemical properties (percent fines, water content, TOC) are summarized in Tables 3 and 4. The mean TOC concentrations are of a similar order of magnitude for all the subsample masses and the coefficient of variation was less than one on all but one sample group.

| <b>Table 3. Physical and chemical properties of the metals subsamples.</b> |                                     |       |       |       |       |       |
|--|-------------------------------------|-------|-------|-------|-------|-------|
| Property   | Sample Groups by Subsample Mass (g) |       |       |       |       |       |
|  | 0.5                                 | 1.0   | 5.0   | 10.0  | 20.0  | 30.0  |
| % Fines <sup>a</sup>   | 87.1                                | 85.2  | 85.7  | 85.8  | 82.4  | 83.0  |
| $\bar{x}_{\text{TOC}}$ <sup>b</sup> (ppm)                                  | 47700                               | 63600 | 37000 | 50800 | 92300 | 75300 |
| S <sub>TOC</sub> <sup>c</sup> (ppm)  | 20500                               | 21100 | 19700 | 16200 | 34100 | 17100 |
| CV <sub>TOC</sub> <sup>d</sup>   | 0.429                               | 0.331 | 0.533 | 0.320 | 0.369 | 0.227 |

a % fines = particles with grain size smaller than 75 µm. A single sample was taken from each sample group for particle size analysis.

b  $\bar{x}_{\text{TOC}}$  = mean TOC concentration.

c S<sub>TOC</sub> = TOC standard deviation.

d CV<sub>TOC</sub> = TOC coefficient of variation.

| <b>Table 4. Physical and chemical properties of the PAH subsamples.</b> |                                     |       |        |       |       |
|---|-------------------------------------|-------|--------|-------|-------|
| Property  | Sample Groups by Subsample Mass (g) |       |        |       |       |
|   | 15.0                                | 30.0  | 45.0   | 60.0  | 75.0  |
| % Fines <sup>a</sup>  | 81.3                                | 82.5  | 82.0   | 81.3  | 83.3  |
| Water Content <sup>b</sup>  | 28.2                                | 28.6  | 28.9   | 27.6  | 30.2  |
| $\bar{x}_{\text{TOC}}$ <sup>c</sup> (ppm)                               | 72900                               | 42500 | 78500  | 45400 | 59100 |
| S <sub>TOC</sub> <sup>d</sup> (ppm)                                     | 29200                               | 20900 | 111000 | 16700 | 29400 |
| CV <sub>TOC</sub> <sup>e</sup>  | 0.400                               | 0.493 | 1.41   | 0.368 | 0.498 |

a % fines = particles with grain size smaller than 75 µm. A single sample was taken from each sample group for particle size analysis.

b Water content = Weight water/Weight solids.

c  $\bar{x}_{\text{TOC}}$  = mean TOC concentration.

d S<sub>TOC</sub> = TOC standard deviation.

e CV<sub>TOC</sub> = TOC coefficient of variation.

The grain size distribution was very similar for each sample group. The percentage of fines, particles with grain size smaller than 75 µm, ranged from approximately 81 to 87 % for each of the sample groups, with an overall mean and standard deviation of approximately 83 % and 2 %, respectively.

**Metals analysis.** The metals subsamples were weighed to the nearest 0.0001 g, with a maximum resulting coefficient of variation of approximately 0.0028.

Statistical measures for results of the metals analysis are given in Table 5, for each sample group. The following relationships were evaluated:

- Mean metals concentration vs. subsample mass (by analyte)
- Magnitude of standard deviation and coefficient of variation within sample groups
- Standard deviation and coefficient of variation vs. subsample mass (by analyte)
- Mean coefficient of variation vs. subsample mass (by sample group)

| <b>Table 5. Regression coefficient of determination and trend for the metals coefficient of variation and standard deviation vs. subsample mass.</b> |                              |              |                             |              |
|--|------------------------------|--------------|-----------------------------|--------------|
| <b>Analyte</b>   | <b>CV vs. Subsample mass</b> |              | <b>S vs. Subsample mass</b> |              |
|  | <b>R<sup>2</sup></b>         | <b>Trend</b> | <b>R<sup>2</sup></b>        | <b>Trend</b> |
| <b>Metals</b>  |                              |              |                             |              |
| Antimony <sup>a</sup>  | ---                          | ---          | ---                         | ---          |
| Arsenic  | 0.657                        | Power        | 0.577                       | Power        |
| Barium   | 0.566                        | Power        | 0.848                       | Power        |
| Beryllium  | 0.137                        | Power        | 0.740                       | Power        |
| Cadmium  | 0.449                        | Power        | 0.357                       | Power        |
| Chromium   | 0.001                        | Linear       | 0.372                       | Linear       |
| Copper   | 0.674                        | Power        | 0.552                       | Power        |
| Lead   | 0.750                        | Log          | 0.509                       | Log          |
| Nickel   | 0.741                        | Log          | 0.643                       | Log          |
| Selenium   | 0.389                        | Log          | 0.194                       | Log          |
| Silver   | 0.421                        | Log          | 0.416                       | Log          |
| Thallium   | 0.615                        | Log          | 0.437                       | Log          |
| Tin  | 0.858                        | Linear       | 0.133                       | Linear       |
| Zinc   | 0.816                        | Power        | 0.748                       | Power        |
| Mean   | 0.785                        | Log          | 0.662                       | Power        |

<sup>a</sup> Antimony concentrations were non-detect.

The mean metals concentration obtained for the different sample groups increased as the subsample mass increased for all metals except tin, which showed an inverse relationship.<sup>1</sup> The increasing mean concentration with increasing subsample mass behavior could be the result of a larger number of contaminated particles being captured in a larger subsample mass; extraction solvent volumes were increased proportionately with subsample mass, thus ruling out a concentration effect due to higher solids/solvent ratios.

The coefficient of determination for mean metals concentration versus subsample mass was statistically significant ( $R^2 > 0.8$ ) for all metals except Cr, Cu, Se, Ag, and Sn, for which  $R^2$  ranged from 0.0384 to 0.709. It is important to note that silver and tin concentrations were non-detect in some replicates and there were fewer data points from which to establish a relationship between mean concentration and subsample mass. Figure 2 illustrates the relationship of the mean concentration versus subsample mass for zinc.

The coefficient of variation within sample groups was generally less than 0.1 for all metals concentrations, indicating limited variability between the replicates.

Variability attributable to subsample mass was evaluated by comparing the coefficient of variation obtained for each sample group. For some contaminants, the coefficient of variation generally decreased (As, Cd, Cu, Pb, Ni, Ag, Tl, Se, and Zn) as subsample mass increased, supporting the initial hypothesis, but in other cases the coefficient of variation generally increased as the subsample mass increased (Ba, Sn) or there was no discernible trend (Ag, Be, Cr) (see Table 5). Only a few regressions were statistically significant, and these suggested an

<sup>1</sup> This is consistent with the findings in the preliminary exercise described in the background section.

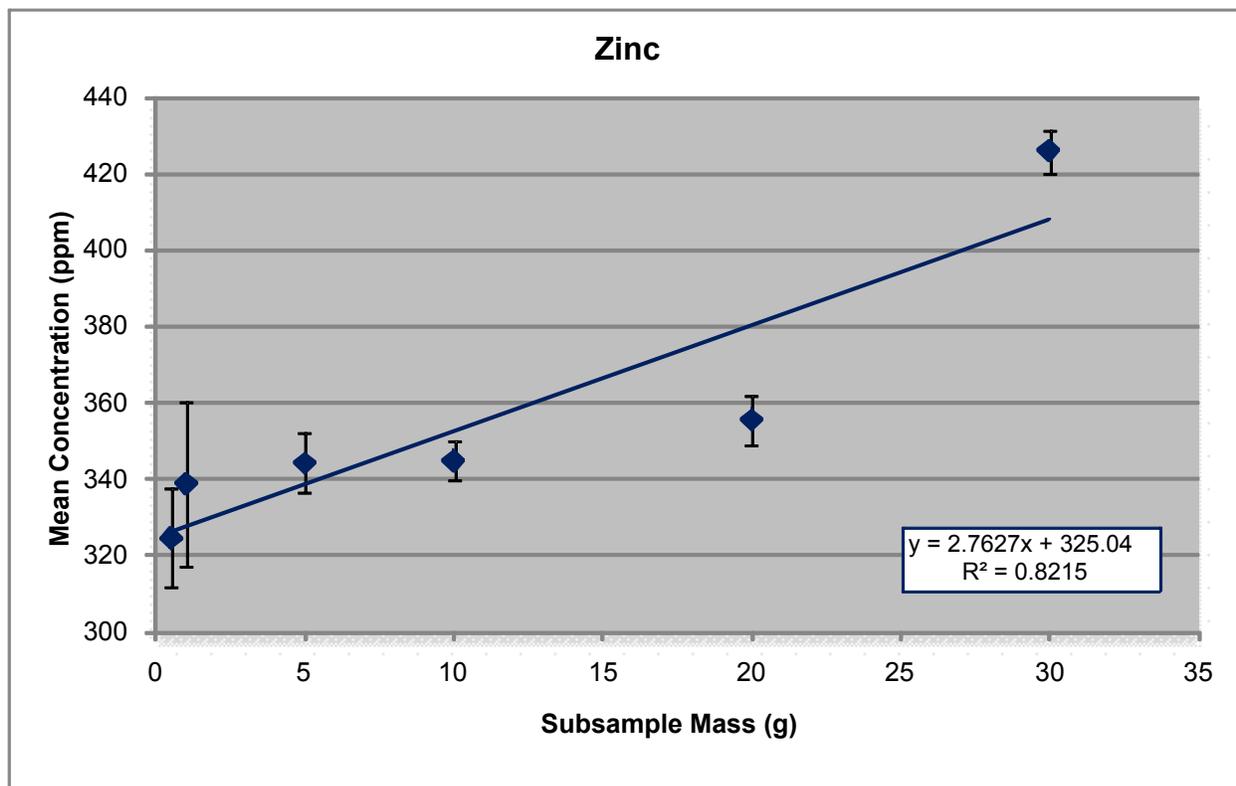


Figure 2. Plot of mean concentration vs. subsample mass for zinc.

inverse relationship between coefficient of variation and subsample mass. Figure 3 shows the plot of coefficient of variation vs. subsample mass for zinc, which was well described by a power function and was statistically significant.

Some interesting qualitative observations can be made by looking at the coefficient of variation values shown in Table 6. For 10 of 13 metals, the minimum coefficient of variation was obtained for subsample masses of 5.0 g and larger (Table 5). The remaining three minimums were obtained for the 1.0-g subsample mass. Conversely, 10 of the 13 maximum coefficients of variation were obtained for the 0.5-g and the 1.0-g subsample masses. These observations are noteworthy given that typical metals extraction subsample masses are 0.5 to 1.0 g in mass; despite the limitations of this data set, clearly the variability of the analysis was greater for the smallest subsample masses. This is also supported by Figure 4, which illustrates the mean metals coefficient of variation versus subsample mass by sample group.

Plots of the standard deviation versus subsample mass were quite similar to the plots of coefficient of variation versus subsample mass, and suggested a decreasing standard deviation with increasing subsample mass generally. The trend observed in the coefficient of variation and standard deviation plots for As, Cd, Cu, Zn, Ba, and Be was best described by a power function. The trend observed for Pb, Ni, Se, Ag and Tl was well described by a log function, and for Cr and Sn by a linear function. Coefficients of determination for the coefficient of variation and standard deviation versus subsample mass are given in Table 6, where it can be observed that only a few were statistically significant.

**Table 6. Statistical measures of the metals subsamples.**

| Analyte   | Subsample Mass (g)   |                         |                           |                    |            |                           |                    |            |               |                    |            |               |                    |            |               |                    |            |               |
|-----------|----------------------|-------------------------|---------------------------|--------------------|------------|---------------------------|--------------------|------------|---------------|--------------------|------------|---------------|--------------------|------------|---------------|--------------------|------------|---------------|
|           | 0.5                  |                         |                           | 1.0                |            |                           | 5.0                |            |               | 10.0               |            |               | 20.0               |            |               | 30.0               |            |               |
|           | $\bar{x}^b$<br>(ppm) | S <sup>c</sup><br>(ppm) | CV <sup>d</sup>           | $\bar{x}$<br>(ppm) | S<br>(ppm) | CV                        | $\bar{x}$<br>(ppm) | S<br>(ppm) | CV            | $\bar{x}$<br>(ppm) | S<br>(ppm) | CV            | $\bar{x}$<br>(ppm) | S<br>(ppm) | CV            | $\bar{x}$<br>(ppm) | S<br>(ppm) | CV            |
| Antimony  | ND                   | ND                      | ND                        | ND                 | ND         | ND                        | ND                 | ND         | ND            | ND                 | ND         | ND            | ND                 | ND         | ND            | ND                 | ND         | ND            |
| Arsenic   | 14.4                 | 0.545                   | <b>0.0379<sup>a</sup></b> | 14.6               | 0.234      | 0.0160                    | 14.7               | 0.282      | 0.0191        | 15.5               | 0.260      | 0.0168        | 15.3               | 0.221      | 0.0145        | 18.3               | 0.196      | <b>0.0107</b> |
| Barium    | 53.4                 | 1.27                    | 0.0237                    | 52.2               | 1.13       | <b>0.0217<sup>a</sup></b> | 55.8               | 1.59       | 0.0285        | 64.1               | 1.83       | 0.0285        | 63.8               | 1.98       | <b>0.0311</b> | 68.5               | 1.79       | 0.0261        |
| Beryllium | 0.846                | 0.0255                  | 0.0301                    | 0.820              | 0.0275     | 0.0335                    | 0.914              | 0.0261     | <b>0.0286</b> | 1.08               | 0.0407     | <b>0.0376</b> | 1.11               | 0.0408     | 0.0367        | 1.27               | 0.0400     | 0.0314        |
| Cadmium   | 1.15                 | 0.0599                  | 0.0522                    | 1.22               | 0.252      | <b>0.206</b>              | 1.18               | 0.0289     | 0.0245        | 1.23               | 0.0264     | <b>0.0215</b> | 1.29               | 0.0472     | 0.0366        | 1.52               | 0.0371     | 0.0245        |
| Chromium  | 40.5                 | 1.83                    | <b>0.0452</b>             | 39.7               | 1.27       | 0.0321                    | 49.6               | 1.17       | <b>0.0237</b> | 66.5               | 2.15       | 0.0324        | 56.0               | 2.02       | 0.0361        | 57.6               | 2.05       | 0.0356        |
| Copper    | 46.7                 | 2.46                    | 0.0526                    | 46.8               | 3.00       | <b>0.0640</b>             | 45.6               | 1.32       | 0.0289        | 51.6               | 2.47       | 0.0479        | 48.5               | 0.885      | <b>0.0183</b> | 58.5               | 1.24       | 0.0212        |
| Lead      | 116                  | 4.69                    | 0.0404                    | 116                | 5.46       | <b>0.0470</b>             | 123                | 3.19       | 0.0260        | 132                | 4.22       | 0.0321        | 128                | 2.64       | <b>0.0207</b> | 155                | 3.83       | 0.0248        |
| Nickel    | 38.9                 | 1.45                    | <b>0.0372</b>             | 39.4               | 0.901      | 0.0228                    | 40.3               | 0.670      | 0.0166        | 44.7               | 0.445      | <b>0.0100</b> | 42.6               | 0.546      | 0.0128        | 48.8               | 0.741      | 0.0152        |
| Selenium  | 1.11                 | 0.0845                  | <b>0.0758</b>             | 1.04               | 0.0591     | 0.0571                    | 1.01               | 0.0641     | 0.0638        | 1.09               | 0.0601     | 0.0552        | 1.06               | 0.0571     | <b>0.0539</b> | 1.17               | 0.0718     | 0.0611        |
| Silver    | 0.376                | 0.0345                  | <b>0.0919</b>             | 0.414              | 0.0167     | <b>0.0402</b>             | ND                 | ND         | ND            | 0.413              | 0.0176     | 0.0426        | ND                 | ND         | ND            | ND                 | ND         | ND            |
| Thallium  | 1.02                 | 0.0308                  | 0.0303                    | 1.05               | 0.0365     | <b>0.0346</b>             | 1.06               | 0.0331     | 0.0311        | 1.19               | 0.0173     | <b>0.0145</b> | 1.15               | 0.0219     | 0.0191        | 1.32               | 0.0261     | 0.0199        |
| Tin       | 1.16                 | 0.0957                  | 0.0827                    | 0.669              | 0.0476     | <b>0.0712</b>             | 0.522              | 0.0454     | 0.0871        | 0.798              | 0.0692     | 0.0867        | 0.759              | 0.111      | <b>0.146</b>  | ND                 | ND         | ND            |
| Zinc      | 325                  | 12.9                    | 0.0398                    | 339                | 21.6       | <b>0.0636</b>             | 344                | 7.82       | 0.0227        | 345                | 5.18       | 0.0150        | 356                | 6.31       | 0.0177        | 426                | 5.61       | <b>0.0132</b> |
| TOC       | 47700                | 20500                   | 0.429                     | 63600              | 21100      | 0.331                     | 37000              | 19700      | <b>0.533</b>  | 50800              | 16200      | 0.320         | 92300              | 34100      | 0.369         | 75400              | 17100      | <b>0.227</b>  |

a Minimum values in shaded cells, maximum values in bold.

b  $\bar{x}$  = mean concentration.

c S = standard deviation.

d CV = coefficient of variation.

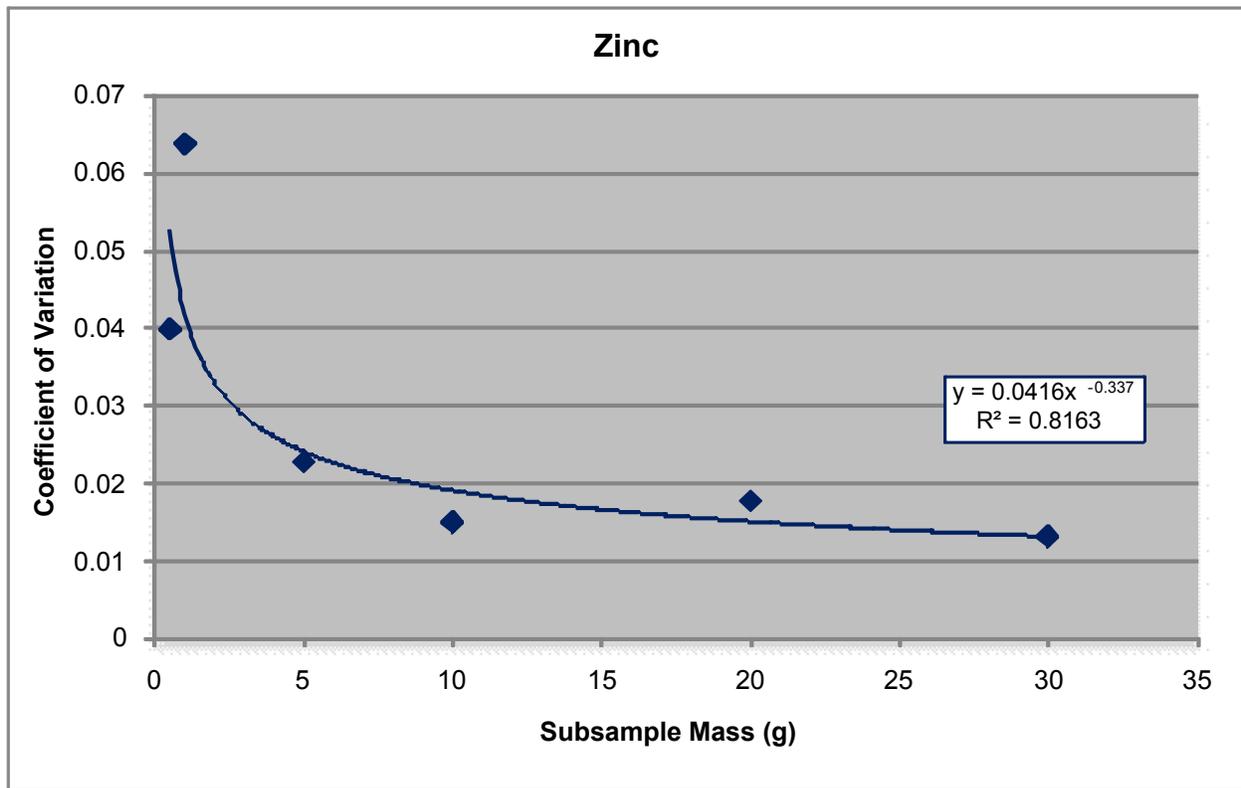


Figure 3. Plot of coefficient of variation vs. subsample mass for zinc.

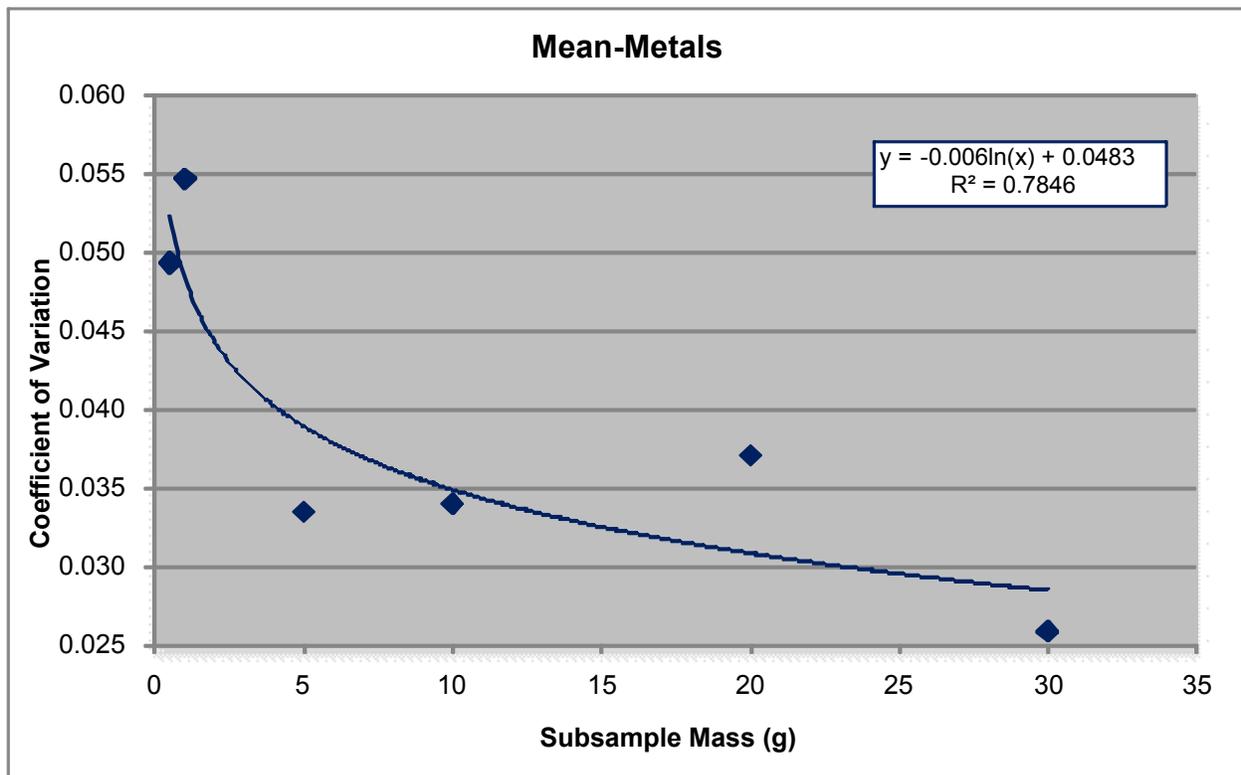


Figure 4. Plot of mean metals coefficient of variation vs. subsample mass.

**PAH analysis.** The PAH subsample masses were weighed to the nearest 0.01 g, with a resulting coefficient of variation ranging from 0.0029 to 0.0096. Table 7 summarizes the statistical measures of the results of the PAH analysis, including the mean, the standard deviation, and the coefficient of variation for each sample group. The following relationships were also evaluated:

- Mean PAH concentration versus subsample mass (by analyte)
- Magnitude of standard deviation and coefficient of variation within sample groups
- Standard deviation and coefficient of variation versus subsample mass (by analyte)
- Mean coefficient of variation versus subsample mass (by sample group)

Most of the PAH contaminants display no significant relationship between the mean concentrations and the subsample mass. A minimum mean concentration could be observed for most of the PAHs for the subsample mass of 45.0 g with the exception of anthracene, acenaphthylene, benzo (a) anthracene, benzo (a) pyrene benzo (b) fluoranthene and benzo (k) fluoranthene; for the first four constituents, the minimum was observed for subsample mass of 15.0 g, and for the last two it was observed for 60 and 75 g, respectively. Figure 5 plots mean concentration versus subsample mass for pyrene.

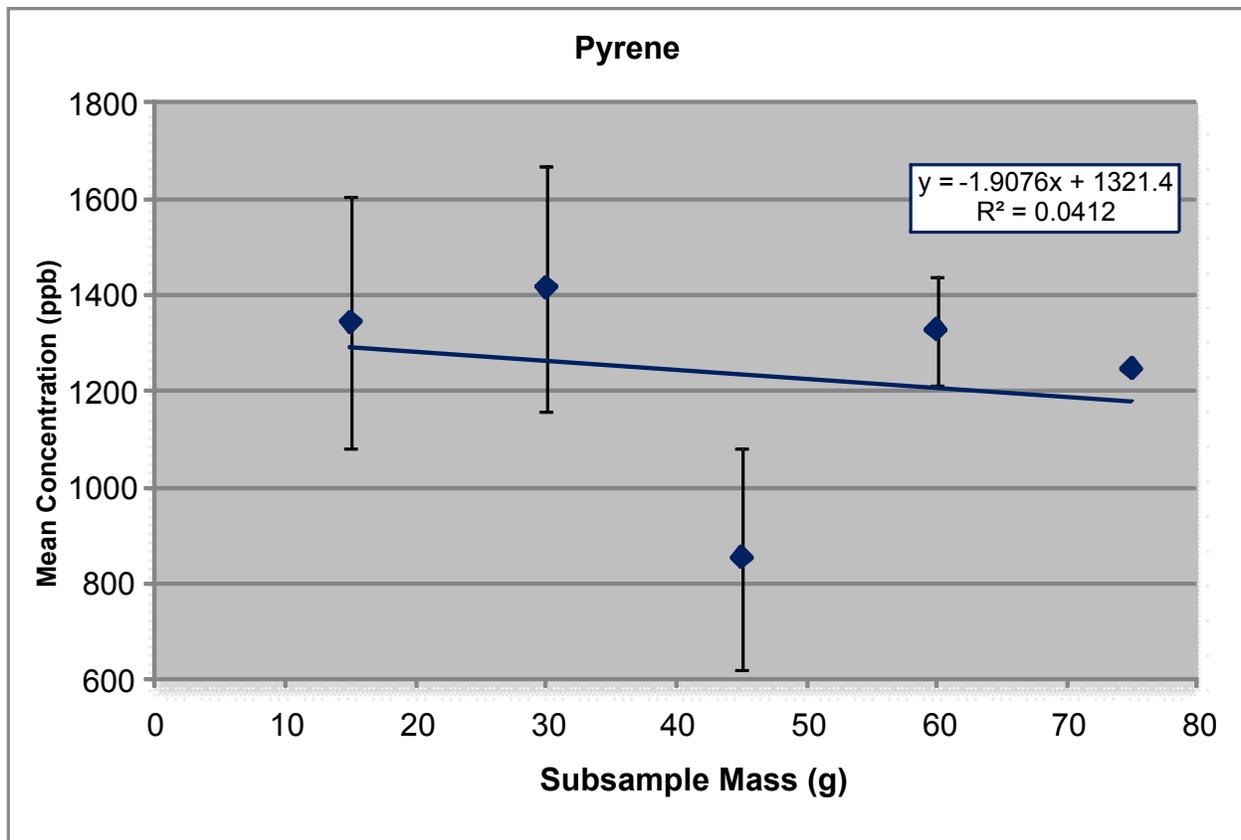


Figure 5. Plot of mean concentration versus subsample mass for pyrene.

| Table 7. Statistical measures of the PAHs subsamples. |                      |                         |                    |                    |            |                    |                    |            |              |                    |            |              |                    |            |        |
|---|----------------------|-------------------------|--------------------|--------------------|------------|--------------------|--------------------|------------|--------------|--------------------|------------|--------------|--------------------|------------|--------|
| Analyte   | Subsample Mass (g)   |                         |                    |                    |            |                    |                    |            |              |                    |            |              |                    |            |        |
|   | 15.0                 |                         |                    | 30.0               |            |                    | 45.0               |            |              | 60.0               |            |              | 75.0               |            |        |
|   | $\bar{x}^b$<br>(ppb) | S <sup>c</sup><br>(ppb) | CV <sup>d</sup>    | $\bar{x}$<br>(ppb) | S<br>(ppb) | CV                 | $\bar{x}$<br>(ppb) | S<br>(ppb) | CV           | $\bar{x}$<br>(ppb) | S<br>(ppb) | CV           | $\bar{x}$<br>(ppb) | S<br>(ppb) | CV     |
| Naphthalene   | 696                  | 140                     | 0.201 <sup>a</sup> | 702                | 114        | 0.162              | 489                | 402        | <b>0.822</b> | 1055               | 227        | 0.215        | 1320               | 288        | 0.219  |
| 2-Methylnaphthalene                                   | 680                  | 184                     | 0.270              | 789                | 160        | 0.203 <sup>a</sup> | 414                | 27         | 0.0653       | 813                | 218        | 0.269        | 956                | 228        | 0.239  |
| Acenaphthylene  | 64.4                 | 21.9                    | <b>0.341</b>       | 97.8               | 12.3       | 0.126              | 65.4               | 14.2       | 0.218        | 68.9               | 10.7       | 0.155        | 69.9               | 6.33       | 0.0904 |
| Acenaphthene  | 356                  | 36.9                    | 0.103              | 374                | 29.0       | 0.0775             | 268                | 31.3       | 0.117        | 339                | 47.8       | <b>0.141</b> | 317                | 16.1       | 0.0507 |
| Fluorene  | 436                  | 62.3                    | 0.143              | 443                | 31.6       | 0.0714             | 317                | 34.5       | 0.109        | 408                | 47.5       | 0.116        | 368                | 16.8       | 0.0458 |
| Phenanthrene  | 1820                 | 449                     | 0.247              | 1740               | 207        | 0.119              | 1340               | 298        | 0.222        | 1540               | 209        | 0.136        | 1410               | 69.8       | 0.0493 |
| Anthracene  | 154                  | 166                     | <b>1.08</b>        | 504                | 69.2       | 0.137              | 399                | 89.5       | 0.225        | 458                | 66.7       | 0.146        | 424                | 26.2       | 0.0619 |
| Fluoranthene  | 1920                 | 825                     | <b>0.430</b>       | 1720               | 284        | 0.165              | 1460               | 548        | <b>0.376</b> | 1760               | 374        | 0.212        | 1540               | 142        | 0.0924 |
| Pyrene  | 1340                 | 395                     | 0.294              | 1410               | 262        | 0.185              | 852                | 255        | <b>0.300</b> | 1320               | 230        | 0.173        | 1240               | 111        | 0.0895 |
| Benzo (a) anthracene                                  | 561                  | 221                     | <b>0.393</b>       | 1040               | 188        | 0.182              | 785                | 210        | 0.268        | 897                | 132        | 0.147        | 831                | 85.5       | 0.103  |
| Chrysene  | 1250                 | 357                     | 0.285              | 1200               | 208        | 0.174              | 875                | 209        | 0.239        | 1060               | 124        | 0.117        | 968                | 138        | 0.143  |
| Benzo (b) fluoranthene                                | 1080                 | 282                     | 0.262              | 1160               | 255        | 0.220              | 1100               | 561        | <b>0.509</b> | 996                | 130        | 0.130        | 1000               | 95.2       | 0.0952 |
| Benzo (k) fluoranthene                                | 684                  | 190                     | 0.277              | 751                | 158        | 0.211              | 678                | 396        | <b>0.584</b> | 681                | 113        | 0.166        | 619                | 105        | 0.169  |
| Benzo (a) pyrene                                      | 771                  | 498                     | <b>0.645</b>       | 1380               | 290        | 0.210              | 1060               | 294        | 0.278        | 1140               | 136        | 0.120        | 1110               | 110        | 0.0989 |
| Indeno (1,2,3-cd) pyrene                              | 570                  | 166                     | 0.292              | 651                | 119        | 0.183              | 372                | 143        | <b>0.385</b> | 588                | 71.5       | 0.122        | 592                | 56.7       | 0.0958 |
| Dibenz (a,h) anthracene                               | 206                  | 53.2                    | 0.258              | 199                | 21.9       | 0.110              | 117                | 35.0       | <b>0.299</b> | 194                | 22.0       | 0.113        | 189                | 53.3       | 0.282  |
| Benzo (g,h,i) perylene                                | 817                  | 229                     | 0.280              | 615                | 84.1       | 0.137              | 321                | 97.8       | <b>0.305</b> | 590                | 66.4       | 0.112        | 597                | 50.0       | 0.0837 |
| Total PAHs  | 11600                | 2420                    | 0.208              | 14000              | 897        | 0.0638             | 9850               | 2200       | <b>0.224</b> | 13200              | 1400       | 0.106        | 13500              | 1110       | 0.0822 |
| TOC   | 72900                | 29200                   | 0.400              | 42500              | 20900      | 0.493              | 78500              | 111000     | <b>1.41</b>  | 45400              | 16700      | 0.368        | 59100              | 29400      | 0.498  |

a Minimum values in shaded cells, maximum values in bold, underlined values were eliminated for comparison (CV>0.3).

b  $\bar{x}$  = mean concentration.

c S = standard deviation.

d CV = coefficient of variation.

The coefficient of variation for PAH replicates within each sample group was less than 0.30 for most of the PAHs, indicating relatively low variability within the replicates. Approximately five PAHs had a coefficient of variation larger than 0.3 for subsample mass of 15.0 g and six PAHs for the subsample mass of 45.0 g. Coefficients of variation larger than 0.3 were eliminated for the comparison of the coefficient of variation versus subsample mass plots, since these values were considered unacceptable for data quality objectives. The coefficient of variation values tended to decrease as the subsample mass increased for most of the PAHs although the regression coefficient of determination was not significant (see Pyrene example, Figure 6) for most of the PAHs, except for benzo (b) fluoranthene, benzo (k) fluoranthene, and indeno (1,2,3-cd) pyrene. For the PAHs, the variability of the analysis was also greater for smaller subsample masses; 14 of 17 minimum coefficients of variation values were obtained for the largest subsample masses (60.0 g and 75.0 g) (Table 7). Two of the remaining three minimums were obtained for subsample mass of 30.0 g and one for a subsample mass of 45.0 g. Conversely, 9 of 17 relative coefficients of variation maximums were obtained for the smallest (15.0-g) subsample mass, with all but one of the remainder obtained for the 45.0-g subsample mass. One maximum was observed for the 60.0-g subsample mass, and none for the 75.0-g subsample mass. The total PAHs minimum coefficient of variation was observed for the subsample mass of 30.0 g and the maximum for the subsample mass of 45.0 g.

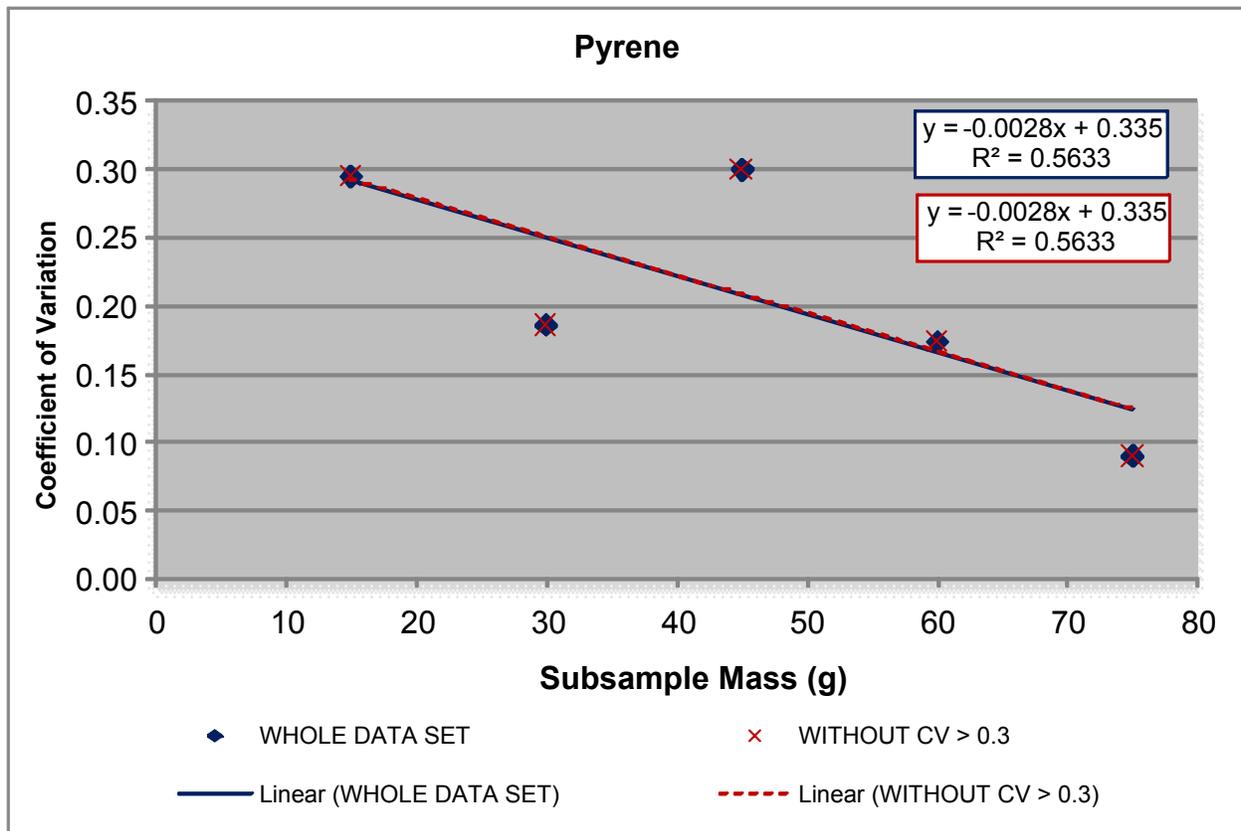


Figure 6. Plot of coefficient of variation versus subsample mass for pyrene.

The plots of the standard deviation versus subsample mass follow a similar tendency to the coefficient of variation plots for most of the PAHs, decreasing with increasing sample mass. The coefficients of determination tended to be higher for the standard deviation plots as compared to coefficient of variation plots. A significant linear regression ( $R^2 > 0.8$ ) was obtained between the standard deviation and the subsample mass for: acenaphthylene, pyrene, benzo (a) anthracene, chrysene, benzo (a) pyrene and indeno (1,2,3-cd) pyrene. Coefficients of determination for PAH coefficient of variation and standard deviation versus subsample mass regressions are given in Table 8. Mean PAH coefficient of variation versus subsample mass is given in Figure 7 (all sample groups) and Figure 8 (45.0-g sample group excluded). The 45.0-g sample group had much higher coefficients of variation for a number of analytes than all other sample groups, suggesting the possibility of analytical error. The trend for mean PAH coefficient of variation versus subsample mass (excluding the 45.0-g sample group) was statistically significant and supports the initial hypothesis (decreasing data variability with increasing sample mass).

**Statistical analysis.** Various statistical tests were conducted to analyze the obtained data using SAS. Because the objective of the study was to reduce analytical variability by increasing extraction/digestion subsample mass, equality of the means and medians for each sample group and each contaminant were compared to determine whether the results obtained actually differed

**Table 8. Regression coefficient of determination and trend for the coefficient of variation and standard deviation versus subsample mass PAHs plots.**

| Analyte                  | CV vs. Subsample Mass <sup>1</sup> |        | S vs. Subsample Mass |        |
|--------------------------|------------------------------------|--------|----------------------|--------|
|                          | R <sup>2</sup>                     | Trend  | R <sup>2</sup>       | Trend  |
|                          | Organics-PAHs                      |        |                      |        |
| Naphthalene              | 0.394                              | linear | 0.307                | linear |
| 2-Methylnaphthalene      | 1.00E-05                           | linear | 0.082                | linear |
| Acenaphthylene           | 0.166                              | linear | 0.820                | linear |
| Acenaphthene             | 0.036                              | linear | 0.097                | linear |
| Fluorene                 | 0.377                              | linear | 0.477                | linear |
| Phenanthrene             | 0.556                              | linear | 0.736                | linear |
| Anthracene               | 0.350                              | linear | 0.750                | linear |
| Fluoranthene             | 0.191                              | linear | 0.587                | linear |
| Pyrene                   | 0.563                              | linear | 0.881                | linear |
| Benzo (a) anthracene     | 0.436                              | linear | 0.816                | linear |
| Chrysene                 | 0.604                              | linear | 0.797                | linear |
| Benzo (b) fluoranthene   | 0.998                              | linear | 0.184                | linear |
| Benzo (k) fluoranthene   | 0.845                              | linear | 0.082                | linear |
| Benzo (a) pyrene         | 0.587                              | linear | 0.898                | linear |
| Indeno (1,2,3-cd) pyrene | 0.901                              | linear | 0.820                | linear |
| Dibenz (a,h) anthracene  | 0.761                              | linear | 8.00E-06             | linear |
| Benzo (g,h,i) perylene   | 0.421                              | linear | 0.693                | linear |
| Total PAHs               | 0.202                              | linear | 0.247                | linear |
| Mean                     | 0.642                              | linear | 0.666                | linear |

<sup>1</sup> R<sup>2</sup> for CV versus subsample mass was estimated after eliminating coefficients of variation greater than 0.3.

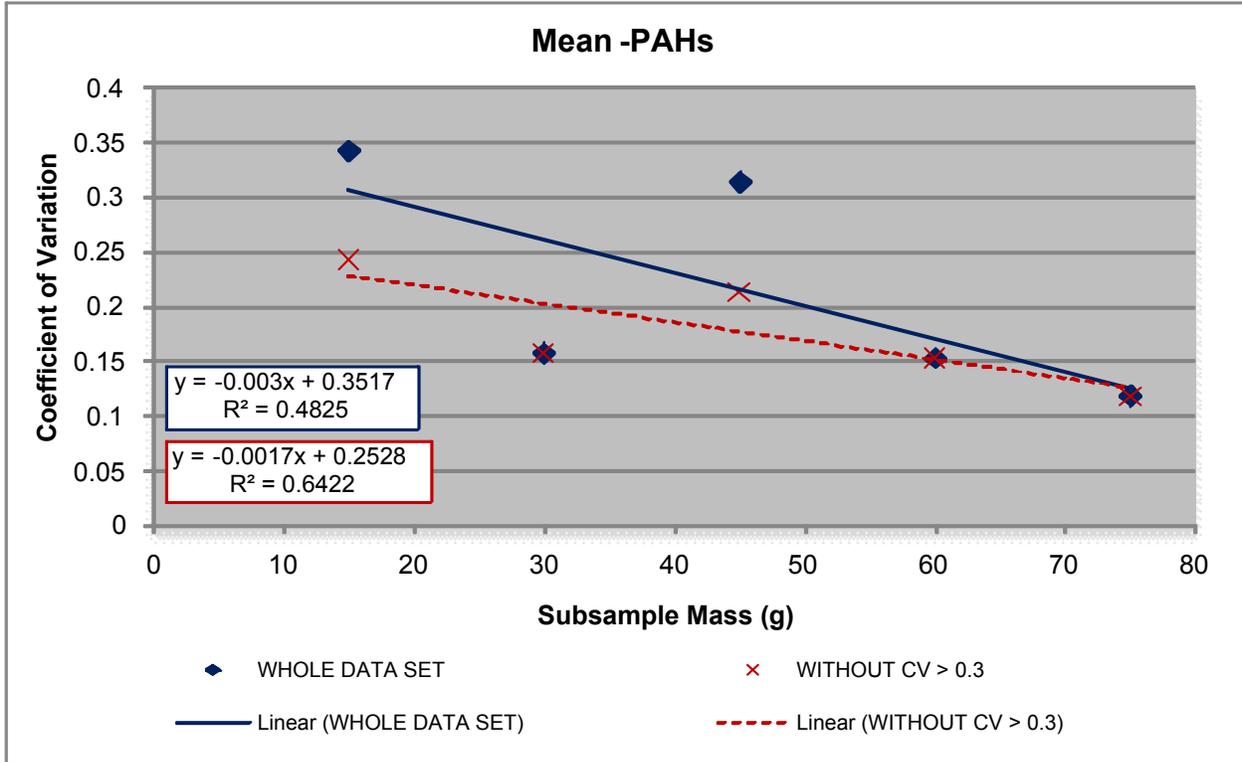


Figure 7. Plot of mean PAHs coefficients of variation vs. subsample mass (all sample groups).

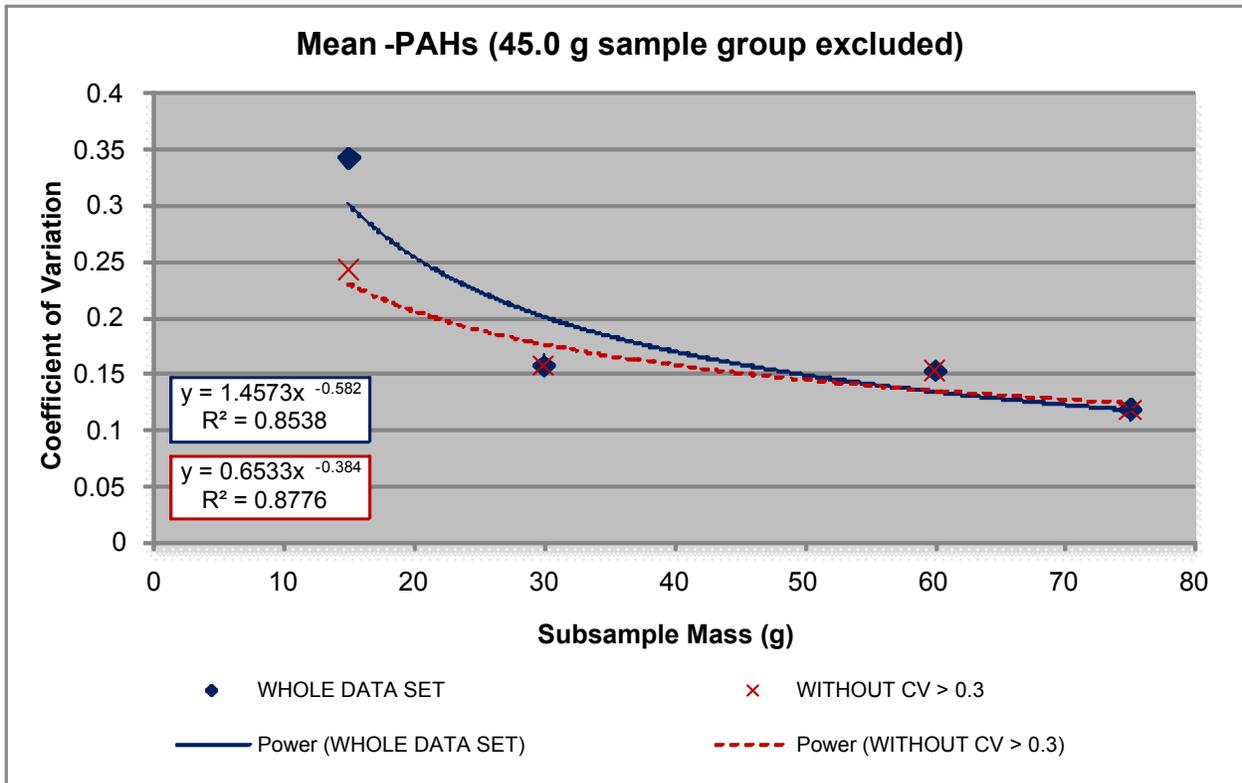


Figure 8. Plot of mean PAHs coefficients of variation vs. subsample mass (45-g sample group excluded).

from each other. A significance level ( $\alpha$ ) of 0.05 was assumed. Normality of the data and equality of variance were evaluated to determine suitability of parametric statistical procedures for analysis of the data.

**Correlation procedure.** Pearson's correlation coefficients were calculated to determine if the percentage of fines and TOC concentration had a relationship with the measured concentrations on each contaminant that might influence interpretation of the overall results. The percentage of fines was measured on an aliquot of sediment from each subsample mass. Correlation of percent fines and mean contaminant concentration for each sample group were evaluated for each individual contaminant. TOC was measured on each replicate and in this case the correlation of TOC to the measured contaminant concentration on each replicate was evaluated. A Pearson's correlation coefficient of less than 0.8 resulted in all cases, indicating that neither percent fines nor TOC was significantly correlated to contaminant concentration.

**Outlier detection.** Although outliers were not eliminated in this study, the data were examined for outliers as one measure of consistency and repeatability in the analyzed data. Two different methods were used to detect outliers within each sample group. The inter-quartile range (IQR) method was conducted using EXCEL and the Rstudent outlier diagnostics were conducted using SAS. The inter-quartile range is estimated based on the first and third quartile. The Rstudent method detects outliers based on the number of standard deviations away from the mean, with outliers being data points more than two standard deviations away from the mean.

Outliers were detected only in some sample groups for some metals and PAHs through the IQR method. The quantity of identified outliers was not greater than two for most of the groups, except for chromium, for which a large quantity of outliers were detected in each sample group, a large quantity of outliers were also detected for an acenaphthylene subsample mass of 75.0 g and a chrysene subsample mass of 45.0 g.

For the metals, the total number of outliers detected by the IQR method for subsample masses of 5.0 and 20.0 g was about half that observed for the other subsample masses. Similarly, the total number of outliers for the PAH subsample masses of 30.0 and 60.0 g was slightly less than half that observed for the other subsample masses.

Outliers were identified for all the analyzed metals and PAHs through the Rstudent method for most of the sample groups. The number of outliers identified by the Rstudent method in each sample group for each contaminant was not greater than two, however.

**Shapiro-Wilk normality test.** The Shapiro-Wilk test was used to determine whether the contaminant concentrations on the replicates of each subsample mass were normally distributed, a requirement of parametric statistical procedures. The univariate procedure was used to perform the Shapiro-Wilk normality test, which was run for each contaminant and sample group separately. The following contaminants were found to be normally distributed: barium, beryllium, chromium, selenium, and fluorene. Therefore, most of the contaminants come from a non-normal distribution, and non-parametric statistical procedures must be employed.

**Levene's test.** Levene's test is used to evaluate equality of variance (homoscedasticity), another requirement of parametric statistical procedures. This test does not assume normality.

This test was conducted through the GLM procedure in SAS. The assumption of equal variance between sample groups was not rejected for most of the PAHs and metals, with the following exceptions: arsenic, chromium, nickel, silver, zinc, acenaphthylene, anthracene, benzo (a) pyrene, and benzo (g,h,i) perylene.

**Selection of parametric versus non-parametric procedures.** Parametric statistical procedures assume equality of variance and a normal distribution of the data. Non-parametric statistical procedures do not require assumptions regarding the distribution of the data. While non-parametric procedures do not require the rigorous assumptions of the parametric procedures, parametric procedures are more powerful (less subject to Type II error). Because data for only some sample groups met the requirements for use of parametric procedures for either the metals or the PAHs, both parametric and non-parametric analysis were conducted for all contaminants; the results were compared to assess consistency of the outcome. With only a few exceptions, the outcome of both parametric and non-parametric procedures was the same.

**Analysis of variance (ANOVA).** The analysis of variance (ANOVA) was conducted to determine if the sample group means obtained for each analyte were statistically different. Three assumptions are made when performing this test including normality, equality of variances, and independence. Based on these assumptions and on the various tests performed to test normality and the equality of variances, only barium, beryllium, selenium, and fluorene meet those assumptions and could be analyzed using ANOVA. P-values for each of these analytes were significantly less than 0.0001, confirming that the subsample group means were statistically different.

**Tukey's test.** Tukey's test is conducted in conjunction with the ANOVA procedure to determine which means are significantly different from each other. This test is used to make a pairwise comparison of the means, and differences are easily visualized based on letters assigned to each Tukey group indicating which means are different and which are similar. Sample groups with the same Tukey grouping letter indicate similarity between the mean concentrations, whereas different letters indicate dissimilarity between the means. The Tukey's test statistic is based on an equation very similar to the t-test. The same assumptions that are made for the ANOVA are also made for this test, including normality, equality of variances, and independence. Based on these criteria, Tukey's test could only be performed on the following contaminants: barium, beryllium, selenium, and fluorene. Table 9 presents the results for these contaminants. It can be observed for barium and beryllium that the mean concentrations corresponding to sample groups of 5 and 30 g are significantly different from the other means. Similarly for fluorene, the mean concentration obtained for the sample group of 45 g is significantly different from the means obtained for the other sample groups. The mean concentrations of the sample groups that were not mentioned have at least one other similar mean (as evidenced by shared Tukey grouping letters in Table 9).

**Kruskal-Wallis test.** The Kruskal-Wallis test, a non-parametric procedure used to evaluate equality of population medians, was also conducted for each contaminant and sample group. Because the test does not require normality of the data, all contaminants could be evaluated using this test. The NPAR1WAY procedure in SAS was used to run this test, for which exact p-values for simple linear rank statistics are computed based on median scores. Significant p-values were obtained for all the metals and most of the PAHs, with the exception of benzo (b) fluoranthene. The results indicate that differences in the median between sample groups were statistically significant for most of the analyzed contaminants.

| <b>Table 9. Tukey groupings of metals and PAHs.</b> |             |          |                           |
|---|-------------|----------|---------------------------|
| <b>Tukey Grouping</b>                               | <b>Mean</b> | <b>N</b> | <b>Subsample Mass (g)</b> |
| <b>Barium</b>                                       |             |          |                           |
| A   | 68.52       | 15       | 30                        |
| B   | 64.1        | 15       | 10                        |
| B   | 63.7533     | 15       | 20                        |
| C   | 55.84       | 15       | 5                         |
| D   | 53.4133     | 15       | 0.5                       |
| D   | 52.2333     | 15       | 1                         |
| <b>Beryllium</b>                                    |             |          |                           |
| A   | 1.274       | 15       | 30                        |
| B   | 1.114       | 15       | 20                        |
| B   | 1.08133     | 15       | 10                        |
| C   | 0.9142      | 15       | 5                         |
| D   | 0.8464      | 15       | 0.5                       |
| D   | 0.8202      | 15       | 1                         |
| <b>Selenium</b>                                     |             |          |                           |
| A   | 1.17467     | 15       | 30                        |
| A,B   | 1.1146      | 15       | 0.5                       |
| B,C   | 1.09007     | 15       | 10                        |
| B,C,D   | 1.06027     | 15       | 20                        |
| C,D   | 1.03653     | 15       | 1                         |
| D   | 1.00547     | 15       | 5                         |
| <b>Fluorene</b>                                     |             |          |                           |
| A   | 442.73      | 15       | 30                        |
| A   | 436.07      | 15       | 15                        |
| A,B   | 408.13      | 15       | 60                        |
| B   | 367.67      | 15       | 75                        |
| C   | 316.67      | 15       | 45                        |

**Comparison of ANOVA and Kruskal-Wallis test.** P-values obtained through ANOVA (parametric analysis of variance) and the Kruskal-Wallis test were similar for all the contaminants with the exception of benzo (k) fluoranthene and fluoranthene. The data for these two contaminants satisfied the parametric assumption of equality of variance for parametric procedures; however, all of the sample groups analyzed for fluoranthene and three of the five sample groups analyzed for benzo (k) fluoranthene failed to meet the assumption of normality. Both benzo (k) fluoranthene and fluoranthene show a significant p-value for the Kruskal-Wallis test and a non-significant p-value for ANOVA.

**Confidence intervals of the mean.** The upper and lower confidence limits of the mean were estimated for each contaminant and sample group to evaluate the impact of large subsample masses on the confidence interval. The means procedure was used to estimate those limits and the gplot procedure was used to plot them along with the mean concentrations. It was observed that the confidence interval generally decreased as subsample mass increased, although the trend

was not statistically significant for most of the contaminants with the following exceptions: barium, beryllium, silver and tin, for which the confidence interval generally increased as subsample mass increased.

### Analytical issues.

**Metals analysis.** Vigorous reaction and overflow of the extraction vessel occurred when performing the acid digestions on the metals subsamples with masses larger than 5 g. This problem can be observed in Figure 9, which shows the 30-g subsample before adding nitric acid, right after adding nitric acid, and after adding hydrogen peroxide. These issues could be attributed to the presence of reactive organics or a large amount of carbonate in the sediment sample. Either of these two constituents could cause a large amount of foaming and boil-over when heating the sediment sample with nitric acid. The likelihood of reactive organics is substantiated by the fact that the foaming issue was also observed with the hydrogen peroxide additions. It is important to note that the overflow could be influenced by the dimensions of the digestion vessel. The overflow became almost impossible to stop when extracting the subsamples larger than 10 g, even though an 18-in.-high digestion tube was used. The laboratory that analyzed the samples usually uses 22.5-cm tubes. In order to control the overflow, the foam was washed down with a squirt bottle of 1% nitric acid; however, it was uncontrollable on the largest subsample (30 g), where the overflow was caused just by adding the hydrogen peroxide with no heat. Although associated material losses were thought to be relatively small as compared to the subsample mass, some analytical error and incomplete extraction may have resulted.

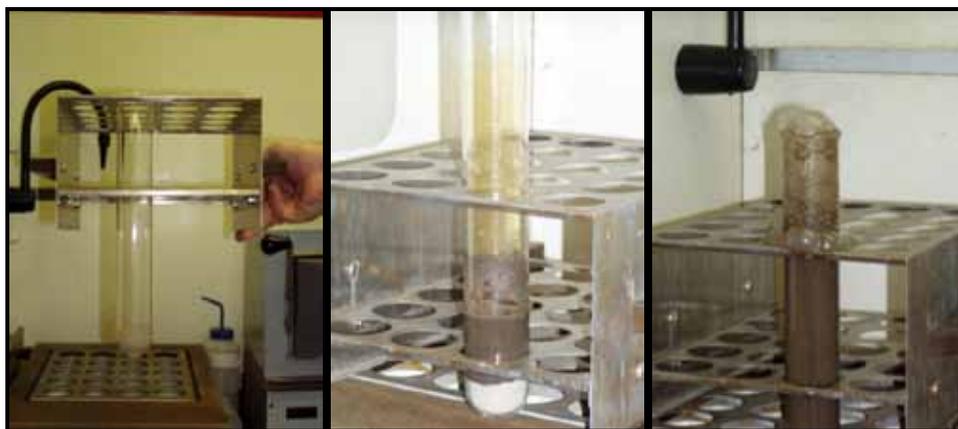


Figure 9. Acid digestion on one of the replicates of the 30-g subsample.

Productivity issues were also encountered when using the large sample masses (i.e. greater than 5 g) that require large digestion vessels. The digestion block that contains small vessels (0.5-g samples) can digest 72 samples in an 8-hr day. However, the digestion block that contains larger vessels can only digest 20 samples and requires longer times to cool between reagent additions. Therefore, it will be hard to complete a full digestion set in 8 hr. This will result in a productivity reduction of approximately one third; there is potentially a tradeoff between accuracy and production/cost. The extractions of the large samples also require a huge amount of acids and reagents, which will also result in increased cost. A less problematic approach would be to digest

smaller samples and combine the extract for analysis, thus realizing the benefit of larger subsamples without the corresponding sample preparation issues.

**Organic analysis.** The 15- and 30-g subsamples did not present any issues when being extracted and analyzed. However, the 45-g subsample began to present issues that became even more evident in the 60- and 75-g subsamples. The larger subsample masses filled the soxhlet completely; this may have resulted in an incomplete extraction and lower extraction efficiency. The normal cleanup procedure was not adequate for the larger subsample masses. Solutions became cloudy when the extract was concentrated, which was attributed to formation of particulates, and samples subsequently had to be diluted (see Figure 10). The dilution resulted in no surrogate recovery for large subsample masses. Taking an equivalent volume of the extraction from the larger sediment aliquots rather than concentrating them to the same volume would appear to be a better procedure. The impact of the “concentration effect” on the overall analysis cannot be determined, however, without repeating the testing.



Figure 10. Extracted samples corresponding to 15-, 30-, and 45-g subsamples, respectively.

**CONCLUSIONS:** For some analytes, the data support the hypothesis that analytical variability can be reduced by extracting larger sediment subsample masses. Where the data was inconclusive, or did not support the hypothesis, sample preparation issues may have been responsible. Material losses that occurred during extraction of larger subsamples for metals and PAHs, incomplete extractions caused by the inadequate contact between the extracting agent and the sediment particles, and interferences introduced by concentrating the larger sample extractions to a smaller volume, were potentially significant to the outcome of this analysis. It is encouraging that in spite of these sample preparation issues, some definite trends were observed supporting the assertion that larger subsamples can reduce analytical variability for soils and sediments. Clearly modification of the extraction/digestion procedures is needed to better assess the benefit of larger

subsamples in terms of data quality. Extracting multiple, smaller subsamples, combining these into a single extraction volume, and then sub-sampling (not concentrating) for analysis should eliminate some of the analytical issues encountered in this study. The sample preparation costs would increase somewhat, but may be offset by higher precision of the analytical results and a reduction in the total number of field samples required to estimate measured parameters with a high degree of confidence.

**POINTS OF CONTACT:** For additional information, contact Damarys A. Acevedo, 601-634-4845, [Damarys.Acevedo-Acevedo@usace.army.mil](mailto:Damarys.Acevedo-Acevedo@usace.army.mil), Dr. Trudy J. Estes, 601-634-2125, [Trudy.J.Estes@usace.army.mil](mailto:Trudy.J.Estes@usace.army.mil), or the program manager of the Dredging Operations and Environmental Research (DOER) program, Dr. Todd S. Bridges, 601-634-3626, [Todd.S.Bridges@usace.army.mil](mailto:Todd.S.Bridges@usace.army.mil). This technical note should be cited as follows:

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