

CDF Characterization for Beneficial Reuse of Dredged Material — Establishing Precedents Based on a Case Study

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PURPOSE: This technical note describes the process of analyzing data collected from a confined disposal facility (CDF), with four fundamental objectives:

- To identify the most useful data analysis tools, and the best application of them
- To illustrate how a structured and sequential evaluation of data can maximize the amount of information obtained
- To evaluate whether the collected data adequately answered the logistical and technical questions posed by the characterization effort
- To provide the foundation for a practical sampling and characterization template for CDFs

In this case, various methods of analyzing and interpreting the data were applied in order to assess the abundance of the desired fraction (sand); the contaminant levels in the sand and residual fractions; the uncertainty of the parameters measured; and the overall adequacy of the characterization effort.

BACKGROUND: Upland disposal capacity for dredged material is diminishing in many U.S. Army Corps of Engineers districts, resulting in the deferral of navigation dredging in some areas. There are many site-specific limitations to the construction or the expansion of CDFs, including high waterfront land values, cost of construction, siting conflicts, and foundation strength limitations. Removal of dredged material from CDFs for beneficial use appears to offer the best potential for sustaining existing CDF capacity. There has been no baseline established, however, regarding the intensity of sampling necessary to adequately characterize materials in a CDF for this purpose, nor has there been any guidance developed to establish evaluation parameters for assessing feasibility and benefit.

Sediment characterization customarily includes determination of physical properties and contaminant analysis. However, for the purposes of material recovery, additional characterization may be needed in order to evaluate sub-fractions of the material, identify treatment or processing needs, and to ensure with a reasonable level of certainty that material specifications, including applicable regulatory criteria, will be met. Due to the fact that chemical characterization and field sampling — particularly coring — are very expensive, the ultimate goal of this document is to develop a strategy for targeted sampling, compositing, and data analysis that will optimize sampling effort, reduce characterization uncertainty, and minimize cost.

APPROACH: Adequate characterization of a CDF for beneficial reuse of material requires sufficient sampling to determine with a reasonable degree of certainty that:

- the amount and distribution of the desired material within the CDF is known;
- all contaminants of concern (COCs) that are present have been identified;
- the concentrations and distribution of the COCs within the CDF and within the sediment fractions are known;
- areas or fractions with potential COC exceedances of regulatory criteria have been identified; and
- beneficial use material specifications can be met in the target material.

Before gathering data, one should know how the data will be used to answer the questions at hand. The following are the sequential steps likely to be employed in order to develop a sampling plan and to structure the data analysis for the purposes of characterizing material in a CDF:

- Identify a beneficial use (BU) or alternative placement for recovered material
- Determinate material specifications and applicable environmental criteria for the identified BU
- Review anecdotal and site data; identify data gaps/needs
- Identify level of acceptable uncertainty
- Evaluate variability of existing data and estimate number of samples required to generate needed data
- Develop a sampling plan for the site
- Characterize the material in keeping with data objectives, including:
 - o physical properties
 - o contaminant levels
 - o engineering properties

Once a preliminary data set has been obtained the data will be used to:

- evaluate suitability of material based on BU specifications and environmental regulations;
- evaluate adequacy of the data and sampling based on uncertainty and data objectives;
- identify excavation boundaries within the CDF;
- estimate volume of recoverable material;
- estimate volume and character of residual materials;
- calculate net capacity gained; and
- calculate cost benefit taking into account facility life cycle, recovery and processing costs, and any material value.

If the uncertainty of the estimated parameters is too great to determine material suitability with confidence, a larger data set may be necessary. In that case, additional sampling would need to be conducted, data sets would be combined if appropriate, and parameter estimation would be repeated. There are issues related to combining data sets that must be considered, including the potential introduction of bias. The complexities of these and other sampling issues are beyond the scope of this document, but are discussed in more detail in a follow-on technical note (Clarke et al. in review).

This technical note will focus primarily on tests that may be used to characterize the materials in the CDF for the purposes of evaluating material suitability, feasibility of recovery, and statistical methods that may be used to assess the level of uncertainty associated with the data. Available data from the Chicago Area CDF will be used to describe the physical and chemical characterization of the CDF and to evaluate the adequacy of sampling based on the requirements described above. The data analysis methods presented will illustrate the association and evaluation of data uncertainty with sample size for a real-world case. The Chicago Area CDF was selected based on the availability of data; the use of these data and the results of data analysis for this technical note do not represent a final or official opinion of U.S. Army Corps of Engineers (USACE) on the quality or potential uses of material stored in the CDF. In addition, criteria comparisons were made to illustrate the potential use of various data analysis methods, and do not represent a rigorous evaluation or official regulatory determination regarding the suitability of the material for any intended uses.

DATA SET: In 2006, sediment samples were collected from the Chicago Area CDF, located immediately south of the mouth of the Calumet River at Lake Michigan in Illinois. The study objective was "to assess the feasibility of mining and processing material from the Chicago Area CDF for beneficial purposes, and to collect geotechnical data for use in CDF expansion designs" (USACE 2006). Core samples were taken at nine terrestrial sites (01-09) and three pond sites (P1-P3) within the CDF (Figure 1). Core samples were examined in the field and in the absence of significant stratification, composited over the length of the core. The terrestrial sites were areas known or thought to contain a substantial amount of coarse material based on surface elevation, surficial materials, and historical discharge points. The pond sites were selected with the intent of potentially ruling out this area for coarse material recovery, given that materials in areas furthest from the dredge discharge are typically predominantly fine-grained.

All samples were analyzed for grain size distribution and organic matter (including total organic carbon, soot, and oil and grease). Seven of the terrestrial cores were also analyzed for chemical contaminants of concern, with two objectives:

- To evaluate the extent to which contaminants might limit beneficial use of the sand or impact the regulatory classification of the fines
- To exploit the correspondence of contaminant concentrations with physical properties of the sediments, such that contaminant concentrations could be estimated in samples for which only physical properties were measured (as a cost savings measure)

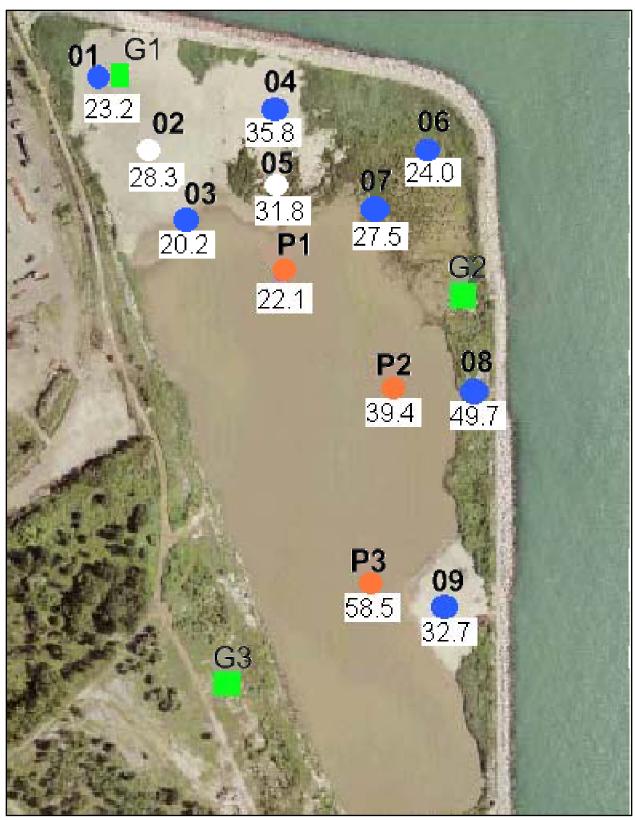


Figure 1. Aerial view of Chicago Area CDF showing sample locations. Values indicated in the figure are percent sand. (Location G3 was not sampled.)

Contaminants analyzed included 12 metals, 17 polynuclear aromatic hydrocarbons (PAHs), and seven polychlorinated biphenyl (PCB) Aroclor mixtures. Sediment cores from two additional locations (G1-G2) were collected for analysis of geotechnical parameters only¹. General parameters measured at each sample location are given in Table 1.

| Tabl | e 1. Chicago | Area C | DF da | ata set | :. | | | | | | | | | | |
|------------------------------|----------------------------|--------------------|-------|---------|-------|-------|--------|----------|-------|-------|----|----|----|----|----|
| Step | | | | | | ; | Sample | Location | 1 | | | | | | |
| | Property | 01 | 02 | 03 | 04 | 05 | 06 | 07 | 08 | 09 | P1 | P2 | P3 | G1 | G2 |
| | Specific gravity | O,C,F ¹ | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | | | | | |
| ĺ | Total organic carbon | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | | | | | |
| u. | Total solids | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | O,C,F | | | | | |
| erizatic | Grain size distribution | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | |
| ract | Bulk density | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | | |
| Cha | Dry density | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | | |
| Physical Characterization | Total combustible organics | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | |
| | Void ratio | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | | |
| | Water content | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | 0 | 0 |
| | Total porosity | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | | |
| | Geotechnical ² | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | 0 | 0 |
| u | Contaminant | | | | | | | | | | | | | | |
| al zatic | PAHs | O,C,F | | O,C,F | O,C,F | | O,C,F | O,C,F | O,C,F | O,C,F | | | | | |
| Chemical racteriza | PCBs | O,C,F | | O,C,F | O,C,F | | O,C,F | O,C,F | O,C,F | O,C,F | | | | | |
| Chemical Characterization | Metals | O,C,F | | O,C,F | O,C,F | | O,C,F | O,C,F | O,C,F | O,C,F | | | | | |
| 5 | Metals - TCLP | С | | С | С | | С | С | С | С | | | | | |

¹ O = Original (bulk sediment), C = Coarse fraction, F = Fine fraction (C and F size fractions obtained by wet sieving at 75 um cut point.) Properties correlated to density fractions (typically above and below specific gravity 2.1) may also be useful in determining appropriate separation unit operations and evaluating potential separation efficiency.

² Atterberg limits, Q-test, R-test, consolidation test.

Grain size distribution was measured on sediment core samples collected from locations 01 through 09 and P1 through P3. Contrary to expectations, the highest percentages of coarse material² occurred in pond samples P2 and P3, and terrestrial samples 08 and 09, and ranged from 44 percent to 62 percent. Sampling locations at the northern end of the CDF had lower amounts of coarse material, ranging from 20 percent at location 03 to 36 percent at location 04. Percent sand is superimposed at each location in Figure 1.

METHODS: The tests and procedures used to obtain and interpret data for the stepwise analysis outlined above are described in the following section. The specific procedures employed are

¹ "Geotechnical measurements" included: Atterberg limits, Q-test, R-test, water content, and consolidation tests.

² Defined as sand + gravel retained on a #200 sieve.

summarized in Table 2 and the procedures and outcomes further described and illustrated with the available data throughout the remainder of this technical note. Data analyses and graphs were prepared using SAS (© SAS Institute Inc. 2003), SigmaPlot (© SPSS Inc. 2001), Department of Defense Groundwater Modeling System (http://www.xmswiki.com/xms/GMS:GMS), U.S. Environmental Protection Agency (USEPA) ProUCL (http://www.epa.gov/esd/tsc/software.htm), and Primer 6 (© PRIMER-E Ltd. 2006).

SAMPLING: There are various approaches to establishing a sampling grid, ranging from those statistically based to those based on practical experience. A summary of current guidance on sampling and compositing to reduce variability can be found in Clarke et al. (in review). Available funding is generally an over-riding limitation to the amount of sampling that is done, as it was in the Chicago Area CDF case. Coring to depth is quite expensive (several thousand dollars per core, although with some economy of scale as core numbers increase). Several approaches to selecting sampling locations for BU characterization of relatively uncontaminated material are outlined in Olin-Estes (2000). These approaches are based on judgmental, random, or systematic methods for selecting sample locations, or some combination thereof. In practice, while random samples may be selected in order to maintain statistical validity of the data, usually some level of judgment is involved, whether in determining the area within which samples will be randomly selected, or in outright selection of sample locations. The number of samples is also generally determined based on judgment and budget, with the provision that additional sampling may be needed if the data are not sufficiently definitive for the specific project requirements. Determining the sufficiency of the data often becomes a largely judgmental process in itself. This technical note is intended to provide a more quantitative, yet practical, approach to evaluating the sufficiency of a data set, coupling simple data and criteria comparisons with statistical tools for evaluating uncertainty.

In the case of the Chicago Area CDF, sample locations were selected based on *a priori* knowledge of placement history, observation of surficial materials, topography and water levels on the site, and budget. Vertical compositing intervals were specified (for the geotechnical samples only) based on observed material properties of the core, such that a three-dimensional picture of the in-situ material might be obtained. Sample locations were limited, but the area is relatively small (43 acres). Evaluating this data set will be a useful exercise, not only to illustrate the protocol proposed in this technical note, but also to determine whether further sampling is needed at this site, and to increase the efficiency of CDF characterization in subsequent efforts.

ASSESSING THE PHYSICAL PROPERTIES OF THE MATERIAL: Customarily, analysis of the homogenized bulk sediment is the only analysis that is performed. Certainly, this provides valuable information regarding the aggregate material. However, where the objective is to recover a given fraction of the sediment, such as sand, then additional testing is needed to characterize adequately the target fraction and the residuals. Two types of fractionation can readily be done — size fractionation and density fractionation — and each offers slightly different information valuable to the process. Size fractionation typically involves wet sieving at a specified cut size and then characterizing the size fractions. From this data, the suitability of the

| | Input Data | Fraction | Test/Analysis | Purpose | | | | |
|------------------------------|---|---|--|---|--|--|--|--|
| | All measured physical properties | Bulk, coarse, fine, P1-P3, G1-G2 | Summary statistics | Establish gross character of the material; comparison to material specifications | | | | |
| Physical | Organic content | Bulk, coarse, fine | Box plots | Illustrate general distribution of different carbon phases | | | | |
| Characterization | Grain size distribution | Bulk, P1-P3 | Surface and contour plots, isopach maps | Visual representations of grain size, sample similarity; potentially useful in establishing | | | | |
| | | | Ternary diagram | excavation boundaries | | | | |
| | Grain size and organic content | Bulk, P1-P3 | Ordination plot | Multivariate graphical illustration of samples with similar grain size and organic content | | | | |
| | Contaminant concentrations | Bulk, Coarse, | Box plots | Location of contaminants, median concentration, interquartile ranges, outlier identification | | | | |
| | | fine | Q-Q plots | Graphical illustration of normality of the data, for distribution-dependent statistical procedures like sample size calculations | | | | |
| | | | Ordination plot | Multivariate graphical illustration of concentra- tions by location, grouping locations with similar concentration levels | | | | |
| | | | Location plots, moving averages | Visual aids to identifying general distribution of materials and contaminants | | | | |
| Observatoral | | | Histogram | Graphical illustration of data distribution, for distribution-dependent statistical procedures like sample size calculations | | | | |
| Chemical Characterization | | | Summary statistics | Establish gross character of the material; comparison to regulatory criteria | | | | |
| | Contaminant concentrations vs organic content Bulk, coarse, find | | Correlation analysis ¹ | Determine the relationship between chemical analytes and different carbon phases | | | | |
| | Metal leachate concentrations vs organic content | Coarse | Correlation analysis ¹ | Identify carbon phases associated with potentially mobile chemical contaminants | | | | |
| | Contaminant concentrations vs organic content (untransformed and/or | Bulk, Coarse, fine | Linear regression (simple and/or multiple) | Determine whether carbon phases can be used to predict contaminant concentrations in samples not analyzed for contaminants | | | | |
| | log-transformed) | | Entropy regression (multiple) | Alternate regression procedure where linear regression is unsuccessful in estimating contaminant levels associated with different carbon phases | | | | |
| | Contaminant concentrations | Bulk, coarse, fine | Estimates of variability (variance, standard deviation, coefficient of variation, confidence limits on the mean) | Calculation of sample size required to determine contaminant levels at a given confidence level, for comparison to regulatory criteria | | | | |
| Uncertainty Analysis | | | Distribution generation (Monte Carlo analysis, bootstrap methods) | Data distribution is synthetically generated on the basis of available data for quantification of sample variability. For determination of sample number requirements/evaluating adequacy of sampling conducted. ² | | | | |
| | | | Sample size vs. relative error plots | Reflects CI around the mean as a function of sample size and relative error and compares the CI to applicable regulatory criteria | | | | |

Spearman's (non-parametric) or Pearson's (parametric) coefficients may be used as appropriate, based on normality of the data ² Distribution generation was evaluated as part of this effort. However, simulation is complex, requires specialized software, and does not provide as direct an estimate of sample size as the standard sample size formulas.

target fraction for the intended use can be determined and any contaminant-related issues identified. Density separation involves the use of heavy media to separate the mineral and organic fractions, which are then characterized in the same manner as the size fractions or bulk sediment. The data obtained from the density separation provides valuable information with respect to contaminated phases that may carry over into the target fraction due to particle size similarities, and also information with respect to the type of separation that will be required to remove them. For example, a coarse organic phase, such as coal fragments, is likely to have high associated contaminant concentrations and may be of a size that will report with the sand in a simple screening process. A separation exploiting differences in particle density may then be required in order to fully remove that phase from the target fraction. In some cases, a portion of the target fraction has to be sacrificed as well in order to more fully remove the contaminated phases.

The use of density separation for contaminant distribution evaluation is relatively new and not widely practiced. Sieving is a common practice, however, and most labs will be able to provide this service with some oversight regarding sample handling to minimize contaminant losses. For this reason, only the size fractions from the Chicago CDF materials were analyzed, though additional samples were archived for possible evaluation of density fractions.

Fractionation. Core samples from locations 01, 03, 04, 06, 07, 08, and 09 were separated into fine and coarse fractions (passing and not passing a #200 sieve, respectively). The original samples (bulk sediment) and the coarse-grained and fine-grained fractions were each analyzed for chemical parameters (metals, PAHs, PCB Aroclors, and organic matter). Potential for leaching of metals from the coarse fraction was also evaluated using the toxicity characteristic leaching procedure (TCLP).

Measurement of carbon phases. Organic matter in the sediment fractions comprises several different phases including amorphous (recently biogenic) organic carbon (OC), condensed carbon phases (soot), and oil and grease. Total organic carbon (TOC), oil and grease (O&G), and soot are measured directly. TOC was measured using Method SW-846 9060; soot using Gustafsson et al. (1997), a modification of the acidification and combustion procedure used for TOC analysis; and O&G by ASTM D1664. OC concentrations are taken to be the TOC not represented by soot and OG concentrations. These three phases significantly influence the relative degree of contamination present in different size fractions, as well as the associated mobility of those contaminants. Clay minerals, having charged surfaces and, in some cases, accessible interlayers where small organic molecules can adsorb, may contribute to the apparent particulate organic content. The physical properties of the organic phases, in part, determine the feasibility of separating them from the target sediment fraction, and the processes required to accomplish this. The issue is complicated by the fact that carbon phases may not exist entirely as discrete particles but rather as coatings on other sediment particles. Although this is a relatively new approach to characterizing material, its value in terms of understanding contaminant distributions in sediments and in evaluating the feasibility of producing a clean target fraction has been demonstrated. Simple measurement of TOC alone may not be sufficient to make these determinations.

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¹ Heavy media: high density liquid diluted to an intermediate density to achieve separation of materials of selected particle density.

Summary statistics. Summary statistics for grain size, organic matter phases, and selected physical parameters are provided in Table 3 for the original bulk sediment and the coarse and fine fractions (where applicable).

| | TOC (%) | O&G (%) | Soot (%) | Clay (%) | Gravel (%) | Sand (%) | Silt (%) | Specific Gravity | Bulk Density (g/cm³) | Dry Density (g/cm³) | Total Porosity (%) | Total Solids (%) | Void Ratio | Water Content (%) |
|--------------|------------|------------|-------------|-------------|---------------|-------------|-------------|---------------------|----------------------------|---------------------------|--------------------------|------------------------|---------------|-------------------------|
| | | | | | | Frac | tion: Bu | ılk Sedime | ent ^a | | | | | |
| n | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 15 | 12 | 16 | 12 | 12 | 12 | 14 |
| Mean | 5.57 | 0.38 | 1.49 | 26.13 | 2.23 | 32.77 | 38.88 | 2.72 | 1.84 | 1.33 | 50.98 | 72.67 | 1.04 | 27.43 |
| Std. Dev. | 2.18 | 0.26 | 1.16 | 6.30 | 3.34 | 11.64 | 10.01 | 0.04 | 0.06 | 0.10 | 3.65 | 3.96 | 0.14 | 3.74 |
| CV | 0.39 | 0.70 | 0.78 | 0.24 | 1.50 | 0.36 | 0.26 | 0.02 | 0.03 | 0.07 | 0.07 | 0.05 | 0.14 | 0.14 |
| Min | 3.20 | 0.14 | 0.44 | 14.90 | 0.00 | 20.20 | 23.00 | 2.61 | 1.73 | 1.15 | 46.90 | 66.00 | 1.00 | 19.00 |
| Q1 | 3.95 | 0.18 | 0.69 | 21.65 | 0.20 | 23.60 | 29.40 | 2.72 | 1.80 | 1.26 | 47.60 | 70.00 | 1.00 | 26.00 |
| Median | 5.35 | 0.31 | 1.05 | 26.35 | 0.95 | 30.05 | 39.30 | 2.73 | 1.82 | 1.34 | 50.50 | 73.00 | 1.00 | 27.00 |
| Q3 | 6.65 | 0.47 | 1.75 | 29.90 | 3.10 | 37.60 | 48.10 | 2.76 | 1.88 | 1.41 | 53.45 | 74.50 | 1.00 | 30.00 |
| Max | 11.00 | 1.00 | 4.40 | 37.70 | 11.70 | 58.50 | 52.30 | 2.77 | 1.95 | 1.49 | 58.40 | 81.00 | 1.50 | 34.00 |
| | | | | | | | Fraction | n: Coarse | | | | | | |
| n | 7 | 7 | 7 | | | | | | | | | 7 | | |
| Mean | 9.26 | 0.09 | 3.94 | | | | | | | | | 76.71 | | |
| Std. Dev. | 5.87 | 0.04 | 4.14 | | | | | | | | | 1.89 | | |
| CV | 0.63 | 0.46 | 1.05 | | | | | | | | | 0.02 | | |
| Min | 4.70 | 0.04 | 0.97 | | | | | | | | | 74.00 | | |
| Q1 | 5.20 | 0.05 | 1.00 | | | | | | | | | 75.00 | | |
| Median | 7.30 | 0.09 | 3.00 | | | | | | | | | 77.00 | | |
| Q3 | 13.00 | 0.13 | 3.60 | | | | | | | | | 77.00 | | |
| Max | 21.00 | 0.16 | 13.00 | | | | | | | | | 80.00 | | |
| | | | | | | | Fracti | on: Fine | | | | | | |
| n | 7 | 7 | 7 | | | | | | | | | 7 | | |
| Mean | 5.94 | 0.25 | 1.38 | | | | | | | | | 65.71 | | |
| Std. Dev. | 1.37 | 0.18 | 0.59 | | | | | | | | | 4.57 | | |
| CV | 0.23 | 0.71 | 0.43 | | | | | | | | | 0.07 | | |
| Min | 4.50 | 0.11 | 0.46 | | | | | | | | | 58.00 | | |
| Q1 | 4.80 | 0.11 | 0.97 | | | | | | | | | 61.00 | | |
| Median | 5.10 | 0.20 | 1.40 | | | | | | | | | 68.00 | | |
| Q3 | 7.40 | 0.46 | 1.50 | | | | | | | | | 68.00 | | |
| Max | 7.80 | 0.56 | 2.40 | | | | | | | | | 71.00 | | |

Box plots. Box plots of the sample data distribution for TOC, OC, soot, and O&G measured in the fine and coarse sediment fractions are shown in Figure 2. Organic matter phases were expressed as mass for statistical comparison between the fine and coarse fractions, and as percent of total (individual phase) mass reporting to each fraction in the box plots (for similarity of scale and visual clarity). OC and O&G mass were significantly higher in the fine fraction than in the coarse fraction, while soot and TOC mass did not differ significantly between the fractions.

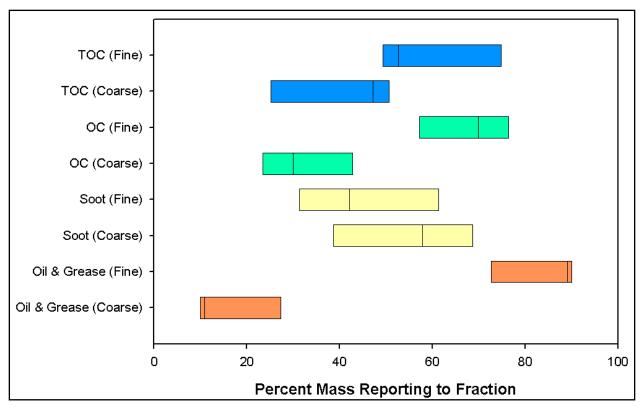


Figure 2. Box plots of sediment organic matter from seven sampled locations. Data for the coarse and fine fractions were expressed as percent of total organic mass in both fractions combined. Each box represents the interquartile range (25th to 75th percentiles) with the bar inside as the median.

Ternary diagram. There are many different ways of plotting both physical and chemical data. Each method provides a different insight into the information contained in the data. Use of histograms, univariate relative location maps, quantile-quantile (Q-Q) plots, scatterplots and other data analysis tools can reveal similarities and trends between groups of one or two variables, as detailed in multiple references on applied geostatistics (e.g., Isaaks and Srivastava 1989). The ternary plot of particle size (Figure 3) provides a slightly different and more complete, three-parameter representation of sample grain size distributions relative to each other than does the plan view and the summary tables. Similarity of locations with respect to their grain size distributions is indicated by proximity within the plot.

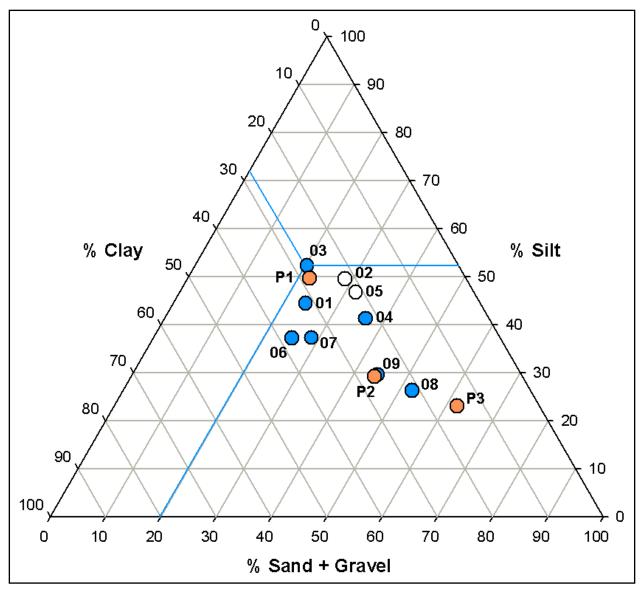


Figure 3. Ternary diagram of Chicago Area CDF sediment particle size composition. White circles are terrestrial, locations and orange circles are pond locations. Both were analyzed for grain size but not contaminants. Blue circles are terrestrial locations analyzed for grain size and contaminants. To determine percentages, read from a sample location diagonally down to the left to the % Sand + Gravel axis, diagonally up to the left to the % Clay axis, and horizontally to the right to the % Silt axis. As an example, blue lines indicate axis values for location 03 (20% sand & gravel, 52% silt, and 28% clay).

Contour plots/isopach maps. Contour plots of sand distribution in the CDF were generated using percent sand and sediment thickness data from the twelve sampled locations. In Figure 4, estimated percent sand contours were superimposed over the CDF map. Figure 5 displays sand isopachs, or contours showing estimated sand volume beneath any square foot of surface area. Both plots required the inclusion of artificial data points along the west margin of the CDF because these areas were not sampled. The contour plots were prepared using the Department of Defense Groundwater Modeling System developed by ERDC and other federal government partners as a graphical interface to construct stratigraphic conceptual models.

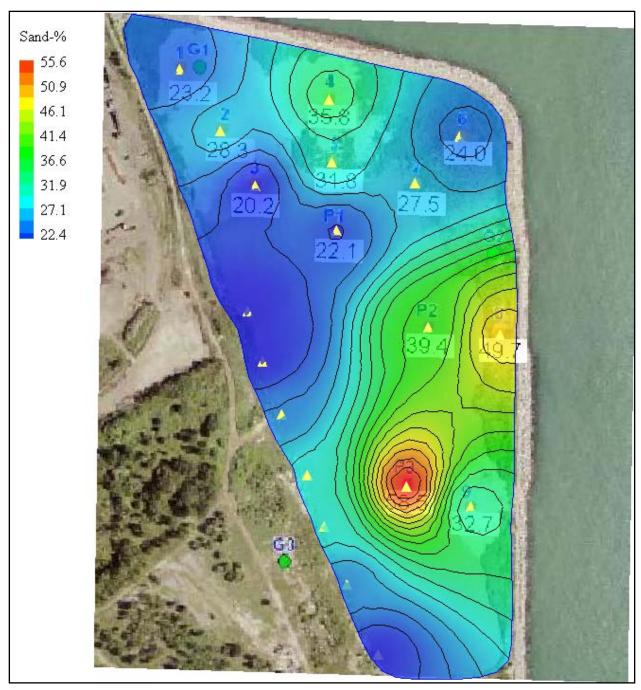


Figure 4. Simple contours of percent sand conditioned on 12 sample locations (01-09 and P1-P3). Data on the west margin are synthetic low estimates (20 percent to 30 percent, with higher values at points west of the peak at P3). These control points along the western boundary are necessary to suppress extreme extrapolation and generate reasonable contours.

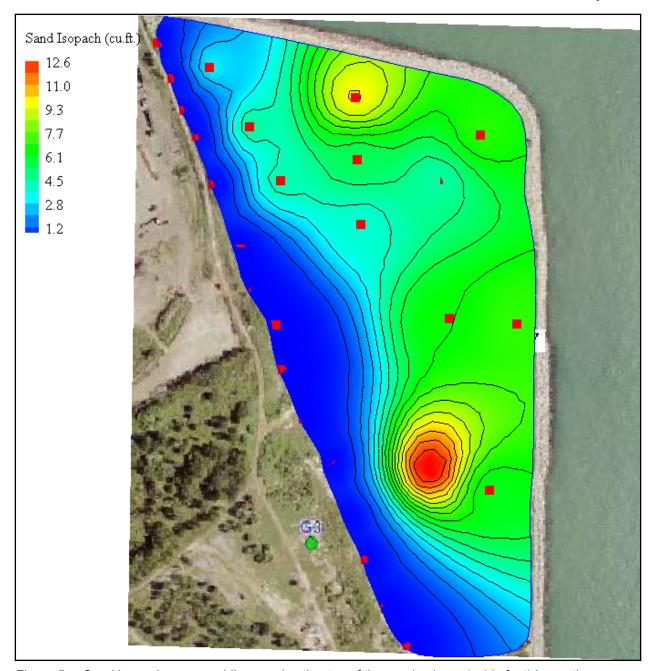


Figure 5. Sand isopach map providing areal estimates of the sand volume (cubic feet) beneath any square foot of surface area. Values are calculated by multiplying percent sand by the local sediment thickness placed in the CDF facility. In the absence of data, sediment at the west margin was assumed to be two feet thick and containing 20-30 percent sand (as in Figure 4); again, these synthetic control points are needed to generate reasonable contours by suppressing extrapolation artifacts.

Ordination plot. To determine the similarity among sampling locations based on physical parameters, data for grain size and organic matter (OC, soot, O&G) from the original fraction were included in a multivariate statistical analysis known as non-metric multi-dimensional scaling (MDS) (Clarke and Warwick 2001). MDS can be used to construct a two-dimensional map or representation of sample locations based on their statistical similarity to each other,

determined using either a similarity index or a distance measure. The resulting map, called an ordination plot, provides a visual display of how "close" (similar) the locations are to each other based on measured values of the multiple parameters included in the analysis rather than on geographic distance, as in a conventional map. Because the MDS similarities among locations are relative, the axes of the ordination plot are shown without scales (hence, "non-metric"), and the plot can be inverted or rotated in any direction. To show groups of similar locations, cluster analysis results are superimposed on the plot as rings of increasing size corresponding to increasing values of the distance measure.

The ordination plot for locations 01-09 and P1-P3 is shown in Figure 6. The size of the bubbles in Figure 6 is proportional to percent sand at each location; colors also indicate ranges of percent sand. Locations cluster into five groups: P3 and 08; P2 and 09; 06 and 07; 01, P1 and 03; and 04, 05 and 02. The first two groups form a larger cluster corresponding to locations near the central and southern part of the CDF. This appears to be the area with the most sand. The remaining three groups also form a larger cluster corresponding to locations in the northern part of the CDF. Note that each of the pond samples falls into a different group, negating the pre-sampling assertion that these locations would be predominantly fine. This may be a result of the site geometry in this case, where flow away from the discharge points was constrained by the opposing bank of the CDF.

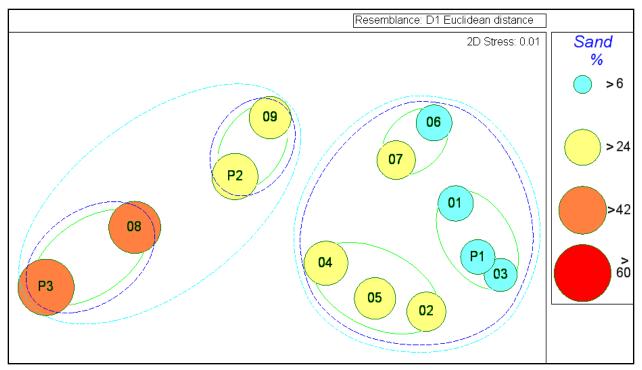


Figure 6. Ordination plot showing similarity of sample locations based on grain size and organic matter analyses for the bulk sediment. The size of the sample circles is proportional to percent sand at each location. Surrounding rings are superimposed from cluster analysis and indicate clusters of increasingly similar locations as rings become smaller.

The location similarities easily observed in the ordination plot can also be discerned in the ternary plot (Figure 3), which is based only on grain size, thus indicating that differences in organic

matter composition among locations are generally slight and do little to distinguish one location from another in this case.

Theoretically, the ordination plot, in conjunction with contour plots, may be useful in establishing preliminary excavation boundaries. In this case, the results obtained with the ordination plot seem intuitive, however, and would probably have been reached on the basis of the preceding information. The ordination plot remains a tool that is relatively easy to utilize and that may be more useful in analysis of larger sets of data where comparisons of multiple site parameters are not as readily made. The tool may be particularly valuable nonetheless, even for small data sets, in discriminating between sample sites on the basis of chemical concentrations, since there are typically many more parameters to be compared.

Comparison to material specifications. The physical properties would normally also be compared to the desired properties in the target fraction to determine whether the material will be suitable without amendment or processing. For example, sand recovered for beach nourishment will typically have a limitation on the percent fines it can contain. Because separation processes are not 100 percent efficient, some of the desired fraction may have to be sacrificed in order to meet such specifications, or additional cleaning steps may be required in order to remove undesirable phases. If the engineering properties are not compatible with the material specifications, amendment with other materials may be required. For the Chicago Area CDF, no material specifications have been determined as yet.

CHEMICAL CHARACTERIZATION

Sample selection. Physical properties are generally less costly to determine than contaminant concentrations, and are often measured in all samples, while chemical analysis is sometimes performed only on a selected subset deemed to be representative based on location, type of material, or other information. At the Chicago Area CDF, the number of samples taken for chemical analysis was largely determined by budgetary constraints. Seven of the 14 samples taken were selected for chemical analysis (locations 01, 02, 04, 06, 07, 08, and 09). These samples reflected a cross section of the CDF, and were located so that the results might be used to infer concentrations expected in nearby samples that were not analyzed for chemical contaminants. In general, further sampling and analysis may be necessary if the initial sampling results are inadequate to fully characterize the materials in the entire CDF with the necessary level of confidence. The need for additional sampling will be evaluated further through comparison to criteria and the uncertainty analysis.

Contaminant concentration summary statistics. All metals and PAHs included in the chemical analyses were detected in at least some of the CDF samples. Nine of 12 metals and all PAHs, except acenaphthylene and dibenzo(a,h)anthracene, were detected in all sediment fractions from all seven locations. PCBs were analyzed as seven Aroclor mixtures, but only Aroclors 1242 and 1254 were detected in any samples. Total PCB was therefore calculated as the sum of these two Aroclors. Nondetects are handled a variety of ways depending upon the objectives of the analysis. In this case, for computation of descriptive statistics, nondetects were assigned values equal to half of the reporting limit. This assumption is consistent with instructions for evaluating compliance with remediation objectives in Illinois Environmental Protection Agency (1997). However, other approaches may be more appropriate, given that remediation and beneficial use objectives are

not entirely consistent. This was not a crucial issue for the purposes of this analysis, but methods of evaluating data sets that do not require assumptions regarding the nondetects are available (Clarke et al. in review). Descriptive statistics for the COCs, grain size categories, and organic matter measurements in each sediment fraction are given in Tables 3 and 4.

| Analyte Class | Contaminant | Sediment Fraction | Mean | Upper 95% Confidence Limit | Standard Deviation | CV (%) | Relative Error (% of Mean) | N | Number of Non- detects |
|------------------|----------------------|----------------------|--------|----------------------------------|-----------------------|-----------|----------------------------------|---|------------------------------|
| | Arsenic | Coarse | 7.29 | 9.74 | 3.35 | 46 | 40 | 7 | 0 |
| | 7 11 301 110 | Fine | 14.26 | 17.56 | 4.49 | 32 | 27 | 7 | 0 |
| | | Original | 13.90 | 16.84 | 4.00 | 29 | 25 | 7 | 0 |
| | Barium | Coarse | 36.74 | 53.15 | 22.34 | 61 | 53 | 7 | 0 |
| | | Fine | 58.04 | 72.64 | 19.88 | 34 | 30 | 7 | 0 |
| | | Original | 55.77 | 64.82 | 12.32 | 22 | 19 | 7 | 0 |
| | Beryllium | Coarse | 0.38 | 0.50 | 0.17 | 45 | 39 | 7 | 0 |
| | | Fine | 0.68 | 0.82 | 0.19 | 28 | 24 | 7 | 0 |
| | | Original | 0.69 | 0.83 | 0.19 | 28 | 24 | 7 | 0 |
| | Cadmium | Coarse | 0.45 | 0.63 | 0.25 | 55 | 48 | 7 | 0 |
| | | Fine | 2.01 | 2.93 | 1.26 | 62 | 54 | 7 | 0 |
| | | Original | 1.67 | 2.32 | 0.89 | 54 | 47 | 7 | 0 |
| | Chromium | Coarse | 18.13 | 22.34 | 5.74 | 32 | 28 | 7 | 0 |
| | | Fine | 52.90 | 67.52 | 19.90 | 38 | 33 | 7 | 0 |
| | | Original | 47.83 | 60.35 | 17.05 | 36 | 31 | 7 | 0 |
| | Chromium, Hexavalent | Coarse | 0.91 | 1.51 | 0.81 | 89 | 77 | 7 | 3 |
| | | Fine | 0.45 | 0.59 | 0.19 | 41 | 35 | 7 | 6 |
| Metal, | | Original | 0.62 | 1.04 | 0.58 | 95 | 83 | 7 | 5 |
| mg/Kg | Copper | Coarse | 28.73 | 35.55 | 9.29 | 32 | 28 | 7 | 0 |
| | | Fine | 72.23 | 92.5 | 27.61 | 38 | 33 | 7 | 0 |
| | | Original | 67.34 | 83.3 | 21.73 | 32 | 28 | 7 | 0 |
| | Lead | Coarse | 70.09 | 102.3 | 43.79 | 62 | 54 | 7 | 0 |
| | | Fine | 195.96 | 272.1 | 103.63 | 53 | 46 | 7 | 0 |
| | | Original | 175.01 | 232.4 | 78.09 | 45 | 39 | 7 | 0 |
| | Mercury | Coarse | 0.17 | 0.28 | 0.15 | 93 | 81 | 7 | 0 |
| | | Fine | 0.29 | 0.49 | 0.28 | 98 | 85 | 7 | 0 |
| | | Original | 0.26 | 0.42 | 0.22 | 83 | 72 | 7 | 0 |
| | Nickel | Coarse | 19.19 | 23.97 | 6.52 | 34 | 30 | 7 | 0 |
| | | Fine | 38.47 | 47.18 | 11.86 | 31 | 27 | 7 | 0 |
| | | Original | 34.36 | 43.96 | 13.07 | 38 | 33 | 7 | 0 |
| | Selenium | Coarse | 0.39 | 0.57 | 0.24 | 60 | 52 | 7 | 6 |
| | | Fine | 0.69 | 0.92 | 0.32 | 46 | 40 | 7 | |
| | | Original | 1.02 | 1.41 | 0.54 | 53 | 46 | 7 | 7 |
| | Silver | Coarse | 1.22 | 3.29 | 2.81 | 230 | 200 | 7 | 4 |
| | | Fine | 1.30 | 2.72 | 1.94 | 149 | 130 | 7 | 0 |
| | | Original | 1.25 | 2.70 | 1.98 | 159 | 139 | 7 | 4 |

| Analyte Class | Contaminant | Sediment Fraction | Mean | Upper 95% Confidence Limit | Standard Deviation | CV (%) | Relative Error (% of Mean) | N | Number of Non- detects |
|------------------|------------------------|----------------------|--------|----------------------------------|-----------------------|-----------|----------------------------------|---|------------------------------|
| | Arsenic, TCLP | Coarse | 7.54 | 8.41 | 1.18 | 16 | 14 | 7 | 0 |
| | Barium, TCLP | Coarse | 452.43 | 531.3 | 107.33 | 24 | 21 | 7 | 0 |
| | Beryllium, TCLP | Coarse | 0.57 | 0.74 | 0.24 | 41 | 36 | 7 | 1 |
| | Cadmium, TCLP | Coarse | 1.19 | 1.78 | 0.81 | 68 | 59 | 7 | 2 |
| | Chromium, TCLP | Coarse | 2.00 | 2.74 | 1.00 | 50 | 44 | 7 | 1 |
| Metal | Copper, TCLP | Coarse | 2.28 | 3.32 | 1.42 | 62 | 54 | 7 | 6 |
| TCLP, µg/L | Lead, TCLP | Coarse | 152.30 | 301.5 | 203.12 | 133 | 116 | 7 | 0 |
| r-3· – | Mercury, TCLP | Coarse | 0.02 | | 0.00 | 0 | 0 | 7 | 4 |
| | Nickel, TCLP | Coarse | 85.73 | 102.0 | 22.20 | 26 | 23 | 7 | 0 |
| | Selenium, TCLP | Coarse | 3.59 | | 0.00 | 0 | 0 | 7 | 7 |
| | Silver, TCLP | Coarse | 1.04 | | 0.00 | 0 | 0 | 7 | 7 |
| | Zinc, TCLP | Coarse | 880.00 | 1179 | 407.77 | 46 | 40 | 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 | 0 |
| | 2-Methylnaphthalene | Coarse | 0.54 | 0.68 | 0.20 | 37 | 32 | 7 | 0 |
| | | Fine | 0.44 | 0.71 | 0.37 | 85 | 74 | 7 | 0 |
| | | Original | 0.61 | 1.20 | 0.79 | 130 | 113 | 7 | 0 |
| | Acenaphthene | Coarse | 0.70 | 0.94 | 0.33 | 47 | 41 | 7 | 0 |
| | | Fine | 0.40 | 0.55 | 0.20 | 50 | 44 | 7 | 0 |
| | | Original | 0.47 | 0.79 | 0.44 | 93 | 81 | 7 | 0 |
| | Acenaphthylene | Coarse | 0.26 | 0.32 | 0.08 | 33 | 29 | 7 | 0 |
| | | Fine | 0.12 | 0.15 | 0.04 | 32 | 27 | 7 | 1 |
| | | Original | 0.16 | 0.24 | 0.11 | 71 | 61 | 7 | 1 |
| | Anthracene | Coarse | 0.93 | 1.29 | 0.49 | 53 | 46 | 7 | 0 |
| | | Fine | 0.37 | 0.49 | 0.16 | 44 | 38 | 7 | 0 |
| | | Original | 0.49 | 0.68 | 0.26 | 53 | 46 | 7 | 0 |
| | Benzo(a)anthracene | Coarse | 1.95 | 2.72 | 1.05 | 54 | 47 | 7 | 0 |
| | | Fine | 0.75 | 0.94 | 0.26 | 34 | 30 | 7 | 0 |
| | | Original | 1.23 | 1.75 | 0.72 | 58 | 51 | 7 | 0 |
| | Benzo(a)pyrene | Coarse | 1.81 | 2.51 | 0.95 | 53 | 46 | 7 | 0 |
| PAH, mg/Kg | | Fine | 0.62 | 0.83 | 0.29 | 48 | 41 | 7 | 0 |
| ilig/itg | | Original | 0.98 | 1.41 | 0.59 | 60 | 52 | 7 | 0 |
| | Benzo(b)fluoranthene | Coarse | 2.18 | 3.10 | 1.25 | 57 | 50 | 7 | 0 |
| | | Fine | 0.94 | 1.20 | 0.35 | 38 | 33 | 7 | 0 |
| | | Original | 1.33 | 1.88 | 0.75 | 56 | 49 | 7 | 0 |
| | Benzo(k)fluoranthene | Coarse | 0.93 | 1.38 | 0.62 | 67 | 58 | 7 | 0 |
| | | Fine | 0.25 | 0.33 | 0.11 | 46 | 40 | 7 | 0 |
| | | Original | 0.39 | 0.59 | 0.26 | 66 | 58 | 7 | 0 |
| | Benzo(g,h,i)perylene | Coarse | 1.05 | 1.50 | 0.62 | 59 | 51 | 7 | 0 |
| | | Fine | 0.35 | 0.45 | 0.15 | 42 | 37 | 7 | 0 |
| | | Original | 0.53 | 0.74 | 0.29 | 56 | 49 | 7 | 0 |
| | Chrysene | Coarse | 2.30 | 3.18 | 1.20 | 52 | 45 | 7 | 0 |
| | | Fine | 0.79 | 1.06 | 0.38 | 48 | 42 | 7 | 0 |
| | | Original | 1.28 | 1.90 | 0.84 | 66 | 57 | 7 | 0 |
| | Dibenzo(a,h)anthracene | Coarse | 0.47 | 0.60 | 0.19 | 40 | 35 | 7 | 0 |
| | | Fine | 0.16 | 0.23 | 0.09 | 52 | 46 | 7 | 2 |
| | | Original | 0.26 | 0.37 | 0.15 | 56 | 49 | 7 | 0 |

| Analyte Class | Contaminant | Sediment Fraction | Mean | Upper 95% Confidence Limit | Standard Deviation | CV (%) | Relative Error (% of Mean) | N | Number of Non-detects |
|------------------|------------------------|----------------------|------|----------------------------------|-----------------------|-----------|----------------------------------|---|-----------------------|
| | Fluoranthene | Coarse | 3.46 | 4.77 | 1.78 | 52 | 45 | 7 | 0 |
| | | Fine | 1.48 | 1.84 | 0.48 | 32 | 28 | 7 | 0 |
| | | Original | 2.09 | 2.85 | 1.03 | 49 | 43 | 7 | 0 |
| | Fluorene | Coarse | 0.78 | 1.20 | 0.57 | 74 | 64 | 7 | 0 |
| | | Fine | 0.47 | 0.60 | 0.17 | 37 | 32 | 7 | 0 |
| | | Original | 0.57 | 0.81 | 0.32 | 57 | 49 | 7 | 0 |
| | Indeno(1,2,3-cd)pyrene | Coarse | 1.12 | 1.58 | 0.63 | 56 | 49 | 7 | 0 |
| | | Fine | 0.41 | 0.52 | 0.16 | 39 | 34 | 7 | 0 |
| PAH, | | Original | 0.66 | 0.87 | 0.29 | 44 | 38 | 7 | 0 |
| mg/Kg | Naphthalene | Coarse | 2.79 | 7.07 | 5.84 | 210 | 182 | 7 | 0 |
| | | Fine | 4.16 | 11.24 | 9.64 | 232 | 202 | 7 | 0 |
| | | Original | 6.68 | 18.77 | 16.46 | 246 | 214 | 7 | 0 |
| | Phenanthrene | Coarse | 3.51 | 5.33 | 2.47 | 70 | 61 | 7 | 0 |
| | | Fine | 1.48 | 2.16 | 0.93 | 63 | 55 | 7 | 0 |
| | | Original | 2.34 | 3.66 | 1.80 | 77 | 67 | 7 | 0 |
| | Pyrene | Coarse | 3.51 | 4.94 | 1.96 | 56 | 49 | 7 | 0 |
| | | Fine | 1.65 | 2.16 | 0.70 | 42 | 37 | 7 | 0 |
| | | Original | 2.19 | 3.23 | 1.42 | 65 | 56 | 7 | 0 |
| | Aroclor 1242 | Coarse | 0.65 | 1.13 | 0.66 | 101 | 87 | 7 | 0 |
| | | Fine | 0.85 | 1.50 | 0.88 | 103 | 90 | 7 | 1 |
| | | Original | 1.47 | 2.66 | 1.62 | 110 | 95 | 7 | 1 |
| | Aroclor 1254 | Coarse | 0.27 | 0.39 | 0.17 | 61 | 53 | 7 | 0 |
| PCB, mg/Kg | | Fine | 0.27 | 0.39 | 0.17 | 62 | 54 | 7 | 1 |
| e, . e, . | | Original | 0.23 | 0.40 | 0.23 | 103 | 90 | 7 | 2 |
| | Total PCB | Coarse | 0.92 | 1.48 | 0.75 | 82 | 71 | 7 | 0 |
| | | Fine | 1.12 | 1.88 | 1.03 | 91 | 80 | 7 | 1 |
| | | Original | 1.70 | 3.02 | 1.80 | 106 | 92 | 7 | 2 |

Box plots provide a visual comparison of contaminant levels in the different sediment fractions, reflecting the interquartile range (25th to 75th percentiles) and the median. For example, median PAH concentrations were consistently higher in the coarse fraction (Figures 7 and 8), indicating that further evaluation of the composition of that fraction will be necessary if the concentrations are high enough to be problematic with respect to the intended BU placement and the applicable criteria. In only one sample did PAH concentrations tend to be higher in the fines (location 08). The elevated PAHs in the coarse fraction may be attributable to the presence of soot, which occurred in higher concentrations in the coarse fraction than in the fine fraction (Figure 2). Contaminant relationships with organic phases should be explored through correlation and regression analysis, in order to identify appropriate unit operations for separation. In some cases (including the case study), however, correlations can be difficult to establish. Where contaminant concentrations present an impediment to BU, physical testing may then be required to empirically establish a contaminant reduction approach.

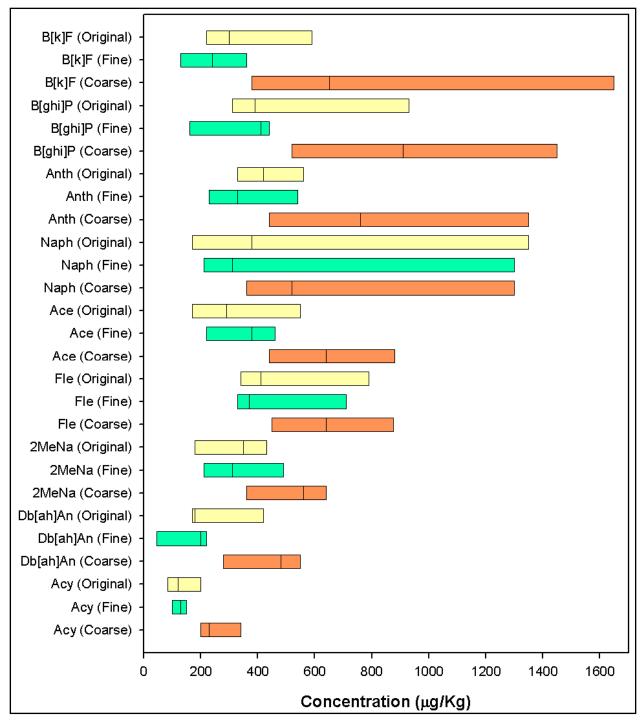


Figure 7. Box plots of PAH concentrations in bulk sediment (Original) and Fine and Coarse sediment fractions. B[k]F, benzo(k)fluoranthene; B[ghi]P, benzo(g,h,i)perylene; Anth, anthracene; Naph, naphthalene; Ace, acenaphthene; Fle, fluoranthene; 2MeNa, 2-methyl naphthalene; Db[ah]An, dibenzo(a,h)anthracene; Acy, acenaphthylene.

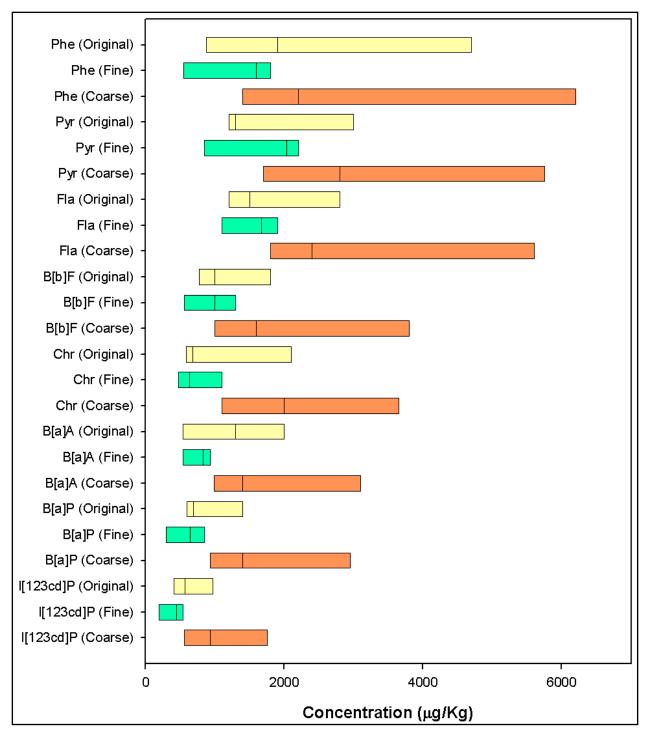


Figure 8. Box plots of PAH concentrations in bulk sediment (Original) and Fine and Coarse sediment fractions. Phe, phenanthrene; Pyr, pyrene; Fla, fluoranthene; B[b]F, benzo(b)fluoranthene; Chr, chrysene; B[a]A, benzo(a)anthracene; B[a]P, benzo(a)pyrene; I[123cd]P, indeno(1,2,3-cd)pyrene.

Ordination plots. These plots were generated for chemistry data, using an entire class of contaminants (e.g., metals or PAHs) in a MDS analysis. Figure 9 illustrates a typical result obtained for the metals, and Figure 10 displays a typical result obtained for the PAHs. Groupings vary

slightly, but for metals, the one sample consistently found to fall outside all of the sample groups was location 09, and for PAHs, location 06. These plots can also be used to display the relative concentrations of any contaminant included in the MDS, for example chromium in the metals MDS (Figure 9) and acenaphthylene in the PAH MDS (Figure 10).

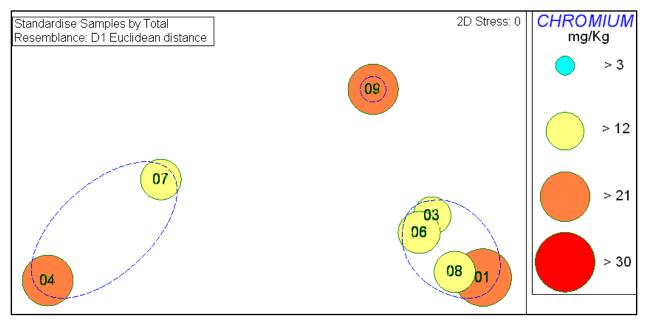


Figure 9. Ordination plot generated using MDS analysis showing similarity of metals concentrations (for all metals) in coarse fraction from different sample locations. Bubble sizes indicate relative concentrations of chromium (mg/Kg).

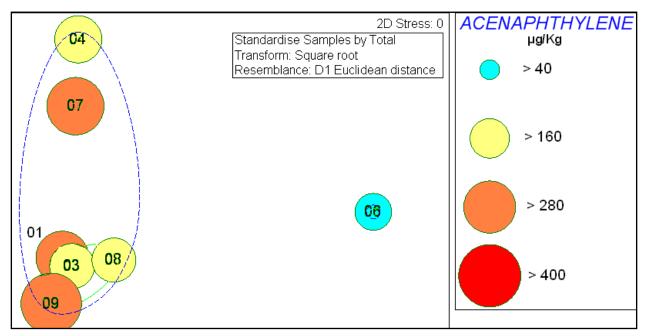


Figure 10. Ordination plot generated using MDS analysis showing similarity of PAH concentrations (for all PAHs) in coarse fraction from different sample locations. Bubble sizes indicate relative concentrations of acenaphthylene (μg/Kg). A square root data transform was employed to improve clarity of the plot.

Q-Q plots, histograms and other tests of distribution. The frequency distribution of the data (e.g., normal, lognormal or non-normal) will determine the statistical tools and models appropriate for a particular data set. Distribution assumptions about the data can be evaluated using methods such as Shapiro-Wilk's test for normality, histograms, and quantile-quantile (Q-Q) plots. Such methods can be valuable in the selection of the most appropriate measures of central tendency (e.g., mean or median), confidence intervals (e.g., normal, lognormal, gamma, or nonparametric), and possible data transformations (e.g., logarithms) for use in subsequent statistical analyses.

Figure 11 shows the histograms for three PAHs, with likely distributional curves. The distributional curves are seen to be skewed, suggesting that the data for these PAHs follow a lognormal or gamma distribution rather than the symmetrical normal distribution.

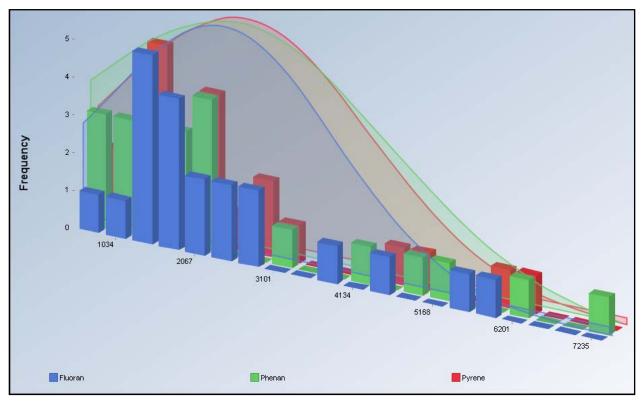


Figure 11. Histogram for the PAHs fluoranthene, phenanthrene, and pyrene (all sediment fractions).

Q-Q plots display the ordered data observations against the theoretical quantiles of the distribution of interest, and often include the regression line relating the two. If the data are distributed as hypothesized, the data points will plot close to the regression line. The distributions of all contaminants were evaluated using Q-Q plots, and an example is given in Figure 12, showing the normal Q-Q plots for fluoranthene, phenanthrene, and pyrene. The ordered observations do not plot close to the regression lines, especially at the extremes of the data range, suggesting again that these data are not normally distributed.

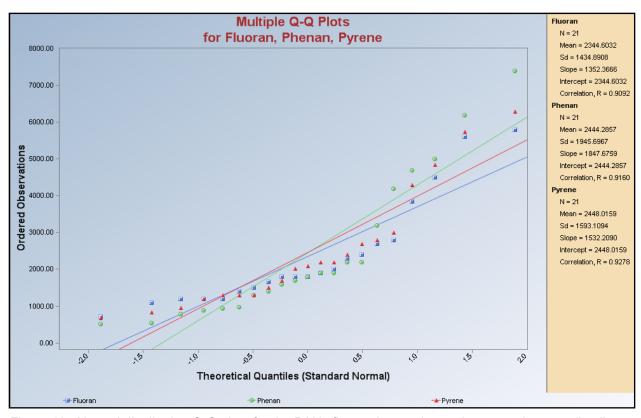


Figure 12. Normal distribution Q-Q plots for the PAHs fluoranthene, phenanthrene, and pyrene (in all sediment fractions).

Similarly, a lognormal Q-Q plot (the ordered logarithms of the data observations plotted against the theoretical normal quantiles) could be developed to verify the assumption of lognormality. Figure 13 displays Q-Q plots for the same three PAHs after the data have been transformed using base 10 logarithms. The central values as well as the tails of the transformed data plot closer to the standard normal regression lines than do the untransformed data (Figure 12), suggesting a good fit to the lognormal distribution.

Analyses of association and prediction. Correlation analysis can be used to evaluate the strength of the association between chemical concentrations and physical properties such as carbon phases. Theoretically, where the association is somewhat consistent, regression analysis can enable estimation of contaminant concentrations in samples where contaminants were not measured, based on the corresponding physical properties. In this way, it may be possible to obtain more information regarding the material in the CDF at lower cost.

Correlation analysis. Spearman's rank correlation analysis was performed in order to evaluate the relationship between chemical analytes and carbon phases (TOC, OC, O&G, soot) in the sediment. Rank correlation is nonparametric and does not require assumptions about the shape of the data distributions. Only a few significant correlations (P < 0.01) were observed; all were positive, indicating increasing contaminant concentration with increasing amounts of organic matter) (Table 5). This result is as expected for hydrophobic organic contaminants, which have a high affinity for carbon phases; similar trends are sometimes observed for metals. Figure 14

illustrates the relationship of soot with barium and benzo(a)pyrene in the different sediment fractions.

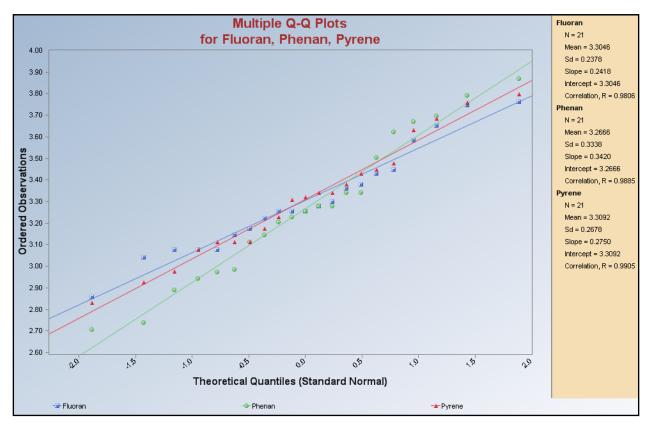


Figure 13. Lognormal distribution Q-Q plots for the PAHs fluoranthene, phenanthrene, and pyrene (in all sediment fractions).

| | Table 5. Significant Correlations of Analytes with Sorptive Phases (Spearman's ρ; P<0.01; n=7) | | | | | | | | | | |
|------|--|----------------------|----------|--|--|--|--|--|--|--|--|
| | Fraction | | | | | | | | | | |
| | Coarse | Fine | Original | | | | | | | | |
| 000 | | Arsenic | Nickel | | | | | | | | |
| O&G | | Nickel | | | | | | | | | |
| тос | | Beryllium | Lead | | | | | | | | |
| | | Barium | | | | | | | | | |
| | | Chromium | | | | | | | | | |
| Soot | | Benzo(a)pyrene | | | | | | | | | |
| | | Benzo(k)fluoranthene | | | | | | | | | |
| | | Fluoranthene | | | | | | | | | |
| ос | Chromium, TCLP | | | | | | | | | | |

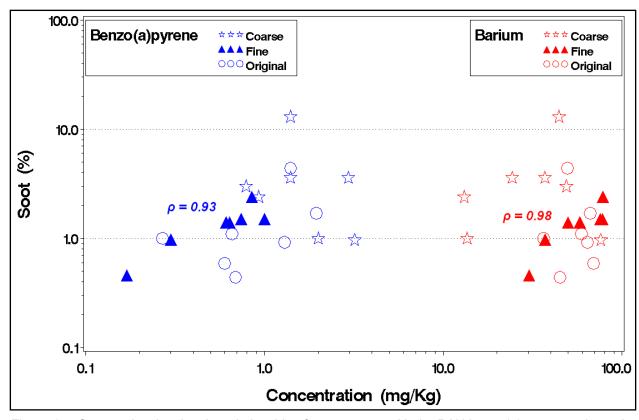


Figure 14. Scatter plot showing the relationship of percent soot with the PAH benzo(a)pyrene and metal barium in each sediment fraction. Spearman's correlation coefficients (ρ) are given for the significant correlations, which occurred only in the fine fraction (solid triangle symbols).

TCLP results are often, though not necessarily appropriately¹, used to assess whether environmentally unacceptable releases would occur as a result of leaching from the dredged material in the upland environment. In the Chicago Area CDF, TCLP testing was done only on the coarse sediment fraction, since that is the fraction targeted for recovery and beneficial use. Previous sorption studies suggest that sorption to hard carbon phases, such as soot, may be largely irreversible, while sorption to more amorphous phases, such as OC, is reversible under favorable conditions. Kan et al. (1998) observed that there was a component of irreversible sorption for each of three sediments studied and proposed a two-phase sorption model to describe reversible and irreversible components. Related research has focused on the existence of organic matter domains. Young, amorphous organic material demonstrates different sorption properties than more condensed or glassy forms such as soot, which has high specificity for organic contaminants (Karapanagioti et al. 2000, Kan et al. 1998).

Correlation of the TCLP concentrations and organic matter phases was evaluated to assess the significance of this factor in the Chicago Area CDF sediments. The only significant TCLP

¹ The TCLP test was designed to reflect conditions present in a municipal landfill; test conditions are not representative of the typical beneficial use placement. Extractions are conducted using either a sodium acetate buffer solution at pH 4.93 or an acetic acid solution at pH 2.88, depending on the alkalinity of the waste. A variety of leaching tests have subsequently been developed, such as the DIWET, RAINWET (ERS 2005) and SLRP (Price and Skogerboe 2000), that may provide more representative results for beneficial use of dredged material.

correlation observed was chromium with OC. The data (seven samples) show that the concentration of TCLP Cr increases with the concentration of OC, which would appear to suggest higher mobility for OC-associated Cr. However, the geochemistry behind this trend is unclear and there is some uncertainty associated with the data, as one of the seven samples was below and two were near the reporting limit.

Observed concentrations in the separate fractions may be helpful in inferring what processes are responsible for contaminant levels in the target fraction. In this case, concentrations of all metals except barium, hexavalent chromium, mercury, and silver were significantly higher in the fine and/or the original sediment fractions than in the coarse fraction. The coarse fraction had significantly higher concentrations of most PAHs than the fine fraction, however. These two observations suggest that carryover of fines into the coarse fraction could be responsible for metals concentration in the sand, but that this would not fully explain the higher concentrations of PAHs in the sand. PCBs did not differ significantly among the sediment fractions, suggesting that the associated phases are distributed throughout the different grain sizes.

Simple linear regression analysis. To determine whether concentrations of any of the identified sorptive phases (soot, O&G, and OC) could be used to predict the concentrations of COCs in un-analyzed samples, simple linear regression analyses were performed on both untransformed and \log_{10} -transformed concentration data using the familiar ordinary least squares (OLS) method. Most OLS regressions were either nonsignificant ($P \ge 0.05$), or were severely affected by influence points² or outliers due to small sample size. Among the few significant regressions, the best example is the regression of arsenic on O&G shown in Figure 15. Although there is considerable scatter, all data points fall within the regression 95 percent confidence limits for prediction of individual values (dashed lines). The potential utility of this analysis is illustrated by superimposing two different criteria that might be applied to dredged material being considered for beneficial use.

Multiple regression analysis. In practice, the single paired variable analysis is usually too simplistic to adequately represent the physical model, where sorption occurs in competition with multiple contaminants and multiple phases, and the results are not reliably predictive. A multivariate approach may be more successful and more accurate in quantifying the desired relationships. Multiple regression analysis, for example, examines the contribution of two or more predictor variables. OLS multiple regressions were done for organics and metals using O&G, soot, and OC as predictor variables, but these were significant predictors for only a very few contaminants.

Entropy is another multivariate procedure that can produce more meaningful results than OLS regressions in some cases. Entropy fits linear regression models by taking prior assumptions about the parameters and errors to obtain parameter estimates. Estimates obtained by this method are biased, but regression mean squared error terms are expected to be smaller than those obtained from traditional regression methods. The method is reported to be more robust than conventional OLS regression for data sets where some distributional assumptions are violated, as when: outliers are present, predictor variables in the model are highly correlated, there are fewer

¹ Analysis of variance and Tukey's HSD means comparison test, P < 0.05

² Influence points are observations that unduly influence the slope of the regression line.

observations than parameters to estimate, or parameter estimates obtained from more traditional methods are counterintuitive (Personal communication SAS Technical Support August 04, 2004). For example, parameter coefficients can be constrained to positive values using Entropy. Entropy procedures are used to solve economics problems where the desired parameter cannot be measured, and only non-experimental observational data are available (Golan et al. 1996). This is essentially analogous to the problem of estimating phase-specific concentrations when the phases cannot be effectively separated for direct measurement of contaminant concentration (Estes 2005). The fractionation data sets are also good candidates for this procedure as they evidence some non-normality, collinearity, and instability of variance. Additionally, conventional regression methods produced negative coefficients having no physical significance.

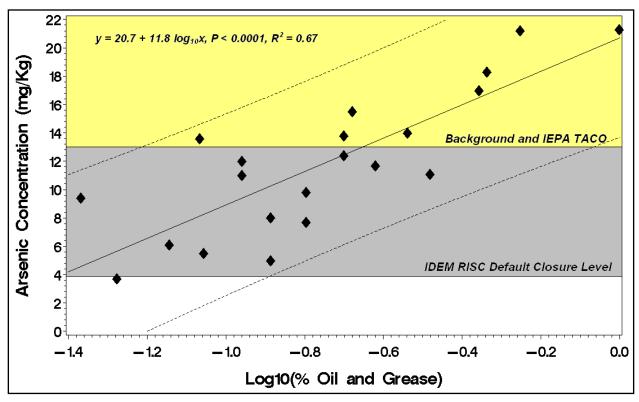


Figure 15. Linear regression of arsenic on percent oil and grease (by weight) for all sediment fractions combined. Diagonal solid and dashed lines indicate regression line and 95 percent confidence limits for prediction of individual values. Illinois and Indiana remediation objectives for arsenic in soil are also shown.

To improve the predictive ability of the regression model (both OLS and Entropy), it can be useful to reduce the full model by eliminating poor quality data points, including outliers and data whose values are uncertain (nondetects). Contaminant outliers were identified through an initial run of the Entropy model. For each contaminant, the predicted values obtained using Entropy were regressed by simple OLS against the observed concentrations, and the studentized residuals were calculated. Since approximately 95 percent of studentized residuals will lie within the bounds (-2, 2) (Draper and Smith 1981), observations with studentized residuals > |2| were

¹ A studentized (or standardized) residual is the residual (the difference between observed and predicted values) divided by its standard error; this puts the residuals for different variables on a similar scale.

considered to be outliers and were removed from the data set prior to the final multiple regression analyses. Predictor variables for the multiple regressions included soot, OC, and O&G, in a no-intercept model for all sediment fractions combined. A no-intercept model was employed in order to assign all the variability of the contaminant concentrations to the sorptive phases, rather than to the intercept (analogous to an unknown cause). This method has been found to be more successful in analysis of fractionation data than use of an unconstrained model. Outliers among the predictor variables were identified using Dixon's test (Barnett and Lewis 1984) and were also removed prior to the reduced model regression analyses.

The coefficients of determination (R²) calculated in the SAS Entropy and OLS regression models are not directly comparable. Therefore, the predicted contaminant concentrations obtained from each model were regressed against the actual observed concentrations using simple OLS to obtain comparable R² for evaluation of the competing models. In a perfect model, all predicted concentrations would be identical to their respective observed concentrations and R² would equal 1. Removal of nondetects and outliers improved the predictive ability of both OLS and Entropy regression models for all contaminants (Figure 16), resulting in higher R² as compared to the full OLS model. An extreme example, hexavalent chromium, is displayed in Figure 17. The data for hexavalent chromium included 14 nondetects and one outlier; eliminating these observations resulted in substantial improvement in predictive ability. For most contaminants, the OLS reduced model ultimately provided a slightly better fit than the Entropy reduced model (Figure 16). It is also clear that the sorptive phases soot, OC, and O&G were poor predictors of PAH concentrations in the CDF sediment samples. This was an unexpected result that was not fully explained by the data analysis conducted. A number of factors may have contributed to this. There is not a clear delineation between amorphous organic carbon (OC) and soot, for example. The soot measurement procedure is based on an arbitrary combustion temperature believed to remove most of the less condensed carbon phases from a sample. Pre-treating a sample at a different temperature would produce different measurements of soot and OC, which might have an impact on the resulting correlation analysis. Potentially there is some overlap of soot and OC measurements. Further, the sorptive phases may or may not exist as discrete phases. Contaminant association with a given phase might then be limited by layering of the phases on other particulates, or on each other. Each soil and sediment is different, and it seems likely that the physical model is therefore different in each. Analytical limitations may have also contributed to poor correlations. There is potentially some overlap of O&G and PCBs measurement, for example, since some PCBs exist as an oily phase. Lastly, small sample size may have been a factor, but typically some association can be seen even with small samples, so this does not fully explain the lack of correlation here.

UNCERTAINTY ANALYSIS is simply the quantification of variability in the parameters of interest. Quantification of variability is typically employed in the comparison of contaminant levels with applicable regulatory criteria, and is a necessary first step in the determination of sample size needed to estimate mean parameter values at a given level of confidence, or within a given margin of error.

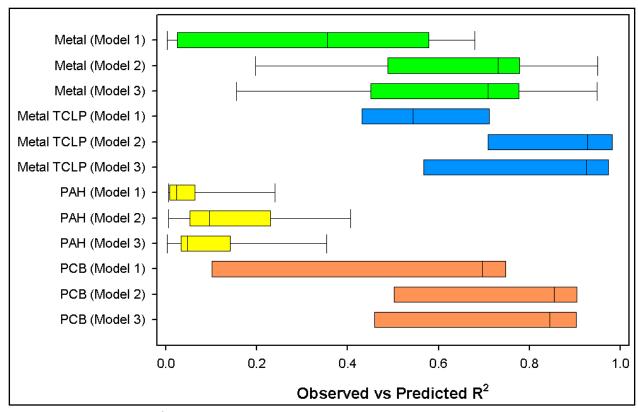


Figure 16. Box plots of R² for three multiple regression models of observed vs predicted analyte concentration values: OLS full (Model 1), OLS reduced (Model 2), and Entropy reduced (Model 3). Reduced models have outliers and nondetects removed. Boxes show the 25th, 50th, and 75th percentiles of R² while the whiskers indicate 5th and 95th percentiles (given sufficient number of analytes in a contaminant class).

Estimates of variability. Analyte uncertainty encompasses both the variability in the quantitative analysis of the analytes, and uncertainty surrounding their spatial distribution within the CDF. Analytical variability is assessed using standard quality assurance/quality control measures such as laboratory replicates. Spatial distribution uncertainty is addressed initially in the development of the sampling plan, utilizing available information to inform sample site selection and compositing. Before selecting a location and initiating the compositing of samples, known factors such as sediment depth and differences between sediment grain size and organic matter should be considered. Spatial variation in such factors can be used as the basis for stratification in a sampling plan, resulting in concentration of samples in areas of greater economic interest (e.g., sandy areas), and leading to more efficient estimates of desired parameters than might be obtained from simple, randomized sampling. Following sample collection and analysis, the spatial variation and uncertainty of the analytes of interest is quantified using measures such as variance, standard deviation, coefficient of variation (CV), and confidence limits. These tools can be used to assess the sufficiency of the data set in characterizing the CDF and the materials for their intended purpose.

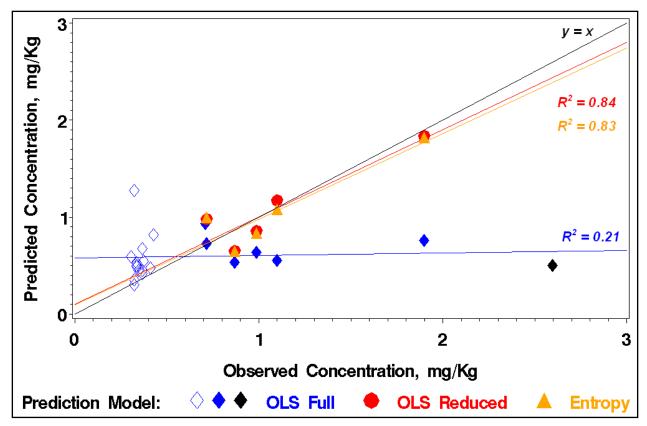


Figure 17. Comparison of predicted and observed concentrations of hexavalent chromium resulting from three multiple regression models using sorptive phases (soot, OC, and O&G) as predictor variables. Open symbols are nondetects, filled symbols are detected concentrations, and the black symbol is a contaminant outlier.

Standard deviation and CV for the CDF sediment analytes are shown in Tables 3 and 4. CV expresses the ratio of the standard deviation to the mean, with high values reflecting high variability in the results and low values reflecting little variability. For the Chicago CDF samples (all sediment fractions), CV ranged from 18 to 105 percent for organic phases, 24 to 150 percent for grain size fractions, 2 to 14 percent for other physical parameters, 22 to 230 percent for metals, 16 to 133 percent for TCLP metals, 32 to 246 percent for PAHs, and 61 to 110 percent for PCBs.

Eleven percent of analytes had CVs greater than 100 percent; only naphthalene and silver had CVs greater than 200 percent. Analytes with high CVs had highly variable concentrations in all three sediment fractions. Besides reflecting data variability, high CVs are often indicative of outliers. An example can be seen in Figure 18 where the coarse fraction soot concentration for location 01 is 13 percent, clearly an outlier, and the corresponding CV for coarse fraction soot is 105 percent. While outlier removal is commonplace for improving the predictive function of regression models, it may be undesirable in other types of data analysis, such as comparison with other treatments or with criteria. In all situations, the data should first be examined to determine whether analytical or transcription errors may have occurred. If no inconsistencies in the results or procedures can be identified, the outlier may reflect a fairly random, but real, condition.

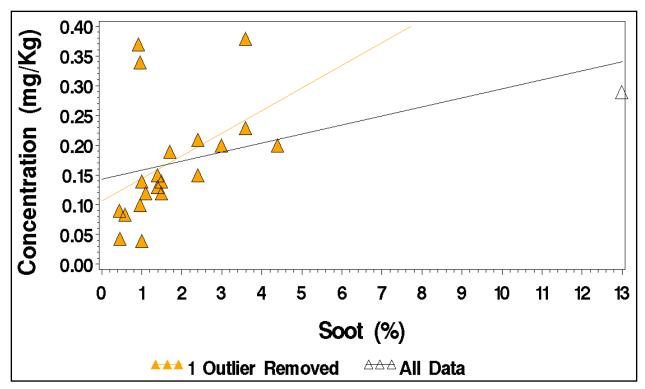


Figure 18. Impact of outlier on OLS regression of acenaphthylene vs. percent soot (for all sediment fractions combined).

Calculation of sample size. Estimates of variability can be used to calculate the approximate number of samples needed to detect a specified difference from numerical criteria. Using the general formula from Appendix D of the Inland Testing Manual (USEPA and USACE 1998) where n is the number of samples and d the difference from a fixed criterion value:

$$n \ge \frac{\left(z_{1-\alpha} + z_{1-\beta}\right)^2 s^2}{d^2} + 0.5 z_{1-\alpha}^2 \tag{1}$$

In Equation 1, z is the standard normal deviate or z-score corresponding to a selected confidence probability $1-\alpha$ and desired power $1-\beta$, and s^2 is the sample variance. The final term of the equation $(0.5z^2_{1-\alpha})$ is a correction factor for small sample size and the use of the sample variance in place of the unknown population variance. Equation 1 is appropriate when a one-tailed comparison is needed, as when the objective is to demonstrate whether a parameter mean is less than some criterion. For a two-tailed comparison (e.g., where it is necessary to demonstrate that the mean of a parameter does not differ from some specified value), one would use a z-score reflecting a confidence probability of $1-\alpha/2$.

To calculate the sample size needed to determine a mean within a measure of error at a given level of confidence $1-\alpha$, when no comparisons with criteria are needed, a simpler formula may be used:

 $^{^{1}}$ A slightly more accurate formula uses Student's t instead of z and does not require a correction factor, but does require iterative solution.

$$n \ge \frac{z_{1-\alpha/2}^2 CV^2}{d^2} + 0.5z_{1-\alpha/2}^2 \tag{2}$$

where CV is expressed as percent and d is the relative error expressed as percent of the mean.

Table 4 gives the relative error for contaminants measured in each fraction, obtained by rearranging Equation 2 to solve for *d* when *n* was the actual sample size used in the Chicago Area CDF characterization study. Assuming a normal distribution and 95 percent confidence level, relative errors ranged from zero to 214 percent of the mean and correlated closely with the CV. High CVs and high relative errors can be considered an indication of inadequate sampling.

Figure 19 displays the approximate minimum required sample size, plotted against the observed CVs, using relative errors of 10, 25, 50 and 100 percent of the mean analyte concentration as d in Equation 2. If the acceptable relative error is high, for example, 100 percent of the mean, the minimum required sample size will be ten or less for all but the most variable analytes (those with CVs of 150 percent or more). Conversely, if extremely small relative error (10 percent) is desired, sample sizes quickly run into the hundreds or even thousands as analyte concentration variability increases.

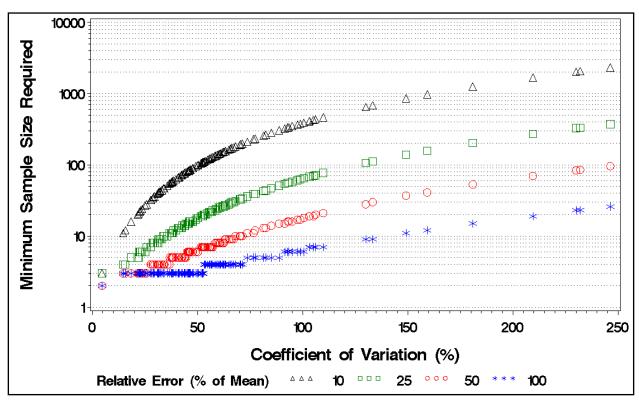


Figure 19. Minimum sample size required to estimate the mean analyte concentration with relative errors of 10, 25, 50, or 100 percent of the mean, plotted as a function of CV. Normal distribution and 95 percent confidence level assumed.

Comparison to criteria. Several remediation objective criteria were applied to the analysis of COC concentrations in the original Chicago Area CDF study (USACE 2006). These included the Illinois Environmental Protection Agency's Tiered Approach to Corrective Action Objectives

(IEPA TACO) Tier I soil remediation objectives for residential properties, and the Indiana Department of Environmental Management Risk Integrated System of Closure (IDEM RISC) residential closure levels. Metals were also compared to IEPA TACO Concentrations of Inorganic Chemicals in Background Soils for Counties within Metropolitan Statistical Areas, and PAHs were compared to available background values from the City of Chicago Department of Environment. Although designed for other uses, the Illinois and Indiana systems for evaluation of remediation objectives provide a set of guidelines that are potentially applicable for beneficial uses of dredged material. Failure to meet appropriately selected criteria indicates that further analysis may be needed in order to demonstrate material suitability for a given use.

For the purposes of illustration, the values for TACO, background, and RISC criteria are given in Table 6, and for each fraction are compared to the COC mean and upper 95 percent confidence limit of the mean. In addition, the number of sample locations at which TACO or RISC criteria were exceeded was noted, except where background concentrations exceeded either TACO or RISC¹. In that case, the number of sample locations exceeding background was noted. Selected criteria are indicated with bold text in Table 6.

In the coarse fraction, the mean exceeded the selected criteria for one metal TCLP (lead), for six PAHs, and for total PCBs. Also in the coarse fraction, the upper confidence limit of the mean exceeded the selected criteria for lead and for TCLP nickel. Mean values exceeding selected criteria are indicated in bold in Table 6. Shaded cells indicate the upper 95 percent confidence limit of the mean exceeded the selective criterion, but the mean did not.

Whether or not the use of mean concentrations is appropriate in the evaluation of regulatory compliance and environmental exposure will be site specific. Regulatory requirements, planned beneficial use placement, potential for exposure or contaminant migration, and the degree of mixing that may be expected to occur when material is processed are all variables that might be considered. Where mean concentrations have been determined to be representative and appropriate to the evaluation, the relative uncertainty of the mean is likely to be important to the decision-making process. It may be desirable, for example, to demonstrate that the upper 95 percent confidence limit of the mean (UCL95) is below the selected criterion, and this will impact the number of samples needed in the data set.

The sample size needed to obtain a confidence interval of a certain width, given the observed variability, can be estimated using Equation 1; in this case, d is the difference between the mean concentration and the criterion. Figure 20 illustrates the PAH indeno(1,2,3-cd)pyrene as an example. An approximate confidence interval for the mean at a given relative error can be calculated as the mean plus or minus the relative error (expressed as a decimal fraction) times the mean; these are represented by the black vertical bars in Figure 20 referenced to the right axis. As the acceptable relative error (horizontal axis) increases, the size of the confidence interval also increases and the required sample size (blue squares assuming normal distribution or green triangles assuming lognormal distribution, referenced to the left axis) decreases. Sample size in

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¹ Both IDEM and IEPA recognize it is unreasonable for states to require concentrations to be below background, and both remediation programs include site-specific approaches to establish background when these concentrations exceed the risk-based criteria (Personal communication with Richard Saichek, August 27, 2009).

Table 6. Comparison of Chicago Area CDF contaminant concentration results with available remediation criteria. Selected criterion and mean values exceeding selected criterion are in bold, shaded boxes indicate that 95% UCL exceeds the selected criterion (lower of TACO or RISC; or background if background > TACO or RISC). Individual exceedances refer to the number of locations exceeding the selected criterion.

| | | | | | | | F | raction | | | |
|------------------|------------------------|--------------|-----------------|--------------|----------------|-------------------------------------|----------------|-------------------------------------|----------------|-------------------------------------|--|
| | | Rem | ediation Criter | ia | | Coarse | | Fine Original | | | |
| Analyte Class | Contaminant | IEPA TACO | Background | IDEM RISC | Mean Result | No. of Individual Exceedances | Mean Result | No. of Individual Exceedances | Mean Result | No. of Individual Exceedances | |
| Metal, | Arsenic | 13 | 13 | 3.9 | 7.29 | 1 | 14.26 | 4 | 13.90 | 3 | |
| mg/Kg | Barium | 5500 | 110 | 1600 | 36.74 | 0 | 58.04 | 0 | 55.77 | 0 | |
| | Beryllium | 160 | 0.59 | 63 | 0.38 | 0 | 0.68 | 0 | 0.69 | 0 | |
| | Cadmium | 78 | 0.6 | 7.5 | 0.45 | 0 | 2.01 | 0 | 1.67 | 0 | |
| | Chromium | 230 | 16.2 | 38 | 18.13 | 0 | 52.90 | 5 | 47.83 | 5 | |
| | Chromium, hexavalent | 230 | 10.2 | 38 | 0.91 | 0 | 0.45 | 0 | 0.62 | 0 | |
| | Copper | 2900 | 19.6 | 920 | 28.73 | 0 | 72.23 | 0 | 67.34 | 0 | |
| | Lead | 400 | 36 | 81 | 70.09 | 2 | 195.96 | 6 | 175.01 | 6 | |
| | Mercury | 10 | 0.06 | 2.1 | 0.17 | 0 | 0.29 | 0 | 0.26 | 0 | |
| | Nickel | 1600 | 18 | 950 | 19.19 | 0 | 38.47 | 0 | 34.36 | 0 | |
| | Selenium | 390 | 0.48 | 5.2 | 0.39 | 0 | 0.69 | 0 | 1.02 | 0 | |
| | Silver | 390 | 0.55 | 31 | 1.22 | 0 | 1.30 | 0 | 1.25 | 0 | |
| Metal | Arsenic, TCLP | 50 | | | 7.54 | 0 | | - | | - | |
| TCLP, | Barium, TCLP | 2000 | | | 452.43 | 0 | | | | | |
| μg/L | Beryllium, TCLP | 4 | | | 0.57 | 0 | | | | | |
| | Cadmium, TCLP | 5 | | | 1.19 | 0 | | | | | |
| | Chromium, TCLP | 100 | | | 2.00 | 0 | | | | | |
| | Copper, TCLP | 650 | | | 2.28 | 0 | | | | | |
| | Lead, TCLP | 7.5 | | | 152.30 | 7 | | | | | |
| | Mercury, TCLP | 2 | | | 0.02 | 0 | | | | | |
| | Nickel, TCLP | 100 | | | 85.73 | 2 | | | | | |
| | Selenium, TCLP | 50 | | | 3.59 | 0 | | | | | |
| | Silver, TCLP | 50 | | | 1.04 | 0 | | | | | |
| | Zinc, TCLP | 5000 | | | 880.00 | 0 | | | | | |
| PAH, | 2-Methylnaphthalene | | | 3.1 | 0.54 | 0 | 0.44 | 0 | 0.61 | 0 | |
| mg/Kg | Acenaphthene | 570 | | 130 | 0.70 | 0 | 0.40 | 0 | 0.47 | 0 | |
| | Acenaphthylene | | | 18 | 0.26 | 0 | 0.12 | 0 | 0.16 | 0 | |
| | Anthracene | 12000 | | 51 | 0.93 | 0 | 0.37 | 0 | 0.49 | 0 | |
| | Benzo(a)anthracene | 0.9 | 1.1 | 5 | 1.95 | 5 | 0.75 | 0 | 1.23 | 4 | |
| | Benzo(a)pyrene | 0.09 | 1.3 | 0.5 | 1.81 | 5 | 0.62 | 0 | 0.98 | 2 | |
| | Benzo(b)fluoranthene | 0.9 | 1.5 | 5 | 2.18 | 4 | 0.94 | 0 | 1.33 | 3 | |
| | Benzo(k)fluoranthene | 9 | 1 | 39 | 0.93 | 0 | 0.25 | 0 | 0.39 | 0 | |
| | Benzo(g,h,i)perylene | | | | 1.05 | 0 | 0.35 | 0 | 0.53 | 0 | |
| | Chrysene | 88 | 1.1 | 25 | 2.30 | 0 | 0.79 | 0 | 1.28 | 0 | |
| | Dibenzo(a,h)anthracene | 0.09 | 0.2 | 0.5 | 0.47 | 7 | 0.16 | 3 | 0.26 | 3 | |
| | Fluoranthene | 3100 | | 880 | 3.46 | 0 | 1.48 | 0 | 2.09 | 0 | |
| | Fluorene | 560 | | 170 | 0.78 | 0 | 0.47 | 0 | 0.57 | 0 | |
| | Indeno(1,2,3-cd)pyrene | 0.9 | 0.86 | 3.1 | 1.12 | 4 | 0.41 | 0 | 0.66 | 2 | |
| | Naphthalene | 12 | | 0.7 | 2.79 | 2 | 4.16 | 3 | 6.68 | 2 | |
| | Phenanthrene | 0000 | | 13 | 3.51 | 0 | 1.48 | 0 | 2.34 | 0 | |
| DOE | Pyrene | 2300 | | 570 | 3.51 | 0 | 1.65 | 0 | 2.19 | 0 | |
| PCB, mg/Kg | Total PCB | 1 | | 1.8 | 0.92 | 2 | 1.12 | 3 | 1.70 | 3 | |

this example drops below ten as relative error increases above 45 percent of the mean. The actual CDF bulk sediment sample mean and 95 percent confidence interval for indeno(1,2,3-cd)pyrene are shown as the large blue circle corresponding to 0.66 on the right axis and relative error of 38 percent on the horizontal axis. Although the sample mean is less than the IEPA TACO (red dashed line on the graph), the UCL95 slightly exceeds the TACO. Reading toward the left, the approximate upper confidence limit calculated from Equation 1 does not exceed the TACO at a point corresponding to relative error of approximately 35 percent of the mean, shown by the vertical dotted reference line. The vertical reference line intersects with the normal distribution sample size line at a sample size of 15 (solid blue square). Thus, given the observed mean and variance and assuming normally distributed data, at least 15 samples would be required to demonstrate that the UCL95 does not exceed the remediation criterion. If the data were lognormally distributed, the necessary sample size would be 10 (solid green triangle).

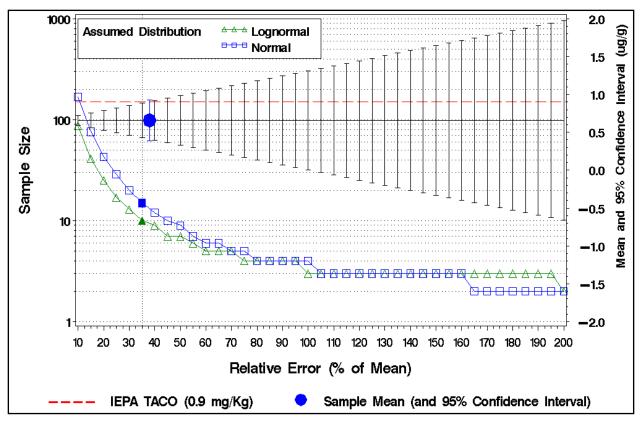


Figure 20. Comparison of sample mean and 95 percent confidence interval (blue circle and error bars) for indeno(1,2,3-cd)pyrene in bulk sediment to IEPA TACO remediation criterion. Calculated minimum sample size assuming normal distribution (blue squares) and lognormal distribution (green triangles) referenced to left axis, and approximate normal confidence intervals (black vertical bars referenced to right axis), are shown as a function of increasing relative error. Solid square and triangle indicate minimum sample sizes that would be required to demonstrate that the UCL95 does not exceed the TACO, assuming normal or lognormal distributions, respectively.

Another permutation of the analysis reflected in Figure 20 would be the consideration of the maximum value of the data set. Some regulations will require that there be no exceedances of a given criterion, as demonstrated by the maximum observed sample value. This could potentially

be addressed using an upper tolerance limit, e.g., the 95 percent upper confidence limit of the 95th percentile of the sample distribution.

The median¹ calculated minimum sample size for each of the classes of analytes is plotted against relative error in Figure 21, assuming normally distributed data. PCBs would require the largest sample sizes, reflecting a relatively high variability in this group. PAHs as a group also have slightly larger sample size requirements than the metals, organic matter phases, and sediment grain size categories. Median sample sizes for all groups are ten or less when the acceptable relative error is at least 70 percent of the mean.

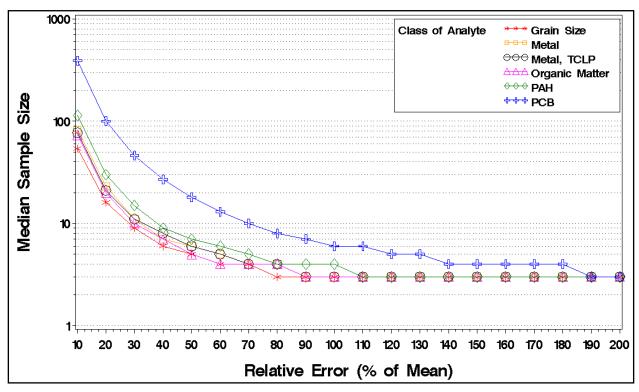


Figure 21. Calculated median sample size for all classes of analytes in all sediment fractions plotted as a function of increasing relative error for assumed normally distributed data.

This type of uncertainty analysis may be applied to existing data prior to sampling, in order to estimate the number of samples required, and after sampling to confirm the adequacy of the data set. If the data fail to meet data quality objectives, additional sampling may be considered.

DATA LIMITATIONS: Data limitations need to be considered for their effect on the accuracy of the CDF characterization and their contribution to uncertainty of the analyses and conclusions.

¹ The distribution of calculated sample sizes tends to be skewed, with several low sample sizes and a few extremely high sample sizes within a class of analytes. Although the maximum sample size would be conservative and seemingly desirable, it would likely also result in a prohibitively large sample number requirement. The median calculated sample sizes were therefore employed for the purposes of this comparison.

Small sample size and variability. Conclusions drawn from the analysis of data from the Chicago Area CDF are limited primarily by small sample size and by the high variability of many analytes. COCs and organic matter were analyzed from only seven locations, and grain size from 12 locations. Coefficients of variation were over 200 percent for naphthalene (all fractions) and silver (coarse fraction), and over 100 percent for gravel, soot, silver, lead (TCLP), 2-methylnaphthalene, and the PCB Aroclors in various sediment fractions. The combination of small sample size and high variability makes it difficult to use surrogate analytes, such as organic carbon measures, to predict concentrations of associated contaminants.

Distribution assumptions. An additional limitation inherent in the attempt to determine minimum sample size for achieving a specified relative error, or for comparison with remediation objectives, is the necessity of assuming a statistical data distribution. In this technical note, the normal distribution was generally assumed for simplicity and ease of illustration. However, normality is not necessarily a realistic assumption for environmental data. For this data set, goodness of fit to normal and lognormal distributions was statistically assessed using the Shapiro-Wilk's test for 44 COCs and organic matter phases in all sediment fractions. Distributional lack of fit was considered significant for P values < 0.05. Of the 44 analytes, 15 passed the test for normality, 39 passed for lognormality, 13 fit both distributions, and three did not significantly fit either distribution. When ProUCL was used to calculate 95 percent upper confidence limits for COCs in each of the three sediment fractions, ProUCL recommended nonparametric or gamma distribution-based confidence limits for 43 percent of the COCs and normal confidence limits for the remainder.

Nondetects. Nondetects (NDs) were reported in the contaminant concentration data for three metals (plus four additional metals in the TCLP analyses), two PAHs, and all Aroclors. Conforming to published Illinois EPA guidance for compliance with remediation objectives (TACOs), NDs were assigned values equal to half of the reported detection limit prior to data analysis. However, most experts in environmental data analysis no longer recommend substitution of detection limit-based values for NDs in analysis of censored data sets (e.g., Helsel 2005; USEPA 2007). A variety of statistical methods can be used instead for computation of summary statistics, comparison of groups, determination of association, or evaluation of trend. These methods utilize the entire data set, including the NDs. Depending upon the software package used, the ND may be set equal to the RL (as a placeholder value) but also coded as ND, and this factors into the algorithm that is then utilized in estimating parameters for the data set. ProUCL, for example, provides appropriate methods for both censored and uncensored data for calculation of summary statistics and UCL95s, hypothesis testing, goodness of fit to various statistical distributions, tests for outliers, and estimation of background threshold values. Nonparametric tests circumvent substitution of RL-dependent values by employing the order of the observations, rather than their values. When some of the RLs are greater than some of the detected values, however, a simple nonparametric test cannot be used. In this case, appropriate censored data methods can be used to estimate values for NDs to permit standard statistical tests.

SUMMARY: The procedures and analyses in this technical note illustrate methods useful for characterizing a CDF for potential beneficial reuse. The process will typically include physical characterization to determine grain size, organic matter content, and spatial distribution of the desired material. Chemical characterization will also be performed to assess the presence,

concentrations, and spatial distribution of contaminants of concern, and to compare COC levels with applicable remediation criteria. Lastly, uncertainty analysis will be completed to determine whether sampling was sufficient for adequate characterization.

The initial challenge in the CDF characterization process is determining the number and location of samples needed for analysis of physical and chemical parameters. A determination of sample size requires estimates of parameter variability and decisions regarding what levels of uncertainty (margins of error) and statistical confidence are acceptable. If previously collected data are available for the materials in the CDF (typically, this will be data obtained on in-situ sediments, prior to dredging), these may provide standard deviations for use in sample size estimation. Although the number of samples should not be determined solely by budget, the sample size equations can be rearranged to calculate what margin of error can be expected for estimation of mean COC concentration given a specified sample size, variability estimate, and confidence level.

In the Chicago Area CDF characterization, COCs were analyzed from a very limited number of locations. Twelve grain-size samples allowed for the construction of a ternary diagram and the plotting of sand contours and isopachs on a map of the CDF. In practice, reliable determination of analyte spatial distribution may require collection of a much larger number of samples at regular intervals on a grid and the application of geostatistical techniques such as kriging. At least some samples should be taken around the perimeter of the facility to provide information regarding boundary conditions and facilitate development of more accurate contour plots and isopachs. However, if enough is known about the facility to make intuitive assumptions about material thicknesses at the facility boundaries, it may not be necessary to sample the entire perimeter. Additional samples in areas of particular interest (zones of expected high sand content, in this case) may be more important, particularly if sampling resources are limiting.

Concentrations of many of the COCs were quite variable, with relative errors (*d* in Eq. 2) ranging from 14 to 200 percent of the mean for metals, 29 to 182 percent for PAHs, and 53 to 87 percent for PCBs. Given the observed variability of the coarse sediment fraction data, to estimate mean COC concentration with a 30 percent relative error for the most variable COCs would require as many as 506 samples for silver, 420 samples for naphthalene, and 171 samples for TCLP lead. The median sample sizes needed to estimate mean COC concentration with a 30 percent relative error would be 33 for metals, 20 for TCLP metals, 29 for PAHs, and 65 for PCBs. Sample sizes to estimate mean COC concentrations with 100 percent relative error would range from two to 47.

Sediment organic carbon phases were less variable than some of the COCs, with relative errors ranging from 40 to 92 percent of the mean. It may be possible to use organic phase concentrations as surrogate measures for the prediction of at least some COCs, especially if historic data are available and reasonable predictive equations can be developed. If historic data and organic phase predictive equations give strong evidence that a class of contaminants (PCBs, for example) is not present in concentrations of concern, it may be possible to achieve cost savings by eliminating that class of contaminants from future analyses (such as in analysis of confirmatory samples taken during excavation). In the Chicago Area CDF, predictive equations developed based on organic phase data did provide reasonable estimates of certain metals and PCBs, but only after nondetects and outliers were identified and removed.

CONCLUSIONS: Clearly, the use of a combination of statistical and graphical data evaluation tools can provide useful insights into the character and variability of materials within a CDF. Some of the measures presented here will have greater utility for larger data sets, due to the fact that sample comparisons are more difficult to make by simple observation; ordination plots are a good example of this. It was apparent from the applied case study that unusual site geometry may make *a priori* estimation of material deposition more difficult, as settling and flow of hydraulically placed material is affected. The evaluation also illustrated the importance of obtaining samples from each side of the site in order to appropriately constrain both 2- and 3-dimensional models with site specific data. If sufficient *a priori* information regarding material thickness at the site boundaries exists, however, then resources may be better focused on additional sampling in areas of particular interest.

Where possible, uncertainty analysis should be applied before sampling as well as after, in order to better ensure that the data set obtained will, and does, meet data quality objectives. More indepth information regarding development of a sampling plan designed to reduce uncertainty is described in the companion document to this technical note (Clarke et al. in review).

A concurrent laboratory effort is being conducted to evaluate the impact of sediment sample extraction size on data variability. Results of that effort will be synthesized into a summary document incorporating the lessons learned from the bench testing, data analysis and literature search.

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