# SUMMARY OF DATA SETS AND DATA QUALITY EVALUATION

## Final Engineering Design
## Kinnickinnic River Environmental Restoration Project

**Wisconsin Department of Natural Resources**
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## I. INTRODUCTION

The Kinnickinnic River Environmental Restoration Project is located in the Milwaukee Estuary Area of Concern in Milwaukee, Wisconsin. The project area is approximately 2,000 feet long with a 200-foot maximum width between Becher Street (the upstream limit) and Kinnickinnic Avenue (the downstream limit). Significant progresses have been made since sediment assessment in 2002. With respect to implementation as the final phase, the project has been and will be conducted in the following five phases:

- Phase I: Sediment Assessment and Site Characterization
- Phase II: Pre-engineering Design and Feasibility Studies (Concept Design)
- Phase III: Final Engineering Design
- Phase IV: Supplemental Design and Remedial Planning
- Phase V: Implementation of the Project

Phases I and II activities were completed in 2002 and 2004. Phase III is on going. This document provides a summary of data that will be used for Phase III work, final engineering design. The summary includes both primary and secondary data. The primary data are those that will be collected during Phase III of the project while the secondary data are those that have been collected prior to Phase III.

This document was developed as part of the project quality assurance and quality control (QAQC) plan of Phase III; therefore, it also provides information on data quality evaluation in the context of a final engineering design for a contaminated sediment remediation project.

## II. PRIMARY DATA

The Kinnickinnic River Restoration project consists of approximately 3,600 linear feet of shoreline. About 2,200 feet of the shoreline are protected with seawalls and the remaining 1,400 feet appear to be natural or unprotected riverbank. Most of the seawalls were built forty years ago with different materials. The types of the seawalls include timber walls with or without a concrete cap and steel sheet piling.

During the pre-engineering design phase (Phase II) of the project, a shoreline inspection was conducted. The results showed that the proposed dredging activities may potentially cause failure of the unprotected riverbank and some of the seawalls. Further stability

analysis has to be conducted and protection alternatives have to be evaluated as part of the final engineering design. Finally, a selected shoreline protection alternative will be designed for construction. Under this grant, the following tasks will be conducted:

- a land survey in the vicinity of the project area. The land survey is essential to identifying characteristics of the shoreline, wall limits, wall length, shoreline profiles, and cross sections of dry land areas at unprotected sections.
- stability analyses for existing steel sheet piling, currently protecting approximately 1,000 feet out of a total of 3,600 feet of the shoreline length.

Evaluation of shoreline protection alternatives and engineering design for the selected alternatives are not included in the scope of work due to a shortage in the project budget and to the complexity of the issues. A final decision on the alternative for shoreline protection will have to be made by incorporating the property owners' recommendations.

The WDNR project manager will assure that the contractor and its subcontractors will follow the survey standard. The land surveying results will be consistent with the specifications used in the WDNR so that the data can be compared to historical records and can be imported to the standard database. The specific quality control requirements are described in Part II of the QA/QC document.

Additional primary data may be needed if the existing secondary data is found to be insufficient for representing the site condition. In that case, separate quality control and quality assurance plans will be developed.

## III. SECONDARY DATA

Various literature values and site specific data collected in the past will be used for the final engineering design. In conjunction with land survey activities, the subcontractors will collect existing information to characterize the locations of utilities, seawalls, soil adjacent to the project area, and river hydraulic conditions. The gathered information will be subject to evaluation.

In this section, detailed summary and analyses will be given to four data sets as listed in Table 1. Emphasis will be placed on Data Set 1, the 2002 sediment assessment results due to its critical role in the delineation of dredging specifications.

**Table 1. Summary of secondary data sets**

| Data set | Description | Purpose | Usage |
|---|---|---|---|
| SET 1 | Results from 2002 sediment assessment | Assessment of the extent of contamination in sediment | • Pre-engineering (concept) design or feasibility study<br>• Final engineering design |
| SET 2 | Results from 2003 sampling at the background reference site | Investigation of contamination levels at the local background reference site | • Pre-engineering (concept) design or feasibility study<br>• Final engineering design |
| SET 3 | Results from 2002 Bathymetry survey and sediment poling | Sediment surface contour development as part of the 2002 sediment assessment | • Pre-engineering (concept) design or feasibility study<br>• Final engineering design |
| SET 4 | Nautical Charts | Historical sounding maps and data collected by the US ACE, Port of Milwaukee, Wiscosnin Board of Harbor Commissioners, and NOAA | • Pre-engineering (concept) design or feasibility study<br>• Final engineering design |

## Data SET 1: Results from 2002 sediment assessment

### Sediment sampling and results

The purpose of the 2002 sediment assessment, a remedial investigation, was to determine the horizontal and vertical extent of contamination in sediment from the project area. The data collected were further used in pre-engineering design (or concept design) to evaluate remedial alternatives and to determine the volume of sediment to be removed. This data set will serve as the basis for the final engineering design as well. The following is a summary of the sediment sampling procedures and analytical results.

In 2002, the USEPA-GLNPO provided funding to US Army Corps of Engineers (ACE), Detroit District, for the assessment work. The Altech Environmental Services Inc. of Southfield, Michigan (Altech), an Architect/Engineering (A/E) contractor to the US ACE, provided sampling and project oversight services.

Between Sep. 9 and 12, 2002, Coleman Engineering of Ironwood, Michigan (Coleman), a subcontractor to Altech, conducted the field work. Samples were collected and handled in accordance with the Quality Assurance and Quality Control (QA/QC) plan (Attachment 1). A total of 106 sediment samples were collected from sixteen locations as shown in Fig. 1. A majority of the samples were core samples collected from the project area between Becher Street and KK Ave. Two grab samples, KK02US01 and KK02US02, were obtained upstream from Becher Street, a location that is considered as a local background reference site. Field duplicate and replicate samples were collected from core locations of KK0203 (KK0203D) and KK0207 (KK0207R), respectively, as defined in the QA/QC plan (Attachment 1). Each sampling location was determined in the field by using a Trimble differential Global Position System (GPS) unit.

Split spoons of 3-inch in diameter and 2-foot in length were used to obtain a sediment core in multiple 2-foot segments. Before a split spoon was placed into the sediment, hollow stem augers (4½“ diameter) were advanced with a Diedrich D-50 auger rig mounted on a Bombardier barge. This sampling technique provided longer sediment cores than in other earlier studies, such as the assessment conducted in 1994 (Li et al., 1995). The obtained cores ranged from 10 to 24 feet in length and were sliced into three to twelve 2-foot segments due to various recovery rates. While balancing the need for defining a complete vertical extent of contamination and a limited budget, a few segments in deeper cores were not saved for chemical analyses.

Sediment samples were analyzed by the Trace Analytical Laboratories, Inc. (Trace) of Trace, Michigan and by the Coleman. Parameters analyzed are listed in Table 2. A summary of the analytical results is provided in Table 3.

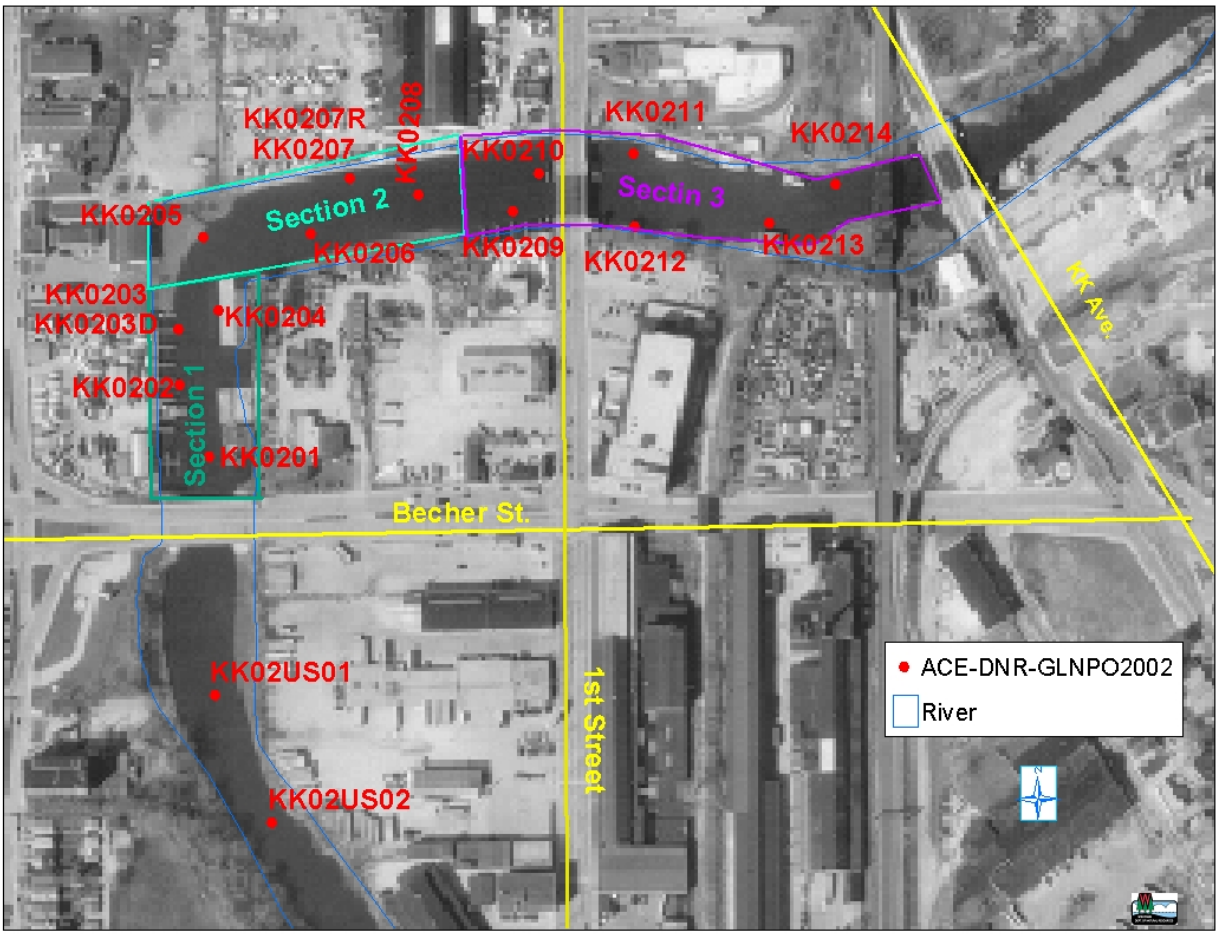



**Figure 1. Sampling locations for 2002 sediment assessment and illustration of the three management sections in the project area**

Total concentrations of PCB (TPCB) and PAHs (TPAH) are the sum of seven Aroclors and sixteen PAH compounds, respectively. A zero value was assigned to an Aroclor or a PAH compound that was detected at or less than the reporting limits. Details of the sampling procedures and analytical results are documented in the report by the Altech (March 2003) and Coleman (October 2002) as listed in Appendix A of this QAPP document.

For dredging purposes, the depths of sediment segments of a core with respect to the vertical distribution of PCB and PAH concentrations are converted to elevation relative to the Lake Michigan Chart Datum (IGLD 1985) of 577.5 feet (LMCD). The conversion from sediment depth to elevation is necessary because sediment removal depth will be referenced to the LMCD. In addition, the same datum has to be used for each sediment core so that average concentrations can be calculated for the purpose of assessing the post remedial concentrations.

Fig. 2 shows the vertical profiles of TPCB and TPAH at fourteen core locations. Each panel in Fig. 2 illustrates the vertical distribution of contaminants of concern in sediment with the bottom x-axis for TPCB concentrations and the top x-axis for TPAH concentrations. The y-axis corresponds to the elevation relative to the LMCD. Concentrations are assigned to the end of each two-foot segment within a core.

For further discussion, the proposed dredging elevations are also shown in Figure D-2. At a few sediment core locations, two lines are displayed. These lines show different dredging elevations. In order to determine the appropriate dredging elevation, the project area was further divided into three management sections, Sections 1 through 3, as shown in Fig. 1. The three sections were divided on the basis of contaminant distribution patterns combined with the hydrological and hydraulic conditions. Section 2 serves as a transition zone from dredging shallower in Section 1 to deeper in Section 3. Within Section 2, the 80-foot channel close to Section 1 is proposed to be dredged to elevation at 557 feet and then gradually sloped to 553 feet as it joins Section 3. Therefore, two lines were plotted in Fig. 2 at some locations. To clarify, these dredging elevations are determined as a result of pre-engineering design. The final dredging specifications may vary slightly after the completion of the final engineering design.

During the pre-engineering design phase, after consulting with the local property owners for recreational boating purposes, the minimum water depth for navigation at the project area was defined as 6-8 ft below the LMCD. Comparison of navigational need to the necessity of removing contaminated sediment indicated that contamination levels would be the driver for determining dredging elevation.

**Table 2 Parameters analyzed in 2002 for sediment from the Kinnickinnic River**

| No. | Parameters | Analyzed by | No. of Samples analyzed | TDL[1] | Precision[1] (RPD) | Analytical Method |
|---|---|---|---|---|---|---|
| A. | Bulk Sediment PCBs[2] | Trace | 106 | Per Method | 50 % | SW-846/8082 |
| B. | Bulk Sediment PAHs[2] | Trace | 106 | Per Method | 50 % | SW-846/8270C |
| C. | Bulk Sediment TOC | Trace | 57 | 1,000 mg/kg | 20 % | Walkely-Black |
| D. | TCLP Procedure | Trace | 7 | N/A | N/A | SW-846/1311 |
| E. | TCLP Procedure for Volatiles | Trace | 7 | N/A | N/A | SW846/1311 |
| F. | TCLP Metals | Trace | 7 | List 1 | List 1 | SW-846 |
| G. | TCLP Volatiles | Trace | 7 | List 2 | List 2 | SW-846/8260B |
| H. | TCLP Semivolatiles | Trace | 7 | List 3 | List 3 | SW-846/8270C |
| I. | TCLP Pesticides | Trace | 7 | List 4 | List 4 | SW-846/8081 |
| J. | TCLP Herbicides | Trace | 7 | List 5 | List 5 | SW-846/8150 |
| K. | Corrosivity | Trace | 7 | N/A | 20 % | SW-846/9040/9045B |
| L. | Reactive Cyanide | Trace | 7 | 0.5 mg/kg | 7.5 % | SW-846 Ch. 7/ EPA 9012 |
| M. | Reactive Sulfide | Trace | 7 | 5.0 | 20 % | SW-846/Ch-7/ EPA 376.2 |
| N. | Ignitability | Trace | 7 | > $200^0$ F | 20 % | SW-846/1010 |
| O. | Paint Filter Test | Trace | 7 | N/A | N/A | EPA 9095 |
| P. | Grain Size | Coleman | 54 | | | |
| Q. | Hydrometer | Coleman | 54 | | | |
| R. | Loss upon ignition | Coleman | 54 | | | |
| S. | Atterberg Limits | Coleman | 8 | | | |

[1] – TDL-Target Detection Limit. For E through J, the TDL and RPD are shown in Lists 1 through 6 below.

[2] - List of PAH compounds and PCB Aroclors analyzed

| PAH Compounds | PCB Aroclors |
|---|---|
| Naphthalene | Aroclor-1016 |
| 2-Methylnaphthalene | Aroclor-1221 |
| Acenaphthylene | Aroclor-1232 |
| Acenaphthene | Aroclor-1242 |
| Fluorene | Aroclor-1248 |
| Phenanthrene | Aroclor-1254 |
| Anthracene | Aroclor-1260 |
| Fluoranthene | |
| Pyrene | |
| Benz(a)anthracene | |
| Chrysene | |
| Benzo(b)fluoranthene | |
| Benzo(k)fluoranthene | |
| Benzo(a)pyrene | |
| Indeno(1,2,3-cd)pyrene | |
| Dibenzo(a,h)anthracene | |
| Benzo(g,h,i)perylene | |

**List 1. Kinnickinnic River TCLP Metals Requirements**

| Analyte | Analytical Method | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|---|
| Arsenic | SW-846 6010/6020/7000 | 0.30 | 20 % |
| Barium | SW-846 6010/6020 | 1.00 | 20 % |
| Cadmium | SW-846 6010B/6020/7000A | 0.10 | 20 % |
| Chromium | SW-846 6010B/6020 | 0.50 | 20 % |
| Lead | SW-846 6010B/6020/7000A | 0.50 | 20 % |
| Mercury | SW-846 7470 | 0.01 | 12 % |
| Selenium | SW-846 6010B/6020 | 0.60 | 20 % |
| Silver | SW-846 7761/6010B/6020 | 0.10 | 20 % |

1 – Target Detection Limit

**List 2. Kinnickinnic River TCLP Volatiles Requirements**

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| Benzene | 0.05 | 50 % |
| Carbon Tetrachloride | 0.05 | 50 % |
| Chlorobenzene | 0.05 | 50 % |
| Chloroform | 0.05 | 50 % |
| Methyl ethyl keytone | 0.25 | 50 % |
| 1,4-Dichlorobenzene | 0.05 | 50 % |
| 1,2-Dichloroethane | 0.05 | 50 % |
| 1,1-Dichloroethylene | 0.05 | 50 % |
| Trichloroethene | 0.05 | 50 % |
| Tetrachloroethylene | 0.05 | 50 % |
| Vinyl chloride | 0.05 | 50 % |

1- Target Detection Limits

**List 3. Kinnickinnic River TCLP Semivolatiles Requirements**

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| 2-Methylphenol | 0.10 | 50 % |
| 3/4-Methylphenol | 0.10 | 50 % |
| Methylphenol(2,3,4) | 0.10 | 50 % |
| 2,4-Dinitrotoulene | 0.10 | 50 % |
| Pentachlorophenol | 0.10 | 50 % |
| Hexachlorobenzene | 0.10 | 50 % |
| Hexachlorobutadiene | 0.10 | 50 % |
| Hexachloroethane | 0.10 | 50 % |
| Nitrobenzene | 0.10 | 50 % |
| Pyridine | 0.10 | 50 % |
| 2,4,5-Trichlorophenol | 0.10 | 50 % |
| 2,4,6-Trichlorophenol | 0.10 | 50 % |

**List 4. Kinnickinnic River TCLP Pesticides Requirements**

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| Chlordane | 0.020 | 50 % |
| Endrin | 0.010 | 50 % |
| Heptachlor | 0.008 | 50 % |
| Heptachlor Epoxide | 0.008 | 50 % |
| 4,4-DD | 0.010 | 50 % |
| Lindane | 0.010 | 50 % |
| Methoxychlor | 0.500 | 50 % |
| Toxaphene | 0.500 | 50 % |

**List 5. Kinnickinnic River TCLP Herbicides Requirements**

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| 2,4-D | 10.0 | 50 % |
| 2,4,5-TP (Silvex) | 1.0 | 50 % |

# Table 3. Summary of analytical results from 2002 sediment assessment[1]

| Core ID | Segmentation | | Segment recovery | Elevation[2] | Trace Analytical Lab. | | | | Coleman Engineering | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | beginning | end | | ave WL | TPCB[3] | TPAH[3] | TOC | Solids | Grain size distribution (%) | | | | Atterberg Limits | | Specific Gravity | Natural Moisture | Organics LOI[4] |
| | | | | | | | | | Gravel | Sand | Silt/Clay | Clay | | | | | |
| | ft | ft | % | ft | ppm | ppm | % | % | | | | | LL | PL | | % | % |
| KK-0201 | 0 | 2 | 0 | 567 | 2.0 | 58.4 | 1.4 | 76 | 0 | 71 | 16 | 13 | | | | 36.8 | 2.1 |
| KK-0201 | 2 | 4 | 80 | 565 | 0.9 | 10.8 | | 81 | | | | | | | | | |
| KK-0201 | 4 | 6 | 50 | 563 | 0.0 | 38.6 | 1.2 | 82 | 0 | 89 | 4 | 7 | | | | 28.3 | 2.4 |
| KK-0201 | 6 | 8 | 40 | 561 | 0.8 | 79.2 | | 81 | | | | | | | | | |
| KK-0201 | 8 | 10 | 80 | 559 | 0.0 | 0.3 | 0.2 | 78 | 0 | 86 | 7 | 8 | | | | 15.1 | 9.1 |
| KK-0202 | 0 | 2 | 80 | 573 | 2.8 | 74.5 | | 82 | | | | | | | | | |
| KK-0202 | 2 | 4 | 20 | 571 | 0.7 | 93.0 | 1.3 | 76 | 0 | 86 | 4 | 10 | | | | 36.9 | 1.8 |
| KK-0202 | 4 | 6 | 80 | 569 | 7.6 | 56.7 | | 79 | | | | | | | | | |
| KK-0202 | 6 | 8 | 80 | 567 | 9.3 | 240.7 | 3.8 | 65 | 0 | 25 | 46 | 29 | | | | 54.0 | 5.2 |
| KK-0202 | 8 | 10 | 80 | 565 | 6.4 | 68.6 | | 77 | | | | | | | | | |
| KK-0202 | 10 | 12 | 80 | 563 | 3.1 | 95.7 | 5.1 | 59 | 0 | 14 | 54 | 32 | | | | 65.6 | 0.0 |
| KK-0202 | 12 | 14 | 80 | 561 | 2.7 | 61.4 | | 73 | | | | | | | | | |
| KK-0202 | 14 | 16 | 80 | 559 | 2.1 | 109.9 | 5.1 | 58 | 0 | 12 | 64 | 25 | 80.0 | 75.3 | 2.334 | 72.2 | 10.5 |
| KK-0202 | 18 | 20 | 80 | 555 | 0.4 | 44.3 | 6.8 | 62 | 0 | 10 | 71 | 19 | 19.4 | 17.0 | 2.708 | 19.3 | 1.7 |
| KK-0203 | 0 | 2 | 50 | 573 | 0.8 | 53.5 | 1.9 | 82 | 0 | 36 | 41 | 23 | | | | 62.9 | 5.6 |
| KK-0203 | 2 | 4 | 25 | 571 | 1.0 | 31.1 | | 81 | | | | | | | | | |
| KK-0203 | 4 | 6 | 80 | 569 | 1.7 | 34.2 | 3.6 | 73 | 0 | 17 | 56 | 27 | | | 2.543 | 63.5 | 6.9 |
| KK-0203 | 6 | 8 | 70 | 567 | 2.7 | 46.6 | | 75 | | | | | | | | | |
| KK-0203 | 8 | 10 | 80 | 565 | 15.7 | 101.9 | 4.0 | 60 | 0 | 15 | 56 | 29 | | | | 66.5 | 3.2 |
| KK-0203 | 10 | 12 | 80 | 563 | 6.3 | 92.2 | | 77 | | | | | | | | | |
| KK-0203 | 12 | 14 | 80 | 561 | 1.9 | 62.2 | 4.3 | 73 | 0 | 11 | 54 | 36 | | | | 63.9 | 6.4 |
| KK-0203d | 0 | 2 | | 573 | 0.9 | 102.0 | 2.2 | 79 | 0 | 29 | 53 | 18 | | | | 63.8 | 6.5 |
| KK-0203d | 2 | 4 | | 571 | 0.9 | 53.0 | | 82 | | | | | | | | | |
| KK-0203d | 4 | 6 | | 569 | 2.5 | 69.7 | 3.5 | 74 | 0 | 16 | 60 | 24 | | | | 65.1 | 7.9 |
| KK-0203d | 6 | 8 | | 567 | 3.2 | 89.2 | | 75 | | | | | | | | | |
| KK-0203d | 8 | 10 | | 565 | 9.5 | 30.9 | 3.8 | 68 | 0 | 23 | 50 | 27 | | | | 57.0 | 5.3 |
| KK-0203d | 10 | 12 | | 563 | 2.9 | 243.5 | | 64 | | | | | | | | | |
| KK-0203d | 12 | 14 | | 561 | 2.4 | 121.5 | 4.7 | 74 | 0 | 15 | 52 | 33 | | | | 63.6 | 7.2 |
| KK-0204 | 0 | 2 | 20 | 570 | 1.4 | 20.9 | | 81 | | | | | | | | | |
| KK-0204 | 2 | 4 | 20 | 568 | 1.1 | 21.9 | 0.3 | 98 | 0 | 94 | 6 | | | | | 26.0 | 0.9 |
| KK-0204 | 4 | 6 | 80 | 566 | 6.3 | 99.0 | | 65 | | | | | | | | | |

**Table 3 (cont'd)**

| Core ID | Segmentation | | Segment recovery | Elevation[2] | Trace Analytical Lab. | | | | Coleman Engineering | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | beginning | end | | ave WL | TPCB[3] | TPAH[3] | TOC | Solids | Grain size distribution (%) | | | | Atterberg Limits | | Specific Gravity | Natural Moisture | Organics LOI[4] |
| | | | | | | | | | Gravel | Sand | Silt/Clay | Clay | | | | | |
| | ft | ft | % | ft | ppm | ppm | % | % | | | | | LL | PL | | % | % |
| KK-0204 | 6 | 8 | 80 | 564 | 3.4 | 71.2 | 2.6 | 81 | 0 | 35 | 41 | 24 | | | | 48.1 | 4.8 |
| KK-0204 | 8 | 10 | 80 | 562 | 4.4 | 56.3 | | 61 | | | | | | | | | |
| KK-0204 | 10 | 12 | 100 | 560 | 1.4 | 53.3 | 3.9 | 76 | 0 | 14 | 54 | 32 | | | | 60.5 | 9.7 |
| KK-0204 | 12 | 14 | 100 | 558 | 2.2 | 70.4 | | 62 | | | | | | | | | |
| KK-0204 | 14 | 16 | 50 | 556 | 0.4 | 33.3 | 4.4 | 76 | 0 | 23 | 55 | 23 | | | | 61.2 | 9.9 |
| KK-0205 | 0 | 2 | 80 | 573 | 1.3 | 8.5 | 4.1 | 59 | 0 | 21 | 65 | 15 | | | | 51.3 | 5.4 |
| KK-0205 | 2 | 4 | 80 | 571 | 1.4 | 24.2 | | 63 | | | | | | | | | |
| KK-0205 | 4 | 6 | 80 | 569 | 8.3 | 26.2 | 4.0 | 64 | 0 | 14 | 57 | 29 | | | | 59.4 | 7.6 |
| KK-0205 | 6 | 8 | 80 | 567 | 7.9 | 65.6 | | 62 | | | | | | | | | |
| KK-0205 | 8 | 10 | 80 | 565 | 12.5 | 21.9 | 3.6 | 65 | 0 | 9 | 52 | 39 | | | | 51.9 | 4.7 |
| KK-0205 | 10 | 12 | 80 | 563 | 2.9 | 99.0 | | 67 | | | | | | | | | |
| KK-0205 | 12 | 14 | 80 | 561 | 2.1 | 71.2 | 5.6 | 61 | 0 | 7 | 62 | 31 | | | | 63.2 | 6.9 |
| KK-0205 | 14 | 16 | 80 | 559 | 0.5 | 56.3 | | 59 | | | | | | | | | |
| KK-0206 | 0 | 2 | 80 | 574 | 1.0 | 53.3 | | 59 | | | | | | | | | |
| KK-0206 | 2 | 4 | 50 | 572 | 0.9 | 70.4 | 1.5 | 76 | 0 | 76 | 12 | 12 | | | | 40.3 | 2.6 |
| KK-0206 | 4 | 6 | 50 | 570 | 1.7 | 33.3 | | 51 | | | | | | | | | |
| KK-0206 | 6 | 8 | 80 | 568 | 6.9 | 58.4 | 5.8 | 56 | 0 | 27 | 45 | 28 | | | | 59.3 | 6.4 |
| KK-0206 | 8 | 10 | 80 | 566 | 3.5 | 10.4 | | 65 | | | | | | | | | |
| KK-0206 | 10 | 12 | 80 | 564 | 3.1 | 38.6 | 4.4 | 64 | 0 | 9 | 55 | 36 | | | | 51.8 | 5.2 |
| KK-0206 | 12 | 14 | 80 | 562 | 3.5 | 79.2 | | 65 | | | | | | | | | |
| KK-0206 | 14 | 16 | 80 | 560 | 0.9 | 0.3 | 6.7 | 60 | 0 | 7 | 53 | 40 | | | | 64.6 | 7.0 |
| KK-0206 | 16 | 18 | 80 | 558 | 0.9 | 8.5 | | 61 | | | | | | | | | |
| KK-0207 | 0 | 2 | 0 | 566 | | | | | | | | | | | | | |
| KK-0207 | 2 | 4 | 0 | 564 | | | | | | | | | | | | | |
| KK-0207 | 4 | 6 | 80 | 562 | 7.0 | 24.2 | 4.1 | 65 | 0 | 17 | 47 | 36 | | | | 54.6 | 6.5 |
| KK-0207 | 6 | 8 | 80 | 560 | 4.3 | 26.2 | | 66 | | | | | | | | | |
| KK-0207 | 8 | 10 | 80 | 558 | 3.1 | 110.8 | 3.4 | 67 | 0 | 31 | 40 | 29 | | | | 52.5 | 6.6 |
| KK-0207R | 0 | 2 | 10 | 566 | 1.9 | 14.9 | 0.6 | 81 | | | | | | | | | |
| KK-0207R | 2 | 4 | 0 | 564 | | | | | | | | | | | | | |
| KK-0207R | 4 | 6 | 100 | 562 | 1.4 | 130.2 | 5.9 | 58 | 0 | 8 | 54 | 38 | | | | 66.9 | 10.3 |
| KK-0207R | 6 | 8 | 80 | 560 | 1.1 | 79.6 | | 67 | | | | | | | | | |
| KK-0207R | 8 | 10 | 80 | 558 | 2.1 | 54.8 | 4.4 | 56 | 0 | 10 | 55 | 35 | | | | 58.2 | 7.5 |

**Table 3 (cont'd)**

| Core ID | Segmentation | | Segment recovery | Elevation[2] | Trace Analytical Lab. | | | | Coleman Engineering | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | beginning | end | | ave WL | TPCB[3] | TPAH[3] | TOC | Solids | Grain size distribution (%) | | | | Atterberg Limits | | Specific Gravity | Natural Moisture | Organics LOI[4] |
| | | | | | | | | | Gravel | Sand | Silt/Clay | Clay | | | | | |
| | ft | ft | % | ft | ppm | ppm | % | % | | | | | LL | PL | | % | % |
| KK-0208 | 0 | 2 | 0 | 571 | | | | | | | | | | | | | |
| KK-0208 | 2 | 4 | 10 | 569 | 0.7 | 17.9 | 0.9 | 77 | 0 | 92 | 3 | 5 | | | | 29.1 | 0.9 |
| KK-0208 | 4 | 6 | 0 | 567 | | | | | | | | | | | | | |
| KK-0208 | 6 | 8 | 80 | 565 | 5.5 | 92.9 | 3.2 | 69 | 0 | 26 | 42 | 32 | | | | 46.2 | 1.3 |
| KK-0208 | 8 | 10 | 80 | 563 | 5.7 | 96.9 | | 64 | | | | | | | | | |
| KK-0208 | 10 | 12 | 80 | 561 | 6.4 | 54.1 | 3.3 | 67 | 0 | 12 | 50 | 38 | | | | 51.8 | 5.6 |
| KK-0208 | 12 | 14 | 80 | 559 | 3.9 | 111.6 | | 63 | | | | | | | | | |
| KK-0209 | 0 | 2 | 80 | 573 | 2.3 | 171.0 | 3.9 | 65 | 0 | 38 | 39 | 23 | | | | 53.6 | 5.5 |
| KK-0209 | 2 | 4 | 80 | 571 | 1.8 | 68.0 | | 60 | | | | | | | | | |
| KK-0209 | 4 | 6 | 80 | 569 | 2.7 | 66.7 | 5.1 | 60 | 0 | 22 | 50 | 28 | | | | 71.0 | 7.2 |
| KK-0209 | 6 | 8 | 80 | 567 | 5.1 | 97.3 | | 57 | | | | | | | | | |
| KK-0209 | 8 | 10 | 80 | 565 | 16.0 | 94.5 | 4.9 | 62 | 0 | 19 | 51 | 31 | | | | 61.3 | 6.6 |
| KK-0209 | 10 | 12 | 80 | 563 | 35.5 | 227.2 | | 60 | | | | | | | | | |
| KK-0209 | 12 | 14 | 80 | 561 | 21.4 | 108.2 | 5.7 | 64 | 0 | 7 | 55 | 38 | | | | 53.9 | 6.0 |
| KK-0209 | 14 | 16 | 80 | 559 | 24.2 | 176.9 | | 67 | | | | | 59.8 | 44.3 | | | |
| KK-0209 | 20 | 22 | 80 | 553 | 1.1 | 42.8 | 5.2 | 65 | 0 | 15 | 61 | 24 | | | | 57.8 | 8.3 |
| KK-0209 | 22 | 24 | 80 | 551 | 0.4 | 72.0 | | 64 | | | | | 55.0 | | | | |
| KK-0210 | 0 | 2 | 10 | 566 | 0.4 | 31.0 | | 59 | | | | | | | | | |
| KK-0210 | 2 | 4 | 20 | 564 | 1.7 | 33.7 | 4.5 | 61 | 1 | 13 | 55 | 31 | | | | | |
| KK-0210 | 4 | 6 | 80 | 562 | 4.5 | 59.8 | | 63 | | | | | | | | | |
| KK-0210 | 6 | 8 | 50 | 560 | 16.8 | 58.0 | 4.7 | 61 | 2 | 13 | 47 | 38 | | | | | |
| KK-0210 | 8 | 10 | 80 | 558 | 8.2 | 96.3 | | 63 | | | | | 51.8 | 31.2 | | | |
| KK-0210 | 10 | 12 | 80 | 556 | | | | | | | | | | | | | |
| KK-0210 | 12 | 14 | 80 | 554 | 2.7 | 63.5 | 5.3 | 62 | 0 | 16 | 49 | 35 | 63.0 | 56.6 | | 64.6 | 1.4 |
| KK-0211 | 0 | 2 | 80 | 570 | 6.1 | 186.9 | 4.7 | 55 | 0 | 10 | 54 | 36 | | | | 77.4 | 1.9 |
| KK-0211 | 2 | 4 | 80 | 568 | 15.3 | 71.1 | | 57 | | | | | | | | | |
| KK-0211 | 4 | 6 | 80 | 566 | 8.9 | 93.8 | 4.0 | 65 | 0 | 9 | 54 | 37 | | | | 74.6 | 7.0 |
| KK-0211 | 6 | 8 | 80 | 564 | 15.3 | 59.8 | | 60 | | | | | | | | | |
| KK-0211 | 8 | 10 | 80 | 562 | 5.2 | 111.8 | 4.2 | 60 | 1 | 10 | 48 | 41 | | | | 65.2 | 6.2 |
| KK-0211 | 10 | 12 | 80 | 560 | 12.1 | 98.7 | | 61 | | | | | | | | | |

**Table 3 (cont'd)**

| Core ID | Segmentation | | Segment recovery | Elevation[2] | Trace Analytical Lab. | | | | Coleman Engineering | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | beginning | end | | ave WL | TPCB[3] | TPAH[3] | TOC | Solids | Grain size distribution (%) | | | | Atterberg Limits | | Specific Gravity | Natural Moisture | Organics LOI[4] |
| | | | | | | | | | Gravel | Sand | Silt/Clay | Clay | | | | | |
| | ft | ft | % | ft | ppm | ppm | % | % | | | | | LL | PL | | % | % |
| KK-0212 | 0 | 2 | 80 | 570 | 4.6 | 153.9 | | 59 | | | | | | | | | |
| KK-0212 | 2 | 4 | 80 | 568 | 2.2 | 77.3 | 4.0 | 60 | 0 | 6 | 54 | 40 | | | | 61.0 | 5.8 |
| KK-0212 | 4 | 6 | 80 | 566 | 6.7 | 124.0 | | 62 | | | | | | | | | |
| KK-0212 | 6 | 8 | 80 | 564 | 5.2 | 179.3 | 4.6 | 59 | 0 | 20 | 48 | 32 | | | | 73.3 | 6.7 |
| KK-0212 | 8 | 10 | 80 | 562 | 3.5 | 122.2 | | 58 | | | | | | | | | |
| KK-0212 | 10 | 12 | 80 | 560 | 12.9 | 139.9 | 4.8 | 59 | 0 | 11 | 55 | 34 | | | | 73.2 | 6.1 |
| KK-0212 | 12 | 14 | 80 | 558 | 5.7 | 169.7 | | 64 | | | | | | | | | |
| KK-0213 | 0 | 2 | 80 | 568 | 3.9 | 86.2 | 4.7 | 57 | 0 | 11 | 58 | 31 | | | | 80.6 | 5.9 |
| KK-0213 | 2 | 4 | 50 | 566 | 3.0 | 84.0 | | 61 | | | | | | | | | |
| KK-0213 | 4 | 6 | 50 | 564 | 2.6 | 123.2 | 4.4 | 59 | 5 | 48 | 28 | 19 | | | | 74.5 | 7.5 |
| KK-0213 | 6 | 8 | 80 | 562 | 5.2 | 180.9 | | 61 | | | | | | | | | |
| KK-0213 | 8 | 10 | 80 | 560 | 10.5 | 147.2 | 4.3 | 61 | 0 | 7 | 59 | 35 | | | | 70.0 | 7.1 |
| KK-0213 | 10 | 12 | 80 | 558 | 7.9 | 115.6 | | 62 | | | | | | | | | |
| KK-0213 | 12 | 14 | 80 | 556 | | | | | | | | | 53.0 | 37.2 | | | |
| KK-0213 | 14 | 16 | 80 | 554 | | | | | | | | | 58.0 | 33.7 | | | |
| KK-0214 | 0 | 2 | 0 | 567 | | | | | | | | | | | | | |
| KK-0214 | 2 | 4 | 10 | 565 | 1.4 | 61.3 | 0.9 | 81 | | | | | | | | | |
| KK-0214 | 4 | 6 | 30 | 563 | 1.9 | 103.4 | | 80 | 7 | 83 | 3 | 8 | | | | 21.8 | 2.1 |
| KK-0214 | 6 | 8 | 30 | 561 | 1.0 | 56.5 | 1.4 | 81 | 11 | 78 | 2 | 9 | | | | 30.1 | 2.8 |
| KK-0214 | 8 | 10 | | 559 | 0.9 | 45.9 | | 70 | | | | | | | | | |
| KK-02US1 | grab sample | | | 574 | 1.2 | 54.4 | 0.9 | 78 | | | | | | | | | |
| KK-02US2 | grab sample | | | 572 | 0.8 | 45.7 | 0.5 | 79 | | | | | | | | | |

[1] Where a sample was not analyzed for a particular parameter the value is left with a blank in the table.
Details of the assessment results can be found in the 1st and 2nd documents as listed in Appendix A of this QAPP.

[2] The elevation (in feet) is adjusted to the average Lake Michigan water level on the sampling days in relative to the Lake Michigan Charter Datum (IGLD 1985) at 577.5 feet

[3] TPCB = total PCBs and TPAH = total PAHs.
TPCB and TPAH are the sum of the concentrations of Aroclors and sixteen individual PAH compounds that exceeded the reporting limits.
PCB Arolors or PAH compounds that were detected at or less than the report limit were treated as "zero" in the sum.

[4] LOI = loss on ignition

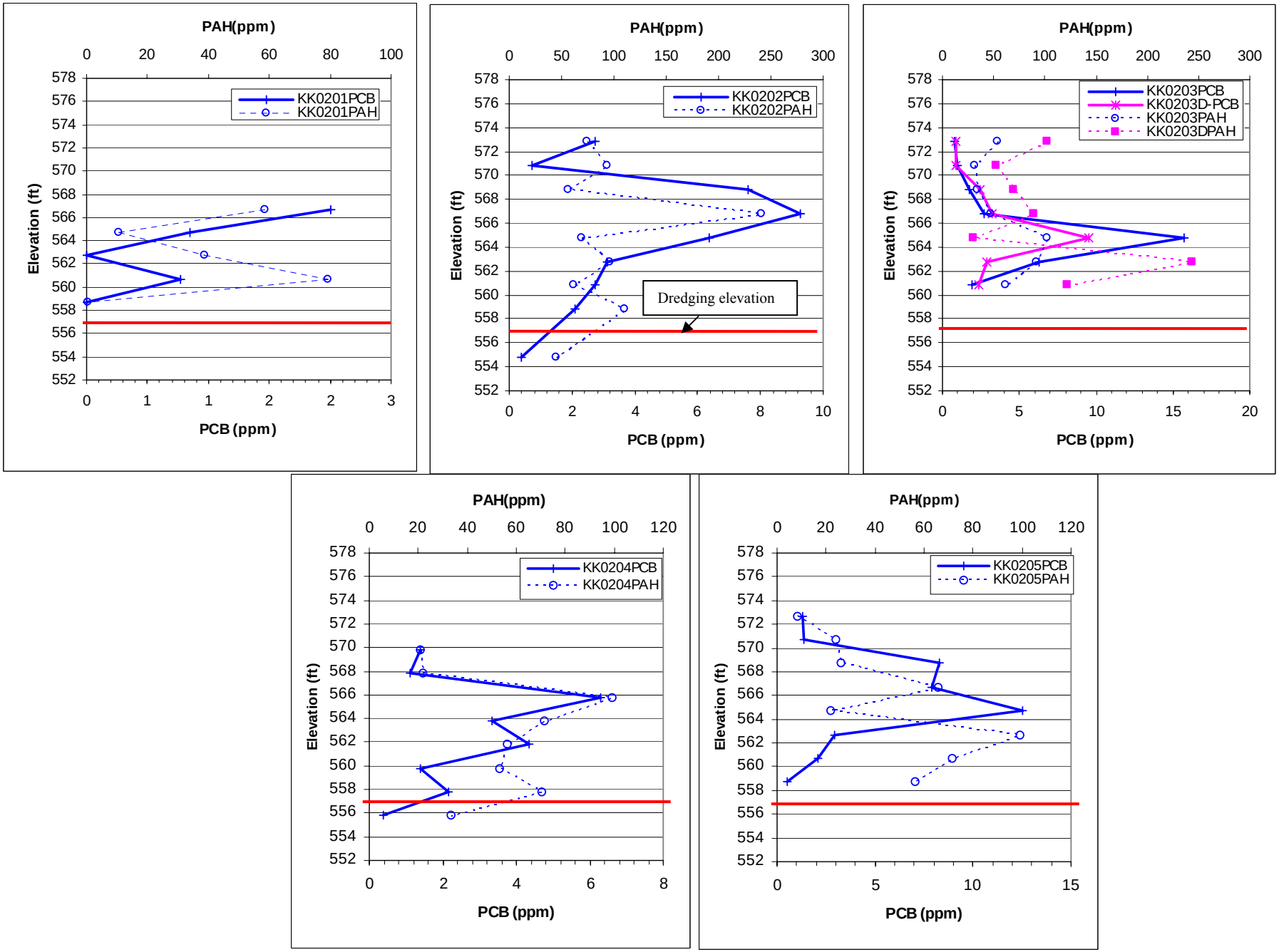



**Figure 2. TPCB and TPAH profiles in sediment cores collected in 2002 ( —proposed dredging elevation)**

**Fig. 2 (Cont'd)**

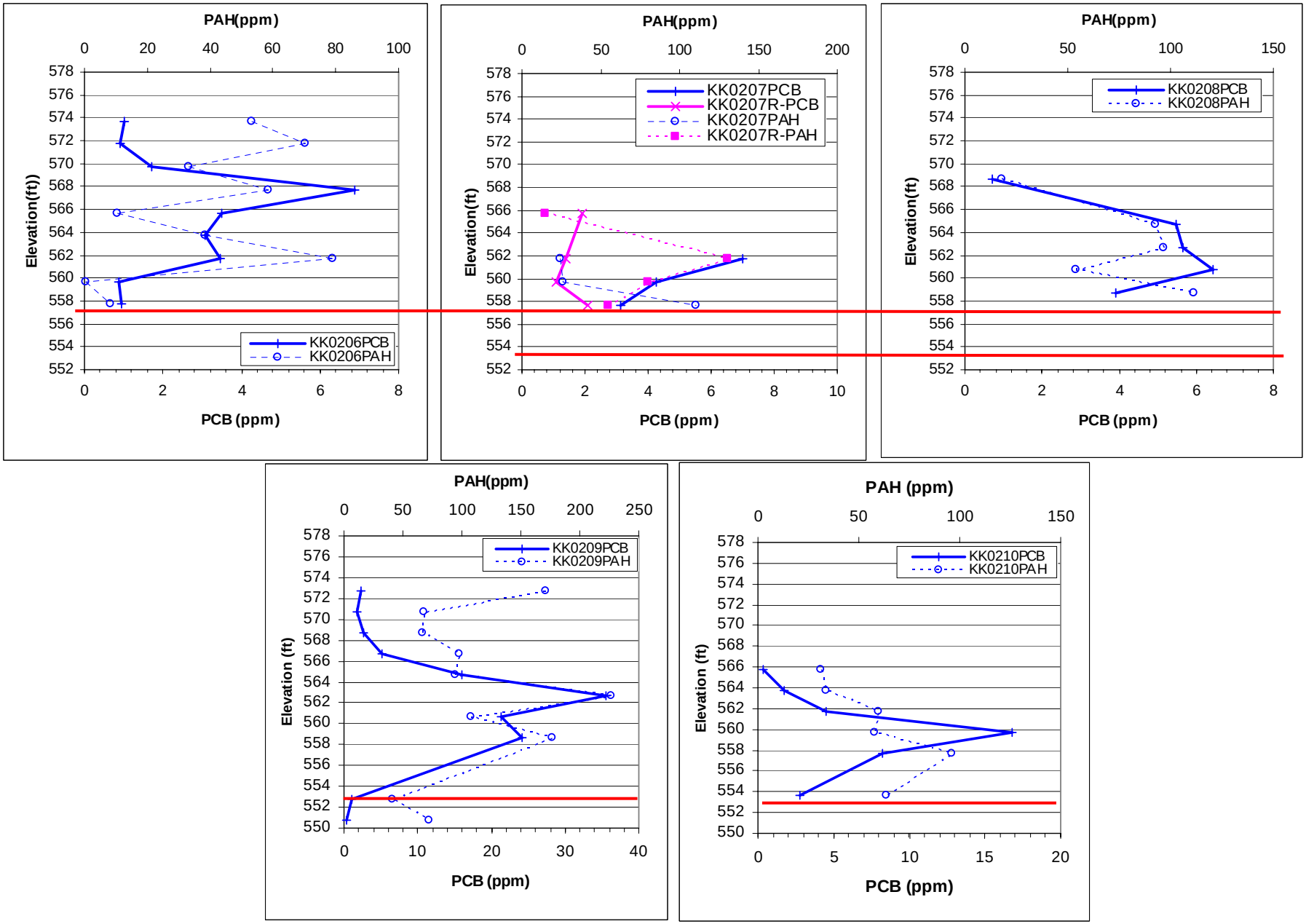
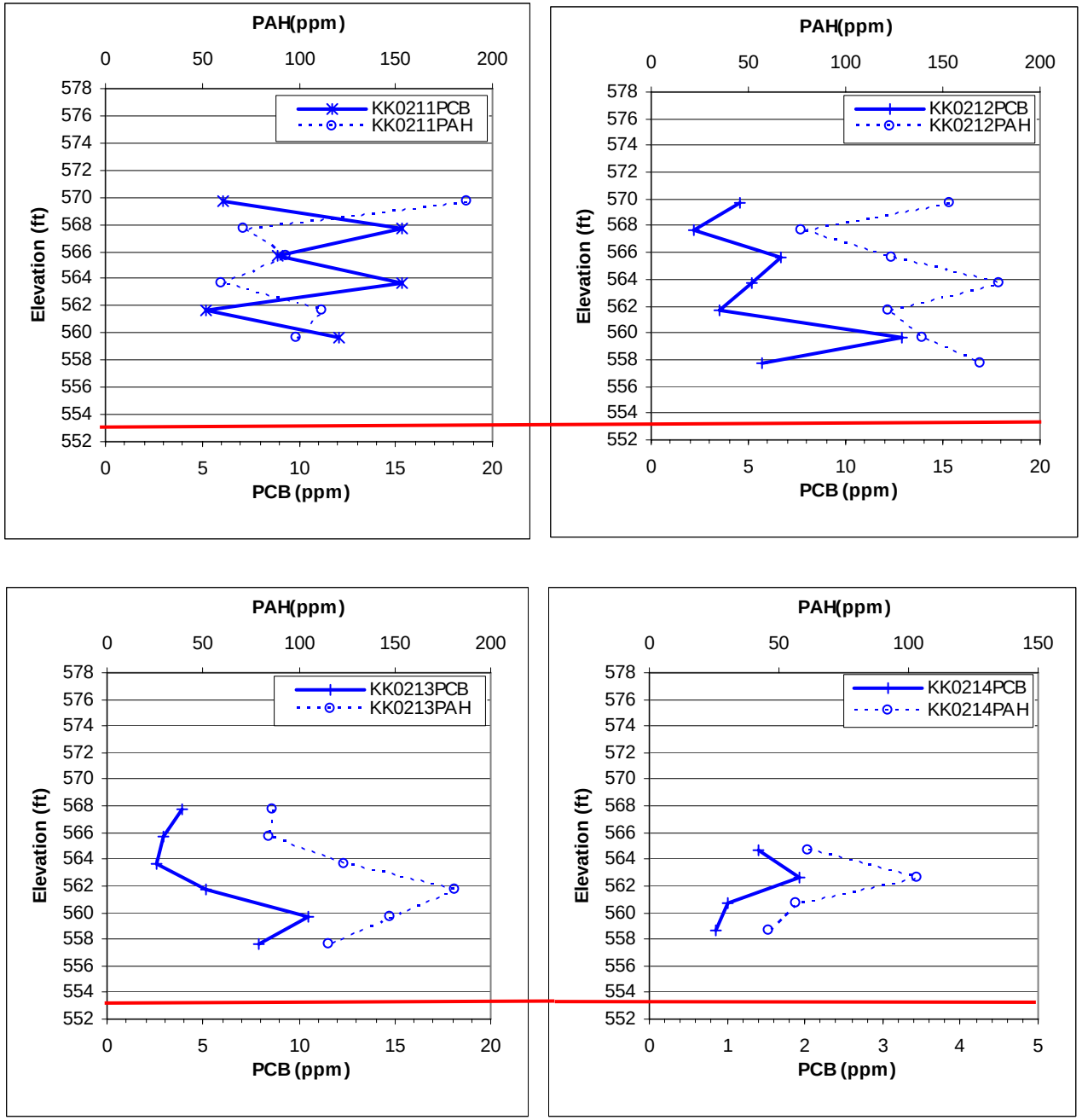

PAH(ppm)
Elevation(ft))
PCB (ppm)
KK0206PCB
KK0206PAH
PAH(ppm)
Elevation(ft)
PCB (ppm)
KK0207PCB
KK0207R-PCB
KK0207PAH
KK0207R-PAH
PAH(ppm)
Elevation(ft)
PCB (ppm)
KK0208PCB
KK0208PAH
PAH(ppm)
Elevation (ft)
PCB (ppm)
KK0209PCB
KK0209PAH
PAH (ppm)
Elevation (ft)
PCB (ppm)
KK0210PCB
KK0210PAH

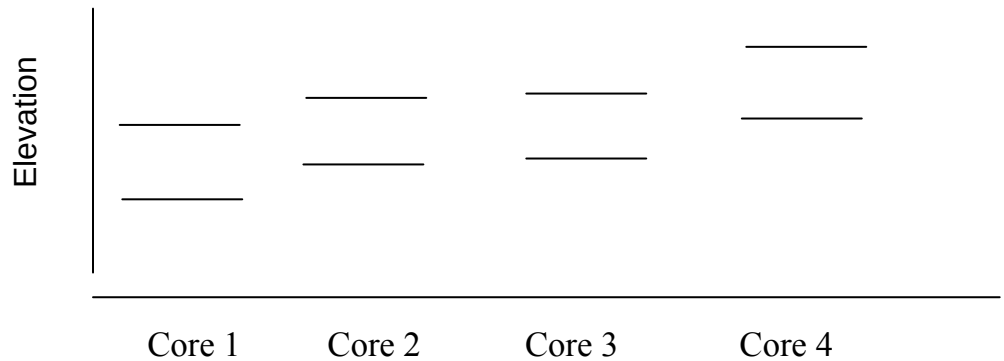
**Fig. 2 (Cont'd)**


PAH(ppm)
0 50 100 150 200
578 576 574 572 570 568 566 564 562 560 558 556 554 552
Elevation (ft)
KK0211PCB
KK0211PAH
0 5 10 15 20
PCB (ppm)
PAH(ppm)
0 50 100 150 200
578 576 574 572 570 568 566 564 562 560 558 556 554 552
Elevation (ft)
KK0212PCB
KK0212PAH
0 5 10 15 20
PCB (ppm)
PAH(ppm)
0 50 100 150 200
578 576 574 572 570 568 566 564 562 560 558 556 554 552
Elevation (ft)
KK0213PCB
KK0213PAH
0 5 10 15 20
PCB (ppm)
PAH(ppm)
0 50 100 150
578 576 574 572 570 568 566 564 562 560 558 556 554 552
Elevation (ft)
KK0214PCB
KK0214PAH
0 1 2 3 4 5
PCB (ppm)

## Average Concentrations

Arithmetic average concentrations calculated for each sediment management section (Fig. 1) will be used as cleanup objective to finalize the target dredging elevations. The following describes how the arithmetic average concentrations are calculated.

As discussed earlier, for dredging purpose, sediment depth is converted to elevation in relative to the LMD. The unevenness of sediment surface naturally existing in the river bottom complicates the calculation of average concentrations. The surface of each sediment core may or may not align to the same elevation as illustrated below.




If sediment surfaces align to the same elevation between cores or differ in a 2-foot interval (Case 1), the average concentration at a particular elevation in a section can be computed simply by averaging the concentrations in the 2-foot interval between the cores because sediment cores were segmented in 2-foot interval in 2002 assessment. If the sediment surfaces do not align to the same elevation between cores or differ in less than 2-foot interval (Case 2), then the data collected from 2002 must be interpreted.

Fig. 3 illustrates the computation processes. As shown in the figure, in Case I, the average concentration is calculated in a straight forward manner.

But it involves slightly more steps for Case II. For example, the average concentration at elevation between 573-572 feet ($X_{572}$) is calculated by averaging concentrations of $x_{1,1,}$ $x_{1,2}$ $x_{2,1,}$ $x_{3,1,}$ and $x_{4,}$ where $X_n$ denotes the arithmetic average concentration at elevation "n"; $x_{i,j}$ denotes the concentrations at the ith segments in the jth core. Similarly, the average concentration at elevation between 572-571 ($X_{571}$) feet is achieved by averaging $x_{1,2}$, $x_{2,1}$, $x_{2,2}$, $x_{3,1}$, $x_{3,1}$, $x_{4,1}$ from corresponding Cores of 1, 2, 3, and 4, respectively. The computation scheme as described in Case 2 creates a profile of average concentration based on 1-foot interval.

As a result, average concentrations of PCB and PAHs were calculated for three sections as shown in Fig. 4. It is worthy to note that sediment in Section 3 contains the highest

level of PCB with a high variation in horizontal and vertical extent comparing to the other two sections. As determined in the pre-engineering design phase, Section 3 will be dredged relatively deeper in order to remove the more contaminated sediment. Based on the average concentrations profiles it is anticipated that the post remedial concentrations in the center channel will be approximately less than 1.5ppm and 65ppm for PCB and PAHs, respectively.

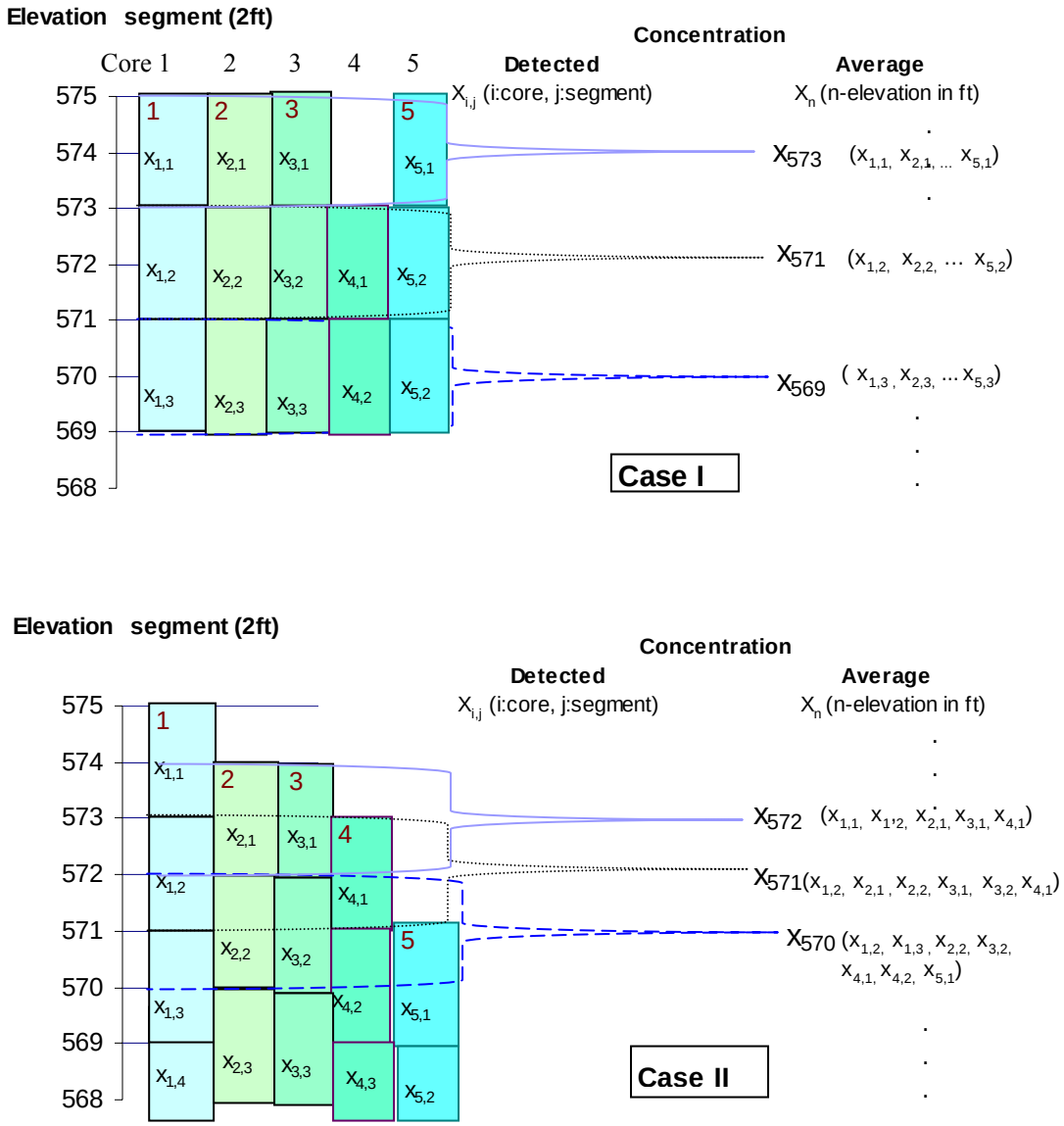



**Figure 3. Illustration of computation processes for the average concentrations at different elevation intervals within a sediment management section**

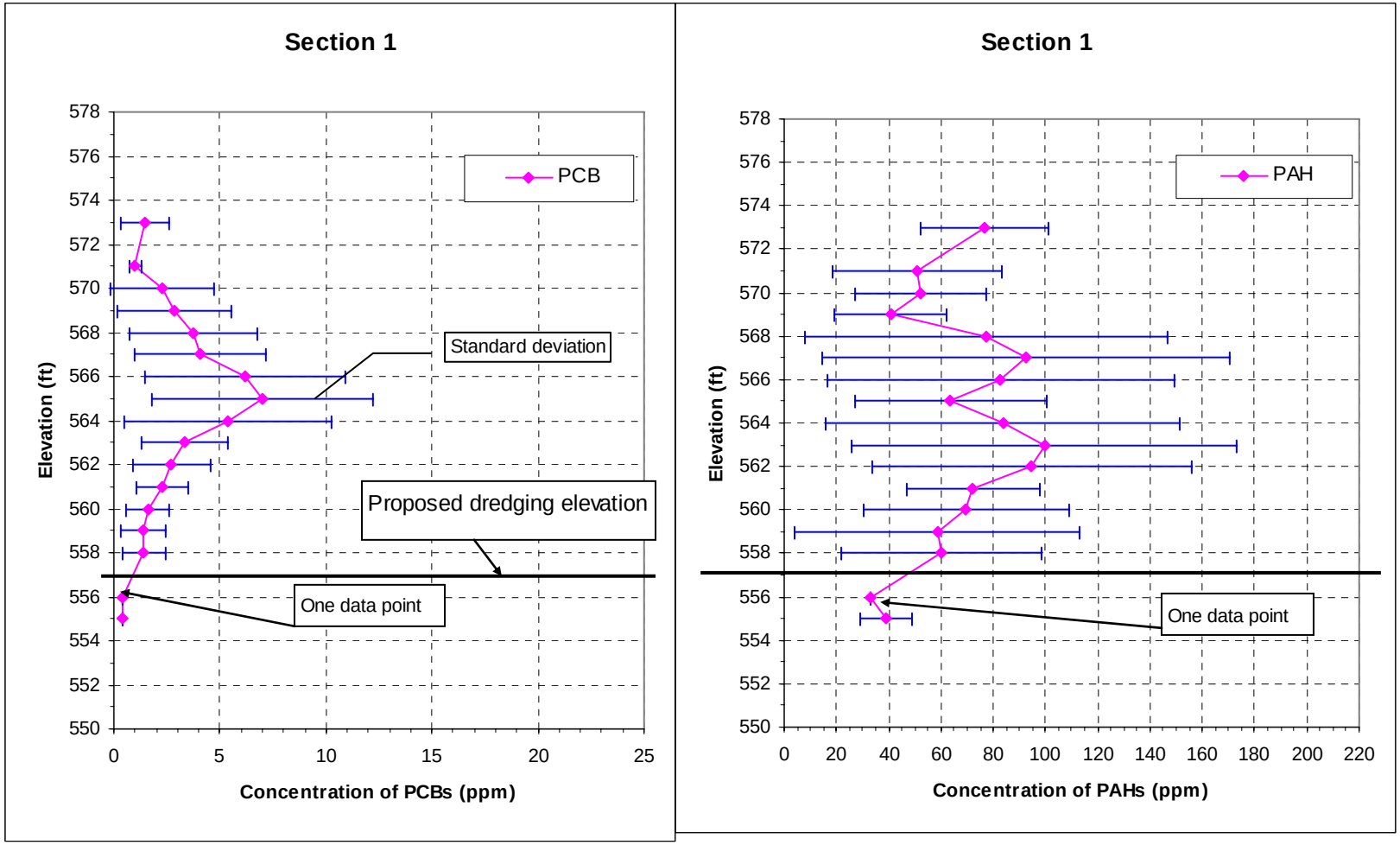
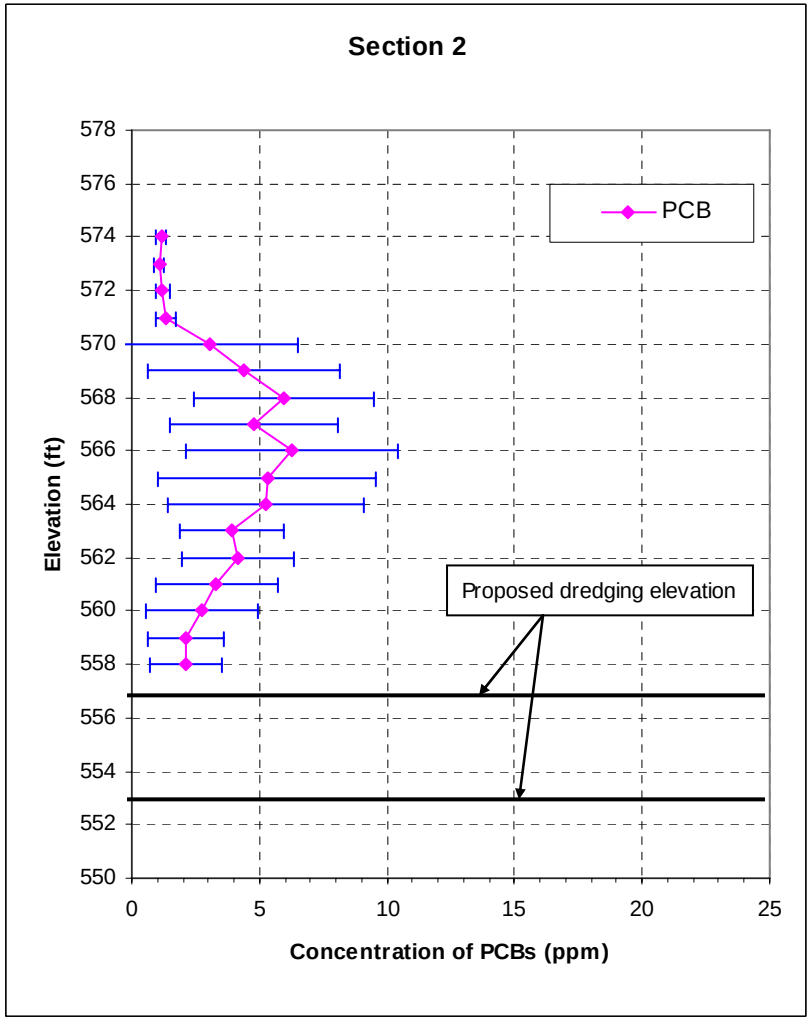



**Figure 4. Arithmetic average concentrations of TPCB and TPAH in each sediment management section**

**Fig. 4 (cont'd)**


Section 2
PCB
Proposed dredging elevation
Elevation (ft)
578
576
574
572
570
568
566
564
562
560
558
556
554
552
550
0
5
10
15
20
25
Concentration of PCBs (ppm)

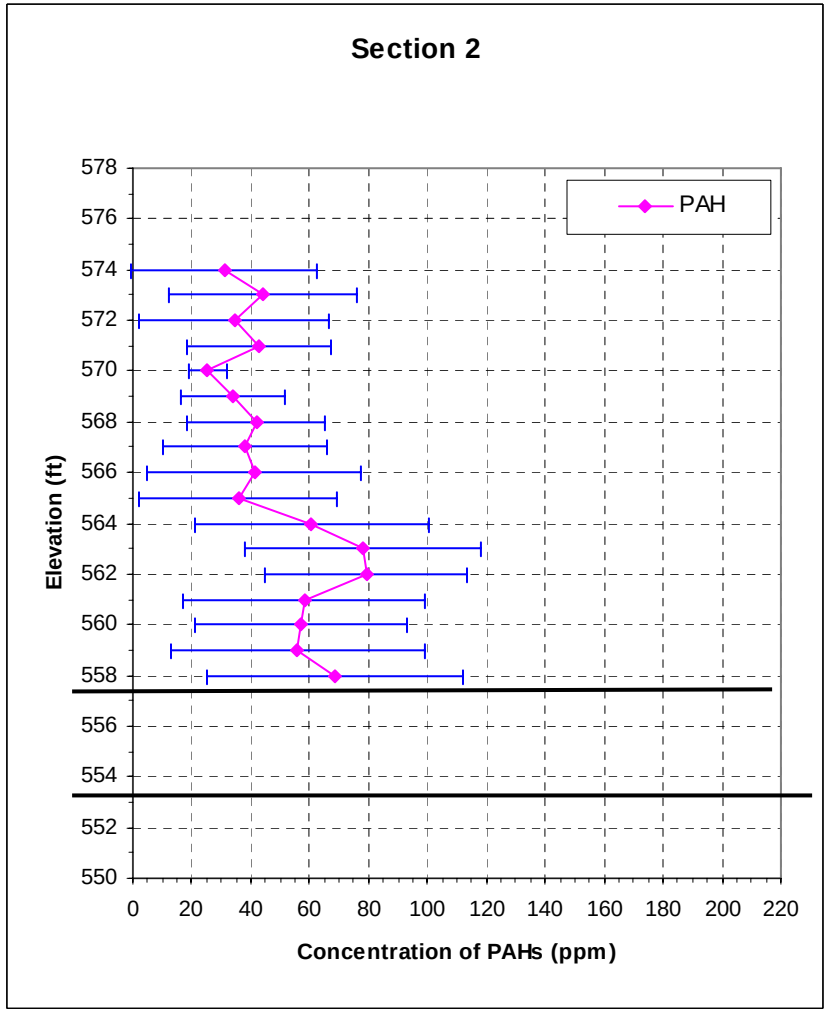
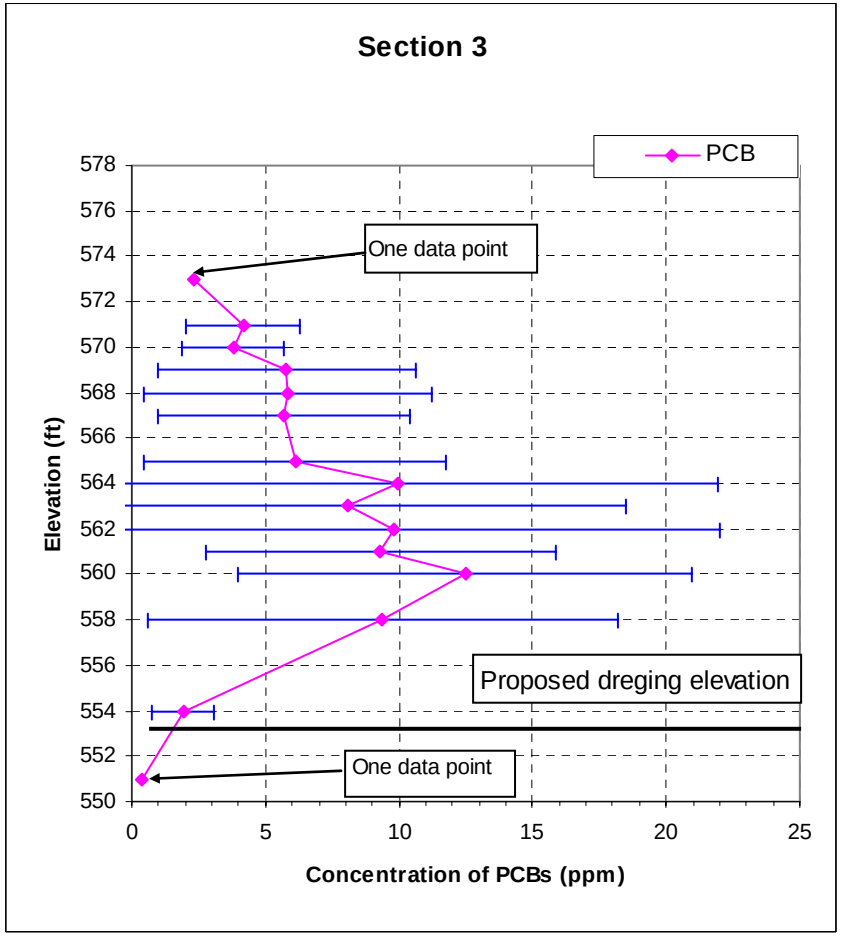
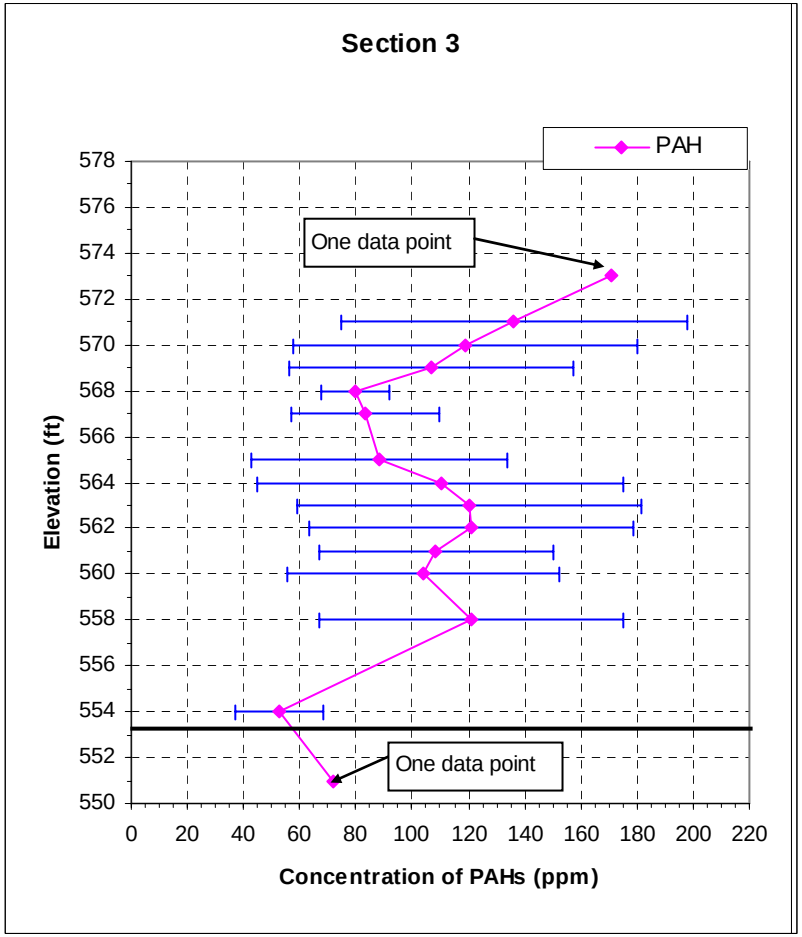

Section 2
PAH
Elevation (ft)
578
576
574
572
570
568
566
564
562
560
558
556
554
552
550
0
20
40
60
80
100
120
140
160
180
200
220
Concentration of PAHs (ppm)

**Fig. 4 (cont'd)**


Section 3
PCB
One data point
One data point
Proposed dreging elevation
Elevation (ft)
578
576
574
572
570
568
566
564
562
560
558
556
554
552
550
0
5
10
15
20
25
Concentration of PCBs (ppm)


Section 3
PAH
One data point
One data point
Elevation (ft)
578
576
574
572
570
568
566
564
562
560
558
556
554
552
550
0
20
40
60
80
100
120
140
160
180
200
220
Concentration of PAHs (ppm)

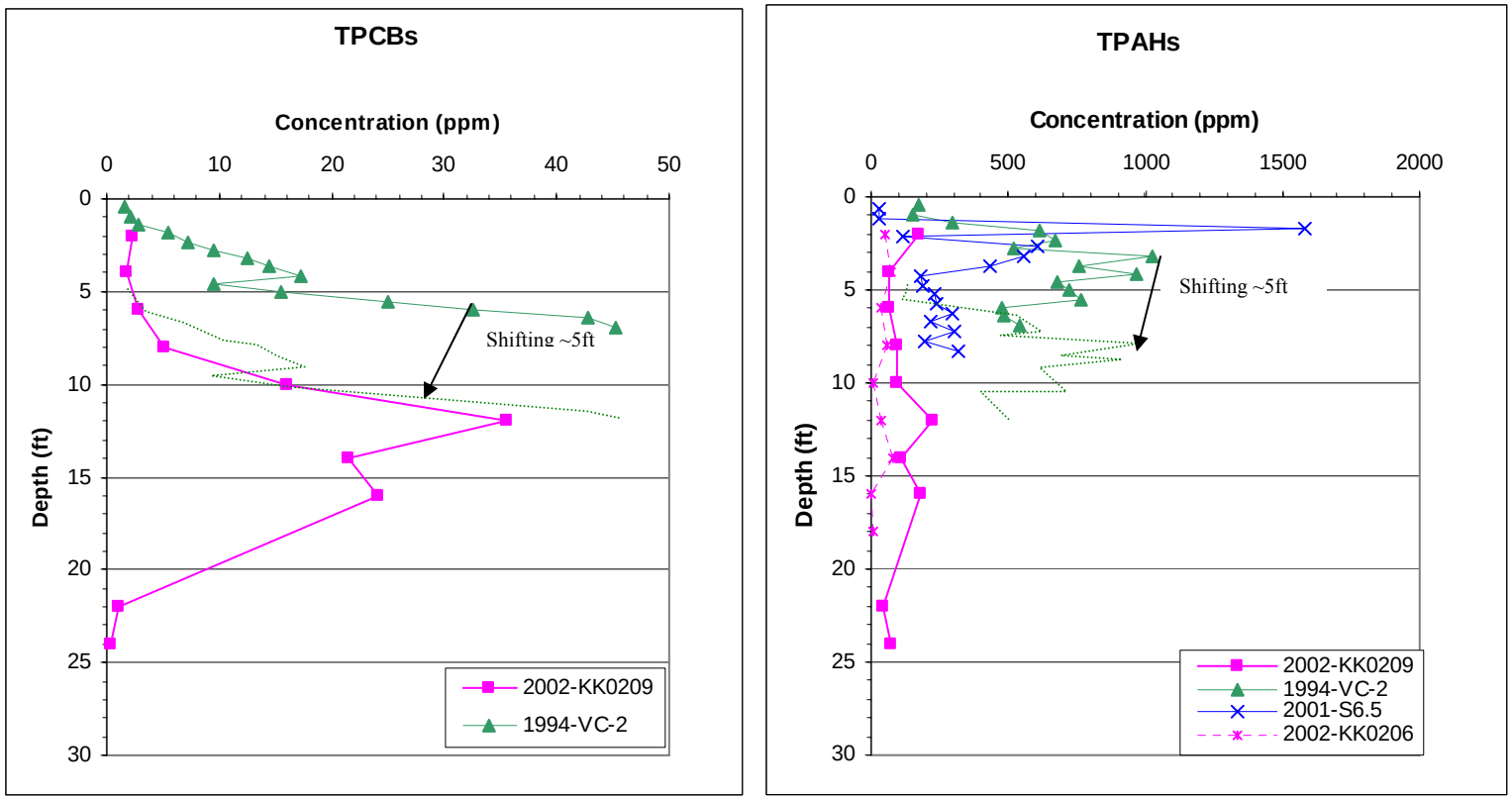



Figure 5. Profiles of TPCB and TPAH in sediment from the KK River (2002-KK0209 and 2002-KK0206 are from 2002 assessment, 1994-VC-2 is adopted form 1994 study by Li and et al.(1995), and 2001-S6.5 is adopted from 2001 study by Grundl (2002) )

## Evaluation of Data Quality

The data quality of TPCB and TPAH with respect to their usage for the restoration project were reviewed and evaluated by the US ACE, WDNR, and USEPA- GLNPO in 2003. During the review process, TPCB and PAH data from different studies were compared. In addition to the 2002 assessment, a number of sediment samples from the project area were collected and analyzed in 1994 and 2001. PCBs and PAHs were analyzed for in the 1994 study (Li and et. al, 1995), while only PAHs were analyzed for in the 2001 study (Grundl, 2001). Comparison of PAH concentrations detected in 2002 with the other two studies revealed a significant difference with respect to the maximum concentrations. The maximum concentration of TPAHs detected in 2002 (241ppm) was much lower than that detected in 1994 and 2001 (greater than 1,000ppm).

Fig. 5 shows the comparison of PCB and PAH concentrations in vertical distribution from different studies at similar sampling locations. Sediment core KK0209 was selected for comparison of PCB concentrations because within its proximity maximum PCB and PAH were detected in 1994 (VC-2) and 2002.

Two sediment cores, KK0209 and KK0206 from 2002 assessment, were selected for comparison of PAH concentrations for the purpose of including the 2001 study. Although there was a sediment core collected from the location close to KK0209 in 2001 study by Grundl, only the top two layers were analyzed, which made the comparison of the vertical distribution impossible. At the vicinity of core KK0206, there was a core (S6.5) collected in 2001. The relative locations of the sediment cores are shown in Fig. 6.

While plotting the TPCB and TPAH profiles at location of Core KK0209, attempts were made to reconstruct the vertical distribution after recognizing the differences between the studies. Reconstruction was conducted by considering recovery rate due to different sampling procedures and sediment accumulation between 1994 and 2002. An average recovery rate of 80% was applied for Core KK0209. Sedimentation rates calculated during the pre-engineering design phase were used to estimate the amount of sediment accumulated between 1994 and 2002 that shifted the surface of VC-2 about 5 inches downwards. Results were not promising. In another word, the differences in terms of PAH peak values and the location of maximum PCB concentrations still exist.

Another approach was carried out to arbitrarily shift the profiles from the 1994 study 5' downwards just for the purpose of comparing distribution shapes. The results are shown in Fig. 5. It is interesting to notice that after the shift, the shape of TPCB distribution profile from the 2002 assessment resembles that from 1994 study for the top 12 feet where data are available from both studies. But TPAH profiles still differ significantly.

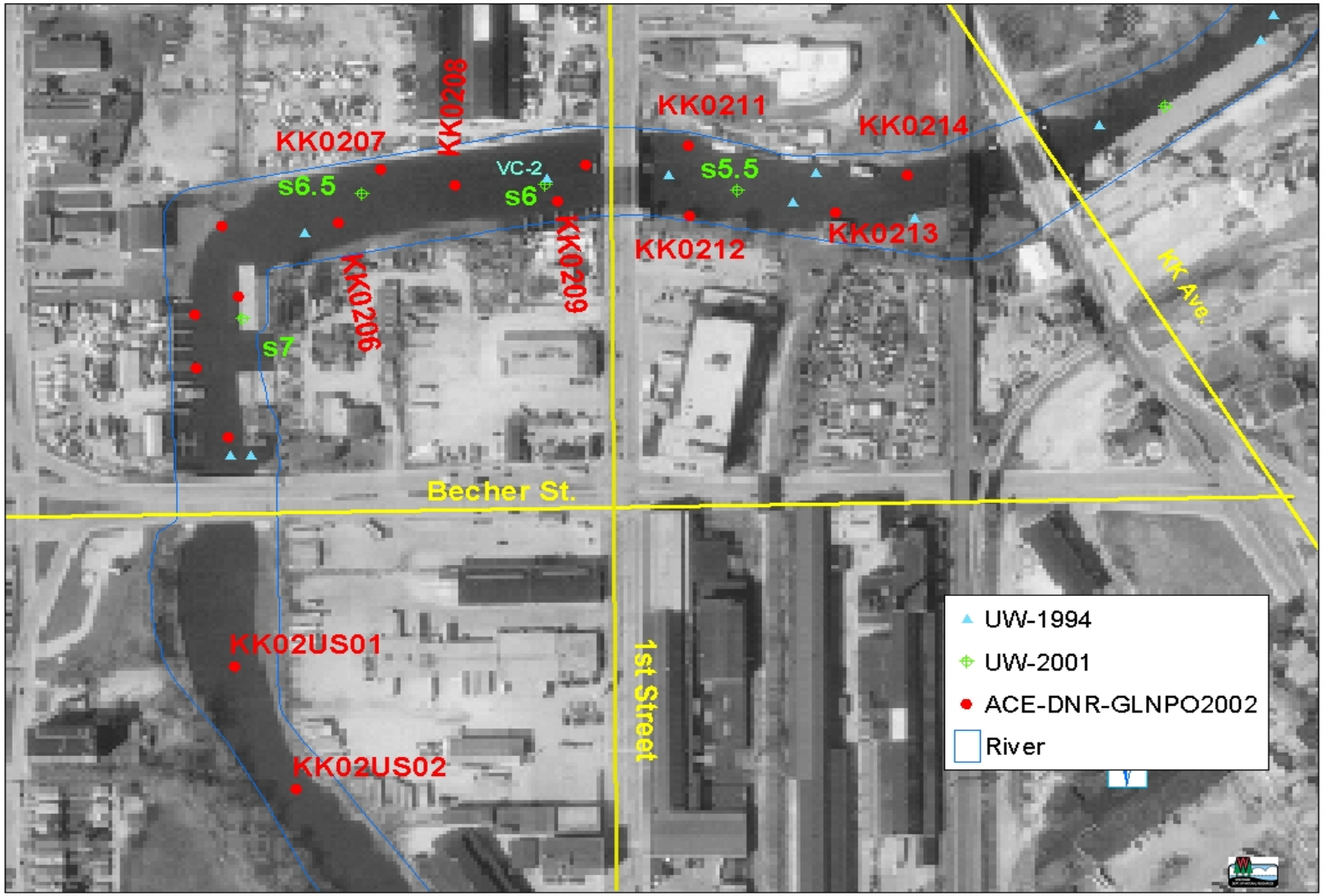



**Figure 6. Relative locations of sediment samples collected from studies in 1994 to 2002** (UW-1994: Li and et. al, 1995; UW-2001: Grundl, 2001; USACE-WDNR-GLNPO 2002: Altech, 2002)

***PCBs***

The similarity of PCB distribution profiles after shifting the 1994 data 5 feet deeper may imply comparable analytical results. But again, Core VC-2 from 1994 was not long enough to represent a complete profile of vertical extent and it is difficult to determine if the peak value would change in a complete 1994 core.

In terms of the maximum peak values, if the concentration of Aroclor 1254 is taken into account for TPCB from 2002 assessment, the peak values of PCB would be much more similar from both 1994 and 2002 studies at the proximity of KK0209. Fig. 7 shows concentrations for seven Aroclors analyzed in selected sediment samples collected from both 1994 and 2002. Results from both assessments show that Aroclor 1242 dominates among seven Aroclors. The second significant Aroclor detected is 1254 for 2002 assessment and 1260 for 1994 study, respectively. However, Aroclor 1254 data from the 2002 assessment were qualified as detected at reporting limits, which were treated as "zero" in calculating the total PCBs. For example, in segment between 565-563 feet at KK0209, Aroclor 1254 was reported at 12 ppm, but was qualified as at reporting limit.

Then TPCB was reported at 36 ppm, excluding Aroclor 1254. Disregarding the qualifier and using simple addition, although not correct, the upper bound TPCB concentration at this sample could reach approximately 48 ppm compared to 45 ppm at VC-2. Clearly there are analytical uncertainties existing among different studies.

To further explain the reasons for the uncertainties of the PCB results is beyond the scope of this document. The difference may or may not be caused by the potential factors or combination of these factors:

- Sediment compaction resulted from various sampling techniques and procedures
- Analytical variations
- Natural heterogeneity of sediment samples
- Continuous sediment dynamic transport processes

***PAHs***

Unlike the TPCB profiles, the maximum concentrations of TPAH detected were profoundly different between the 1994 and 2002 data sets. At locations KK0209 and KK0206, the peak PAH concentrations observed in 1994 and 2001 were not detected in the 2002 profiles. The shapes of distribution remain significantly different even if the 1994 profile was shifted 5 feet downward as shown in Fig. 5.

It is fully recognized that the factors as discussed above for the PCB profiles could contribute to the variation of TPAH concentrations among different data sets at similar locations. Nevertheless, the significant difference of the maximum concentrations between data sets warrants further evaluation of the 2002 data with respect to potential analytical errors while the other factors are less controllable.

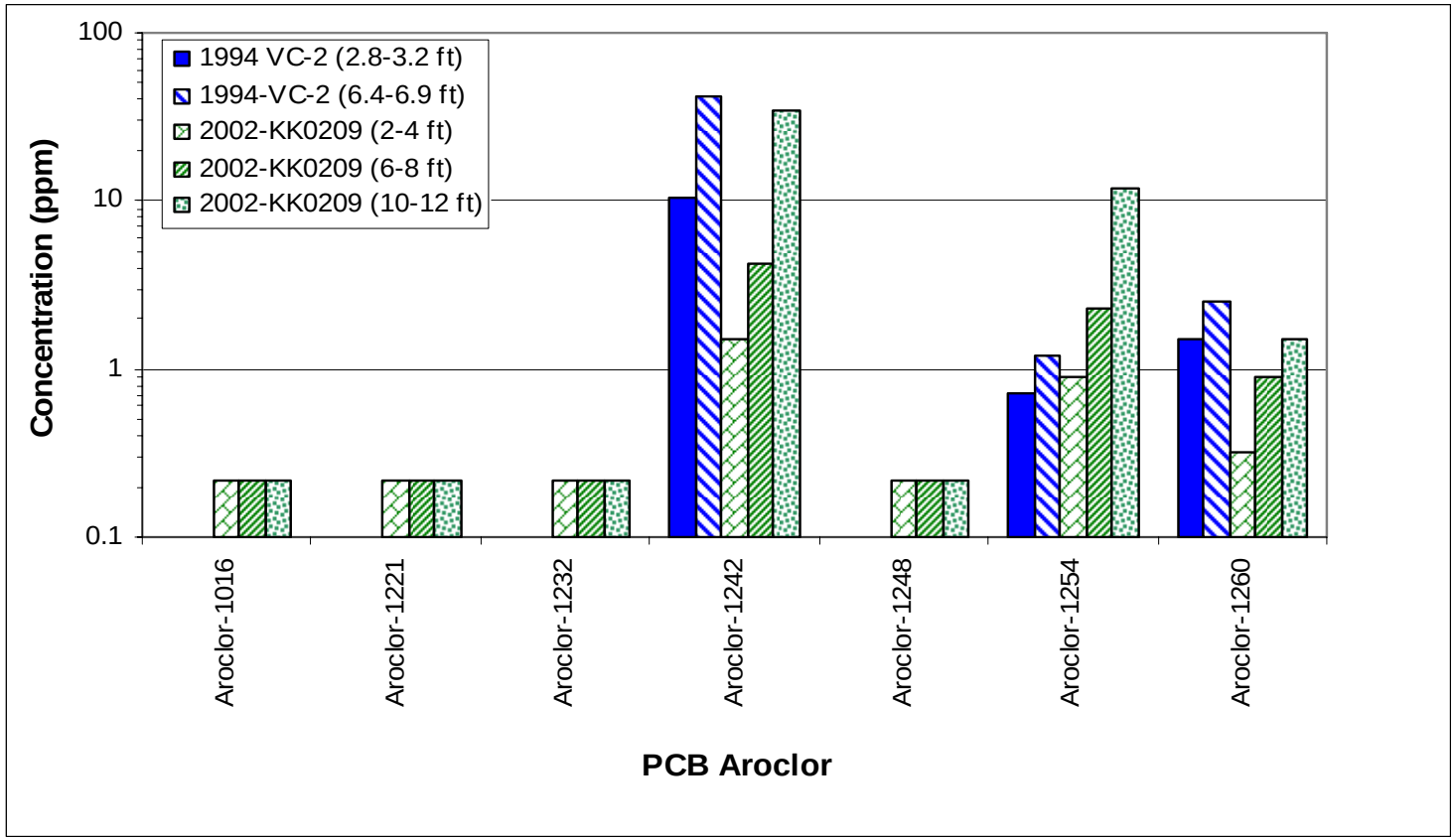



**Figure 7. PCB Aroclors detected in selected sediment samples (**1994-VC-2 (6.4-6.9ft) and 2002-KK0209 (10-12 ft) were where the maximum PCB concentrations were detected in 1994 and 2002, respectively. Aroclor 1254 was not taken into account for the total PCB in 2002 dataset, because it was detected at the reporting limit).

**Evaluation of PAH Data**

The question of what may cause the high discrepancies among the three data sets lead to multiple data quality evaluation processes. The first step was to verify whether or not the same PAH compounds were analyzed and used for calculation of TPAHs. After reviewing the original records, it was confirmed that the same sixteen PAH compounds were analyzed, reported, and summed up for TPAH under the three studies in question.

However, the verification revealed that the three studies had different laboratory reporting limits for individual PAH compounds and varied in methods of treating the values equal to or less than reporting limits for summation of PAH concentrations. Subsequently, the reporting limits under the three studies were compared. It was concluded that variation originating from reporting limits would not significantly influence the representation of TPAH concentrations. This conclusion is supported by the facts as follows:

- Reporting limits under the three studies were all at a relatively low level (less than 1.5 ppm for individual PAH compounds). Compounds that were detected at this level were all low molecular weight compounds. By nature, they are more susceptible of degradation in the environment.
- Similar predominant PAH compounds were found under the three studies as demonstrated in Fig. 8. Although only selected results are displayed in the figure, they are typical of compound distribution patterns from the three studies. Clearly, those compounds that were detected at a level equal to or less than the reporting limits, defined as "undetected", were not the predominant compounds among the sixteen analyzed.

After ruling out the possibility that variation of reporting limits could cause high discrepancy in TPAH concentrations among tree studies, follow-up procedures as listed below were undertaken to further evaluate and verify the 2002 assessment data.

1) The Trace Laboratory reanalyzed two samples with different sample preparation methods
2) A total of ten samples were sent to the Severn-Trent Lab. of North Canton, Ohio, (STL) from Trace Laboratory for an inter-laboratory cross check.
3) The WDNR selected six samples for analysis by the Wisconsin State Lab of Hygiene (SLOH).
4) The USACE Omaha District performed an independent QA/QC audit on the 2002 data reported by the Trace Laboratory.

The purpose of the 1$^{st}$ procedure was to evaluate potential errors associated with different sample preparation methodology within the Trace Lab, serving as an internal laboratory check up.

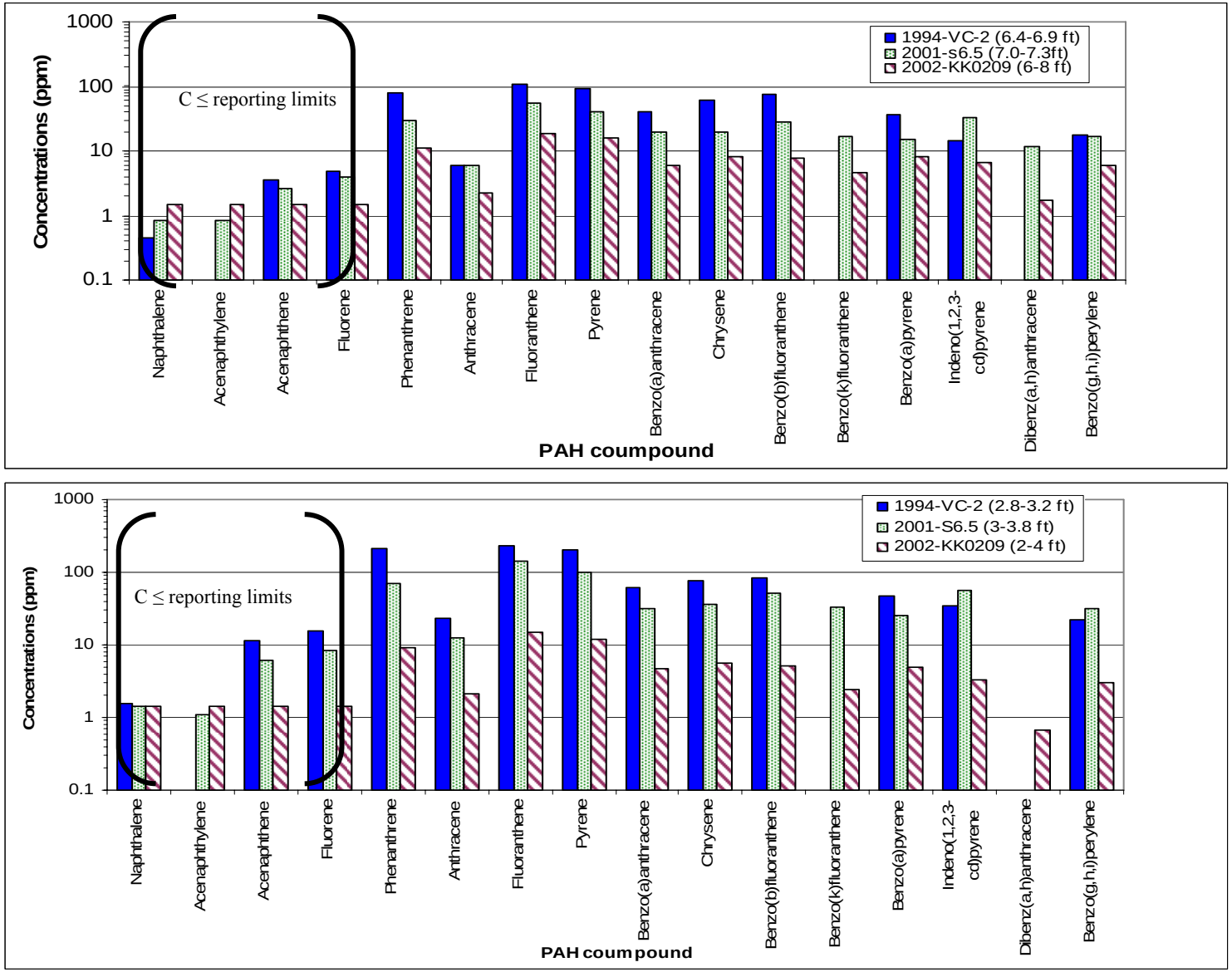



**Figure 8. Distribution of PAH compounds in selected sediment samples colleted in 1994 and 2002** (for 1994 dataset, compounds Benzo(b)fluoranthene and Benzo(k)fluoranthene was reported with one value as well as Indeno(1,2,3-cd)pyrene and Dibenzo(a,h)anthracene)

The 2nd and 3rd procedures were performed to evaluate inter-laboratory analytical uncertainties. Ideally, for a true inter-laboratory cross check, standard materials should be used for analyses. The results can then be used to check the systematic uncertainties caused by different labs. However, the standard inter-laboratory cross check does not reflect uncertainties that can be associated with real field samples. Therefore, the inter-laboratory cross check for these procedures serves the purpose of finding out how different the results could be if the real samples were analyzed by different laboratories. The uncertainties resulting from this inter-laboratory cross check not only included systematic errors from a lab but also those caused by sediment samples.

The objective of the 4th procedure was to make a final decision on whether or not the PAH data obtained in 2002 could be accepted for the subsequent engineering design work. The results from the evaluation are summarized as follows:

1. The re-analyses by the Trace laboratory with different sample preparation methods did not provide a conclusive result. Sonication extraction may or may not cause a bias towards lower recovery and lower concentration of PAH as assumed. As shown in Table 3, for sample KK02US1, the Soxhlet extraction resulted in higher TPAH concentration (116 ppm) compared to Sonication extraction (78 ppm). In contrast, for sample KK0201-0204, the Soxhlet extraction method resulted in lower concentration of TPAH (55ppm) compared to the Sonication method (68 ppm). The difference could be originated from the methods or from the heterogeneity of samples.

2. Results from the inter-laboratory cross check were also inconclusive. Concentrations of individual PAH compounds that exceeded the reporting limits from different laboratories for the same sample were compared among Trace, STL, and SLOH laboratories. Here, the "same sample" is defined as the sample aliquots from a sediment segment with the same identifications.

   It should be noted that the value of 815 ppm of TPAHs reported by STL laboratory for sample KK02US1 was later disqualified because the surrogate recovery was out of the laboratory QA/QC limits.

   Fig. 9 shows the comparison of the concentrations of selected individual PAH compounds analyzed by the Trace and STL laboratories. Concentrations reported by the Trace and STL are displayed on the x-axis and y-axis, respectively. There is a slight trend that the STL's results biased high for the compounds detected in low levels by the Trace.

   A similar trend is also observed by comparing the data from the SLOH to that from Trace. As shown in Fig. 10 the results from SLOH are relatively higher than that from Trace. The variation again may come from laboratory analysis or from sample

matrix. The SLOH and Trace laboratories used different instruments and different sample preparation methods. HPLC was used by the SLOH while GCMS was used by the Trace. Regarding sample preparation, Soxhelet was used by the SLOH while Sonication was used by Trace. Studies have shown that HPLC is more sensitive for analyzing PAHs at low levels compared to GCMS (verbal communication with SLOH).

The inconclusiveness of the inter-laboratory cross check is also reflected in the statistical aspect of the data as summarized in Table 3. As shown in table, there are three occasions that the same samples were analyzed by the three laboratories. The standard deviation was high (122 ppm) for sample KK0207-0608 with the original concentration detected at less than 100 ppm by the Trace lab. But the standard deviation was 24 ppm for sample KK0203-0810 with the original concentration detected at 102 ppm by the Trace.

3. Because both the internal check and inter-laboratory cross check were not conclusive, an independent data audit was conducted by the USACE Omaha District Office. The audit concluded that the Trace laboratory performed within its stated data quality acceptance limits and these measures generally support the usability for the follow up engineering design [Attachment 2]. Therefore, the PAH data from 2002 assessment have been verified for use in the pre-engineering design and will be used for the final engineering phase. The data collected in 1994 by UW-Milwaukee researcher were not and will not be used further except for as references.

**Conclusions**

The PAH analyses carried high uncertainties, particularly in the samples with low concentrations, for example, less than 100ppm. Using PAH data as one of the cleanup criteria could possibly lead to high decision errors. Consequently the PCB data from the 2002 assessment will be the primary parameter for establishing site cleanup objectives. PAHs data will be used as references when needed. This decision can be further supported by two facts: 1) to a large extent the vertical distribution patterns of PAH concentrations in sediment at each location follows the similar trend of PCB profiles as shown in Figure D-2. In some locations, the maximum PCB concentrations in sediment cores coincide with the PAH peaks; 2) as displayed in Fig. 2, although the dredging depths were determined based on PCB distributions, sediment contaminated with high level of PAHs will be removed as well under the current proposed dredging specifications.

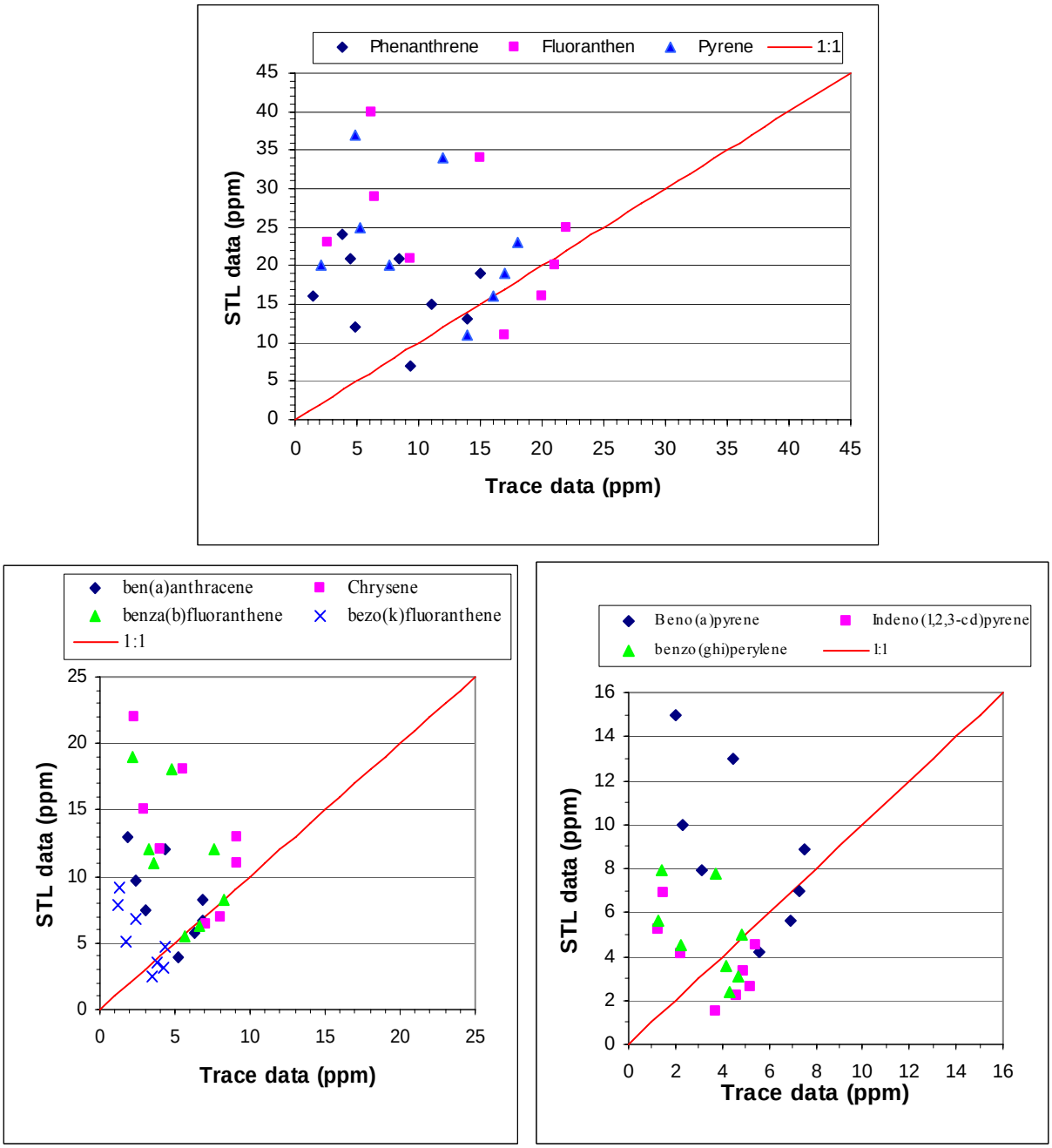



**Figure 9. Comparison of inter-laboratory cross check analyses (STL and Trace) for selected PAH compounds**

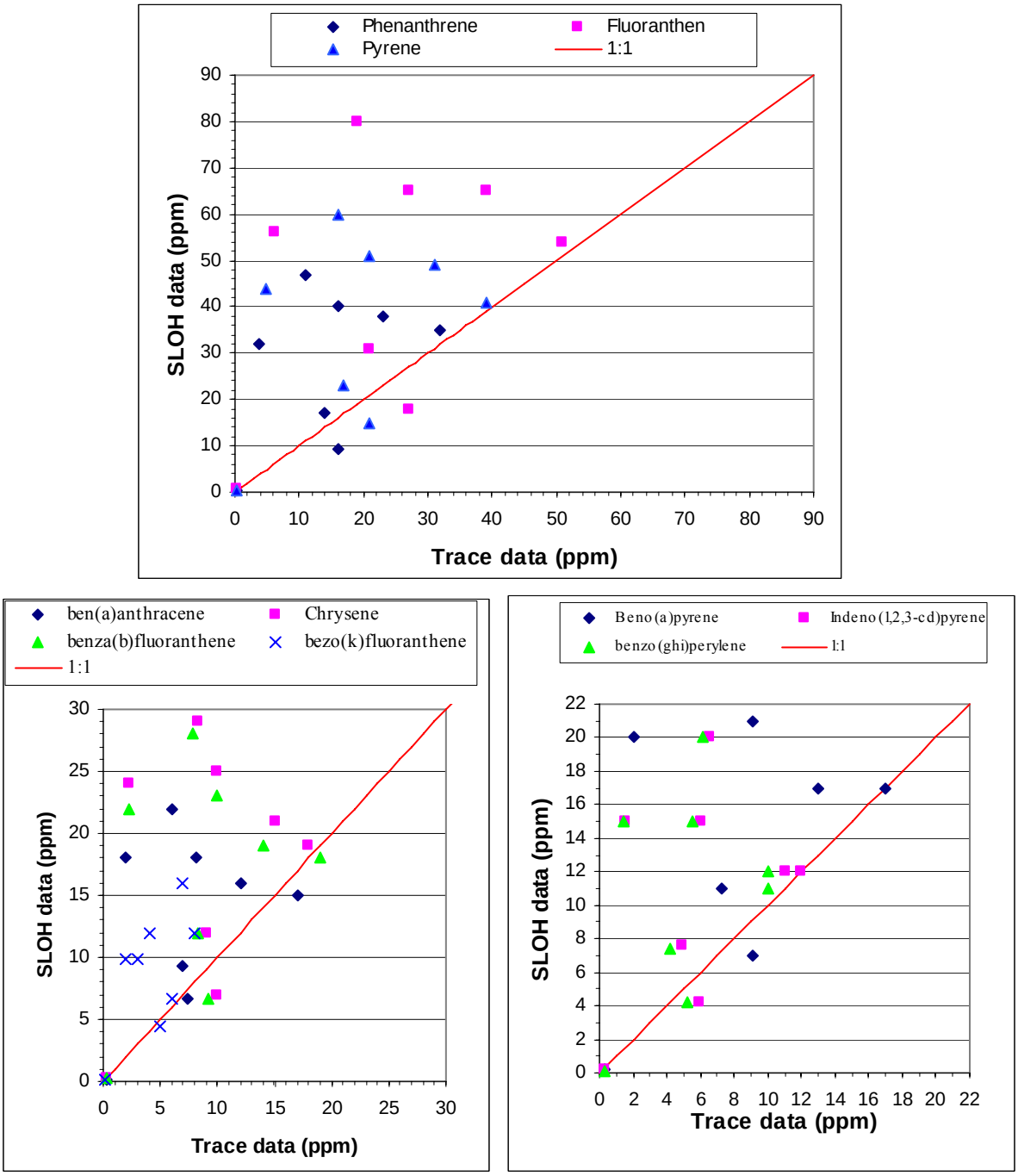



**Figure 10. Comparison of inter-laboratory cross check analyses (SLOH and Trace) for selected PAH compounds**

## Table 4. PAH results for confirmation samples

| **Sample ID** (extraction method) | **Total PAHs Concentrations (ppm)** | | | Note |
|---|---|---|---|---|
| | **Laboratories*** | | | |
| | Trace | STL | SLOH | |
| KK02US1 (Sonication) | 54 | | | **Under "Trace"** original result |
| KK02US1 (Sonication) | 78 | | | Rerun |
| KK02US1 (Soxhlet) | 116 | 815 | | Trace's rerun |
| KK02US1( Soxhlet) | --- | 112 | | STL's rerun |
| ****Ave (KK02US1)** | **83** | | | |
| *****Stdev (KK02US1)** | **31** | | | |
| KK0201-0204 (Sonication) | 10 | | | original result |
| KK0201-0204 (Sonication) | 68 | | | Trace's rerun |
| KK0201-0204 (Soxhlet) | 55 | 105 | | Trace's rerun |
| **Ave (KK0201-0204)** | **44** | | | |
| **Stdev (KK0201-0204)** | **30** | | | |
| KK0201-0810 | 0.33 | | 3.1 | |
| KK0202-0608 | 241 | | 239 | |
| KK0203-0810 | 102 | 95 | 140 | **Ave=112 Stdev =24** |
| KK0203-0810D | 30 | 140 | | |
| KK0204-0204 | 93 | 81 | | |
| KK0207-0608 | 26 | 194 | 264 | **Ave=161 Stdev =122** |
| KK0207R-0608 | 90 | 56 | | |
| KK0209-0406 | 67 | 171 | | |
| KK0209-0608 | 97 | | 357 | |
| KK0209-1214 | 108 | 123 | | |
| KK0209-2022 | 177 | 105 | | |
| KK0211-0002 | 187 | | 264 | |
| KK0212-0406 | 124 | | 292 | |
| KK0214-0810 | 46 | | 85 | |

* Different laboratories used different sample preparation and analytical methods.
For extraction, Sonication was used by Trace while Soxhlet was used by STL and SLOH.
The Trace Laboratory reran some of the samples by using both Sonication and Soxhlet extraction as indicated in the parentheses in the first column.
For instrumental analyses, GC-MS was used by Trace and STL while HPLC was used by SLOH.
The preparation and analytical methods were both EPA approved methods.

** Ave = average concentration

*** Stev = Standard deviation

**Data SET 2: Results from 2003 sampling at background reference site**

The KK River is a typical urban river in that most of the area of the watershed is developed either for residential or commercial and industrial uses. Contaminants from anthropogenic sources are ubiquitously present in the KK River sediment, particularly at the project area where the river becomes wider and deeper compared to the upstream. Multiple contaminants, PCB, PAHs, and potentially heavy metals coexist in sediment. In developing the cleanup criteria, it is impractical to target the post remedial concentrations to sediment quality criteria based on empirical approaches by linking the lower level of individual contaminant in sediment to adverse effects on biota in a laboratory. For that reason a local background reference site was established in 2002. The stretch of the river between Becher Street and Chase Ave, approximately 1,200 feet in length within the Milwaukee Estuary AOC and upstream of the project area, was selected as the local background reference site during the 2002 assessment. Fig. 11 shows the location of the background reference site in relation to the project area.

The decision for selecting the background reference site was made based on the characteristics of the KK River and the potential of transport of sediment to the project area from upstream. Chase Avenue is the upper boundary of the KK River portion of Milwaukee AOC. Further upstream of Chase Avenue, the river channel is lined with concrete. Little, if any, sediment deposits in these concrete lined channels. Sediments from the upper portion of the KK River watershed readily settle on the riverbed starting downstream from Chase Avenue. Throughout of the years, the long term hydrodynamic sediment transport processes have created a pattern in the distribution of solids. Coarser and sandy materials have deposited in the area close to Chase Avenue., creating sand bars in the river. Finer sediment particles have transported further downstream to the project area or immediately upstream of the project area. After remediation, sediment deposited between Chase Avenue and Becher Street may potentially transport downstream and deposit in the project area. Therefore, the concentrations of PCB and PAHs in sediment in this stretch of the river are representative as background levels and can be considered as upper bound of cleanup criteria.

To establish the background TPCB and TPAH concentrations, sediment samples were collected in 2002 and 2003 from the locations as shown in Fig. 11. As part of the 2002 sampling protocol, two grab samples (KK-02US1 and KK-02US2) were collected [Altech, 2002]. These two samples were collected between Becher Street and Lincoln Avenue, just upstream of the project area. Later in 2002, WDNR realized that additional samples were needed to better characterize the entire background reference site.

On Feb. 27, 2003, nine additional samples were collected from potentially depositional areas that are representative of nonpoint and point sources including the areas up- and down-stream of outfalls, at the exposed sand bars, and close to truck roads. These

**Figure 11. Location of sediment samples at the background reference site relative to the samples in the project area**

samples are denoted with the identification keys of KKUS0301 through KKUS0309 as shown in Fig. 11. Samples KKUS0301 and KKUS0302 served as field replicates. Six out of nine samples were selected for PCB analyses. All nine samples were analyzed for PAH and particle size distribution.

The details of sample collection and analysis are documented in sampling report [Altech, 2002] for the 2002 samples and in Appendix C of the Concept Design Documentation Report (CDDR) for 2003 samples, respectively. A brief summary of the 2003 sampling and analytical results is provided below. Also along with the presentation of data, a discussion regarding the data quality will be provided.

**Sampling and Analyses in 2003**

Sampling locations were determined by using a Trimble global positioning system (GPS) unit. On the sampling day, the river upstream from Becher Street was frozen with approximately 1-2 feet of ice. WDNR staff carried the equipment on a sled and walked from Becher Street to Chase Avenue. A power auger was used to break through the ice before a petite ponar dredge was advanced to collect the samples. A core sampler was not used because based on the past experiences, particularly from the 1994 studies (Christensen, 1995, personal communication), sediment cores were not obtained due to the coarse material deposited in the stretch of the river. We encountered difficulties at a few places where it was not possible to obtain sediment materials by using the ponar. A stainless steel spoon was used to scoop up the materials.

Upon retrieval, sediments were mixed in a stainless steel mixing bowl, subsampled into a 500ml Mason jar, and stored in a cooler on ice under the air temperature of $0^{o}C$. By the end of the day, samples were transported from Milwaukee to Madison and stored in a refrigerator in the WDNR's office building. Next day, on Feb. 28, 2003, the samples were delivered to the Wisconsin State Laboratory of Hygiene (SLOH), Madison, Wisconsin for analysis.

The same QA/QC sampling procedures used in 2002 assessment [Appendix D-1] were followed for the 2003 sampling event. But the sample preparation in laboratory and instrumental analyses differed. Samples were prepared by using Soxhlet extraction followed by clean-up procedures (SW846 3550B/3630). SLOH method Section 1581 (equivalent to the SW846/8310) with HPLC used for PAH analyses. Section 1510 (SW846/8080A) was applied for PCB analyses with GC/ECD.

Table 5 summarizes the sampling locations and physical characteristics of the sediment samples. The surficial sediment from the background reference site (~top 6"-12") had a high percentage of sand, ranging from 88-98% with an average of 96%. In some areas, particularly near Lincoln Ave, the stream bed was covered by large boulders, rocks, and gravel with little sediment present in surface.

## Table 5. General parameters for samples collected from the background reference site (upstream of Becher Street)

| Sample ID | WD* | D ** | W** | Time*** | Color & Texture | Sand | Silt | Clay | Analyses | | Notes**** | Location | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ft | ft | ft | | | % | % | % | | | | Lat | | | Long | | |
| KKUS0301 | 4.0 | 230 | 230 | 11:30 | Sandy | 98 | 0 | 2 | PAH | PCB | | 43° | 00' | 21" | 87° | 54' | 50" |
| KKUS0302 | 2.2 | 230 | 230 | 11:45 | Sandy | 97 | 1 | 2 | PAH | PCB | | 43° | 00' | 21" | 87° | 54' | 50" |
| KKUS0303 | 3.5 | 820 | 164 | 12:00 | Sandy | 97 | 1 | 2 | PAH | | | 43° | 00' | 15" | 87° | 54' | 47" |
| KKUS0304 | 5.2 | 1,214 | 197 | 12:15 | Sandy, black asphalt, mussel shells | 95 | 4 | 1 | PAH | PCB | | 43° | 00' | 12" | 87° | 54' | 44" |
| KKUS0305 | 9.8 | 1,640 | 72 | 12:30 | Silty sand | 93 | 5 | 2 | PAH | | | 43° | 00' | 09" | 87° | 54' | 42" |
| KKUS0306 | 3.2 | 2,066 | 82 | 12:45 | Sewer smell, gravel, stones, silty sand | 97 | 2 | 1 | PAH | PCB | | 43° | 00' | 05" | 87° | 54' | 40" |
| KKUS0307 | 1.8 | 2,329 | 98 | 13:00 | gravel, stones, silt sand. | 98 | 0 | 2 | PAH | | 1 | 43° | 00' | 02" | 87° | 54' | 40" |
| KKUS0308 | 0 | 3,346 | 115 | 13:40 | exposed deposit materials, sandy | 88 | 4 | 8 | PAH | PCB | 2 | 42° | 59' | 52" | 87° | 54' | 42" |
| KKUS0309 | 0 | 4,264 | 66 | 14:00 | exposed deposit materials, sandy | 98 | 0 | 2 | PAH | PCB | 2 | 42° | 59' | 46" | 87° | 54' | 48" |

* WD: Water depth

** D- distance from Becher Street to the sample location. W-stream width at the sample location.
D and W are measurements from the aerial photo (Fig. 11) by using GIS tool.

*** Time- when the sample was collected

**** 1. No materials could be retained by the ponar. A spoon was used to collect the sample
2. There was no standing water above sand bars. The samples for 08 and 09 were composite samples generated from three subsamples collected with a spoon from two transects. The middle of a transect was considered as the sample location.

**Data Evaluation**

As summarized in Table 6, the data collected from the background reference site varied from 0.5 ppm to 2.2 ppm for PCBs and 14 ppm to 347 ppm for PAHs, respectively. As a first step for establishing cleanup criteria, average concentrations of PCB and PAHs need to be calculated. However, there are issues regarding the computation of average concentration as listed below:

- Temporal difference: whether or not the two datasets collected in Sep. 2002 and Feb. 2003 can be combined.

- Extreme value: whether or not the sample KKUS0306 with a high PAH concentration (347ppm) should be included although it has been discussed in Appendix C of CDDR [USACE and WDNR, 2004] that the PAH high concentration of 347 ppm observed at location KKUS0306 is considered as an isolated case.

- Spatial difference: whether or not the concentrations in sediment immediately upstream from Becher Street (between Lincoln and Becher Street) better represent the background reference levels.

With consideration of the above issues, average concentrations were calculated under different options as follows:

- Option 1: two datasets combined. Further evaluation for PAHs with or without the result from KKUS0306.
- Option 2: average concentration based on 2002 data only
- Option 3: average concentration based on 2003 data only. Further evaluation for PAH with or without the result from KKUS0306.
- Option 4: average concentration in sediment in the area immediately upstream of Becher Street, defined as between Becher Street and Lincoln Ave. Because KKUS0306 is located further upstream, no further evaluation for PAHs is needed.

Table 6 summarizes the evaluation results. For PCBs, comparison of the average concentrations does not show significant variations under Options 1, 2, and 3. It ranges from 0.8 ppm to 1.0ppm. The standard deviation ranges from 0.7 ppm to 0.8 ppm. PCB average concentrations are relatively higher in the immediate upstream (1.2 ppm and 1.4 ppm) than in the overall background site ( 0.9 and 0.8 ppm) when results from option 1a and 4a are compared or from option 3a and 4b are compared as shown in Table 6. It is concluded that because the insignificant temporal and spatial differences in the averaged PCB concentrations, the two data sets from the entire reference site will be used for establishing the final cleanup criteria.

## Table 6. Concentrations of PCB and PAHs in sediment from the background reference site (upstream of Becher Street)*

| Options | Sample Events | | Sample ID | TPAH | TPCB | PCBs (Aroclor) |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
| | **Year 2003** | | KKUS0301 | 21.4 | 1.1 | PCB 1242 |
| | | | KKUS0302 | 48.5 | 2.2 | PCB 1242 |
| | | | KKUS0303 | 30.7 | | |
| | | | KKUS0304 | 29.1 | 0.9 | PCB 1242 |
| | | | KKUS0305 | 39.2 | | |
| | | | KKUS0306 | 346.8 | 0.5 | PCB 1242 |
| | | | KKUS0307 | 13.6 | | |
| | | | KKUS0308 | 50.8 | 0.2 | PCB 1248/1254 |
| | | | KKUS0309 | 23.9 | 0.1 | PCB 1248/1254 |
| | **Year 2002** | | KK-02-U-1 | 54.4 | 1.2 | PCB 1242 |
| | | | KK-02-U-2 | 45.7 | 0.8 | PCB 1242 |
| **1** **2002 and 2003 data combined** | **1a** including KKUS0306 | Average | | 64.0 | 0.9 | |
| | | STDEV (Standard deviation) | | 94.7 | 0.7 | |
| | **1b** excluding KKUS0306 | Average ( PAHs) | | 35.7 | | |
| | | STDEV (PAHS) | | 14.0 | | |
| **2** **2002 data only** | | Average | | 50.1 | 1.0 | |
| **3** **2003 data only** | **3a** including KKUS0306 | Average | | 67.1 | 0.8 | |
| | | STDEV | | 105.6 | 0.8 | |
| | **3b** excluding KKUS0306 | Average | | 32.2 | | |
| | | STDEV | | 13.1 | | |
| **4 immediate upstream of Becher Street**** | **4a** 2002 and 2003 data combined | Average | | 38.3 | 1.2 | |
| | | STDEV | | 13.0 | 0.6 | |
| | **4b** 2003 data only | Average | | 32.4 | 1.4 | |
| | | STDEV | | 11.5 | 0.7 | |

* The table include data collected both in 2002 and 2003. TPAH and TPCB do not include PAH compounds or PCB Aroclors that are detected at or less than the reporting limits (unit in mg/kg).

** Samples located between Becher Street and Lincoln Ave. were used for the calculation. These samples include KKUS0301 through KKUS0304 and KK-02-U-1 & KK-02-U-2

For PAHs, in general, the extreme value observed at KKUS0306 does significantly influence the average concentrations. The average concentrations differ about two times because of the extreme value (comparing 1a to 1b or 3a to 3b in Table 6). In the area immediately upstream from Becher Street, the data from 2002 shows higher concentrations compared to the 2003 data (comparing Option 2 with Option 4).
Due to high variations between laboratory analyses and also to be conservative, the average concentration of 36 ppm, resulted from the calculation including the two data sets but excluding the extreme data value from KKUS0306 (1b in Table 6), is considered as the average PAH background level.

**Data SET 3: Results from 2002 Bathymetry Survey and Sediment Poling**

Prior to sediment sampling, the Kewaunee office of the Army Corps of Engineers conducted a sediment thickness poling and bathymetry survey on August 27, 2002. The bathymetry survey was performed in accordance with the US ACE guidance entitled "Engineering and Design Hydrographic Survey" [USACE, 2004] (http://www.usace.army.mil/inet/usace-docs/eng-manuals/em1110-2-1003/toc.htm).

Results from sediment thickness poling were used as a reference to identify general depositional areas for determination of sampling locations during sampling plan phase. The geographical location from the bathymetry survey or sediment poling were not used to identify the actual sampling location. Sediment core locations were determined in the field by using the GPS unit as discussed previously in Data SET 1 and 2.

The core length obtained in September 2002 varied significantly to the sediment thickness recorded in August 2002. For instance, at the vicinity of Core KK0209, the poling recorded a sediment thickness of approximately 5 feet while the sediment core collected reached 24 feet. This discrepancy may be contributed to the composition of sediment. The sediment poling rod was not able to penetrate through tightly compacted sand layers that might exist intermittently between soft sediment layers in the area.

Because of the incomparable results from actual coring compared to sediment poling, in the pre-engineering design phase, the poling data was rejected as bench marks for sediment volume calculation. No further use of the data is anticipated in this final engineering design work.

Bathymetric survey data collected in 2002 were used to estimate the sediment removal volume in pre-engineering design phase and will be further used in the final design phase. Based on the 2002 survey results, computer program, Surfer (Golden Software, Inc., Version 8), a contouring and 3D surface mapping program, was and will be used to calculate the volume of sediment to be removed in the final engineering design phase. The details of how the volume was calculated are documented in Appendix E of CDDR [USACE and WDNR, 2003].

**Data SET 4: Nautical Charts**

The project area is a portion of the Milwaukee Harbor. As a result, a series of nautical charts were created by the US ACE, National Oceanic and Atmospheric Administration (NOAA), and Port of Milwaukee from different time periods. Compilation of these historical nautical charts provides a record of chronology of the river bathymetry.

As discussed in Appendix C of CDDR [USACE and WDNR, 2004], efforts were made to obtain nautical charts dated between 1915 and 2002 for the purpose of sediment dating and supporting design. In addition to the 2002 sounding map created from the bathymetric survey in 2002, a total of seven historical charts were obtained from the Milwaukee City Library, Port of Milwaukee, and Map Library in the University of Wisconsin-Madison. These charts were dated 1915, 1936, 1944, 1951, 1960, 1969, and 1978. Water depth shown on the charts, although in a coarse scale, was of primary interest to investigate the change of river bathymetry and sedimentation.

Based on these maps, elevation of the surface sediment at the time the charts were created was determined from the water depth and further converted to elevation relative to the Lake Michigan Chart Datum (IGLD 1985). Among these charts, the deepest water column was recorded in 1936. After 1936, the project area has become progressively shallower due to sedimentation. Fig. 12 is an example of the recorded change of water column between 1936 and 1944. The difference of water depth between the two maps in sequential mapping dates was then interpreted as the depth of sediment accumulated for the time period. As shown in Fig. 12, a maximum of 3 feet of sediment accumulated in the area between 1936 and 1944. Sedimentation rates were then estimated by dividing the amount of sediment accumulated over the time period.

There are challenges associated with the sediment dating using the historical nautical charts. Uncertainties originating from different accuracy and precision in measurements for creating the nautical charts and interpretation of water depth from the charts could lead to errors in sediment dating. However, this method is applicable with respect to the coarse segmentation scale of sediment cores and to the nature of dredging operations. Sediment cores were segmented in 2-foot intervals. This coarse segmentation scheme which was necessary for defining the vertical extent of contamination diminished the demand for higher accuracy in estimates of sedimentation rates.

Details of sediment dating processes are documented in Appendix C of CDDR. Fig. 13 represents the results at core locations of KK0202 and KK0209. The figure shows the vertical profiles of total PCBs (PCB) and total PAHs (PAHs) with the potential dates assigned at the bottom of each 2-foot segment.
The vertical profiles (Fig. 13) exhibit that PCB concentrations increased steadily since the1940s (KK0202) or the late 1930s (KK0209) and reached a peak in approximately the

1960s (KK0202) or between the mid 1940s and 1960 (KK0209). After reaching the peak, the PCB concentrations followed a general decreasing pattern. The long time period of about 20 years assigned to the PCB peak at KK0209 implied high uncertainties in the sediment record that will be further discussed later.

Regardless of the uncertainties, the overall trend of PCB concentrations in sediment is comparable to the PCB sales or usage in the US. PCBs were commercially manufactured starting in 1929. Prior to 1957, they were used exclusively in electrical transformers and capacitors. Only after 1957, were PCBs used widely. It is reasonable to assume that fewer PCBs were manufactured and used prior to 1957. By 1977 PCB manufacturing in the US ceased. Fig. 14 is a record of PCB sales which reflects the usage in the US for time period between1957 and 1974 [http://www.cdc.gov/niosh/78127_7.html]. The figure shows that the sales of PCBs peaked in 1970.

Comparing PCB concentrations in sediment (Fig. 12) and the sales record (Fig. 13), similar trend is observed with some discrepancies on the temporal scale. The discrepancy is small at KK0202 but significant at KK0209. Based on the sediment dating results, PCB concentrations at KK0209 were relatively high between 1936 and 1940s compared to that in KK0202. According to the overall sales trend, it is safe to assume that the sales between 1936 and 1940s would be equivalent to 1970s and the PCB concentrations in sediment may be lower than the results have shown. The sediment age assigned to the sediment in KK0209 deeper than 564 feet is questionable. There is a need to obtain sounding data in higher spatial and temporal resolutions for better sediment dating.

A series of sounding maps that were created in the 1940s and later was then obtained from the Port of Milwaukee. Sounding data in 40 feet grid resolution (e.g. Fig. 15 and -16) were recorded in 1940 by the Wisconsin Board of Harbor Commissioners. The 1940 maps show that the KK River was approximately 20 feet and 13 feet (NGVD 1929) deep in the vicinity of KK0202 and KK0209, respectively. Converting the sounding data relative to the NGVD1929 to the LMCD (IGLD85), the sediment surface would be at an elevation of 557 feet and 564 feet at KK0202 and KK0209, respectively (Fig. 13).

At KK0202, the sediment surface elevation at 557 feet on the 1940 map agreed well to the chronological record (approximately 556 feet) based on the sediment dating. That supports the dating of PCB profiles in sediment, placing PCB peak concentration after 1940.

At KK0209, the sediment surface elevation at 564 feet on the 1940 map is not significantly different from that at 561 feet which was determined based on the sedimentation rates. But this slight difference in elevation caused problems with respect to PCB concentrations. If the 1940 map is referenced as sediment age at the elevation of 564 feet, the PCB peak value would occur prior to 1940, which is not in agreement with the manufacturing and sales record. Therefore, further analyses of the sediment dating at

KK0209 is necessary because ultimately we have to determine whether or not the 1940 sounding map could be used to finalize dredging configurations so that we could reduce the possibilities of either over-dredging or under-dredging at the project area.

There are a few factors that may cause the uncertainties of temporal records of vertical distribution of PCBs at KK0209 as analyzed and summarized below.

- ***Sounding data in 1940***. A close look at the 1940 map revealed a steep lateral slope transitioned from 13 feet (elevation at 564 feet) near KK0209 to 19 feet (elevation at 558 feet) about 40 feet downstream. Further downstream, the maximum water depth was 22 feet (elevation at 555 feet). There is a possibility that the water depth at KK0209 was not 13 feet. Current GPS technology provides higher accuracy in determining locations than the previous tools used in 1940s. The water depth could fall within a range of 13 and 22 feet, most likely between 13 and 19 feet. If the water depth at KK0209 area was 19 feet deep in 1940, the date assigned for PCB profile at 1936 (Fig. 13) would be changed to 1940. Then the PCB peak concentration would be present after 1940.

- ***Sediment dating.*** Sediment dating using the set of nautical charts in low spatial resolution can cause high uncertainty in assignment of sediment age. The uncertainty of the sediment dating is supported by comparing PCB distribution in similar locations between the1994 and 2002 assessments. As shown in Fig. 5, high concentrations of PCBs were entrapped in sediment closer to surface compared to the 2002 result. The variation implies that sediment age assignment based on the sediment dating carries high uncertainties with respect to the PCB profiles.

- ***Hydrodynamic processes.*** River hydrodynamic processes in conjunction with potential human activities may have redistributed PCBs in sediment. The sharp decrease of PCB concentrations from 24 ppm at segment 559-561 to 1.1 ppm at segment 555-553 at KK0209 implies that PCB deposition started sometime when the sediment surface was at elevation between 555-559 feet. Unfortunately, the sediment segments between 559 and 555 were not analyzed for PCBs. The starting point could be changed due to redistribution of sediment because the existing First Street bridge was built after 1940.

Based on the above discussion, it is concluded that if the sediment in the vicinity of KK0209 and downstream, basically management Section 3, is dredged to elevation at 555 feet that is equivalent to 22 feet of water column, PCB mass removal will be achieved. In addition, for the areas without chemistry data available, the 1940 sounding data can be used as a surrogate dredging contour to finalize the dredging configuration. The

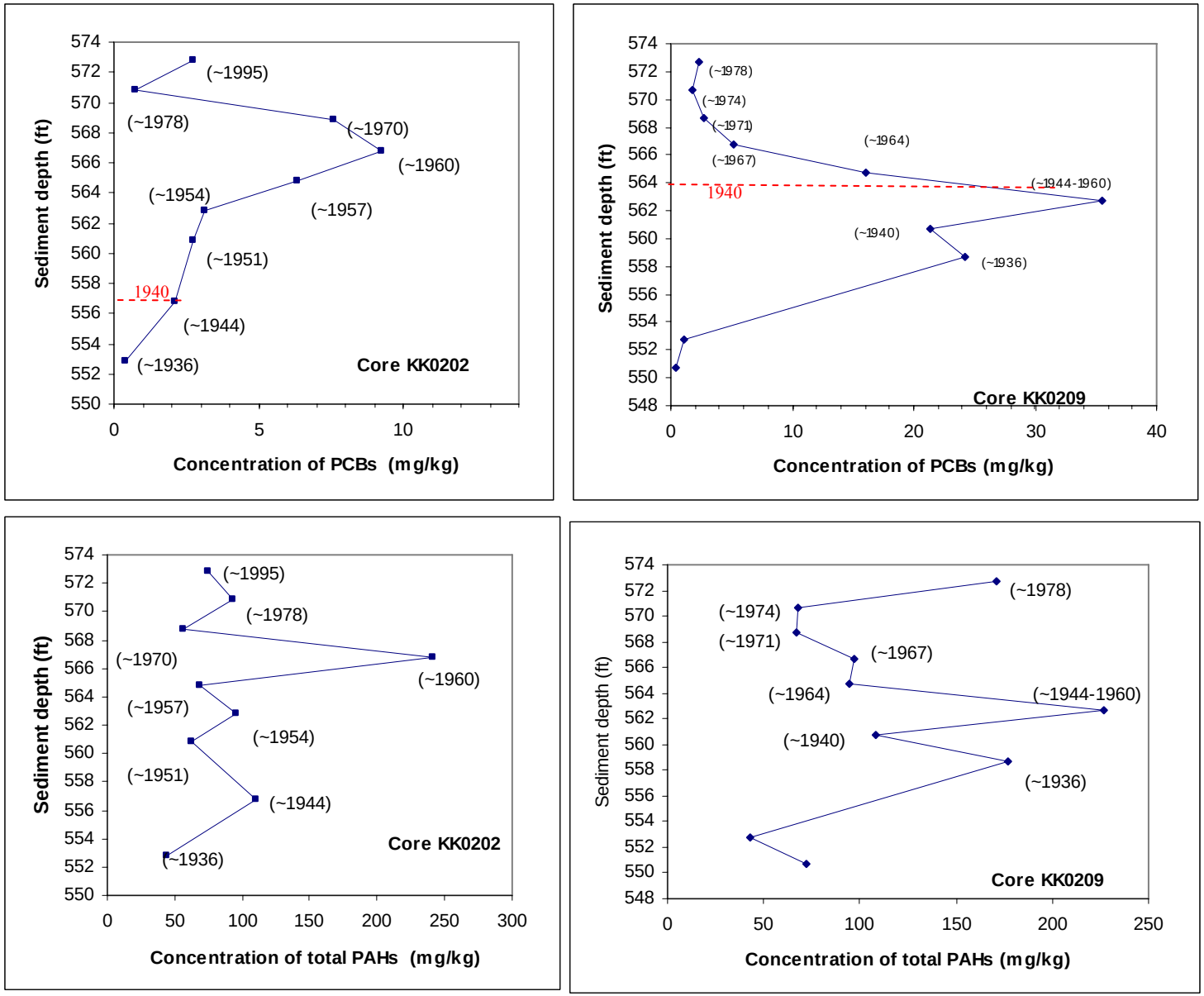



**Figure 12. Profiles of PCBs and PAHs in sediment cores KK0202 and KK0209 with estimated sedimentation dates based on the historical nautical charts** ( ---- sediment age based on 1940 sounding map)

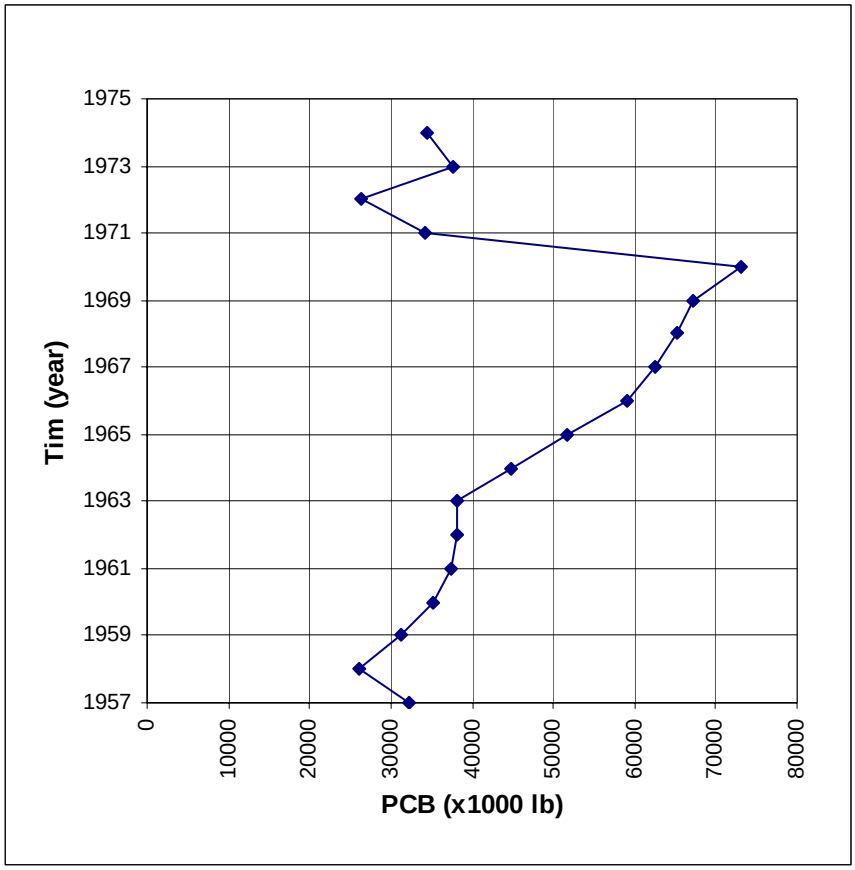



**Figure 13. Record of PCB sales between 1957 and 1975(www.cdc.gov/niosh/78127_7.html)**

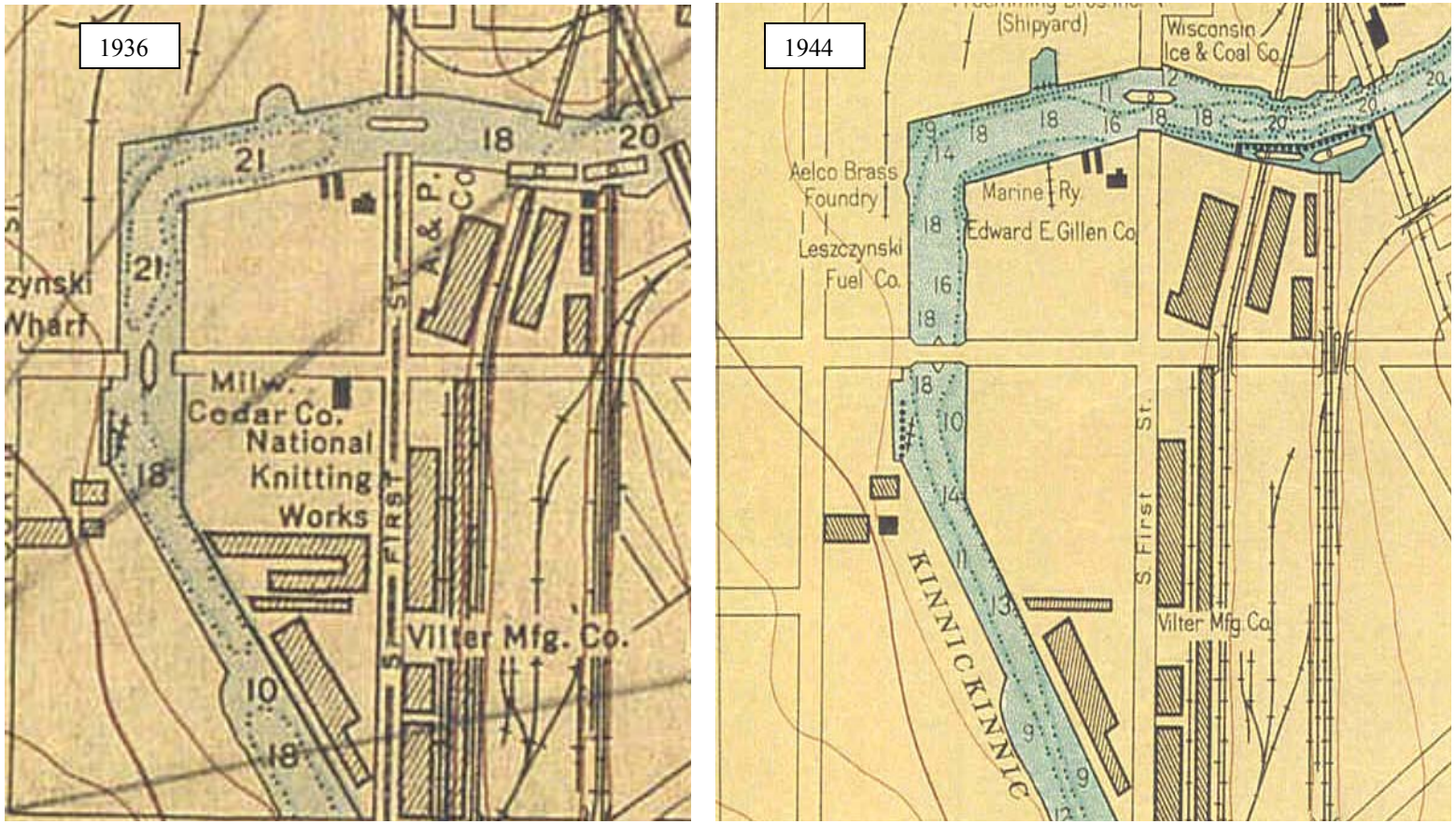



**Figure 14. Comparison of nautical charts created in 1936 and 1944**

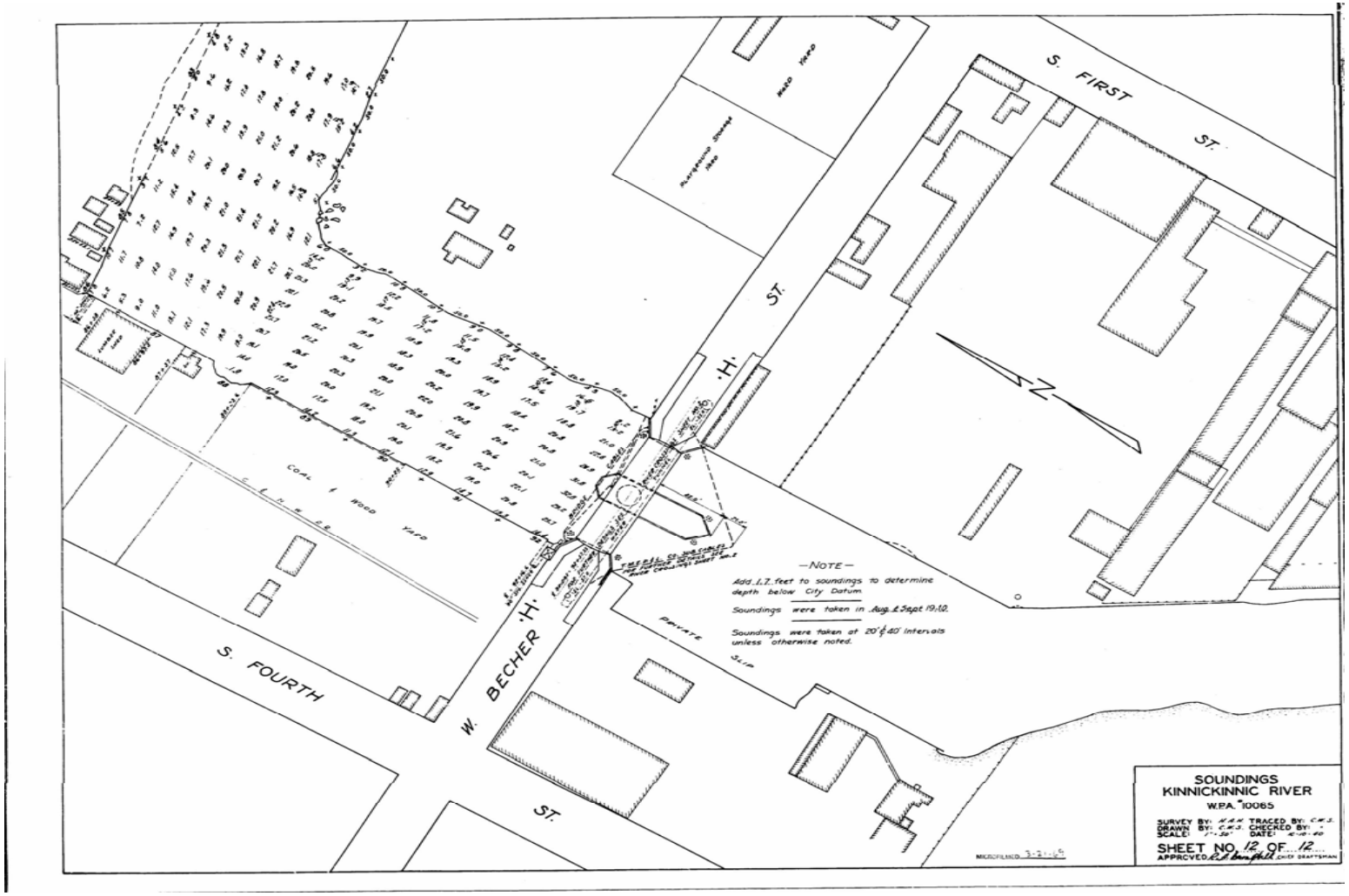



**Figure 15. The 1940 Sounding data for the area between Becher Street and upstream of First Street**

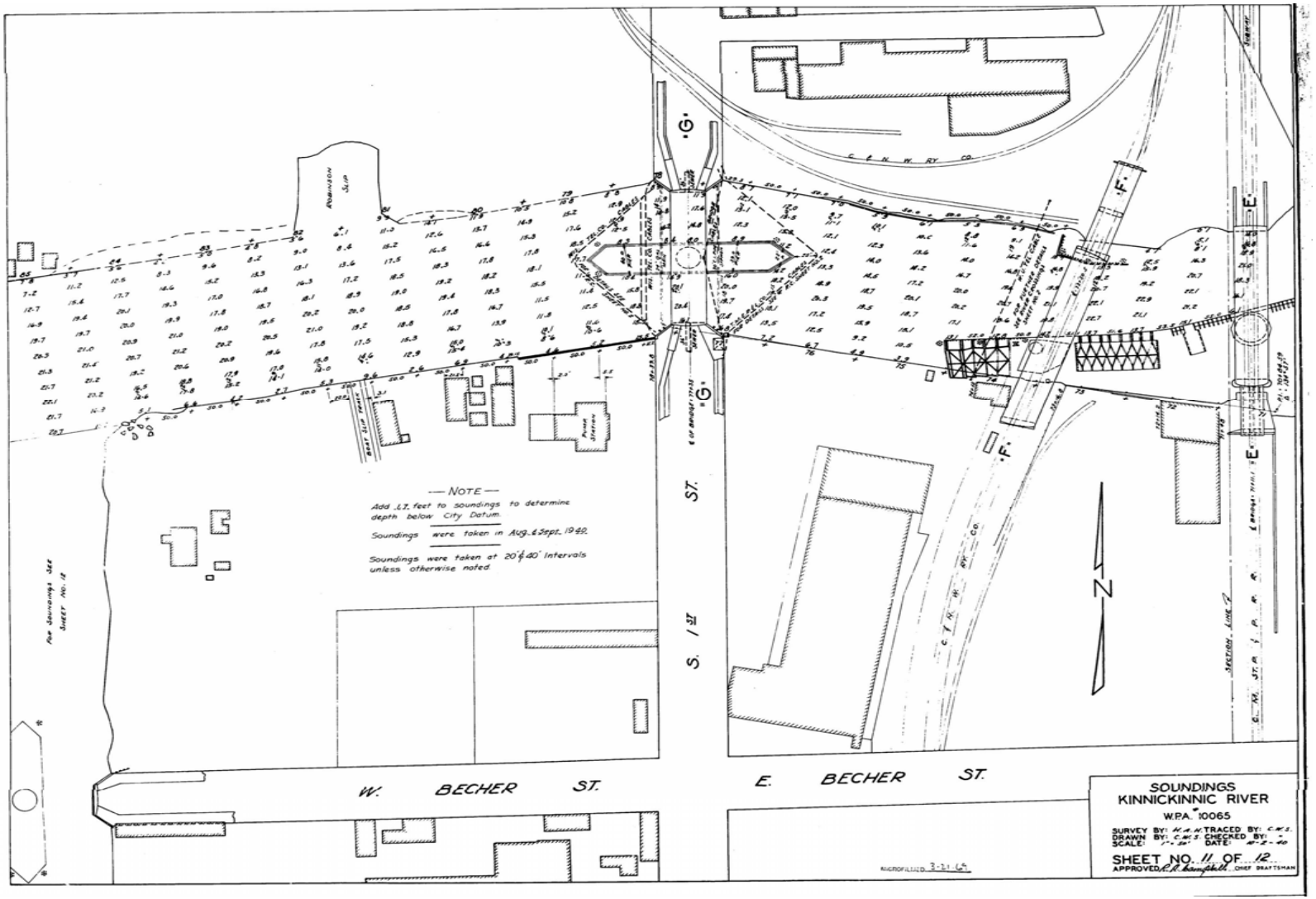



**Figure 16. The 1940 sounding data for the area between First Street and KK Avenue**

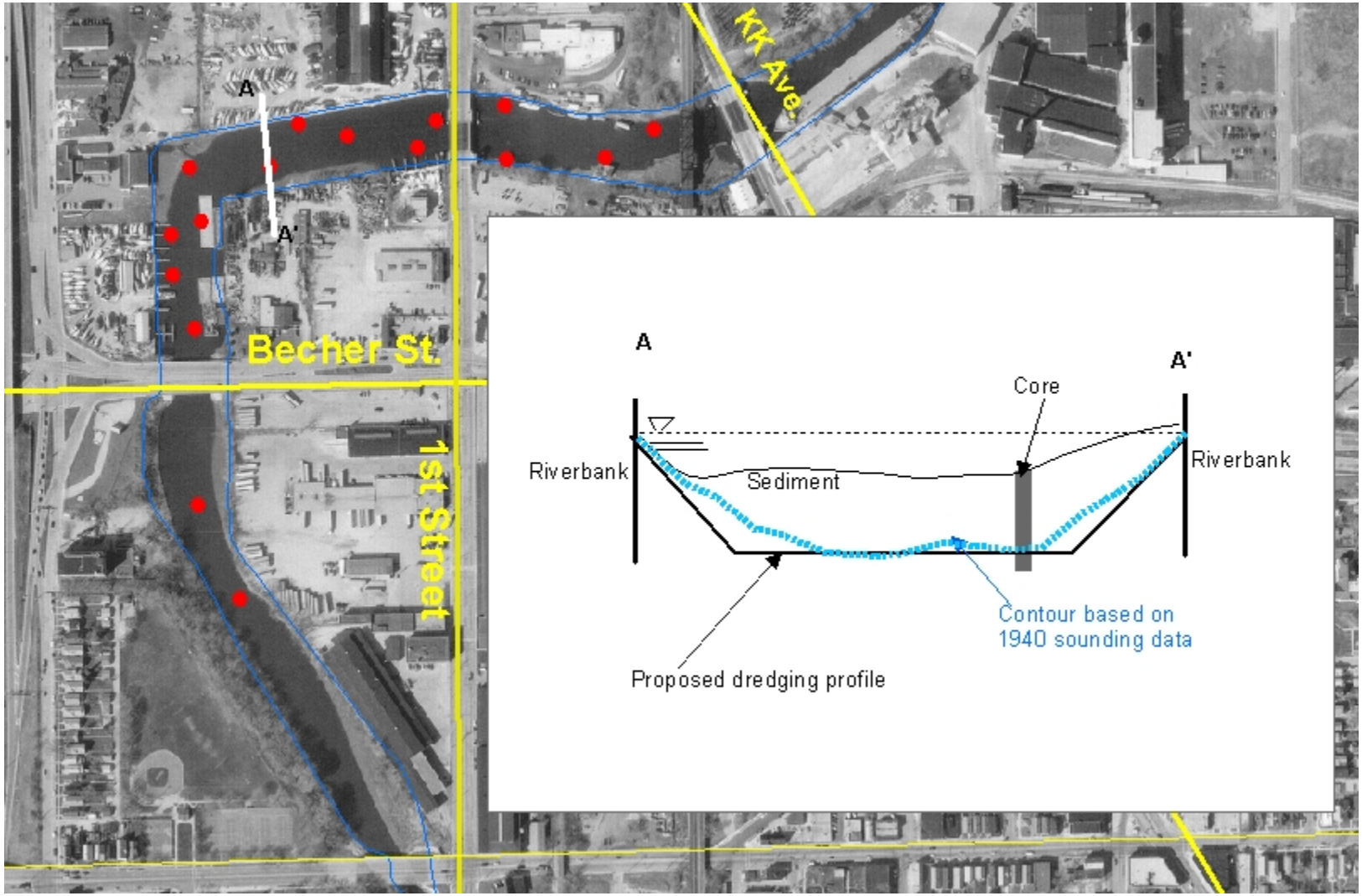



**Figure 17. Illustration of using 1940 sounding data to modify the dredging configuration** (scales are not in proportion)

application of the sounding data is illustrated in Fig. 15. This proposal is a modification to the dredging depth to elevation 553 feet for 80-foot channel as defined in the CDDR. Using the 1940 sounding data may reduce the potential of over dredging. However, caution will be taken with respect to removing contaminated sediment. Confirmation samples will be collected during dredging and post dredging to assure that sediment contaminated with high PCB concentrations will be removed.

## IV. REFERENCES

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US EPA, Sep. 2002. Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites.

US Army Corps of Engineers, Detroit District and Wisconsin Department of Natural Resources, April 2004. Kinnickinnic River, Wisconsin, Milwaukee Estuary Area of Concern Deepening/Remediation Concept Design Documentation Report (CDDR). Prepared by the Barr Engineering, Inc.

# Attachment 1

# Quality Assurance Project Plan
# Kinnickinnic River Sediment Sampling in 2002

US Army Corps of Engineers, Omaha District
April, 2002

# Quality Assurance Project Plan
# Title and Approval Sheet
# Draft, April 2002
# Kinnickinnic River Sediment Sampling in FY2002:

## IAG#DW96947964-01

_____
Demaree Collier, Project Officer, GLNPO
77 West Jackson Blvd (G-17J), Chicago, Illinois 60604-3590,
Phone:312-886-0214, Fax: 312-353-2018

_____
Paul Baxter, Project Coordinator, U.S. Army Corps of Engineers
Detroit District, 477 Michigan Ave., Detroit, Michigan 48226,
Phone (313) 226-7555, Fax (313) 226-2013

_____
Xiaochun Zhang, Project Investigator,
Wisconsin Department of Natural Resources
101 Webster St., Box 7921
Madison, WI 53707-7921
Phone: (608) 264-8888
Fax (608) 267-2800

_____
Ian Kerr, Project Manager, Altech Environmental Services, Inc.
24209 Northwestern Hwy., Suite 230, Southfield, Michigan 48219,
Phone (248) 353-3832, Fax (248) 353-5485

_____
Ann Preston, Project Manager, Trace Analytical Laboratories, Inc.
2241 Black Creek Rd., Muskegon, Michigan 49444-2673,
Phone (231) 773-5998, Ex. 224, Fax (231) 773-6537

_____
Scott Strigel, Project Geologist, Coleman Engineering Company
635 Industrial Park Drive, Iron Mountain, Michigan 49801
Phone (906) 774-3440, Fax (906) 774-7776

_____
Louis Blume, Quality Assurance Manager, GLNPO
77 W. Jackson Blvd. (G-17J), Chicago, IL 60604
Phone (312) 353-2317, Fax (312) 353-2018

## QAPP Distribution List

Demaree Collier, Project Officer
USEPA- GLNPO
77 West Jackson Blvd (G-17J)
Chicago, Illinois 60604-3590
phone: 312-886-0214
E-mail: Collier.Demaree@epamail.epa.gov

Paul Baxter, Project Coordinator
U.S. Army Corps of Engineers - Detroit District
477 Michigan Avenue
Detroit, MI 48226
phone: 313-226-7555
E-mail: paul.r.baxter@lre02.usace.army.mil

Xiaochun Zhang,
Project Investigator
Wisconsin Department of Natural Resources
101 Webster St., Box 7921
Madison, WI 53707-7921
Phone : (608)264-8888
E-mail: ZHANGX@DNR.STATE.WI.US
E-mail: ZhangX@mail01.dnr.state.wi.us

Ian Kerr
Altech Environmental Services, Inc.
24209 Northwestern Hwy., Suite 230
Southfield, Michigan 48219
Phone (248) 353-3832
E-mail: ikerr@altechenvironmental.com

Ann Preston, Project Manager
Trace Analytical Laboratories, Inc.
2241 Black Creek Rd., Muskegon, Michigan 49444-2673
phone: (231) 773-5998, Ex. 224
E-mail: traceanalytical@mad.scientist.com

Scott Strigel
Coleman Engineering Company
635 Industrial Park Drive, Iron Mountain, Michigan 49801
Phone (906) 774-3440
E-mail: colemanengineering@uplogon.com

Lou Blume, QA Manager
USEPA- GLNPO
77 West Jackson Blvd (G-17J)
Chicago, Illinois 60604-3590
phone: 312-886-0214
E-mail: blume.louis@epa.gov

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# 1. SUMMARY

## 1.1 Purpose

The sampling efforts detailed in this document outlines a plan to determine the extent of contamination in a stretch of the Kinnickinnic River, Milwaukee Wisconsin. The data collected during this study will be used to determine alternatives to perform environmental clean-up of the contaminated sediments. Proposed testing for this sampling include: PCBs, PAHs, TOC, and Toxicity Characterization. Samples for particle size distribution, hydrometer, loss upon ignition, and Atterberg limits will be collected but not analyzed within the scope of this project.

Primary Objective: Collect sufficient data to ascertain the current state of contamination in a stretch of the Kinnickinnic River.

Secondary Objective: Collect samples for geotechnical analysis to generate sufficient data to create plans and specifications for dredging the contaminated sediments.

## 1.2 Background

Site Location
The Kinnickinnic flows primarily east through the southeast corner of Wisconsin, discharging into Lake Michigan after a convergence with the Milwaukee River in Milwaukee, Wisconsin. The stretch of the Kinnickinnic River subject to this sediment sampling investigation begins at the State Highway 32 bridge and extends approximately 1,700 ft. upstream to the Becher Street bridge.

Historical Sampling
A limited amount of sediment chemistry data is available to document contamination conditions at the site. If available, the following historical data sets will be evaluated as part of this project:

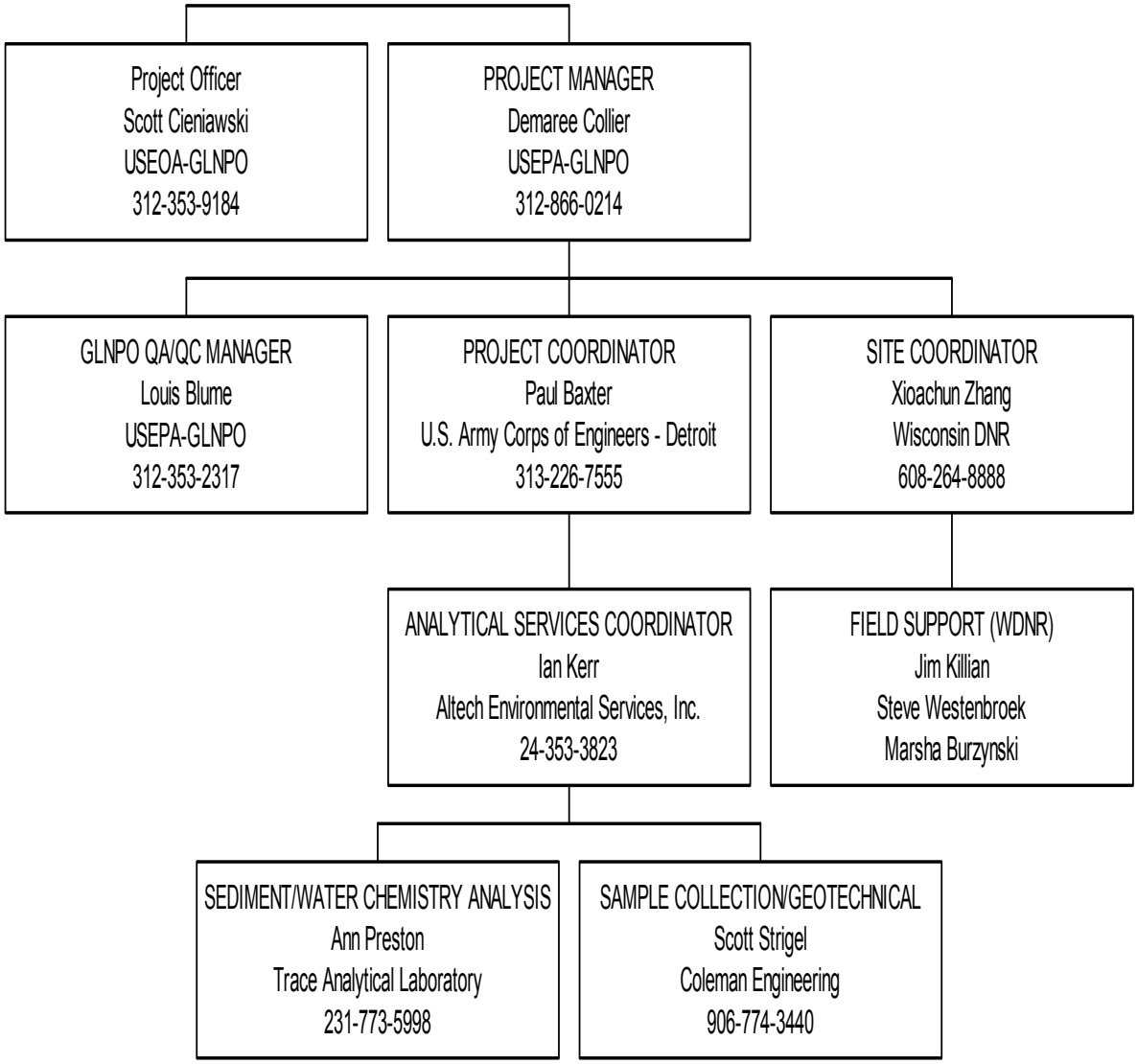
1. Wisconsin DNR sediment testing;
2. University of Wisconsin, Milwaukee sediment testing;
3. 2001 Tetra Tech Em, Inc (EPA Superfund Sampling).

The above sediment sampling and analytical projects revealed sediments within this project area to have sufficient contamination at least to the depth of 7 feet to warrant further investigation. This project is designed to delineate the full extent of contamination within the project area.

## 1.3 Project Organization

Figure 1 provides a summary of the project organization for this project. A description of the duties of each individual is provided below.

**Figure 1.** Organizational Chart




USEPA-GLNPO

USEPA-GLNPO is the principal investigating agency for this sediment survey. They are responsible for coordination and approval of the Scope of Work and QAPP as well as the principal client for the final data. USEPA-GLNPO staff associated with this project include:

| ***Person:*** | ***Responsibilities:*** |
|---|---|
| Scott Cieniawski<br>Project Manager<br>77 W. Jackson Blvd. (G-17J)<br>Chicago, IL 60604<br>Phone: 312-353-9184<br>Cieniawski.Scott@epamail.epa.gov | Coordinate Project Funding |

| | |
|---|---|
| Demaree Collier<br>Project Manager<br>77 W. Jackson Blvd. (G-17J)<br>Chicago, IL 60604<br>phone: 312-886-0214<br>collier.demaree@epa.gov | Project Management<br>Review/Approve QAPP<br>Perform Project Management Tasks |
| Louis Blume<br>GLNPO QA Manager<br>77 W. Jackson Blvd. (G-17J)<br>Chicago, IL 60604<br>phone: 312-353-2317<br>blume.louis@epa.gov | Review/Approve QAPP |

U.S. Army Corps of Engineers - Detroit District

The U.S. Army Corps of Engineers will provide laboratory contracting support, and an initial QA/QC review of the project data. The USACE representative will be responsible for developing a project Scope of Work and QAPP, contracting collection of sediment samples and analysis of sediment samples, contacting USEPA-GLNPO/WDNR regarding any concerns regarding the data received from the laboratories, and advising USEPA-GLNPO/WDNR regarding any concerns expressed by the laboratory. USACE individual involved in this project is:

| ***Person:*** | ***Responsibilities:*** |
|---|---|
| Paul Baxter<br>Project Coordinator<br>477 Michigan Av.<br>U.S. Army Corps of Engineers<br>Detroit, Michigan 48226<br>313-226-7555<br>Paul.R.Baxter@lre02.usace.army.mil | Prepare Scope of Work and Project QAPP<br>Contract Sampling and Analytical Testing<br>Perform Contract Management Activities<br>Initial QA/QC Review |

Wisconsin DNR

The Wisconsin DNR (WDNR) will provide oversight/coordination and field support to this project. Field support will be provided during sediment sampling. WDNR will also provide historical data, results, and information on sampling and analysis methods used during historical studies. WDNR will be responsible for evaluation of analytical test results which will be submitted to EPA-GLNPO Project Manager. The WDNR staff involved in this project are:

| ***Person:*** | ***Responsibilities:*** |
|---|---|
| Xiaochun Zhang<br>Project Investigator - WDNR<br>Wisconsin DNR<br>101 Webster St., Box 7921<br>Madison, Wisconsin 53707-7921<br>608-264-8888<br>ZhangX@mail01.dnr.state.wi.us | Oversee/Coordinate Project Sampling Activities<br>Provide Information on Historical Sampling Results and Analytical Methods<br>Review/Approve QAPP<br>Analyze Data and Prepare Report |

| | |
|---|---|
| Steve Westenbroek<br>Water Resources Engineer<br>Wisconsin DNR<br>2300 N. Dr. Martin Luther King Jr. Dr.<br>Milwaukee, Wisconsin 53212<br>414-263-8576<br>westes@dnr.state.wi.us | Provide Field and Technical Support |
| Jim Killian<br>Water Resources Specialist<br>Bureau of Watershed Management<br>Wisconsin DNR<br>101 S. Webster St., Box 7921<br>Madison, Wisconsin 53707-7921<br>608-264-6123<br>killij@dnr.state.wi.us | Provide Field and Technical Support |
| Marsha Burzynski<br>Water Resources Planner<br>Southeast Region-Milwaukee<br>Wisconsin DNR<br>2300 N. Martin Luther King Jr. Dr.<br>Milwaukee, Wisconsin 53212<br>414-263-8708 | Provide Field and Technical Support |

Laboratory

Laboratory analyses for this project will be performed by Trace Analytical Laboratories, Inc. Altech Environmental Services, Inc. (Altech) will coordinate analytical services from the laboratory under a contract agreement with the USACE. Altech will be responsible for sub-contracting for sample analysis. Trace Analytical Laboratories, Inc. will have sample analysis and review responsibilities on this project. The laboratory will have their own provisions for conducting an internal QA/QC review of the data before it is released to the U.S. Army Corps of Engineers. The laboratory contract supervisor listed below will contact the USACE project coordinator with any data concerns.

Written QA/QC reports will be filed by the analytical laboratory when data is submitted to the USACE. Corrective actions will be reported to the USACE project coordinator along with the QA/QC report (see Section 9). The laboratory may be contacted directly by USEPA or USACE personnel to discuss QA concerns. Altech will act as laboratory coordinator on this project and all correspondence from the laboratory should be coordinated with Altech. Responsibilities of the laboratory and the laboratory coordinator are provided below:

| ***Person:*** | ***Responsibilities:*** |
|---|---|
| Ian Kerr<br>Project Manager<br>Altech Environmental Services, Inc.<br>313-535-7882<br>ikerr@altechenvironmental.com | Review/Approve QAPP<br>Review final analytical report<br>Ensure Sub-Contract Laboratory Resources are Available on an As-required Basis<br>Review Final Analytical Report |

| | |
|---|---|
| Ann Preston<br>Client Services Manager<br>Trace Analytical Laboratories, Inc.<br>2241 Black Creek Rd.<br>Muskegon, Michigan 49444-2673<br>231-773-5998<br>traceanalytical@mad.scientist.com | Coordinate Chemical Analyses<br>Ensure Laboratory Resources are<br>Available on an As-required Basis<br>Supply Required Sample Bottles<br>and Coolers (including temperature blanks) |
| Gregory J. Hayes<br>QA/QC Manager<br>Trace Analytical Laboratories, Inc.<br>2241 Black Creek Rd.<br>Muskegon, Michigan 49444-2673<br>traceanalytical@mad.scientist.com | Review/Approve QAPP<br>Perform QA/QC Review on Analytical Test Results<br>Prepare a QA/QC Case Narrative |

Sample Collection

Sample collection will be accomplished utilizing the services of Coleman Engineering Company (Coleman). Coleman will perform sample collection under the direction of the on-site field coordinator. Coleman will be responsible for preparing sample boring logs and supplying all equipment necessary for sample collection and containers for geotechnical testing of the sediments. Coleman's on-site project manager is:

| | |
|---|---|
| Scott Strigel<br>Project Manager<br>Coleman Engineering Company<br>635 Industrial Park Dr.<br>Iron Mountain, Michigan 49801<br>906-774-3440<br>colemanengineering@uplogon.com | Review/Approve QAPP<br>Coordinate and Perform Sample Collection |

## 2. Project Description

### 2.1 Data Uses and Expected Measurements

GLNPO proposes an assessment of contamination. Work would be coordinated with the Wisconsin DNR to insure mapping the extent of contamination will be thorough. The proposed work components are summarized below.

Determination of Existing Data Availability

The first step of this project will be to identify sources and availability of data for this site. The Wisconsin DNR, University of Wisconsin, Milwaukee, U.S. EPA have collected data at or near the project site.

GLNPO will coordinate with Wisconsin DNR to determine the quality and availability of existing data.

Sediment Chemistry Sampling

Sediment chemistry sampling will consist of the collection of a sediment core samples at approximately 16 locations. Two (2) of the locations will be upstream of the project area and 14

of the locations will be within the project area. All sediment cores will be sectioned into sub-samples of 0'-2', 2'-4', 4'-6', 6'-8', 8'-10', 10'-12', 12'-14', 14'-16', 16'-18', and 18'-19'. At four locations cores will extend an additional 7 ft for geotechnical testing. It is anticipated there will be a minimum of 5 and a maximum of 10 samples per boring for chemical testing. The two locations upstream of the project area will be surficial grab (ponar) samples. All sediment samples collected will be analyzed for PCBs Aroclors and PAHs. Seven of the borings (borings ending with an odd number) will also have vertical composites for toxicity characterization testing as defined in 40 CFR Ch 1 Part 261 as well as TOC analysis on the boring discrete samples. Refer to Figure 5 for illustrations of sediment borings. Table1 summarizes the anticipated water and boring depths and number of samples.

Table 1. Kinnickinnic River Approximate Station Boring Depths

| Station I.D. | Water Depth (Ft.) | Boring Depth (Ft.) | No. Environmental Samples | No. Geotechnical Samples |
|---|---|---|---|---|
| KK0201 | 3 | 16 | 8 | 4 |
| KK0202 | 5 | 14 | 7 | 3 |
| KK0203 | 0[1] | 19 | 10[1] | 4 |
| KK0204 | 7 | 12 | 6 | 3 |
| KK0205 | 0[1] | 19[1] | 10[1] | 4 |
| KK0206 | 0[1] | 19[1] | 10[1] | 4 |
| KK0207 | 9 | 10 | 5 | 2 |
| KK0208 | 0[1] | 19 | 10[1] | 4 |
| KK0209 | 3 | 16 | 8 | 4 |
| KK0210 | 6 | 13 | 7 | 3 |
| KK0211 | 3 | 16 | 8 | 4 |
| KK0212 | 6 | 13 | 7 | 3 |
| KK0213 | 8 | 11 | 6 | 3 |
| KK0214 | 7 | 12 | 6 | 3 |
| KK02US1 | N/A | N/A | 1 | 1 |
| KK02US2 | N/A | N/A | 1 | 1 |
| **Totals** | | | **100[1-2]** | **50[1]** |

1 - Estimated
2- Does not include field QA/QC samples

## 2.2 Criteria and Objectives

### 2.2.1 Sediment Chemistry

Tables 2 through Table 7 provide the requirements necessary for sediment chemistry testing. Standard Operating Procedures for analysis of sediments for this project are available upon request to the USACE Project Coordinator, Paul Baxter.

Table 2. Kinnickinnic River Sediment Testing Requirements

| Parameter | No. of Samples | TDL[1] | Precision (RPD) | Analytical Method |
|---|---|---|---|---|
| Bulk Sediment PCBs | 122 | Per Method | 50 % | SW-846/8082 |
| Bulk Sediment PAHs | 122 | Per Method | 50 % | SW-846/8270C |
| Bulk Sediment TOC | 61 | 1,000 mg/kg | 20 % | Walkely-Black |
| TCLP Procedure | 7 | N/A | N/A | SW-846/1311 |
| TCLP Procedure for Volatiles | 7 | N/A | N/A | SW846/1311 |
| TCLP Metals | 7 | Table 3 | Table 3 | SW-846 (Table 3) |
| TCLP Volatiles | 7 | Table 4 | Table 4 | SW-846/8260B |
| TCLP Semivolatiles | 7 | Table 5 | Table 5 | SW-846/8270C |
| TCLP Pesticides | 7 | Table 6 | Table 6 | SW-846/8081 |
| TCLP Herbicides | 7 | Table 7 | Table 7 | SW-846/8150 |
| Corrosivity | 7 | N/A | 20 % | SW-846/9040/9045B |
| Reactive Cyanide | 7 | 0.5 mg/kg | 7.5 % | SW-846 Ch. 7/EPA 9012 |
| Reactive Sulfide | 7 | 5.0 | 20 % | SW-846/Ch-7/EPA 376.2 |
| Ignitability | 7 | $> 200^0$ F | 20 % | SW-846/1020A |
| Paint Filter Test | 7 | N/A | N/A | EPA 9095 |

1 – Target Detection Limit

Table 3. Kinnickinnic River TCLP Metals Requirements

| Analyte | Analytical Method | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|---|
| Arsenic | SW-846 6010/6020/7000 | 0.30 | 20 % |
| Barium | SW-846 6010/6020 | 1.00 | 20 % |
| Cadmium | SW-846 6010B/6020/7000A | 0.10 | 20 % |
| Chromium | SW-846 6010B/6020 | 0.50 | 20 % |
| Lead | SW-846 6010B/6020/7000A | 0.50 | 20 % |
| Mercury | SW-846 7471A | 0.01 | 12 % |
| Selenium | SW-846 6010B/6020 | 0.60 | 20 % |
| Silver | SW-846 7761/6010B/6020 | 0.10 | 20 % |

1 – Target Detection Limit

Table 4. Kinnickinnic River TCLP Volatiles Requirements

| Analyte | TDL[1] (mg/l) | Precision |
|---|---|---|
| Benzene | 0.05 | 50 % RPD |
| Carbon Tetrachloride | 0.05 | 50 % RPD |
| Chlorobenzene | 0.05 | 50 % RPD |
| Chloroform | 0.05 | 50 % RPD |
| Methyl ethyl keytone | 0.25 | 50 % RPD |
| 1,4-Dichlorobenzene | 0.05 | 50 % RPD |
| 1,2-Dichloroethane | 0.05 | 50 % RPD |
| 1,1-Dichloroethylene | 0.05 | 50 % RPD |
| Trichloroethene | 0.05 | 50 % RPD |
| Tetrachloroethylene | 0.05 | 50% RPD |
| Vinyl chloride | 0.05 | 50 % RPD |

1- Target Detection Limits

Table 5. Kinnickinnic River TCLP Semivolatiles Requirements

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| 2-Methylphenol | 0.10 | 50 % |
| 3/4-Methylphenol | 0.10 | 50 % |
| Methylphenol(2,3,4) | 0.10 | 50 % |
| 2,4-Dinitrotoulene | 0.10 | 50 % |
| Pentachlorophenol | 0.10 | 50 % |
| Hexachlorobenzene | 0.10 | 50 % |
| Hexachlorobutadiene | 0.10 | 50 % |
| Hexachloroethane | 0.10 | 50 % |
| Nitrobenzene | 0.10 | 50 % |
| Pyridine | 0.10 | 50 % |
| 2,4,5-Trichlorophenol | 0.10 | 50 % |
| 2,4,6-Trichlorophenol | 0.10 | 50 % |

Table 6. Kinnickinnic River TCLP Pesticides Requirements

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| Chlordane | 0.020 | 50 % |
| Endrin | 0.010 | 50 % |
| Heptachlor | 0.008 | 50 % |
| Heptachlor Epoxide | 0.008 | 50 % |
| 4,4-DD | 0.010 | 50 % |
| Lindane | 0.010 | 50 % |
| Methoxychlor | 0.500 | 50 % |
| Toxaphene | 0.500 | 50 % |

Table 7. Kinnickinnic River TCLP Herbicides Requirements

| Analyte | TDL[1] (mg/l) | Precision (RPD) |
|---|---|---|
| 2,4-D | 10.0 | 50 % |
| 2,4,5-TP (Silvex) | 1.0 | 50 % |

## 2.3 Special Personnel, Training, and Equipment Requirements

Sediment Sampling
Sediment sampling will require the use of the Coleman Engineering's barge and associated drilling rig or an equivalent. Equipment requirements for collecting sediment core samples are contained in Appendix A.

Under normal operations, the minimum Personal Protective Equipment (PPE) required to be worn by personnel working on deck aboard the drill rig barge is Modified Level D Protection. Modified Level D Protection includes: hard hat with face shield, steel toed footwear, tyvek coveralls, boot covers, Personal Floatation Device, and double gloves. Modified Level D indicates that no respiratory protection is required.

This survey will require PPE suitable for normal operating conditions as described above. The main method to avoid exposure to the contaminants present, is to avoid direct contact with skin. Washing hand immediately after sampling will also reduce potential exposures to the contaminants.

## 2.4 Project Schedule

A tentative project schedule is provided in Table 8. All personnel shown in Figure 1 should be contacted regarding significant schedule changes.

**Table 8. Tentative Project Schedule**

| Task | Completion Date |
|---|---|
| Scope of Work Acceptance | May 2002 |
| QAPP Development and Approval | May 2002 |
| Sediment Sampling | June 2002 |
| Completion of Sediment Analysis | July 2002 |
| Draft Analytical Report Due to USACE | July 2002 |
| Final Analytical Report Due to USACE | August 2002 |
| Report Due to GLNPO and WDNR | September 2002 |
| QA/QC Review Due to GLNPO and WDNR | November 2002 |

# 3. Sampling Plan

## 3.1 Sampling Network Design and Rationale

The purpose of this sampling survey is to determine the quality of the sediments in the project area. In order to obtain a full picture of the extent of contamination a large number of samples need to be collected. Sediment chemistry and geotechnical test samples will be collected. These samples will allow WDNR and the COE to determine the levels of contaminants present in the sediments and development of disposal options of the dredged sediments.

Figure 2 presents an overview of the project area and approximate locations for collection of sediment samples. Latitude/longitude of the sampling points within the project area are provided in Appendix E. Exact sample locations may be relocated by the on-site field coordinator during

sampling. This will be dependent upon, but not limited to; site characteristics and ability of the sampling team to collect sufficient sample material.

The sampling locations are designed to provide focused coverage of the project area as well as some general coverage upstream of the project area. Table 9 summarizes the types of data and analyses to be collected at each type of sampling location.

**Table 9. Summary of Data and Analyses at Sampling Locations**

| Core Sample (14 locations) | Grab Samples (2 Locations) |
|---|---|
| Sediment Chemistry | Sediment Chemistry |
| Sediment Depth | Water Depth (Actual & Corrected) |
| Water Depth (Actual & Corrected) | Physical Descriptions of Samples |
| Geotechnical Sample Collection | Photographs of Samples |
| Physical Descriptions of Samples | |
| Photographs of Samples | |

## 3.2 Definition of Sample Types

Three types of sediment samples will be collected during this survey; Routine Field Samples (RFS), Field Replicates (FR), and Field Duplicates (FD). Each sample type is described below.

*Routine Field Samples (RFS)*: Prepared by collecting a section of a sediment core, homogenizing the sediments collected, and filling all required sample jars. Routine field samples will be collected at fourteen (14) locations. Refer to Figure 3 for locations of the RFS.

*Field Duplicates (FD)*: Prepared by filling a second set of sample jars from a sediment core after the cores have been homogenized. FDs will be collected at one (1) sediment core location. This is approximately equivalent to a ratio of FDs to RFSs of 1 to 10 (10%). Location of the FDs will be determined in the field by the on-site sample collection coordinator.

*Field Replicates (FR)*: Prepared by collecting a second, sediment core sample, homogenizing the material separately from the RFS and filling the required sample bottles. FRs will be collected at one (1) sediment core location. This is approximately equivalent to a ratio of FRs to RFSs of 1 to 10 (10%). Locations of the FRs will be determined in the field by the on-site sample collection coordinator.

## 3.3 Type and Number of Samples

Table 10 summarizes the type and number of samples to be collected during this sampling event. The estimated number of samples does include all RFS, FD, and FR samples.

**Table 10. Summary of Type and Number of Samples to be Collected**

| Sample Type | Estimated Number of Samples[1] | Sample Matrix | Analysis Required |
|---|---|---|---|
| Sediment Chemistry | 122 | Sediment | PCBs Aroclors and PAHs |
| Sediment Chemistry | 61 | Sediment | TOC |
| Sediment Chemistry | 7 | Sediment | Toxicity Characterization |
| Geotechnical Samples[2] | 50 | Sediment | Grain Size with Hydrometer and Loss Upon Ignition |
| Geotechnical Samples[2] | 8 | Sediment | Atterberg Limits |

[1]- Includes field QA/QC samples.
[2] - To be analyzed at a later date, analysis is not included within this project.

All of the data listed in Table 10 is considered critical to the success of this assessment project.

### 3.4 Field Data Collection

Three sets of field data will be collected that are critical to the data quality objectives for this project.

*Latitude/Longitude Location*: This data is critical for use in determining where sediment samples were collected. The Differential Global Positioning Systems (DGPS) onboard the Coleman Engineering barge will be capable of ascertaining horizontal locations with < 5 meters of accuracy. To achieve this accuracy, it is important that the DGPS is in good working order and are obtaining strong satellite signals. The field team will be responsible for checking the satellite signal strength for the DGPS system prior to recording this data and for ensuring that the system is recording equivalent horizontal locations. Any problems with signal strength shall be recorded on in the field boring log. If problems are noted, the field team should provide a qualitative description of the sampling location utilizing any available, permanent landmarks. The DGPS unit will have the accuracy checked prior to each days sampling activities by locating one of the USACE survey markers shown on Figure 3. The DGPS unit's antennas will be located as close to the marker as possible and the reading will be compared to those on Figure 3.

*Sediment Depth:* Sediment depth data is critical for determining the volume of sediments with a potential for being contaminated. Sediment depth will be measured to the nearest 0.1 ft.

*Water Depths:* Water depths will be taken directly over the location of the sampling site prior to sample collection with a weighted measuring tape. Water depths will be reported as actual depth measured and as water depth corrected to Low Water Datum. Low Water Datum is available for Milwaukee Harbor at the closest daily and hourly water levels

station for Lake Michigan, which can be obtained from the Internet at the NOAA home page for water elevations. Water depths will be measured to the nearest 0.1 ft.

*[Note: Low Water Datum is available in 6 minutes intervals. The address is: http://www.opsd.nos.noaa.gov/data_res.html. From this address under Preliminary Water Level Data select Great Lakes Stations then choose Milwaukee and display recorded water levels in feet.]*

# 4. Sample Collection and Handling

## 4.1 Sample Collection

### 4.1.1 Sediment Cores

Sediment cores will be collected utilizing a two inch and/or three inch diameter (depending on amount of recovery) split spoon sampler and associated hollow stem auger (ASTM Method D-1586-84, Standard Method for Penetration Test and Split-Barrel Sampling of Soils). The split spoon sampler is capable of collecting continuous sediment cores to the depths required for this project. All sediment cores will be analyzed for sediment chemistry as summarized in Table 10 and explained in detail in Section 5.

Once the barge has been positioned over a given sampling station, the following activities will take place, but not necessarily in this order:

1. Water depth will be measured through the hole in the barge where the samples will be collected;
2. Location coordinates will be recorded by placing the GPS antenna over the sampling hole;
3. The split spoon sampler will be lowered penetrating two feet into the sediment, if applicable, the sampler will be hammered into the sediment with a 30 inch free fall of a 140 lb. hammer and the blow counts per every six inches will be recorded in the boring log. The split spoon sampler will be retrieved to the barge deck for sample handling. The hollow stem auger will be lowered to the sediment surface. If upon retrieval, the split spoon sampler did not retain/collect any sample, the hollow stem auger will be slowly rotated to a depth of two feet and slowly retrieved to the surface of the barge. A sediment sample will be collected from the hollow stem auger fins representative of the two foot sample depth.
4. After the 0 to 2 ft. depth has been sampled, the hollow stem auger will be advanced to the 2 foot depth and flushed with site water to remove any residual sediments within the auger.
5. The split spoon sampler will then be advanced to the 4 ft. depth and retrieved for sample handling;
6. This procedure will continue until either native material (such as clay) is encountered or the predetermined depth for a given boring is achieved.

### 4.1.2. Sediment Grab Samples

Sediment grab samples will be collected utilizing a ponar dredge sampler.

### 4.1.3. Hand Augured Samples

Four of the sampling locations within the project area are not accessible to the drill rig barge. Therefore, samples will be collected from these locations utilizing a bucket hand auger. Samples will be collected to the deepest depth as practical depending upon but not limited to hole collapse, complete resistance, obtaining the project sample depth of 19 ft., etc.

## 4.2 Sample Handling

### 4.2.1 Sample Processing

Samples not analyzed for TCLP Toxicity Characterization.

Upon retrieval of the split spoon/ponar sampler, the sampler will be carefully opened, sample retained within the split spoon sampler will be measured for recovery, transferred to a clean stainless steel mixing bowl or equivalent, photographed, a description will be recorded, thoroughly homogenized, and transferred into the appropriate sample containers. Samples for chemical analysis will be placed on ice within a cooler for shipment to the laboratory. Samples for geotechnical testing will be placed into an appropriate sample container ensuring that there will be no loss of moisture from the samples and then stored in a storage container for transport to Coleman Engineering Company's testing facility.

Samples analyzed for TCLP Toxicity Characterization.

Upon retrieval of the sediment sample, the sample will be transferred to a clean stainless steel mixing bowl or equivalent, photographed, and a description will be recorded. For TCLP volatiles, an aliquot will be transferred into the appropriate laboratory supplied sample container (TCLP volatiles samples will be composited at the laboratory). Another aliquot will be transferred to the sample container for TOC analysis. The remainder of the material will be thoroughly homogenized and a sufficient aliquot will be transferred into a second stainless steel mixing bowl for compositing. This process will be repeated for each 2 ft. split spoon sample collected from the boring. Upon completion of the boring, the sediment placed into the second stainless steel mixing bowl will be photographed and thoroughly homogenized and transferred into the proper TCLP extractable sample container.

### 4.2.2 Equipment Decontamination

Immediately after the samples have been transferred from the split spoon/ponar sampler, the equipment will be scrubbed with on-site water, scrubbed with a alconox/liquinox solution, and followed by a on-site water rinse. The on-site water wash and rinse may be disposed of on-site. The alconox/liquinox wash solution will be retained by the sampling team and disposed of properly at the completion of this sampling project. Disposal should be to a wastewater treatment facility.

### 4.2.3 Sample Containers

After processing, sediment samples will be placed into the appropriate sample containers as summarized in Table 6. A field sample log shall be filled out for each sampling location.

*Note: The analyzing laboratory will supply all required Chain-of Custody forms, sample containers, and sample coolers, including a temperature blank with each sample cooler.* ***The coolers and sample bottles shall be shipped to the following address no later than June 14, 2002****:*

*Scott Strigel*
*Coleman Engineering Company*
*635 Industrial park Dr.*
*Iron Mountain, Michigan 49801*

**Table 11. Sample Container and Preservation Requirements**

| Analyses | Container | Preservation Technique | Holding Times |
|---|---|---|---|
| PCBs | 8 oz Glass | Cool/dark, ≤ 4 $^{o}$ C | 14 days/40 days[2] |
| PAHs | | Cool/dark, ≤ 4 $^{o}$ C | 14 days/40 days[2] |
| TOC | 4 oz Glass | Cool/dark, ≤ 4 $^{o}$ C | 28 days |
| TCLP Volatiles | 4 oz Glass | Cool/dark, ≤ 4 $^{o}$ C | 14 days/40 days[2] |
| TCLP Extractables[1] | 16 oz Glass | Cool/dark, ≤ 4 $^{o}$ C | 14 days/40 days[2] |
| Ignitability, Corrosivity, and Reactivity | | Cool/dark, ≤ 4 $^{o}$ C | Analyze as soon as practical |
| Grain Size | 16 oz., Widemouth Plastic | Cool/dark, ≤ 4 $^{o}$ C, No head space[3] | No hold time |
| Hydrometer | Included in grain size | Cool/dark, ≤ 4 $^{o}$ C | No hold time |
| Atterberg Limits | Included in grain size | Cool/dark, ≤ 4 $^{o}$ C | No hold time |
| Loss upon ignition | Included in grain size | Cool/dark, ≤ 4 $^{o}$ C | No hold time |
| Percent Moisture | Included in PCBs | Cool/dark, ≤ 4 $^{o}$ C | 28 days |

[1] As, Ba, Cd, Cr, Cu, Pb, Hg, Ag, Semivolatiles, Pesticides, and Herbicides
[2] From time of collection to extraction/From time of extraction to analysis

### 4.2.4 Sample Labeling

Each sample bottle shall be individually labeled using a waterproof pen. The label shall contain, but not be limited to, the following information:

- Unique Sample Number: KK02XX-XX/XX; where "KK02" refers to the Kinnickinnic River 2002 sampling event, "XX-XX/XX" refers to the numerical sequence of the sample locations and the depth interval of the sample (KK0201-00/02 is sample number 1 collected from the sediment depth of 0 to 2 feet). Field duplicates and field replicates shall have a suffix of "R" for replicate and "D" for duplicate.
- Sample Date (MM-DD-YYYY)
- Sample Time (HHMM, on a 24-hour clock)
- Analysis to be performed (e.g. PCBs, PAHs, etc.)
- Sampler's Initials
- Client: Altech Environmental Services
- Project: Kinnickinnic River

An example label is shown in Figure 4. Clear tape will be placed over the label after the label has been completely filled out and attached to the sample container. The sample identification number and date of sample collection will be written on the sample container closure with a water proof marker.

**Figure 4. Example Sample Label**

**Project: Kinnickinnic River**
**Client: Altech Environ. Services**
**K0201-00/04 6-18-2002**
**PCBs & PAHs 1300 hrs.**
**DC**

### 4.2.5 Shipment and Chain-of-Custody

After collection and labeling, all glass containers shall be placed in a zip-lock bag, wrapped in bubble wrap and placed in an appropriate sample cooler. Within 24 hours of sample collection, the samples will be sent to the analyzing laboratory. After samples are collected each day, the Field Team Coordinator shall be responsible for shipping and/or arranging pickup of samples. A Shipping Container Checklist is provided for guidance (Appendix D). The Field Team Coordinator shall insure that:

1. The coolers contain sufficient ice to keep the sample below $4^{o}$ C during the shipment process and samples are immobilized with bubble pack to reduce the risk of breakage,
2. The chain of custody form (see example in Appendix A) is properly filled out,
3. A copy of the chain-of-custody form shall be retained and provided to the project manager,
4. A copy of the chain-of-custody form will be placed in a "ziploc" bag and taped to the inside lid of the cooler,
5. A temperature blank is included in each sample cooler (temperature blank to be supplied by the laboratories),
6. The outside of the container will be sealed using fiberglass or duct tape,
7. The laboratory name, phone number, and address, as well as the return name and address, will be clearly labeled on the outside of the cooler,
8. The samples will be sent to the contract laboratory by an overnight courier, and
9. Receipts of bills of lading will be retained as part of the permanent documentation and a copy of the air bill and/or bill of laden will be sent to Altech Environmental Services Project Manager, Ian Kerr,.
10. Commercial couriers are not required to sign off on the sample tracking form,
11. Laboratories are contacted prior to shipment to insure they are prepared for sample arrival.

***Note:*** *The analyzing laboratory will supply chain-of custody forms to the Project Field Sample Collection Team Leader, Scott Strigel, prior to the sampling event.*

Table 11 summarizes where each of the respective types of samples shall be shipped.

**Table 12. Addresses for Shipment of Samples**

| Analysis | Laboratory Contact Information |
|---|---|
| PCBs, PAHs, TOC, and Toxicity Characterization | Ann Preston<br>Trace Analytical Laboratories, Inc.<br>2241 Black Creek Rd.<br>Muskegon, Michigan 49444-2673<br>(231) 773-5998 Ext. 224 |
| Grain Size with Hydrometer, Atterberg limits, and Loss Upon Ignition[1] | Coleman Engineering - Scott Strigel<br>635 Industrial Park Rd.<br>Iron Mountain, Michigan 49801<br>(906) 774-3440 |

[1] - Geotechnical samples may be held on-site and in custody by Coleman Engineering Company and taken to Coleman Engineering's facility with the sampling team after completion of the project.

### 4.2.6 Receipt of Samples

Upon receipt of project samples for chemical analysis the laboratory shall

- Complete their portion of the chain-of-custody forms,
- Contact the Altech Environmental Services Project Manager to inform him of sample receipt and to discuss any problems or issues,
- Insure that the samples are maintained at < 4$^{o}$C,
- Complete a Cooler Receipt Form (See example in Appendix C).
- If there are any sample shipment problems, the laboratory should contact Altech Environmental Services Project Manager (Ian Kerr) and the Altech Environmental Services Project Manager shall contact the USACE Project Coordinator (Paul Baxter) and the USEPA Project Manager (Demaree Collier) as soon as the sample shipment problem is discovered,
- Fax a copy of the chain-of-custody form to the Altech Environmental Services Project Manager, Ian Kerr at (248) 353-5485

## 5. Laboratory Analysis

### 5.1 Analytical Methods

Analysis and preparation methods for all required analyses are provided in Table 2.

### 5.2 Data Quality Objectives (DQOs)

Data from the historical sampling events contains very little information regarding the extent of contamination within the project area. Additionally, the analytical obtained in the historical sampling events is not sufficient to meet the primary and secondary objectives of this project.

Therefore, the DQOs chosen for this project will be based on the objectives required to adequately assess the current state of contamination within the project area.

The DQOs for the laboratory analysis portion of this project are defined according to the following four quality assurance objectives.

Definitions

*Instrument Detection Limit (IDL)*: The instrument detection limit (IDL) is the lowest analyte concentration that an instrument can detect. The IDL is determined on samples that have not gone through any sample preparation (e.g. calibration standards).

*Limits of Quantification (LOQ)*: The limits of quantification is the lowest analyte concentration that can be accurately measured and reported, as opposed to simply detected.

*Method Detection Limit (MDL)*: Method detection limits (MDL) will be determined by making repeated measurements (a minimum of seven) over several non-consecutive days of either a calibration blank or a low-level standard with a concentration within 1-5 times the IDL. The MDL is calculated, at the 95 percent confidence level, as 3 times the standard deviation of the measured sample concentrations.

*Target Detection Limit (TDL)*: The target detection limit (TDL) is the concentration at which each analyte must be detected and quantified in order to meet the study objectives. This means that, if possible, all IDLs, MDLs and LOQs, should be less than the TDLs for all analytes. If the laboratory expects any of the IDLs, MDLs, or LOQs to exceed the required TDLs, they must contact the USACE and USEPA project managers to develop corrective action procedures.

### 5.2.1 Method Detection Limits and Level of Quantification

For quantitative chemical analyses, the analytical laboratory will be required to determine the instrument detection limit (IDL) prior to any analysis of the routine samples. The target detection limit (TDL) is the concentration at which the presence of an analyte must be detected to properly be able to assess and satisfy the DQOs. To be acceptable, a laboratory must demonstrate that the MDL is less than or equal to the TDL through use of laboratory quantitation standards. The laboratory shall also strive to set the dry sample Levels of Quantification (LOQs) below the applicable TDLs. Tables 2 through 7 contain the threshold effect concentrations (TECs) for the chemicals to be analyzed that have actually had the TECs calculated and contain the exact information, plus a few additional parameters that do not have calculated TECs, which are all also listed at the TDL for each parameter.

Target detection limits for all required sediment chemistry are provided in Tables 2 through Table 7.

**Note:** If a laboratory is unable to obtain MDLs and LOQs that are below the respective TDLs for each analyte, the laboratory shall contact the U.S. Army Corps of Engineers Project Coordinator and/or the U.S. Environmental Protection Agency's Project Manager to discuss required course of action. Decisions to be made could include: implementation of additional sample clean-up procedures prior to analysis, USEPA acceptance of higher MDLs and LOQs, or implementation of other potential suggestions.

**Note**: It is understood that potential high moisture contents of the sediments could impact MDLs and LOQs achieved by the laboratory. In an effort to reduce the impact of high water content on MDLs and LOQs the labs shall decant free water from the surface of the sediment samples prior to analysis.

### 5.2.2 Bias

Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction. Bias assessments for environmental measurements are made using personnel, equipment, and spiking materials or reference materials as independent as possible from those used in the calibration of the measurement system. When possible, bias assessments should be based on analysis of spiked samples rather than reference materials so that the effect of the matrix on recovery is incorporated into the assessment. A documented spiking protocol and consistency in following that protocol are important to obtaining meaningful data quality estimates. Spikes should be added at concentrations approximately at the mid-range. Spiked samples shall be used in accordance with the specified method.

Bias will be assessed through the use of certified reference materials (CRMs), standard reference materials (SRMs: a reference material certified by the U.S. National Institute of Standards Technology [U.S. NIST]), or other standards, such as, matrix spikes. The use of spiked surrogate compounds for GC and GC/MS procedures for PCB and PAH compounds, respectively, will be used to assess for bias.

Matrix spike and matrix spike duplicate samples (MS/MSD) also will be used to assess bias as prescribed in the specified methods. Acceptable recovery values will be within the recoveries specified by each of the analysis methods. Control samples for assessing bias will be analyzed at a rate as specified in the analytical SOPs and specified analytical methods.

### 5.2.3 Precision

Precision is a measure of agreement among replicate measurements of the same property, under prescribed similar conditions. This agreement is calculated as either the range ® or as the standard deviation (s). It may also be expressed as a percentage of the mean of the measurements, such as relative percent difference (RPD) or relative standard deviation (RSD) (for three or more replicates).

Laboratory precision is assessed through the collection and measurement of laboratory duplicates. The laboratories shall follow the protocols in the specified method and corresponding SOPs regarding the frequency of laboratory duplicates. This allows intra-laboratory precision information to be obtained on sample acquisition, handling, shipping, storage, preparation, and analysis. Both samples can be carried through the steps in the

measurement process together to provide an estimate of short-term precision. An estimate of long-term precision can be obtained by separating the two samples and processing them at different times, or by different people, and/or analyzed using different instruments. Acceptable RPDs will be in accordance to those specified by each analysis method.
For duplicate measurements, relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|D_1 - D_2| \times 100\%}{(D_1 + D_2)/2}$$

RPD = relative percent difference
$D_1$ = sample value
$D_2$ = duplicate sample value

For three or more replicates:

$$RSD = (s/x) \times 100$$

RSD = relative standard deviation
s = standard deviation of three or more results
x = mean of three or more results

Standard deviation is defined as follows:

$$s = ((\sum(y_I - \text{mean } y)^2 \times 1/(n-1)))^{0.5}$$

s = standard deviation
$y_I$ = measured value of the replicate
mean y = mean of replicate measurements
n = number of replicates

Quality control limits for Precision, Accuracy, and Completeness are summarized in Tables 2 through Table 7.

### 5.2.4 Accuracy

Accuracy measures how close analytical results are to a true or expected value. Accuracy objectives will be determined by calculating the percent recovery range of laboratory matrix spikes and matrix spike duplicates. Accuracy measures are calculated using the RPD between the expected value and the actual analytical results.

### 5.2.5 Representativeness

Representativeness is the degree to which the sampling data properly characterize the study environment. For the field-sampling phase, the previously established sampling sites reasonably cover the entire project area, and have been previously deemed to adequately represent any various sub-units within the project area.

In the analytical phase, and as specified elsewhere in this document, appropriate sample storage and preservation, and sample homogenization will insure that the samples analyzed adequately reflect conditions as they existed in the natural environment.

### 5.2.6 Comparability

Comparability states the confidence with which one data set can be compared to another. Comparability will be enhanced by the consistent use of standardized sampling methods and

specified protocols for the sampling phase and through the use of standard documented methodologies for analyte determinations. Any deviations from the standardized, selected methods or protocols will be clearly documented by the laboratories and noted in the final analytical report. There are a number of issues that can make two data sets comparable, and the presence of each of the following items enhances their comparability:

- Two data sets should contain the same set of variables of interest
- Units in which these variables were measured should be convertible to a common metric
- Similar analytical procedures and quality assurance should be used to collect data for both data sets
- Time measurements of certain characteristics (variables) should be similar for both data sets
- Measuring devices used for both data sets should have approximately similar detection levels
- Rules for excluding certain types of observations from both samples should be similar
- Samples within data sets should be selected in a similar manner
- Sampling frames from which the samples were selected should be similar
- Number of observations in both data sets should be of the same order or magnitude.

These characteristics vary in importance depending on the final use of the data. The closer two data sets are with regard to these characteristics, the more appropriate it will be to compare them. Large differences between characteristics may be of only minor importance, depending on the decision that is to be made from the data.

For this investigation, comparability will be satisfied by ensuring that the field sampling plan is followed, standard EPA Methods of analysis are used for sample analysis and that proper sampling techniques are used.

### 5.2.7 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Field completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. Field completeness objectives for this project will be greater than 90%. Laboratory completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. Laboratory completeness for this project will be greater than 90% of the total number of samples submitted to the analytical laboratories.

The calculation for percent completeness is as follows:

$$\%C = 100\% \times (V/n)$$

%C = percent completeness
V = number of valid measurements
n = number of measurements planned

# 6. Documentation and Records

## 6.1 Field Documentation

Field logs, boring logs, ship logs, and chain of custody documents will be used to record appropriate sample collection information in the field.

Sediment Sample Collection/Boring Logs: A sediment sample collection and/or boring log will be filled out by the field crew for each sample collected. All original field data sheets shall be turned over to the Project Coordinator at the conclusion of the field sampling and shall be kept as part of the permanent project file. A summary of sample collection information shall be maintained for each day of field sampling. Information to be included in the field log shall include but not be limited to: sample location ID, latitude/longitude of each sampling location, time of sample collection, water depth, etc.

Chain-of-Custody Forms:
An example chain of custody form is provided in Appendix A. A chain-of-custody form will be filled out for each set of samples shipped to the laboratory. A copy of the chain-of-custody form will be faxed to the Altech Environmental Services' Project Manager at the end of the field sample portion of this project.

## 6.2 Laboratory Reports

All laboratory data and records will be included in the final analytical report submitted to the project manager. A complete copy of the QAPP will be provided to the lab. The project manager will be responsible for maintaining the reports in the permanent project file. The following laboratory-specific records will be compiled by the laboratory and included in the final analytical report submitted to the project manager.

*Sample Data*. These records contain the times that samples were analyzed to verify that they met holding times prescribed in the analytical methods. Included should be the overall number of samples, sample location information, any deviations from the SOPs, time of day, and date. Corrective action procedures to replace samples violating the protocol also should be noted.

*Sample Management Records*. Sample management records document sample receipt, handling and storage, and scheduling of analyses. The records verify that sample tracking and proper preservation were maintained, reflect any anomalies in the samples (such as receipt of damaged samples), note proper log-in of samples into the laboratory, and address procedures used to ensure that holding time requirements were met.

*Test Methods*. Unless analyses are performed exactly as prescribed by SOPs, this documentation will describe how the analyses were carried out in the laboratory. This includes sample preparation and analysis, instrument standardization, detection and reporting limits, and test-specific QC criteria. Documentation demonstrating laboratory proficiency with each method used should be included (i.e. LCS data).

*QA/QC Reports*. These reports will include the general QC records, such as instrument calibration, routine monitoring of analytical performance, calibration verification, etc. Project-specific information from the QA/QC checks such as blanks (e.g., reagent, method), spikes (e.g.,

matrix, matrix spike duplicate, surrogate spike), calibration check samples (e.g., zero check, span check, and mid-range check), replicates, and so on should be included in these reports to facilitate data quality analysis.

*Data Reporting Package Format and Documentation Control Report:* The format of all data reporting packages must be consistent with the requirements and procedures used for data validation and data assessment described in Sections 8, 9, and 10 of the QAPP. The Field Sampling Coordinator will ensure that data are being recorded appropriately on the sample labels, sample tracking forms, and in the field notebook. All entries will be made using permanent ink, signed, and dated, and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark that is signed and dated by the sampler. A similar data entry process will be followed by the contract laboratory. Only QC/Calibration summary forms will be provided at this time, unless analytical raw data is necessary.

Contract laboratory will be expected to provide a data package with the following components:

- Case Narrative:
- Date of issuance
- Laboratory analyses performed
- Any deviations from intended analytical strategy
- Laboratory batch number
- Numbers of samples and respective matrices
- Quality control procedures utilized and also references to the acceptance criteria
- Laboratory report contents
- Project name and number
- Condition of samples "as received"
- Discussion of whether or not sample holding times were met
- Discussion of technical problems or other observations which may have created analytical difficulties
- Discussion of any laboratory QC checks which failed to meet project criteria
- Signature of the Laboratory QA Manager.

*Chemistry Data Report*:

- Case narrative for each analyzed batch of samples
- Summary page indicating dates of analyses for samples and laboratory quality control checks
- Cross referencing of laboratory sample to project sample identification numbers
- Descriptions of data qualifiers
- Sample preparation and analyses for samples
- Sample and laboratory quality control results
- Results of (dated) initial and continuing calibration checks
- Matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, calibration check compounds, and system performance check compound results
- Results of tentatively identified compounds.

*** An electronic copy of the Analytical Data Report will be submitted in an MS Excel format on CD containing the analytical test results***

## 7. Special Training Requirements

No special training requirements are required for this project.

## 8. Quality Control Requirements

All analytical procedures are documented in writing as SOPs and each SOP includes QC information, which addresses the minimum QC requirements for the procedure. The internal quality control checks might differ slightly for each individual procedure. Examples of some of the QC samples that will be used during this project include:

- Method blanks
- Reagent/preparation blanks
- Instrument blanks
- Surrogate spikes
- Analytical spikes
- Field replicates
- Laboratory duplicates
- Matrix Spike/Matrix Spike Duplicate
- Laboratory control standards
- Internal standard areas for GC/MS or GC/ECD analysis; control limits.

The actual QC samples requirements will be dictated by the method requirements. Details on the use of each QC check are provided in the analytical SOPs provided for each measurement. Method detection limits will be calculated for each analyte.

**Note:** Instrument calibration concentrations, method validation procedures, internal quality control protocols, analytical routines, maintenance and corrective actions, and the data reduction procedures are included in and will be performed as specified in the Standard Operation Procedures as required by the designated analytical methods.

### 8.1 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The purpose of this section is to discuss the procedures used to verify that all instruments and equipment are maintained in sound operating condition, and are capable of operating at acceptable performance levels.

*Testing, Inspection, and Maintenance*
The success of this project is dependent on well functioning field, analytical, and toxicological equipment. Preventative maintenance of this equipment is the key to reduce possible project delays due to faulty equipment.

As part of each laboratory's QA/QC program, a routine preventative maintenance program will be conducted to minimize the occurrence of instrument failure and other system malfunctions. All laboratory instruments are maintained in accordance with manufacturer's specifications and the requirements of the specific method employed. This maintenance is carried out on a regular, scheduled basis and is documented in the laboratory instrument service logbook for each instrument.

## 8.2 Instrument Calibration and Frequency

This section concerns the calibration procedures that will be used for instrumental analytical methods and other measurement methods that are used in environmental measurements. Calibration is defined as checking physical measurements against accepted standards.

*Instrumentation Requiring Calibration*
All of the equipment used to analyze the sediment samples will require calibration.

*Calibration Methods That Will Be Used For Each Instrument*
Instrument calibration procedures are dependent on the method and corresponding SOP. All ongoing calibration measurements must be within the requirements of the corresponding SOP to be considered adequate

*Calibration Apparatus*
None of the analytical instruments will be calibrated using a calibration apparatus.

*Calibration Standards*
The working linear range of an instrument should be established prior to performing sample analyses. Calibration standards as specified in the applicable methods and SOPs will be used when establishing the working linear range. The working linear range for a specific analysis should bracket the expected concentrations of the target analyte in the samples to be analyzed.

*Calibration Frequency*
Instrument calibration is performed before sample analysis begins and is continued during sample analysis at the intervals specified within the applicable methods and SOPs in order to ensure that the data quality objectives are met. The verification of instrument stability is assessed by analyzing continuing calibration standards at regular intervals during the period that sample analyses are performed. Standards will be analyzed on a schedule as specified in the analytical SOPs. The concentration of the continuing calibration standard should be equivalent to the midpoint of the working linear range of the instrument.

Equipment logbooks will be maintained at the laboratory, in which will be recorded the usage, maintenance, calibration, and repair of instrumentation. These logbooks will be available during any audits that may be conducted.

## 8.3 Inspection/Acceptance Requirements for Supplies and Consumables

The purpose of this section is to establish and document a system for inspecting and accepting all supplies and consumables that may directly or indirectly affect the quality of the project or task.

*Identification of Critical Supplies and Consumables*
Critical supplies and consumables include sample bottles, gases, reagents, hoses, materials for decontamination activities, and distilled/deionized water. The laboratory will utilize high quality supplies and consumables to reduce the chances of contaminating the samples. All water purification systems are tested on a regular basis to ensure that water produced is acceptable for use. Solvent blanks are run to verify the purity of solvents used in the organic analyses. The contract laboratory may also incorporate other measures, such as the dedicated use of glassware for certain analyses.

*Establishing Acceptance Criteria*
Acceptance criteria must be consistent with overall project technical and quality criteria. The laboratory should utilize their own acceptance criteria for normal operations with analyzing and/or testing contaminated sediments.

*Inspection of Acceptance Testing Requirements and Procedures*
The contract laboratory should document inspections of acceptance testing, including procedures to be followed, individuals responsible, and frequency of evaluation. In addition, handling and storage conditions for supplies and consumables should be documented.

*Tracking and Quality Verification of Supplies and Consumables*
Procedures should be established to ensure that inspections or acceptance testing of supplies and consumables are adequately documented by permanent, dated, and signed records or logs that uniquely identify the critical supplies or consumables, the date received, the date tested, the date to be retested (if applicable), and the expiration date. These records should be kept by the responsible individual(s) at the laboratory. In order to track supplies and consumables, labels with the information on receipt and testing should be used. These or similar procedures should be established to enable project personnel to: 1) verify, prior to use, that critical supplies and consumables meet the project objectives; and 2) ensure that supplies and consumables that have not been tested, have expired, or do not meet acceptance criteria are not used for the project.

## 8.4 Data Management

This section will present an overview of all mathematical operations and analyses performed on raw data to change their form of expression, location, quantity, or dimensionality. These operations include data recording, validation, transformation, transmittal, reduction, analysis, management, storage, and retrieval.

*Laboratory Data Recording*
All raw analytical and toxicity data will be recorded in numerically identified laboratory notebooks or data sheets. The data will be promptly recorded in black ink on appropriate forms that are initialed and dated by the person collecting the data. Changes to recorded data are made in black ink, with a single line cross-out, initials, and date. No “whiteout” will be allowed.

If a laboratory has the capability to directly enter or download the data into a computerized data logger, then this is preferable. All labs shall download data directly into a computerized database. Sample data are recorded along with other pertinent information, such as the sample identification number. Other details which will also be recorded include: the analytical method used (SOP #), name of analyst, the date of analysis or toxicity test, matrix sampled, reagent concentrations, instrument settings, and the raw data. Each page of the notebook or data sheet will be signed and dated by the analyst. Copies of any strip chart printouts (such as gas chromatograms) will be maintained on file. Periodic review of these notebooks by the Laboratory Supervisors will take place prior to final data reporting. Records of notebook entry inspections are maintained by the Laboratory QA/QC Officer.

*Data Verification*
The method, instrument, or system should generate data in a consistent, reliable, and accurate manner. Data validation will be shown by meeting acceptable QC limits for analytical parameters and sediment toxicity tests. In addition, the application of preventative maintenance activities and internal QA/QC auditing will ensure that field and laboratory generated data will be valid. Quality control data (e.g., laboratory duplicates, matrix spikes, matrix spike duplicates, and performance of negative controls) will be compared to the method acceptance criteria. Data considered to be acceptable will be entered into the laboratory computer system. Data verification is performed by a second designated senior/experienced staff at the technical level where QC results, hold times, and instrument calibration is evaluated. All QA requirements are programmed into automated systems and flagged where appropriate.

*Data Transformation*
Data transformations result from calculations based on instrument output, readings, or responses. The procedures for converting calibration readings into an equation that will be applied to measurement readings are given in the SOPs for analytical parameters.

*Data Transmittal*
Data transmittal occurs when data are transferred from one person or location to another or when data are copied from one form to another. Some examples of data transmittal are copying raw data from a notebook onto a data entry form for keying into a computer file and electronic transfer of data over a computer network. The transmittal of field data will be double-checked by the PI. The transmittal of laboratory data will be checked by the individual analyst with periodic checks by the Laboratory Project Manager and/or QA/QC Officer.

*Data Reduction*
Data reduction includes all processes that change the number of data items. The laboratory has their own data reduction techniques, as is usually documented in their QA Manual. For the analytical results, data reduction will involve calculating the arithmetic mean and standard deviation of field and laboratory replicates.

*Data Analysis*
Data analysis will involve comparing the surficial contaminant concentrations to qualitative values contained in Tables 2 through 7. The analysis shall be performed by the WDNR Project Manager.

*Data Tracking*
Data management includes tracking the status of data as they are collected, transmitted, and processed. The laboratory will have its own data tracking system in place.

*Data Storage and Retrieval*
The contract laboratory will have its own data storage and retrieval protocols. USEPA-GLNPO will retain all the analytical data packages in the project files for this study. In addition, the sediment contaminant data will be added to GLNPO's contaminated sediment database.

### 8.5 Data Acquisition Requirements (Non-Direct)

Additionally, sets of screening values will be used to evaluate the potential impacts of the contaminant concentrations found in the sediments during this survey. All parameter data will be compared to existing sediment quality guidelines available in *MacDonald et. Al*. (2000) and *Persuad et. Al* (1993). All of these screening levels were specifically developed for freshwater ecosystems and have been published in peer reviewed journals and documents. Therefore, these guidelines are considered sufficient for a screening level analysis of sediment data.

Water surface elevation data will be obtained from the NOAA web page. Only data from the "verified/historical water level data" page will be utilized in the study. However, NOAA has attached the following disclaimer on data from this web page:

**"These raw data have not been subjected to the National Ocean Service's quality control or quality assurance procedures and do not meet the criteria and standards of official National Ocean Service data. They are released for limited public use as preliminary data to be used only with appropriate caution."**

Since the water surface elevation data is non-critical data, this preliminary data is sufficient for our needs.

## 9. Assessment and Oversight

### 9.1 Assessment and Response Actions

During the planning process, many options for sampling design, sample handling, sample cleanup and analysis, and data reduction are evaluated and chosen for the project. In order to ensure that the data collection is conducted as planned, a process of evaluation and validation is necessary. This section of the QAPP describes the internal and external checks necessary to ensure that:

- All elements of the QAPP are correctly implemented as prescribed.
- The quality of the data generated by implementation of the QAPP is adequate.
- Corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

The most important part of this section is documenting all planned internal assessments. Generally, internal assessments are initiated or performed by the QA Officer.

*Assessment of Subsidiary Organizations*

Two types of assessments of the subsidiary organizations can be performed as described below.

- *Management Systems Review (MSR).* A form of management assessment, this process is a qualitative assessment of a data collection operation or organization to establish whether the prevailing quality management structure, policies, practices, and procedures are adequate for ensuring that the type and quality of data needed are obtained. The MSR is used to ensure that sufficient management controls are in place and carried out by the organization to adequately plan, implement, and assess the results of the project.
- *Readiness Reviews.* A readiness review is a technical check to determine if all components of the project are in place so that work can commence on a specific phase.

It is anticipated that a readiness review by each contract laboratory project manager will be sufficient for this project. No management systems review is anticipated for this project. A pre-project QA/QC conference call (already held) and submittal of laboratory certifications and/or QA plans shall suffice as a MSR.

*Assessment of Project Activities*
Assessment of project activities can involve the following tasks:

- Surveillance
- Technical Systems Audit (TSA)
- Performance Evaluation (PE)
- Audit of Data Quality (ADQ)
- Peer Review
- Data Quality Assessment.

Surveillance will be the primary assessment technique of project activities. This will most readily occur by the Project Manager and QA Officer of the contract laboratory.

*Number, Frequency, and Types of Assessments*
Due to the short-term nature of this project for the contract laboratory, no types of assessments are planned other than general surveillance, a data quality assessment by USACE representatives, and peer review by USACE and USEPA.

*Assessment Personnel*
Internal audits of the contract laboratory are regularly performed by their respective QA Officers.

*Schedule of Assessment Activities*
External audits by the GLNPO QA Officer and/or the GLNPO Project Manager is up to his/her discretion. The scheduling of regular internal audits at contract labs is at the discretion of the respective QAQC Officer.

*Reporting and Resolution of Issues*
Any audits or other assessments that reveal findings of practice or procedure that do not conform to the written QAPP need to be corrected as soon as possible. The Laboratory Project Manager and Laboratory QA/QC Officer need to be informed immediately of critical deviations that compromise the acceptability of the test. For any critical deviations from the QAPP (i.e.,

elevated detection levels, surrogate recoveries outside control limits, etc.) that cannot be corrected within the laboratories standard procedure, the Laboratory Project Manager must contact both the USEPA Project Manager and the USACE Project Coordinator within 24-hours of being informed of the deviation. The laboratory project manager should be ready to provide suggestions for corrective action. For non-critical deviations, they need to be informed by the next business day.

Corrective actions should only be implemented after approval by both the USACE Project Coordinator and the USEPA Project Manager. If immediate corrective action is required, approvals secured by telephone from the USEPA Project Manager should be documented in an additional memorandum. In general communications from the laboratory should follow the chain-of-command as shown in Figure 1. However, if the contract laboratory is unable to contact the Altech Environmental Services Project Manager on any time-critical matter, the laboratory shall contact either the USACE Project Coordinator or USEPA Project Manager as necessary.

For noncompliance problems, a formal corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem will be responsible for notifying the project manager. Implementation of corrective actions will be confirmed in writing through the same channels. The laboratory shall issue a nonconformance report for each nonconformance condition.

Corrective actions in the laboratory may occur prior to, during, and after initial analysis. A number of conditions, such as broken sample containers, multiple phases, and potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with laboratory analysts and section leaders, it may be necessary for the Laboratory QA/QC Officer to approve the implementation of corrective actions. The submitted SOPs specify some conditions during or after analysis that may automatically trigger corrective actions of samples, including additional sample extract cleanup and automatic re-injection/reanalysis when certain quality control criteria are not met.

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event.

Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- There are unusual changes in detection limits
- QC limits for sediment toxicity tests are not met
- Deficiencies are detected by the Laboratory and/or GLNPO QA Officer(s) during any internal or external audits or from the results of performance evaluation samples
- Inquiries concerning data quality are received.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, experimental set-up, and so on. If the problem persists or cannot be identified, the matter is referred to the Laboratory Project Manager and/or

Laboratory QA/QC Officer for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the Laboratory QAQC Officer.

These corrective actions are performed prior to release of the data from the laboratory. The corrective actions will be documented in both the laboratories corrective action log and the narrative data report sent from the laboratory to the Altech Environmental Services Project Manager.

If corrective action does not rectify the situation, the laboratory will contact Altech Environmental Services Project Manager who will then contact the USACE Project Coordinator and USEPA Project Manager to discuss details of the corrective actions and required future actions.

## 9.2 Reports to Management

*Responsible Organizations*
Written QC data and appropriate QA/QC reports generated by the laboratory shall be included in the Analytical Data Report. The Analytical Data Report will be provided by the laboratory to the Project Manager by the persons identified in Section 1.3 whenever sample measurements are reported. The QC section of the Analytical Data Report should include the QC data (including results, recoveries, and RPDs), any non-conformance reports, and chains of custody. The report should give detailed results of analysis of QC samples, and provide information on the precision, accuracy, and completeness for each sample run. These written reports will note any significant QA/QC problems encountered during sample analyses, as well as state the corrective actions taken.

Any serious QA problems needing immediate decisions will be discussed orally between the USACE Project Coordinator and laboratory staff, with such discussions denoted in writing. Communication should follow the chain-of-command summarized in Figure 1. These problems will be noted in the final project report to the USEPA Project Manager.

The USACE Project Coordinator will provide summary QA/QC information in the final written report to USEPA. This report will include information on adherence of measurements to the QA objectives. The final report will contain detailed discussions of QA/QC issues, including any changes in the QAPP, a summary of the contract laboratory QA/QC reports, results of any internal performance audits, any significant QA/QC problems, detailed information on how well the QA objectives were met, and their ultimate impact on decision making. The following is a list of items to be included in the final project report:

- Changes in the QAPP
- Results of any internal system audits
- Significant QA/QC problems, recommended solutions, and results of corrective actions
- Data quality assessment in terms of precision, accuracy, representativeness, completeness, and sensitivity
- Indication of fulfillment of QA objectives
- Limitations on the use of the measurement data.

## 10. Data Validation and Usability

The USEPA Project Manager will make a final decision regarding the validity and usability of the data collected during this project. The project manager will evaluate the entire sample collection, analysis, and data reporting processes to determine if the data is of sufficient quality to meet project objectives. Data validation involves all procedures used to accept or reject data after collection and prior to use. These include screening, editing, verifying, and reviewing through external performance evaluation audits. Data validation procedures ensure that objectives for data precision and bias will be met, that data will be generated in accordance with the QA project plan and SOPs, and that data are traceable and defensible. The process is both qualitative and quantitative and is used to evaluate the project as a whole.

*Procedures Used to Validate Field Data*
Procedures to evaluate field data for this project primarily include checking for transcription errors and reviewing field notebooks. This task will be the responsibility of the WDNR project manager.

*Procedures Used to Validate Laboratory Data*
The Laboratory QAQC Officer will conduct a systematic review of the analytical data for compliance with the established QC criteria based on the spike, duplicate, and blank results provided by the laboratory. All technical holding times will be reviewed, the laboratory analytical instrument performance will be evaluated, and results of initial and continuing calibration will be reviewed and evaluated.

Upon receipt of the draft laboratory report, the U.S. Army Corps of Engineers will perform a QA/QC review of the analytical report. At a minimum, this review will include an analysis of:

- Sample Receipt Verification/Documentation
- Detection Limits
- Surrogate Recoveries
- Laboratory QC Documentation and Results
- Holding Time Data
- Process Bias and Sensitivity
- MS/MSD Recoveries
- Analytical Method Documentation

At the conclusion of the review, the U.S. Army Corps of Engineers will prepare a report describing the results of the review, providing recommendations on data items requiring corrective action or further documentation/information, and drawing conclusions as to the usability of the data provided. A draft report will be provided to the analyzing laboratory and the U.S. EPA project manager for review and comment prior to finalizing conclusions and recommendations.

The data review will identify any out-of-control data points and data omissions, and the Laboratory QA Officer will interact with the laboratory to correct data deficiencies. Decisions to repeat sample collection and analysis may be made by the USEPA Project Manager based on the extent of the deficiencies and their importance in the overall context of the project.

Additionally, the USEPA project manager will compare all field and laboratory duplicates for RPD. Based on the results of these comparisons, the USEPA project manager will determine the acceptability of the data. One hundred percent of the analytical data will be validated. Reconciliation of laboratory and field duplicates shall be the responsibility of the USEPA project manager.

Finally, the USACE project coordinator will compare the laboratory methods and results to the QA/QC Review checklist contained in Appendix B. Any critical problems identified by these checklist that we are unable to rectify through corrective actions, may be cause for rejecting portions or all of the data provided.

**APPENDIX A**

**U.S. Army Corps of Engineers, Detroit District**
**Environmental Analysis Branch**

| Address: | Project Name: | Requested Analysis | | | | | | | | | Lab Comments: |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Project # | | | | | | | | | | |
| To: | P.O.# | | | | | | | | | | |
| Phone:<br>Fax: | Sampled by:<br>Name: Initials: | | | | | | | | | | |
| Turnaround time: | Samples Received:<br>Cold: Y N _____ $^0$C Intact: Y N | | | | | | | | | | |

| # | Sample Identification | Date | Time | Comp | Grab | Matrix | # | | | | | | | | | | |
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| Relinquished By: | Received By: | Date/Time: | Notes: |
|---|---|---|---|
| Relinquished By: | Received By: | Date/Time: | |

# APPENDIX B

## Minimum QA/QC Checklist for Data Evaluation

Upon receipt of the Draft Analytical Report, the draft report will be checked to verify that the following are included:

1. Project name and number
2. Date of issuance
3. Laboratory report contents
4. Case Narrative
5. Numbers of samples analyzed
6. Laboratory analysis performed
7. Condition of the samples "as received"
8. Copy of the cooler receipt form
9. Any deviations from the intended analytical strategy
10. Discussion of whether or not sample hold times were met
11. Discussion of technical problems or other observations which may have created analytical difficulties
12. Discussion of any laboratory QC checks which failed to meet project criteria
13. Analytical test results in spreadsheet format using USACE sample I.D.s and laboratory sample I.D.s
14. Summary page indicating dates of analyses for samples and laboratory quality control checks
15. Analytical test methods utilized
16. Quality control test results
17. Descriptions of data qualifiers
18. Matrix spike/matrix spike duplicate recoveries, laboratory control samples, method blank results calibration check compounds, system performance check compound results, and precision results
19. Statement signed by laboratory QA/QC officer that all data and information submitted is valid.

# APPENDIX C

## COOLER RECEIPT FORM

LIMS #_____ Number of Coolers _____

PROJECT:_____ Date/Time Received _____

A. PRELIMINARY EXAMINATION PHASE:
Cooler opened by (print)_____ (sign) _____

1. Did cooler come with a shipping label (air bill, etc)?……YES NO
   If yes, enter carrier name & air bill number _____

2. Were custody seals outside of cooler?……YES NO
   How many & where _____, sealed date:_____seal name:_____

3. Were seals unbroken and intact at the date and time of arrival?…….YES NO

4. Were Chain-of-Custody papers in a plastic bag & taped to the cooler lid?…….YES NO

5. Were Chain-of-Custody papers filled out properly?…….YES NO

6. Did you sign the Chain-of-Custody papers in the appropriate location?…….YES NO

7. Were temperature blanks used?……..YES NO
   Cooler Temperature_____($^0$C) Thermometer ID No.
   _____

8. Have designated person initial here to acknowledge receipt of
   cooler:_____ Date/time_____

Comments:

Continued

**COOLER RECEIPT FORM Continued**

B. LOG-IN PHASE: Date samples were logged in:_____

By (print) _____ (sign)_____

11. Describe type of packing in cooler:_____

12. Were all bottles sealed in separate plastic bags?…….YES NO

13. Did all bottles arrive unbroken with labels in good condition?……...……YES NO

14. Were all bottle labels complete (ID, date, time, initials, etc.?)……...YES NO

15. Did all labels agree with Chain-of-Custody?……..YES NO

16. Was a sufficient amount of sample sent for tests indicated?……...YES NO

17. If answered NO to any of the above, was laboratory manager notified and project manager called to discuss……..YES NO

Document discussion/comments:

# APPENDIX D

**SHIPPING CONTAINER CHECKLIST SUMMARY**

Failure to properly handle or document the Project samples could jeopardize the usability of the sample results and ultimately the Project. Prior to sending a cooler to the Analytical Laboratory please check the following items:

* Is the Project clearly identified on the Chain-of-Custody (official project name, project location)?
* Are all enclosed sample containers clearly labeled with waterproof ink, is the label covered with clear tape, enclosed in a plastic bag, and wrapped in bubble wrap?
* Are the sample labels complete?
* Are the desired analyses indicated on the bottle labels and Chain-of-Custody?
* Does the information on the Chain-of-Custody match the information on the sample container labels?
* Is the sample identification clearly marked on the sample container enclosure with waterproof ink?
* Has the Chain-of-Custody been placed into a plastic bag and attached to the inside of the cooler lid?
* Is the shipping Bill of Laden been properly and clearly filled out including laboratory contact name and phone number?
* Is there sufficient ice (double bagged in ziploc baggies) or "blue ice" in the cooler?
* Are the sample container secured (no free space between containers) with bubble wrap or equivalent?

# APPENDIX E
## Sampling Station Coordinates

| Station Identification | Degrees Minutes Seconds | Degrees Minutes | State Plane NAD 83 |
|---|---|---|---|
| KK0201 | N 43$^0$ 00' 24.582" | N 43$^0$ 00.4097' | N 373938.5418 |
| | W 87$^0$ 54' 49.461" | W 87$^0$ 54.8244' | E 2526476.8398 |
| | | | |
| KK0202 | N 43$^0$ 00' 26.052" | N 43$^0$ 00.4342' | N 374084.8365 |
| | W 87$^0$ 54' 50.774" | W 87$^0$ 54.8462' | E 2526375.5895 |
| | | | |
| KK0203 | N 43$^0$ 00' 27.127" | N 43$^0$ 00.4521' | N 374193.0581 |
| | W 87$^0$ 54' 51.121" | W 87$^0$ 54.8520' | E 2526374.0692 |
| | | | |
| KK0204 | N 43$^0$ 00' 27.587" | N 43$^0$ 00.4598' | N 374242.5581 |
| | W 87$^0$ 54' 49.501" | W 87$^0$ 54.8250' | E 2526466.2548 |
| | | | |
| KK0205 | N 43$^0$ 00' 29.083" | N 43$^0$ 00.4847' | N 377391.5662 |
| | W 87$^0$ 54' 50.804" | W 87$^0$ 54.8467' | E 2526365.6385 |
| | | | |
| KK0206 | N 43$^0$ 00' 28.793" | N 43$^0$ 00.4799' | N 374368.3612 |
| | W 87$^0$ 54' 47.492" | W 87$^0$ 54.7915' | E 2526612.4021 |
| | | | |
| KK0207 | N 43$^0$ 00' 30.135" | N 43$^0$ 00.5022' | N 374505.5048 |
| | W 87$^0$ 54' 46.746" | W 87$^0$ 54.7791' | E 2526664.4580 |
| | | | |
| KK0208 | N 43$^0$ 00' 29.027" | N 43$^0$ 00.4838' | N 374397.3218 |
| | W 87$^0$ 54' 44.620" | W 87$^0$ 54.7437' | E 2526825.1040 |
| | | | |
| KK0209 | N 43$^0$ 00' 29.594" | N 43$^0$ 00.4932' | N 374455.7424 |
| | W 87$^0$ 54' 44.067" | W 87$^0$ 54.7344' | E 2526864.7492 |
| | | | |
| KK0210 | N 43$^0$ 00' 30.668" | N 43$^0$ 00.5111' | N 374570.0809 |
| | W 87$^0$ 54' 41.053" | W 87$^0$ 54.6842' | E 2527085.9289 |
| | | | |
| KK0211 | N 43$^0$ 00' 30.479" | N 43$^0$ 00.5080' | N 374554.1841 |
| | W 87$^0$ 54' 39.337" | W 87$^0$ 54.6556' | E 2527213.8477 |
| | | | |
| KK0212 | N 43$^0$ 00' 29.352" | N 43$^0$ 00.4892' | N 374444.6494 |
| | W 87$^0$ 54' 36.910" | W 87$^0$ 54.6152' | E 2527396.9646 |
| | | | |
| KK0213 | N 43$^0$ 00' 29.196" | N 43$^0$ 00.4866' | N 374432.3383 |
| | W 87$^0$ 54' 35.002" | W 87$^0$ 54.5834' | E 2527539.0922 |
| | | | |
| KK0214 | N 43$^0$ 00' 30.198" | N 43$^0$ 00.5033' | N 374540.8733 |
| | W 87$^0$ 54' 31.186" | W 87$^0$ 54.5198' | E 2527819.9944 |

# Attachment 2

# Report of Data Audit for 2002 Sediment Assessment Kinnickinnic River, Milwaukee, Wisconsin

US Army Corps of Engineers, Omaha District
March 25, 2003

DATE: March 25, 2003
SUBJECT: Review of selected Kinnickinnic River sediment samples for overall quality

A set of ten samples were randomly selected and provided to the USACE HTRW-CX by the USACE Detroit District for a QA data review. These samples were from the Kinnickinnic River project; the review entailed an evaluation of report completeness, and an evaluation of the reported quality control measures. In particular the samples were reviewed for the polychlorinated Biphenyls (PCB) and Polynuclear hydrocarbon (PNA) analyses data quality.

The project report documents and materials provided by Trace Analytical Laboratories, Inc. of Muskegon, Michigan for the River Project were reviewed first for completeness. This involved verifying that all samples selected for review (Table 1) were present in the document package provided in both a data report form and as raw instrumental data printouts. All samples listed in Table 1 were definitively linked to report sheets in the document package with the single exception of sample KK0203D-0810. This sample appears to be referenced incorrectly and actually is sample KK0203-0810D, which was identified and located in the package. All identified samples were then traced to their associated preparatory and analysis batches (see Tables 3 & 4). These batches were reviewed, and it was determined that all of the batch quality control data reports and raw instrumental data printouts were present for each batch.

Having determined that all required information was present; a review of the content was completed. The content review involved examination of sample specific quality control information (e.g. surrogates, etc.), batch specific quality control information (e.g. matrix spike recoveries, etc.), and method specific quality control information (e.g. laboratory control sample recoveries, etc.) for both completeness and performance (see Table 5 for items reviewed). The laboratory non-conformance reports were also reviewed for every one of the out of acceptance limits excursions that were noted during the content review process. The non-conformance reports in general adequately addressed the exceptions that were noted.

Samples with levels of analytes exceeding the highest calibration standard were consistently reanalyzed with a greater dilution. Calculations for the quantitation of PCBs and PAHs were manually verified to the extent possible, particularly with respect to dilutions. The values reported were consistent and appear to have been properly adjusted for dilutions. The detail provided related to the sample preparation and analysis sequence for the PAH analysis did not include enough information to confirm the adjustments were being completed for percent solids and amount (mass) of sample. Based on the values reported for the PCBs and the raw values given on instrument report sheets the adjustments for percent solids and amount used would have to have been made by the analysis software, as it was confirmed that these values were not post-analysis corrected for these items. The detail provided in the analysis sequence for the PCB analysis did not include enough information to confirm the adjustments were being completed for percent solids and amount (mass) of sample

For the PCB analysis, it appears that primarily single point calibrations were used to quantitative Aroclors other than 1260 and 1016. While this meets method requirements, if Aroclors other than 1260 and 1016 are expected to be found routinely it would be advisable to use multi-point calibration for those Aroclors. Additionally it was observed that different integration techniques

were routinely used for the different Aroclors. In general, the 1260 and 1016 Aroclors (analyzed simultaneously) were analyzed using a "valley baseline" while the other Aroclors generally used a "baseline mapping" and/or extending technique. The valley baseline method works well when there is good baseline resolution of peaks while the "baseline mapping" can provide good results when optimal peak resolution is not observed. Not all peaks were baseline resolved in the 1260 and 1016 Aroclors therefore; baseline mapping may have been a better option. It should be noted that the significance of the baseline drawing technique choice is reduced the greater the amount of PCB present. This is because the magnitude of the peak area increases while the variations in the area due to the different assignments of the baseline remains nearly constant and the overall affect is that the baseline selection becomes relatively less significant. Finally, it was noted that the calibration standards were treated in the same manner as the unknown samples this also lessens the impact of baseline technique and therefore selection of the alternate (mapping) technique may provide only a slight increase in data quality. In conclusion, no significant impact to the reported quantitation of the individual Aroclors resulted from this practice. It is however, recommended that the laboratory use the "baseline mapping" method as a default technique for all Aroclors as this would be a better overall option, particularly when it is not known if the sample to be analyzed may have low or high levels of PCBs.

Overall conclusion - the content review indicated that the laboratory generally performed within its stated acceptance limits and these measures generally support the usability of the reported data.

## TABLES

Table 1, Samples Selected for Review

| |
|---|
| Randomly Selected |
| KKO202-1820 |
| KKO203D-0810* |
| KKO205-1012 |
| KKO207-0608 |
| KKO208-1012 |
| KKO210-1214 |
| KKO211-0204 |
| KKO213-0406 |
| KKO214-0608 |
| Non-Random Selection |
| KKO2US1 |

*Sample KK0203-0810D was reviewed not KK0203D-0810.

Table 2, Sample Identification Cross Reference

| Altech | TRACE |
|---|---|
| KKO202-1820 | CJ100-26 |
| KKO203-0810D | CJ100-13 |
| KKO205-1012 | CJ100-45 |
| KKO208-1012 | CJ100-62 |
| KKO207-0608 | CJ100-82 |
| KKO210-1214 | CJ100-80 |
| KKO213-0406 | CJ100-92 |
| KKO214-0608 | CJ100-99 |
| KKO2US1 | CJ100-116 |
| KKO211-0204 | CJ100-110 |

| Table 3, PNA batching of samples | | |
|---|---|---|
| PNA batch | Altech | TRACE |
| PNA091101S | KKO203-0810D | CJ100-13 |
| PNA091201S | KKO202-1820 | CJ100-26 |
| PNA091301S | KKO205-1012 | CJ100-45 |
| | KKO208-1012 | CJ100-62 |
| PNA091701S | KKO207-0608 | CJ100-82 |
| | KKO210-1214 | CJ100-80 |
| PNA091801S | KKO213-0406 | CJ100-92 |
| | KKO214-0608 | CJ100-99 |
| | KKO211-0204 | CJ100-110 |
| PNA091901S | KKO2US1 | CJ100-116 |

| Table 4, PCB batching of samples | | |
|---|---|---|
| PCB prep | Altech | TRACE |
| PCB091201S | KKO202-1820 | CJ100-26 |
| PCB091501S | KKO203-0810D | CJ100-13 |
| | KKO205-1012 | CJ100-45 |
| | KKO208-1012 | CJ100-62 |
| PCB091601S | KKO207-0608 | CJ100-82 |
| | KKO210-1214 | CJ100-80 |
| PCB091701S | KKO213-0406 | CJ100-92 |
| | KKO214-0608 | CJ100-99 |
| | KKO2US1 | CJ100-116 |
| PCB091801S | KKO211-0204 | CJ100-110 |

Table 5, Summary of Items Checked in Report Content Review

| | Report Present | Holding Time | Surrogate Recovery | Spike Recovery | Relative Percent Difference | Spike and Surrogate Acceptance Limits Reasonable* |
|---|---|---|---|---|---|---|
| Samples | X | X | X | | | X |
| Method Blank | X | | X | | | X |
| MS & MSD | X | | X | X | X | X |
| LCS & LCSD | X | | X | X | X | X |

*Surrogate and spike recoveries (MS, MSD, LCS and LCSD) we considered reasonable if they were similar to typically reported limits. Limits were not reviewed for consistency with any project specific requirements in the SAP and/or QAPP.

MS & MSD = Matrix Spike and matrix spike duplicate
LCS & LCSD = Laboratory control sample and laboratory control sample duplicate

Richard J. Meyer, Ph.D.
*Chemist*
*USACE, HTRW-CX*
*Voice: (402) 697-2571*
*Fax: (402) 697-2595*