WRI SR 00-01

Evaluation of the Effectiveness of Remediation Dredging: The Fox River Deposit N Demonstration Project
November 1998 – January 1999

Fox River Remediation Advisory Team
Madison, Wisconsin

June 2000

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Water Resources Institute Special Report
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Water Resources Institute
University of Wisconsin-Madison
1975 Willow Drive
Madison, Wisconsin

2000

EXECUTIVE SUMMARY

The presence of PCB-contaminated sediments in the Lower Fox River, Wisconsin has been implicated as a cause of water quality degradation and as a source of PCB bioaccumulation in fish and other wildlife in Green Bay of Lake Michigan. Various remediation strategies have been proposed for the Lower Fox River, including dredging and permanently removing sediments from the river. As a result of a cooperative agreement between the State of Wisconsin and the Fox River Group (a coalition of seven former and present paper companies-Appleton Papers, Ft. James, P.H. Glatfelter Co., NCR Corp., Riverside Paper Corp., U.S. Paper Mills Corp. and Wisconsin Tissue Mills, Inc.) a demonstration project was developed to assess the effectiveness of dredging as a remediation option for PCB-contaminated sediments in the Lower Fox River.

The Fox River Remediation Advisory Team (FRRAT) was established in April 1998 to review plans for monitoring the effectiveness of dredging at the Fox River Deposit N demonstration site, near Kimberly, Wisconsin. After reviewing various revisions of monitoring plans, FRRAT reached the consensus that the best method for assessing the effectiveness of dredging was a mass balance approach. The mass balance approach suggested by FRRAT compares the mass of contaminant removed from a sediment deposit with the mass recovered onshore and that mass transported downstream in the Lower Fox River. The three essential components of the mass balance approach for Deposit N were the Deposit Mass Balance, River Transport, and Process Mass Balance. These three mass balance components are considered when determining the effectiveness of dredging at Deposit N.

The results presented here focus on Phase I of the remediation, which encompasses pre-dredge periods, dredging (16 Nov.–29 Dec. 1998) and post-dredge coring (Jan. 1999). Activities occurring at Deposit N after Phase I are not considered in this report because the monitoring needed for complete mass balances was not in place. Post-Phase I activities, however, are briefly discussed in the Appendices.

During Phase I, approximately 17.1 kg of PCBs and 2.3 kg of mercury were removed from the west lobe of Deposit N. This represented 89% of the PCBs and 81% of the mercury in this lobe of the deposit. The press cake material that was trucked away from the site accounted for most of the contaminants removed from the deposit, representing 96% of the PCBs and 87% of the mercury. The concentrations of PCBs and mercury in treated waters discharged back to the Fox River were less than 0.01% of the concentrations in the sediment slurry transported to the shoreside treatment site.

Based on the results of Phase I activities, the following conclusions are made regarding the effectiveness of dredging at Deposit N: 1) Environmental dredging is an effective mechanism for removal of contaminated sediments from Deposit N in the Lower Fox River; 2) A mass balance approach is the most scientifically defensible measure for assessing the effectiveness of a dredging operation; 3) Shoreside processing was an effective means of concentrating and permanently removing contaminated sediments from the river; 4) Dredging on the Fox River should be conducted during a period when monitoring is sufficient to determine losses from the activity; 5) Common techniques such as measurement of total suspended solids (TSS) and turbidity do not adequately describe riverine transport of PCBs; 6) Prior to dredging, Deposit N represented an active source of PCBs to the Lower Fox River and was not "naturally" capping with clean sediments; 7) The demonstration project at Deposit N provided information important for future shoreside processing design; 8) The demonstration project at Deposit N provided information important for water column sampling designs; and 9) The mass balance framework is a feasible and useful approach for future dredging activities.

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ACRONYMS

BBL - Blaslund, Bouck and Lee, Inc., Syracuse, NY

DOC - dissolved organic carbon

d/s - downstream

ECL - En Chem Laboratories, Madison, WI

FRG - Fox River Group, a coalition of seven former and present paper companies - Appleton Papers, Ft. James, P.H. Glatfelter Co., NCR Corp., Riverside Paper Corp., U.S. Paper Mills Corp. and Wisconsin Tissue Mills, Inc.

FRRAT - Fox River Remediation Advisory Team

GIS - Geographic Information System

GLNPO - Great Lakes National Program Office

Hg - mercury

LMMB - Lake Michigan Mass Balance Study

PCBs - polychlorinated biphenyls

RI/FS - remedial investigation/feasibility study

STL - Severn-Trent Laboratory, Colchester, VT

TOC - total organic carbon

TSS - total suspended solids

u/s - upstream

USEPA - U.S. Environmental Protection Agency

USGS - U.S. Geological Survey

WDNR - Wisconsin Department of Natural Resources

ACKNOWLEDGMENTS

Based on an agreement between the Wisconsin Department of Natural Resources (WDNR) and the Fox River Group (FRG) on January 31, 1997, it was agreed that FRG would perform the monitoring phase of the Deposit N dredging demonstration project. The Fox River Remediation Advisory Team (FRRAT) was formed at the request of the WDNR to evaluate FRG monitoring plans that were developed by Blasland, Bouck and Lee, Inc. The FRG provided funding to the University of Wisconsin Water Resources Institute (UW-WRI) through WDNR (Contract no. NMI 00001571).

We thank several staff members from the U.S. Geological Survey in Middleton, Wisconsin for their efforts in obtaining field samples in Kimberly. At times, samples were collected during difficult weather conditions. Their dedication resulted in obtaining samples that form the basis of this report.

Kari Sherman and Cynthia Walder, UW-WRI, provided editorial support for this document.

1. INTRODUCTION

The Lower Fox River, flowing from Lake Winnebago to Green Bay (Figure 1-1), has been impacted by the presence of sediment-bound contaminants that have accumulated over the last several decades. The Wisconsin Department of Natural Resources (WDNR) has determined that release of contaminants from sedimentary deposits in the Fox River cause exceedances of state water quality standards and lead to the posting of fish consumption advisories. From a human health and ecological risk perspective, the principal contaminants of concern are polychlorinated biphenyls (PCBs) and mercury (Hg). Sampling has confirmed that sediment-associated PCBs and Hg are accumulating within the aquatic food chain and are actively being transported within the river and out into Green Bay and Lake Michigan.

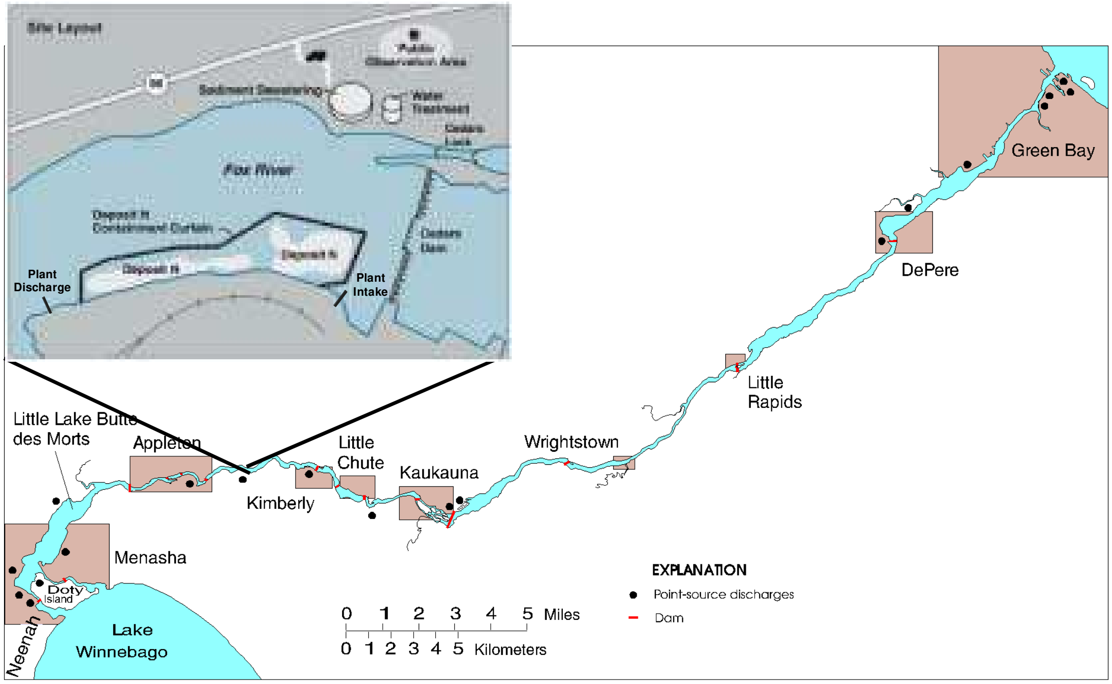


Figure 1-1 – The Lower Fox River from Lake Winnebago to Green Bay. Inset shows location of Deposit N. (Maps courtesy of Wisconsin Department of Natural Resources)

The Fox River Coalition conducted a Remedial Investigation/Feasibility Study (RI/FS) at Deposit N in Kimberly, Wisconsin (Graef, Anhalt, Schloemer & Associates, Inc. and Science Applications International Corporation, 1996) to provide the information needed to develop a whole river clean-up plan. The RI/FS concluded that feasible options for Deposit N were in-place containment or removal and offsite disposal. To provide specific information for developing a whole river clean-up plan for the Lower Fox River, as well as begin active remediation of the river, WDNR, with financial assistance from U.S. Environmental Protection Agency (USEPA) Great Lakes National Program Office (GLNPO) and the Fox River Coalition, identified Deposit N as a site to conduct a sediment removal pilot project. The goal of this remediation demonstration project was to implement a remedial design, protective of human health and the environment, for the removal and disposal of sediments from Deposit N. Implementation will result in a mass removal of PCBs from the Lower Fox River. Additional plans for the project included:

- Sediment removal by hydraulic dredging;
- Minimization of resuspension of sediment, PCBs, and other constituents to the river;
- Protection of water quality, including the industrial water intake at the Inter Lake Papers paper mill;
- Removal of as much PCB-contaminated sediment from the deposit as is practicable within the confines of the project budget;
- On-shore dewatering of the sediments; and
- In-state landfill disposal of the sediments.

The Deposit N remediation project was a joint effort between the State of Wisconsin and the Fox River Group (FRG). An agreement on January 31, 1997 stated that the FRG would perform the monitoring phase of the Deposit N dredging demonstration project. The FRG was asked to develop and submit a monitoring plan to the WDNR. On November 7, 1997 an initial draft of the Deposit N environmental monitoring plan was forwarded to the WDNR. The FRG received written comments in a letter from Mr. Robert Paulson of WDNR dated December 8, 1997. In response to this letter, the FRG, in a letter from Mr. Joseph Heimbuch dated December 23, 1997, provided WDNR with a plan for proceeding with development of an environmental monitoring plan for Deposit N. On January 28, 1998, representatives of WDNR and the FRG met at the WDNR offices, Madison, Wisconsin to discuss the draft monitoring plan. At this meeting, WDNR provided additional explanation of the comments presented in the December 8, 1997 letter. It was agreed that the FRG would revise and resubmit the monitoring plan to WDNR. To provide additional review of the FRG draft documents, WDNR formed an advisory group with funding from the FRG called the Fox River Remediation Advisory Team (FRRAT) (Table 1-1).

The FRRAT reviewed FRG monitoring plans in April 1998 and advised FRG to use a mass balance approach in determining the effectiveness of dredging at Deposit N. This approach was preferred over the concentration-based assessment originally proposed by FRG through its consultants, Blaslund, Bouck and Lee, Inc. (BBL). Concentration of a contaminant has often been used to specify the level of contamination in an environmental compartment like river sediments. By extension, a change in concentration resulting from cleanup activities may be used to evaluate the extent of remediation. Some cleanup strategies may be deemed successful if contaminant concentrations decrease after treatment. This position is largely site-focused, without the broad ecosystem concerns.

The FRRAT, however, believes that measuring only concentration for assessment results in erroneous conclusions regarding the effectiveness of environmental dredging. For instance, concentration-based studies may falsely indicate no change, effective remediation, or ineffective remediation whether or not

Table 1-1. Members of the Fox River Remediation Advisory Team (FRRAT).

Name	Affiliation
James P. Hurley, Ph.D., Chair	University of Wisconsin Water Resources Institute and Bureau of Integrated Science Services, Wisconsin Department of Natural Resources, Madison
David E. Armstrong, Ph.D.	Water Chemistry Program, University of Wisconsin-Madison
J. Philip Keillor, M.S.	Sea Grant Institute, University of Wisconsin-Madison
Jon Manchester, Ph.D.	Water Chemistry Program, University of Wisconsin-Madison
Jeffrey J. Steuer, M.S.	U.S. Geological Survey, Middleton, Wisconsin

the targeted mass of contaminated sediment has been removed. Factors such as clean or contaminated material sloughing from a river bank or sides of a dredge cut, or from a movement of upstream particles into the dredging area may mask the actual effects of dredging. Surficial sediment concentrations are the result of short-term, as well as longer-term, hydraulic processes working on a contaminated mass of sediments. From an ecosystem perspective, dredging contaminated sediments permanently removes them from the affected area, insuring that these contaminants in a river system can no longer be transported downstream to other areas by typical or event-related flows. A true measure of the effectiveness of environmental dredging as a remediation strategy must include an assessment of the amount, or mass, of contaminant removed from the affected location. This mass can then be applied to risk assessment calculations to determine the reduction in risk to the environment resulting from the permanent removal of the contaminant.

The mass balance approach suggested by FRRAT compares the mass of contaminant removed from a sediment deposit with the mass that was recovered onshore and the mass transported downstream in the Lower Fox River. A mass balance of dredging at Deposit N requires a calculation of the amount of PCB removed from the river, the amount of PCB processed onshore, and the amount transported downstream. The three essential components of the mass balance approach for Deposit N (Figure 1-2) are deposit mass balance, river transport, and process mass balance.

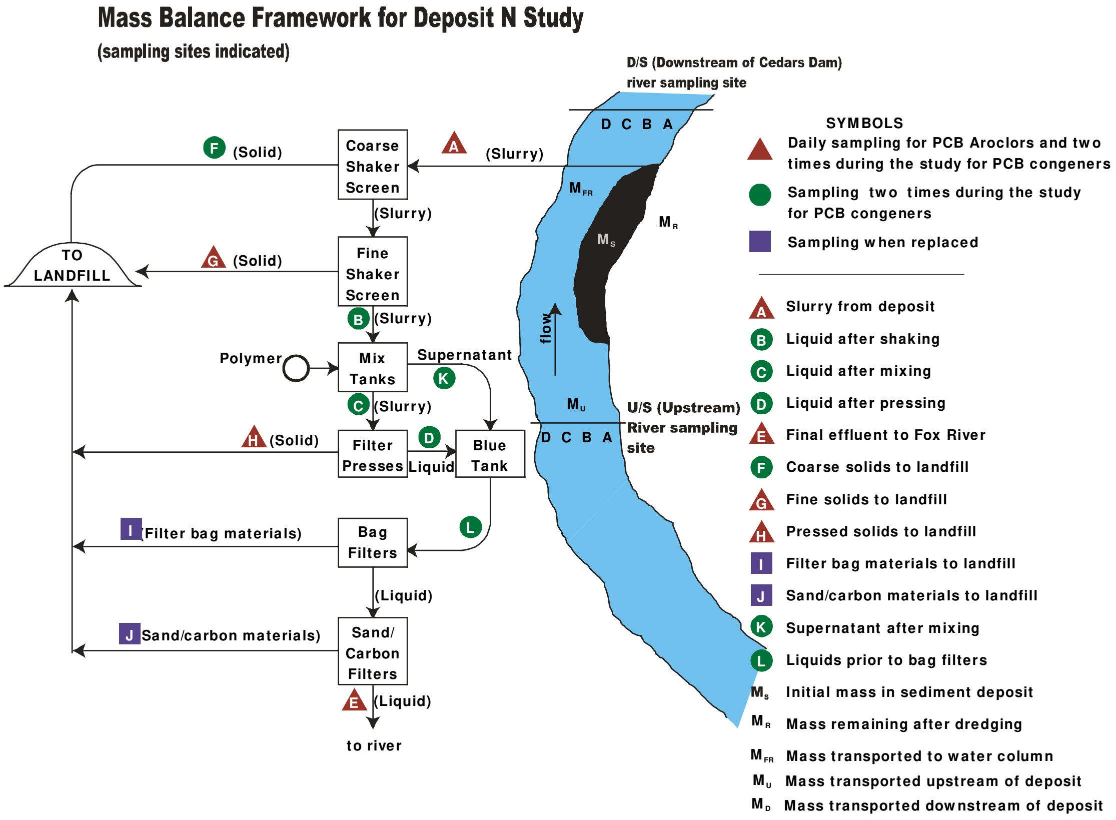


Figure 1-2. Map of Deposit N with shoreside processes schematic.

DEPOSIT MASS BALANCE

The deposit mass balance is the ***principal component of the monitoring plan for evaluating the effectiveness of dredging***. This mass balance is a materials flow accounting of the original amount of PCBs in the deposit and a daily accounting of the material dredged and trucked away. It compares the amount of material originally in Deposit N to that remaining after dredging is complete. Continuous monitoring of the slurry pipe inflow to the shoreside processing facility serves as a check of materials being removed from the river.

RIVER TRANSPORT

The assessment of riverine conditions before, during, and after dredging estimates the amount of contaminant that is released during dredging relative to background conditions upstream in the river. Water column sampling was conducted both upstream and downstream of the dredge site, that was enclosed with an impermeable barrier. It is critical that all concentration data obtained in this phase of the mass balance be coupled with flow data to quantify mass transport downstream.

PROCESS MASS BALANCE

This secondary mass balance assesses the potential losses during on-shore processing of the dredged materials. Several sampling sites were located within the treatment facilities and sampled less often than the sites identified necessary for the previous two focus areas.

The mass balance approach is tailored to the dredging remediation option. The dredging option seriously consider the possibility of future resuspension of unremoved PCBs in Fox River sediments by extreme floods. These resuspended sediments could then become new sources of PCBs to aquatic organisms and waterfowl in Green Bay and Lake Michigan and to the people who consume fish from these waters. Extreme floods have become more frequent in Wisconsin, repeatedly overwhelming storm water drainage systems designed for 100-year frequency rainfall events.

The Deposit N remediation project utilized several sampling techniques designed during the Green Bay Mass Balance Study and the tributary monitoring phase of the Lake Michigan Mass Balance (LMMB) study. A sampling site for the Fox River during the LMMB study was located at the mouth of the river at Green Bay and provides a basis for comparison of dredging activities to typical fluxes at the river mouth.

Data from the LMMB Fox River site clearly show a seasonal trend during 1994-95 (Figure 1-3). During the winter, PCB fluxes decrease dramatically, most likely due to low particle levels and ice-cover conditions on the river. Although intensive sampling did not occur at the mouth of the Fox River during the 1998-99 water year, these data identify a general trend of decreasing loading during a period similar to that of dredging at Deposit N (November through January). If conditions in winter 1998-99 were similar to 1994-95, one would expect low background PCBs in the river during dredging. These conditions allow for better detection of increases in PCB inputs during dredging activities relative to other times during the year (Figure 1-3).

This report summarizes the data collected from November 1998 through January 1999 (Phase I) of the demonstration dredging at Deposit N. During this period field-sampling crews obtained samples that could be used in the three mass balance approaches discussed previously. Our determination of effectiveness and suggestions for future dredging activities is based on the period during which conditions allowed successful sampling at all necessary sites. In the Appendices, we discuss trends observed during Phases II and III. However, the inability to collect sufficient samples precluded the use of the mass balance approach during these phases of the project.

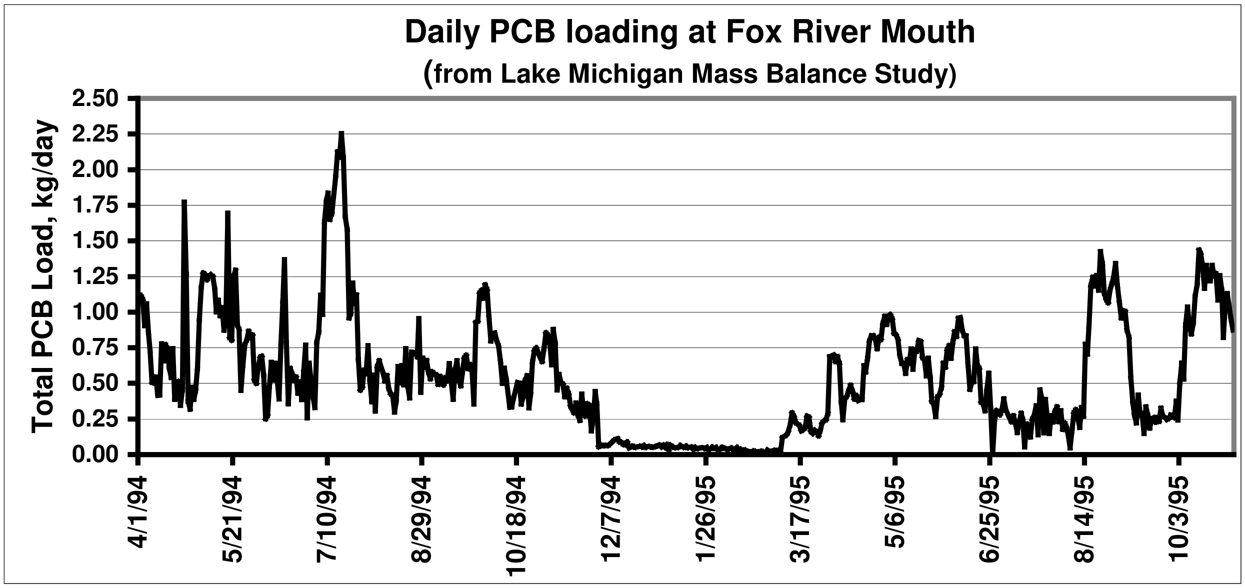


Figure 1-3. Results of the Lake Michigan Mass Balance (LMMB) study for daily discharges of PCBs at the mouth of the Fox River, 1994-95.

2. METHODS

The three study phases incorporate the mass balance approach and are described as follows. Sampling sites for the focus areas are shown in Figure 1-2. Dates and activities associated with dredging are listed in Table 2-1.

DEPOSIT MASS BALANCE

This mass balance is a materials flux accounting of the original amount of PCBs in the deposit, a daily accounting of the material dredged and trucked away, and the deposit mass at the conclusion of dredge operations. The deposit mass balance includes the following components:

M_S = mass (solids, PCBs, Hg) initially present in the deposit;
M_R = mass remaining after dredging operations are completed;
M_A = mass transported from the deposit in the dredged slurry; and
M_{FR} = mass transported from the deposit area to the Fox River during dredging.

Table 2-1. Dates and activities during Deposit N remediation.

Date(s)	Activity
22 Oct. 1998	First water column sample collected to establish background deposit
22-29 Oct. 1998	Deposit N cored to establish Deposit N initial conditions
10 Nov. 1998	Began installation of sediment curtain (anchor bolts and cable); extreme wind conditions
12 Nov. 1998	Continued turbidity curtain installation
15 Nov. 1998	Continuous turbidity monitors installed
19-20 Nov. 1998	Sediment poling conducted to establish Deposit N initial volume
26 Nov. 1998	Dredging and shoreside sediment processing began
4 Dec. 1998	Turbidity curtain completed
22 Dec. 1998	Dredging and shoreside processing stopped
28 Dec. 1998	Dredging and shoreside processing reconvened
29 Dec. 1998	Continuous upstream and downstream turbidity monitors no longer operating
30 Dec. 1998	Opening cut in downstream side of turbidity curtain to allow ice removal; ice breaking operations commenced
31 Dec. 1998	Dredging and shoreside operation shutdown due to freeze-up
1 Jan. 1999	Icebreaking operations outside of barrier to retrieve monitors
6 Jan. 1999	Icebreaking in preparation for diver coring operations
11-16 Jan. 1999	Deposit N cored to establish final conditions
21 Dec. 1998, 15-19 Jan. 1999	Sediment poling conducted to establish Deposit N final volume
19 Jan. 1999	Began turbidity barrier removal; icebreaking operations to remove barrier
20 Jan. 1999	Final water column sample collected
27 Jan. 1999	Completed turbidity barrier removal
20 Aug. to 4 Oct. 1999	Sediment dredged from downstream (east) Lobe–Phase II
5-14 Oct.1999	Sediment dredged from upstream (west) lobe–Phase III

The mass balance equation for the overall calculation of downstream releases is:

$$M_S - M_R - M_A = M_{FR}. \qquad \textbf{\textit{Equation 1}}$$

The before and after masses in the deposit are calculated using Equation 2:

$$M_{PCB} = VRC_{PCB} = ADRC_{PCB}, \qquad \textbf{\textit{Equation 2}}$$

where:

M_{PCB} = mass of PCB in the river sediments, before or after dredging;
V = volume of river sediments;
A = area of river sediments;
D = depth of river sediments;
R = in-place density of river sediments; and
C_{PCB} = concentration of PCBs in river sediments

Equation 2 states that four parameters (A, D, R, and C_{PCB}) must be known to calculate the mass of PCB in river sediments. Three of these values, D, R, and C_{PCB}, must be measured and may change as a result of dredging. Conversely, the fourth parameter, A, representing the area of remediation, is chosen to reflect the area of the river sediments impacted by dredging. This area, once chosen, is constant before and after dredging.

The mass of PCB in river sediments is related to the area of the river sediments containing PCBs. Proper choice of river sediment area, A, requires that it be large enough to contain the area of dredged sediments, but as small as possible so that Equation 1 does not produce a very small difference of two large numbers. Several aspects of the dredging project at Deposit N aid in selecting an appropriate value for sediment area, A, in Equation 2.

Deposition of sediment at Deposit N is a result of a clockwise gyre in Fox River flow as the river approaches the Cedars Dam. The gyre produces a gradually diminishing current along the south bank of the river that flows in a direction opposite to the overall easterly flow of the river. As this current slows, sediment particles are sorted as they settle to the river bottom. Larger particles fall out early while finer particles are carried farther west along the south shore. This produces a deposit along the shore with two distinct lobes. The east lobe has coarser particles and lower PCB concentrations, while the west lobe is composed of finer particles and has higher PCB concentrations. It also should be noted that Deposit N consists of sediment resting on bedrock.

Dredging at Deposit N proceeded in three phases. During Phase I much of the sediment in the west lobe of the deposit was removed. The east lobe was dredged during Phase II and a small amount of additional sediment was removed from the west lobe during Phase III. Monitoring of onshore activity, including an assessment of PCB collected, occurred only during Phase I. In addition, a silt containment curtain surrounded the dredging activity during Phase I, which occurred about 9 months earlier than the remainder of the dredging. Given these aspects of the dredging operation and the characteristics of Deposit N, the area chosen for consideration in this discussion is the portion of the west lobe of Deposit N that was bounded by the silt containment curtain. This area is equal to about 9300 m^2. The calculations presented here quantify the mass of PCB removed from this area. This mass may be compared with the amount of PCB processed onshore during Phase I dredging to assess the effectiveness of environmental dredging as a remediation strategy. Results for Phases II and III are summarized in Appendices I and II.

All three measured parameters in Equation 2 vary spatially and temporally in river sediments at Deposit N, due to either natural conditions, or as a direct result of dredging, or both. Dredging and monitoring during Phase I occurred within a relatively short time frame. It was possible, therefore, to assess temporal variability in measured parameters, as well as obtain the information required by Equation 1, by sampling at only two points in time, once before and once after Phase I dredging. Spatial variability over the area of interest was much greater. Previous sediment coring, as well as information from other environmental dredging efforts, indicated that 20 sediment cores were necessary to properly characterize the PCB concentrations and the in-place sediment densities at the dredge site in the West Lobe. Sediment depth also varies greatly, in large part due to the removal of sediment by dredging.

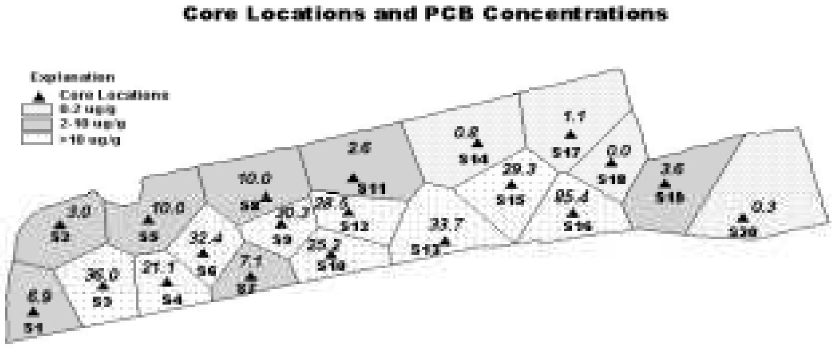
The use of Equation 2 to calculate the mass of PCB in river sediments in the west lobe of Deposit N is made more complex by the spatial variability of the measured parameters describing PCB concentration and in-place density. Several techniques are available to integrate a spatially variable data set so that Equation 2 may be solved. These techniques include simple global averaging, interpolative methods such as inverse distance weighting and kreiging, and discrete methods such as Theisen polygons. While providing a fast solution, simple global averaging discards much of the information in the data set. In contrast, interpolative methods augment the available data and sometimes introduce methodological artifacts. This is acceptable and necessary if the data set is limited in size. Discrete methods divide the original space into subunits, calculate values of interest for each subunit, and then sum the values calculated for each subunit to arrive at a value for the original space. Previous work (Graef, Anhalft, Schloemer & Associates Inc. and Science Applications International Corporation, 1996) had established the sample size necessary to characterize the dredge site, making it possible to collect the required samples. Therefore, it was desirable to retain all available data and it was not necessary to augment the data set. For these reasons, an approach using Theisen polygons was chosen to integrate the measured values for PCB concentration, in-place density, and sediment depth and calculate the PCB mass in the dredging area. The west lobe of Deposit N, the silt containment curtain, the 20 Theisen polygons that subdivide the dredge area, and the locations of the sediment sampling cores that define the boundaries of the polygons are shown in Figure 2-1.

Two sets of values for the four parameters in Equation 2, representing conditions before and after dredging, were tabulated for each of the 20 polygons shown in Figure 2-1. These values were used to calculate the mass of PCB in the sediment bounded by each polygon before and after dredging. The mass of PCB in the dredge area sediments before and after dredging is equal to the sums of the PCB masses in the polygons in each case. Equation 3 expresses this algebraically:

$$M_{PCB} = \Sigma\, A_i D_i R_i C_{PCBi} \qquad \textbf{\textit{Equation 3}}$$

where:

i = polygon number 1 to 20.



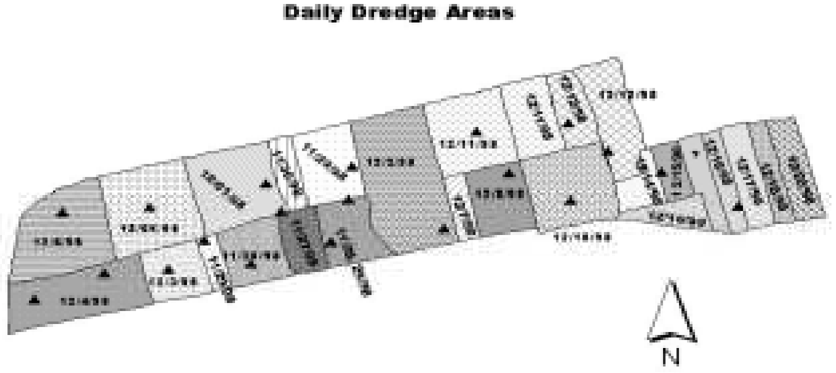


Figure 2-1. Pre-dredge concentrations of PCBs and dates of dredging during Phase I Deposit N activities.

Other important quantities describing the dredging effort may be calculated from equations related to Equation 3. For example, as suggested by Equation 2, sediment volume is equal to the product of sediment area and depth:

$$V = \Sigma A_i D_i, \qquad \textbf{\textit{Equation 4}}$$

and

$$M_{SEDIMENT} = \Sigma A_i D_i R_i, \qquad \textbf{\textit{Equation 5}}$$

where:

$M_{SEDIMENT}$ = mass of dry sediment in the dredge area, and other parameters are as previously defined.

Sediment Depth Measurements

Depth data used in calculations presented here were obtained by Miller Engineering, Kimberly, Wisconsin. The sediment surface elevation at Deposit N was surveyed before the start of dredging (19-21 Nov. 1998) and after completion of Phase I (21 Dec. 1998 and 15, 18, and 19 Jan. 1999). The elevation of bedrock under Deposit N was also measured. Measurements were reported as feet above sea level and referenced to benchmark 54, elevation 716.52 by the U.S. Geological Survey (USGS).

Sediment surface elevations before and after dredging, and of bedrock, were surveyed at more than 100 locations. Two spatial grids defined the survey locations, one over each of the two deposit lobes. Other than covering the same portion of the river, the surveying grids had no inherent relationship to the 20 sediment-coring locations described previously, nor to the Theisen polygons surrounding the coring locations. Thus, it was necessary to systematically combine the elevation measurements in order to generate representative sediment depths–before and after dredging–for each polygon. Geographic Information System (GIS) computer software was used to overlay surveying locations and associated depth measurements on the Theisen polygons generated from sediment core locations (Figure 2-1). Elevation measurements were then separated into 20 groups, representing measurements located inside each polygon. All elevations for sediment before dredging, for sediment after dredging, and for bedrock inside a given polygon were averaged to give the average sediment elevation before and after dredging and the average bedrock elevation for that polygon. Finally, the depth of sediment before and after dredging was calculated for each polygon by subtracting the average bedrock elevation from the average sediment elevations before and after dredging for that polygon.

Sediment PCB Concentrations and Sediment In-place Density

Sediment PCB concentrations were measured on samples taken from sediment cores, Ponar grab samples, or sediment samples collected in bottles by divers. Sampling was done before the start of dredging on 22-29 Oct. 1998 and after dredging on 11-16 Jan. 1999. Twenty locations within the dredge area were sampled for sediment before and after dredging.

All but three of the sampling locations were sampled by sediment coring before dredging began; a Ponar grab sampler was used to sample locations 2, 14, and 19. In addition, site and tray duplicates were collected from locations 10, 13, and 16. As noted, Deposit N rests on bedrock and many locations had little remaining sediment after dredging. Therefore, it was possible to collect cores from only eight locations (3, 5, 6, 9, 10, 12, 16, and 18) after dredging. Divers collected available surface sediment in bottles at the remaining locations. A tray duplicate was collected at location 10 and a bottle duplicate was collected at location 20.

Location 18 was sampled before dredging and location 11 was sampled after dredging. However, due to laboratory error, no concentration data was available from these samples. The missing values were set equal to the values after and before dredging for locations 18 and 11, respectively. The calculations were also performed with the two missing values set equal to zero. Because before and after PCB masses decreased by the same small amount when zero values were used, there was no difference in the mass of PCB removed.

Additional sediment cores collected before dredging from about half of the sampling locations were sectioned to produce depth-resolved sediment samples. Typically, this resulted in a sample representing the first 10 cm of sediment and a sample representing the remainder of the core, although the lower portion of some cores was divided into two or three sections. Thus, depth-resolved PCB concentrations were available for part of the dredge site before dredging.

Sediment in-place density could be measured on sediment samples collected by coring and, in one case (location 2), by Ponar grab. Thus, locations 14 and 19 did not have a value for in-place density before dredging. The value used for location 14 was the average of nearby locations 11, 15, and 17, and the value for location 19 was obtained by averaging values from locations 16, 18, and 20. Also, less than half of the coring locations after dredging had measured in-place densities because many sediment samples after dredging were collected in bottles. In-place sediment densities measured before dredging were used for those locations lacking a measured value after dredging. This approach was justified in two ways. Those values measured after dredging were similar to their counterparts before dredging. In addition, sediment in-place density was measured after Phase III of Deposit N dredging. The locations of the measurements after Phase III differed somewhat from those used during Phase I, however, values measured in similar locations were comparable.

RIVER TRANSPORT

Riverine conditions must be assessed before, during, and after dredging in order to estimate the amount of contaminant that is released during dredging. During dredging, a silt curtain was in place and affected transport due to dredging activities. River transport includes periods both pre- and post-dredging, including samples taken as during curtain installation and removal (if weather conditions allowed for safe sampling).

Equation 1 may not be sensitive enough for assessing releases to the water column because M_S and M_A are large terms, and small errors in the measurements of M_A, M_R, and M_S may give substantial uncertainty in calculated values of M_{FR}. As a result, the direct measurement of water column transport is necessary. Water column sampling was designed to support mass transport calculations. In equation form, the net mass transported to the Fox River (M_{FR}) from the deposit area is calculated by:

$$M_{FR} = (M_D - M_U)_{\text{during dredge ops}}, \qquad \textbf{\textit{Equation 6}}$$

where:

M_U = the mass in the water column upstream of the dredge site; and
M_D = the mass downstream of the dredge site.

Water column samples were collected from four discrete locations along a transect. Figure 1-2 details the four upstream (U-a, U-b, U-c, U-d) and downstream (D-a, D-b, D-c, D-d) locations. The four sites were flow-proportioned; sites were spaced closer together in areas of focused flow. At each sub-site water was collected from two depths; 0.2 and 0.8 of the total water depth. During the dredging operation two to three transect pairs (upstream and downstream) were collected per sample day. For a given transect (upstream or downstream), water from the four sub-sites was composited throughout the day to provide a representative concentration for each cross-section. In addition to transect composites, discrete total suspended solids (TSS) samples and water quality parameters (temperature, turbidity, pH, and specific conductance) were obtained.

Upstream and downstream composite samples were analyzed for congener-specific PCB (dissolved and particulate), TSS, dissolved organic carbon (DOC), and total organic carbon (TOC). The dredging contractor also collected continuous turbidity data at several sites during most of the dredge operation.

Eighty-liter composite water column samples were filtered through 0.7-µ glass fiber filters to determine particulate congener PCB concentrations. Filtrate was pumped through an absorbent resin column (e.g. XAD-2) to concentrate PCBs for the operationally defined “dissolved” phase. Complete procedures for 80-liter PCB water column samples are described in the QAPP (Fox River Group, 1999). Total PCB concentrations were calculated by summing the dissolved and particulate fractions.

A continuous discharge record for Deposit N was based on the 15-min flow data generated from the Appleton Acoustic Discharge meter (USGS site 04084445) located approximately 5 miles upstream of Deposit N. The continuous record was increased by 6% based on a comparison to periodic discharge measurements made at the dredge site. Mean daily river discharge was used in conjunction with the water column concentration values (collected over an 8- to 12-hour period) to calculate daily TSS and PCB loads.

Four sets of duplicate PCB and TSS samples were collected. The mean relative percent differences were calculated for total PCB (combined dissolved and particulate phases) (15%), composite TSS samples (17%), and discrete TSS samples (5%).

PROCESS MASS BALANCE

The process mass balance assesses the potential losses during processing of the dredged materials. Several sampling sites were located within the treatment facilities and sampled less often than the sites identified as necessary for the overall mass balance. The process mass balance includes:

M_A = Mass (solids, PCBs, Hg) transported in the dredged slurry to the coarse shaker screen;
M_B = Mass in the slurry transported from the fine shaker screen to mixing tanks;
M_C = Mass in the slurry transported from mixing tanks to filter presses;
M_D = Mass in liquid transported from filter presses to bag filters and sand/carbon filters;
M_E = Mass in liquid transported from sand/carbon filters to the river;
M_F = Mass in solids transported from coarse shaker screen to landfill disposal;
M_G = Mass in solids transported from fine shaker screen to landfill disposal;
M_H = Mass in solids transported from filter press to landfill disposal;
M_I = Mass retained by bag filters; and
M_J = Mass retained by sand/carbon filtration media.

Sampling methods and frequencies for these locations (Figure 1-2) are summarized in Section 2.2 of the QAPP (Fox River Group, 1999). Measurements were used to assess potential PCB releases during the on-shore handling of dredged sediments. Possible routes of PCB loss may be mechanical loss, volatilization to the air, or return to the Lower Fox River following water treatment. The magnitude of PCB losses to the air due to sediment processing can be calculated from the overall Process Mass Balance equation:

$$M_A - M_F - M_G - M_H - M_I - M_J - M_E = M_{loss,\ process}. \qquad \textit{\textbf{Equation 7}}$$

As is true for the Deposit Mass Balance, small errors in measurements of total PCBs may provide insufficient sensitivity to adequately quantify potential processing losses of PCBs. Therefore, total PCB (Aroclors) measurements were supplemented with congener-specific PCB analyses to allow monitoring of changes in congener patterns resulting from potential desorption losses.

Each of these methods is discussed in the QAPP (Fox River Group, 1999). The calculation of individual masses, rather than simple concentrations, is of great importance in every step of the mass balance. Each concentration measured during this assessment must be accompanied by a measurement that will enable calculation of a mass (including TSS, sediment density, and percent water content).

3. RESULTS

DEPOSIT MASS BALANCE

Sediment depth before and after dredging is presented in Figure 3-1A, while average sediment PCB concentration before and after dredging at each sampling location is shown in Figure 3-1B. Also, depth-weighted averaged concentrations are shown for those locations where core sectioning occurred. For the calculations presented here, all available measured PCB concentrations from a given sampling location were averaged to produce one representative PCB concentration for each location. This approach used all available data and did not differentiate between collection techniques or sediment depth. However, because some depth-resolved data was available, a calculation of the mass of PCB in the dredge site before dredging was also done using depth-resolved concentrations where available. These concentrations were averaged using depth weighting to give a concentration for each location with depth-resolved concentrations. This technique increased the calculated amount of PCB present before dredging by about 5%. Using in-place density (Figure 3-1C), mass in each polygon (an area of the deposit that the core represents; the core concentrations are taken as mean for calculation of mass for the entire polygon) can be calculated (Figure 3-1D).

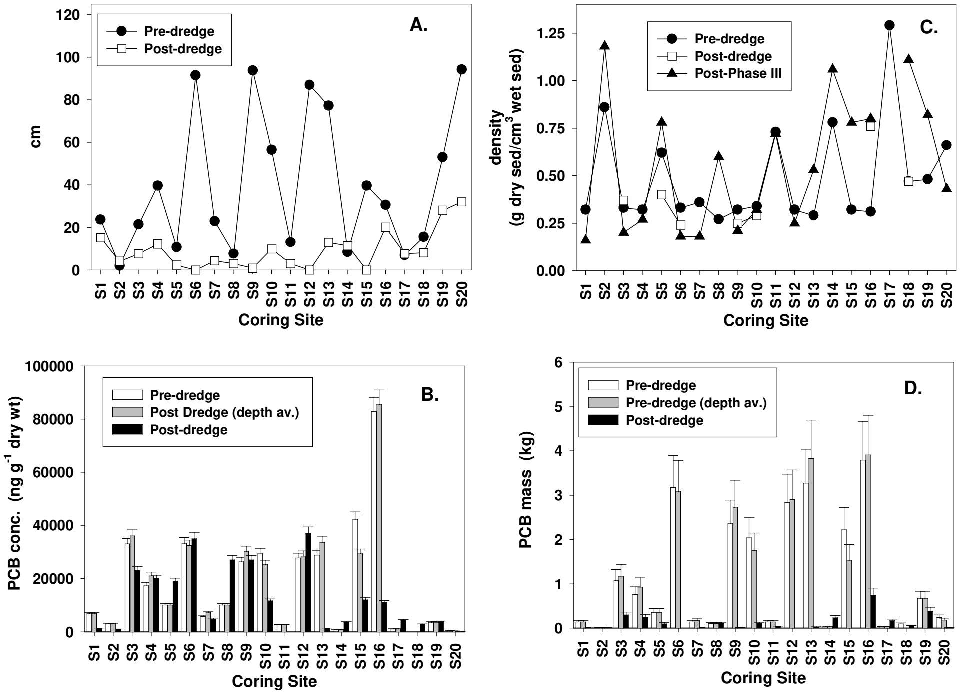


Figure 3.1. A) Sediment depth before and after Phase I of dredging at Deposit N; B) Sediment PCB concentrations before and after Phase I; C) Sediment in-place density before and after Phase I; and D) Pre- and post-dredging PCB mass in sediment polygons.

Using Equations 3, 4, and 5, the mass of PCB, the volume of sediment, and the mass of dry sediment in the dredge area before and after dredging were calculated. Sediment volume and mass and PCB mass, before and after dredging, are listed in Tables 3-1 and 3-2, respectively. Table 3-2 also includes global averages of PCB concentrations before and after dredging in the dredge area. Although Equation 3 was developed to determine the mass of PCB in sediments, the concentration of any sediment-bound substance may be substituted for C_{PCB} to calculate the mass of that substance associated with sediments. Mercury was also measured during this project, and the mass of Hg in the dredge area has been calculated. These values are listed in Tables 3-1, 3-2, and 3-3.

Table 3-1. Deposit N west lobe bulk sediment dredging results (Phase I dredging).

	Pre-dredge	Post-dredge	Net	Change (%)
Sediment Volume (m^3)	3,809	1,058	2,751	- 72
Sediment Dry Mass (tonnes)	1,699	606	1,093	- 64

Table 3-2. Deposit N west lobe PCB dredging results (Phase I dredging).

	Pre-dredge	Post-dredge	Net	Change (%)
PCB Mean Concentration (µg/kg dry)	18,395	12,409	5,986	- 33
PCB Mass (kg)	23.5	2.6	20.9	- 89

Table 3-3. Deposit N west lobe Hg dredging results (Phase I dredging).

	Pre-dredge	Post-dredge	Net	Change (%)
Hg Concentration (µg/kg dry)	3,039	2,325	714	- 23
Hg Mass (kg)	3.29	0.63	2.66	- 81

Pre- and Post-Dredging PCB Mass in Sediment Polygons

Finally, the amount of sediment, PCB, and mercury (Hg) removed by dredging were calculated (using Equation 1 for PCB mass and analogous equations for sediment volume, dry sediment mass, and Hg) and are listed in Tables 3-1, 3-2, and 3-3, respectively.

The values in Tables 3-1, 3-2, and 3-3 indicate that 2,751 m^3 of sediment, with a dry weight of 1,093 tonnes, was removed from the Phase I dredge area of Deposit N. These sediments were contaminated with PCB and Hg, and so, 21 kg of PCB and 2.7 kg of Hg were also removed by dredging this portion of the river. In relative terms, Phase I dredging removed 72% of the targeted sediment volume and 64% of the sediment dry mass from the dredge area of the west lobe of Deposit N. This resulted in the removal of 89% of the targeted PCB mass and 81% of the Hg mass from this area of the Lower Fox River.

The use of the mass balance approach strongly identifies the weaknesses of a concentration approach. For instance, in polygons S6 and S12, the concentration of PCBs in surface sediments increased after dredging (Figure 3-1B). However, essentially all of the PCBs in these two polygons (3.2 and 2.8 kg, respectively – Figure 3-1D) were permanently removed from the Fox River. A simple concentration-based assessment would term dredging in these polygons unsuccessful despite the fact that nearly 100% of the PCBs in these polygon areas was removed.

Error Analysis

An estimate of the error associated with the values listed in Table 3-4 is found by differentiating, and substituting from, Equation 2:

$$dM_{PCB} = \left(\partial M_{PCB}/\partial A\right)dA + \left(\partial M_{PCB}/\partial D\right)dD + \left(\partial M_{PCB}/\partial R\right)dR + \left(\partial M_{PCB}/\partial C_{PCB}\right)dC_{PCB};$$

Equation 8

and, for small changes in measurements; and

$$\left(\partial M_{PCB}/\partial A\right) = DRC_{PCB} = \frac{M_{PCB}}{A}$$
$$\left(\partial M_{PCB}/\partial D\right) = ARC_{PCB} = \frac{M_{PCB}}{D}$$
$$\left(\partial M_{PCB}/\partial R\right) = ADC_{PCB} = \frac{M_{PCB}}{R}$$
$$\left(\partial M_{PCB}/\partial C_{PCB}\right) = ADR = \frac{M_{PCB}}{C_{PCB}}$$

Equations 9A-9D

$$\Delta M_{PCB} = \frac{M_{PCB}}{A}\Delta A + \frac{M_{PCB}}{D}\Delta D + \frac{M_{PCB}}{R}\Delta R + \frac{M_{PCB}}{C_{PCB}}\Delta C_{PCB}.$$

Equation 10

Unlike the other values, A is chosen and constant, so ΔA is zero. Rearranging,

$$\frac{\Delta M_{PCB}}{M_{PCB}} = \frac{\Delta D}{D} + \frac{\Delta R}{R} + \frac{\Delta C_{PCB}}{C_{PCB}}.$$

Equation 11

Equation 11 states that the relative error in PCB mass is equal to the sum of the relative errors of the measured parameters used to calculate PCB mass. The relative errors of the measured parameters are defined as range divided by mean for in-place density and PCB concentration, for those measurements that include several duplicates (contaminant concentration, in-place density). Depth measurement relative error is defined as measurement interval divided by sediment depth, where the measurement interval is equal to the smallest observable change, here equal to 3 cm. In all cases, the values used are averages of all available values for the specific relative error. This information is summarized in Table 3-4.

The appropriate measurement relative errors are summed to find the relative errors in the calculated masses of PCB and Hg removed from the river. These values are 53.6% and 44.6% for PCB and Hg, respectively. Because measurement error assessments are based on ranges and means, an estimate of the uncertainty in the calculated masses would be equal to the calculated value plus or minus one-half the relative errors. Thus, for PCB the error is $M_{PCB,\ Removed}$ +/- 26.8%, and for Hg the error is $M_{Hg,\ Removed}$ +/- 22.3%.

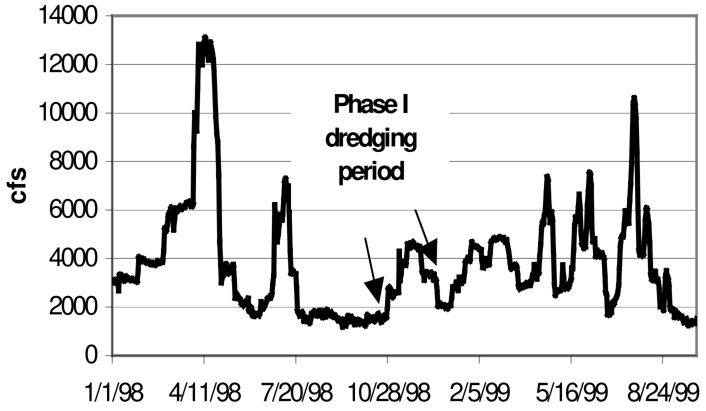
Table 3-4. Relative errors of Deposit N west lobe measured parameters.

	Relative Error Definition	n	Average Relative Error (%)
PCB Concentration	Duplicate Range/Mean	5	18.0
Hg Concentration	Duplicate Range/Mean	7	9.0
In-place Density	Duplicate Range/Mean	6	9.7
Sediment Depth	Measurement Interval/Depth	107	25.9

RIVER TRANSPORT

Fox River Characteristics during Dredging

Flow Conditions. The dredging operation occurred during moderate river discharges (Figure 3-2), but included low temperatures when the river surface became ice-covered, which limited monitoring operations.



`**Figure 3-2.** Discharge of the Fox River in Appleton, Wisconsin, U.S. Geological Survey gage, during 1998.

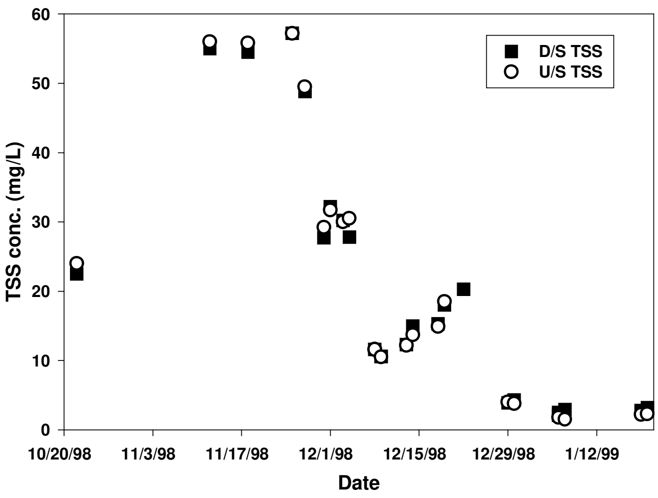


Figure 3-3. Upstream (upstream) versus downstream (downstream) TSS in the Fox River during dredging.

Suspended Solids Transport. Daily TSS loads were calculated by multiplying daily river discharge with daily TSS concentrations. Initially, the discrete site (sub-sites a, b, c, d) TSS values were averaged to calculate daily TSS concentration. Linear interpolation between TSS data points was used for days in which no water samples were collected. There was very little difference between upstream and downstream TSS concentrations (Figure 3-3). Examination of the total suspended solids % change (see next section -Figure 3-8C) indicates there was an increase in TSS after the curtain was breached (30 Dec. 1998) to enhance ice breaking operations. Turbidity data indicated a similar trend.

Continuous turbidity data collected by the site contractor was used as a second approach to calculate water column suspended solids. Turbidity-TSS relationships (Figure 3-4) were used to calculate daily TSS values for the upstream and downstream sites for the period 19 Nov. to 28 Dec. 1998. However, for the overall period of turbidity meter operation

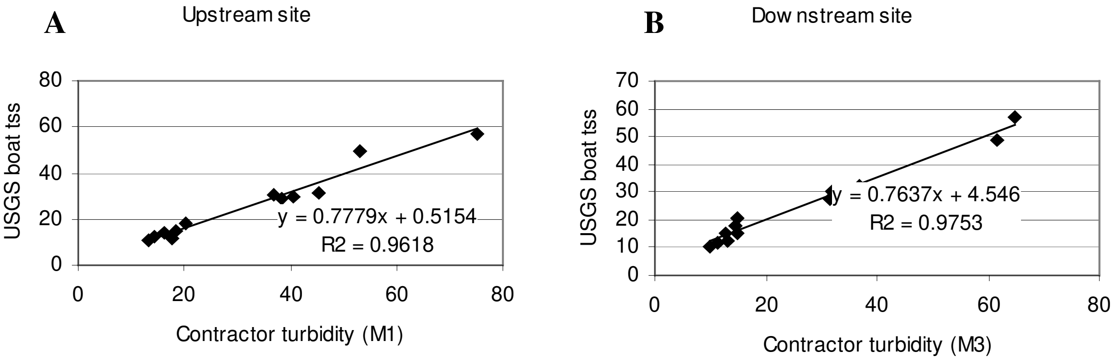


Figure 3-4. A) Upstream turbidity versus TSS; B) Downstream turbidity versus TSS.

(26 Nov. to 28 Dec. 1998) the regressed solids loading was a negative 23 tonne (net settling). After 28 Dec. 1998 ice conditions made the continuous turbidity meters inoperable. From 29 Dec. 1998 to the termination of curtain removal (20 Jan. 1999), TSS loading was estimated using linear interpolation between the six daily concentration values. This resulted in 109 tonne of solids transport downstream.

Using the previous two approaches, from 26 Nov. 1998 (start of dredging operations) to 20 Jan. 1999, there were 86 tonne more TSS transported past the downstream (6,784 tonne) site than the upstream site (6,698 tonne). This 1% increase is much smaller than the measurement error and if applied to the mean discharge (3,570 cfs) for 56 days, would amount to a TSS increase of 0.2 mg/liter.

The paper mill discharged approximately 0.3 tonne/day (1.4 tonne maximum) of suspended solids between the upstream and downstream sites for the period 26 Nov. 1998 to 20 Jan. 1999. Taking into account the total point discharger solids (16.8 tonne), the estimated solids mass resuspended from the deposit during the dredging operation was 69 tonne (86 tonne less 16.8 tonne). From 26 Nov. to 30 Dec. 1998, net solid loading from the deposit area was –21 tonne.

Concentrations of PCBs in the Fox River

Background PCB levels prior to dredging were calculated to evaluate the PCB flux that would have occurred if no dredging had taken place. To assist in this assessment, prior to the start of dredging four sets (upstream and downstream) of samples were collected (Figure 3-5). On 3 of the 4 days there was a net PCB loading from the deposit area of 5 to 16 g/day (Figure 3-7). On 12 Nov. 1998, however, PCB concentration at the upstream site exceeded the downstream site. On this date, there was rapidly changing flow and river discharge was uncertain at the Deposit N site during the time of upstream and downstream sample collection, based on flow data from the USGS gage at Appleton, Wisconsin. Because of this uncertainty in flow and resulting changes in bottom sediment and PCB flux, the 12 Nov. 1998 sample is not included in the background PCB flux assessment. Several studies (House et al., 1993; Steuer et al., 1995; Hall, 1999) have documented the winter decrease in water column PCB concentration in the Fox River. This is a direct result of reduced PCB flux from the in-place contaminated sediments. Thus, it is appropriate to assume that as the upstream PCB concentration decreased by an order of magnitude, the background deposit flux would also have decreased. To estimate that decrease, a relationship between upstream concentrations and pre-dredge deposit flux was approximated (Figure 3-7). These results suggest that from 26 Nov. 1998 to 20 Jan. 1999 Deposit N would have contributed 0.4 kg of PCB to the water column if no dredge operation had taken place. Following a similar approach, one can estimate the *annual* PCB flux from Deposit N. In 1998, had no dredging taken place, it is estimated using field data and transport modeling that Deposit N would have contributed 4 to 5 kg to the water column and air (volatilization) (Steuer et al., 1995).

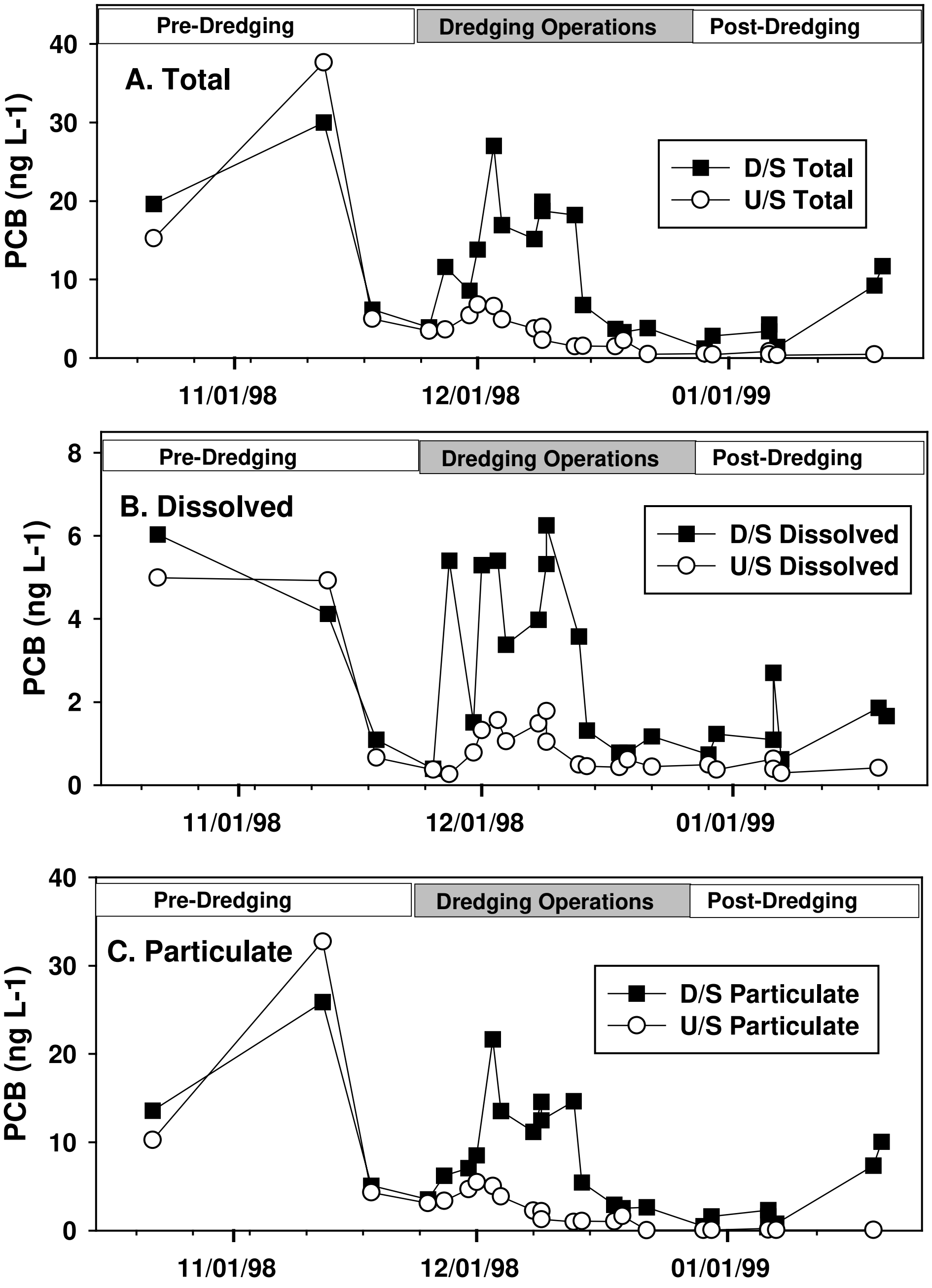


Figure 3-5. Concentrations of PCBs A) Total; B) Particulate; and C) “Dissolved” [<0.45 um] from sites upstream and downstream of Deposit N.

PCB Transport during Dredging

There was a consistent concentration increase at the downstream site in the dissolved and particulate phases (Figure 3-5) after dredging began on 26 Nov. 1998. A two-sample “t” test (assuming unequal variances) indicated this difference to be statistically significant at 95% ($t_{critical} = 2.2$; $t_{stat} = 4.4$). The mean upstream PCB concentration was 3.2 ng/liter and the downstream PCB concentration was 11.5 ng/liter. This is a substantially larger difference than that of the sample duplicates (15%). Removal of the sediment curtain on 19 and 20 Jan. 1999 appears to have produced an additional increase in water column PCB concentration.

It appears contradictory that there was a positive PCB load to the water column with negative suspended solids loading (settling) during the dredge operation. However, material exposed to or resuspended in the water column during dredging increased the dissolved PCB concentration (Figure 3-5B). In addition, the

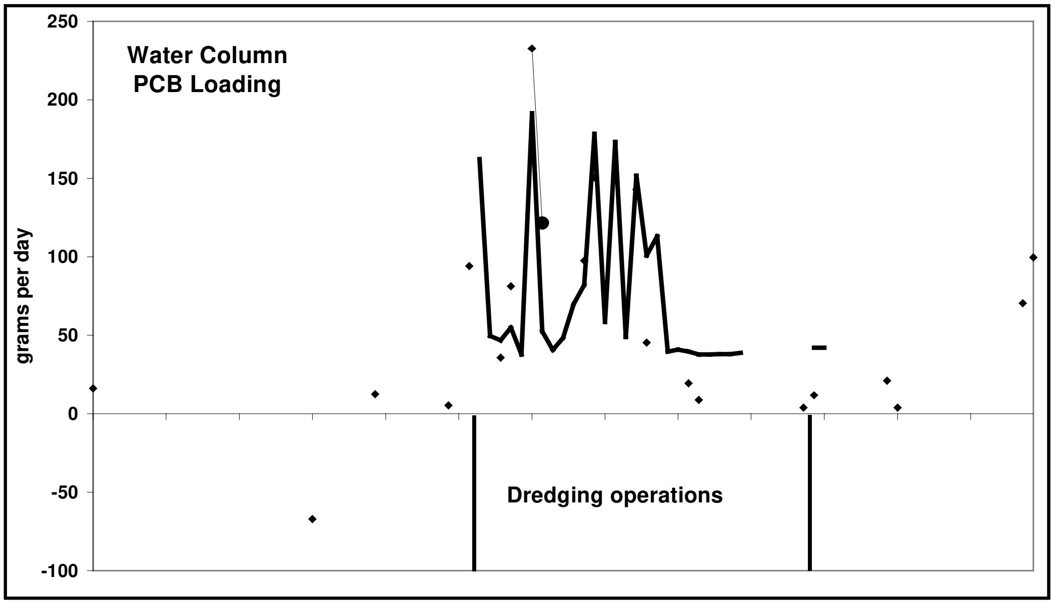


Figure 3-6. Water column PCB loading before, during and after dredging at Deposit N. Solid line is from slurry concentrations. Diamonds are actual data from the Fox River.

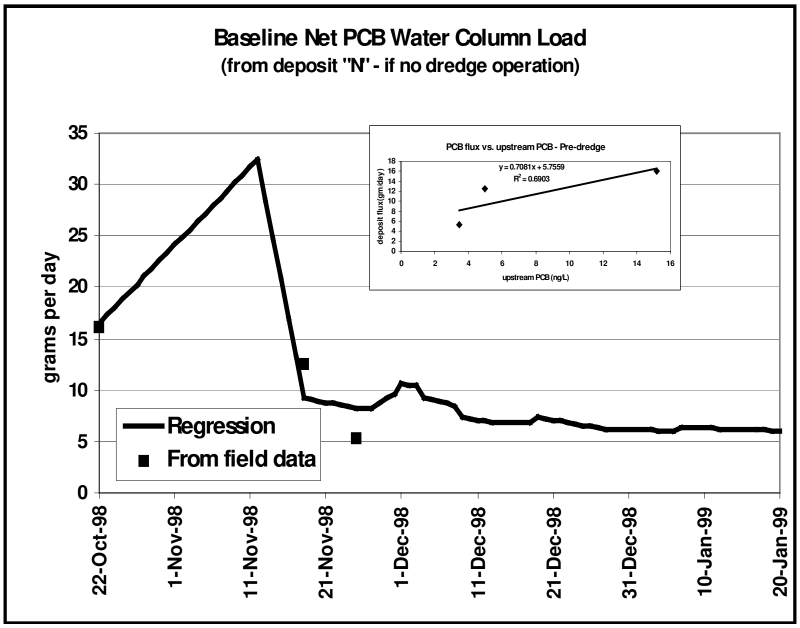


Figure 3-7. Regression approach to assess PCB input from Deposit N had no dredging taken place.

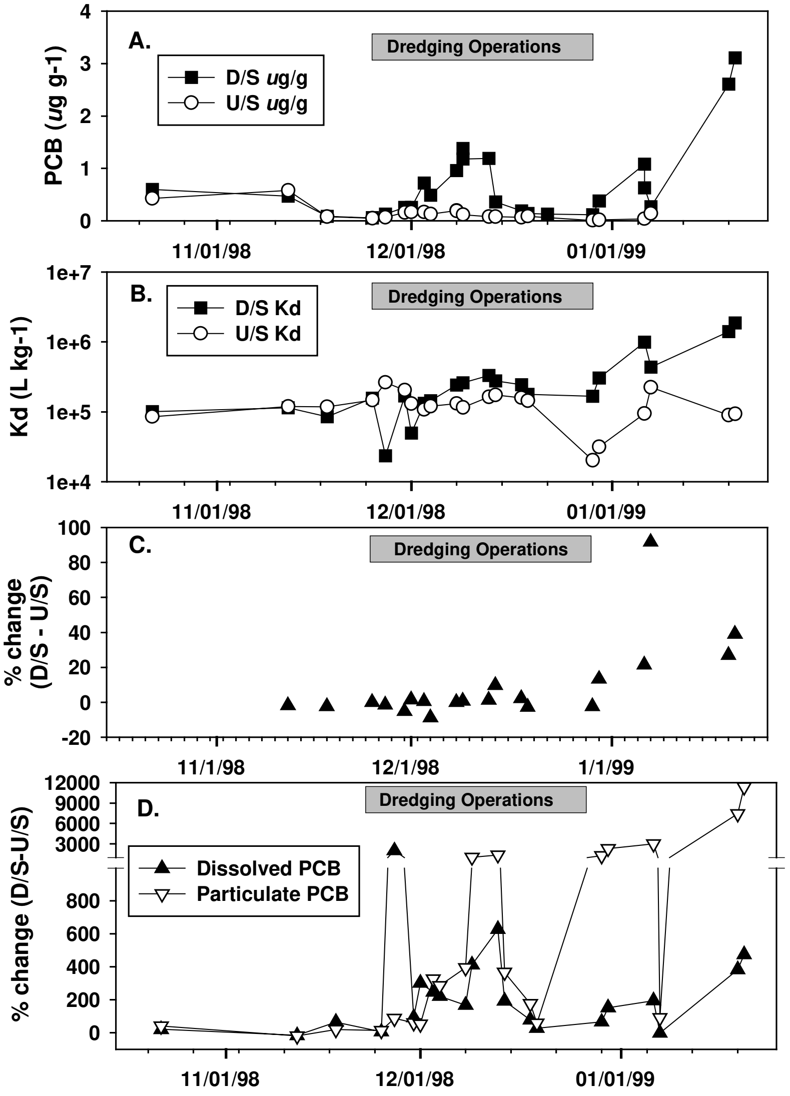


Figure 3-8. A) Particle concentration of PCBs on particles in the Fox River above and below dredging site at Deposit N; B) Partition coefficient of particles and water in the Fox River above and below Deposit N; C) Percent difference in suspended solids; and D) Congener summation of upstream versus downstream differences.

PCB concentration on a given particle also increased (Figure 3-8A). Therefore, even though the overall mass of particles transported downstream did not increase, the PCB transported on the particles did increase. The median PCB concentration of a suspended particle at the upstream site was 0.08 µg/g; while at the downstream site it was 0.43 µg/g (Figure 3-8A). This is consistent with the resuspension or exposure of higher PCB-concentrated bottom sediment particles to the overlying water column.

The TSS and PCB percent differences (downstream-upstream) comparison (Figure 3-8C) illustrates that TSS is not a good indicator of PCB transport during a dredging operation. Note that no TSS difference is detected on the deposit side of the river until the curtain is breached. However, an increase in PCB concentration is observed throughout the remediation. (Figure 3-8D). Thus, if one is to monitor PCB transport during a remediation operation it is not adequate to solely measure turbidity or TSS. The contaminant of interest must also be directly measured since exposed (highly concentrated) pore waters can contribute to particle and dissolved phase PCB concentrations in downstream waters.

The change in the distribution coefficient further substantiates that the PCB load increased. Figure 3-8B details the distribution coefficient (Kd = particulate PCB/dissolved PCB) for the upstream and downstream water column sites. During the pre-dredge period, Kd is very similar at the upstream and downstream transects. After 4 Dec. 1998 there is a marked increase in the downstream Kd. This increase is consistent with particles resuspended from the bed sediments into the particle-poor (low TSS) water column with lower PCB levels. Resuspended particles would not have sufficient time to arrive at the same state of equilibrium that existed at the upstream site. Elevated Kds (1.4 to 1.8 x 10^6) observed during the curtain removal (19 and 20 Jan. 1999) are consistent with particles that traveled rapidly from the upstream to the downstream water column site.

To consider the concentration increase in a useful context it is necessary to calculate mass fluxes. Table 3-5 details daily loading at the upstream and downstream sites on days that water column samples were collected. The mean daily net PCB load (80 g/day; with a coefficient of variation of 86%) was multiplied by 35 days to calculate an initial loading approximation of 2.8 kg during Phase I of the project.

A second approach calculated daily net PCB loading using a linear interpolation between the 22 sample day PCB loads (Figure 3-7). This resulted in a net PCB loading of 2.3 kg during the active dredge period of 26 Nov. to 30 Dec. 1998.

A third approach to calculate daily PCB loading utilized a regression variable that was measured on a frequent basis. It was felt that the concentration or mass of the material being processed (slurry, cake, or sand) could indicate how much PCB was transported downstream. Thus, daily variables such as press cake, sand, settled slurry, and slurry supernatant were examined in light of water column transport. The best indicator of water column PCB transport was concentration of the settled slurry sample ($r^2 = 0.71$) with a 2-day offset. For example, a high PCB concentration in the settled slurry sample on 3 Dec. 1998 indicated there would be increased PCB transport on 5 Dec. 1998. This offset may be a result of the very low velocities that existed inside the curtain area.

The resulting regressed load result of 2.2 kg is very similar to the 2.3 kg calculated from the linear interpolation approach over that same time period and is considered the most reliable estimate. This slurry regression relationship could only be applied during the active dredge period (26 Nov. to 30 Dec. 1998) at times when slurry was being generated. Using the linear interpolation results (on days of no slurry) in conjunction with the regression relationship, the water column load for the period 26 Nov. 1998 to 20 Jan. 1999 was 2.9 kg. The increased PCB transported during dredging was more than the 0.4 kg that would have been released had no dredging taken place. It should be noted that from 28 Dec. 1998 to the end of curtain removal on 20 Jan. 1999, there were no turbidity data collected except for water sampling on 29 and 30 Dec. 1998 and 6, 7, 19, and 20 Jan. 1999. Conditions are unknown from 1 Jan. 1999 through 18 Jan. 1999, except for the two sampling days.

The PCB Aroclor analyses provided the foundation for the overall PCB mass balance calculations (Fox River Group, 1999); however, to reduce the limits of detection the 80-liter water column samples were analyzed on a congener-specific basis. Therefore, to compare the water column results with the deposit or shore process mass balances it was necessary to estimate an Aroclor concentration (Aroclor*1242) from the congener-specific data. The congener distribution for the manufactured 1242 mixture (Manchester-Nesvig 1993) is depicted in Figure 3-9. The six Aroclor peaks (10 congeners) commonly used in the Aroclor*1242 quantification are highlighted; these constitute 51.9% of the 1242 mixture mass.

Table 3-5. PCB phase distribution and loads for riverine samples.[†]

		Downstream (ng/L)				Upstream (ng/L)			Discharge	d/s Load	u/s Load	Net Load
		Diss .	Part .	Total		Diss.	Part.	Total	(cfs)	g/day	g/day	g/day
22 Sep. 1998		6.0	13.6	19.6		5.0	10.2	15.2	1,505	72.2	56.1	16.1
12 Nov. 1998		4.1	25.9	30.0		4.9	32.7	37.7	3,583	262.9	330.0	-67.1
18 Nov. 1998		1.1	5.1	6.2		0.7	4.3	5.0	4,282	64.6	52.1	12.5
25 Nov. 1998		0.4	3.5	3.9		0.4	3.1	3.4	4,940	47.1	41.7	5.4
		26 Nov. 1998 started dredging operations										
27 Nov. 1998		5.4	6.2	11.6		0.3	3.3	3.6	4,802	136.3	42.3	93.9
30 Nov. 1998		1.5	7.1	8.6		0.8	4.7	5.4	4,664	97.9	62.1	35.8
1 Dec. 1998		5.3	8.5	13.8		1.3	5.5	6.8	4,738	160.0	78.8	81.2
3 Dec. 1998		5.4	21.6	27.0		1.6	5.0	6.6	4,653	307.8	75.1	232.8
4 Dec. 1998		3.4	13.5	16.9		1.0	3.8	4.9	4,123	170.7	49.4	121.3
8 Dec. 1998		4.0	11.2	15.1		1.5	2.3	3.7	3,530	130.7	33.2	97.6
8 Dec. 1998					Dup.	1.8	2.2	3.9				
9 Dec. 1998		5.3	14.6	19.9		1.0	1.3	2.3	3,615	170.9	20.3	150.5
9 Dec. 1998	Dup.	6.3	12.5	18.7								
13 Dec. 1998		3.6	14.6	18.2		0.5	1.0	1.5	3,487	155.5	12.6	142.9
14 Dec. 1998		1.3	5.4	6.7		0.4	1.1	1.5	3,540	58.4	13.1	45.3
18 Dec. 1998		0.8	2.9	3.7		0.4	1.0	1.5	3,530	31.9	12.6	19.3
19 Dec. 1998		0.8	2.5	3.3		0.6	1.6	2.2	3,350	27.1	18.3	8.7
22 Dec. 1998		1.2	2.6	3.8								
29 Dec. 1998		0.7	0.5	1.2		0.4	0.0	0.5	2,173	6.5	2.5	3.9
30 Dec. 1998		1.2	1.6	2.8		0.5	0.1	0.5	2,099	14.5	2.8	11.7
6 Jan. 1999		1.1	2.3	3.4		0.4	0.1	0.4	2,523	23.7	2.7	21.0
6 Jan. 1999	Dup.	2.7	1.6	4.3								
7 Jan. 1999		0.6	0.8	1.4		0.6	0.2	0.8	2,968	10.1	6.1	4.0
		19 Jan. 1999 - Superior removed u/s* portion of curtain										
19 Jan. 1999		1.9	7.4	9.2		0.4	0.1	0.5	3,286	74.1	3.7	70.4
		20 Jan. 1999 - Superior removed d/s* portion of curtain										
20 Jan. 1999		1.7	10.0	11.7		0.3	0.1	0.4	3,604	103.2	3.6	99.6
20 Jan. 1999					Dup.	0.4	0.1	0.5				
Dredge operation period (26 Nov. to 30 Dec. 1998)												
Mean		3.1	8.4	11.4		0.9	2.3	3.2	3,716	112.9	32.5	80.4
Median		3.4	7.1	11.6		0.7	1.9	3.0	3,540	130.7	20.3	81.2
Dredge - Curtain operation period (26 Nov. 1998 to 20 Jan. 1999)												
Mean		2.7	7.4	10.1		0.8	1.8	2.5	3,570	98.8	25.8	72.9
Median		1.8	6.6	8.9		0.5	1.1	1.5	3,530	97.9	13.1	57.5

[†] Diss. is dissolved; Part. is particulate; and Dup. is duplicate.

*u/s is upstream; d/s is downstream.

Therefore, to convert the water column congener specific data to an Aroclor*1242 concentration, the above six Aroclor peaks (nine highlighted congeners) were summed and divided by 0.519.

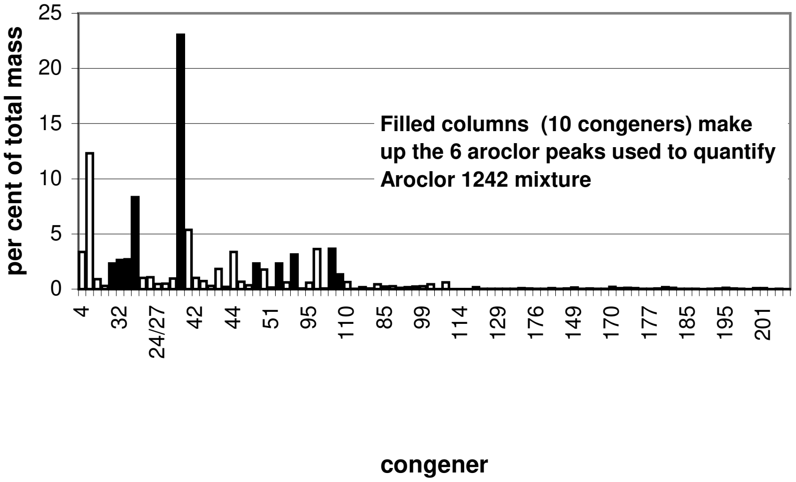


Figure 3-9. Congeners used to quantify Aroclor* 1242 mixture.

Table 3-6. Comparison of congener-specific and Aroclor*1242 PCB analyses for Deposit N.

Sample Type	Congener Sum (ng/liter)	Aroclor* 1242 (ng/liter)	Aroclor* 1242/ Congener Sum Ratio
u/s dissolved	25.2	26.3	1.04
d/s dissolved	65.7	63.7	0.97
u/s particulate	83.7	62.9	0.75
d/s particulate	195.6	157.8	0.81

For example, the dissolved phase, upstream site congeners (10 highlighted congeners in Figure 3-9) taken in total (all 24 samples) had a summed mass of 13.7 ng/liter. Dividing by 0.519 yields an Aroclor*1242 concentration of 26.3 ng/liter. The congener summation total for all the upstream dissolved samples was 25.2 ng/liter, very little difference from the Aroclor*1242 value. For the upstream *particulate* phase, PCB congener summation total (all congeners) was 83.7 ng/liter and the Aroclor* 1242 concentration was 62.9 ng/liter. Clearly, the particulate water samples differed substantially from an Aroclor*1242 mixture. If the laboratory PCB analysis method had been on an Aroclor basis, a substantially lower PCB concentration would be expected than that resulting from summation of specific congeners.

Table 3-6 details the comparative results for dissolved and particulate phases at both sites. At the upstream and downstream sites the particulate phase constituted 74% of the total PCB (Table 3-5). Based on Table 3-6, one can assume no difference between the congener sum and Aroclor*1242 values for the dissolved phase, however, the particulate phase has a 0.78 ratio.

The 26 Nov. to 30 Dec. 1998 water column load (2.2 kg from congener summation) was adjusted to an Aroclor*1242 basis as follows:

$$\text{Aroclor*1242} = \underbrace{(0.26)(2.2\text{ kg})(1)}_{\textit{(Dissolved)}} + \underbrace{(0.74)(2.2\text{ kg})(0.78)}_{\textit{(Particulate)}} = 1.8\text{ kg.}$$

Equation 12

The 26 Nov. 1998 to 30 Jan. 1999 water column load (2.9 kg from congener summation) was adjusted to an Aroclor*1242 basis as follows:

$$\text{Aroclor*1242} = \underbrace{(0.26)(2.9\text{ kg})(1)}_{\textit{(Dissolved)}} + \underbrace{(0.74)(2.9\text{ kg})(0.78)}_{\textit{(Particulate)}} = 2.4\text{ kg.}$$

Equation 13

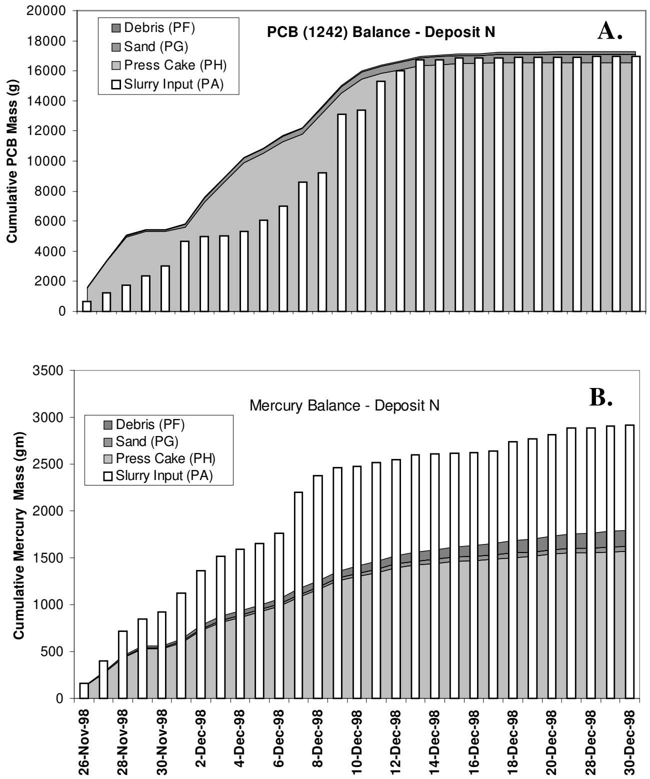


Figure 3-10. A) Mass flux of PCBs removed during dredging at various sites in shoreside processing; B) Hg mass balance of shoreside processing.

Table 3-7. Total PCB and Hg mass removed during various phases of shoreside processing.

	Max. Conc.	Min. Conc.	Med. Conc.	Load (kg)
		PCBs		
Slurry	1012 µg/liter	1.1 µg/liter	192 µg/liter	17.0
Press Cake	78 µg/g	0.1 µg/g	19 µg/g	16.5
Sand Pile	29 µg/g	0.1 µg/g	5.0 µg/g	0.55
Debris Pile	1.4 µg/g	1.0 µg/g	1.2 µg/g	0.21
Filter Bags	68 µg/g	0.8 µg/g	37.5 µg/g	0.005
Sand/Carbon	2.0 µg/g	0.6 µg/g	0.95 µg/g	0.09
Effluent	4.98 ng/liter	4.00ng/liter	4.49 ng/liter	0.0002
		Hg		
Slurry	184 µg/liter	2.6 µg/liter	29 µg/liter	2.9
Press Cake	4.7 µg/g	0.2 µg/g	3.6 µg/g	1.6
Sand Pile	2.6 µg/g	0.06 µg/g	0.28 µg/g	0.05
Debris Pile	-	-	-	0.12
Filter Bags	-	-	-	-
Sand/Carbon	-	-	-	-
Effluent	0.27 ng/liter	0.20 ng/liter	0.24 ng/liter	0.00001

PROCESS MASS BALANCE

Mass Transported in the Dredged Slurry (M_A)

The dredge operated intermittently over a 24-hour period. Slurry material was transported from the dredge to the processing site via the slurry pipe. After entering the processing site the slurry entered an 8-inch riser pipe before being discharged on the coarse (debris) shaker screen (Figure 1-2). Dredge slurry velocity (1-min intervals) was measured via an external Doppler meter on the 8-inch (inside diameter) riser pipe. These velocity data were used to calculate a daily discharge.

One daily composite sample of the dredged slurry, consisting of four to six grab samples, was collected from the slurry stream just prior to entry on to the shaker screen. To analyze for TSS and PCB in these heavily sediment-laden samples, the entire slurry sample was gravity settled and a supernatant sample and settled solids sample were separated. Volume measurements were recorded for the supernatant and the settled fraction. The supernatant was analyzed for Aroclor PCBs and TSS and the settled slurry solids sample was analyzed for Aroclor PCBs, percent moisture, and bulk density. Overall sample concentrations were calculated and multiplied by the daily slurry volume to determine TSS and PCB masses.

The slurry pipe delivered an estimated 1,207 tonne of dry sediment from 26 Nov. to 30 Dec. 1998. The daily slurry PCB concentration (settled and supernatant fractions) was multiplied by the daily slurry inflow volume to calculate PCB influx via the slurry pipe. Overall PCB mass via the slurry pipe was 17,000 g with more than 98% of the PCB removed from the deposit in the first 18 days of the operation (Figure 3-10A). Mercury concentration, as determined from the entire slurry sample (Fox River Group, 1999), was multiplied by the daily slurry volume to calculate daily Hg mass. Overall Hg influx was 2,900 g with 89% of the Hg removed during the first 18 days of operation

(Figure 3-10B). A summary of ranges and means of concentrations at each site of the process mass balance is given in Table 3-7.

Mass Transported in the Coarse Material (Debris) (M_F)

The dredge slurry material was deposited on a vibrating shaker screen to remove material with a diameter of ≥0.95 cm. This material was sampled on only 2 of the 29 days because it was anticipated that this would be a minor pathway for PCB and Hg. On 10 and 16 Dec. 1998, composite samples were collected as material fell from the shaker screen. These composites were analyzed for TSS, congener-specific PCB, percent moisture, and in-place dry density. The debris piles were removed with a bobcat tractor to storage piles that were later removed from the remediation site by truck. The site contractor recorded the number of bobcat bucket loads of debris removed per 12-hour shift.

The number of daily bobcat bucket loads, TSS, estimated bucket volume (10.6 ft^3), and in-place density were used to calculated a daily dry solids flux. A median in-place dry density of 0.92 g/cm^3 was used for all days. An estimated 168 tonne of debris solids were removed during the remediation period.

The mean of the two PCB concentration (1.2 µg/g) values was applied to the above solids to estimate daily PCB mass leaving via coarse solids pile. Overall PCB mass via the debris pile was 0.21 kg, with a maximum value of 17.2 g/day. Daily debris pile PCB made up a small portion of the overall process PCB mass (Figure 3-10A). An estimated Hg concentration of 1.0 µg/g was applied to the above solids to calculate daily Hg mass leaving via the debris pile. Overall Hg mass via the debris pile was 0.17 kg (Figure 3-10B).

Mass Transported in the Sand ($M_{G.}$)

The slurry material, after it passed through the coarse shaker screen, was processed through two hydrocyclones to remove the sand fraction. Composite samples (consisting of 4 to 6 grab samples) were collected as sand dropped from the hydrocyclones to a temporary storage pile. Composite samples were analyzed for TSS, PCB, percent moisture, and in-place dry density. The temporary sand piles were removed via a bobcat tractor to outdoor storage piles that were later trucked from the site. The site contractor recorded the number of bobcat bucket loads of sand removed per 12- hour shift. The number of daily bobcat bucket loads, TSS, estimated bucket volume (10.6 ft^3), and in-place density were used to calculate a daily dry sand flux. The daily PCB concentrations (dry weight basis) were applied to the above dry solids to calculate daily PCB mass. The median PCB concentration was 5.0 µg/g with a maximum value of 29 µg/g (1 Dec. 1998). Overall PCB out-flux via sand piles from 26 Nov. to 30 Dec. 1998 was 0.55 kg with a maximum value of 89 g/day. The PCB sorbed to the sand fraction made up a relatively small portion of the overall PCB mass (Figure 3-10A).

The daily Hg concentrations (dry weight basis) were applied to the above dry solids to calculate daily Hg mass. The median concentration was 0.28 µg/g with a maximum value of 2.6 µg/g. Overall, Hg removed in the sand pile was 0.06 kg, with a maximum value of 8.0 g/day.

Mass Transported in the Filter Press Cake (M_H)

After the slurry passed through the sand removal area (mix tank and cyclotron, M_B) it was routed into tanks in which a polymer was added. After a period of mixing, the slurry was allowed to settle. The supernatant was removed and the settled fraction was pumped into two parallel lines of filter presses (M_C). Composite samples were collected as the filter cake was removed from the press filters and analyzed for TSS, PCB, percent moisture, and in-place dry density. The resulting press cake piles were removed via tractor to storage piles that were later trucked from the site. The site contractor recorded the number of press dumps per 12-hour shift.

The number of daily press cycles, TSS, filter press volume (7.3 yd^3), and in-place density were used to calculate a daily dry solids flux. An estimated 592 tonne of dry press cake solids were removed during the study. The daily PCB concentrations (dry weight basis) were applied to the above dry solids to calculate daily PCB mass. The median press cake PCB concentration was 19.0 µg/g with a maximum value of 78 µg/g (8 Dec. 1998). Overall PCB mass removed via press cake from 26 Nov. to 30 Dec. 1998 was 16.5 kg, with a maximum value of 1,763 g/day.

The daily press cake Hg concentrations (dry weight basis) were applied to the above dry solids to calculate daily Hg mass. The median concentration was 3.6 µg/g with a maximum value of 4.7 µg/g. Overall Hg removed by the press cake was 1.6 kg with a maximum value of 162 g/day. Processed Hg solids (debris, sand, and press cake) is consistently less than the slurry mass. The daily comparison indicates much of the difference occurred prior to 9 Dec. 1998, a period when coal was observed in the debris.

Mass Retained by the Bag Filters (M_I)

The mix tank supernatant (M_K) and the filter press effluent (M_K) were combined into a storage tank that was intermittently pumped through two rows (plumbed in parallel) of bag filters (M_K). Each row consisted of four bags that were changed several times per 8-hour shift; more than 715 filter bags were used during the remediation period. Sub-samples, periodically removed from the bag filters, were analyzed for congener-specific PCB and on an Aroclor basis. The daily number of bags, the median bag PCB concentration (37.5 µg/g), and the dry bag weight were used to calculate the daily PCB mass retained by the bag filters. The entire PCB mass retained by the bag filters was 0.005 kg. There were no Hg or solid analyses conducted on the bag filter material.

Mass Retained by the Sand and Carbon Filters (M_J)

Effluent from the bag filters was pumped directly through two rows (plumbed in parallel) of sand and carbon filter tanks. Bag filter effluent passed through three sand tanks (10-ft diameter) and one carbon media tank (8-ft diameter) prior to discharge to the river. At the completion of the remediation operation there were six PCB samples (congener-specific and Aroclor basis) collected from the sand tanks and two PCB samples collected from the carbon tanks. The PCB concentrations from the sand media ranged from 0.91 to 2.0 µg/g while carbon PCB concentrations ranged from 0.6 to 0.7 µg/g (Aroclor basis). Consistent with organic carbon partitioning theory, the carbon media retained more of the lesser-chlorinated congeners than did the sand media. These less chlorinated congeners are prevalent in the dissolved phase. Thus, the carbon filter was more proficient at removing the dissolved phase PCBs than were the sand filters.

Based on tank geometry and estimated levels of media, sand and carbon volumes were estimated at 60.5 and 46 yd^3, respectively. To calculate the PCB removed via the filter media, volume was multiplied by an estimated in-place dry density (1.1 g/cm^3 for both carbon and sand), which was multiplied by the PCB concentration. The sand tanks contained an estimated 64 g of PCB, while the carbon tanks contained 25 g. This approach utilized a number of gross assumptions; if the filter media is the focus of attention, a more elaborate computational method could be used.

Despite the fact that Hg or solids analyses were not conducted on the sand or carbon filters, we assume that Hg was retained on either of these filters, presumably the carbon filters. This assumption is made because of the strong affinity of Hg for organic carbon and the fact that final effluent (next section) was extremely low in Hg.

Mass Transported from Sand/Carbon Filters to the River (M_E)

Flow from the sand/carbon filters passed through the contractor ISCO flow meter prior to discharge back to the river. In general, the contractor effluent flow meter was 40% less than the daily flow as measured by the slurry Doppler meter. The reason for the difference in effluent meter and slurry meter results is unknown. This uncertainty is accounted for in the error analysis.

On 10 and 16 Dec. 1998, two composite samples were collected from the sand/carbon filter effluent in the vicinity of the contractor flow meter. These consisted of four to six discrete sub-samples collected over an 8- to 12-hour interval and were analyzed for TSS and congener-specific PCB. The two total suspended solids sample concentrations were less than detection (2 mg/liter).

The 80-liter congener-specific PCB effluent samples were filtered using 0.7-μ glass fiber filters to determine particulate congener PCB concentrations. The operationally dissolved phase PCB sample was obtained by pumping the filtrate through an absorbent resin column (e.g., XAD-2) to concentrate PCBs. Whole-water PCB concentrations were calculated by summing the operationally dissolved and particle-bound fractions (less than detection was assigned a zero value). Levels of detection range from 0.006 to 0.43 ng/liter. Congener summation (dissolved and particulate phases) was 4.98 and 4.00 ng/liter.

Applying the contractor flow meter volume (or the Doppler meter volume) to the median PCB concentration (4.49 ng/liter) resulted in an effluent PCB mass of < 1 g for the overall remediation period.

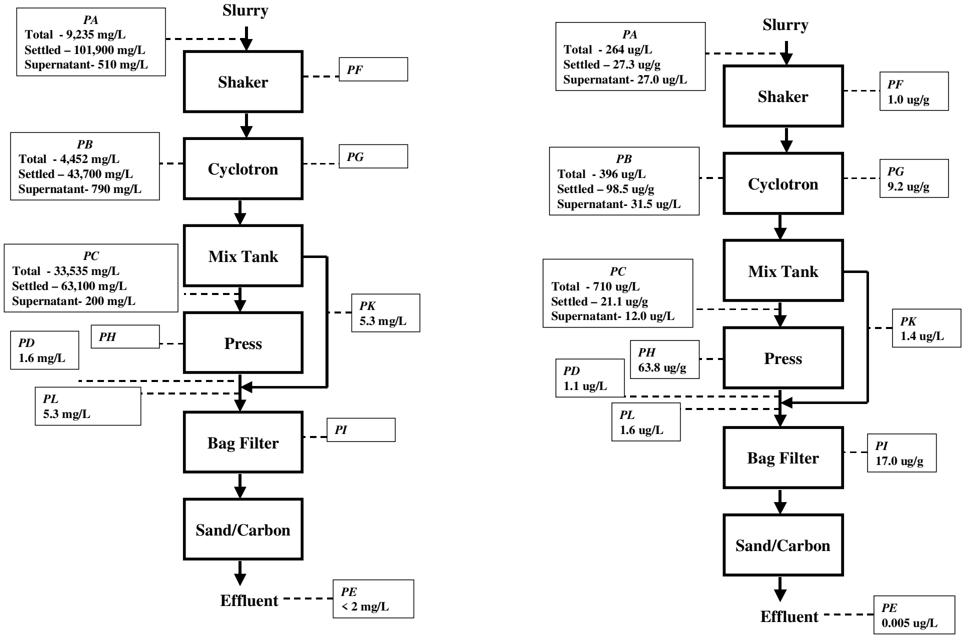
Results from Sampling at Increased Process Locations

On 10 and 16 Dec. 1998 the process was sampled at five additional locations (Figure 1-2):

- Slurry transported from the fine shaker screen to mixing tanks (B);
- Slurry transported from mixing tanks to filter presses (C);
- Liquid transported from filter presses (D);
- Supernatant removed from the mix tanks (K); and
- Liquid in-flow into the bag filters (L).

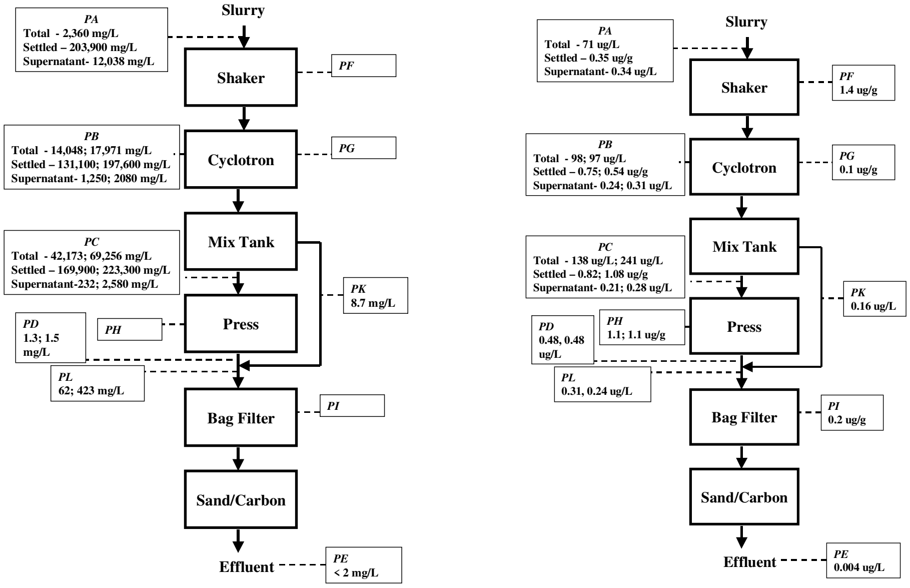
These samples were analyzed for congener-specific PCB to support the congener fractionation analyses. It was not possible to measure flow volume in all steps of the process; thus, daily masses were not computed at all locations. On 10 Dec. 1989 the operation was dredging in an area of the deposit with the highest depth-averaged PCB concentrations (Figure 2-1). On 16 Dec. 1998 deposit PCB concentrations were much lower (Figure 2-1). This is reflected in higher concentrations throughout the entire shore process (Figure 3-11 B, D). The sole exception was the debris fraction (location H), which had a slightly higher concentration on 16 Dec. 1998. On both days the hydrocyclones increased the slurry PCB concentration (location A to B) in the process of removing the sand fraction.

The supernatant skimmed from the mix tanks (location K) and the liquid squeezed from the filter presses (location D) had similar PCB concentrations (0.16 to 1.4 μg/liter). The combination of bag filters and sand/charcoal filters reduced this concentration by two orders of magnitude (0.0045 μg/liter). Over the duration of the study the bag filters retained 5 g, the sand filters retained 64 g, and the carbon filters retained 25 g of PCB (Figure 3-12). Filter order in the flow stream must be considered when comparing effectiveness of the filter media.



A. Dry Solids Processing – 12/10/98

B. PCB Processing – 12/10/98
(Congener summation)



C. Dry Solids Processing – 12/16/98

D. PCB Processing – 12/16/98
(Congener summation)

Figure 3-11 Dry solids processing on detailed shoreside processing activities (A and C); and PCB processing on detailed shoreside processing activities (B and D)

The suspended solids concentration entering the mix tanks (in which a polymer was added to promote flocculation) ranged from 4,500 to 18,000 mg/liter (Figure 3-11A and C; location B). The settling/flocculation processes concentrated the solids so that input to the filter presses (location C) was 33,500 to 69,000 mg/liter while the skimmed supernatant had a TSS concentration of <10 mg/liter (location K).

Table 3-7 illustrates how efficiently PCBs were removed from the incoming slurry stream prior to its return to the river system. On 10 Dec. 1998 the incoming slurry PCB concentration (264,000 ng/liter; Figure 3-11B) was reduced by 99.998% at the point that it was released back to the river (effluent was 4.98 ng/liter). Similarly, on 16 Dec. 1998 the slurry PCB concentration (71,000 ng/liter) was reduced by 99.994% at the point that it was released back to the river (effluent was 4.00 ng/liter).

Mercury was not sampled at the internal locations in the process. It was, however, sampled at the slurry inflow (PA) and effluent locations (PE) on the above 2 days. On 10 Dec. 1998 the incoming slurry Hg concentration (6,241 ng/liter) was reduced by 99.997% at the point that it was released back to the river (effluent Hg concentration was 0.2011 ng/liter). On 16 Dec. 1998 the slurry Hg concentration (3,463 ng/L) was reduced by 99.992% at the point that it was released back to the river (effluent concentration was 0.2728 ng/liter).

Results from Congener Sampling at Process Locations

The magnitude of PCB losses (to the air or mechanical) due to sediment processing can be calculated from the overall Process Mass Balance equation (Equation 7):

$$M_A - M_F - M_G - M_H - M_I - M_J - M_E = M_{loss,\ process}. \qquad \textbf{\textit{Equation 14}}$$

It was anticipated that total PCB mass fluxes, because of measurement error, would not be sensitive enough to adequately quantify the potentially small processing losses of PCBs. Therefore, during the two days detailed previously, total PCB (Aroclor) measurements were supplemented with congener-specific PCB analyses to allow monitoring of changes in congener patterns resulting from potential desorption losses. It was hypothesized that this approach would provide an estimate of PCB loss between the internal processes and that this knowledge would prove useful in future remediation system design. The congener enrichment approach is based upon a consistent congener pattern in the incoming slurry. The congener fractions from the ten core locations that were analyzed for congener-specific patterns were highly variable. For the co-eluting congeners 141/153, anticipated conservative congeners, fractionation ranged over an order of magnitude from 0.34 to 3.8%. Due to the variable congener patterns found in deposit sediment cores and the resulting process slurry stream it was not possible to determine mass loss such as volatilization between process locations.

Duplicate Sample and Error Analysis Results

The shoreside processing was prematurely terminated due to cold weather. As a result a limited number of field duplicate samples were collected. All duplicates (Tables 3-8 and 3-9) were collected with separate sampling equipment and collection containers (QAPP).

The shoreside mass fluxes were calculated on a daily basis using flow (volume) and concentration. A first order error analysis incorporating the above field duplicates was used to estimate loading error.

Using press cake solids load as an example, the daily solids load was calculated by multiplying the volume (press cycles per day times press volume) with the solids concentration (or bulk density).

Table 3-8. Duplicate sample analyses during dredging activities for process samples.

Shoreside Processing Duplicates		
Date	PCB-Aroclor*1242 (µg/g)	Bulk density (g/cm^3)
	Sand Fraction	
7 Dec. 1998	4.4	0.73
7 Dec. 1998	5.0	0.77
	Press Cake	
7 Dec. 1998	21.0	0.34
7 Dec. 1998	22.0	0.36
16 Dec. 1998	0.64	0.57
16 Dec. 1998	0.50	0.60
	Dredge Slurry Duplicates	
	PCB-Aroclor*1242	TSS (mg/liter)
	Settled Fraction (µg/g)	
7 Dec.1998	84.0	77,670
7 Dec. 1998	99.0	87,379
	Supernatant (µg/L)	
7 Dec. 1998	43	685
7 Dec. 1998	41	660
	Total Slurry (µg/L) *(Supernatant and Settled) Computed*	
7 Dec. 1998	526	6,418
7 Dec. 1998	682	7,118

Table 3-9. Duplicate sample analyses during dredging activities for water column samples.

Water Column Duplicates

Date	Total PCB (ng/liter)	Computed TSS (mg/liter)	Discrete TSS (mg/liter)
8 Dec, 1998	3.74	13	-
8 Dec. 1998	3.94	11	-
9 Dec. 1998	19.90	12	-
9 Dec. 1998	18.74	11	-
18 Dec. 1998			15.8
18 Dec. 1998			15.5
18 Dec. 1998			14.8
18 Dec. 1998			14.8
6 Jan. 1999	3.39	4	2.1
6 Jan. 1999	4.28	3	2.5
20 Jan. 1999	0.35	3.2	2.3
20 Jan. 1999	0.46	2.8	2.3

$$L_i = V_i * C_i \qquad \textbf{\textit{Equation 15}}$$

where:

C_i = the daily solids concentration; and
V_i = the daily solids volume.

The **daily** variance of the error in a load can be determined as the product of two independent random variables (Benjamin and Cornell, 1970).

$$\sigma^2_{Load} = (\sigma^2_{Vol} * C_i^2) + (\sigma^2_{Con} * V_i^2) \qquad \textbf{\textit{Equation 16}}$$

where:

σ^2_{Load} = the variance of error in the daily solids load;
σ^2_{Vol} = the variance of the error in the daily volume; and
σ^2_{Con} = the variance of the error in the daily solids concentration.

Because the volume and concentrations (bulk densities) were determined independently, the assumption of independence should be valid.

Dividing Equation 16 by the squared expected value of the daily load $(V_i * C_i)^2$ yields an expression for the variance of the error in the daily load as a function of relative variations, namely

$$\sigma^2_{Load} /(Vi * C_i)^2 = (\sigma_{Vol} /V)^2 + (\sigma_{Con} /C)^2$$

Equation 17

where:

$(\sigma_{Vol} /V_i)^2$ = relative variation of the volume error; and
$(\sigma_{Con} /C)^2$ = relative variation of the concentration error.

The relative variation of error calculated from a field sample duplicate pair (Box et al., 1978) is

$$(\sigma_{Con}/C)^2 = 2 * (C_1 - C_2)^2/(C_1 + C_2)^2. \qquad \textbf{\textit{Equation 18}}$$

Based on the bulk density field duplicates and Equation 18, the relative variation of concentration $[(\sigma_{Con}/C)^2]$ was 0.0015. The relative variation of error for volume was estimated to be $(0.25)^2$. On 26 Nov. 1998 the calculated press cake solids load was 31.9 tonne. Substituting these values into Equation 17, the variance of the error for the solids load for 26 Nov. 1998 was

$$\sigma^2_{Load} = (31.9)^2 * (0.25^2 + 0.0015) = 65.1 \text{ tonne}^2. \qquad \textbf{\textit{Equation 19}}$$

The 28 daily variances were summed to calculate a total loading variance of 926 tonne^2 and a loading error standard deviation (σ_{Load}) of $\sqrt{926}$ = 30.4 tonne. Table 3-10 details the relative loading variations used in the error calculations for shoreside and water column fluxes. All relative variations were determined from field duplicates (Tables 3-8 and 3-9) and Equation 18 unless otherwise noted.

Table 3-10. The relative loading variations used in error calculations for shoreside and water column fluxes.

Media Masses		Relative variance (unitless) $(\sigma_{Con}/C)^2$	Relative Standard Deviation (%)	Total Variance	Total Standard Deviation
Press Cake Solids	Bulk Density	0.0015	4	926 tonne^2	30.4 tonne
	Volume	0.0625†	25		
Press Cake PCB	PCB Conc.	0.0156	12	1.6 kg^2	1.3 kg
	Solids Mass	0.0640	25		
Sand Fraction Solids	Bulk Density	0.0014	4	576 tonne^2	24 tonne
	Volume	0.2500†	50		
Sand Fraction PCB	PCB Conc.	0.0081	9	0.0058 kg^2	0.08 kg
	Solids Mass	0.2514†	50		
Debris Fraction Solids	Bulk Density	0.0014†	4	319 tonne^2	18 tonne
	Volume	0.2500†	50		
Debris Fraction PCB	PCB Conc.	0.0081†	9	0.0005 kg^2	0.02 kg
	Solids Mass	0.2514†	50		
Dredge Slurry Solids	TSS	0.0053	7	14,024 tonne^2	118 tonne
	Flow	0.1600†	40		
Dredge Slurry PCB	PCB Conc.	0.0335	18	5.6 kg^2	2.4 kg
	Flow	0.1600†	40		
u/s Water Column TSS	Solids Conc.	0.0147‡	12	50,126 tonne^2	223 tonne
	Discharge	0.0100	10		
d/s Water Column TSS	Solids Conc.	0.0098‡	9	37,107 tonne^2	192 tonne
	Discharge	0.0100	10		
Net Water Column TSS	(add u/s and d/s variances)			87,233 tonne^2	295 tonne

† Values were estimated.

‡ Values are from regression equations.

The relative variance associated with total suspended solids concentration resulted from the turbidity-TSS regression relationship (Figure 3-4) percent standard errors.

The net PCB transport error estimate was calculated from the standard error (39.8 g) resulting from the loading regression relationship. This standard error was squared to estimate daily load variance. The 35 daily variances were summed to calculate a total loading variance of 55,441 g^2 and a loading standard error deviation (σ_{Load}) of $\sqrt{55{,}441}$ = 235 g or 0.24 kg.

The above error analysis only considers random sampling error; therefore, the results should be considered a lower bound. It did **not** include sample bias. Possible biases may include press cake bulk density (may be low); slurry volume (Doppler slurry meter was consistently greater than the effluent slurry meter); slurry PCB concentration on the settled sample (may be low); and sampling procedures, sample collection was conducted on an 8- to 10-hour day while dredging, shore processing, and transport occurred throughout a 24-hour period.

It should be noted that overall loading error (if only considering random error) decreases as the number of sample days increases. Sample bias error, however, does not decrease with sample frequency. The above error estimates are depicted in the mass balance Figures 3-12. Only the major mass pathway errors were computed.

Overall Mass Balance for Dredging Operations

Summing the various mass balance components listed previously, it is possible to calculate an overall mass balance for the dredging period, 26 Nov. through 30 Dec. 1998. Figure 3-13 depicts dry solids, PCB, and Hg mass balances for most phases of the dredging operation.

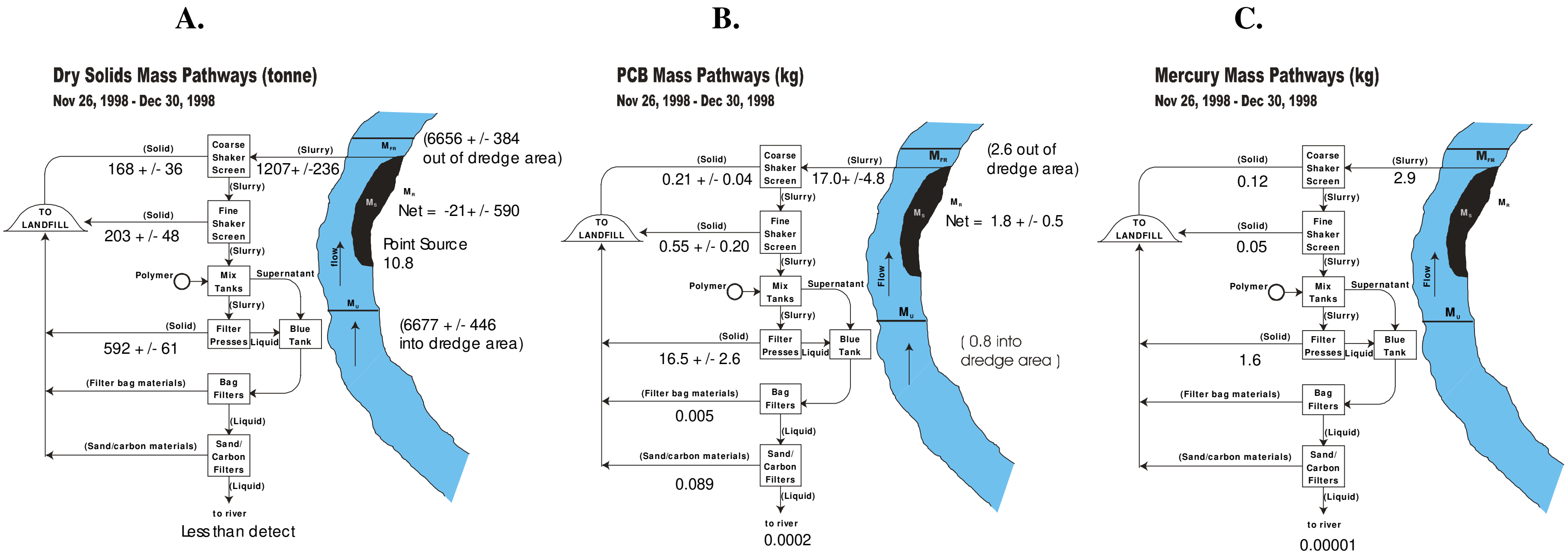


Figure 3-12. Mass pathways for A) Total solids, B) PCBs, and C) Hg at the shoreside processing facility and the Fox River at Deposit N.

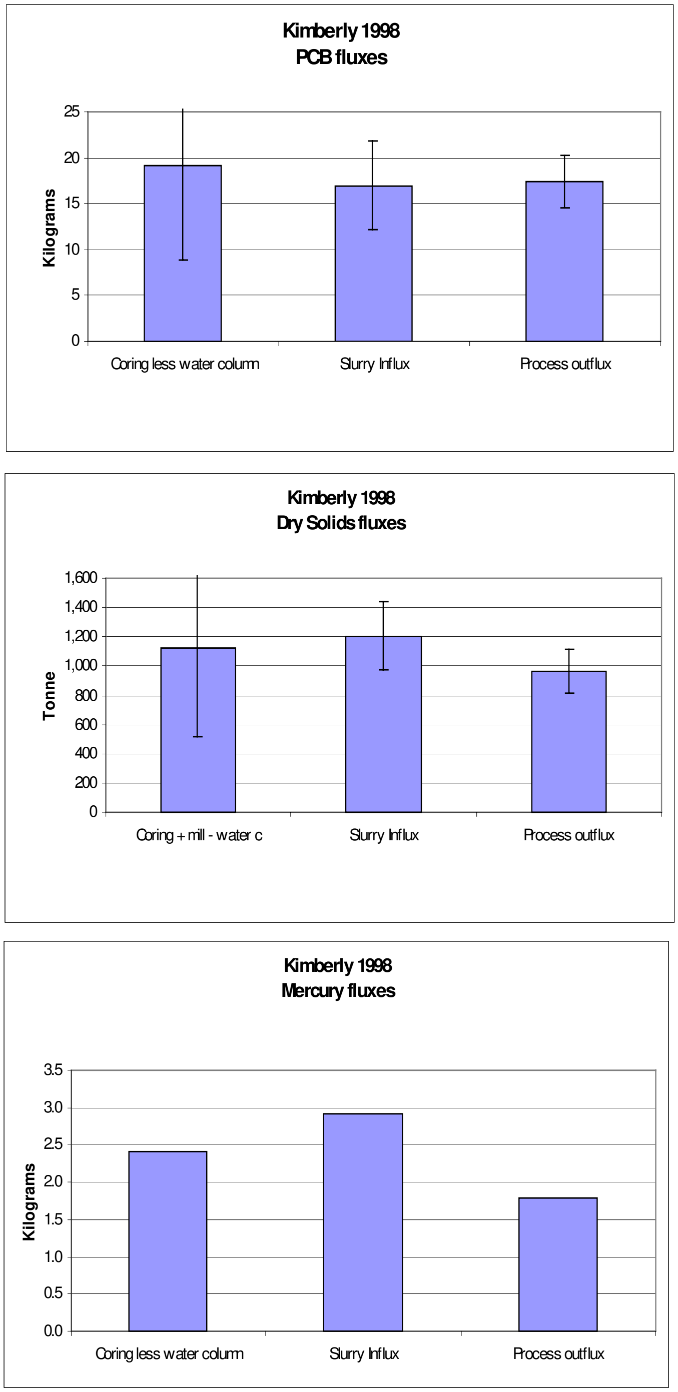


Figure 3-13. Dry solids, PCB, and Hg mass balances for most phases of the dredging operation.

4. CONCLUSIONS

Analysis of data from Phase I dredging of contaminated sediments at Deposit N of the Lower Fox River at Kimberly, Wisconsin led to the following conclusions:

1. ***Environmental dredging is an effective mechanism for removal of contaminated sediments from Deposit N in the Fox River.*** During the period of dredging encompassed by Phase I (26 Nov. to 31 Dec. 1998), 17.1 kg of PCB and 2.3 kg of Hg were permanently removed from the west lobe of the deposit. This is a mass of contaminants that will not be transported to the water column and relocated downstream in a depositional area to become a new source of contamination, nor will it be volatilized to the atmosphere for global transport. The 2.6 kg of PCB that remain in the deposit lobe is a small mass when compared to the estimated 4 to 5 kg that the deposit could have contributed to the column or atmosphere during 1998 if no dredging had occurred. During Phase I of the dredging operation 1.8 kg of the dredged PCB mass was lost to the water column during the cutter-head operation.

2. ***A mass balance approach is the most scientifically defensible measure for assessing the effectiveness of a dredging operation.*** A concentration-based approach has been suggested by FRG, but concentration does not account for the quantity of PCBs and contaminated sediments that have been permanently removed from the river system. Data from Phase I dredging demonstrates that a concentration-based assessment would be misleading for the Deposit N dredging project. The average surface concentration of PCBs declined by 33%, however, 89% of the PCB mass was removed. The after-dredging PCB concentration represents a small mass (2.6 kg); a mass that is about 50% of the annual contribution prior to dredging.

3. ***Shoreside processing was an effective means of concentrating and permanently removing contaminated sediments from the river.*** The shoreside process removed > 99.99% of the Hg and PCB mass from the incoming slurry mixture prior to returning more than 11 million gallons of water back to the river. Less than 1 g of PCB was returned to the river from the shoreside process. On 10 Dec. 1998, the incoming slurry PCB concentration (264,000 ng/liter) was reduced by 99.99% at the point that it was released back to the river (effluent was 4.98 ng/liter). Similarly, on 16 Dec. 1998 the slurry PCB concentration (71,000 ng/liter) was reduced by 99.99% at the point that it was released back to the river (effluent was 4.00 ng/liter). On 10 Dec. 1998 the incoming slurry Hg concentration (6,241 ng/liter) was reduced by 99.997% at the point that it was released back to the river (effluent Hg concentration was 0.2011 ng/liter). On 16 Dec. 1998 the slurry Hg concentration (3,463 ng/liter) was reduced by 99.992% at the point that it was released back to the river (effluent concentration was 0.2728 ng/liter).

4. ***Dredging on the Fox River should be conducted during a period when seasonal weather extremes are not a concern.*** Our assessment of the overall level of effectiveness for the entire project was hampered, constrained by cold weather conditions after 30 Dec. 1999. Appendices A and B discuss problems encountered during icing conditions and possible losses from the deposit. The east lobe losses occurred during the period when there was no dredge cutter-head operation in the eastern lobe of the deposit. An apparent loss of fine-grained contaminant-laden surface sediments was probably due to ice-breaking operations. As a pilot operation, this study underscores the problems that cold weather conditions can create.

5. ***Common techniques such as measurement of total suspended solids and turbidity are inadequate to describe riverine transport of PCBs.*** There was little or no measurable difference between the upstream (u/s) and downstream (d/s) TSS concentrations (or loads) over the length of the operation. At the u/s and d/s sites there was a strong correlation between turbidity and TSS. However, neither turbidity nor TSS was sufficient in predicting PCB transport because the PCB concentration on

suspended particulate matter and the dissolved phase PCB concentrations were variable and at least partially dependent on the deposit concentration in which the dredge was operating. If chemical transport assessment is to be done during PCB remediation, TSS and turbidity monitoring are not adequate. Approximately 25% of the PCB load at the d/s site was in the dissolved phase (< 0.45 μ) and this distribution between dissolved and particulate PCBs cannot be detected through simple TSS or turbidity measurements.

6. ***Prior to dredging, Deposit N represented an active source of PCBs to the Fox River and was not "naturally" capping with low-PCB content particles from the water column.*** The median u/s particle concentration was 0.08 μg/g–one or two orders of magnitude lower than the upper (0 to 4 in) deposit core concentration (12 μg/g). This indicates that the deposit has not been buried and that it is still loading the water column. Deposit N would have contributed about 0.4 kg of PCBs during the dredging interval had no dredging taken place (background flux). It is estimated that in 1998 the annual background flux from Deposit N would have been 4 to 5 kg had no dredging taken place.

7. ***The demonstration project at Deposit N provided information important for future shoreside processing design.*** The press cake appeared to be the most important step for removal of PCBs (96%) and Hg (87%). The supernatant skimmed from the mix tanks (location K) and the liquid squeezed from the filter presses (location D) had similar PCB concentrations (0.16 to 1.4 μg/liter). The combination of bag filters and sand/charcoal filters led to a reduction of PCB concentrations by two orders of magnitude (0.0045 μg/liter). Over the duration of the study the bag filters retained 46 g, the sand filters retained 64 g, and the carbon filters retained 25 g of PCB. Filter order in the flow stream must be considered when comparing effectiveness of the filter media. The PCB concentrations from the sand media ranged from 0.91 to 2.0 μg/g while carbon PCB concentrations ranged from 0.6 to 0.7 μg/g (Aroclor basis). Consistent with organic carbon partitioning theory, the carbon media retained more of the lesser chlorinated congeners than did the sand filters. These less chlorinated congeners are prevalent in the dissolved phase. Thus, the carbon filter was more proficient at removing the dissolved phase PCBs than were the sand filters.
8. ***The demonstration project at Deposit N provided information important for water column sampling designs.*** Collecting discrete TSS and turbidity data laterally in the river cross-sections provided insight into solids transport. The TSS resulting from the multiple transects collected over the course of a sampling day indicated that river conditions (especially the d/s site) were variable. Had water column samples not been collected over an extended period of time (8 to 10-hour sample period), samples would have been substantially less representative of the entire day. The increased distribution coefficient and suspended particle concentration at the d/s site provided transport insight; thus, it is useful to measure both the dissolved and particulate phase PCB. The slurry mass (g/day) and slurry settled fraction PCB concentration (μg/g) were both indicators ($r^2 = 0.71$) of net PCB flux to the water column.

9. ***The mass balance framework is a feasible and useful approach.*** The mass (dry solids, mercury, and PCB) balance approach was determined to be successful (Figure 3-13). This approach provides assurance in the major flux conclusions; fluxes such as changes in the sediment PCB deposit, quantity of PCBs trucked from the site, and water column loading. A successful mass balance allows reliable comparison of specific mass pathways. For example, the PCB mass removed in the press cake can be compared to that collected on the cloth bag filters. It also provides information for future remediation designs, such as size of sand or carbon filters needed to retain specific masses. If time and space scale are not composited together, insight can be gained into specific phases of an operation and even into daily operations. Lastly, the mass balance approach (deposit, shore process, and water column) provides a backup system that can be invaluable when cold weather conditions terminate traditional monitoring approaches.

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APPENDICES

APPENDIX A

CESSATION OF PHASE I DREDGING AND REMOVAL OF SILT CURTAIN

On 29 Dec. 1998 sub-freezing temperatures in Kimberly, Wisconsin caused conditions that were unfavorable for successful dredging and concomitant monitoring at Deposit N near Kimberly. Essential equipment became inoperable, including upstream and downstream turbidity monitors. Therefore, information necessary for mass balance calculations was not attainable. The State of Wisconsin, together with the on-site contractor, decided to cease dredging operations at the site. At this point, Phase I of the dredging demonstration was considered complete. All mass balance measurements and calculations, with the exception of post-dredge coring, encompassed samples prior to and including 29 Dec. 1998. Since mass balance calculations required simultaneous collection of several sample types, both within the river and at the shoreside processing operation, FRRAT was constrained to only using the mass balance approach prior to 30 Dec. 1998.

During the period of 30 Dec. 1998 to 20 Jan. 1999 the following operations were conducted under challenging cold weather conditions: breaching the turbidity barrier and breaking ice to enhance flow to remove the ice and continue dredging; icebreaking operations in support of coring; turbidity meter removal and barrier removal; removal of frozen turbidity meters; coring; and sediment mapping (Table 2-1). ***The effectiveness of these operations could not be assessed*** due to the inability of field crews to properly monitor in close proximity to the operations.

The dredge did not operate in the East Lobe (Figure A-1, polygons S21-S29) prior to ceasing operations

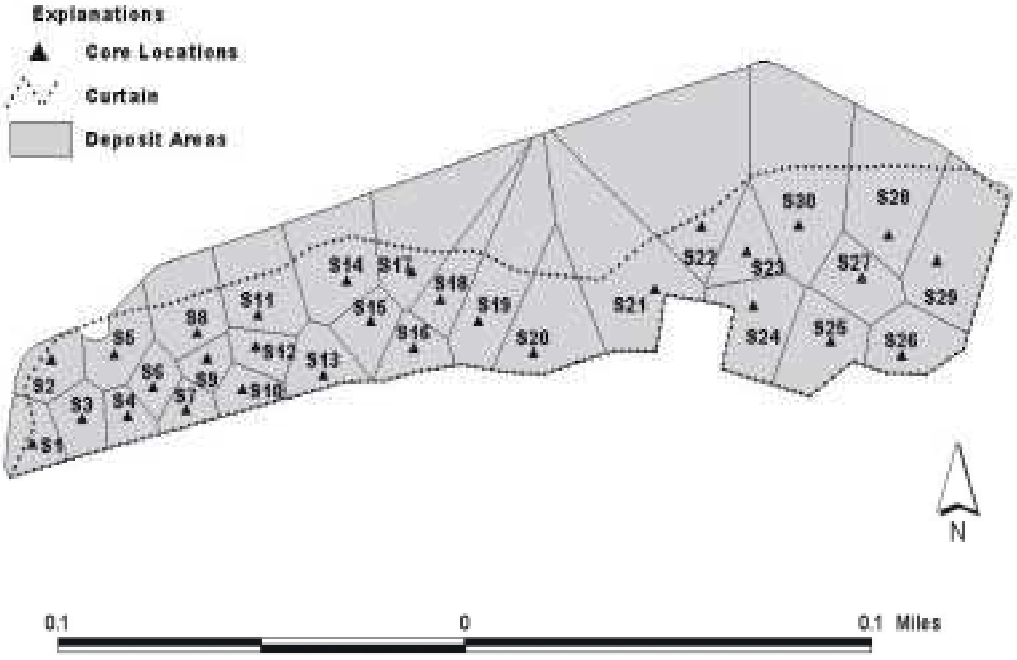

Figure A-1. Theisen polygons developed for the entire Deposit N sediment remediation site.

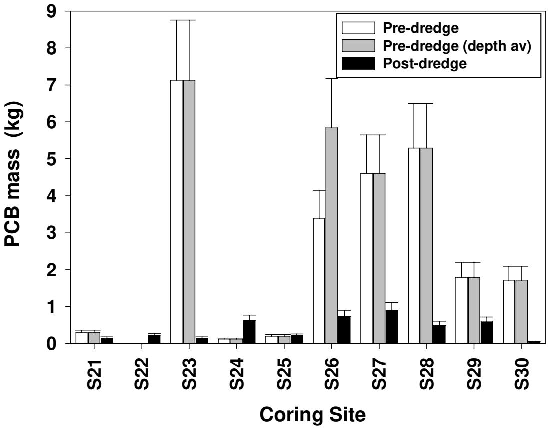

Figure A-2. PCB mass in east lobe sediments not dredged during Phase I.

due to cold weather on 30 Dec. 1998. However, coring conducted in January 1999 indicated this deposit lobe lost 300 tonne of dry solids. Loss of this amount of solids from the site could amount to approximately 20.4 kg of PCB and 0.3 kg of Hg (Figure A-2).

Due to the inability to conduct proper monitoring during the curtain-removal process, it is not possible to determine the exact physical condition that created these losses. Ice breaking is one probable cause of significant resuspension, sorting, and transport of sediments. The ice-breaking boat had a 4 ft draft with two 160 horsepower engines. The combined draft of the boat and the size of the engines, coupled with the physical tilting of the boat during ice-breaking operations, is comparable to the common use of commercial fishing boats and small tug boats to clear shoals in channels and at docks by pressing the bow of the boat against a dock or streambank and using the propeller wash to move sediment. Boat operations intended to clear ice probably resuspended bottom sediments in shallow waters of the East Lobe. Since the turbidity barrier had been breached to enhance ice-breaking activities, significant flow through the dredge site probably transported resuspended sediment downstream.

Ice cover conditions also prevented USGS sampling crews from obtaining samples from upstream and downstream sites until 7 Jan. 1999. During this sampling gap, ice-breaking operations were conducted over the entire site so that conditions were favorable for SCUBA divers to obtain post-dredge sediment cores. Downstream samples indicate a slight increase in total PCB on 7 Jan. 1999, but the majority of increase appears to be in the “dissolved” phase (Figure 3-5).

Icing conditions also prevented complete downstream monitoring during the turbidity curtain removal. The process began on 19 Jan. and continued until 27 Jan. 1999; the final water samples were obtained on 20 Jan. 1999. While the total mass of PCB transported downstream could not be calculated for the entire curtain-removal process, significant increases were observed downstream for both dissolved and particulate PCB on 20 Jan. 1999 (Figure 3-5). Furthermore, the concentration of PCBs on particles was greater than at any time during dredging when the curtain was fully in place (Figure 3-8A). Although the concentration on particles was elevated, mass flux estimates for 20 Jan. 1999 were about 70 to 1,000 g of PCB/day, which was about mid-range for PCB transport during dredging. The sum of 20.4 kg of PCB applied to the 300 tonne of sediment results in an estimated particle concentration of ~68 µg/g for these areas of the deposit. Similarly, the Hg particle concentration would be approximately 0.9 µg/g. Both of these concentrations were exceeded in the processed cake material in the upstream lobe during dredging activities in Phase I.

It is unfortunate that all of the contractor water column turbidity meters were frozen during these operations. However, the sole operational turbidity meter was on the industrial intake, located just downstream of the dredge site (Figure 1-1). This meter was located behind a second turbidity barrier that further protected the industrial intake water. Nevertheless, an increase in turbidity is observed during the ice operations (Figure A-3).

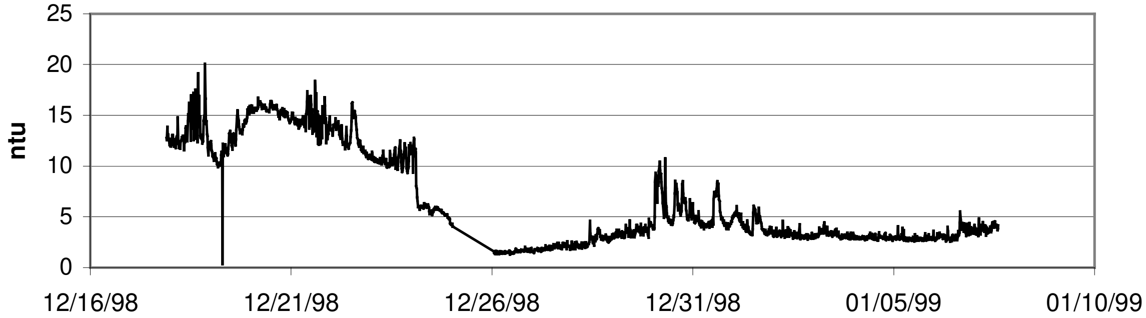

Figure A-3. Turbidity data from industrial intake located downstream of Deposit N remediation site.

WATER COLUMN TRANSPORT DURING THE 1999 DREDGE OPERATIONS

Although the full mass balance approach was not used during Phases II and III, WDNR did require water column monitoring in the Fox River during dredging. Techniques applied during these phases were similar to our Phase I sampling. Daily net loading to the water column from the deposit during the 1999 dredging operation was lower than in the 1998 operation (Figure A-5). During 1999 the dredge was primarily operating in a less contaminated (eastern lobe) area than in 1998. Applying the mean net daily load (44 g/day; coefficient of variation is 91%) to 56 days results in a net PCB flux to the water column of 2.5 kg (congener summation; 2.1 kg Aroclor*1242 basis). This net flux compares to 2 net flux of 2.3 to 2.9 kg during Phase I dredging.

Based on Deposit N cesium concentration (Steuer et al., 1995) it is probable the deposit has been in existence since the early 1960s. Therefore, it is likely the deposit has contributed hundreds of kilograms of PCB to the water column. A loss of 20.4 kg during a pilot study is unfortunate but small when compared to historical transport.

PCB MASS REMOVED DURING THE 1999 DREDGE OPERATIONS OF PHASES II AND III

Data obtained during Phases II and III were coupled with Phase I data to calculate a provisional, overall deposit mass balance for the remediation site. Due to the lack of complete mass balance monitoring conducted in Phase I, FRRAT is less confident in calculations made because of ice-breaking, curtain removal, and uncurtained activities used during Phases II and II. The lack of a curtain after 27 Jan. 1999 allowed for new material from upstream to be transported into the remediation area and allowed for particulate matter to more easily leave the site. The major mass fluxes of PCBs associated with the November 1998 to October 1999. Deposit N remediation are depicted in upper panel of Figure A-4A. It should be noted that had the remediation operation been conducted under non-winter conditions, it is likely the "non- cutter head east lobe PCB flux" (Figure A-4) would have been smaller, if it had occurred at all. The solids balance (A-4B) lends further credibility to the mass balance approach.

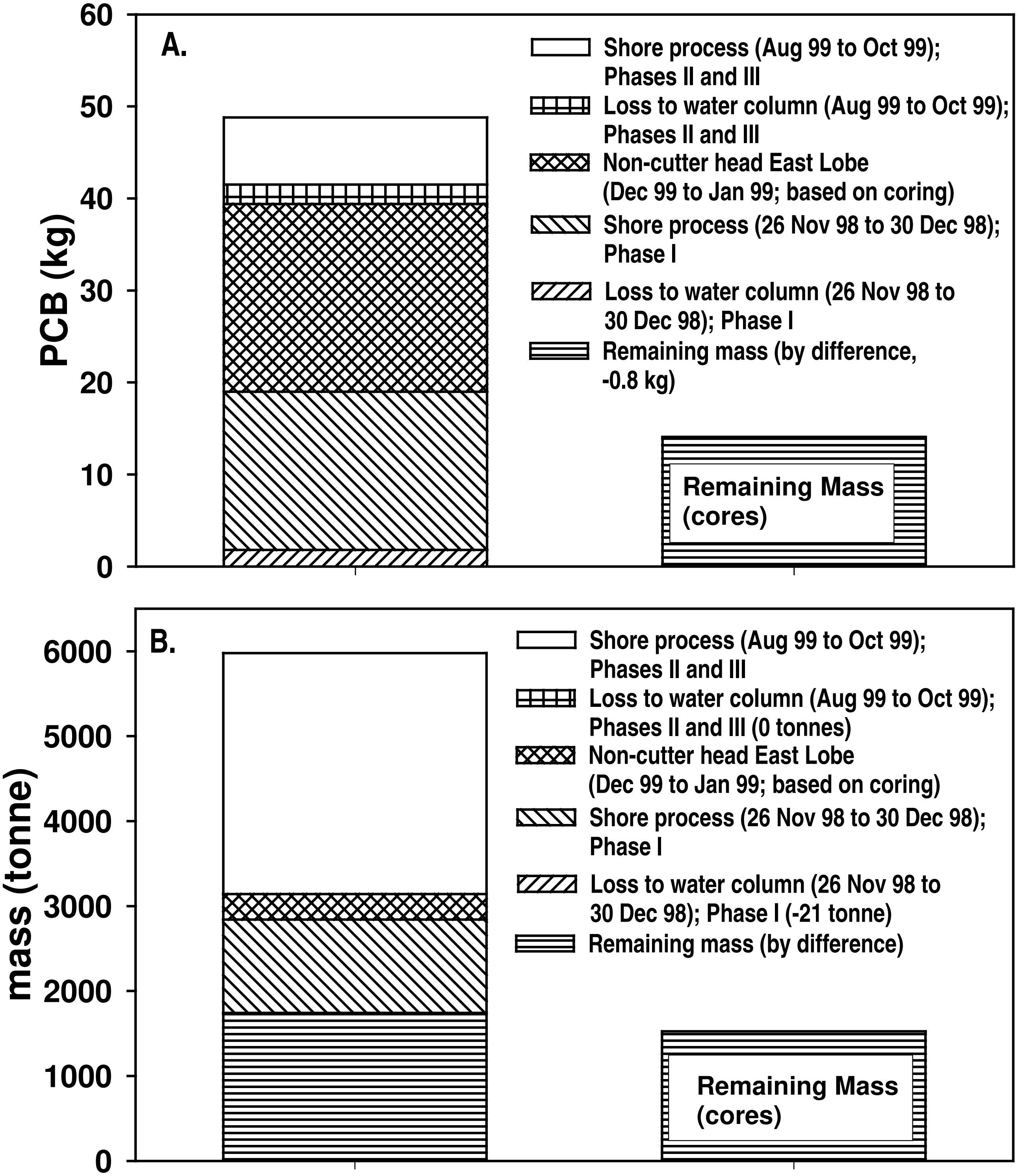

Figure A-4. Provisional overall mass balance for Deposit N remediation site. A. PCB mass balance. B. Dry solids mass balance.

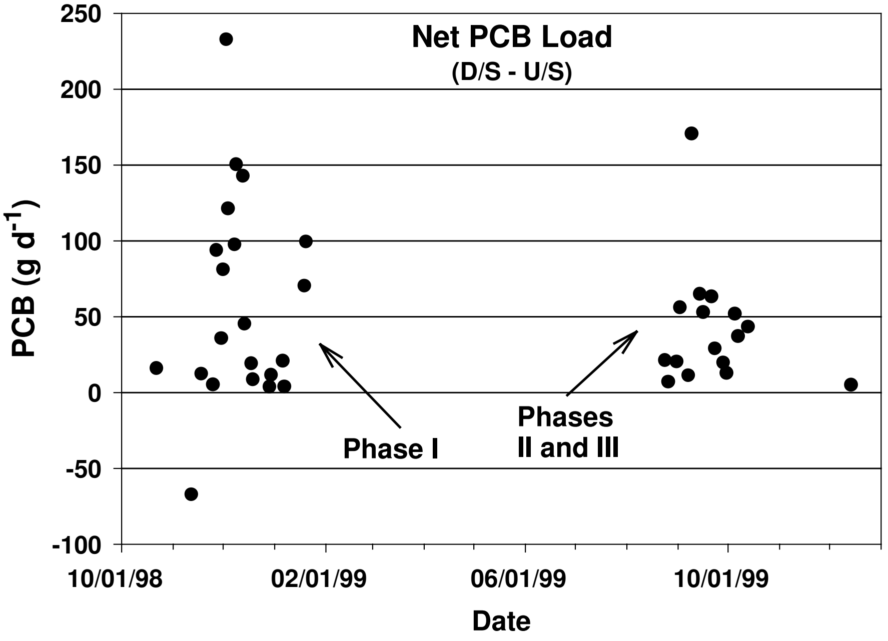

Figure A-5. Net PCB loading to the Fox River during Phases I, II, and III of dredging at Deposit N.

APPENDIX B

COMPARISON WITH SITE CONTRACTOR PCB MASS FLUXES

All of the PCB analyses utilized in the main body of this report were conducted at Severn-Trent Laboratories (STL) (Fox River Group, 1999). The sole exceptions were the water column samples; these were analyzed at the Wisconsin State Laboratory of Hygiene, Madison, Wisconsin.

As part of an operational monitoring plan, the site contractor also monitored various media for PCB concentration; these samples were analyzed at Enchem Laboratories. The largest PCB mass was processed via the press cake (Figure 3-12A). The site contractor collected sub-samples from each press cake storage pile that consisted of approximately 30 press cycles. These data were used, in part, to determine the appropriate landfill destination.

Laboratory comparison of press cake concentrations (Figure B-1) indicates that the Enchem results were consistently greater than those from STL. [It should be noted that the STL sample was collected daily with the daily concentration composited (weighted mean based upon solids mass) to arrive at a specific storage pile concentration]. In an attempt to resolve this difference a split sample laboratory comparison is being conducted as this report is being written.

In the overall Deposit N mass balance, to account for the laboratory difference, the median Enchem/STL ratio of 1.8 (from Figure B-1) can be applied to the samples that were analyzed at STL. This results in an improved balance (Figure B-2) in which the overall deposit mass residual (7.5 kg) is comparable to the remaining mass as determined from coring (14.1 kg). The overall dredged mass is 38.3 kg with 10% transported to the water column during cutter-head operation. This processed PCB mass is less than the mass (111 lbs; 50.4 kg) reported by the site summary report (Foth and Van Dyke, 2000). This difference is primarily due to the difference in press cake percent dry solids Figure B-3).

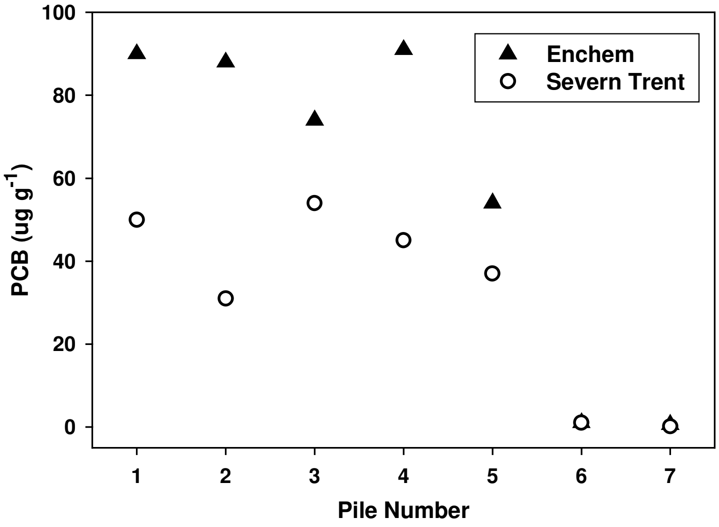

Figure B-1. Comparison of Enchem Laboratories and Severn Trent Laboratory PCB levels in cake solid piles.

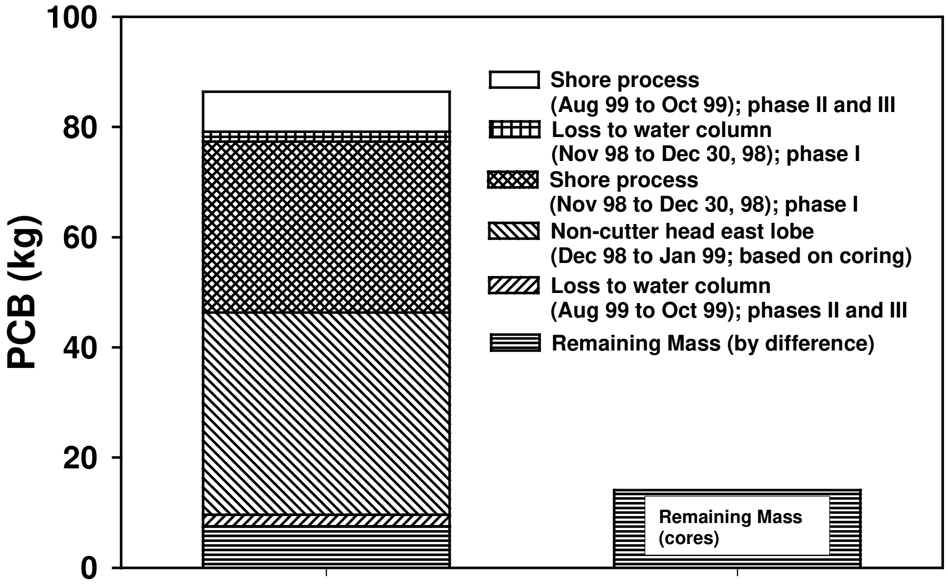

Figure B-2. Overall mass balance with increased STL values.

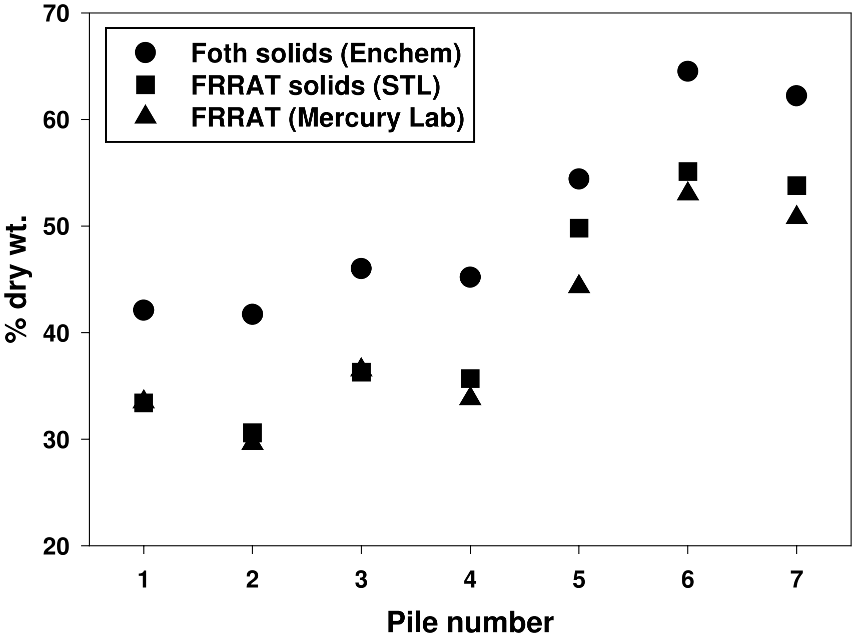

Figure B-3. Comparison of percent dry weight from press cake piles determined by three different laboratories

APPENDIX C

FOX RIVER REMEDIATION ADVISORY TEAM RECOMMENDATIONS BASED ON POST-PHASE I ACTIVITIES

The FRRAT is confident that dredging during Phase I of the Deposit N demonstration project was a successful operation for both river and shoreside operations. Clearly, once sediment was removed from the river, it was effectively dewatered and permanently removed from the Fox River. However, FRRAT also found that information is not available to use the same scientific scrutiny of the mass balance approach for activities conducted at the site after 29 Dec. 1999. Based on data that we feel are not as complete as the Phase I methods, we make the following recommendations:

1. ***First and foremost, all activities associated with dredging must take place prior to deterioration of weather conditions at the dredge site.*** Icing conditions on the Fox River, monitoring equipment failures, and the inability of field crews to collect prescribed samples led FRRAT to attempt to assess causes and effects with an incomplete set of data. We strongly recommend that post-dredge assessment coring and curtain removal be conducted well in advance of ice formation at the dredge site.
2. ***Silt curtains should remain intact and in-place for the entire dredge operation.*** It is extremely unfortunate that it was necessary to breach the curtain before cores were taken for post-dredge assessment during Phase I. While it was understandable that breaching was done to aid ice-breaking activities, it compromised the ability to completely quantify post-dredge conditions.
3. ***No excessive motor operations should occur within the curtained dredge site.*** While FRRAT has no direct evidence due to non-functioning turbidity monitoring equipment, it is apparent from coring activities that material from the East Lobe of Deposit N was moved by a process other than cutterhead movement of the dredge. Indirect evidence supports an assumption that icebreaking in shallow regions resuspended fine, contaminant-laden sediments.
4. ***Complete monitoring during all phases of dredging is warranted.*** While a detailed mass balance approach suggested by FRRAT and implemented during Phase I may not be feasible for all dredging activities, specific contaminant monitoring is warranted to validate approaches used for dredging. This will certainly benefit both the current assessment of methods and aid in determination of best practices of future ventures.
5. ***Similar techniques, or preferably laboratories, should be used for all phases of assessment.*** The problems encountered with laboratories using different methods for a measurement such as density of solids (Appendix B) further complicated the interpretations of the mass balance approach.