A Mass-Balance Approach for Assessing PCB Movement During Remediation of a PCB-Contaminated Deposit on the Fox River, Wisconsin

The U.S. Geological Survey, in cooperation with the Wisconsin Department of Natural Resources, collected water samples during the September 1–December 15, 1999 removal of sediment contaminated with polychlorinated biphenyls (PCBs) from a reach of the Lower Fox River designated Sediment Management Unit (SMU) 56/57. Results of analyses of the samples, along with monitoring activities of several other organizations, were used to delineate and compare PCB mass pathways during the cleanup effort (fig. 1). Results indicate that the cleanup at SMU 56/57 had the following effect on PCB mass: dredging permanently removed more than 650 kg (1441 lb) of PCBs, transported 14.5 kg (32 lb) downstream, and volatilized 2.6 kg (5.7 lb) to the atmosphere; associated activities on the shore returned 0.1 kg (0.3 lb) to the river. This report documents the USGS data-collection efforts and details the mass-balance approach for PCB pathway delineation.

Introduction

Water quality and aquatic life in the Lower Fox River, which flows from Lake Winnebago to Green Bay (fig. 2), have been affected by contaminants that have accumulated in streambed sediments over the last several decades. The Wisconsin Department of Natural Resources (WDNR) has determined that contaminants released from Fox River sediment deposits cause exceedances of State water-quality standards and necessitate fish-consumption advisories. From the perspective of human health and ecological risk, polychlorinated biphenyls (PCBs) and mercury are the principal contaminants of concern. Sampling has confirmed that sediment-associated PCBs and mercury are accumulating within the aquatic food chain and are actively being transported within the river and out into Green Bay and Lake Michigan (Brazner and DeVita, 1998).

Figure 1. Pathways of polychlorinated biphenyl (PCB) mass (Aroclor 1242) during the September 1–December 15, 1999 remediation at SMU 56/57. Amounts are in kilograms.

Figure 2. Location of the Fox River point-source discharge sites, dams, and the SMU 56/57 remediation project.
The Sediment Management Unit 56/57 (SMU 56/57) remediation project was a joint effort between the State of Wisconsin and the Fox River Group (FRG), a coalition of paper companies. A primary purpose of the project was to remove PCB-contaminated sediment by dredging and thereby generate information relevant to the effectiveness of large-scale dredging and disposal of the sediments (in this case, 7–11 million cubic yards) from the Lower Fox River (ThermoRetec Consulting Corp., 1999; Blasland, Bouch, and Lee, Inc., 1999; Montgomery Watson, 2000). A hydraulic dredge was used to pipe a sediment slurry from the river bottom to a settling basin; the onshore operation consisted of filter-pressing the slurry, filtering the liquid effluent and returning it to the stream, and trucking away the solids. In support of the sampling plan designed by the FRG and WDNR, a mass-balance approach (a combined examination of concentration and flow) was used to determine the effectiveness of dredging in removing the PCBs from the river environment.

**Description of the study area**

In 1995, sediment mapping by the WDNR in the 7-mile reach of the Fox River between the De Pere dam and the river mouth revealed a nearly continuous mass of soft sediment deposits. SMU 56/57 is approximately midway between the De Pere Dam and Green Bay. A papermill is adjacent to SMU 56/57; its discharge pipe is upstream from the dredged site and the upstream water-column sampling transect. A permeable silt curtain fabric was deployed around the dredged area that allowed passage of water but reduced transport of sediment and protected the papermill water intake (fig. 3).

This area is a commonly used offloading area for coal ships. The offloading slip is immediately downstream from SMU 56/57, and the turning basin used by these deep-draft vessels is adjacent to the deposit area (fig. 3). Fifteen coal ships offloaded cargo during the 15-week dredging operation.

SMU 56/57 has a surface area of approximately 9 acres with overlying water depths of 2–14 ft. Maximum sediment thickness was 16 ft with an overall average PCB concentration of 53 ppm (parts per million). Maximum PCB concentration was 710 ppm, the highest concentrations being in the top 2–5 ft. Total PCB mass in the deposit was estimated to be between 2,090 and 3,000 kg (4,600–6,600 lb) (Montgomery Watson, 2000; Blasland, Bouch, and Lee, Inc., 1999).

The lower 7-mile reach of the Fox River has an ever-changing flow and depth oscillation commonly found in estuaries. Flow reversals (from Green Bay toward De Pere Dam) are common in this reach (fig. 4). A continuous streamflow record for the river at SMU 56/57 was based on stream-velocity data collected at 15-minute intervals with a double-path acoustic velocity meter located approximately 2.7 mi downstream from the deposit and 0.8 mi upstream from the river mouth at Green Bay (USGS site 040851385, fig. 2). Because the dredging-site location was upstream from the acoustic-velocity-meter site and the inflow point of the East River, the daily mean streamflow was adjusted by a factor of 0.98 to account for the basin area difference.

The average water depth in this reach of the river is a function of Lake Michigan and Green Bay water levels, wind speed and direction, and flow over the De Pere Dam (which depends on precipitation and control at nine upstream dams). During 1999, the river depth at the USGS acoustic-velocity-meter site varied by more than 6 ft; during the dredging period (September 1–December 15, 1999) depth varied by more than 4.2 ft. River depth is important to sediment and PCB transport in that, for a given flow, water velocity increases as river depth decreases. An increase in water velocity results, in turn, in an increase to the fourth power for sediment resuspension (Jepsen and others, 1997).

**Sampling methods**

Water-column samples collected before, during, and after dredging operations were analyzed to support calculations of the mass transport of PCBs. The samples were collected from four discrete sites along an upstream transect and five sites on a downstream transect (fig. 3). Site spacing was closest in areas of focused flow (as determined by a portable Doppler flow meter). The southeast side of the channel is the deeper part and contains most of the flow; therefore, sample-collection sites are skewed toward that side. At
each site, water was collected from two depths, at 20 percent and 80 percent of the total water depth. For a given transect (upstream or downstream), water from the transect sites was composited throughout the day to provide a representative PCB concentration for each transect. During the dredging operation, each transect (upstream and downstream) was sampled 2-3 times per sample day, resulting in 36 sample (daily composite) pairs. In addition to transect composites, discrete total suspended solids (TSS) samples, and water-quality field measurements (temperature, turbidity, pH, and specific conductance) were obtained from each site. At the original downstream site A, it appeared that dredging could produce a contamination plume that could remain close to shore and not be collected. Therefore, section A was divided to create sites A1 and A2, with collection volumes halved.

Water-column samples were collected over an 8-12 hour period on each of 36 sample days during the 15-week dredging operation. Efforts were made to collect water only during periods of outgoing flow (fig. 4).

Upstream and downstream composite samples were analyzed for 101 individual PCB congeners (dissolved and particulate), TSS, dissolved organic carbon (DOC), and total organic carbon (TOC). The dredging contractor also collected turbidity data continuously at several sites during most of the dredging operation (fig. 3).

Composite water-column samples (80-L volume) were filtered through 0.7-μm glass fiber filters to determine particulate congener PCB concentrations. Filtrate was pumped through an absorbent resin column (that is, XAD-2) to concentrate PCBs for the operationally defined “dissolved” phase. Complete procedures for 80-L PCB water-column samples are described in the dredging-project quality assurance plan (Blasland, Bouck, and Lee, Inc., 1999). Total PCB concentrations were computed by summing the dissolved and particulate fractions; concentrations reported as being less than the laboratory detection limit were given a zero value. Daily mean river discharge was used in conjunction with the water-column concentration data to compute daily TSS and PCB loads.

On certain days, the entire sampling process was repeated to produce sample duplicates for analysis of PCB (6 duplicates) and TSS (3 duplicates). The purpose of the sample duplicates was to assess the ability to detect real change in the environment (that is, isolate laboratory and sampling artifacts from environmental change). The mean relative percent differences between sample duplicates were 5 percent for total PCB samples (combined dissolved and particulate phases); 10 percent for composited TSS samples; and 12 percent for discrete TSS samples. These duplicate results are similar to those from previous sampling efforts (Fox River Remediation Advisory Team, 2000).

**Suspended-solids transport during dredging**

When averaged over the length of the dredging operation, little difference was found between the upstream and downstream TSS and turbidity values. Periodic differences, however, were substantial (fig. 5). These differences were not consistent—at times net TSS increased over the dredging area, and at other times it decreased.

A consistent lateral pattern was evident at the upstream site (fig. 6). TSS concentrations were generally highest closest to the papermill wastewater-treatment plant discharge pipe (570 lb/d), and concentrations decreased away from this pipe.

The TSS concentrations at the sample-collection sites provided insight regarding shipping operations. On the mornings of October 8 and November 3, 1999, coal-ship departure appeared to have resuspended PCB-laden sediment (fig. 7). This increase in suspended sediment was in agreement with the continuous turbidity data collected by the site contractor (Montgomery Watson, 2000). A similar effect was observed on the two other days (October 14 and November 23) when PCB water-column samples were collected coincident with vessel movement.
**PCB concentration changes during dredging**

After dredging started on September 1, a consistent PCB concentration increase was evident at the downstream site (fig. 8A). The mean upstream concentration of PCB was 50.7 ng/L and the downstream PCB concentration was 92.0 ng/L. The paired upstream-downstream samples had a mean relative percent difference of 59 percent, substantially larger than the 5-percent difference between sample duplicates.

Initially, it seems contradictory that PCB concentration increased while suspended solids loading remained the same or decreased (because of settling) during the dredging operation. However, material exposed to or resuspended into the water column during dredging increased the dissolved PCB concentration (fig. 8B), as well as the PCB concentration on a given particle (fig. 8C). Therefore, even though the overall mass of particles transported downstream did not increase, the PCB in solution and transported on the particles did increase.

The TSS and PCB comparison (downstream minus upstream) illustrates that TSS is not a reliable indicator of PCB transport during a dredging operation. For example, from September 1 to October 6, a period of negative TSS loading (less at the downstream than at the upstream site), the PCB loading was positive. Thus, if one is to monitor PCB transport during a remediation operation, sole reliance on turbidity or TSS measurements is inadequate. One must also directly measure the concentration of the contaminant of interest because exposed layers of contaminated sediment and exposed concentrated pore waters can contribute to particle- and dissolved-phase PCB concentrations in downstream waters. Concentration data, however, do not form a complete picture of the effects of dredging; the mass of transported PCBs also must be taken into account.

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**Figure 7.** Total suspended solids concentrations at the site locations on October 8 and December 13, 1999, Fox River, Wis.

**Figure 8.** PCB concentrations at the upstream and downstream transects before and during dredging operations, Fox River, Wis.
PCB loading in the Fox River due to the dredging operation

Putting the PCB concentration increase in a useful context requires calculation of mass fluxes, such as the daily PCB load (expressed as mass) to the water due to dredging operations and the amount of PCB processed in the onshore operations. For a given sample-collection day, the PCB load due to dredging operations was calculated by multiplying daily streamflow by total PCB concentration (summation of all congeners, dissolved and particulate).

A daily net PCB load due to dredging (fig. 9) was computed by multiplying the difference between the downstream and upstream PCB concentrations on a given sample day by the daily discharge. Net PCB loads, in general, increased after November 15. This result is consistent with a change in operations: the dredge had been moved to an area of the deposit that contained higher PCB concentrations and was closer to the downstream transect (Blasland, Bouck, and Lee, Inc., 2000). Additionally, streamflow increased substantially after November 15 (fig. 10).

An initial overall PCB load estimate was calculated using the median daily PCB load for the two intervals (before November 16 and after November 15). The median was used, rather than the mean, because daily PCB loads were not normally distributed for either interval. The median daily PCB loads for each interval (42.4 gm and 364.3 gm, respectively) were multiplied by the median flows to provide initial load estimates of 3.2 kg and 10.9 kg, respectively.

Further PCB loading analyses examined relations with variables that were measured daily (dredge-slurry settled-fraction concentrations and supernatant concentrations). Concentrations of the material being removed from the deposit or the amount of dredging per day might be indicators as to how much PCB was transported downstream. Frequently monitored variables such as turbidity, streamflow, and stream depth also were examined. A usable regression relation could not be developed for the interval prior to November 16. For the dredging interval after November 15, however, a regression was developed in which four factors explained much of the variability ($r^2 = 0.88$): daily PCB concentration of the incoming slurry mixture (settled fraction (Set) and supernatant (Sup)), time spent dredging on a given day (T), and stream depth (D).

$$\text{Daily PCB load (gm)} = (-507.9)(D) - (1237.9)(T) - (5.69)(\text{Set}) + (32.5)(\text{Sup}) + 293,703$$

The daily PCB loads resulting from this regression equation (fig. 9) were summed to arrive at a load of 13.7 kg for the post-November 15 dredging period. The standard error was 25 percent of the mean.

The final estimated PCB load (16.9 kg), combining the median based pre-November 16 load (3.2 kg) with the regression-based post-November 15 load (13.7 kg), was selected as a conservative approach.

An estimated PCB load entering into the dredged area from upstream (fig. 1) was computed by applying the median daily upstream PCB concentration (51.4 ng/L) to the median daily flow (1.842 ft/s) for the 106 days. The result was an estimated overall PCB load of 24.5 kg entering the deposit cross-section from upstream.

Congener distribution changed noticeably during dredging (fig. 11). Congeners 5/8, 4/10, and 6—congeners that readily volatilize to the atmosphere—are noticeably less prevalent at the upstream site than at the downstream site. Air monitoring during remediation has shown that the river routinely volatilizes PCB to the atmosphere; thus depletion of these congeners is not surprising at the upstream site. Sub-surface sediments and pore waters that are newly exposed during the dredging may replenish these congeners, as is reflected by concentrations at the downstream site.

The Fox River Mass Balance Study (Steuer and others, 1995) estimated a PCB volatilization-to-advection ratio of 13 percent. Applying this ratio to the upstream PCB advection (20.9 kg; Aroclor*1242) yields an estimated 2.7 kg volatilization from the Fox River upstream from SMU 56/57 during the dredging period. Air monitoring at the shore-processing site indicated that between 0.3 to 4.9 kg of PCB volatilized from that facility during the 106 days of onshore processing (Blasland, Bouck, and Lee, Inc., 2000; David Grande, Wisconsin Department of Natural Resources, written comm., 2000).

To put into context the PCB input to the water column during the dredging operation (16.9 kg), one can consider PCB loading from
PCB transport back into the river from the onshore-processing operation

After filter presses removed most solids from the incoming slurry, the effluent was passed through sand and carbon filters before being discharged back to the river at a rate of more than 700,000 gal/d. On five days, 80-L samples were collected by the USGS (over an 8–12 hour period) from the shore-process-discharge pipe. Total PCB concentrations in the effluent ranged from 82–676 ng/L with a mean concentration of 422 ng/L. These values did not appear to be normally distributed. A conservative approach, applying the median concentration (509 ng/L) to the effluent volume discharged during the entire dredging operation (76,213,900 gallons), resulted in 0.147 kg of PCBs being returned to the river.

Of the 654 kg of PCBs that were processed onshore or held in the settling basins (Montgomery Watson, 2000; Richard Weber, Montgomery Watson, written comm., 2000), less than 0.03 percent was returned to the river. Additionally, the congener distribution (fig. 13) of these effluent samples was markedly different from that in the water column samples—most of the more chlorinated congeners (higher health risk) had been removed. Thus, a very small PCB mass was returned to the river, and this small mass was made up of a less toxic PCB mixture.

Postdredging PCB concentrations and loads

Dredging was discontinued on December 15, 1999. Low temperatures and freezing water in pipelines, process equipment, and the river surface required too many operating adjustments in all aspects of the hydraulic-dredging, water-treatment, and dewatering processes for the operation to continue.

Three sets of water-column samples at the two transects were collected after the termination of dredging. Net daily PCB transport decreased (range was −12 g/d to 2 g/d) from that during active dredging. The dissolved-phase PCB concentration, however, still increased substantially from upstream to downstream (fig. 14) due to the deposit (a 15–21 percent increase). On two of the sampled postdredging days, the particulate PCB concentration decreased (as did TSS concentration) at the downstream site. Apparently, the dredged area may be functioning, at least temporarily, as a depositional area. Daily mean flows during the postdredging sampling were moderate—less than 3,000 ft³/s (fig. 10)—and also may have tended to promote deposition.

Even though a new sediment layer is exposed—with greater PCB concentrations at the sediment surface than before the start of dredging (thus the observed increase in dissolved PCB)—the overall PCB concentration has decreased because of settling of particles in the dredged area. These data do not indicate how long this settling will continue, or at what rate of streamflow the deposition will cease, or whether net scour of the exposed PCB sediment will occur. The dredging operation was planned to resume in summer or fall of 2000. The preceding observations were based on three sets of data points; more postremediation sampling would provide a stronger basis for conclusions.
Adjusting water-column PCB concentrations to allow comparison with onshore-sample PCB data

PCB aroclor analyses provided the foundation for the onshore-processing (slurry, trucked press cake) PCB concentrations (Blasland, Bouck, and Lee, Inc., 1999). However, to reduce the limits of detection, the 80-L water column samples were analyzed on a congener-specific basis. The congener-specific analysis approach is expensive ($835 per sample); thus, only a few onshore-processing samples were analyzed to this level of detail. Most samples collected onshore were examined with the less expensive Aroclor-basis PCB analysis. Therefore, to compare water-column results with the onshore-process PCB masses, a water-column PCB Aroclor concentration had to be estimated (Aroclor* 1242) from the congener-specific data. This was done by an approach developed in a previous remediation assessment (Fox River Remediation Advisory Team, 2000). The conversion was based on the dissolved (35 percent) and particulate (65 percent) average phase distributions (figs. 8B and 8C) and the Aroclor/congener sum ratios as calculated in the previous assessment.

The congener sum PCB load of 16.9 kg was adjusted to an Aroclor* 1242 basis as follows:

$$\text{Aroclor}^{*} 1242 \text{ PCB load} = (0.35)(16.9 \text{ kg})(0.88) + (0.65)(16.9 \text{ kg})(0.85) = 14.5 \text{ kg},$$

where 0.88 and 0.85 are the Aroclor/congener sum ratios for the dissolved and particulate phases. Thus, the net water-column load due to dredging is estimated to be 14.5 kilograms on an Aroclor* 1242 basis. A similar conversion on the congener summation PCB load entering the deposit area from upstream (24.5 kg) resulted in 20.9 kg PCB mass on an Aroclor* 1242 basis.

Lessons learned

Commonly used techniques such as measurement of total suspended solids (TSS) and turbidity were inadequate to describe transport of PCBs during a dredging operation in the Fox River. Little or no measurable difference was found between the upstream and downstream TSS concentrations (or loads) over the length of the operation. However, neither turbidity nor TSS was sufficient to predict PCB transport because of increased PCB concentration on a particle and dissolved-phase PCB concentration. Approximately 35 percent of the PCB load at the downstream site was in the dissolved phase. Results of the study described here indicate that if chemical transport is to be quantified during a PCB remediation, then monitoring of TSS and turbidity alone is not adequate.

The study illustrates the importance of collecting water-column samples at numerous vertical and lateral locations to represent an entire transect concentration. The study found lateral concentration differences that would skew a sample if the entire cross-section was not adequately sampled. Additionally, in a dynamic situation (dredging operation), even in a large river, sampling over a prolonged interval is necessary to obtain a representative daily concentration of a constituent of interest.
Furthermore, the results of this study illustrate that a concentration-based approach to assessing remediation can be misleading. Clearly, the water-column PCB concentration increased as a result of dredging, but until this concentration is converted to a mass basis, comparisons such as the following cannot be made: that the PCB load into the water-column mass represented less than 2.5 percent of what was dredged from the deposit and approximately 9 percent of what was annually transported by the Fox River in 1994–95. The onshore-process effluent median PCB concentration of 509 ng/L may initially appear substantial, but when converted to a mass (0.147 kg), one can conclude that this is negligible compared to the mass of PCBs that was permanently removed from the deposit. Lastly, concentration-based approaches do not necessarily require a sample that represents an entire cross-section. Such sampling, if done only on the deposit side of the river (fig. 6), would have provided a biased data set.

Dredging ceased during arrival and departure of the coal vessels; ship movement apparently increased PCB transport in the area. On four sampling days, vessels moved in or out of the area shortly before or during sample collection (fig. 9). On the two days when ship movement coincided with sample collection, the PCB transport increase was more pronounced (400–600 g). The PCB loading increase due to vessel movement was probably not sustained throughout the entire day; thus, applying a daily mean flow to this concentration probably biased the resulting PCB load on the high side. The concentration increase during vessel movement (figs. 7 and 9), however, is substantially higher than the predredging days in August or the postdredging days (fig. 14). Vessel movement is a continuing PCB transport mechanism regardless of dredging operations.

In summary, hydraulic dredging, by means of a horizontal auger cutter head and permeable silt curtain, resulted in a net PCB load (Aroclor 1242) of 14.5 kg to the water column in the Fox River while 654 kg were permanently removed from the deposit. At the same time, less than 0.15 kg was discharged back to the water column from the onshore processing (fig. 1). This is compared to an annual load (congener summation) (1994–95) of 186 kg from the Fox River into Green Bay.

References

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