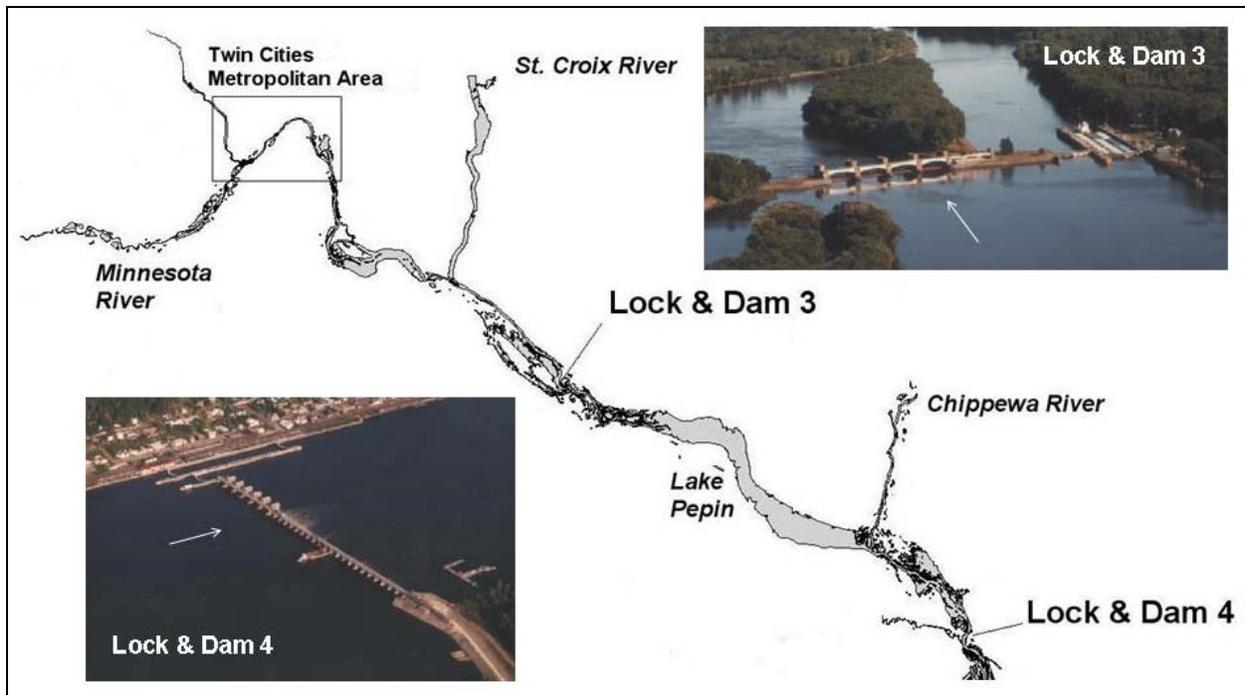


# Temporal Changes in Contaminant Levels in Suspended Sediment at Locks and Dams 3 and 4 on the Mississippi River



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## **Introduction**

Suspended sediment provides an important matrix for sampling pollutants in aquatic environments since trace elements, chlorinated hydrocarbons and other polar organic compounds have a strong affinity to bind or adsorb to fine-grained sediments, particularly those with high levels of organic matter (Horowitz 1991; Karickhoff et al. 1979). Whole-water concentrations of these pollutants are typically found in highest concentrations in the particulate fraction in turbid river systems and represent an important component in downstream transport in the Mississippi River (Meade 1995; Balogh et al. 1997; Rostad et al. 1999). Contaminant analysis of sediment trap samples provides an efficient and simple method for collecting and estimating particulate-bound contaminants and can provide reasonable estimates of particulate-phase contaminant concentrations in water if ambient concentrations of suspended particulate matter are available during trap deployment (Sullivan 1995; Sullivan and Steuer 1999). Resuspension of contaminated bed sediments contributes to increased water column concentrations, affects partitioning of these pollutants into the dissolved phase, and provides direct exposure pathways to aquatic organisms, especially filter feeding biota.

In the late 1980s, the Wisconsin Department of Natural Resources began using sediment traps to collect time-composited samples of suspended sediment to evaluate contaminant concentrations in the Mississippi River, especially PCBs and trace metals from upstream point and non-point source inputs from the Minneapolis-St. Paul (MN) Metropolitan Area (Sullivan 1995). Sediment traps have been used as a common limnological tool for over 100 years (Reynolds et al. 1980). It was believed these simple devices could provide useful information for evaluating long term contaminant trends in the Upper Mississippi River at a time when low-level water column contaminant measurements were not available, costly or difficult to collect.

This report provides a summary of the long term sediment trap data collected at US Army Corps of Engineers navigation locks and dams at Red Wing, Minnesota (LD 3) and Alma, Wisconsin (LD 4) on the Upper Mississippi River. The main objectives of this evaluation are to summarize the sediment trap data, discuss factors influencing the results and provide an assessment of long term changes in contaminant concentrations. This review will provide information for evaluating the effectiveness of this sediment monitoring effort and determining the need for possible modifications in this monitoring program.

## **Methods**

Suspended sediment samples were collected seasonally in the upstream auxiliary lock chambers at Mississippi River Locks and Dams 3 and 4 from 1987 through 2005 using cylindrical glass sediment traps (see map on cover). The auxiliary lock chambers are not functional and provide a relatively quiescent and secure area for deploying the traps near the main channel of the river. Vertical (0.5-1.5 m deep) and seasonal (spring, April-June; summer, June-August; and fall, September-November) composite samples were obtained for analysis of heavy metals, chlorinated hydrocarbons (primarily PCBs),

nutrients and organic matter (total volatile solids and total organic carbon). Sampling was primarily limited to spring and fall seasons. Field sampling and laboratory analytical methods have been previously described (Sullivan 1995). The Wisconsin State Laboratory of Hygiene in Madison, Wisconsin analyzed the sediment samples following U.S. EPA approved procedures. A summary of laboratory method detection levels and associated quality assurance information is presented in Table 1. The PCB data presented in this summary represent total PCBs as derived by an Arochlor-based analysis prior to September 1991 and a congener-based analysis (congener sum) after this date. The Arochlor-based method had a detection limit of 50 ng/g (Sullivan 1995). The switch to a congener-based method was implemented to improve the analytical detection limit since sediment trap PCB concentrations declined rapidly and were usually less than 50 ng/g at LD 4.

River flows during trap deployment periods were obtained from the nearest USGS gaging stations at Prescott, WI (for LD 3) and Winona, MN (for LD 4). Data for 2005 were supplemented by USCOE flow data for these two dams when USGS data were not available.

Statistical evaluations were completed using STATISTIX, version 8.0 (Analytical Software 1994). Graphs were created using Microsoft Excel, then imported into Microsoft PowerPoint for report layout.

## **Results and Discussion**

### **Organic Matter and Manganese**

Particle size and organic matter content strongly influence the ability of suspended sediment to bind or adsorb heavy metals, chlorinated hydrocarbons and nutrients. To accurately assess the enrichment of suspended sediment by these chemicals, it is necessary to account for differences in particle size, including surface area, and organic matter content. Although direct measurements of particle size were not determined in this study, surrogates for particle size were estimated by measuring manganese (Mn) (Wiener et al. 1984; Moody et al. 1999) and organic matter content (Horowitz 1991). Organic matter was measured directly by total organic carbon (TOC) analysis and estimated using loss on ignition (total volatile solids, TVS).

Mn is a common trace element found in the earth's crusts and soils (Hem 1970 and Baudo and Muntau 1990). Mn oxide is known to be an "excellent scavenger" of trace elements (along with iron) and is found as a coating on mineral grains and fine sediment (Horowitz 1991). Mn provides another method for normalizing sediment for grain size effects provided local enrichment sources are not present. This element has been used successfully to evaluate the enrichment of heavy metals in Upper Mississippi River bed sediments (Wiener et al. 1984; Sullivan and Moody 1996).

The TOC content in sediment trap samples from LD 3 and 4 typically ranged from about 2 to 6 % with generally higher values found during the fall deployment period (Figure 1).

An unusually high value (9.6%), at LD 3 in the fall sample from 1988, may be an anomaly since a similar elevated TVS level was not evident in this sample. In general, suspended sediment collected at LD 4 had a higher TOC content than LD 3 samples, likely reflecting inorganic solids settling and algae production in Lake Pepin. LD 4 samples may have also been influenced by suspended particulate matter input from the Chippewa and Buffalo Rivers, which enter upstream of this dam. However, the specific influence of these tributaries was not evaluated in this study.

TVS levels in suspended sediment were moderately variable and ranged from about 6 to 13% at LD 3 and 4, with higher levels normally found during the fall collection period (Figure 1). As is evident with TOC, the TVS level in samples from LD 4 was higher than that in samples from LD 3. The highest TVS levels typically occurred during fall low flow periods. TVS exhibited a significant ( $P \leq 0.05$ ) positive correlation with TOC in samples collected at LD 4, but not at LD 3 (Table 2).

Mn concentrations in LD 3 and 4 sediment traps ranged from about 1,000 to 6,000  $\mu\text{g/g dw}$  (Figure 1). The highest levels were typically found during low flow periods and were consistent with the patterns described for TOC and TVS. Possible exceptions to these patterns were high Mn concentrations in fall samples from LD 4 during low flow periods. It is hypothesized that the Mn enrichment of trapped sediment at LD 4 may reflect a release of dissolved Mn from Lake Pepin's sediments during periods of bottom water anoxia (Ruttner 1972). The dissolved Mn may have been assimilated by phytoplankton or formed particulate-bound suspensoids that were transported out of the lake and then collected by traps deployed downstream at LD 4.

The TOC and TVS levels in suspended sediments exhibited many significant positive correlations with trace metal concentrations (Cu, Pb, Mn, Zn), PCBs, and total Kjeldahl N (Table 2). These responses are likely particle size related, as discussed previously, and again support the need to account for this sediment property when evaluating sediment enrichment of these chemicals in trap samples.

### Effects of River Flow

River flows during trap deployment periods ranged from about 16,000 to 140,000 cfs (Figure 1). The highest flows were recorded during spring runoff, especially in 2001. The lowest flows were encountered during fall deployments in the late 1980s, late 1990s, and early 2000s. River flow normally exhibited significant ( $P \leq 0.05$ ) Spearman rank correlations with the rate of sediment accumulation in the sediment traps (gross sedimentation) and organic matter (TOC/TVS) and Mn composition of trapped materials (Table 2). Regression analysis indicated these relationships were non-linear (Figure 2). Since river flow had a strong influence on suspended sediment organic matter and Mn contents (and hence particle size), flow also exhibited significant correlations with many other sediment constituents measured in this study (Table 2).

Gross sedimentation rates were substantially greater and the trapped materials contained lower organic matter and Mn contents during periods of high flow (Figure 2).

Higher flows likely resulted in increased turbulence and greater potential for carrying suspended inorganic particulate material, especially fine sands. In contrast, low flows likely carried suspended material with smaller particle size and greater organic matter content, as reflected in higher TOC and TVS levels. Low flows also favor increased algal production in the Mississippi River and its large tributaries as a result of increased residence time, reduced turbulence and improved light penetration (lower suspended solid concentrations). As a result, sestonic algae would be expected to contribute to higher particulate organic matter flux into the sediment traps during periods of low flow.

### Gross Sedimentation Rates at Lock and Dam 3

Seasonal data evaluation allowed a closer examination of factors influencing gross sedimentation rates at LD 3, which varied from about 0.05 to 0.2 cm/d (Figure 3). The highest rates were recorded during spring flow periods, but gross sedimentation rates were strongly correlated to river flow during both the spring and fall seasons, with greater than 50% of the explained variation due to changes in river flow. High river flows are typically associated with greater total suspended solids (TSS) concentrations and are likely an important factor influencing sediment accumulation rates. This was verified by comparing gross sedimentation rates at LD 3 to TSS data collected at this location during sediment trap deployments from separate monitoring programs (UMRCC, 2002). Gross sedimentation rates were significantly and positively correlated with river TSS during both spring and fall periods, but spring periods yielded greater accumulation rates at equivalent TSS concentrations (Figure 3).

### Temporal Changes in Sediment Composition

Temporal changes in suspended sediment contaminant levels were evaluated following two approaches. The first method utilized a Spearman rank correlation analysis (constituent x year) of all data collected for a particular site, including normalization for organic matter and particle size effects using TOC, TVS and Mn where appropriate (Table 2). Those constituents showing significant correlations ( $P \leq 0.05$ ) were also plotted and fitted with linear or non-linear regression (Figures 4 to 10) as a means of generally visualizing patterns in long term trends. For clarity, the regression equations were omitted from these figures. For each contaminant, a trend was considered to be real if both the raw data (non-normalized concentrations) and at least two of the normalized concentrations revealed significant correlations by year.

Long term trend assessment using Spearman rank correlation revealed significant temporal decreases in Cd, Cu, Pb, Hg, ammonia-N (NH<sub>x</sub>), total phosphorus (TP) and PCBs at LD 3. Significant decreasing trends in Cd, Hg and PCB concentrations were also noted at LD 4 (Table 2). The highest correlation coefficients were observed for Hg and PCBs at LD 3 and 4 and for TP at LD 3. It was interesting to note that no contaminant measured in this study exhibited an increasing temporal correlation. These results suggest a broad decrease in the measured pollutants carried on suspended sediment during the monitoring period and are consistent with previous studies demonstrating reduced loadings of pollutants from upstream sources, especially

industrial and municipal point sources in the Twin Cities area of Minneapolis and St. Paul (Balogh et al. 1999; U.S. EPA 2000). The significant reductions in TP concentrations at LD 3 are particularly noteworthy and likely reflect major efforts to remove P from municipal wastewaters in the Twin Cities Metropolitan Area in the past decade (Metropolitan Council 2006, MPCA 2004).

Regression plots of the suspended sediment contaminant concentrations and associated organic matter and Mn-normalized concentrations revealed both linear and non-linear temporal trends (Figures 4 – 10). Linear regressions were fit to Cd (Figure 4), Cu (Figure 5), NHx (Figure 8) and TP (Figure 9) data. For Pb (Figure 6), Hg (Figure 7) and PCBs (Figure 10), polynomial regressions seemed to best fit the data. The regression lines and corresponding regression coefficients ( $R^2$ ) in these trend plots were only provided where Spearman rank correlation analyses of the temporal data were statistically significant (Table 2) as discussed above. The only exception was for Cd at LD 3, where a high value of 8.4 ug/g was measured in the fall sample in the fall 2004 sample, resulting in a flattened regression line (not shown). It is believed that Cd levels have decreased significantly at both LD 3 and 4 over the time period, but the single outlier at LD 3 skewed the regression for this site (Figure 4).

A second approach for assessing temporal changes in suspended sediment contaminant levels was performed by dividing the data for each site into two equal assessment periods (1987-1995 and 1997-2005) with segregation by season (spring versus fall). Data for 1996 and summer data were excluded. This approach resulted in a decreased sample size for assessing temporal changes and likely decreased the power to detect trends. However, this method provided a means for evaluating trends on a seasonal basis that was missed in the first approach described above.

This trend assessment by site and season evaluated all measured constituents (Table 3), including the organic matter and Mn-normalized contaminant concentrations (Table 4). Temporal differences in suspended sediment contaminant levels between assessment periods were established using Kruskal-Wallis AOV ( $P \leq 0.05$ ), a non-parametric method applied to the ranks. The percentage change in the average measurement between assessment periods was calculated to provide a general indication of the magnitude of the change.

Concentrations of Cd, Cu, Hg and PCBs in spring-deployed sediment traps at LD 3 and 4 decreased significantly between the two assessment periods (Table 3). The typical percent change in contaminant concentrations ranged from about -17 to -47%. Gross sedimentation rates in spring traps at LD 4 increased significantly (44%). Unfortunately, accompanying total suspended solids data were not available for this site to corroborate this response.

Temporal changes in suspended sediment contaminant concentrations in fall-deployed traps varied between sites. Only PCB concentrations showed a significant decrease at both LD 3 and 4 between the two assessment periods (Table 3). Pb and Hg

concentrations decreased significantly at LD 3, but only Cd concentrations exhibited a significant decline at LD 4.

TOC, TVS and Mn-normalized contaminant concentrations provide a better means for evaluating temporal changes since these adjustments account for organic matter and particle size effects as discussed above. Significant reductions in two or more normalized concentrations of Cd, Hg and PCBs were apparent in spring-deployed traps at LD 3 and 4 between the two assessment periods (Table 4). In addition, normalized Pb concentrations decreased significantly at LD 3 between these time intervals. The percent change in average normalized concentrations between assessment periods ranged from about -30 to -50%.

In fall-deployed traps, significant reductions in two or more normalized contaminant concentrations were evident for PCBs at LD 3 and LD 4 between the two assessment periods (Table 4). In addition, Hg decreased significantly at LD 3 and Cd and TP decreased at LD 4 over the two time periods. Mn-normalized concentrations of Cu, Pb, Hg and Zn decreased significantly in fall-deployed traps at LD 4 between the two assessment periods; however, these trends were not corroborated when normalized for organic content (TOC or TVS). The decreasing concentration trends observed for some Mn-normalized concentrations at LD 4 were likely associated with higher Mn levels in suspended sediments in the fall-deployed traps during the second assessment period (1997-2005, Figure 1).

### **Summary and Conclusions**

Levels of organic matter (TOC and TVS) in suspended sediment collected with sediment traps varied spatially and seasonally. Samples from LD 3 typically yielded lower organic matter levels than samples from LD 4, likely reflecting inorganic solids settling and autochthonous organic matter (algal) production in Lake Pepin, just upstream of LD 4. The lowest organic matter levels were normally observed in spring-deployed traps, reflecting suspended sediments that contain higher inorganic material due to increased turbulence during periods of higher river flow. The Mn concentrations in suspended sediment exhibited spatial and seasonal patterns similar to those observed for organic matter content. Changes in the organic matter and particle size content of suspended sediments are important factors to consider for sediment quality and trend assessments since these properties influence the ability of suspended sediment to bind or adsorb metals, chlorinated hydrocarbons and nutrients.

Gross sedimentation rates in sediment traps were strongly correlated with river flow and reflect higher TSS concentrations during periods of higher flow. Sedimentation rates were typically greatest during spring trap deployments, with the highest rates measured at LD 3.

Significant decreases in trace element, nutrient and PCB concentrations in suspended sediment were noted during the 1987-2005 monitoring period, indicating reduced enrichment of suspended sediment in the river. The most consistent temporal changes

were decreased Cd, Hg, PCB concentrations at both LD 3 and LD 4, with an average reduction ranging from about 30 to 50% during the monitoring period. Significant reductions in Cu, Pb, ammonia-N and total P were also noted in sediment trap samples, but these reductions varied by site and season. None of the contaminants measured in this study exhibited an increasing temporal trend. Reduced enrichment of suspended sediment suggests reductions of pollutant inputs from upstream nonpoint and point sources during the monitoring period.

The use of sediment traps to monitor contaminants of concern in the Mississippi River has provided valuable information for assessing water quality trends and for evaluating pollutant abatement activities. It is recommended that this monitoring program continue with some minor modifications. Suspended sediment-bound contaminants that have not shown a significant increasing trend (Cr, Zn) or present at low concentrations (nitrite-nitrate-N) or present in concentrations below levels of concern, can be omitted from future monitoring. The frequency of sampling for PCBs at LD 4 can be reduced since these contaminants are found at relatively low concentrations at this site. Future phosphorus analysis should include partitioning into biologically available and refractory forms since this information may provide more detailed information for evaluating watershed phosphorus load reductions associated with the Lake Pepin TMDL. When funding and laboratory support are available, considerations should be given to periodically screening for other contaminants of concern that bind or adsorb on suspended sediment particles.

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