Mississippi River Long Term Sediment Trap Contaminant Trends: Lock and Dam 3 and 4 (1987-2017)

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Suspended Sediment Contaminant Concentration Trends

The Wisconsin Department of Natural Resources (WDNR) has been conducting long term monitoring of suspended sediment contaminant concentrations in the Mississippi River at Lock and Dam 3 (Red Wing,

MN) and Lock and Dam 4 (Alma, WI) since 1987 (Figure 1). Suspended sediment is collected passively through the deployment of glass sediment traps for roughly 60 days in a slack water area immediately upstream of both lock and dams during spring, summer and fall (Figure 2). 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. 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. The primary purpose of this monitoring has been to assess long term trends and to provide an estimate of whole-water particulate-phase concentrations.



Figure 1. Location of sediment trap sampling sites at Lock and Dam 3 (Red Wing, MN) and Lock and Dam 4 (Alma, WI).



Figure 2. Example of sediment trap deployment at Lock and Dam 3. The traps are lowered below the water surface for roughly 60 days of passive sampling.

Suspended sediment or particulate matter in river water represents a major portion of contaminant transport, especially in turbid rivers like the Mississippi River. Organic chemicals that don't dissolve readily in water such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) or organochlorine pesticides and elements such as heavy metals, adsorb to fine-grained suspended sediment particles, especially those high in organic matter content. Some sources of contaminant input include runoff from urban and agricultural land use, deposition from coal and waste incineration, resuspension of contaminated bed sediments and wastewater discharges.

An illustration of PCB and mercury concentrations in suspended sediment at both monitoring sites is shown in Figure 3. River discharge, season, sediment particle size, organic matter content, and changes in contaminant inputs influence contaminant concentrations in suspended sediment. Spring sediment traps are generally characterized as having higher sedimentation rates, lower organic matter content and larger particle size than fall-deployed traps.



Figure 3. Long term sediment trap polychlorinated biphenyl (PCB) and mercury (Hg) trends at Lock and Dam 3 and 4 (1987-2017). PCB concentration is in nanograms/g and mercury concentration is in micrograms/g.

The WDNR consensus-based sediment guidelines are based on the effect level at which toxicity to benthic-dwelling organisms are predicted to be unlikely and probable, respectively (Table 1). There is an incremental increase in toxicity as the contaminant concentrations increase between the threshold effects concentration (TEC) and probable effects concentration (PEC), although specific numeric values relating to degree of toxicity can't be derived. Based on the ranges of concentration related to the TEC and PEC values, a qualitative system was developed to provide a basis of relative levels of concern with

increasing contaminant concentrations. The levels of concern can be used to rank and prioritize sites for additional investigation. The midpoint effect concentration (MEC) is a concentration midway between the TEC and PEC concentrations.

Table 1. Consensus-based sediment quality guidelines (CBGQGs) based on toxicity to benthic-dwelling organisms. Adapted from MacDonald et al. (2000).

Level of Concern	Threshold Effect Concentration (TEC)	Level of Concern	Midpoint Effect Concentration (MEC)	Level of Concern	Probable Effect Concentration (PEC)	Level of Concern
Level 1	From	Level 2	TEC + PEC /2	Level 3	From	Level 4
≤ TEC	CBSQGs	< TEC ≤ MEC	= MEC	> MEC ≤ PEC	CBSQGs	> PEC

PCB and mercury concentrations in suspended sediments are normally higher in samples collected from Lock and Dam 3 than at Lock and Dam 4 (Figure 3). This is due to the closer proximity to the Twin Cities Metropolitan Area, a major source of these contaminants. In addition, Lake Pepin, a natural riverine lake located in Pool 4, acts as a natural sediment trap, which results in decreased transport of these contaminants downstream. The mercury (Hg) samples shown indicate the spring, summer and fall samples, therefore the annual variability is evident in the data plots.

In the case of non-polar organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and PCBs, the bulk sediment concentrations should be normalized to the total organic carbon (TOC) content for site to site comparison purposes. It has been established that the organic carbon content of sediment is an important factor influencing the movement and bioavailability of nonpolar organic compounds (e.g. PAHs and PCBs) between the organic carbon content in bulk sediments and the sediment pore water and overlying surface water. Biological responses of benthic organisms to nonionic chemicals in sediments are different across sites when the sediment concentrations are expressed on a dry weight basis, but similar when expressed on an organic carbon normalized basis. Figure 4 shows the PCB data normalized for total organic carbon content.



Figure 4. Long term sediment trap polychlorinated biphenyl (PCB) trends at Lock and Dam 3 and 4 (1987-2017). PCB concentration is in nanograms/g and normalized to 1% total organic carbon content. Long term total organic carbon (TOC) concentrations are show in the lower panel.

A suite of select metals of concern (Cd, Pb, Cr, Mn, Cu and Zn) of which limited sampling has occurred during the past ten years were sampled in 2017 (Figure 5). The sampling frequency of these parameters was reduced over the past ten years due to declining concentrations and funding constraints. However, it is important to revisit these parameters on a periodic basis to ensure that concentrations are continuing to decline. These parameters will be sampled every five years moving forward to ensure concentrations are continuing to decline. The 2017 sampling confirmed continued declines for all six parameters and is an encouraging result. The success of metals reductions in the Mississippi River is a

potent reminder of the overwhelming success of pollution reduction policies in the United States since the passage of the Clean Water Act in 1972. The lessons of the past indicate that it is much better to be proactive rather than reactive in dealing with environmental contaminants. It is always more costeffective to prevent environmental damage than it is to "clean up" environmental damage after it has occurred.



Contaminant Concentrations in Mississippi River Suspended Sediments at LD3 and LD4

Figure 5. Long term sediment trap metals concentrations (1987-2017). Concentrations are in mg/kg.

In the interest of broadening the scope of the assessment, sampling for PAHs also took place in 2017 (Figure 6). It is useful to have a PAH baseline value established at these sites for future investigations. This group of toxic hydrocarbons has caused considerable environmental damage, therefore establishing a baseline for these contaminants is important. Carbon normalized total PAH concentrations at both LD3 and LD4 were substantially less than those collected from bed sediments near both sampling sites in recent years. Presently, it is unclear if this is a function of differences in sediment and contaminant transport at the sampling site or reflective of more recent PAH concentration reductions. These mechanisms need to be explored further and should be the topic of future work.



Total Polycyclic Aromatic Hydrocarbons 2017



Temporal trends indicate a decrease in PCB and metal concentrations at both monitoring sites. PCB concentrations are presently one-third to one-fourth those observed in the late 1980s, while present mercury concentrations are less than one-half of concentrations measured during the late 1980s. Pollution abatement efforts to reduce the use and discharge of these contaminants have led to these reductions in contaminant concentrations. These findings underscore the need for the management community to pivot efforts toward non-point pollution reduction efforts while continuing to reduce legacy contaminants. Additional efforts should also be directed toward efforts to better understand and quantify emerging and less understood environmental contaminants such as: polybrominated diphenyl ethers (PBDEs), hexabromocyclodecane (HBCD), triclosan, phthalates, microplastics, and estrogenic compounds.

References

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