Contaminants in Mississippi River Suspended Sediment Collected with Cylindrical Sediment Traps

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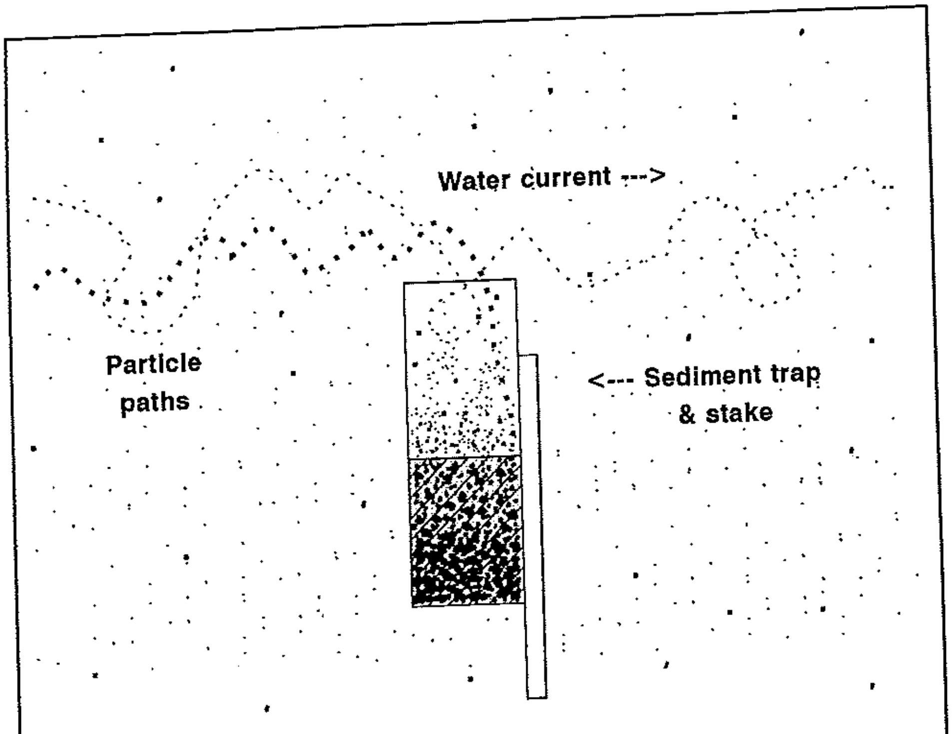

Suspended sediment is collected through a process of fluid exchange where particles are carried into traps by eddies - W.D. Gardner 1979

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SUMMARY AND CONCLUSIONS

Glass sediment traps were deployed in the Upper Mississippi River to collect composite samples of suspended sediment for contaminant analysis between 1987 and 1994. Most of this monitoring was conducted at Lock and Dam 2 (L/D 2, Hastings, Minnesota), L/D 3 (Red Wing, Minnesota) and L/D 4 (Alma, Wisconsin). After the summer flood of 1993, this monitoring effort was expanded to include 13 Upper Mississippi River sites between Champlin, Minnesota and Dubuque, Iowa and one station on the Minnesota River near Ft. Snelling, Minnesota. The objectives of this work were to assess the contaminant concentrations of suspended sediments in the Upper Mississippi River, evaluate factors influencing contaminant concentrations, assess temporal trends and compare contaminant concentrations in suspended sediments to recent contaminant investigations on the river.

Polychlorinated biphenyls (PCBs) and cadmium concentrations in sediment traps exhibited a distinct longitudinal profile with highest concentrations observed in suspended sediments collected from navigation Pools 2 to 4 with concentrations decreasing downriver. These spatial trends reflect point and nonpoint source pollution contributions from within the Twin Cities metropolitan area, resuspension of contaminated bed sediments, and dilution by less contaminated suspended sediment input below Lake Pepin. Copper, mercury, lead and zinc concentrations in suspended trap samples exhibited a more variable longitudinal profile in the study reach. Chromium concentrations showed an increasing trend downstream. This spatial trend was absent when chromium values were normalized for organic matter and particle size.

Differences in the particle size and organic matter content of sediment trap samples were addressed by normalizing the contaminant concentrations for total volatile solids, total organic carbon and manganese content. Manganese was used to provide an independent normalization for sediment particle size exclusive of organic matter content. Normalized data provided a relative assessment of suspended sediment contaminant enrichment due to anthropogenic inputs. Suspended sediments collected between Pools 2 and Lake Pepin (Pool 4) were enriched with PCBs and cadmium as reflected by high normalized concentrations. The absence of high normalized values for other trace elements (copper, chromium, mercury, lead and zinc) in this same reach suggests lower enrichment of suspended sediment from local point and nonpoint source inputs.

Suspended sediments collected from the lower Minnesota River were enriched with most trace elements and phosphorus when normalized for organic matter and manganese content. These data indicate this tributary provides an important source of these contaminants to the Mississippi River at Pool 2. In contrast, PCBs were not detected (< 1 ng/g) in suspended sediment collections from this tributary.

The longitudinal distribution of PCBs and cadmium in the Upper Mississippi River paralleled similar river contaminant profiles that have been reported for bed sediments, mayflies, fish and other environmental matrices. These results reflect the importance of suspended sediments in influencing the distribution, transport and bioavailability of these contaminants in the river's ecosystem.

Sediment traps were influenced by current velocity and turbulence that affected the particle size and organic content of trapped sediments collected at several sites above L/D 2, including the Minnesota River site. Monitoring sites with current velocity exceeding approximately 15 cm/s trapped less organic matter (< 2% total volatile solids) and more sand.

A definite seasonal pattern (spring versus fall) was observed in the gross sedimentation rate, total volatile solids and manganese content of trapped sediment. Changes in river flow and differences in the contribution of allochthonous versus autochthonous organic matter were believed responsible for these observations. Spring sediment trap samples were characterized as having higher sedimentation rates, lower organic matter content and increased particle size than fall-deployed traps. Sediment traps collected in the fall likely contained a greater proportion of autochthonous organic matter. These seasonal differences influenced contaminant concentrations since hydrophobic organic contaminants and trace elements have a strong affinity to bind to fine particles, especially those high in organic matter content.

Long term monitoring at L/D 3 between 1987 to 1994 indicated a significant reduction in PCBs, cadmium, copper, mercury, lead and zinc bound on suspended sediment. However, when contaminants were normalized for organic matter or manganese content, temporal trends were weak or not observed. The major factor influencing long term suspended sediment contamination was river flow that showed a significant increase during the study period. Higher flows increased the size of the particles in suspension and resulted in decreased organic matter content in suspended sediments. This resulted in a reduction in the surface area (binding sites) of the particles in suspension and contributed to lower sediment trap contaminant concentrations. In contrast to sediment trap contaminant concentrations, particulate phase contaminant mass transport and whole-water particulate phase contaminant concentrations increased due to greater total suspended solid (TSS) concentrations and mass transport during high flows. The impact of the 1993 summer flood did not appear to appreciably influence suspended sediment contaminant concentrations or mass transport over what has been observed historically.

Accurate estimates of whole-water particulate phase trace element concentrations were derived from sediment trap contaminant and TSS data at L/D 3. This was based on a comparison to independent trace element analysis of water samples using "clean-sampling" and "low-level" analytical methods. Maximum particulate phase contaminant concentration estimates for PCBs and mercury were 5.5 and 11 ng/L, respectively. These concentrations exceeded Wisconsin's water quality standards for PCBs (0.49 ng/L) and mercury (2 ng/L) by more than five fold. Actual exceedance was greater, since the dissolved and colloidal phases were not included in these estimates.

INTRODUCTION

Suspended sediments play an important role in the transport of contaminants in aquatic systems. It is well known that chlorinated hydrocarbons and heavy metals have a strong affinity to adsorb to fine-grained sediments, especially those high in organic matter content. Resuspension of contaminated bed sediments can contribute to increased water column concentrations and may allow for increased partitioning of contaminants into the dissolved phase. Contaminants in suspended particulate material represent another form of exposure to aquatic life, especially bivalves, which filter large volumes of water during normal feeding activity. Therefore, monitoring of contaminants in suspended sediments provides an important matrix upon which to further evaluate contaminant problems in riverine systems.

Sediment traps have been used as a limnological tool for over 100 years (Reynolds et al. 1980). Recent studies on the Mississippi River have demonstrated that cylindrical sediment traps can provide an efficient and simple device for collecting suspended sediments that are representative of the particle sizes found in the water column (Bartsch 1991, et al. 1995). In addition, these devices provide an inexpensive approach for collecting time-integrated suspended sediment samples. Sediment traps have also been used to evaluate the input of polychlorinated biphenyls (PCBs) from a source of contamination in Pool 5A of the Upper Mississippi River (Sullivan and Steingraeber 1995).

The Wisconsin Department of Natural Resources has been monitoring contaminant concentrations in suspended sediments in the Mississippi River through the use of sediment traps since 1987 (Sullivan 1992). This effort has largely focussed on two or three sites above and below Lake Pepin, a reach of the river known to have problems with contaminants, especially PCBs. As a result of funding provided by the U.S. EPA through the Wisconsin Flood Assessment Grant in 1993, this effort was expanded to include a 288 mile reach of the Upper Mississippi River extending from Champlin, Minnesota, to Dubuque, Iowa. The objectives of this work were to:

- assess the contaminant concentrations of suspended sediments in the Mississippi River from the Twin Cities metropolitan area to a few hundred miles downstream.
- evaluate factors that may be influencing contaminant concentrations in suspended sediments, especially river flow, and point and nonpoint source inputs.

- evaluate temporal changes in contaminant concentrations observed since monitoring initiation in 1987.

- compare contaminant concentrations measured in suspended sediments to biological samples and other recent contaminant monitoring investigations on the Upper Mississippi River.

Study Area

Initial contaminant studies using sediment traps were conducted at Lock and Dams (L/D) 2 (Hastings, Minnesota), 3 (Red Wing Minnesota), and 4 (Alma, Wisconsin) between 1987 and 1989 and at L/Ds 3 and 4 through 1994. As a result of the basin-wide flooding in the summer of 1993, this effort was expanded to include Mississippi River sites near Champlin, Minnesota; Lower St. Anthony Falls (SAF) L/D (Minneapolis, Minnesota); L/D 1 (Minneapolis, Minnesota); Lambert's Landing (St. Paul, Minnesota); L/D 2; lower Lake Pepin near Pepin, Wisconsin; L/D 5 (Minneiska, Minnesota); L/D 8 (Genoa, Wisconsin); L/D 9 (Lynxville, Wisconsin) and L/D 11 (Dubuque, Iowa). In addition, the Minnesota River, a highly turbid tributary to upper Pool 2, was sampled near Fort Snelling, Minnesota (Figure 1). A description of each monitoring site is provided in Table 1.

METHODS

Cylindrical, glass sediment traps were used to collect suspended sediment. Glass was selected to allow testing of chlorinated hydrocarbons, metals and nutrients. The traps were tall, wide-mouth jars that were manually cleaned prior to deployment (years 1987-90). Cleaning consisted of scrubbing traps with liquid detergent and rinsing with tap water. Next, traps were rinsed with 10% HCL followed by deionized water. Final rinses were accomplished with pesticide grade hexane followed by deionized water. Since 1991, ICHEM® certified-clean (model 221-500) 500 ml glass jars have been utilized for sediment traps. The sediment traps had a aspect ratio (height/diameter) of 2.4 between 1987 and 1990 and 3.0 since 1991. The inside diameter of the traps was approximately 5.5 cm.

A vertical composite sample of suspended sediment was collected by attaching 3 to 5 traps to a 3 m long, galvanized 1.9 cm o.d. pipe using vinyl tape. Traps were spaced at equal intervals along this pipe and suspended in the water column between 0.5 and 3.5 m. All traps were flushed several times with ambient river water prior to deployment.

Traps were normally deployed for 50-70 days during spring (April-June) and fall (September-November) periods. One collection was made during the summer (June-early September) of 1992 at L/Ds 3 and 4. Monitoring sites were near the main channel but were normally protected from strong currents, tow boat traffic and vandalism. The primary objective was to select sites that had relatively low current velocity (< 15 cm/s) to minimize turbulent scouring within the traps which can bias the collection towards coarser sediments. The upstream portion of auxiliary lock chambers provided optimal and uniform conditions meeting these objectives. It was more difficult finding suitable monitoring locations at St. Paul and at sites further upstream. As a result, some of the deployment sites were in areas of greater current velocity and turbulence.

At the completion of the exposure period, teflon-lined screw caps were added to the traps and the outside glass surfaces were cleaned with ambient river water and then placed in a cooler packed with ice during transit. Samples were allowed to settle overnight before measuring the mean sediment accumulation (±1 mm) of each trap. Notes were made regrading the color and presence of live or dead invertebrates. Water was carefully decanted down to about 1 cm of the sediment surface. Occasionally, small larval fish (mainly channel catfish) or crayfish were found to be inhabiting a trap. Under these conditions, sediments collected in these traps were discarded from the composite sample. Sediment trap samples were then shaken vigorously for several minutes and transferred to a quality-assured (clean) 1 qt mason jar (provided by the analytical laboratory) to form a vertical composite sample for a specific site. If sediment was too thick to pour, samples were shaken and transferred to the compositing jar with a stainless steel spoon. The composite sample was then mixed by shaking or stirring for several minutes. Subsamples for trace element, total volatile solids and nutrient analyses were then placed in separate 250 ml quality-assured polyethylene bottles. The remaining sample in the compositing jar was analyzed for chlorinated hydrocarbons (primarily PCBs) and total organic carbon.

Sediments samples were stored refrigerated prior to analysis by the Wisconsin State Laboratory of Hygiene (WSLOH) in Madison, Wisconsin. A summary of method detection limits and associated quality assurance information is provided in Table 2. Analytical methods have been described elsewhere (WSLOH 1992, 1993). However, some general descriptions are warranted. Sediment samples were air dried, mixed and passed through a 2 mm sieve to remove large debris prior to analyte extraction.

PCB analysis was performed on a total Aroclor® basis on samples collected prior to September 1991. This involved the use of a packed-column gas chromatograph with electron capture detection (GC-ECD). Congener-based PCB analysis was utilized on all samples collected from L/D 4 after October 1991 and all other sites after September 1993. This latter method utilized capillary column GC-ECD. This method yielded 85 detectable congeners, some co-eluting as pairs or triplets. The sum of these congeners provided an estimate of total PCBs. A comparison of both methods using reference samples from Lake Pepin (n=2) revealed the congener-based PCB results (congener sum) were greater than the Aroclor® totals by 17% (Sullivan, 1994). No adjustment in the PCB data reported here were made to account for this difference.

Sediment digestions for mercury analysis were performed using a block digester with a sulfuric-nitric acid mixture and a second digestion cycle using a potassium permanganate solution. The digestate was analyzed using cold vapor atomic absorption spectroscopy.

Sediment analysis for the remaining trace elements (cadmium, chromium, copper, lead, manganese, and zinc) were digested with nitric acid followed by hydrogen peroxide. The digestate was refluxed with dilute hydrochloric acid for inductively coupled plasma emission spectroscopy (ICP) analysis of trace elements. Dilute nitric acid was used as the final acid for furnace atomic absorption analysis of cadmium or lead.

Mississippi River flow data were obtained from the U.S. Geological Survey for their gaging station at Prescott, Wisconsin. Total suspended solids (TSS) data were available from Wisconsin's and Minnesota's ambient water quality monitoring data stored in the U.S. EPA STORET data base. Additional information for TSS was provided by the Metropolitan Council, Wastewater Services for sites near or within the Twin Cities area.

Sediment trap contaminant concentrations were normalized for organic matter and grain size differences using total volatile solids, total organic carbon and manganese concentration. The normalization procedure was accomplished by dividing the contaminant concentrations by the respective normalization parameter.

Whole-water particulate phase (ie. bound to suspended material) concentrations of PCBs and trace elements at L/D 3 were estimated by multiplying the average TSS concentration (g/l) measured during trap deployment at a nearby monitoring site by the suspended sediment contaminant concentrations (μg or ng/g dry wt).

Particulate phase contaminant mass transport (kg/d) was estimated using the average daily river flow during the trap exposure period.

Statistical procedures followed methods in STATISTIX, version 4.1 (Analytical Software 1994). Levels of significance were determined at a 0.05 level of probability.

RESULTS AND DISCUSSION

Total Suspended Solids and Gross sedimentation

Total suspended solid (TSS) concentrations in the study reach exhibited a distinct longitudinal profile (Figure 2) with highest concentrations found at St. Paul, Minnesota (RM 840), lowest values at lower Lake Pepin (RM 766), and an increase below Lock and Dam 4 (RM 753). This response mainly reflects high suspended solid mass transport from the Minnesota River and sedimentation within Lake Pepin (Sullivan 1989). Total suspended solids are normally positively correlated with river flow and as a result, concentrations are usually greatest during periods of runoff, especially high spring flows.

The rate of sediment accumulation within a cylindrical trap provides an estimate of the gross downward flux of sediment in suspension. The geometry of the trap and hydrodynamic factors restrict the resuspension of collected materials residing on the bottom of the trap, provided a non-turbulent boundary layer is established for quiescent settling (Gardner 1980a,b). Under highly turbulent conditions, scouring of trapped materials can bias the collection of particles and result in increased trapping of fine sands. Sediment trap samples collected from the Mississippi River at St Paul and Champlin, Minnesota (RM 840 and 871, respectively) and the Minnesota River at Fort Snelling, appeared to be dominated by fine sands and were likely influenced by greater current velocities and turbulence at these monitoring sites.

Gross sedimentation rates in the fall of 1993 and spring of 1994 showed a similar longitudinal response to that observed for TSS concentrations (Figure 2). Highest sedimentation rates (>0.25 cm/d) were found in trap samples collected in the Mississippi River at St. Paul (RM 840) and the Minnesota River, sites with TSS concentrations ranging from 50 to 150 mg/l. Lock and Dam 11 also exhibited a relatively high gross sedimentation rate (about 0.2 cm/d) in the spring of 1994 and would suggest high TSS concentrations during trap deployment at this site. Long term sediment trap data collected at L/D 3 revealed a significant positive correlation between TSS and gross sedimentation rate measurements (Table 3).

A very distinctive seasonal pattern was apparent when comparing long term sedimentation rates at L/Ds 3 and 4 (Figure 14). Spring rates were noticeably greater than fall measurements. This difference is likely attributable to greater spring river flows which may have influenced the mass and size of particles in suspension. Further, it is possible that the ultimate source(s) and composition of the suspended sediment may vary during these two periods. For example, watershed contributions of soil and stream bank erosion may be important during the spring period. However, fall samples may reflect greater contributions of organic matter associated with allochthonous (leaf fall) and autochthonous production (senescence of aquatic plants). This is partially supported by the higher organic matter content (total volatile solids) observed in fall sediment trap samples (Figure 2 and 14).

Long term trends at L/D 3 indicate a significant increase in TSS concentrations and gross sedimentation rates over the 7-year period (Figure 14 and Table 3). This trend reflects increased river flow over the study period.

Total Volatile Solids and Total Organic Carbon

Total volatile solids (TVS) and total organic carbon (TOC) are measurements of the organic matter content of a sample. Organic matter has a strong affinity to concentrate trace elements through adsorption, cation exchange, organometallic bonding, complexation and physical trapping (Horowitz 1991). In addition, there is normally a strong positive correlation between organic matter and sediment surface area or decreasing grain size. As a result, organic matter is actually an indirect measure of sediment grain size. The importance of grain size in influencing the capacity of sediments to concentrate trace elements is well known (Horowitz 1991). The organic carbon content of sediment also plays a direct role in binding nonpolar organic compounds (Karickhoff et al. 1979).

Both TVS and TOC were utilized in this study to normalize sediment trap data for differences in grain size and organic content. This dual approach was utilized since there was no significant correlation between TVS and TOC based on long term sediment trap data from L/D 3 (Table 3). This lack of correlation may be attributable to method differences and variation in the nature of trapped organic matter. TVS involves the ignition of a relatively large sample mass (about 25 g) with the loss in weight representing an estimate of organic matter. A much smaller sample size (about 0.5 g) is used in the TOC method. Further, carbonates are removed in the TOC analysis using a relatively strong acid (6M HNO_3) before ignition and measurement of the evolved CO_2. This acidification procedure may have resulted in the loss of labile organic matter in sediment trap samples. However, TOC analysis of bed sediments oxidized with 6 M H_3PO_4 did not reveal a significant difference from samples oxidized with nitric acid based on TOC method testing by the laboratory used in this work (WSLOH 1995). Therefore, the reason for the lack of correlation between TVS and TOC in sediment trap samples remains unclear.

TVS and TOC contents of sediment trap materials collected in the fall of 1993 and spring 1994 showed a similar longitudinal response (Figure 2). Highest values (>10% TVS and >4% TOC) were normally found above L/D 1 (RM 848) and lower Lake Pepin (RM 766). However, some exceptions included the Champlin, MN site (RM 871) and the St. Anthony Falls site (RM 853) in the spring of 1994 when lower TVS and TOC were found. The Minnesota River site also had relatively low TVS (2%) and TOC (0.8-0.9%) contents in both spring and fall collections. Similarly, the Mississippi River at St. Paul (RM 839) had reduced TVS (4%) and TOC (1.6-1.7%) in comparison to downstream sites. In general, current velocity and turbulence were more variable at these upstream sites and likely influenced the composition of materials collected by the sediment traps.

The TVS and TOC content of suspended sediments were negatively correlated to river flow, total suspended solids and gross sedimentation rates (Table 3). These variables are closely interrelated. High flows enhance the transport and resuspension of larger particles, which are likely dominated by greater inorganic materials, especially coarse silts and fine sands. Under low flow conditions, suspension of sands is reduced and autochthonous production of organic matter (ie. phytoplankton) is greater due to increase hydraulic retention time within the large riverine pools.

Long term trends in the TVS and TOC contents of sediment trap samples collected at L/D 3 and 4 have indicated a definite decline between 1987 and 1994 (Figure 14). Correlation analysis of TVS and TOC against time (year) at L/D 3 indicated this temporal trend was statistically significant (Table 3). This response is attributed to a change in river flow which showed a significant increase over the 7-year period. There was an apparent seasonal influence on TVS concentrations during the lower flow years (1987-1990) with spring sediment trap collections yielding lower values than fall exposures (Figure 14). In contrast, differences in TOC concentrations between spring and fall deployments were not apparent. These results may again reflect differences in the methods as well as possible changes in the composition of organic matter present during these two seasons. The high TOC value of 9.6% at L/D 3 in the fall of 1989 is suspect since this value seems unusually large relative to its TVS content (ie. 9.5 %). Further, a substantially lower TOC value of 5.7% was found at L/D 2 during this period (Table 4). The summer flood of 1993 did not appear to influence TVS and TOC concentrations measured during the following fall period.

Manganese

Manganese (Mn) is a common trace element that is found at relatively high concentrations in the earth's crust and soils (Hem 1970 and Baudo and Muntau 1990). This element is generally not considered to represent a significant environmental threat in most aquatic systems. Manganese and iron oxides are known to be "excellent scavengers" of trace elements and are often found as coatings on mineral grains and fine sediments (Horowitz 1991). As a result, these elements can be utilized as a surrogate for particle size or sediment surface area provided there is no local enrichment (source inputs) of these elements. Manganese has been successfully used in the Upper Mississippi River to normalize sediment trace element data (arsenic, cadmium, mercury, and lead) to evaluate anthropogenic enrichment longitudinally in the river (Wiener et al. 1984). Manganese provided a third parameter in this study, in addition to TVS and TOC, as another method for normalizing sediment trap materials for differences in grain size.

The Mn content of sediment traps ranged from 470 to 3300 μg/g based on data collected in the fall of 1993 and spring of 1994 (Table 4). There was no discernable longitudinal profile in the study reach (Figure 3). Highest concentrations (3200-3300 μg/g) were found at Coon Rapids, Minnesota (RM 866 μg/g) in the fall of 1993 and at lower Lake Pepin (RM 766) during the spring of 1994. Both samples were characterized as having high organic matter contents as reflected in TOC or TVS data (Table 4).

Correlation analysis of sediment trap Mn concentration with TVS or TOC indicated a significant positive correlation based on long term data collected at L/D 3 (Table 3). Mn was negatively correlated to gross sedimentation rate, river flow and TSS. This latter response was similar to that reported for TVS and TOC discussed above and suggests similar processes were influencing all three parameters. In general, normalizing Mn concentrations by TVS or TOC did not indicate any localized enrichment relative to organic matter content (Figure 3). The normalized data revealed a relatively flat profile through the study reach. An exception was the site at Champlin, MN (RM 871) in the spring of 1994 which was likely influenced by very low organic matter content

(1% TVS and 0.4 % TOC, Table 4). In general, sites with lowest Mn concentrations (< 700 μg/g) were influenced by greater trapping of fine sands.

Mn concentrations of sediment trap samples collected at L/D 3 and 4 indicated decreasing concentrations over the 7-year monitoring period (Figure 15). Concentrations were highest in the fall of 1988 (3500 μg/g) at L/D 3 and the fall of 1989 (4700 μg/g) at L/D 4, periods of low flow. In general, spring Mn concentrations were normally lower than fall samples and were likely flow-related. These differences probably reflect smaller sediment grain size in the fall collections in addition to increased organic matter composition. Terrestrial and aquatic plants may accumulate Mn during the growing season and their resultant decay and input during the fall period may be an additional source of Mn (Hem 1970).

Mn concentrations in fall trap samples collected at L/D 4 were noticeably greater than corresponding samples collected at L/D 3 in 1989 and 1990 (Figure 15), periods of relatively low flow (<20,000 cfs, Figure 14). This suggests an enrichment of particulate-bound Mn between these two sites. It is hypothesized this increased enrichment was associated with a release of dissolved Mn from anoxic sediments (Ruttner 1972) from Lake Pepin during periods of late summer or early fall stratification. Lake Pepin experiences low dissolved oxygen concentrations in bottom waters during summer periods of low flow (Minnesota Pollution Control Agency 1993). The reduced form of Mn could be assimilated by phytoplankton or form particulate suspensions as anoxic hypoliminetic waters are mixed with aerobic waters. The subsequent transport of this particulate-bound Mn could explain the increased Mn concentrations observed in downstream sediment trap samples collected at L/D 4.

Whole-water particulate phase Mn concentration estimates at L/D 3 ranged from about 25 to 95 μg/L (Figure 22) based on the 7-year study period. Particulate phase Mn concentrations indicated an increasing trend and reflected increasing TSS concentrations over the monitoring period. An even greater temporal trend was observed with particulate Mn mass transport which was highly influenced by increasing river flow. The greatest mass transport occurred in the spring of 1993. Whole-water particulate phase Mn concentration or mass transport estimates in the fall of 1993 or spring of 1994 did not reveal any unusual response attributable to the 1993 summer flood.

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are a group of chlorinated organic compounds that were produced commercially by chlorination of biphenyl with anhydrous chlorine (Eisler 1986a). This process yielded a complex mixture of chlorinated biphenyls with varying chlorine content. In the United States, PCB mixtures were commonly sold under the trade name of Aroclor® and were produced by Monsanto Corporation. There are a total of 209 separate PCB congeners that comprised the original formulations (Mullin and Pochini 1984). However, the typical number present in environmental samples is normally substantially fewer (McFarland and Clarke 1989). PCBs have been widely used since the 1930s, especially in electrical equipment, lubricants and fire retardants (Eisler 1986a). State and Federal regulations were enacted in the mid 1970s to restrict the production, use and disposal of these compounds.

The input of PCBs into the Upper Mississippi River has been a water quality problem for more than 20 years, especially in the river reach immediately below the Twin Cities metropolitan area (Sullivan 1988 and Steingraeber et al. 1994). PCB contamination of sport and commercial fish has resulted in the issuance of consumption advisories by Wisconsin since 1977 (Amrhein 1995). In 1989, Wisconsin adopted a water quality criterion concentration of 0.49 ng/L total PCBs (for Aroclors® 1254 or 1260) for warm water sport fish communities (ch. NR 105, Wis. Adm. Code 1989). This use designation includes the Mississippi River.

Sediment trap PCB concentrations collected in the fall of 1993 and spring of 1994 exhibited a marked longitudinal profile with greatest concentrations (90-140 ng/g) occurring at L/D 3 (RM 797) and Lake Pepin (RM 766), (Figure 4). Concentrations decreased rapidly below Lake Pepin but were still found at detectable concentrations (2-10 ng/g) at the furthest downstream sites. PCB concentrations in sediment traps in fall of 1993 exceeded concentrations found at the same sites the following spring. This seasonal difference was likely a result of greater organic matter content in the fall suspended sediment collections. Normalizing the PCB data by TVS, TOC and Mn resulted in a similar longitudinal profile with greatest enrichment occurring between L/D 2 (RM 815) and Lake Pepin (RM 766), (Figure 4). These PCB profiles are consistent with previous environmental PCB samples collected in this river reach (Sullivan 1988 and Steingraeber et al. 1994).

Total PCB concentrations in sediment trap samples were negatively correlated to river flow and TSS based on long-term data collected at L/D 3 (Table 3). A positive correlation was observed with TOC, TVS and Mn. This latter response is expected since PCBs have greater affinity to adsorb to fine-grained sediments with high organic matter and content, factors that are enhanced during low river flow. Further, increased phytoplankton development during low flow (MPCA 1993) may be especially important since phytoplankton may accumulate PCBs directly (Swackhamer et al. 1991) and they comprise part of the biogenic particles found in sediment trap samples.

Long-term trends in PCB concentrations in sediment trap samples from L/D 3 and 4 indicated a decline over the 7-year monitoring period (Figure 16). This trend was not as obvious at L/D 4 since samples collected prior to the fall of 1991 were analyzed using the less sensitive Aroclor®-based method. This latter method has consistently revealed PCBs resembling Aroclor® 1254 in sediment trap samples collected at L/D 3 and 4 when present at concentrations above the method detection limit (50 ng/g). Correlation analysis of L/D 3 PCB concentrations against time (year) indicated a significant decreasing temporal trend (Table 3). This was also found when PCBs were normalized for TVS content. This temporal trend was absent when PCBs were normalized using TOC or Mn (Figure 16 and Table 3). These data indicate PCB enrichment of suspended sediment has not shown a consistent temporal decline and suggests continued direct or diffuse inputs, especially from the Twin Cities metropolitan area.

Estimates of whole-water particulate phase PCB concentrations at L/D 3 ranged from 2.5 to 5.5 ng/L during the 7-year monitoring period (Figure 23). These concentrations exceeded Wisconsin's PCB water quality criterion (0.49 ng/L) by a factor of 5 to 11. Total water column PCB concentrations were greater since these particulate phase estimates do not include PCBs dissolved in water and in the colloid phase. Dissolved phase PCB concentration are approximately 10-50% of whole-water particulate phase concentrations based on a partitioning approach described by Sullivan (1988). Particulate phase PCB concentration estimates indicated highest values in the fall of 1991 and summer of 1992, periods of greatest TSS concentration (Figure 14). Periods of low flow (1987-1990, Figure 14) had relatively uniform PCB concentrations of 2.5-3.0 ng/L.

Particulate phase PCB transport at L/D 3 increased substantially in the early 1990s as a result of higher flows and associated increases in TSS concentrations. Highest PCB transport occurred during spring periods in 1991, 1993 and 1994 (Figure 23). The summer flood of 1993 did not appear to contribute to a change in PCB mass transport over what has been observed historically.

The percent composition of di- and tri-chlorinated biphenyl PCB homologues in suspended sediment revealed a change in samples collected above and below L/D 1 (RM 848). Suspended sediment samples collected above L/D 1 contained a greater percentage of di- and tri-chlorinated biphenyls and lower penta-chlorinated biphenyl congeners as compared to downstream sites (Figure 29). Steingraeber et al. (1994) described a distinct change in the PCB composition of mayflies collected between upper and middle Pool 2. They also reported a greater proportion of the lower chlorinated homologues (e.g. di-, tri- and tetra-chlorinated biphenyls) in mayfly samples collected 1 mile above the Metro Plant outfall (RM 835). This site was several miles below the Minnesota River confluence (RM 844). There were no PCBs detected in suspended sediments collected from the Minnesota River in the present study (Table 4). This change in congener composition likely reflects a change in source contribution between Pool 1 and 2. It is suspected that PCB contributions above L/D 1 are influenced by greater atmospheric inputs where the lower molecular weight PCBs (ie. less chlorinated) are dominant (Hornbucke et al. 1993 and Baker and Eisenreich 1990). Point and local nonpoint source PCB mass transport to Pool 2, including contaminated bed sediments, likely represent the major PCB inputs below L/D 1.

Other Organic Contaminants

Sediment trap samples were analyzed for a selected group of pesticides (e.g. cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, p,p-DDE and hepatachlor epoxide) at L/Ds 2, 3 and 4 in 1987 and 1988. None of these contaminants were present above the laboratory's detection limit (10 ng/g) based on 2 sets of samples collected from these locations. As a result, these contaminants were omitted in subsequent analysis of sediment trap samples collected from the river.

Cadmium

Cadmium (Cd) is a relatively rare metallic, divalent element found in igneous and sedimentary rocks (Hem 1970). It is a common byproduct in the refining of zinc, copper and lead. Cd has common uses associated with electroplating, pigment production, and battery manufacturing. Important anthropogenic sources include smelting operations, fossil fuels, fertilizers and municipal sludges from urban industrialized areas (Eisler 1985). Cd is normally found at relatively low concentrations in surface waters and its toxicity is reduced by increasing water hardness and complexation by dissolved organic material (Sprague 1987). Wisconsin's chronic toxicity criterion for Cd is related to water hardness (Ch. NR 105, Wis. Adm. Code 1989). The chronic warm water sportfish criterion for the Mississippi River is 1 µg/L (total recoverable Cd) at a total hardness of 200 mg/L $CaCO_3$, a value typical for the Mississippi River at L/D 3 (Sullivan 1989).

Past environmental assessments of Cd in bed sediments (Wiener et al. 1984 and Boyer 1984), mayflies (Dukerschein et al. 1992 and Beauvais et al. 1995) and mussels (Sullivan 1990) in the Upper Mississippi River have indicated elevated concentrations in samples collected from Pools 2 to 4. Stratigraphic analysis of bed sediments from Lake Pepin indicated relatively high concentrations (6 to 7 µg/g) in sediment strata dated from the 1970's (Rada et al. 1990). The source of this Cd was attributed to anthropogenic inputs from the Twin Cities metropolitan area.

Cd concentrations in sediment traps deployed in 1993 and 1994 revealed a longitudinal profile (Figure 5) somewhat similar to that previously described for PCBs. Highest Cd concentrations were found at L/D 3 (about 1 µg/g) with lowest concentrations (0.04-0.2 µg/g) observed at the furthest upstream sites (Minnesota River and above L/D 1). In contrast to PCBs, Cd concentrations did not decline in the lower study area between L/D 4 to L/D 11 (RM 753-583), but seemed to reach a plateau concentration of 0.5 µg/g.

TOC-, TVS- and Mn-normalized Cd values indicated an increasing longitudinal trend below L/D 4 (RM 753, Figure 5). This increasing enrichment may suggest transport of contaminated sediments or biogenic particles from upstream sources or input from point and nonpoint sources in the lower reaches of the study area. The relatively high Mn-normalized value observed at L/D 5 (RM 738) in the spring of 1994 is suspect due to an abnormally low Mn concentration in this sample (670 µg/g) relative to its TVS and TOC content (8 and 2.4 %, respectively), (Table 4). Cd concentrations in fall sediment trap samples were greater than spring samples and are related to greater organic matter content and smaller particle size in the fall collections. The Minnesota River suspended sediments were enriched with Cd when normalized for TVS, TOC and Mn in comparison to samples collected from the Mississippi River above L/D 1 (RM 848, Figure 5). Mass transport of particulate-bound Cd from this tributary likely represents a major influx of this contaminant to Pool 2 since this tributary provides a major source of suspended sediment to this pool (Sullivan 1989).

Cd concentrations in sediment trap samples showed a significant negative correlation to river flow and TSS based on long term data collected at L/D 3 (Table 3). Cd exhibited a significant positive correlation with Mn, but was not correlated with TOC and TVS.

Long-term trends in sediment trap Cd concentrations at L/D 3 and 4 showed a variable response over the 7-year period (Figure 17). In general, higher concentrations were observed between 1988 and 1990, a period with below average river flow. Temporal trend analysis indicated a significant decline in Cd concentrations at L/D 3 between 1987 and 1994 (Table 3). However, this response was absent when Cd was normalized by TOC, TVS and Mn. This would indicate that Cd enrichment of suspended sediment at L/D 3 has not decreased over the last several years. Cd analysis of samples collected prior to 1991 was performed using the less sensitive ICP method and may have influenced the observed temporal trends.

Whole-water particulate phase Cd concentration estimates at L/D 3 ranged between 20 and 70 ng/L between 1987 and 1994 (Figure 24). Lowest concentrations were observed during the initial deployments in 1987 and 1988, periods with low flow and TSS concentrations (Figure 14). Highest particulate phase Cd concentrations occurred during periods with high TSS concentrations. Particulate phase concentration estimates compared favorably to independent grab samples collected using low-level sampling and analytical techniques (Webb 1994). Particulate phase Cd concentrations were substantially below Wisconsin's chronic water quality criterion (1000 ng/L). This is true even if dissolved Cd concentrations (about 20-25 ng/L) are considered (Webb 1994).

Estimates of particulate phase Cd transport at L/D 3 indicated an increasing temporal trend (Figure 24) and reflects increased flow and TSS concentrations during this period. The flood of 1993 did not seem to be an important factor influencing sediment trap or whole-water particulate phase Cd concentrations based on a comparison of pre- and post-flood samples.

Copper

Copper (Cu) is a widely distributed element that is essential in both plant and animals as a trace nutrient (Hem 1970). This metallic element has been used by man since prehistoric times. Cu has been used in coins, plumbing supplies, electrical equipment, metal plating, metal alloys, fungicides, pesticides and algicides (USEPA 1977). Wisconsin has adopted a chronic warm water sportfish criterion for Cu that is based on total hardness (Ch. NR 105, Wis. Adm. Code 1989). A chronic criterion of 22 μg/L (total recoverable Cu) is calculated for L/D 3 at a total hardness of 200 mg/L $CaCO_3$, a value typical for the Mississippi River at this location (Sullivan 1989).

A survey of Mississippi River bed sediments collected between lower Pool 4 to Pool 10 by the US Fish and Wildlife Service in 1985 yielded Cu concentrations of 6-26 µg/g (Mahaffy et al. 1991). A review of their data did not indicate any spatial trend in this river reach. Boyer (1984) reported highest bed sediment Cu concentrations (31 µg/g) above L/D 2 based on a survey of bed sediments collected between Coon Rapids, Minnesota and Lower Pool 2. Boyer also found highest Cu concentrations in carp livers (7 µg/g wet wt) collected above L/D 2 and attributed this response to the increased Cu concentrations in bed sediments in lower Pool 2 as compared to upstream sites.

Sediment trap samples collected in the fall of 1993 in the Mississippi River indicated greatest Cu concentrations (28-29 µg/g) from Coon Rapids, Minnesota (RM 866) and St Anthony Falls L/D (RM 853), (Figure 6). Corresponding samples collected in the following spring from this reach had substantially lower Cu concentrations (4-8 µg/g) and were influenced by low organic matter content (< 4% TVS) and greater trapping of fine sands.

TVS-normalized Cu concentrations revealed a decreased enrichment in suspended sediment based on samples collected above L/D 3 (RM 797) to those collected from Lower Lake Pepin (RM 766) and below (Figure 6). However, this response was not apparent when Cu was normalized by TOC or Mn. Sediment trap samples collected from the Minnesota River were enriched with Cu based on TVS, TOC and Mn normalization. This may indicate this tributary is an important source of particulate-bound Cu for the Mississippi River due to the high suspended sediment transport of this tributary.

Cu concentrations at L/D 3 collected over the 7-year monitoring period were negatively correlated to river flow and TSS (Table 3). This response likely reflects an increase in suspended sediment particle size and decreased organic matter content as a result of increased river flows over this time period. Sediment trap Cu concentrations were positively correlated to TOC, TVS and Mn.

Long-term sediment trap Cu concentrations at L/D 3 and 4 indicated a sharp increase (about 35 µg/g) in suspended sediment Cu concentrations in the fall of 1989 (Figure 18). This was also apparent when data were normalized by TVS and TOC. Mn-normalized Cu concentrations were more variable and the enrichment was not as clearly defined. Cu concentrations at L/D 3 fell gradually from 60 µg/g in the fall of 1989 to 23 µg/g in the spring of 1991. This temporal pattern suggests a plume of particulate-bound Cu was moving through this study reach during this time. The temporal pattern observed with Cu was not observed with the other contaminants measured in this study with the possible exception of Cd (Figure 17). The reason for the Cu enrichment of suspended sediments in 1989 was not established.

Sediment trap estimates of whole-water particulate phase Cu concentrations at L/D 3 ranged from about 0.5 to 1.3 µg/L during the 7-year study (Figure 25). Concentrations were lowest prior to the fall of 1989 and averaged about 1 µg/L between 1990 and 1994. Sediment trap estimates of particulate phase Cu concentrations were generally comparable to grab samples collected by independent methods using low-level sampling and analytical techniques (Webb, 1994). This latter work indicated Cu was primarily present in the dissolved phase (60%) with an average concentration of 1.3 µg/L (n=3). As a result, total water column Cu concentrations at L/D 3 were approximately an order of magnitude below the Wisconsin's water quality criterion of 22 µg/L derived for L/D 3.

Mass transport of particulate phase Cu increased over the 7-year study period (Figure 25). This is attributed to increased river flow and TSS concentrations during this period.

Chromium

Chromium (Cr) is a hard metallic element that is widely used in industrial and domestic products. This element has several oxidation states (-2 to +6) with the trivalent (Cr^{+3}) and hexavalent (Cr^{+6}) forms representing the most common forms in aquatic systems. The Cr^{+6} compounds readily oxidize organic matter which results in the formation stable Cr^{+3} complexes with negatively charged inorganic or organic compounds (Eisler 1986b). The average Cr^{+3} concentration in the earth's crust is reported to be 100 µg/g (Baudo and Muntau 1990). Cr is used in stainless steel production, chrome plating, pigments and paints. Some of the anthropogenic inputs include: chrome alloy industries, coal combustion, municipal incinerators, cement production, cooling towers, wastewater treatment plants, tanneries, steel foundries and urban and residential runoff (Eilser 1986b). Wisconsin's chronic water quality criterion for Cr is related to water hardness (Ch. NR 105, Wis. Adm. Code 1989). A trivalent Cr criterion concentration of 95 µg/L (total recoverable Cr^{+3}) is calculated for L/D 3 at a total hardness of 200 mg/l $CaCO_3$, a hardness typical for the Mississippi River at this location (Sullivan 1989).

Cr concentrations in Mississippi River backwater bed sediments collected by the U.S. Fish and Wildlife Service between lower Pool 4 and upper Pool 10 in 1985 indicated a slight decreasing longitudinal trend (Mahaffy et al. 1991). Their survey yielded bed sediment Cr concentrations of 8 to 34 µg/g in this reach. Boyer (1984) reported an increase in Cr concentrations in bed sediments below the Twin Cities area with highest concentrations reported for lower Pool 2. Similarly, Boyer found Cr accumulation in carp tissue was greater in samples collected from Pool 2 as compared to upstream sites. Cr concentrations in 3-ridge (Amblema plicata) and pimpleback (Quadrula pustulosa) mussel samples collected from upper Pool 4 in 1989 were found to be about two times greater than similar samples collected from Pools 8 and 10 (Sullivan 1990).

Cr concentrations in sediment trap samples collected from the Mississippi River in the fall of 1993 and spring of 1994 indicated an increasing trend downstream (Figure 7). Lowest concentrations (7-11 u/g) were found in spring samples collected above St. Anthony Falls L/D (RM 853) which were characterized as having low organic matter content (TVS <4%, Table 4). The Minnesota River samples also had low Cr and organic matter contents in both spring and fall collections. Highest Cr concentrations (30-36 μg/g) were found in spring samples collected at L/D 3 (RM 797), L/D 4 (RM 753) and L/D 9 (RM 648). In general, the longitudinal and seasonal responses observed with Cr were different than other contaminants measured in this study. The reason for this difference was not established.

Normalized Cr concentrations by TVS and TOC did not yield any definite longitudinal trend in enrichment (Figure 7). Mn-normalized Cr concentrations of spring samples collected in 1994 indicated greater enrichment between L/D 3 (RM 797) and L/D 11 (RM 583) as compared to samples collected during the previous fall period. The exception was the lower Lake Pepin site (RM 766) which was influenced by a relatively high Mn concentration (3500 μg/g). The Mn-normalized response for Zn (Figure 10) indicated a similar pattern and may suggest similar processes and sources were influencing both trace elements. Normalized Cr concentrations observed in sediment trap samples collected from the Minnesota River were enriched with Cr, especially in the fall 1993 collection. The mass transport of particulate-bound Cr from this tributary likely represents a major source of Cr to Pool 2 as a result of high mass transport of TSS from this tributary (Sullivan 1989).

Whole-water particulate Cr concentration estimates of samples collected at L/D 3 in the fall of 1993 and spring of 1994 ranged from about 1 to 1.5 μg/L. Low-level monitoring of Cr concentrations near L/D 3 in the fall of 1992 and spring of 1993 provided an average total and dissolved concentration of 0.9 μg/L and 0.19 μg/L, respectively (Webb 1994). This yields an average particulate concentration of 0.7 μg/L which was slightly below that estimated using sediment trap and TSS data. Total Cr concentrations were substantially below Wisconsin's chronic criterion of 95 μg/L (total recoverable Cr^{+3}) which would be applicable for the Mississippi River at L/D 3.

Mercury

Mercury (Hg) is a liquid, metallic element that has been used by man for over two thousand years (Eisler 1987). It is normally found at low concentrations in environmental samples. However, mercury can be biomagnified through the food chain and can result in serious environmental problems. Hg has been used in slimacides, fungicides, mining, electrical controls, thermometers, dental amalgams, batteries, fluorescent lights and in the chemical production industry. Incinerations of Hg containing wastes or the burning of fossil fuels can contribute significantly to anthropogenic inputs to the atmosphere (Eisler 1987). Hg can be present in the environment in many different forms and has a complex cycling process (D'Itri 1990). Organomercurial compounds likely represent the greatest threat in aquatic systems, and are especially apparent in waters with low alkalinity (Spry and Wiener 1991). Wisconsin has adopted a wild and domestic animal water quality criterion concentration of 2 ng/L for all surface waters (Ch. NR 105, Wis. Adm. Code 1989).

The Hg content of bed sediments from the Upper Mississippi River (Pools 1-10) has been shown to be elevated in Pools 2 to Pool 4 (Wiener et al. 1984 and Beauvais et al. 1995). Bioaccumulation of Hg by mayflies was also found to be greater in these pools as compared to downstream pools bordering Wisconsin (Dukerschein et al. 1992 and Beauvais et al. 1995). Sentinel mallards placed in Spring Lake (Pool 2) and Lake Pepin (Pool 4) exhibited greatest Hg bioaccumulation in liver tissue samples from Mallard exposures in Pool 2 (Ensor et al. 1993).

Hg concentrations in sediment trap samples exposed in 1993 and 1994 exhibited the highest concentrations (0.11 to 0.16 μg/g) in fall samples collected between Coon Rapids, Minnesota (RM 866) and L/D 3 (RM 797, Figure 8). Lowest concentrations (<0.05 μg/g) were typically found in spring samples with low organic matter content (< 4% TVS, Table 4). The profile of suspended sediment Hg concentrations in the river showed a general decline from 0.15 to 0.05 μg/g between L/D 3 (RM 797) and L/D 11 (RM 583). Normalizing Hg concentrations by TOC, TVS and Mn resulted in a more variable longitudinal response. Only the TVS-normalized Hg data indicated reduced enrichment at the downstream sites.

Correlations of L/D 3 sediment trap Hg concentrations with other physical and chemical variables provided a different response as compared to other contaminants evaluated in this work (Table 3). Sediment trap Hg concentrations were not correlated to river flow and TSS in contrast to other contaminants measured in this study. In addition, no correlation was evident between Hg and TVS or Hg and TOC. A significant positive correlation was apparent between Hg and Mn.

Temporal analysis of the Hg content of sediment trap samples exposed at L/D 3 and 4 has indicated a gradual decline over the 7-year monitoring period (Figure 19). Correlation analysis of Hg versus time (year) indicated this trend was statistically significant (Table 3). However, when Hg was normalized by TVS, TOC and Mn, the temporal trend was more obscure. Only TVS-normalized data indicated a significant decline in suspended sediment enrichment over the study period. TVS-, TOC- and Mn-normalized Hg data revealed the suspended sediments were enriched with Hg in the spring trap samples collected in 1992 at L/D 3 and 4 (Figure 19). This was especially apparent in samples collected from L/D 4. This may suggest increased point or nonpoint source inputs during spring deployment in 1992. The Mn-normalized data from both L/D 3 and 4 and the TVS-normalized data for L/D 3 indicated that spring samples were generally enriched with Hg as compared to fall samples.

Whole-water particulate phase Hg concentration estimates at L/D 3 ranged from about 4 to 11 ng/L during the 7-year period (Figure 26). All values exceeded Wisconsin's surface water quality criterion of 2 ng/L for total Hg. A grab sample for total and dissolved Hg was collected near L/D 3 in the spring of 1993 as part of a separate low-level trace metal study (Webb 1984). The particulate phase concentration for this sample (6 ng/L) was essentially similar to that estimated using sediment trap and TSS data (Figure 26).

Estimates of particulate phase Hg mass transport at L/D 3 indicated an increasing trend over the study period (Figure 26). This response was attributed to increased river flow and TSS concentrations during the study period.

Lead

Lead (Pb) is a dense metallic element that is present in over 200 minerals. Its use by man dates back to more that 5,000 BC (Eisler 1988). Pb has been used in batteries, gasoline additives, pigments, paint, ceramics, solder, plumbing and ammunition. Mining, smelting and vehicle emissions have represented major anthropogenic inputs to the environment (Eisler 1988). Pb loads to the Gulf of Mexico from the Mississippi River have been decreasing due to discontinued use of leaded gasolines (Trefry et al. 1985). Further, they reported that over 90% of the riverborn lead transport was attributable to suspended sediments. Atmospheric input is considered to be the primary source of Pb found in aquatic sediments (D'Itri 1990). Wisconsin has established a chronic toxicity of criterion for Pb that is hardness related (Ch. NR 105, Wis. Adm. Code 1989). For a total hardness of 200 mg/L $CaCO_3$, a value typical for the Mississippi River at L/D 3 (Sullivan 1989), the chronic Pb criterion is approximately 24 μg/L (total recoverable Pb).

Previous environmental monitoring of Pb in the Upper Mississippi River has indicated elevated Pb accumulation in carp livers from samples collected at Fridley, Minnesota and Pool 2 (Wiener et al. 1984). They also reported greatest bed sediment Pb concentrations (22-86 μg/g) were present in Pool 2 and Lake Pepin. Sediment cores from Lake Pepin indicated Pb concentrations showed the greatest anthropogenic enrichment (5-8 times background) in a study of trace metal influxes to this large riverine lake (Rada et al. 1990). They reported a maximum concentration of 72 μg/g from sediments dated from the 1970s. Bed sediment surveys conducted between lower Pool 4 and Pool 10 in 1985 by the U.S. Fish and Wildlife Service did not reveal any definite longitudinal pattern in Pb concentrations (Mahaffy 1991). They reported highest concentrations ranging from 20-26 μg/g.

The longitudinal profile of Pb concentrations of sediment trap samples collected in the fall of 1993 and spring of 1994 (Figure 9) revealed highest concentrations (24-41 μg/g) in the reach between Coon Rapids (RM 866) and L/D 4 (RM 753). Samples collected below L/D 4 were less than 20 μg/g. In general, these results were consistent with previous bed sediment studies discussed above. Lowest sediment trap Pb concentrations (< 7 μg/g) were associated with samples collected at Champlin, Minnesota (RM 871) and the Minnesota River. Both of these latter samples were influence by low organic matter content (1-2% TVS, Table 4).

TVS-normalized Pb concentrations indicated a decreased enrichment through the study reach (Figure 9). This was not observed when Pb was normalized by TOC or Mn. The spring sample from the Minnesota River revealed a substantial enrichment of Pb relative to TOC, TVS and Mn contents. Transport of suspended sediment from the Minnesota River to Pool 2 is very high and has a major influence on the Mississippi River below its confluence (Sullivan, 1989). This suggests this tributary may provide a major source of particulate-bound Pb to the Mississippi River.

Long-term sediment trap Pb concentrations at L/D 3 indicated significant negative correlations to river flow and TSS (Table 3), a response attributed to a reduced suspended sediment particle size and increased organic matter content at lower flows. A significant positive correlation was found between Pb and TOC, but was absent with TVS or Mn.

Temporal trend evaluation of sediment trap Pb data collected at L/D 3 has indicated a significant decline over the 7-year monitoring period (Table 3 and Figure 20). However, when Pb concentrations at L/D 3 were normalized for TOC, TVS and Mn, no significant temporal trend was found. Suspended sediment collected in the spring of 1988 and fall of 1989 were especially enriched with Pb at L/D 3. In contrast, this was not observed at L/D 4. Moderate increases in sediment trap Pb concentrations, including normalized data, were found at L/D 4 in the fall of 1993. However, the significance of this increase is questionable considering the large difference in duplicate field sample results observed at L/D 3 during this period (Figure 20).

Whole-water particulate phase Pb concentration estimates at L/D 3 ranged from about 0.4 to 1.5 μg/L over the 7-year study period (Figure 27). These results compared reasonably well with independent grab samples collected as part of a low-levels metal sampling program conducted near L/D 3 (Webb 1994). The latter work revealed particulate phase Pb concentrations of 0.9 to 1.8 μg/L which represented about 94% of the total Pb concentration. Therefore, total water column Pb values are substantially below Wisconsin's chronic water quality criterion of 24 μg/L applicable at L/D 3.

Estimates of particulate phase Pb mass transport at L/D 3 indicated an increasing trend over the 7-year monitoring period (Figure 27). This is a reflection of increasing river flow and TSS concentrations over this period of time.

Zinc

Zinc (Zn) is an essential trace element necessary for all organisms and is a common constituent in rocks and soils (Eisler 1993 and Hem 1970). Zn is used in electroplating, noncorrosive alloys, galvanized metals, photocopying paper, pigments, medicine, and fungicides. Anthropogenic inputs include: electroplaters, smelting, mining, domestic and industrial sewage, burning of fossil fuels and solid waste, road surface runoff, corrosion of Zn alloys and galvanized surfaces and erosion of agricultural land (Eisler 1993). Baudo and Mauntau (1990) referenced a mean concentration of 75 μg/g for the earth's crust. Similarly, Boyer (1984) listed a value of 106 μg/g for bed rocks in the Northern Great Plains region. Wisconsin has established a chronic toxicity of criterion for Zn that is a function of water hardness (Ch. NR 105, Wis. Adm. Code 1989). For total a hardness of 200 mg/L $CaCO_3$, a value typical for the Mississippi River at L/D 3 (Sullivan 1989), the Zn criterion is 89 μg/L (total recoverable Zn).

Zn concentrations in backwater bed sediments of Upper Mississippi River collected from Pool 4 to upper Pool 10 revealed a range of 42-109 μg/g with no apparent longitudinal trend (Mahaffy et al. 1991). Rada et al. (1990) reported anthropogenic enrichment of Zn in sediment cores collected from Lake Pepin (Pool 4), but this enrichment was less than other trace elements (Pb, Cd, Cu and Cr). Boyer (1984) found an increasing sediment Zn concentrations (19 to 131 μg/g) in a reach extending immediately above and below the Twin Cites metropolitan area. Highest concentrations were reported for a site in Lower Pool 2 (RM 815). Boyer also reported Zn bioaccumulation was greater in carp tissues collected above the Twin Cites area than samples collected from lower Pool 2.

Concentrations of Zn in sediment trap samples collected in the Mississippi River in the fall of 1993 and spring of 1994 revealed a response similar to Cu (Figure 6 and 10). Highest concentrations (120-160 μg/g) were found in fall samples collected above St. Anthony Falls L/D (RM 853) and in the spring sample from lower Lake Pepin (RM 766). As with Cu and other trace elements evaluated in this study, lowest Zn concentrations (< 40 μg/g) were associated with trap samples with low organic matter content (≤ 2% TVS, Table 4) and increased trapping of fine sands.

Normalizing Zn concentrations by TVS indicated a sharp decrease in enrichment in the river reach between Champlin, Minnesota (RM 871) and L/D 5 (RM 738, Figure 10). Zn concentrations normalized by TOC or Mn failed to show this response. Sediment trap samples from the Minnesota River were enriched with Zn as indicated by TVS- and TOC-normalized data. This tributary likely contributes a large load of particulate-bound Zn to the Mississippi River when one considers the high suspended sediment transport of this tributary (Sullivan 1989).

Sediment trap Zn concentrations collected at L/D 3 during the 7-year monitoring period were negatively correlated to river flow and TSS (Table 3). These relationships likely reflect an increase in suspended sediment particle size associated with increasing river flows during the study period. Zn was positively correlated to TVS and Mn, but no correlation was found with TOC.

Long term trends in sediment trap Zn concentrations collected at L/D 3 and 4 indicated a slight decline over the 7-year monitoring period (Figure 21). Temporal trend analysis of data collected at L/D 3 indicated this trend was statistically significant (Table 3). This temporal trend was absent when Zn was normalized by TOC, TVS and Mn. A distinct seasonal trend was observed with Mn-normalized Zn concentrations (Figure 21). Spring trap samples were enriched with Zn relative to Mn. This is attributed to a seasonal fluctuation of particulate-bound Mn concentrations which were generally greater in the fall sediment traps (Figure 15). A similar response was observed with other trace elements (Cd, Cu and Hg) measured in this study.

Whole-water particulate phase Zn concentration estimates for L/D 3 ranged from about 2 to 6 μg/L (Figure 28). These values compared very well to independent grab samples collected using low-level trace element sampling and analytical techniques (Webb 1994). Dissolved Zn normally represents less half of the total water column concentrations in river systems (Baudo and Muntau 1990). Limited data for L/D 3 (n=3) indicated an average dissolved concentration of 1.1 μg/L and a total concentration of 5.6 μg/L (Webb 1994). Therefore, the total Zn concentrations were more than an order of magnitude below Wisconsin's Zn chronic criterion of 89 μg/L determined for the Mississippi River at L/D 3.

Estimates of particulate-bound Zn mass transport indicated an increasing trend during 7-year study (Figure 28). This reflects an increase in river flow and TSS concentrations over the monitoring period.

Nitrogen

Molecular nitrogen (N_2) is the primary gas in the atmosphere and is present in soils and biological material in both organic and inorganic forms. Nitrogen is a major plant nutrient that may affect the productivity of aquatic systems (Hem 1970 and Wetzel 1975). Nitrogen fixation of molecular N_2 by soil-born bacteria represents a major global source of nitrogen compounds (Wetzel 1975). In sediments, N is primarily present as dissolved molecular N_2 organic N (both dissolved and particulate) and ammonia-N. Examples of anthropogenic sources of nitrogen include: industrial and municipal wastewater discharges, fertilizers, and animal feed lots.

Ammonia-N and Total Kjeldahl-N (TKN) were the two N forms measured in this study. TKN analysis includes ammonia-N and nitrogen bound in organic materials. N analysis of surface water is commonly performed to assess nutrient enrichment and to determine the concentration of un-ionized ammonia-N, a form that is toxic to aquatic life. Previous surface water analysis of ammonia-N and TKN at several Mississippi River main channel sites between L/D 2 and L/D 9 have revealed a definite longitudinal gradient (Sullivan 1989). Highest concentrations occurred at L/D 2 and reflect N inputs from the

Minnesota River and the Metro Plant, a 250 mgd wastewater treatment facility for the Twin Cities metropolitan area.

Some problems were encountered in the analysis of sediment trap materials for both ammonia-N and TKN (Table 4). The holding time for ammonia-N was exceeded and there were problems with spike recoveries on several TKN samples. As a result, these data should be treated as estimates only. In general, highest, ammonia-N and TKN concentrations were associated with samples of greatest organic matter contents. Low TKN values were found in samples that had little organic matter and contained appreciable fine sands. The spring ammonia-N concentration in suspended sediments collected from lower Lake Pepin (RM 766) was more than 3-fold higher than all other samples (Figure 11). This site was likely greatly influenced by the high organic matter content (14% TVS, Table 4) present in this sample. Autochthonous production of phytoplankton within Lake Pepin and losses of coarse inorganic particulate matter through sedimentation contribute to these changes in the organic and TKN content of suspended material in lower Lake Pepin. The river profile of TKN (Figure 12) in suspended sediment samples paralleled changes in organic matter (TVS, Figure 2). This was not surprising since TKN analysis is essentially an indirect measure of organic content since N is an important constituent in biogenic material.

Normalizing ammonia-N data by TVS, TOC and Mn revealed a rather flat river profile. A noted exception occurred in the sample of suspended sediment collected from lower Lake Pepin which was enriched with ammonia-N (Figure 11). This sample likely reflects a greater input of fresh organic material from autochthonous sources, most likely Lake Pepin phytoplankton. The elevated Mn-normalized N concentration at L/D 5 (RM 738) is suspect due to the low Mn concentration measured at this site (Figure 3).

The atomic ratio of carbon-to-nitrogen (C/N) (Figure 30) showed a decreasing longitudinal trend between Champlin, Minnesota (RM 871) and L/D 4 (RM 753). This response may be due to an increase in the contribution of autochthonous organic matter to the large riverine pools (lower Pool 2 and Lake Pepin) that is enriched with nitrogen as compared to allochthonous organic matter derived from the watershed above Pool 2 (Wetzel 1975, Ward et al. 1990 and Leenheer et al. 1995). In addition, the longer hydraulic retention time afforded by these pools may allow for greater differential mineralization of C and N and increased sedimentation which may alter the C/N ratio as the suspended sediments are transported downstream.

Phosphorus

Phosphorus (P) is an important element that is necessary for biological organisms. There are many oxidation states possible for this element (Hem 1970). Elemental P is highly toxic, but this form is rarely present in most aquatic systems (Thurston et al. 1979). In aquatic systems, particulate P may be present in live organisms, adsorbed to dead organic material or attached to soil particles (Wetzel 1975). P is often cited as being the limiting nutrient in aquatic systems and when present in excess, contributes to the eutrophication of lakes and reservoirs (Vollenweider 1968 and Wetzel 1975). Major cultural sources of P include fertilizers, industrial and municipal wastewater discharges, detergents, and heat treatment compounds (Hem 1970).

Total P (dissolved plus particulate) measurements are routinely made in surface waters to assess eutrophication problems. Total P concentrations in surface waters of the Mississippi River main channel in the study area usually indicate highest concentrations (0.3 mg/l) in Pool 2 and lowest values (0.1 mg/l) at L/D 4 (Sullivan 1989). As with TKN, the high P concentrations observed in Pool 2 are primarily attributed to P contributions from the Minnesota River and the Metro Plant.

Laboratory analysis of Total P in sediment trap samples revealed quality assurance problems associated with spike recoveries on several samples (Table 4). This problem also occurred on the same samples analyzed for TKN. As a result, these data were considered as approximate values for this evaluation.

Similar to TKN, P concentrations were greatest at sites with high organic matter content (Table 4). Fall sediment trap samples collected in 1993 exhibited greater P concentrations than samples collected from the same sites the following spring (Figure 13). This is again attributed to greater organic matter content (TVS and TOC) in the fall samples.

Normalizing P by TVS, TOC and Mn did not indicate any distinct spatial trend. However, it was noted that the Minnesota River sample collected in the fall of 1993 was enriched with P relative to its TVS, TOC and Mn contents (Figure 13). This is consistent with previous studies that have indicated this tributary provides a major source of P to Pool 2 (Sullivan 1989 and MWCC 1993). Greatest P enrichment was noted at L/D 4 (RM 753) based on TVS-, TOC- and Mn-normalized data collected in the fall of 1993. This may reflect the export of particulate-bound P from Lake Pepin (MPCA 1993) or tributary inflows. The relative high Mn-normalized P value found at L/D 5 (RM 738) in the spring of 1994 is suspect due to the low Mn concentration reported for this sample (670 μg/g, Table 4).

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Table 1. Location of sediment trap monitoring sites in the Upper Mississippi River system collected by the Wisconsin Department of Natural Resources between 1987 and 1994. Position coordinates based on the North American Datum 1927.

Location	Nearest City	STORET No.[1]	River Mile	Latitude Deg. Min.	Longitude Deg. Min.	Sediment Trap Sample Collection Years[2]								Additional Site Comments
						87	88	89	90	91	92	93	94	
U.S. Hwy. 169 Br.	Champlin, MN	483068	871	45 11.5	93 23.7	-	-	-	-	-	-	-	S	I-Beam supports on new brige, fast current
Coon Rapids Dam	Coon Rapids, MN	483053	866	45 9.7	93 18.7	-	-	-	-	-	-	F	-	Below concrete walkway near turbine housing
Lower St. Anthony Falls Lock and Dam	Minneapolis, MN	483054	853	44 58.8	93 14.8	-	-	-	-	-	-	F	S	Bullnose at upstream guide wall
Lock & Dam 1	Minneapolis, MN	483066	848	44 54.9	93 12.1	-	-	-	-	-	-	-	S	At notch in upstream guide wall
Minnesota River	Ft. Snelling, MN	483055	3.5	44 52.8	93 11.5	-	-	-	-	-	-	F	S	Outside piling of MWCC's auto. monitoring station
Lambert's Landing	St. Paul MN	483056	839	44 56.5	93 5.5	-	-	-	-	-	-	F	S	On piling below eddy
Lock & Dam 2	Hastings, MN	483026	815	44 46.4	92 53.5	-	-	-	-	-	-	F	S	Above auxiliary lock gate
St. Croix River	Prescott, WI	483001	0.1	44 45.0	92 48.2	-	*	-	-	-	-	-	-	On railroad br. support
Lock & Dam 3	Red Wing, MN	483027	797	44 36.6	92 36.6	F	SF	SF	SF	SF	SMF	SF	S	Above auxiliary lock gate
Lower Lake Pepin	Pepin, WI	473015	766	44 26.05	92 8.47	-	-	-	-	-	-	-	S	Depth 18 ft, Traps mounted between 5-15 ft from surf.
Lock & Dam 4	Alma, WI	063029	753	44 19.6	91 55.1	F	S	SF	SF	SF	SMF	SF	S	Above auxiliary lock gate
Lock & Dam 5	Minneiska, MN	063051	738	44 9.6	91 48.7	-	-	-	-	-	-	-	S	Above auxiliary lock gate
Lock & Dam 8	Genoa, WI	633038	679	43 34.2	91 13.8	-	-	-	-	-	-	F	S	Above auxiliary lock gate
Lock & Dam 9	Lynxville, WI	123016	648	43 12.7	91 5.9	-	-	-	-	-	-	-	S	Above auxiliary lock gate
Lock & Dam 11	Dubuque, IA	223263	583	43 32.4	90 38.7	-	-	-	-	-	-	-	S	Above auxiliary lock gate

1 - U.S. EPA's Storage and Retrieval (STORET) computer data base system
2 - Collection periods: S = Spring (April-June), M = Summer (June-September), F = Fall (September-November), * = September 1987 to June 1988

Table 2. Summary of laboratory quality assurance information for sediment analyses at the Wisconsin State Laboratory of Hygiene in Madison, Wisconsin.

Parameter	MDL[1]	Precision[2] R % D	Accuracy[3] % recovery
Total PCBs ng/g *	50	6.1	94.5
PCB IUPAC # 28/31 ng/g +	1.4	7.0	90.7
PCB IUPAC # 77/110 ng/g +	0.40	7.4	96.1
PCB IUPAC # 180 ng/g +	0.35	8.4	96.0
Total organic carbon %	0.2	6.8	ND
Total volatile solids %	NA	11.1	ND
Cd AA ug/g	0.1	9.7	93.5
Cr ICP ug/g	5	16.9	95.1
Cu ICP ug/g	2	14.8	96.1
Pb ICP ug/g	5	18.2	96.3
Mn ICP ug/g	2	7.7	102.5
Hg AA cold vap. ug/g	0.02	7.1	94.8
Zn ICP ug/g	1	13.1	100.4

1 - Method detetection limit (MDL)
2 - Average relative % difference (R % D)
3 - Average spike recovery
ND - No data
NA - Not available
* - Arochlor-based method
+ - Selected congeners using congener-based method
IUPAC - International Union of Pure and Applied Chemists
AA - Atomic absorption spectrometry
ICP - Iductively coupled plasma emission spectrometry

Table 3. Spearman rank-order correlation coefficients of sediment trap data collected in the Mississippi River at Lock and Dam 3 near Red Wing, Minnesota. Based on data collected between September 1987 and June 1994.

Variable			Raw Data	Variable 2 Normalization[a]		
1		2		TOC	TVS	Mn
Flow	vs	Year	0.710 *	-	-	-
		Srate	0.953 *	-	-	-
		TSS	0.693 *	-	-	-
		TVS	-0.594 *	-	-	-
		TOC	-0.669 *	-	-	-
		PCB	-0.886 *	-0.199	-0.783 *	-0.156
		Cd	-0.558 *	0.163	-0.385	0.276
		Cu	-0.592 *	0.286	-0.308	0.318
		Pb	-0.510 *	0.150	-0.360	0.233
		Mn	-0.750 *	0.081	-0.716 *	-
		Hg	-0.477	-0.002	-0.229	0.441
		Zn	-0.630 *	0.309	-0.026	0.668 *
Year	vs	Srate	0.688 *	-	-	-
		TSS	0.705 *	-	-	-
		TVS	-0.533 *	-	-	-
		TOC	-0.543 *	-	-	-
		PCB	-0.787 *	-0.145	-0.679 *	-0.264
		Cd	-0.471 *	0.080	-0.343	0.021
		Cu	-0.507 *	0.269	-0.141	0.163
		Pb	-0.604 *	-0.054	-0.395	0.034
		Mn	-0.519 *	0.108	-0.455	-
		Hg	-0.845 *	-0.449	-0.644 *	-0.067
		Zn	-0.646 *	0.250	-0.080	0.309
TSS	vs	Srate	0.560 *	-	-	-
		TVS	-0.580 *	-	-	-
		TOC	-0.716 *	-	-	-
		PCB	-0.776 *	0.059	-0.665 *	-0.129
		Cd	-0.546 *	0.060	-0.460	-0.028
		Cu	-0.809 *	0.153	-0.570 *	0.042
		Pb	-0.762 *	-0.118	-0.609 *	-0.106
		Mn	-0.617 *	0.226	-0.554 *	-
		Hg	-0.504	-0.084	-0.268	0.284
		Zn	-0.780 *	0.233	-0.239	0.378

Table 3. Continued.

Variable			Raw Data	Variable 2 Normalization[a]		
1		2		TOC	TVS	Mn
TOC	vs	Srate	-0.593 *	-	-	-
		TVS	0.255	-	-	-
		PCB	0.718 *	-	0.781 *	0.052
		Cd	0.445	-	0.293	-0.308
		Cu	0.502 *	-	0.246	-0.468
		Pb	0.591 *	-	0.573 *	-0.079
		Mn	0.616 *	-	0.651 *	-
		Hg	0.361	-	0.188	-0.479
		Zn	0.484	-	0.221	-0.513 *
TVS	vs	Srate	-0.533 *	-	-	-
		PCB	0.663 *	0.282	-	-0.013
		Cd	0.332	0.093	-	-0.201
		Cu	0.714 *	0.232	-	-0.025
		Pb	0.277	-0.109	-	-0.338
		Mn	0.614 *	0.243	-	-
		Hg	0.353	0.195	-	-0.362
		Zn	0.629 *	0.196	-	-0.455
Mn	vs	Srate	-0.693 *	-	-	-
		PCB	0.777 *	0.757 *+	0.677 *+	-
		Cd	0.693 *	0.767 *+	0.507 *+	-
		Cu	0.625 *	0.846 *+	0.346 +	-
		Pb	0.469	0.358 +	0.290 +	-
		Hg	0.619 *	0.714 *+	0.289 +	-
		Zn	0.510 *	0.826 *+	-0.057 +	-

a - Variable 2 divided by TOC, TVS or Mn
* - Significant at 0.95 probability level
\+ - Both variables 1 and 2 normalized
Srate - Gross sedimentation rate measured in trap
TVS - Total volatile solids
TOC - Total organic carbon
TSS - Total suspended solids

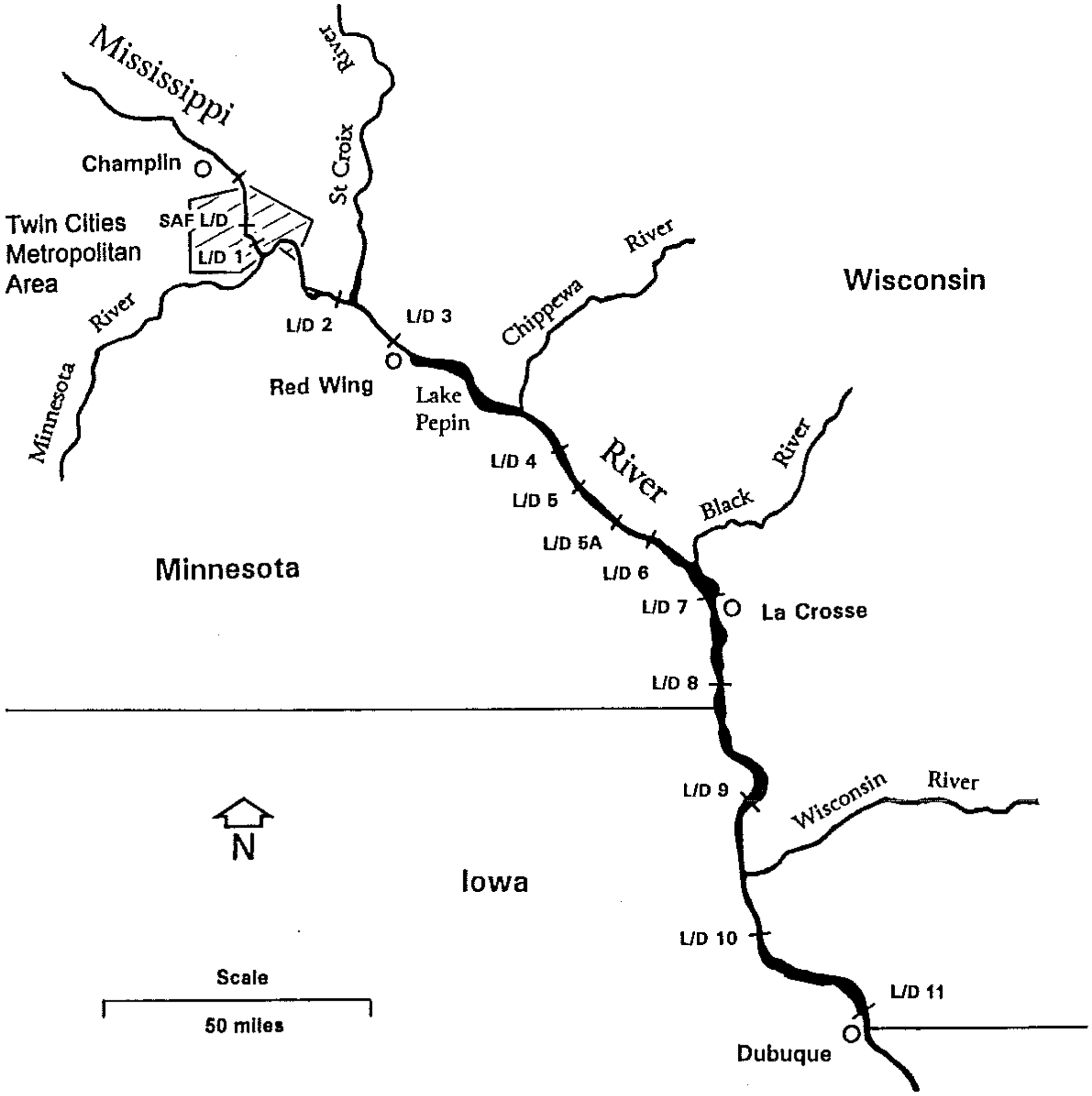
Table 4. Sediment trap contaminant data collected by the Wisconsin Department of Natural Resources with assistance from the Minnesota Pollution Control Agency. Sediments analyzed by the Wisconsin State Laboratory of Hygiene, Madison, Wisconsin.

Trap Location	1 STORET ID No.	River Mile	2 Trap Collect yr mo dy	3 Exp days	4 Gross Accum cm	5 Sed. Rate cm/d	TVS %	TOC %	6 Tot. PCB ng/g	Cd µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Mn µg/g	Hg µg/g	Zn µg/g	NH4-N µg/g	TKN µg/g	TP µg/g
1993 Flood Evaluation Work - Fall 1993																			
MINNESOTA RIVER	483055	3.5	93 10 20	34	10.0	0.29	2	0.8 <	1	0.23	12	7	6	470	0.03	32	12	690	710
COON RAPIDS DAM	483053	866	93 11 17	72	1.5	0.02	-	8.3	55	0.33	24	28	24	3300	0.13	130	-	-	-
ST ANTHONY FALLS	483054	853	93 11 17	72	3.0	0.04	12	5.2	83	0.50	21	29	39	2300	0.12	120	400	7500	2400
ST PAUL	483056	839	93 11 17	72	8.0	0.11	4	1.6	5.8	0.27	14	12	13	950	0.04	49	96	1900	1000
LOCK & DAM 2	483026	815	93 10 20	34	7.0	0.21	7	3.0	80	0.94	23	21	16	1400	0.11	91	62	3700 #	1600 #
LOCK & DAM 3	483027	797	93 11 15	68	7.0	0.10	7	3.0	92	1.04	24	23	32	1800	0.16	95	130	4300	1700
LOCK & DAM 3 REP	483027	797	93 11 15	68	7.0	0.10	8	3.4	99	1.08	27	24	18	1700	0.13	92	170	3900 #	1400 #
LOCK & DAM 4	063029	753	93 11 15	68	3.5	0.05	8	2.5	25	0.59	27	19	29	1600	0.09	79	240	5400	2900
LOCK & DAM 5	063051	738	93 11 15	61	3.3	0.05	9	3.9	43	0.70	28	18	20	2500	0.09	90	76	5900 #	2400 #
LOCK & DAM 8	633038	679	93 11 17	62	5.2	0.08	8	3.0	23	0.62	29	17	16	1600	0.09	86	49	4700 #	2200 #
1993 Flood Evaluation Work - Spring 1994																			
MINNESOTA RIVER	483055	3.5	94 6 6	42	11.6	0.28	2	0.9 <	1	0.19	9	8	15	540 <	0.02	37	74	950	570
CHAMPLIN, MN.	483068	871	94 6 6	83	8.8	0.11	1	0.4 <	1	0.04	7	4	3.8	480 <	0.02	19	5	260	190
ST ANTHONY FALLS	483054	853	94 6 6	82	6.6	0.08	3	1.2	11	0.13	11	8	16	690	0.04	52	89	1500	540
LOCK & DAM 1	483066	848	94 6 6	82	8.4	0.10	7	3.7	27	0.26	15	14	27	1500	0.08	72	200	3100	850
ST PAUL	483056	839	94 6 6	42	11.3	0.27	4	1.7	1.5	0.27	12	12	18	1200	0.04	55	150	2000	760
LOCK & DAM 2	483026	815	94 6 6	83	6.4	0.08	5	2.5	67	0.72	18	18	18	1100	0.08	73	95	2000	920
LOCK & DAM 3	483027	797	94 6 1	58	8.3	0.14	8	2.6	66	0.99	33	23	19	1300	0.12	95	256 @	4000 #	1200 #
LOCK & DAM 3 REP	483027	797	94 6 1	58	8.5	0.15	7	2.4	66	0.99	31	23	22	1200	0.12	94	252 @	3500 #	1200 #
LOWER LAKE PEPIN	473015	766	94 6 30	79	3.7	0.05	14	4.9	143	0.96	27	26	41	3200	0.10	160	1700	10000	2500
LOCK & DAM 4	063029	753	94 6 1	58	6.1	0.11	8	2.8	16	0.49	36	21	19	1200	0.08	83	274 @	4100 #	1700 #
LOCK & DAM 5	063051	738	94 6 1	58	6.7	0.12	8	2.4	15	0.52	18	8	11	670	0.06	51	282	3800	1200
LOCK & DAM 8	633038	679	94 6 2	58	6.8	0.12	5	2.1	5.3	0.42	25	13	16	920	0.06	69	191	2300	880
LOCK & DAM 9	123016	648	94 6 2	58	7.2	0.12	7	2.0	9.5	0.56	34	17	19	1300	0.10	88	251	3500	1200
LOCK & DAM 11	223263	583	94 6 4	58	11.1	0.19	5	1.5	2.0	0.49	22	12	16	780	0.04	55	192	2200	760
Historical Data - Fall 1987 - Spring 1993																			
LOCK & DAM 2	483026	815	87 11 23	60	2.5	0.04	7.9	-	-	2	-	26	20	2100	-	120	-	-	-
LOCK & DAM 2	483026	815	88 6 13	51	6.9	0.14	9	5.4	160	2	-	28	24	1700	-	140	-	-	-
LOCK & DAM 2	483026	815	88 8 29	77	9.3	0.12	8.3	5.3	170	2	-	25	28	2200	0.24	150	-	-	-
LOCK & DAM 2	483026	815	88 11 29	61	4.5	0.07	8.5	5.7	180	2	-	27	29	2200	0.24	100	-	-	-
LOCK & DAM 2	483026	815	89 6 13	63	6.0	0.10	8.8	4.2	120	2	-	25	24	2100	0.23	110	-	-	-
ST CROIX RIVER	483001	0.1	88 6 13	262	2.2	0.01	-	3.2 <	50	-	-	-	-	-	-	-	-	-	-

Table 4. Continued.

Trap Location	1 STORET ID No.	River Mile	2 Trap Collect yr mo dy	3 Exp days	4 Gross Accum cm	5 Sed. Rate cm/d	TVS %	TOC %	6 Tot. PCB ng/g	Cd µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Mn µg/g	Hg µg/g	Zn µg/g	NH4-N µg/g	TKN µg/g	TP µg/g
Historical Data - Fall 1987 - Spring 1993																			
LOCK & DAM 3	483027	797	87 11 23	60	2.7	0.05	8.7	5.1	140	1	-	28	23	2500	-	110	-	-	-
LOCK & DAM 3	483027	797	88 6 13	51	4.3	0.08	8	4.6	120	1	-	25	51	1300	-	130	-	-	-
LOCK & DAM 3	483027	797	88 11 23	62	3.1	0.05	9.5	9.6	150	2	-	27	35	3500	0.23	100	-	-	-
LOCK & DAM 3	483027	797	89 6 15	70	9.6	0.14	7.8	3.3	100	2	-	22	32	1700	0.24	100	-	-	-
LOCK & DAM 3	483027	797	89 11 21	68	3.8	0.06	10	2.7	160	2	-	60	53	2600	0.21	130	-	-	-
LOCK & DAM 3	483027	797	90 5 29	62	6.1	0.10	9	2.7	110	2	-	43	24	1800	0.22	110	-	-	-
LOCK & DAM 3	483027	797	90 11 27	69	3.8	0.06	10	2.8	110	2	-	35	21	2800	0.17	120	-	-	-
LOCK & DAM 3	483027	797	91 6 4	63	7.3	0.12	7	2.7	70	1.14	-	23.4	23.5	1400	0.17	92	-	-	-
LOCK & DAM 3	483027	797	91 11 6	49	4.1	0.08	8	2.6	80	1	-	21	21	1600	0.15	93	-	-	-
LOCK & DAM 3	483027	797	92 6 3	56	7.9	0.14	8	2.3	80	0.7	-	23	15	1400	0.23	110	-	-	-
LOCK & DAM 3	483027	797	92 9 2	91	7.8	0.09	7	2.3	80	1.06	-	19.1	14	1300	0.14	79	-	-	-
LOCK & DAM 3	483027	797	92 11 3	62	5.7	0.09	7	3.4	80	1.05	-	22	20	1700	0.13	99	-	-	-
LOCK & DAM 3	483027	797	93 6 1	63	9.8	0.16	8	2.0	50	0.88	24	21	15	1300	0.10	82	194	3300	1200
LOCK & DAM 4	063029	753	87 11 23	60	2.5	0.04	12.3	6.3	70 <	1	-	15	25	1800	-	100	-	-	-
LOCK & DAM 4	063029	753	88 6 13	51	3.9	0.08	10	4.8 <	50 <	1	-	20	20	2100	-	85	-	-	-
LOCK & DAM 4	063029	753	89 6 15	70	6.4	0.09	10.8	4.4 <	50	2	-	22	21	2500	0.17	94	-	-	-
LOCK & DAM 4	063029	753	89 11 21	68	2.0	0.03	13	2.6	90	1	-	52	25	4700	0.17	110	-	-	-
LOCK & DAM 4	063029	753	90 5 29	62	5.7	0.09	11	2.6 <	50	1	-	27	17	2100	0.12	85	-	-	-
LOCK & DAM 4	063029	753	90 11 27	69	2.5	0.04	12	3.9 <	50	2	-	22	17	3500	0.10	100	-	-	-
LOCK & DAM 4	063029	753	91 6 4	63	7.0	0.11	9	3.6 <	50	0.51	-	22.4	18.8	1400	0.12	84	-	-	-
LOCK & DAM 4	063029	753	91 11 6	49	1.7	0.04	10	3.3	33	1	-	21	12	2400	0.09	93	-	-	-
LOCK & DAM 4	063029	753	92 6 3	56	5.8	0.10	10	3.3	32	0.79	-	21	12	1400	0.23	87	-	-	-
LOCK & DAM 4	063029	753	92 9 2	91	10.6	0.12	10	2.5	34	0.63	-	23.8	12	2300	0.11	86	-	-	-
LOCK & DAM 4	063029	753	92 11 3	62	4.6	0.07	8	4.5	39	0.61	-	21	15	2300	0.08	83	-	-	-
LOCK & DAM 4	063029	753	93 6 1	63	5.8	0.09	7	2.5	20	0.62	29	21	13	1100	0.08	77	70	3200	1600

1 - U.S. EPA's Storage and Retieval (STORET) computer data base system
2 - Date of sediment trap collection
3 - Sediment trap exposure period
4 - Gross sediment accumulation in trap
5 - Sedimentation rate
6 - Sum of PCB congeners at or above the method detection limit
@ - Holding time exceedance, results are approximate
# - Spike quality control exceeded matrix group, results are approximate
nd - Not detected
na - Not available
\- - No sample



L/D = Lock and Dam
SAF = St. Anthony Falls

Figure 1. Upper Mississippi River study area.

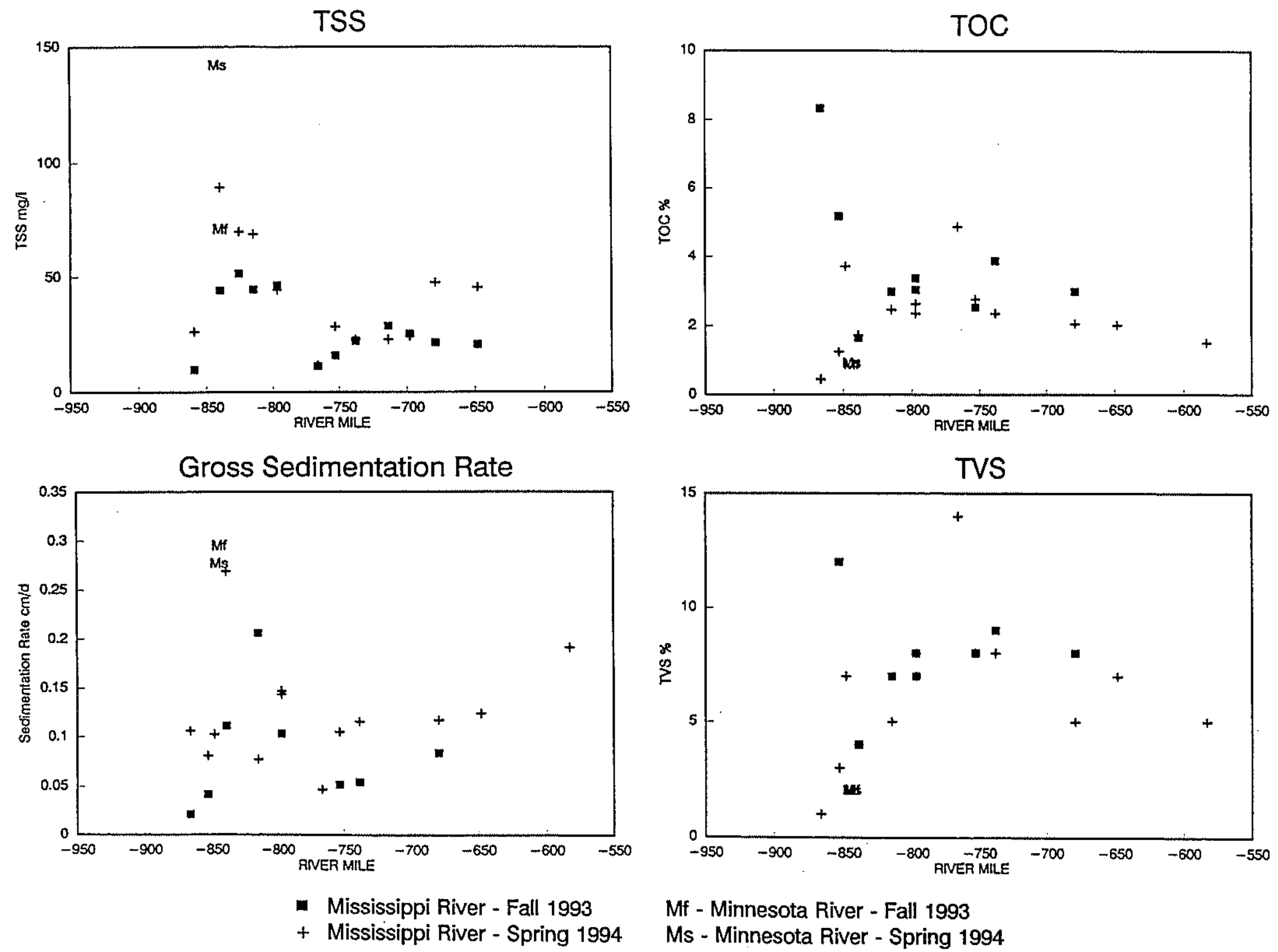


Figure 2. Longitudinal profile of total suspended solids (TSS), total organic carbon (TOC), gross sedimentation rate and total volatile solid (TVS) concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

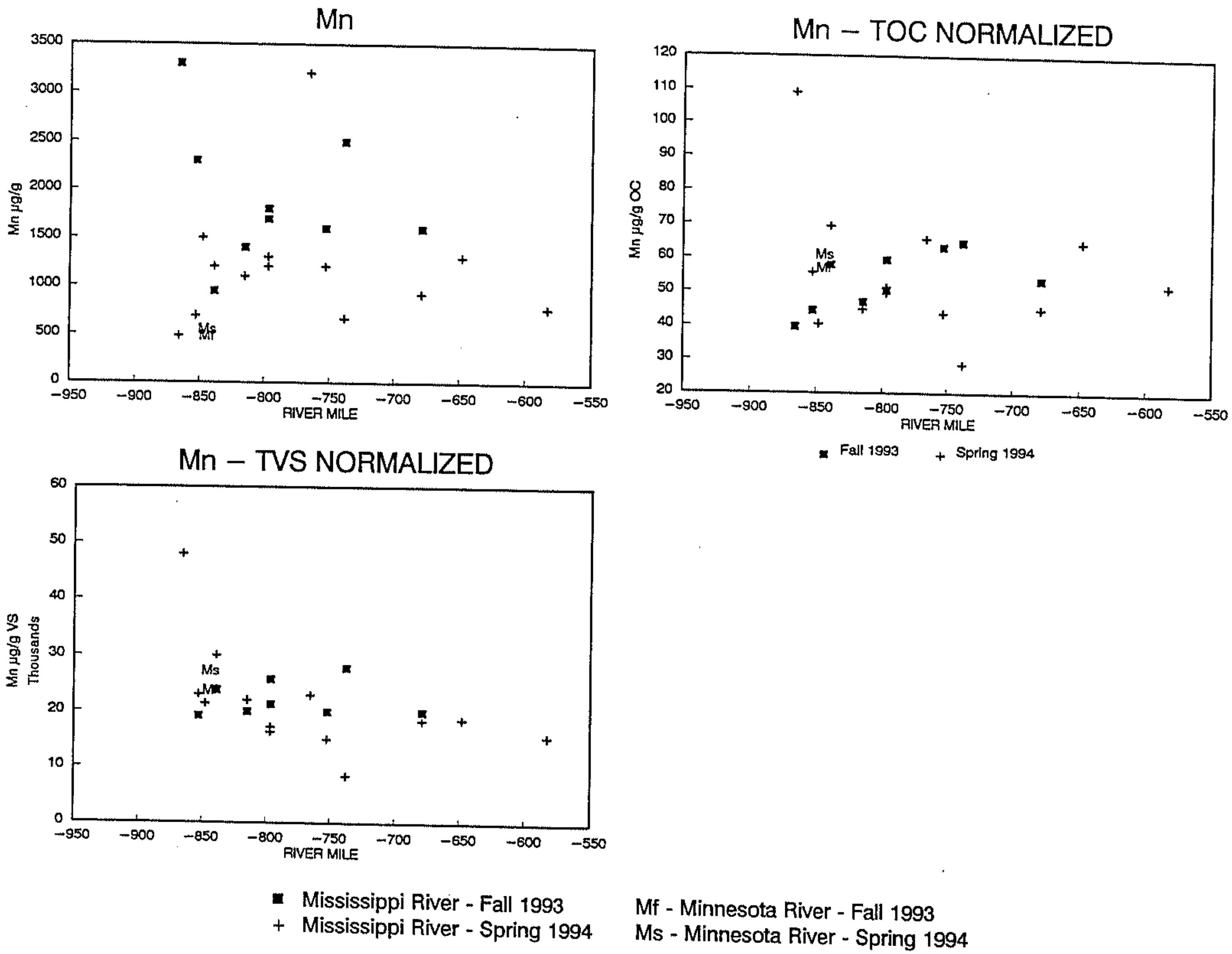


Figure 3. Longitudinal profile of manganese (Mn), total organic carbon-normalized Mn and total volatile solids-normalized Mn concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

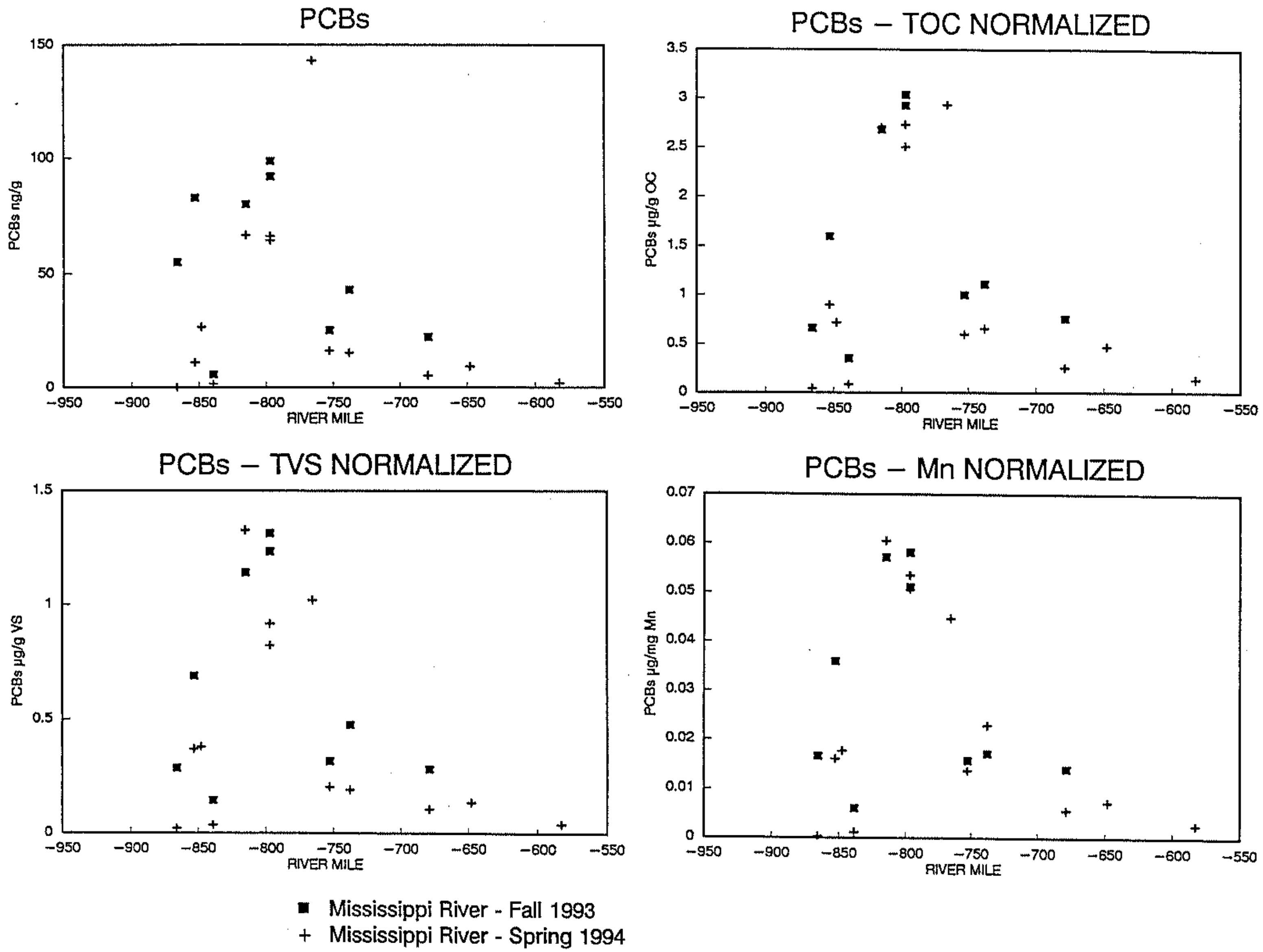


Figure 4. Longitudinal profile of total polychlorinated biphenyls (PCBs), total organic carbon-normalized PCBs, total volatile solids-normalized PCBs and manganese-normalized PCB concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

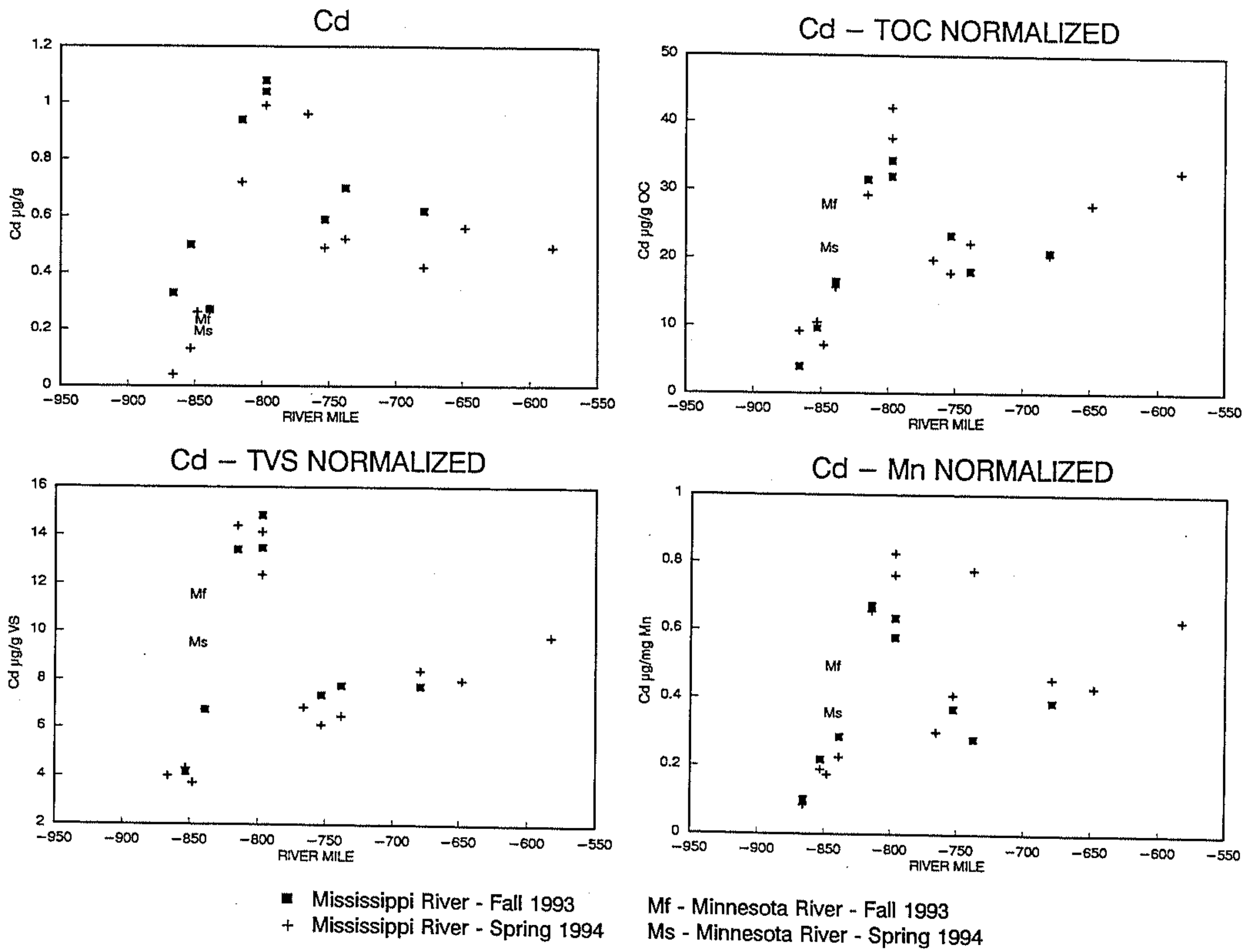


Figure 5. Longitudinal profile of cadmium (Cd), total organic carbon-normalized Cd, total volatile solids-normalized Cd and manganese-normalized Cd concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

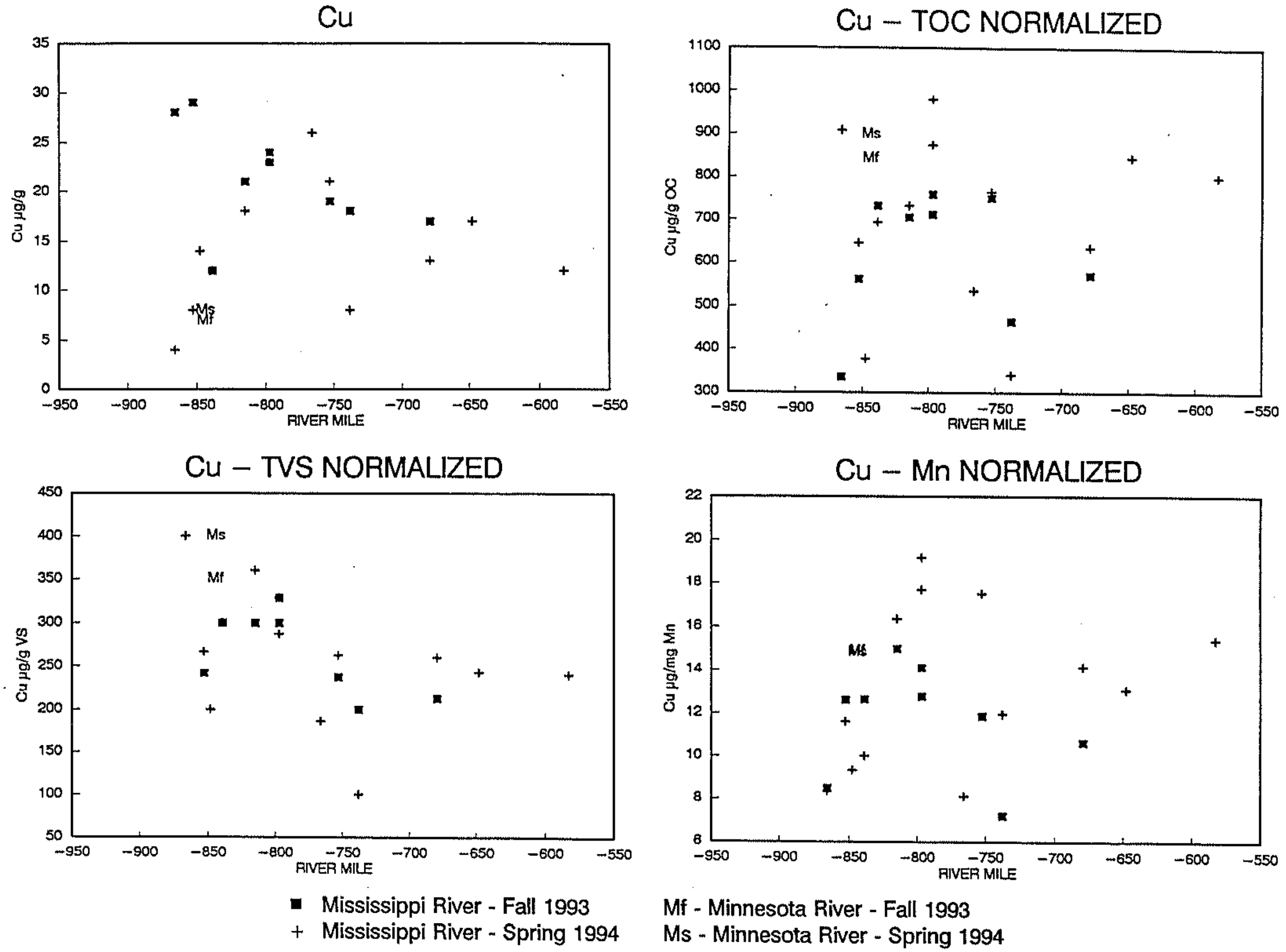


Figure 6. Longitudinal profile of copper (Cu), total organic carbon-normalized Cu, total volatile solids-normalized Cu and manganese-normalized Cu concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

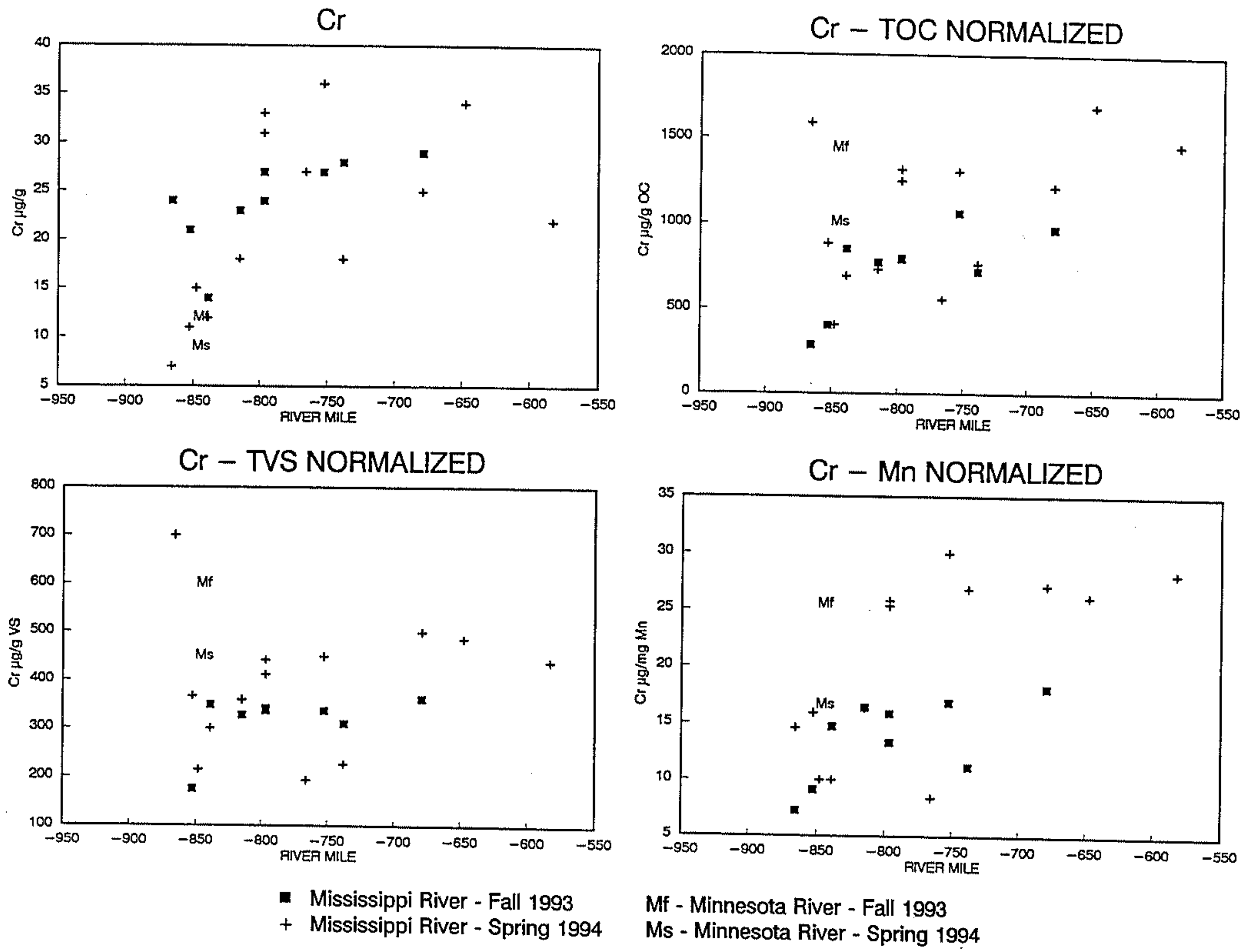


Figure 7. Longitudinal profile of chromium (Cr), total organic carbon-normalized Cr, total volatile solids-normalized Cr and manganese-normalized Cr concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

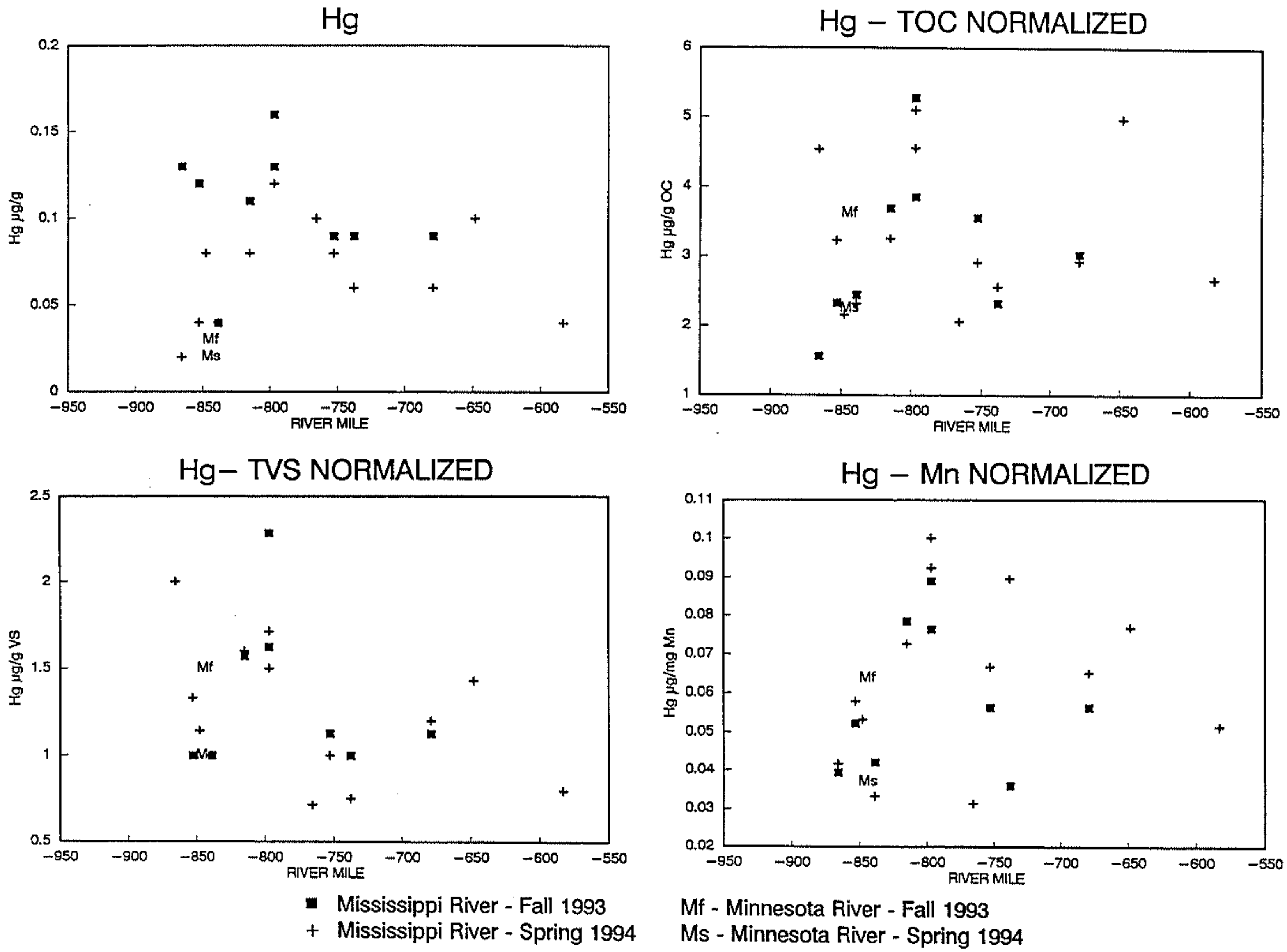


Figure 8. Longitudinal profile of mercury (Hg), total organic carbon-normalized Hg, total volatile solids-normalized Hg and manganese-normalized Hg concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

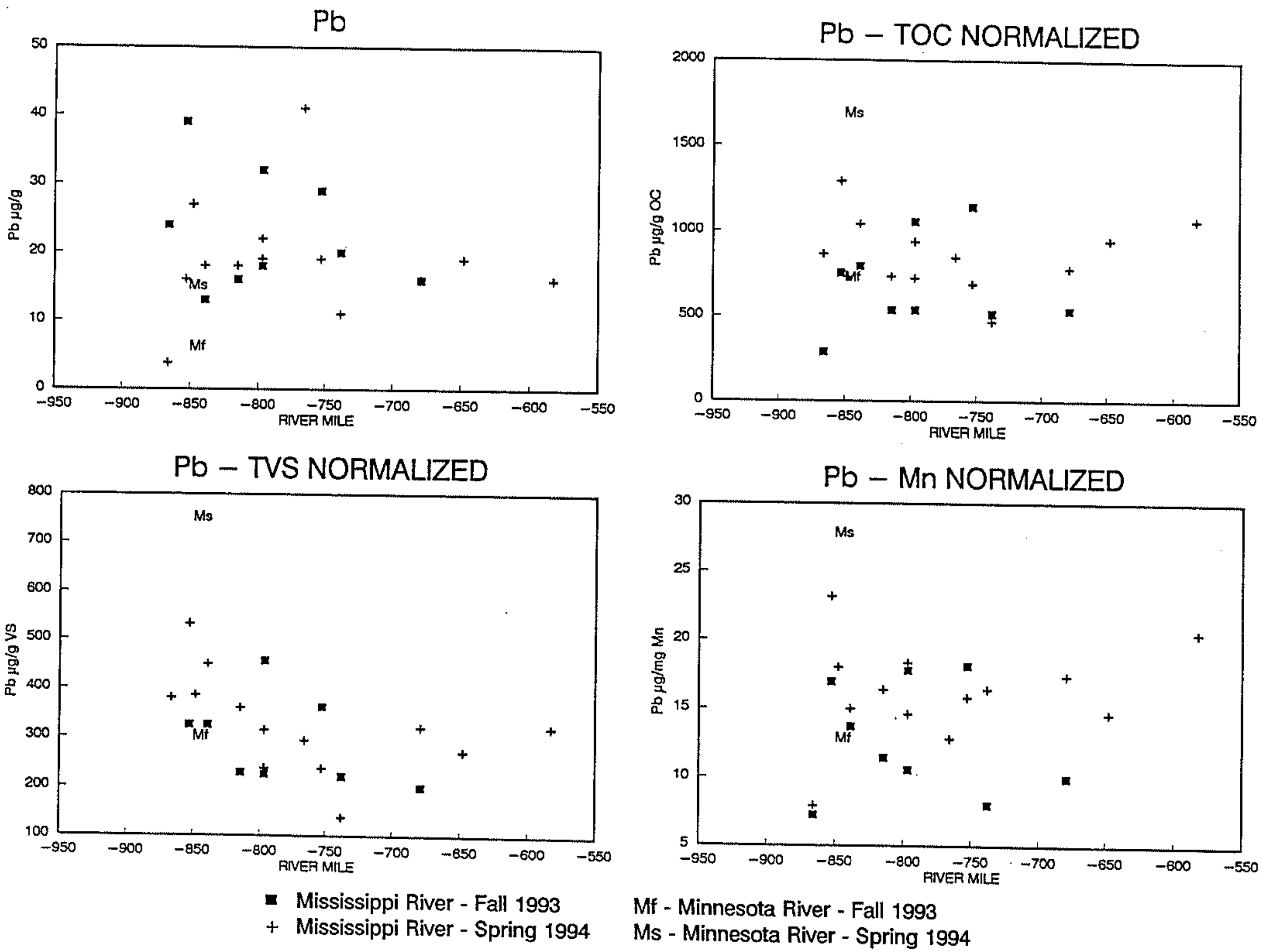


Figure 9. Longitudinal profile of lead (Pb), total organic carbon-normalized Pb, total volatile solids-normalized Pb and manganese-normalized Pb concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

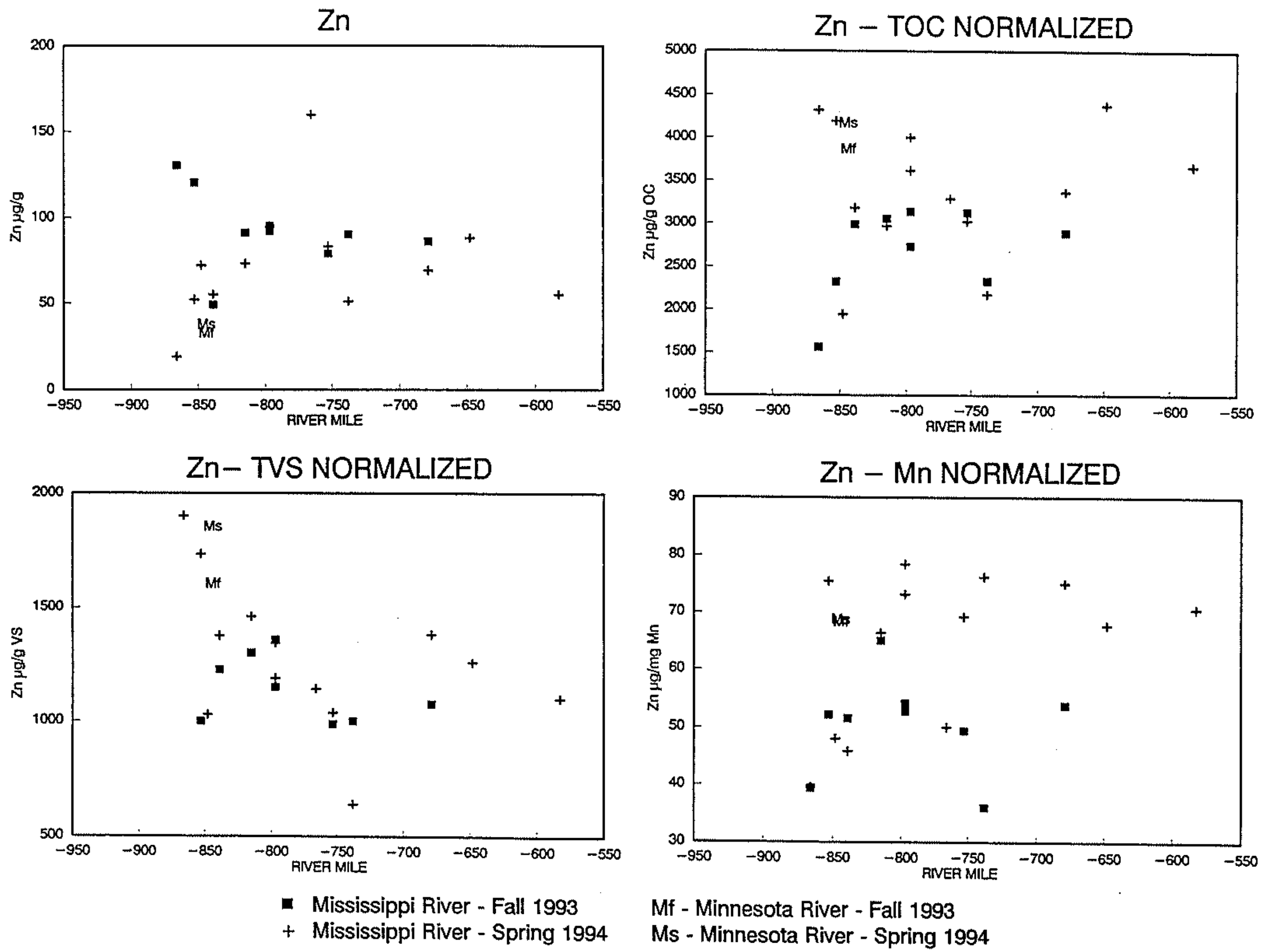


Figure 10. Longitudinal profile of zinc (Zn), total organic carbon-normalized Zn, total volatile solids-normalized Zn and manganese-normalized Zn concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

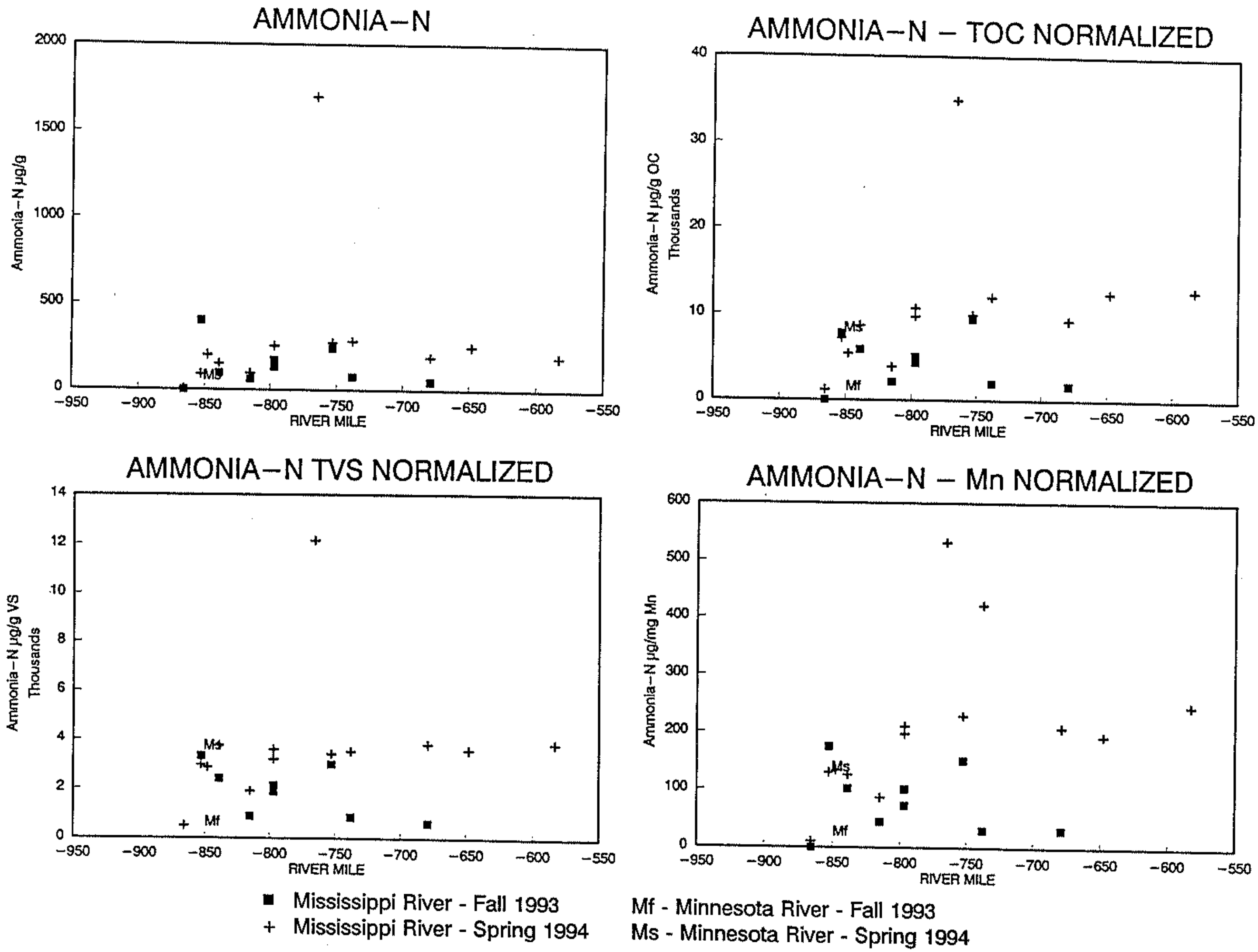


Figure 11. Longitudinal profile of ammonia-nitrogen (N), total organic carbon-normalized ammonia-N, total volatile solids-normalized ammonia-N and manganese-normalized ammonia-N concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

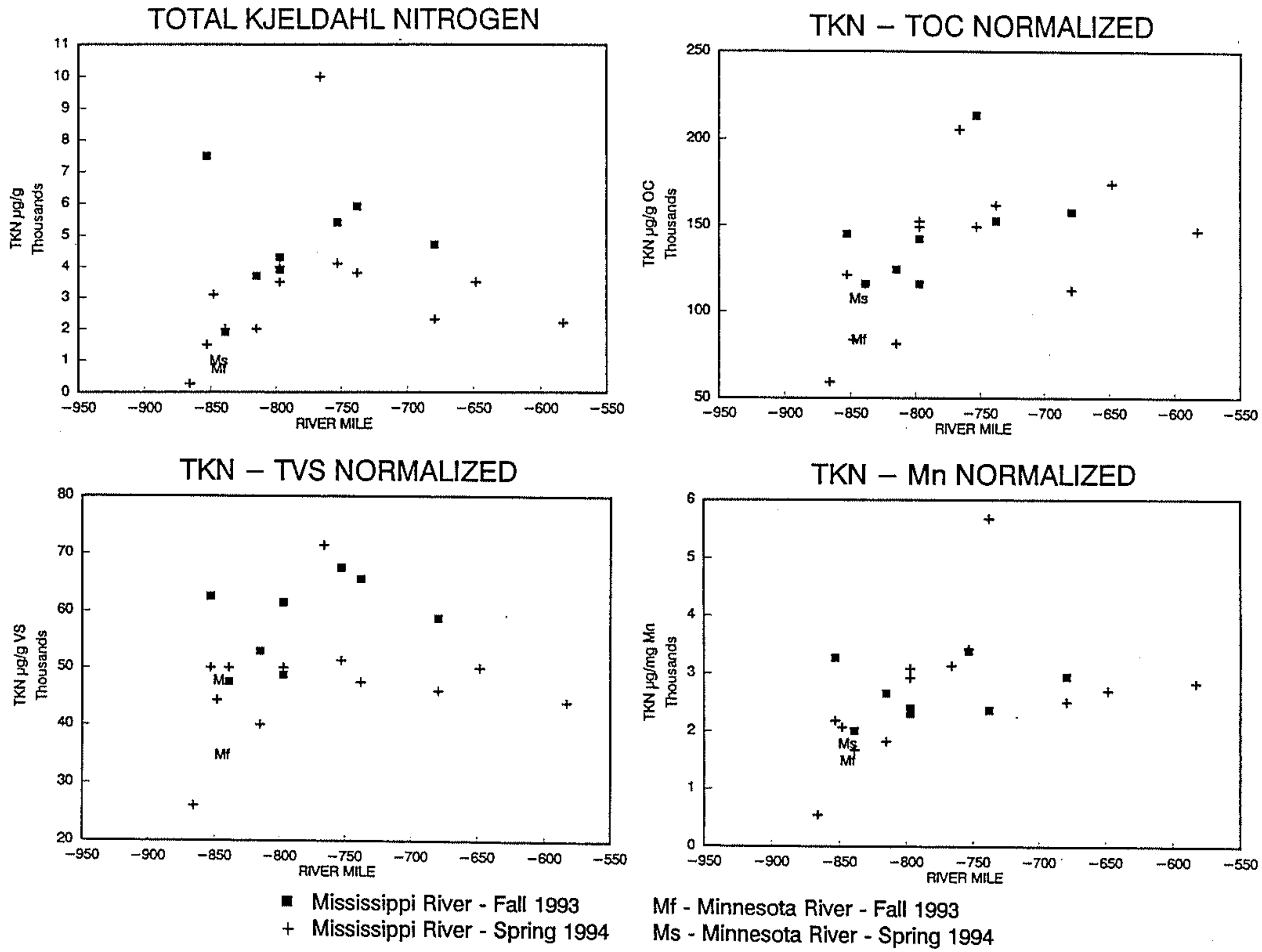


Figure 12. Longitudinal profile of total Kjeldahl nitrogen (TKN), total organic carbon-normalized TKN, total volatile solids-normalized TKN and manganese-normalized TKN concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.

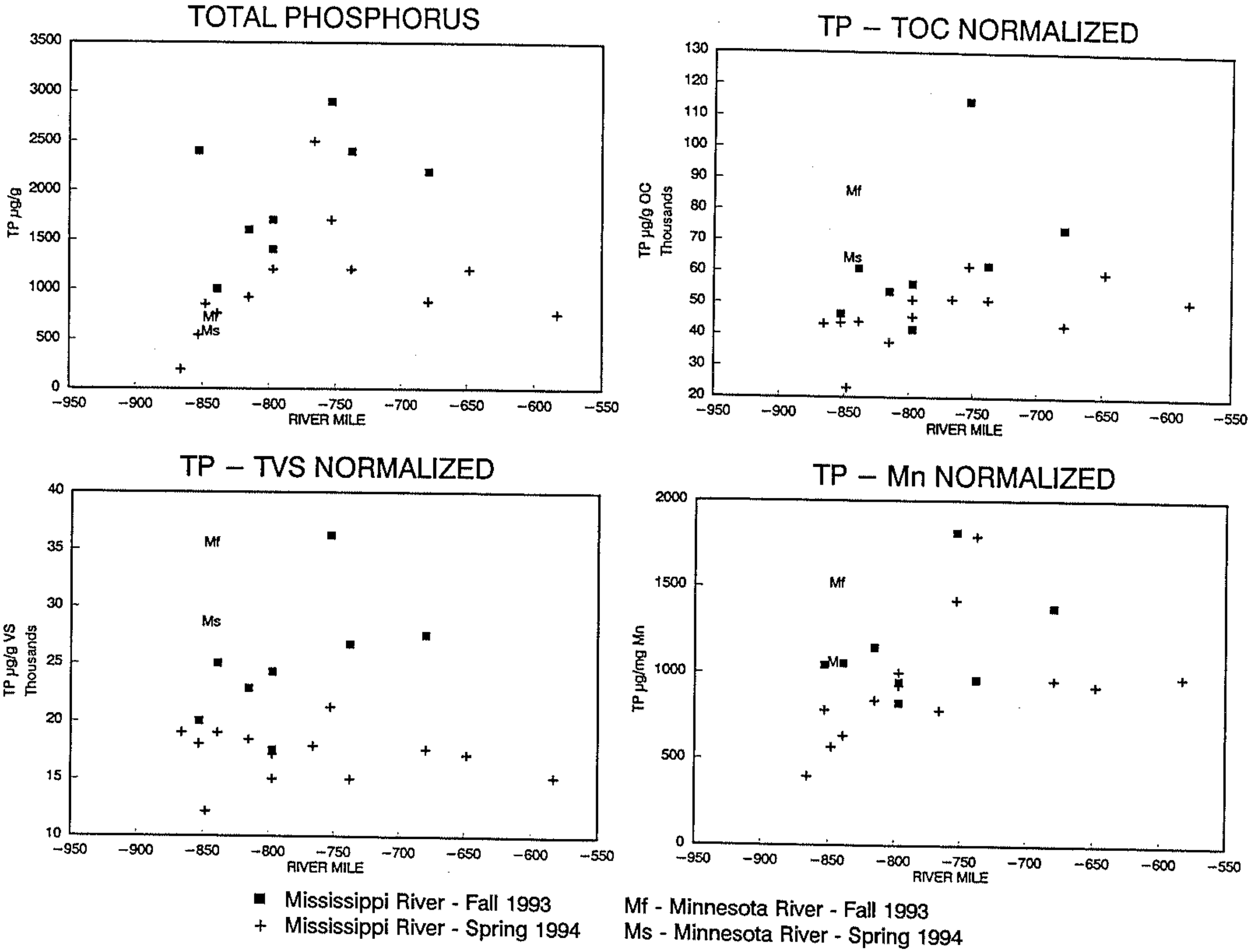
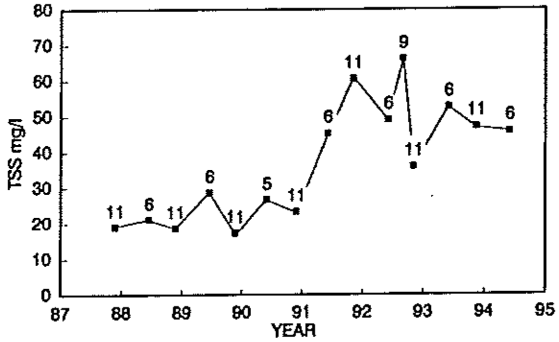
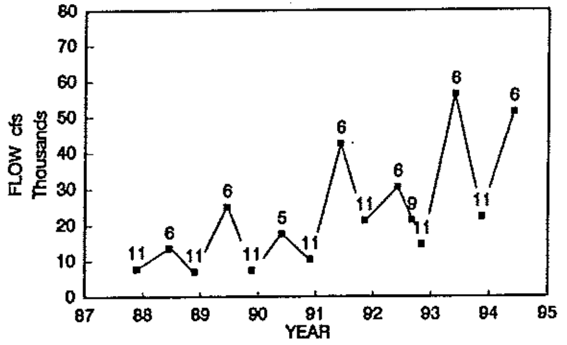


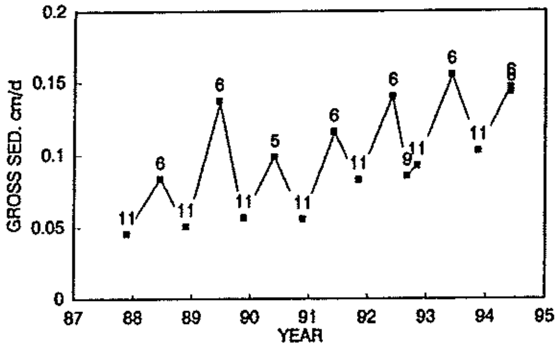
Figure 13. Longitudinal profile of total phosphorus (TP), total organic carbon-normalized TP, total volatile solids-normalized TP and manganese-normalized TP concentrations in sediment trap samples collected from the Upper Mississippi River in the fall of 1993 and spring of 1994.



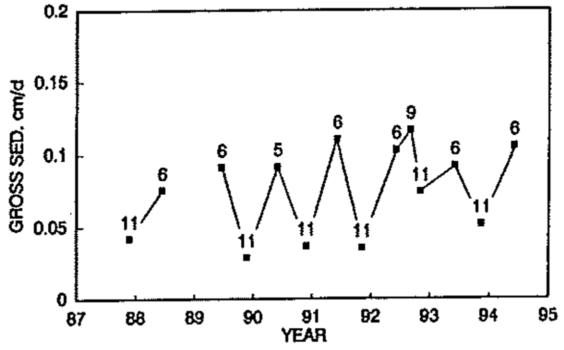
TSS – L/D 3



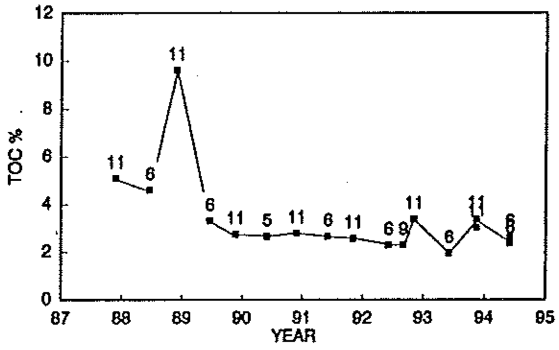
RIVER FLOW AT PRESCOTT, WI



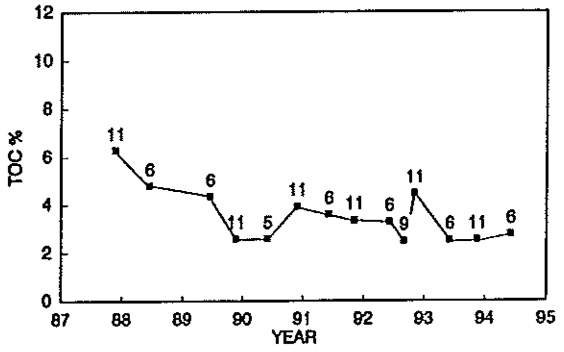
GROSS SED. RATE – L/D 3



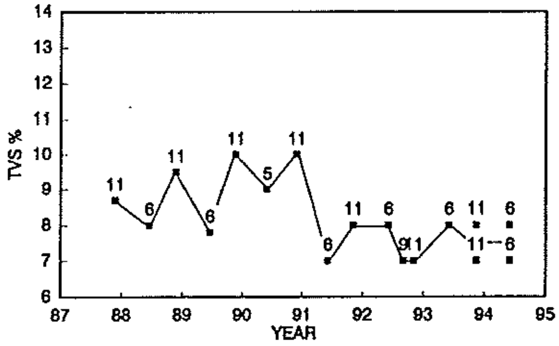
GROSS SED. RATE – L/D 4



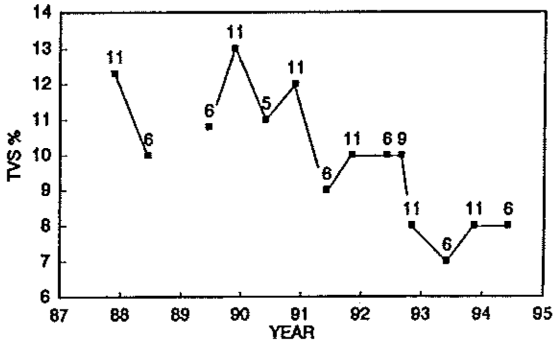
TOC – L/D 3



TOC – L/D 4



TVS – L/D 3



TVS – L/D 4

Figure 14. Total suspended solids (TSS) at L/D 3, river flow at Prescott, Wisconsin, and gross sedimentation rate, total organic carbon (TOC) and total volatile solid (TVS) concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.

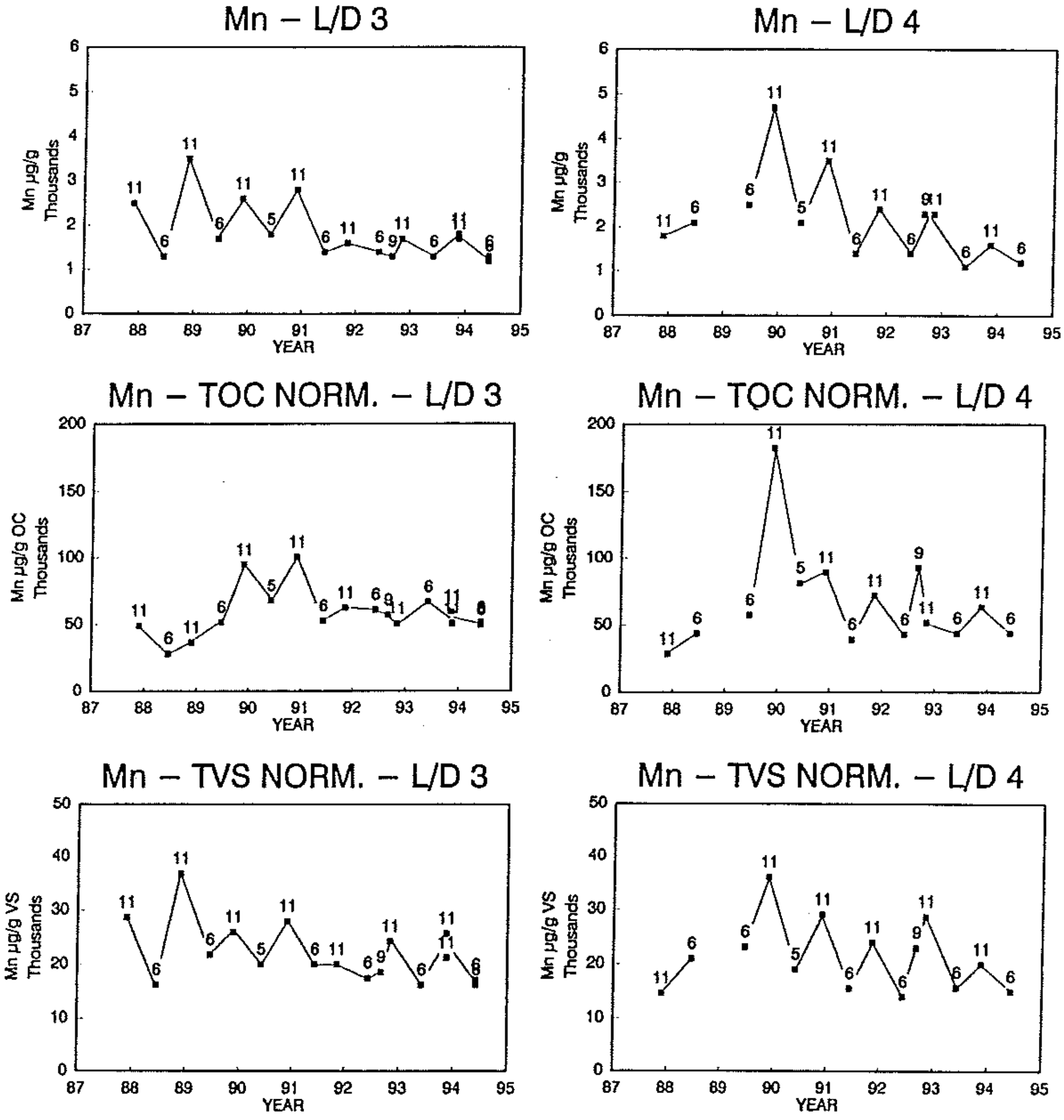
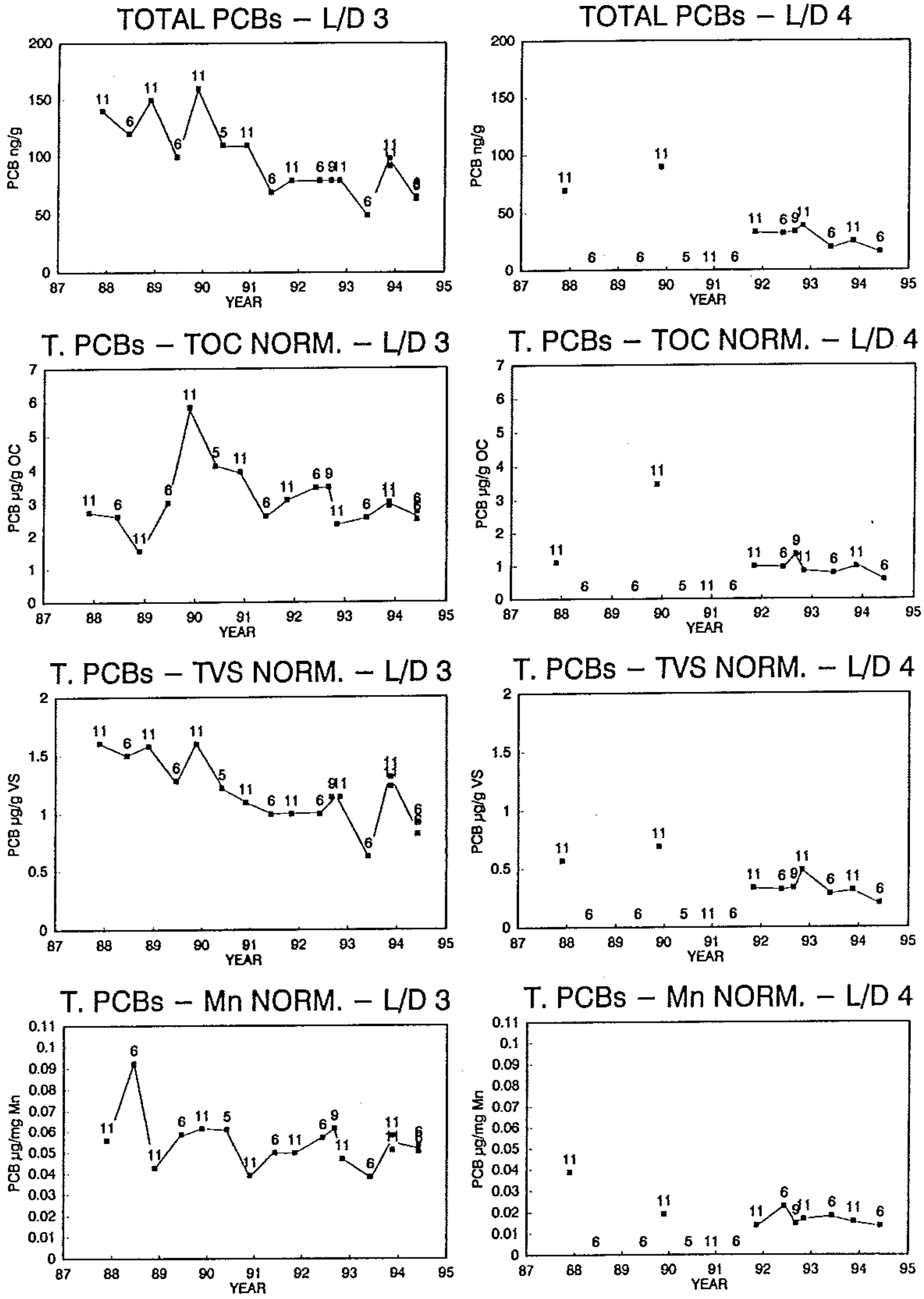


Figure 15. Manganese (Mn), total organic carbon-normalized Mn and total volatile solids-normalized Mn concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.


TOTAL PCBs – L/D 3

TOTAL PCBs – L/D 4

T. PCBs – TOC NORM. – L/D 3

T. PCBs – TOC NORM. – L/D 4

T. PCBs – TVS NORM. – L/D 3

T. PCBs – TVS NORM. – L/D 4

T. PCBs – Mn NORM. – L/D 3

T. PCBs – Mn NORM. – L/D 4

Figure 16. Total polychlorinated biphenyls (PCBs), total organic carbon-normalized PCBs, total volatile solids-normalized PCBs and Manganese (Mn) - normalized PCB concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.

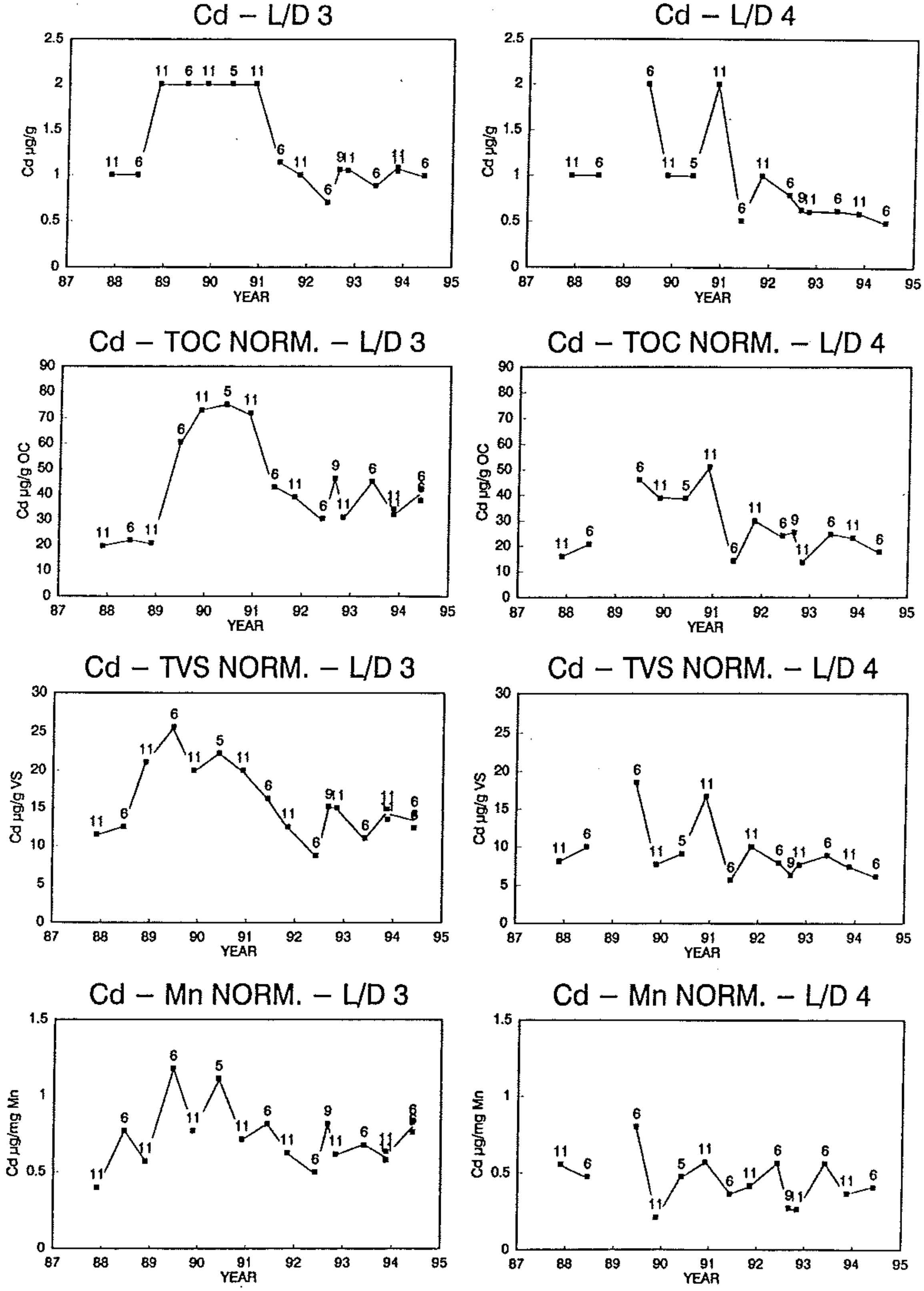


Figure 17. Cadmium (Cd), total organic carbon-normalized Cd, total volatile solids-normalized Cd and Manganese (Mn) - normalized Cd concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.

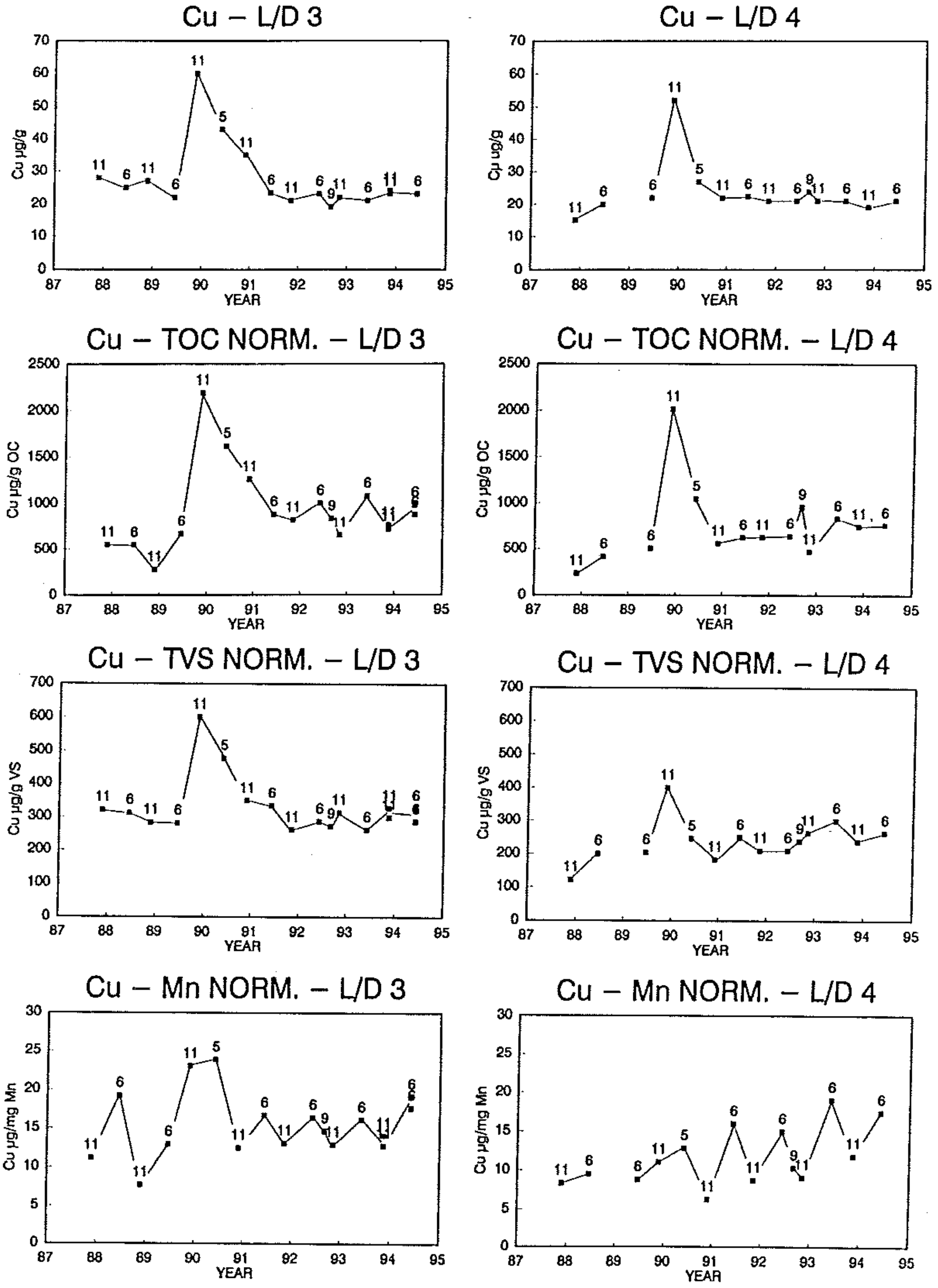


Figure 18. Copper (Cu), total organic carbon-normalized Cu, total volatile solids-normalized Cu and Manganese (Mn) - normalized Cu concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.

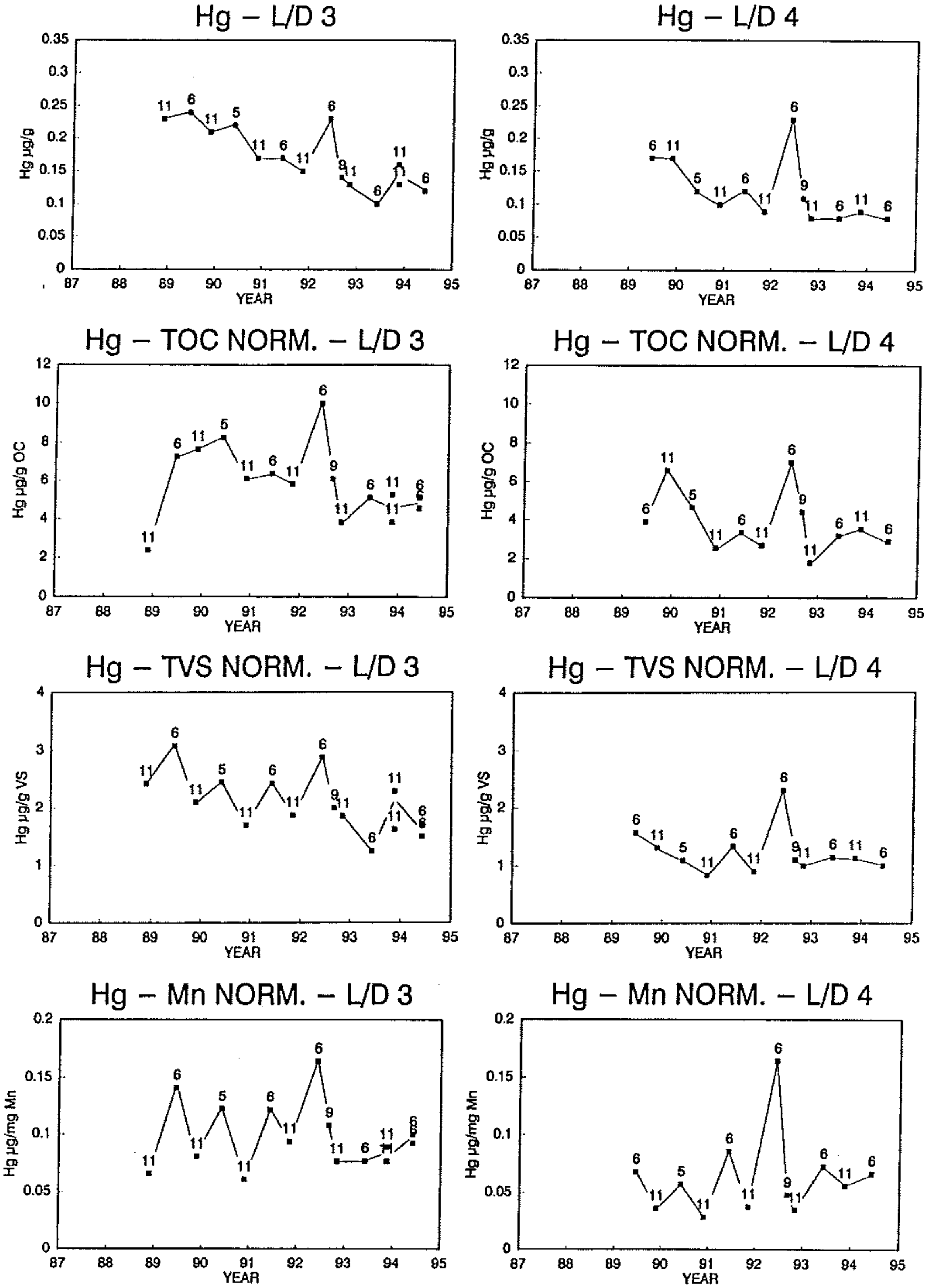


Figure 19. Mercury (Hg), total organic carbon-normalized Hg, total volatile solids-normalized Hg and Manganese (Mn) - normalized Hg concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.

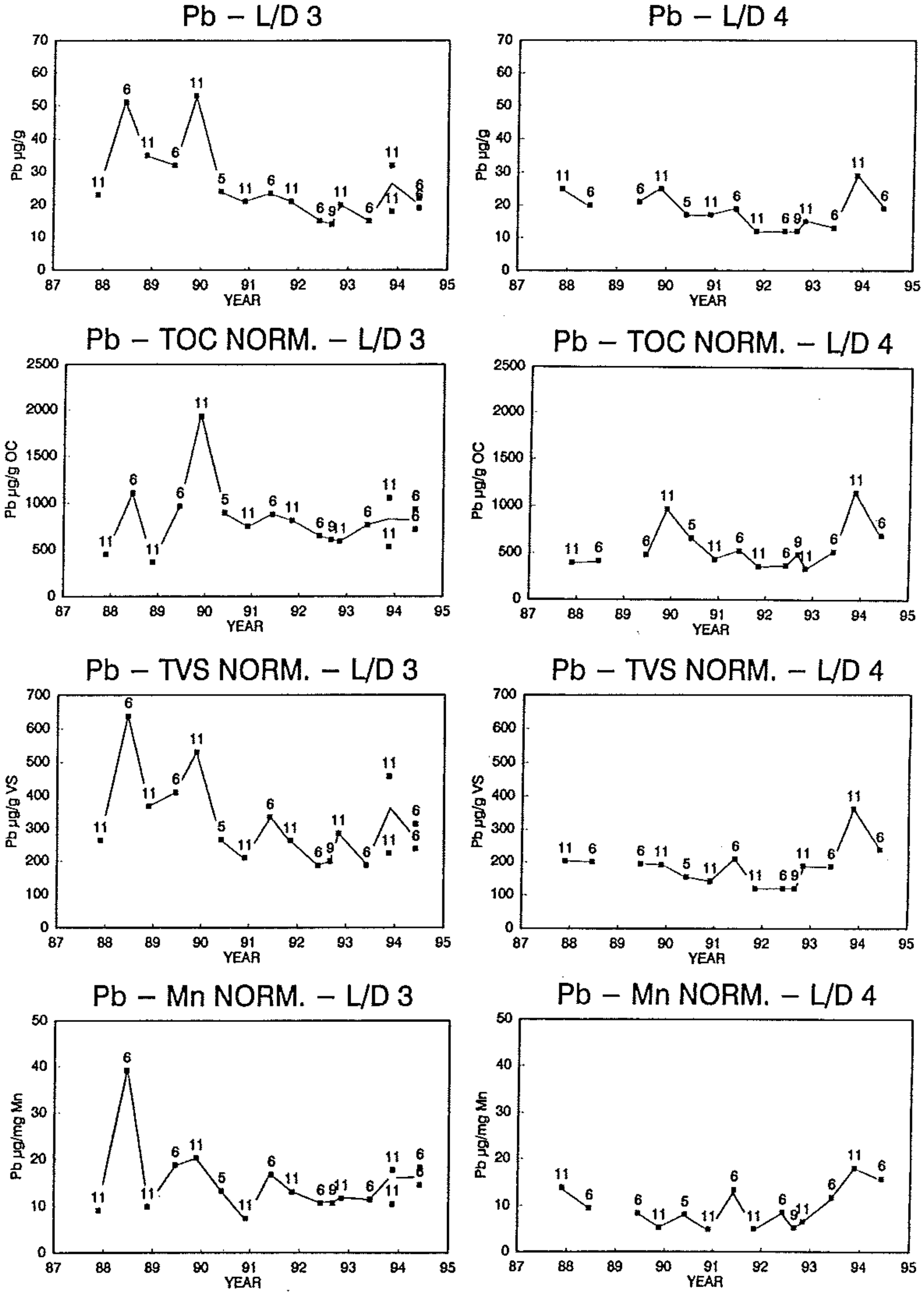
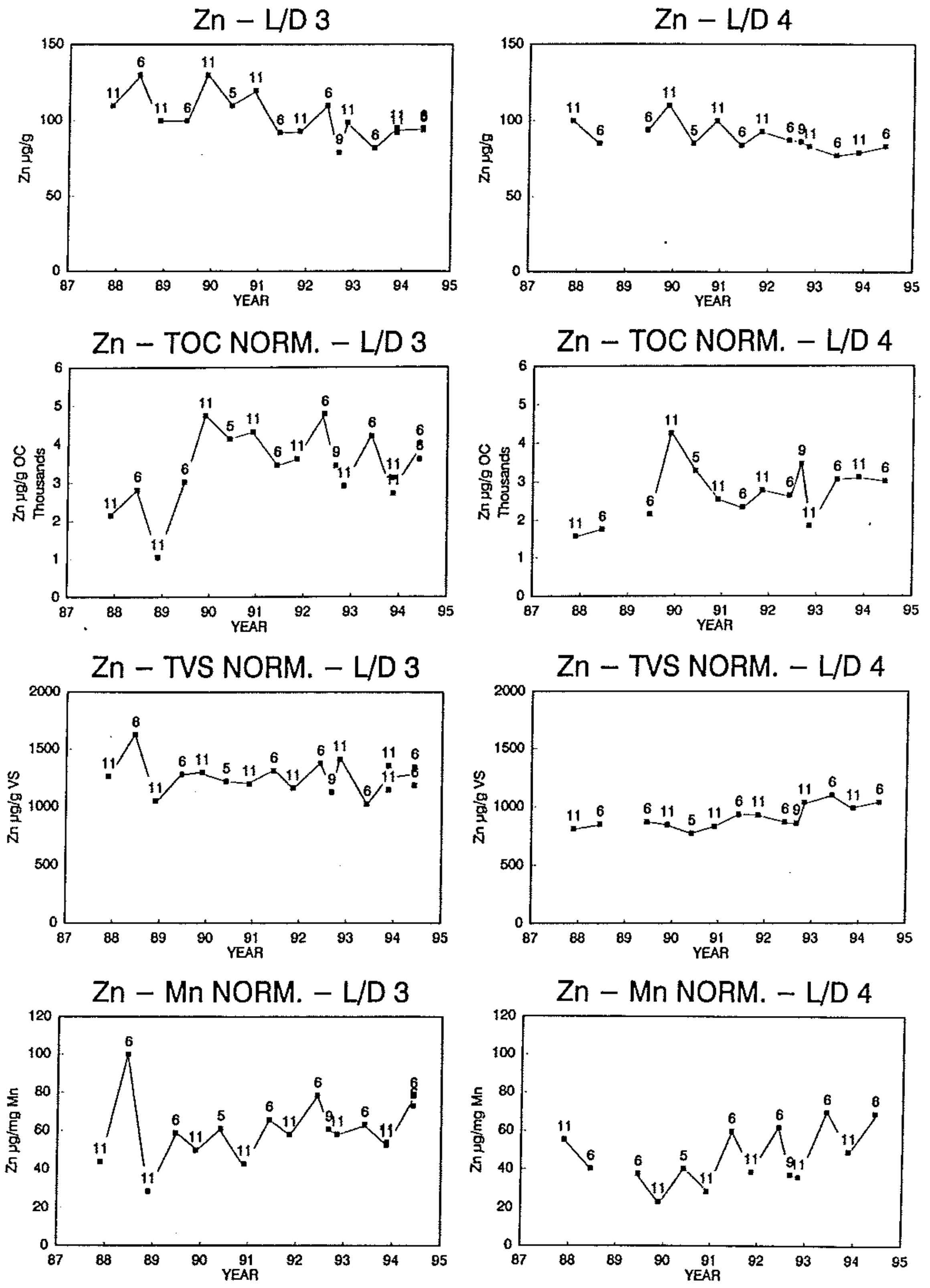


Figure 20. Lead (Pb), total organic carbon-normalized Pb, total volatile solids-normalized Pb and Manganese (Mn) - normalized Pb concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.



Zn – L/D 3

Zn – L/D 4

Zn – TOC NORM. – L/D 3

Zn – TOC NORM. – L/D 4

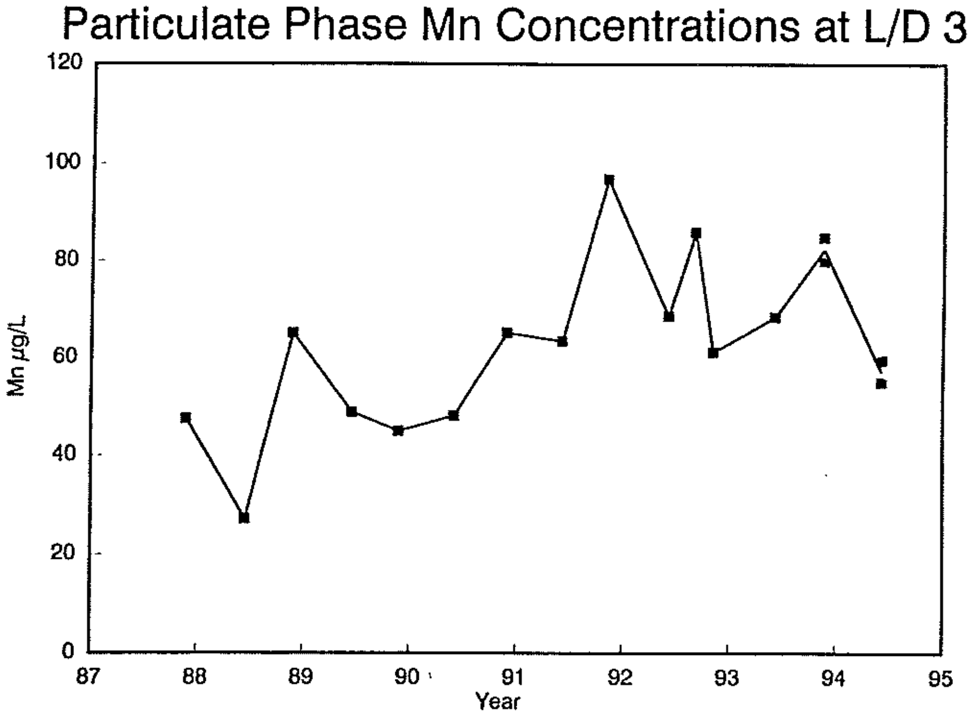
Zn – TVS NORM. – L/D 3

Zn – TVS NORM. – L/D 4

Zn – Mn NORM. – L/D 3

Zn – Mn NORM. – L/D 4

Figure 21. Zinc (Zn), total organic carbon-normalized Zn, total volatile solids-normalized Zn and Manganese (Mn) - normalized Zn concentrations in sediment trap samples collected from the Upper Mississippi River at Lock and Dams 3 and 4 for the period 1987 to 1994. Numbers above points in graphs represent the month samples were retrieved from the river.


Particulate Phase Mn Concentrations at L/D 3

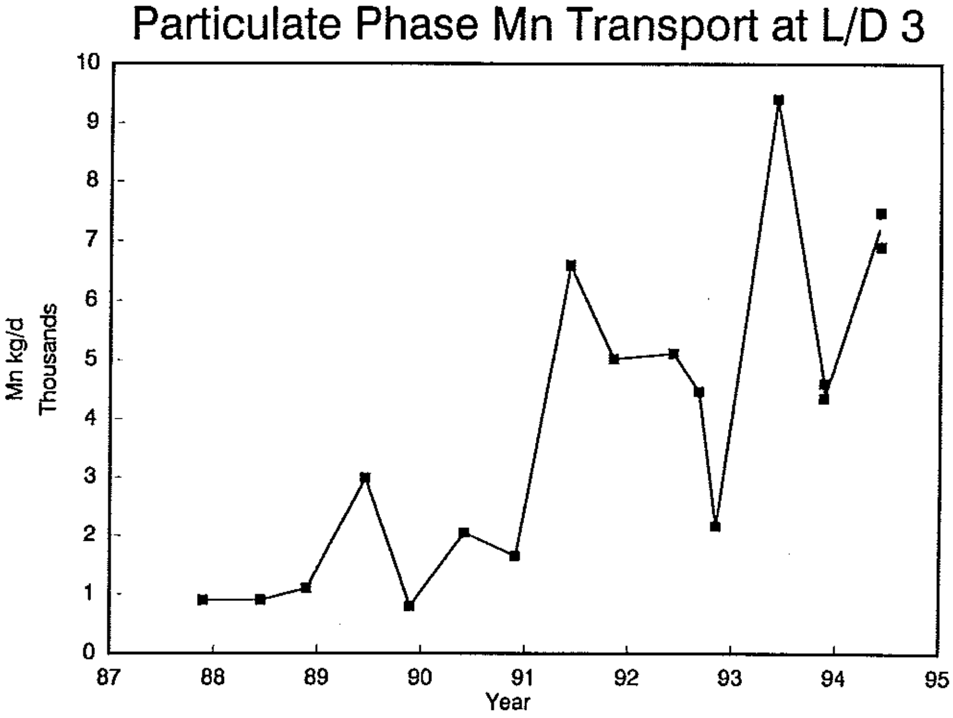
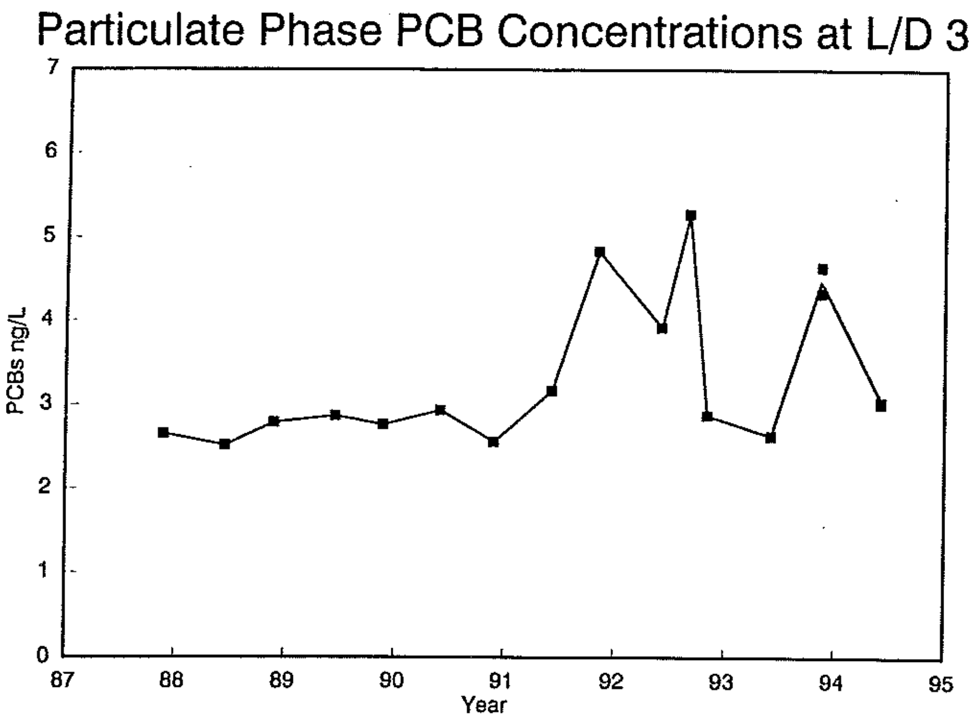

Particulate Phase Mn Transport at L/D 3

Figure 22. Whole-water particulate phase manganese (Mn) concentrations (µg/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1987 to 1994. Mn concentrations estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment.



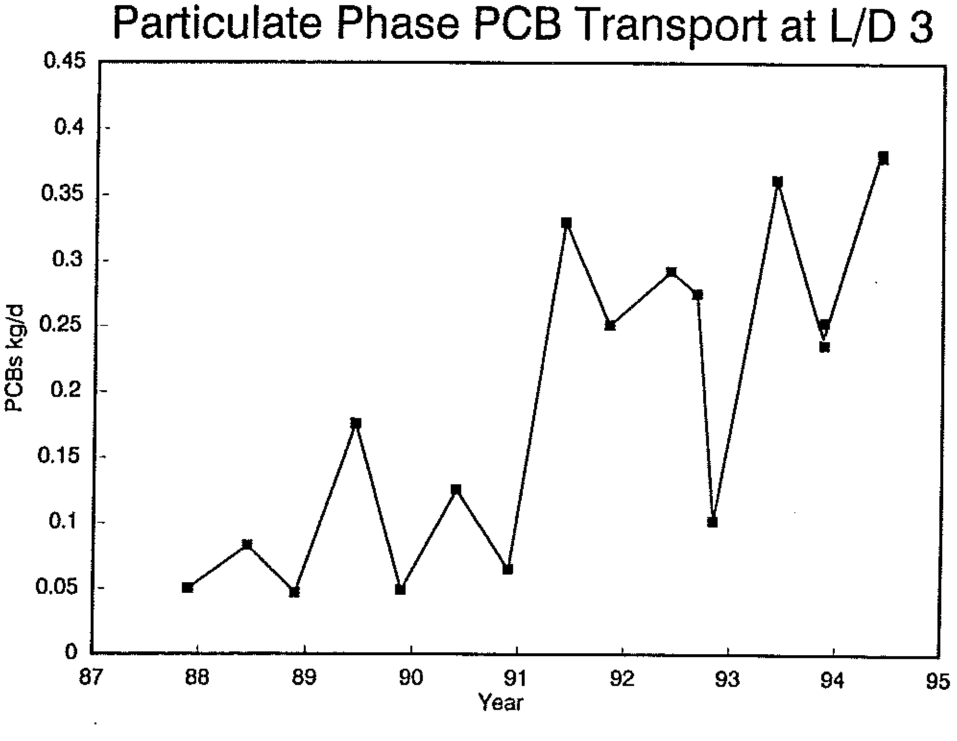
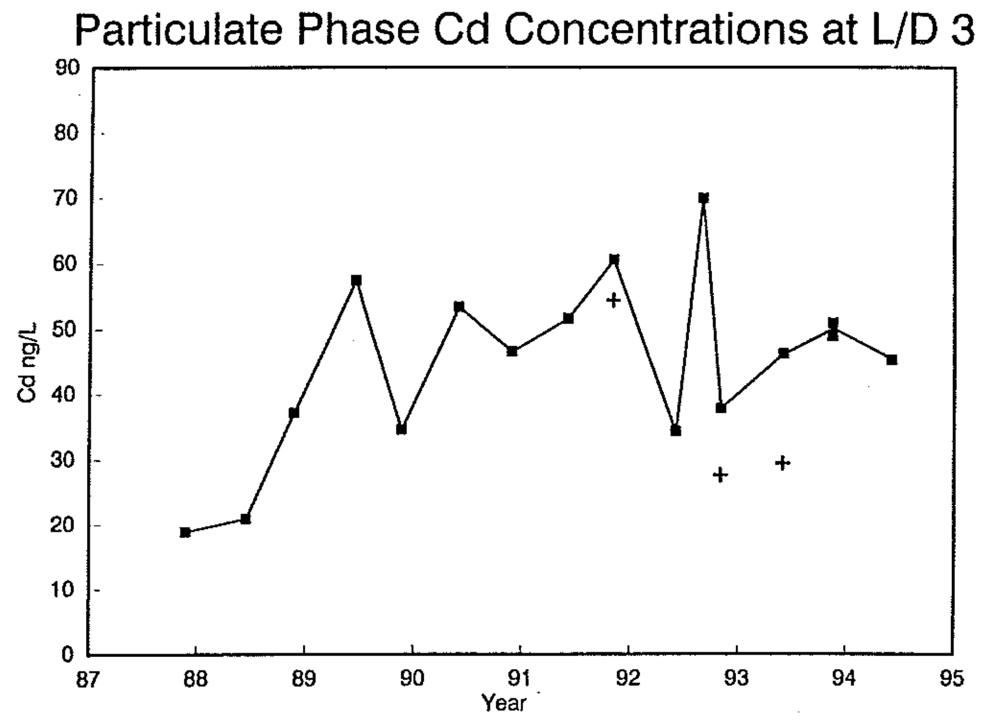


Figure 23. Whole-water particulate phase polychlorinated biphenyl (PCB) concentrations (ng/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1987 to 1994. PCB concentrations estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment.



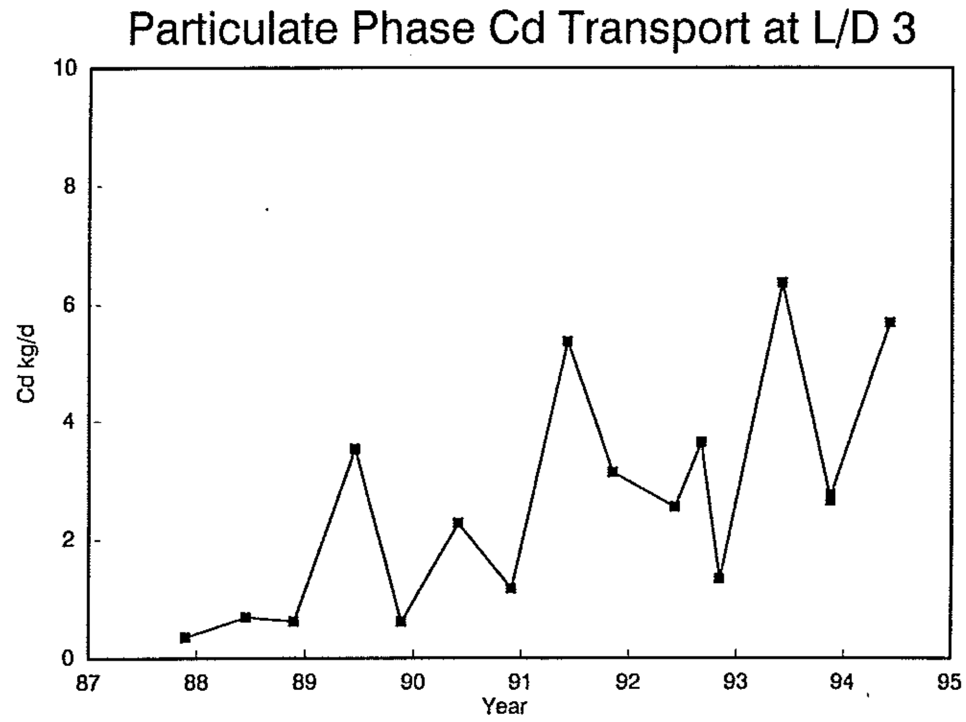
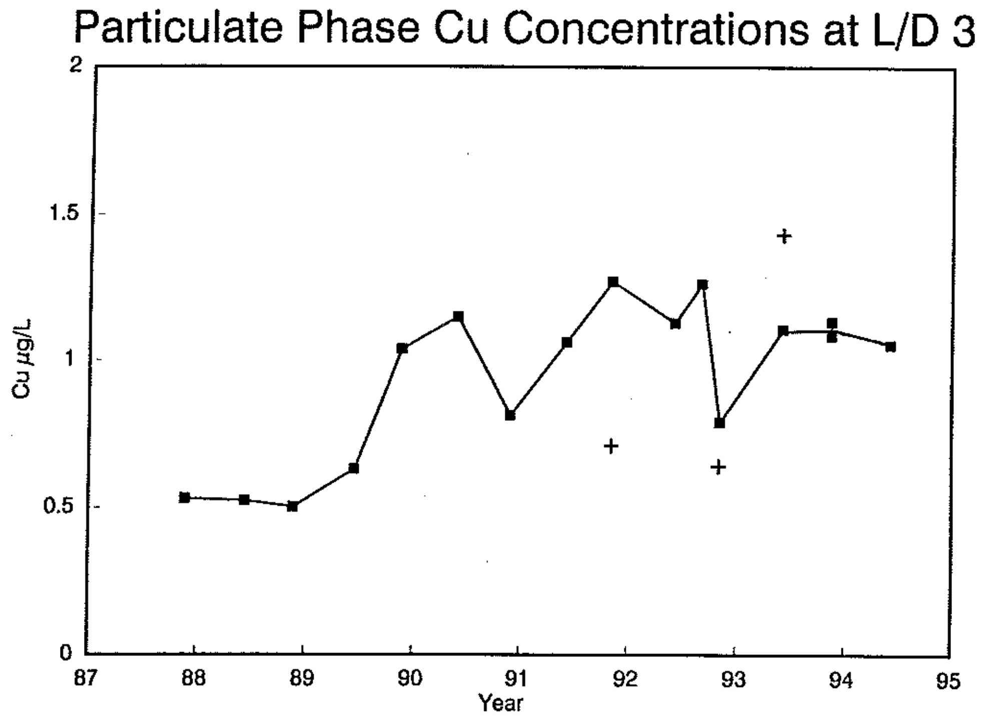


Figure 24. Whole-water particulate phase cadmium (Cd) concentrations (ng/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1987 to 1994. Cd concentrations (■) estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment. Other Cd concentrations (+) obtained from grab samples analyzed using low-level analytical methods (Webb 1994).



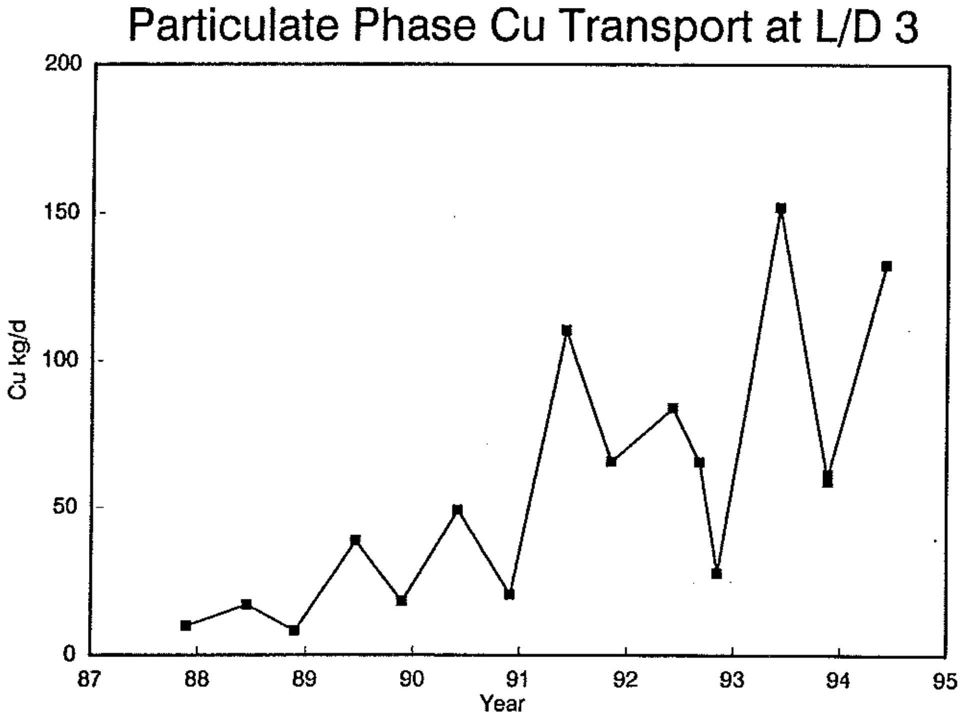


Figure 25. Whole-water particulate phase copper (Cu) concentrations (µg/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1987 to 1994. Cu concentrations (■) estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment. Other Cu concentrations (+) obtained from grab samples analyzed using low-level analytical methods (Webb 1994).

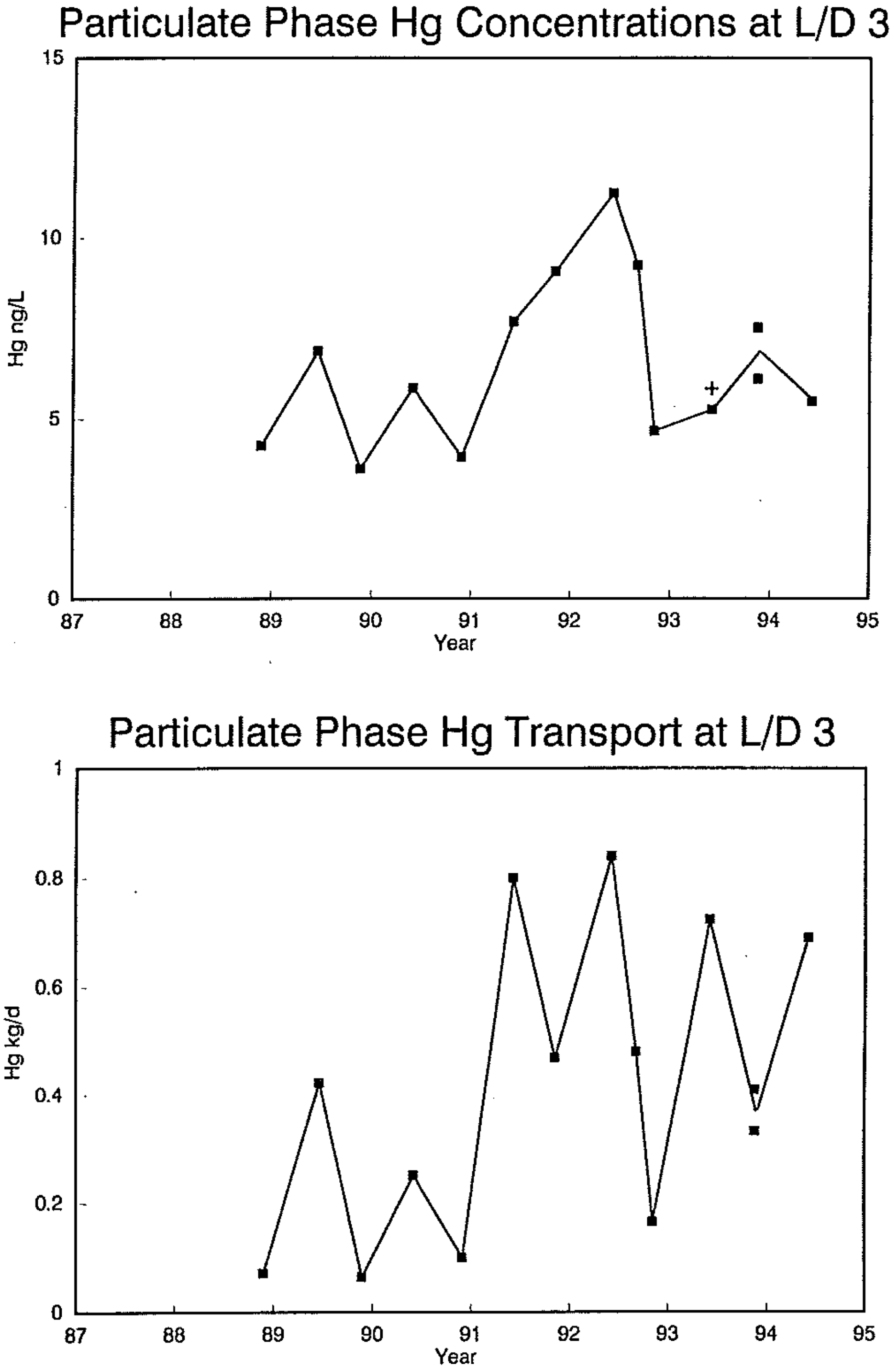
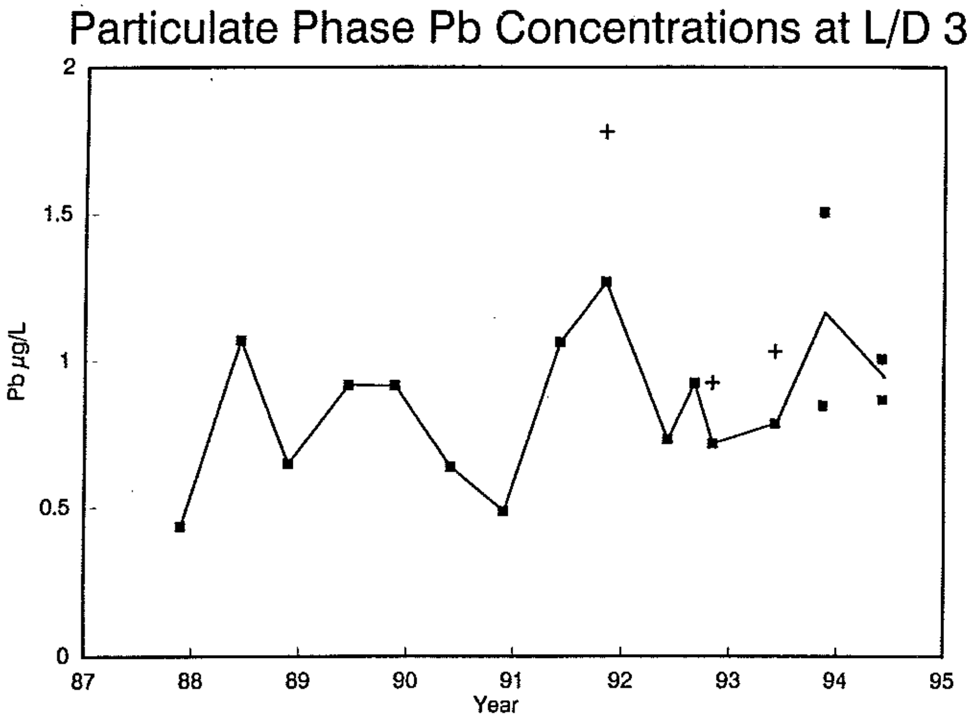


Figure 26. Whole-water particulate phase mercury (Hg) concentrations (μg/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1988 to 1994. Hg concentrations (■) estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment or a single grab sample (+) obtained using low-level analytical methods (Webb 1994).



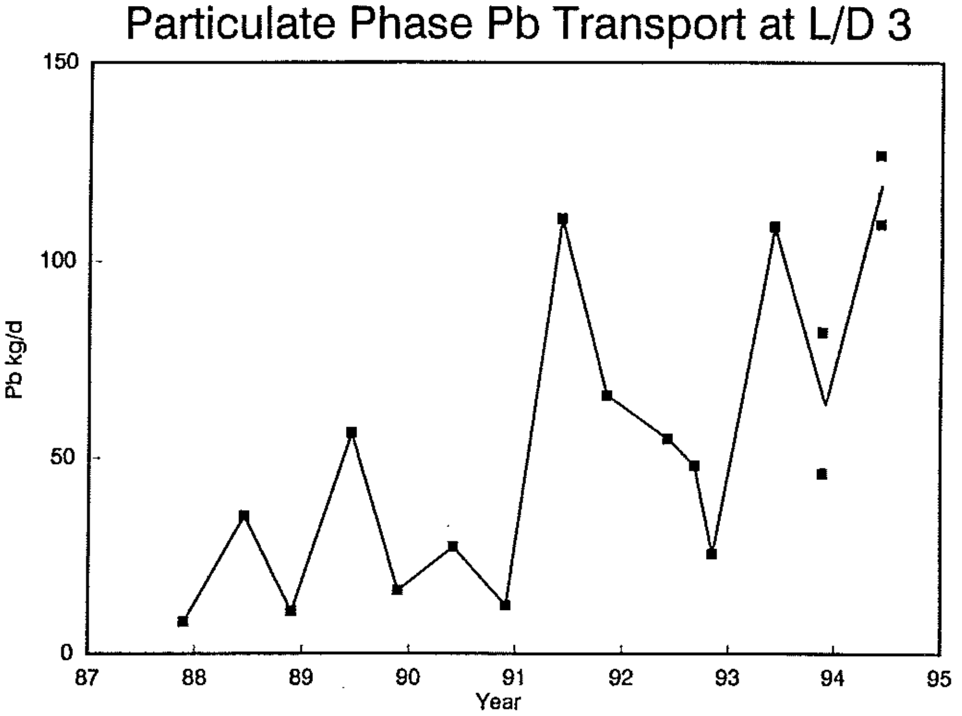
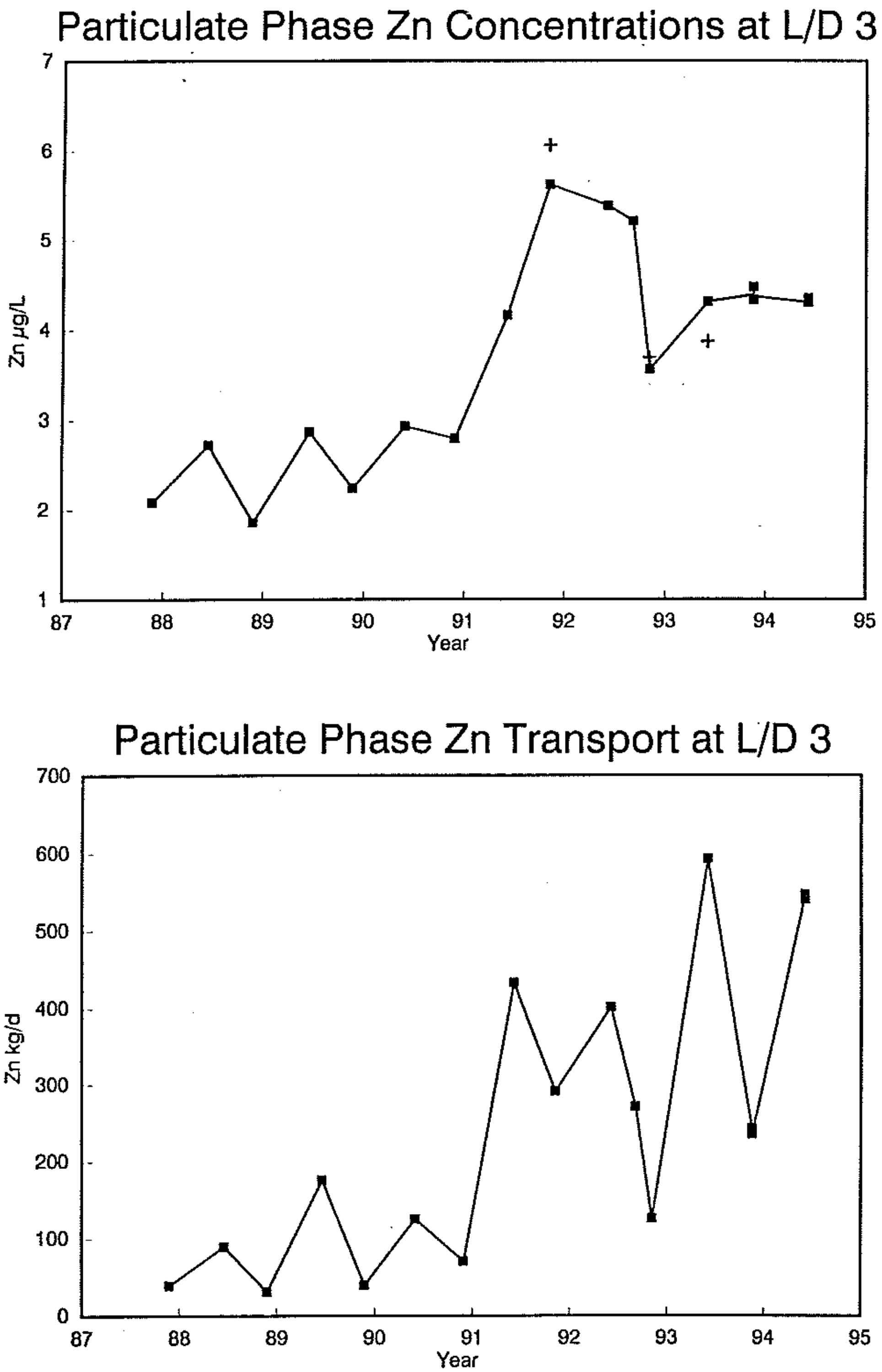


Figure 27. Whole-water particulate phase lead (Pb) concentrations (µg/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1987 to 1994. Pb concentrations (■) estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment. Other Pb concentrations (+) obtained from grab samples analyzed using low-level analytical methods (Webb 1994).


Particulate Phase Zn Concentrations at L/D 3

Particulate Phase Zn Transport at L/D 3

Figure 28. Whole-water particulate phase zinc (Zn) concentrations (µg/L) and mass transport (kg/d) in the Upper Mississippi River near Lock and Dam 3 (L/D 3) for the period 1987 to 1994. Pb concentrations (■) estimated from bulk sediment trap data and ambient total suspended solid concentrations during trap deployment. Other Pb concentrations (+) obtained from grab samples analyzed using low-level analytical methods (Webb 1994).

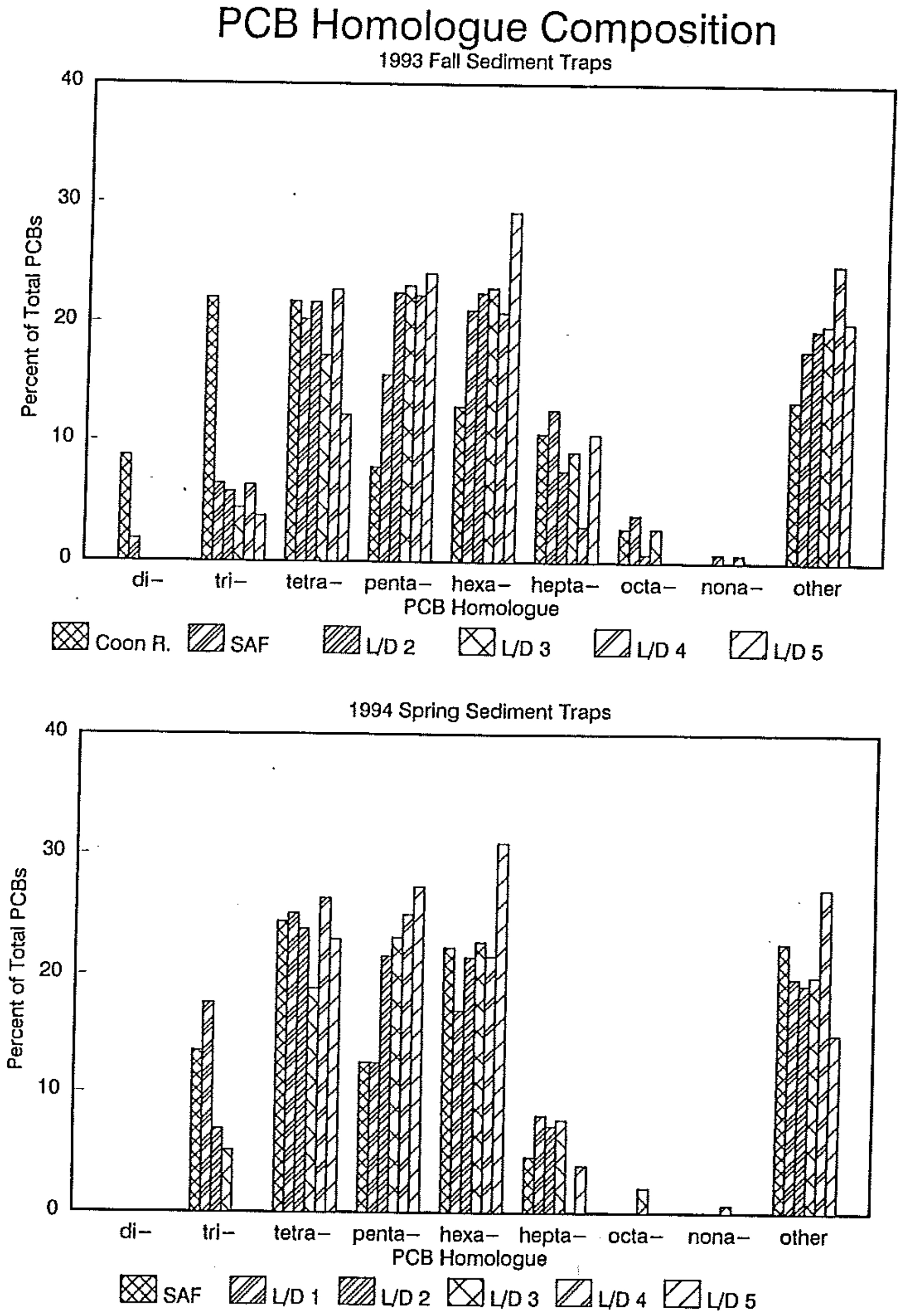


Figure 29. Polychlorinated biphenyl (PCB) homologue composition in sediment trap samples collected in the fall of 1993 and spring of 1994 from the Upper Mississippi River between Coon Rapids (Coon R.), Minnesota and Lock and Dam (L/D) 5. Co-eluting PCB congeners representing multiple homologues are marked "other". SAF = St. Anthony Falls Lock and Dam (lower dam).

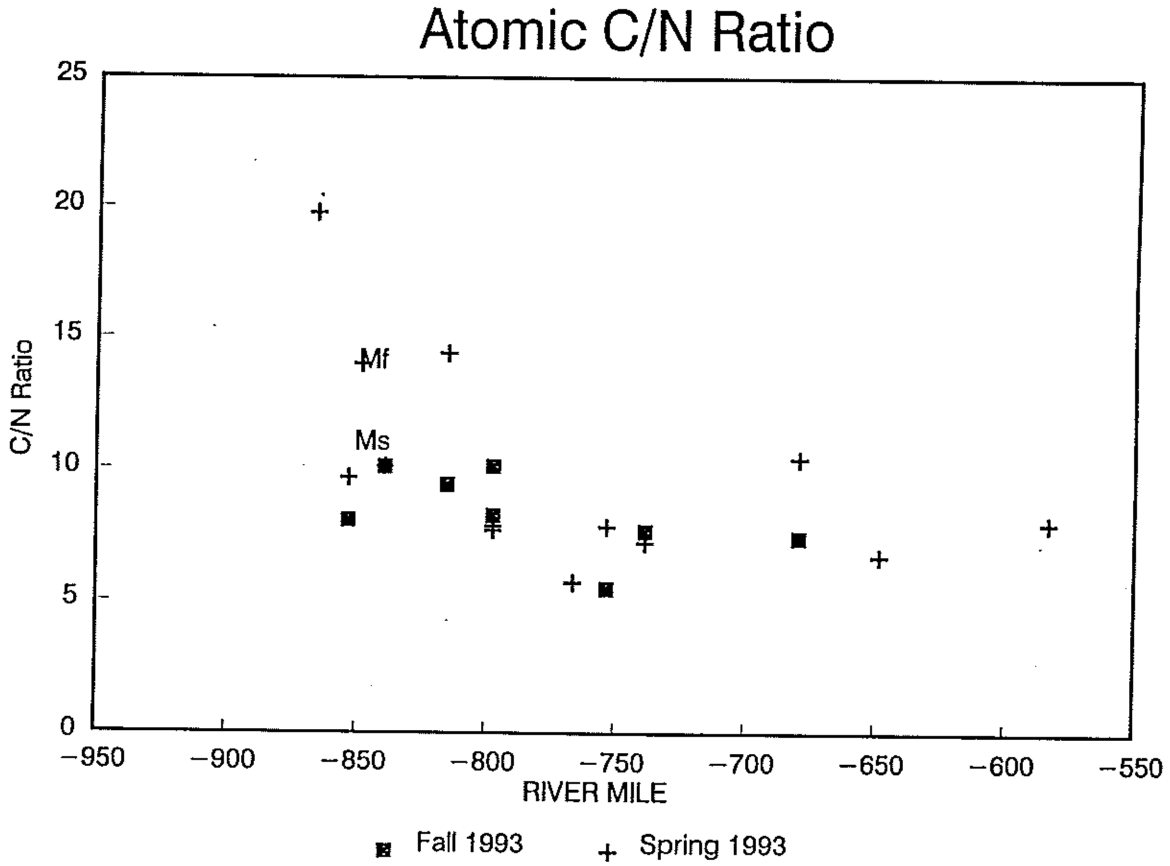


Figure 30. Longitudinal profile of atomic carbon-to-nitrogen (C/N) ratio of sediment trap samples collected in the fall of 1993 and spring of 1994 from the Upper Mississippi River between Champlin, Minnesota (RM 871) and Lock and Dam 11 (RM 583).