

# Impact of the 1993 Flood on the Distribution of Organic Contaminants in Bed Sediments of the Upper Mississippi River

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The 1500 km Upper Mississippi River (UMR) consists of 29 navigation pools and can be divided into the upper reach (pools 1–4), the middle reach (pools 5–13), and the lower reach (pools 14–26). Comparison of composite bed sediment samples collected from the downstream third of 24 pools before and after the 1993 UMR flood provides field-scale data on the effect of the flood on sediment organic compound distributions. The sediments were analyzed for organic carbon, coprostanol, polynuclear aromatic hydrocarbons including pyrene, linear alkylbenzenesulfonates, polychlorinated biphenyls (PCBs), and organochlorine pesticides. Most of the target compounds were detected in all of the sediment samples, although concentrations were generally <1 mg/kg. The highest concentrations typically occurred in the upper reach, an urbanized area on a relatively small river. Pool 4 (Lake Pepin) is an efficient sediment trap, and concentrations of the compounds below pool 4 were substantially lower than those in pools 2–4. Differences in concentrations before and after the 1993 flood also were greatest in the upper reach. In pools 1–4, concentrations of pyrene and PCBs decreased after the flood whereas coprostanol increased. These results suggest that bed sediments stored in the pools were diluted or buried by sediments with different organic compound compositions washed in from urban and agricultural portions of the watershed.

## Introduction

The Upper Mississippi River (UMR) runs 1500 km from northern Minnesota to its confluence with the Ohio River (Figure 1) and is characterized by a series of 29 pools formed by a lock and dam network erected for navigation. Land use in the river basin includes urban, industrial, and agricultural areas, and the river receives direct effluent discharges from a variety of industries and municipalities. The UMR can be divided into three distinct reaches. The upper reach (pools 1–4) receives significant point and nonpoint source contaminant inputs from the Twin Cities (Minneapolis/St. Paul, MN) and the Minnesota River, and is terminated by Lake Pepin (pool 4), a natural sediment trap. The middle reach (pools 5–13) consists of a series of long shallow pools bordered by bluffs. The lower reach (pools 14–26) is

characterized by diminished bluffs and the river is constrained by a levee system. A study of contaminants throughout the entire Mississippi River system (Twin Cities to New Orleans, LA) was conducted during 1991 and 1992 (1). As part of this study, bed sediments were collected from 24 of the pools on the UMR. During the summer of 1993, the UMR experienced widespread flooding and peak discharges exceeded the 100 year flood magnitude at 46 locations in the UMR and Missouri River basins (2). Following the 1993 flood, the 24 pools sampled in 1991 and 1992 were resampled to evaluate the effect of the flood on bed sediment contaminant distributions.

Several classes of organic compounds commonly associated with municipal and agricultural sources and that accumulate in bed sediments were evaluated (3–6), including coprostanol, linear alkylbenzenesulfonates (LASs), polynuclear aromatic hydrocarbons (PAHs), organochlorine (OC) pesticides, and polychlorinated biphenyls (PCBs). Coprostanol is a molecular tracer of contamination by fecal matter of mammals and concentrates in bed sediments (7–13). The organic carbon normalized sediment/water distribution coefficient ( $\log K_{oc}$ ) of coprostanol is  $\sim 10^5$  (3). Biodegradation half-lives for coprostanol range from  $\sim 1$  day under aerobic conditions to >400 days under anaerobic conditions (8, 14). Polynuclear aromatic hydrocarbons are widespread bed sediment contaminants derived from combustion processes and petroleum sources (15–17). Molecular structures of PAHs are variable, resulting in  $\log K_{oc}$  values ranging from  $10^3$  to  $10^7$  (18). Biodegradation half-lives for PAHs in anaerobic systems range from 7 to >800 days (19). Linear alkylbenzenesulfonates are anionic surfactants widely used in laundry detergents and are commonly present in sewage effluent (20, 21). Commercial formulations of LASs consist of a mixture of 26 homologues and positional isomers that have  $\log K_{oc}$  values ranging from  $10^4$  to  $10^5$  (22). Under aerobic conditions, LASs have biodegradation half-lives of  $\sim 1$  day, but under anaerobic conditions, they are resistant to biodegradation (23, 24). Many OC pesticides, such as *p,p'*-DDT and its metabolites *p,p'*-DDD and *p,p'*-DDE, have widespread distribution in the environment because they are resistant to degradation or form stable metabolites (25). The *p,p'*-DDT-related compounds have  $\log K_{oc}$  values ranging from  $10^4$  to  $10^6$  (26, 27) and biodegradation half-lives from 730 to >5000 days (19). Polychlorinated biphenyls can consist of 209 congeners, but the actual numbers present in environmental samples are less due to original compositions and differential partitioning and degradation rates (28–30). Although the use of PCBs was restricted in mid-1970, they continue to be a water quality issue in the UMR and cause fish consumption advisories (31). The PCBs have  $\log K_{oc}$  values ranging from  $10^4$  to  $10^8$  and are resistant to biological degradation (19, 32).

## Materials and Methods

The sampling program evaluated sediments from 24 of the navigation pools in the UMR (Figure 1A). Composite bed sediment samples were collected from the downstream third of each pool, a reach characterized by fine-grain sediments. Sediments were not collected from the main navigation channel because they consist predominantly of sand with lower sorption capacity than silt and clay. During the 1991–1992 study, sampling locations were plotted on topographic maps and located in the field using a microwave navigation system (5). During the 1994 study, sampling locations were reoccupied using a global positioning system (6). The composite bed sediment samples consisted of approximately

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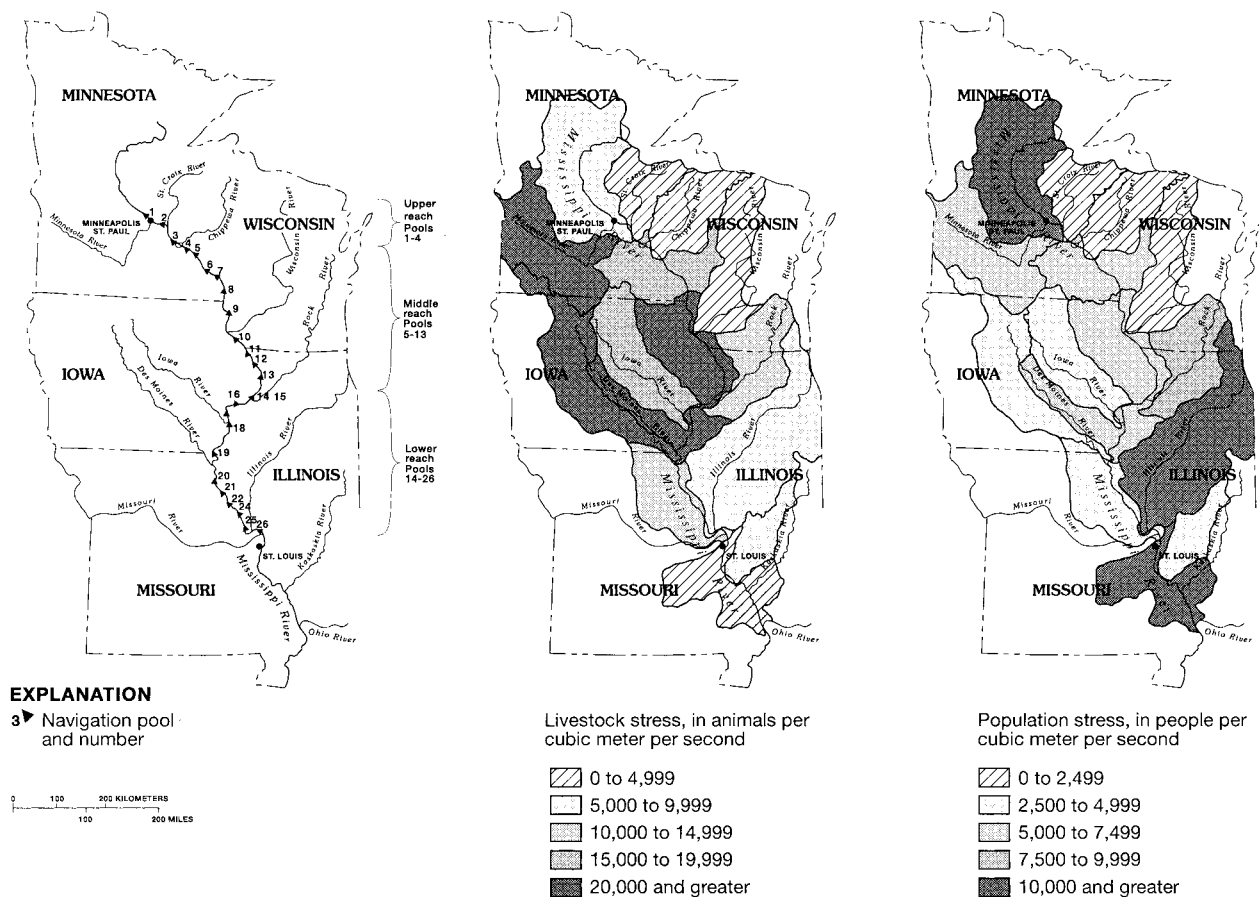


FIGURE 1. (A) Location of navigation pools on the Upper Mississippi River, (B) livestock stress (livestock stress = total number of cattle and pigs in the respective watershed divided by average annual discharge), and (C) population stress (population stress = total number of people in the respective watershed divided by average annual discharge). (Data Sources: Livestock, U.S. Department of Commerce, 1987 Census of Agriculture; Population, U.S. Department of Commerce, 1990 Census of Population and Housing; Streamflow, U.S. Geological Survey National Water Information System and U.S. Army Corp of Engineers.)

20 subsamples collected from 2 to 3 transects across the backwater areas (water depth 0.3–3 m) of each pool. The number of subsamples and transects for each pool was identical for the pre- and postflood samplings. Sediment was collected using a modified van Veen grab sampler (20 cm × 20 cm) and a subsample was taken from the top ~5 cm of each sample using a Teflon syringe. Subsamples for coprostanol, PAHs, and LASs were composited, preserved with chloroform (1% v/v), and stored at 4 °C until analysis. Subsamples for OC pesticides and PCBs were composited and stored at 4 °C until analysis. Separate composite samples were collected for total sediment organic carbon (SOC) analysis.

Preflood SOC concentrations were determined by combustion, acidification, and colorimetric detection, and postflood concentrations were determined by combustion, acidification, and infrared detection (5, 6). Results from the two methods were comparable (6). Coprostanol (and other fecal sterols) and PAHs were extracted from the bed sediments and measured by gas chromatography/mass spectrometry (GC/MS) (33, 34). The sediments were saponified and extracted by refluxing with potassium hydroxide in methanol/benzene, followed by partitioning into methylene chloride. The extracts were fractionated on a column of neutral silica over neutral alumina by sequential elution with hexane, benzene, and methanol. The hexane and benzene extracts were analyzed for PAHs. Coprostanol was eluted in the methanol fraction and derivatized with *N*-trimethylsilylimidazole in pyridine to form the trimethylsilyl ether. The extracts were analyzed by GC/MS in full scan and selected

ion monitoring (SIM) modes. The stereoisomers coprostanol and epicoprostanol coelute and were not differentiated (fecal matter is a primary source for both compounds). Coprostanol was quantified using *d*<sub>7</sub>-cholesterol added at the beginning of the extraction procedure, and the detection limit was ~0.01 mg/kg. Sixteen PAHs (EPA priority pollutants) were measured in the benzene and hexane fractions described above. Concentrations of PAHs were determined using deuterated standards, and the detection limits for individual PAHs were ~0.01 mg/kg. Linear alkylbenzenesulfonates were determined by extraction, derivatization, and GC/MS analysis (33–35). The sediments were extracted with methanol, and the extracts were derivatized with phosphorus pentachloride and 2,2,2-trifluoroethanol to form the trifluoroethyl esters of LASs. The derivatized LASs were analyzed in full scan and SIM modes. Concentrations of the 26 individual isomers were quantified using a single isomer C<sub>9</sub>-LAS surrogate standard added prior to extraction, and the detection limit was ~0.01 mg/kg total LASs. Organochlorine pesticides and total PCBs were extracted with acetone/hexane and analyzed by dual-column gas chromatography with electron capture detection (36, 37).

The methods used in this study were designed to obtain representative bed sediment samples from the lower reach of the pools and to allow comparison of concentrations and distributions of compounds in the pre- and postflood samples. Concentrations were considered substantially different if the relative percent difference (RPD) between pre- and postflood samples was greater than 3 times the field/analytical variability given in Table 1. Evaluation of

**TABLE 1. Summary of Analytical Methods and Quality Assurance Results for Select Organic Compounds Determined in Pre- and Postflood Bed Sediments from the Upper Mississippi River (GC/MS, Gas Chromatography/Mass Spectrometry; GC/ECD, Gas Chromatography/Electron Capture Detector; RPD, Relative Percent Difference)**

compd	method	recovery	analytical variability (% RPD)	field/analytical variability (% RPD)
SOC	coulometric <sup>a</sup> or IR <sup>b</sup>	99 <sup>c</sup>	15 <sup>d</sup>	19 <sup>e</sup>
coprostanol	GC/MS	na <sup>f</sup>	20 <sup>g</sup>	6 <sup>e</sup>
sterol ratio	GC/MS	na <sup>h</sup>	na <sup>h</sup>	14 <sup>e</sup>
LASs	GC/MS	88 <sup>i</sup>	33 <sup>j</sup>	18 <sup>e</sup>
pyrene	GC/MS	na <sup>f</sup>	10 <sup>k</sup>	15 <sup>e</sup>
<i>p,p'</i> -DDE	GC/ECD	82 <sup>l</sup>	5 <sup>m</sup>	29 <sup>e</sup>
<i>p,p'</i> -DDD	GC/ECD	91 <sup>l</sup>	6 <sup>m</sup>	61 <sup>e</sup>
total PCBs	GC/ECD	99 <sup>l</sup>	3 <sup>m</sup>	16 <sup>e</sup>

<sup>a</sup> Preflood SOC analyses by combustion, acidification, and coulometric detection. <sup>b</sup> Postflood SOC analyses by combustion, acidification, and infrared detection. <sup>c</sup> SOC recovery is the average percent recovery from replicate analysis of NIST Buffalo River sediment reference standard. <sup>d</sup> SOC analytical variability is the average relative standard deviation (RSD) from replicate analysis of NIST Buffalo River sediment reference standard. <sup>e</sup> Field/analytical variability is the average RPD between duplicate postflood samples (pools 2, 8, 19). <sup>f</sup> Coprostanol and pyrene were quantified by deuterated surrogate standards. Detailed recovery studies were not performed. <sup>g</sup> Coprostanol and sterol ratio analytical variability is the average RSD of triplicate analyses on preflood samples (pools 1, 10, 13) and postflood sample (pool 3). <sup>h</sup> Not applicable. <sup>i</sup> LAS recovery is the average percent recovery of the C<sub>9</sub>-LAS surrogate standard for all samples. <sup>j</sup> LAS analytical variability is the average RSD of the C<sub>9</sub>-LAS surrogate standard for all samples. <sup>k</sup> Pyrene analytical variability is the average RSD of triplicate analysis on preflood (pool 1) and postflood (pool 3) samples. <sup>l</sup> *p,p'*-DDE, *p,p'*-DDD, and total PCBs recovery is the average percent recovery for 20 spiked samples. <sup>m</sup> *p,p'*-DDE, *p,p'*-DDD, and total PCBs analytical variability is the RPD calculated from 10 sets of duplicate samples (pre- and postflood).

the data based on the nonparametric sign test (38) was used to determine the significance of observed differences (negative or positive) between paired pre- and postflood concentrations.

## Results

Concentrations of SOC in the preflood samples ranged from 0.1 to 3.5% compared to 0.1 to 3.8% in the postflood samples (Figure 2A). Concentrations increased from pool 1 to a maximum at pool 4 followed by a decrease below pool 4. Concentrations of SOC in pools 5–26 were relatively uniform, although several pools had elevated concentrations.

A number of fecal sterols were identified, but only coprostanol (coprostanol + epicoprostanol), cholesterol, and cholestanol were quantified. Coprostanol concentrations in the preflood samples ranged from 0.10 to 0.72 mg/kg compared to 0.04 to 1.64 mg/kg in the postflood samples (Figure 2B). The highest concentrations of coprostanol occurred in pools 1–4 in both the pre- and postflood samples. Pool 4 (Lake Pepin) functions as a settling basin where sediment-bound contaminants are deposited. The distribution of coprostanol was similar in the pre- and postflood samples, although several pools had substantial differences in concentrations (Table 2). A positive linear correlation was observed between coprostanol and SOC concentrations in the 1991–1992 ( $r^2 = 0.32$ ) and 1994 ( $r^2 = 0.69$ ) samples. The sterol ratio (coprostanol/cholestanol + cholesterol) provides a better indication of the extent of sewage and livestock contamination than coprostanol alone and also removes SOC related bias. A sterol ratio of >0.06 indicates sewage or livestock contamination (3). Sterol ratios ranged from 0.04 to 0.28 in preflood and from 0.02 to 0.25 in postflood samples (Figure 2C). Postflood coprostanol concentration and sterol ratio in pool 4 were twice as high as preflood values. Coprostanol concentrations in pools 9, 12, 15, and 16 were substantially higher in the postflood samples than the preflood samples, as were the sterol ratios in pools 12, 15, and 16. Pools 15 and 16 are downstream from the Quad Cities (Davenport and Bettendorf, IA, Moline and Rock Island, IL).

Concentrations of LASs in the preflood samples ranged from 0.01 to 0.95 mg/kg, and those of postflood samples ranged from 0.03 to 1.07 mg/kg (Figure 2D). The distribution of LASs was more variable than coprostanol. Concentrations were similar between pre- and postflood sampling events, with the exception of substantial postflood decreases in pools

**TABLE 2. Sign Test Statistical Evaluation of Changes in Concentrations of Select Organic Compounds in Upper Mississippi River Bed Sediments Collected before and after the 1993 Flood (Bold Values Indicate That Observed Change Was Significant at  $\alpha = 0.05$ ; na, Not Applicable)**

compd	pools 1–26		pools 1–4		pools 5–13		pools 14–26		pools where change was 3× field/analytical variability <sup>b</sup>
	observed change <sup>a</sup>	<i>p</i> -value	observed change <sup>a</sup>	<i>p</i> -value	observed change <sup>a</sup>	<i>p</i> -value	observed change <sup>a</sup>	<i>p</i> -value	
SOC	decrease	0.08	no change	na	decrease	0.09	decrease	0.17	(+) 1 (-) 10, 20, 25
coprostanol	increase	0.15	increase	0.31	increase	0.09	decrease	0.50	(+) 4, 9, 12, 13, 15, 16, 21, 26 (-) 1, 6, 20, 22, 24, 25
sterol ratio	increase	0.41	increase	0.31	decrease	0.50	increase	0.50	(+) 4, 12, 15, 16, 18 (-) 13, 20
LASs	increase	0.27	decrease	0.31	increase	0.25	increase	0.27	(+) 7, 8, 11, 13, 21, 24, 25 (-) 1, 3, 12, 16
pyrene	decrease	0.15	decrease	0.06	increase	0.50	decrease	0.27	(+) 7 (-) 1, 2, 3, 4, 6, 8, 16, 18, 19, 21, 22
<i>p,p'</i> -DDE	<b>decrease</b>	<b>0.01</b>	decrease	0.50	decrease	0.25	<b>decrease</b>	<b>0.04</b>	(+) none (-) none
<i>p,p'</i> -DDD	increase	0.12	increase	0.50	<b>increase</b>	<b>0.03</b>	increase	0.50	(+) none (-) none
total PCBs	<b>decrease</b>	<b>0.01</b>	decrease	0.06	<b>decrease</b>	<b>0.004</b>	<b>decrease</b>	<b>0.001</b>	(+) none (-) 1, 2, 4, 5, 7, 10, 11, 19, 22, 24

<sup>a</sup> Pre- and postflood sample pairs were evaluated using the sign test. Increase (+) indicates concentrations increased after the flood. Decrease (–) indicates concentrations decreased after the flood. <sup>b</sup> See Table 1 for field and analytical variability data.

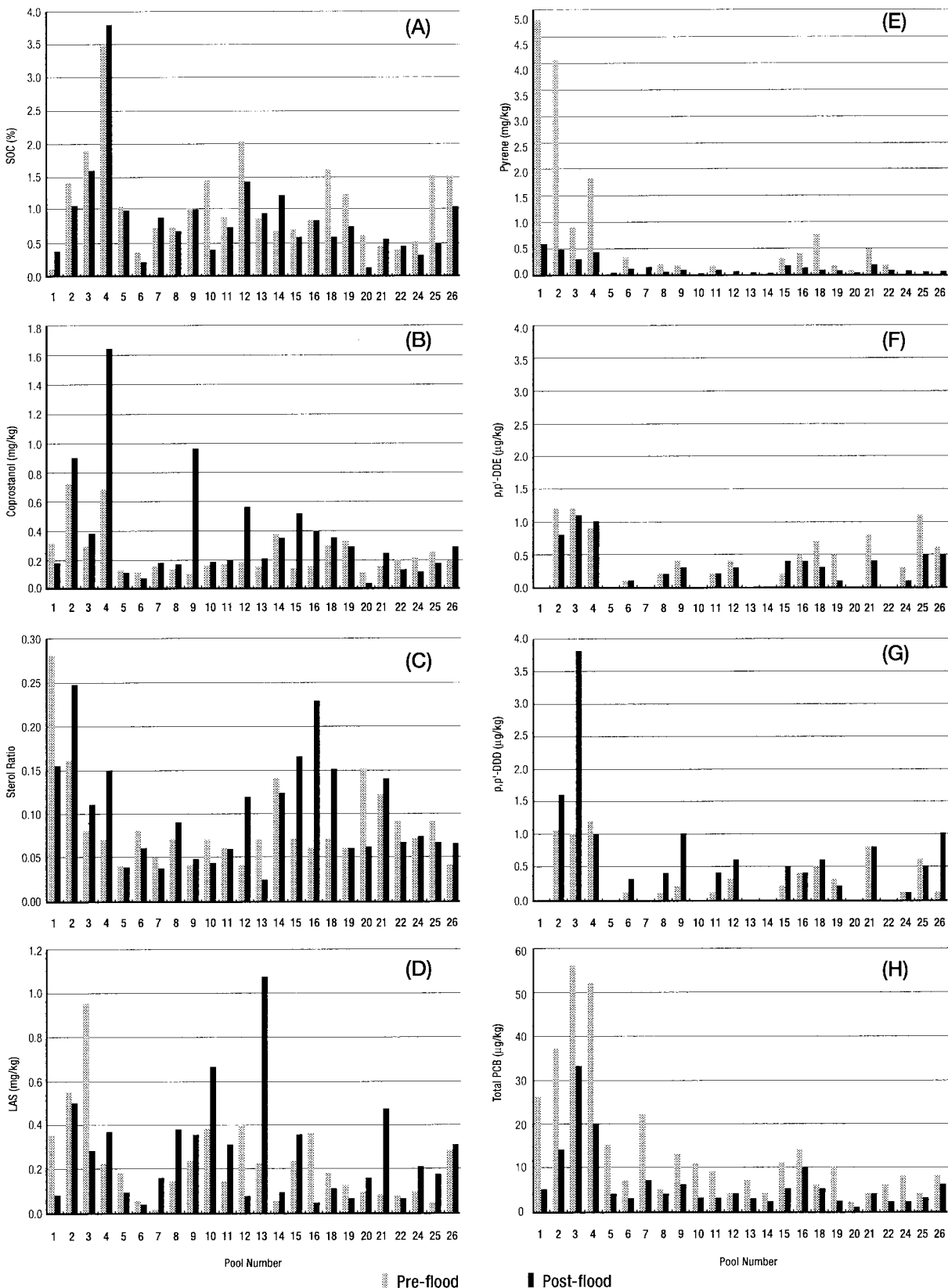


FIGURE 2. Pre- and postflood Mississippi River bed sediment profiles for (A) sediment organic carbon, (B) coprostanol, (C) sterol ratio, (D) linear alkylbenzenesulfonates, (E) pyrene, (F) *p,p'*-DDE, (G) *p,p'*-DDD, and (H) total PCBs.

1, 3, 12, and 16 and increases in pools 13 and 21. In both the pre- and postflood samples, elevated concentrations of LASs were observed downstream of elevated coprostanol concentrations, possibly due to the ionic nature of LASs and their resulting enhanced mobility.

Several PAHs were detected (naphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]-anthracene, and chrysene) in the pre- and postflood samples. Fluoranthene and pyrene were major components (22–29%) of the summed (total) concentration of the 16 individual

PAH compounds. Concentrations of total PAHs ranged from <0.01 to 16.6 mg/kg in the pre-flood samples and from 0.09 to 2.64 mg/kg in the postflood samples. Pyrene concentrations ranged from <0.01 to 4.80 mg/kg in the pre-flood and from <0.01 to 0.58 mg/kg in the postflood samples (Figure 2E). The highest pyrene concentrations were observed in pools 1–4, an area receiving a large proportion of stormwater runoff from the Twin Cities metropolitan area. Pyrene concentrations in pools 1–4 decreased substantially in the postflood samples indicating burial or dilution by sediments with lower concentrations of PAHs. Below pool 4, there was a slight decrease in postflood pyrene concentrations, although distributions between pre- and postflood samples were similar.

Concentrations for most of the target OC pesticides were below detection limits. All of the pools had detectable concentrations of *p,p'*-DDE and *p,p'*-DDD. Dieldren, *p,p'*-DDT, and technical chlordane were detected in sediments from several pools. Concentrations of *p,p'*-DDE ranged from 0.1 to 1.2  $\mu\text{g}/\text{kg}$  in the pre-flood and from 0.1 to 1.1  $\mu\text{g}/\text{kg}$  in the postflood samples, and *p,p'*-DDD ranged from 0.1 to 1.2  $\mu\text{g}/\text{kg}$  in the pre-flood and from 0.1 to 3.8  $\mu\text{g}/\text{kg}$  in the postflood samples (Figure 2, panels F and G). Preflood concentrations of *p,p'*-DDE and *p,p'*-DDD were about the same and were elevated in the upper reach, decreased in the middle reach, and increased again in the lower reach. The relative concentrations of *p,p'*-DDD increased in the postflood samples whereas *p,p'*-DDE decreased.

In a manner similar to the other target compounds, total PCBs were greatest in the upper reach and decreased significantly below pool 4 (Figure 2H), although they were detected in all of the pools. Three methods were used to measure total PCBs in the UMR sediments, and the results were in general agreement. Only the USGS schedule 1325 data are presented here because it is the most complete set. Preflood concentrations ranged from 2 to 56  $\mu\text{g}/\text{kg}$  and postflood concentrations ranged from 2 to 33  $\mu\text{g}/\text{kg}$ . Concentrations of total PCBs in the postflood samples were lower than in the pre-flood samples, although their spatial distributions were similar.

## Discussion

Measurable concentrations of coprostanol, LASs, PAHs, OC pesticides, and total PCBs in bed sediments throughout the UMR indicate the widespread influence of point and non-point source contamination. However, the UMR is less contaminated than many aquatic systems impacted by industrial and municipal sources. Coprostanol concentrations of >1 mg/kg have been measured in bed sediments proximal to sewage-sludge disposal sites (7–12). Concentrations of total PAHs greater than 10 mg/kg have been measured in areas affected by urban runoff (15–17). Concentrations of LASs in sediments across the U.S. range from 0.2 to 340 mg/kg (20, 21). Concentrations of *p,p'*-DDE and *p,p'*-DDD of >100  $\mu\text{g}/\text{kg}$  have been reported for contaminated agricultural soils (39). Concentrations of total PCBs of >100  $\mu\text{g}/\text{kg}$  have been reported for contaminated sediment (31). The UMR sediments have relatively low levels of contamination due to large stream dilution factors (river flow divided by cumulative effluent discharge) that range from 50 at the Twin Cities to 500 at St. Louis (40).

Comparison of concentrations of contaminants in the pre- and postflood bed sediments using the sign test for the entire data set and the individual reaches are presented in Table 2. Significant differences between the entire pre- and postflood data set ( $\alpha = 0.05$ ) were observed for *p,p'*-DDE (decrease) and total PCBs (decrease). Contaminant distribution patterns grouped by reach show that *p,p'*-DDD increased in the middle reach, and *p,p'*-DDE and total PCBs

decreased in the lower reach. Other reach comparisons show no significant changes between pre- and postflood samples.

The distribution patterns of coprostanol, LASs, PAHs, OC pesticides, and total PCBs in both the pre- and postflood samples were dominated by the influence of the Twin Cities and Minnesota River (Figure 2). Elevated concentrations were observed from pool 1 downstream to pool 4, indicating that sediment-bound contaminants from the Twin Cities and Minnesota River are introduced into the Mississippi River and eventually deposited in pool 4. Historically, pools 2–4 have had elevated levels of sediment contamination (41). Increased sediment contamination by PCBs in pools 1–4 relative to the other pools of the UMR also is indicated by the levels of PCBs in emergent mayflies (31). Concentrations of target compounds were generally lower from pools 5–26 due to the absence of large municipalities and dilution by less contaminated sediment inputs. Coprostanol concentrations below the Twin Cities (pool 2) to Lake Pepin (pool 4) exhibited opposite trends to pyrene and total PCBs between pre- and postflood samples. Coprostanol concentrations increased after the flood, and pyrene and total PCBs decreased. The Minnesota River, which discharges into pool 2, was severely flooded (2), and the high flows likely introduced coarser sediments that were less contaminated with PCBs and PAHs. The increase in coprostanol levels below the Twin Cities could be attributed to runoff from livestock areas in the Minnesota River watershed (Figure 1B). The decrease in concentrations of pyrene and total PCBs in pools 1–4 indicates that runoff-derived sediment had lower concentrations of these compounds than the bed sediments.

The postflood increase in coprostanol concentrations and sterol ratios in pools 15 and 16, an area completely inundated by floodwaters, indicate that flooded sewage-treatment plants and/or feedlots also affect the bed sediments in this region. There is a high concentration of livestock upstream from these pools (Figure 1B). Pools 15 and 16 also had elevated concentrations of PCBs in the pre-flood samples. This is consistent with the results of Steingraeber et al. (31) who reported that PCB congener analyses of mayflies collected along the UMR indicate that a documented point source of PCBs in the Quad Cities had contaminated sediments in pool 15. As was observed in pools 1–4, concentrations of PCBs decreased in the postflood samples whereas concentrations of coprostanol increased.

The coprostanol and sterol ratio data show that in some pools the 1993 flood resulted in redistribution of contaminated bed sediments or input of sewage/livestock contaminated sediments. In contrast, the pyrene results indicate little redistribution or inputs of sediments contaminated with PAHs. Under aerobic conditions, *p,p'*-DDT is dechlorinated to the metabolite *p,p'*-DDE, whereas under anaerobic conditions, *p,p'*-DDD is formed (39). The input of these chemicals probably originates from runoff of *p,p'*-DDT contaminated sediments in the upper watershed. Resuspension of buried sediments in the UMR probably is not the source of *p,p'*-DDD because sediment scouring also would increase post-flood concentrations of PCBs, which was not observed.

Sediment quality guidelines are available for SOC, *p,p'*-DDD, *p,p'*-DDE, total PCBs, and pyrene (42). Concentrations above the organic carbon normalized no effects level (NEL) indicate potential for biomagnification, and concentrations above the organic carbon normalized lowest effect level (LEL) indicate potential for adverse impact on sediment-dwelling organisms. Although most of the pre- and postflood sediment samples had *p,p'*-DDE, *p,p'*-DDD, and total PCBs concentrations exceeding the NEL, almost all of the concentrations were below the LEL (43). Pyrene concentrations in pools 1, 2, 6 (pre- and postflood), and 4 (preflood) exceeded the LEL guidelines. Pools 1 and 6 are influenced by very low SOC

concentrations. There are no sediment quality guidelines for LASs or coprostanol. Concentrations of LASs in all of the samples were below sediment toxicity thresholds of >100 mg/kg (44).

Figure 1, panels B and C, show livestock and population stress in the UMR and associated tributaries. The watersheds most impacted by population stresses are the headwaters of the UMR (pool 1), the Illinois River (pool 26), and the Meramec River (below pool 26), all relatively small rivers with large metropolitan areas (Twin Cities, Chicago, St. Louis). In contrast, the Minnesota River (pool 2), the Middle UMR (pools 7–19), and the Des Moines River (pool 20) have the greatest livestock stress. These stresses are reflected in the bed sediment chemistry of the UMR.

Scouring and resuspension/deposition of fine-grained bed sediments do not appear to be the primary mechanisms influencing postflood contaminant distributions in the UMR. This is indicated by no increase in concentrations of pyrene or total PCBs downstream from the historically contaminated pools 1–4. Despite the magnitude of observed peak discharges (5–10 times the normal mean discharge) in the UMR and its tributaries during the 1993 flood (6) changes in the organic bed sediment chemistry were not substantial. Apparently, the high discharge volumes did not result in sheer velocities sufficient to resuspend cohesive, fine-grain sediments in the lower third of the pools. Most of the changes in bed-sediment chemistry at individual pools are probably the result of burial by coarse-grained sediments, which typically have lower contaminant concentrations, derived from overland runoff. Although changes in bulk sediment contaminant concentrations were relatively small, large amounts of sediment-bound contaminants probably were transported out of the UMR system during the 1993 flood (45). Even relatively minor changes in bed sediment chemistry can increase the equilibrium concentrations of contaminants within the overlying water as was observed in a similar pre- and postflood study of the Missouri River basin (46).

Various physical mechanisms control the fate and transport of sediment bound organic compounds in the UMR including discharge volume, flow velocity, sedimentation, resuspension, and loading rates from point and nonpoint sources. In addition, although not specifically addressed in this study, a number of other important mechanisms including sorption/desorption and biodegradation also control the environmental fate of bed sediment contaminants. The similar distribution patterns for bed sediment contaminants between the pre- and postflood samples show that concentrations are strongly influenced by the Twin Cities and diminish downstream. Although the postflood samples indicate some departures from this pattern, the 1993 flood appears to have had minimal effects on the overall distribution of organic compounds in the fine-grained bed sediments of the UMR.

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