

Distribution and Transport of Polychlorinated Biphenyls and Associated Particulates in the Milwaukee River System, Wisconsin, 1993–95

By Jeffrey S. Steuer, Sharon A. Fitzgerald, and David W. Hall

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CONTENTS

Abstract	1
Introduction	1
Purpose and scope	3
Environmental setting and hydrology	3
Site descriptions	4
Sampling and analytical methods	5
Distribution and transport of PCB's and associated particulates	6
PCB congeners	6
Phase partitioning of PCB's	12
Total suspended solids load and chlorophyll <i>a</i> concentrations	13
Total suspended solids load.....	16
Concentrations and loads of transported PCB's in the Milwaukee River system.....	21
Summary	26
References cited	28
Appendixes 1–2:	
1. PCB congeners found during laboratory analysis of water and sediments in the Milwaukee River Basin and their respective limits of detection and quantification	32
2a. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Cedar Creek at Columbia Avenue (USGS station 04086525), 1994–95	33
2b. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Cedar Creek at Highland Road (USGS station 04086528), 1994–95.....	34
2c. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Highway T (USGS station 04086528), 1994–95	34
2d. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Pioneer Road (USGS station 04086600), 1994–95.....	35
2e. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Thiensville (USGS station 04086710), 1994–95	36
2f. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Estabrook Park (USGS station 04087000), 1994–95	37

FIGURES

1. Map showing location of Cedar Creek and Milwaukee River sampling sites.....	2
2–7. Graphs showing:	
2a. Dissolved PCB congener distributions from the two highest field-equipment-blank concentrations and two Milwaukee River field sites.....	7
2b. Particulate PCB congener distributions from the two highest field-equipment-blank concentrations and two Milwaukee River field sites.....	8
3a. Dissolved PCB congener distributions for Milwaukee River and Cedar Creek sites and one Aroclor mixture	9
3b. Particulate PCB congener distributions for Milwaukee River and Cedar Creek sites and one Aroclor mixture	10
3c. Bed-sediment PCB congener distributions for Milwaukee River and Cedar Creek sites and one Aroclor mixture	11
4. Apparent distribution coefficients at two Milwaukee River Basin sites.....	14
5. Correlation of point-sampled (POINT) and equal-width-increment (EWI) sampled suspended solids at four Milwaukee River and Cedar Creek sites	15
6. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Highland Road site on the Milwaukee River.....	17
7. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Pioneer site on the Milwaukee River.....	18

CONTENTS—Continued

FIGURES—Continued

8–13. Graphs showing:	
8. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Thiensville site on the Milwaukee River.....	19
9. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Estabrook Park site on the Milwaukee River.....	20
10. Cumulative suspended solids-loads at three Milwaukee River sites and discharge at the Estabrook site.....	22
11. Net suspended-solids loads for two Milwaukee River reaches and Estabrook discharge.....	22
12. Pioneer PCB concentration regression residuals.....	25
13. Cumulative summed PCB congener loads at three Milwaukee River sites and discharge at the Estabrook Park site.....	27

TABLES

1. Summed PCB congener concentration in bottom sediment and accumulated PCB mass estimates resulting from the Wisconsin Department of Natural Resources bottom sediment surveys.....	3
2. Calculated $\log K_D$ and $\log K_{POC}$ values for selected PCB congeners and summed PCB congener concentrations at all sampling sites.....	13
3. Total-suspended-solids loads computed for four Milwaukee River Basin sites.....	21
4. Summed PCB congener concentration regression relations and characteristics at Highland Road (Cedar Creek) and three Milwaukee River sites.....	23
5. Computed total loads for the Milwaukee River Basin sites using PCB regression relations (RLOAD).....	26
6. Computed summed PCB congener loads based on three computation approaches for the Milwaukee River Basin sites.....	28

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To Obtain
acre	0.4048	hectare
mile (mi)	1.609	kilometer
square mile (mi ²)	2.590	square kilometer
foot (ft)	0.3048	meter
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
micrometer (μm)	0.00003937	inch
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilogram (kg)	2.205	pound
kilogram (kg)	0.00326	ton
gram (g)	1 x 10 ⁹	nanogram
gram (g)	1 x 10 ⁶	microgram
gram (g)	1 x 10 ³	milligram
liter (L)	0.2642	gallon
ton	0.9072	megagram

Temperature in degrees Fahrenheit (°F) can be converted to degrees Celsius (°C) by use of the following equation:

$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32.$$

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated water-quality units used in this report: Chemical concentrations are given in metric units. Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (μg/L), or nanograms per liter (ng/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

Miscellaneous abbreviations:

ΣPCB is a total PCB concentration obtained by summing all dissolved and particulate-phase congeners in a sample.

POINT samples are those water samples collected from a single point in a river, such as a sample obtained from the intake pipe of an automated sampler.

EWI samples are water samples collected from equal-width-increments across a cross section of a river.

CHURN samples consist of four subsamples collected at equal-width-increments across a stream cross section that are subsequently composited in a teflon churn splitter.

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MMSD is the Milwaukee Metropolitan Sewage District in Milwaukee, Wisconsin.

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Abstract

The distribution and transport of polychlorinated biphenyl (PCB) congeners were determined at various sites on Cedar Creek and its receiving stream, the Milwaukee River. PCB congener distributions were determined in the operationally defined dissolved phase, suspended-particle phase, and surficial bed sediments (0–2 centimeters depth). At most sites, the relative abundances of PCB congeners in the suspended particles and surficial bed sediments were similar to each other, and in some cases, to known Aroclor mixtures (1242 and 1260). Dissolved PCB congener distributions were higher in the less chlorinated congeners as predicted by their lower hydrophobicity and higher solubility. Log partition coefficients for the dissolved and the particle-associated organic carbon phases ranged from 5.0 to 5.8 and 6.5 to 7.5, respectively, for Σ PCB's (congener summation). Particle-associated PCB's exhibited two patterns: (1) a general increase in spring and summer associated with algal growth and, (2) episodic increases associated with resuspension of bed sediments during storms. Total suspended solids loads in water year 1994 ranged from 8,700 tons at Pioneer Road to 15,800 tons at Estabrook Park. PCB loads decreased from Highland Road (3.7 kilograms) to Pioneer Road (1.8 kilograms) from August 1994 to August 1995, indicating PCB deposition between those sites. PCB transport at Estabrook Park was 8 to 16 kilograms during this same time period.

INTRODUCTION

Polychlorinated biphenyl (PCB) congener mixtures were used extensively in the United States from 1929 until their manufacture was banned in the 1970's. Each of the 209 possible PCB congeners consists of 1 to 10 chlorine atoms attached to a biphenyl ring. The physical

and chemical properties of the PCB congeners vary as a function of their structure. As a group, however, the congeners are substantially resistant to heat and degradation, properties that made them valuable for a wide variety of uses. Congener mixtures marketed under the trade names Aroclor (Monsanto, U.S.) and Askerele were extensively used in electrical equipment such as transformers, capacitors, switchgear, and manufacturing machinery. Aroclor mixtures also were used in printing inks, carbonless copy paper, heating coils, specialized cookware, fireproof panels, lubricating oils, resins, synthetic rubber, sealants and coatings, wax, waterproofing compounds, adhesives, and cutting oils (Cairns and others, 1986). Although manufacture of PCB's was banned in the United States in the 1970's, approximately 50 to 60 percent of all PCB's ever manufactured are still in use, with an additional 20 to 30 percent of the manufactured PCB's cycling in the environment from discarded waste materials (Anders Andren, University of Wisconsin-Madison, oral commun., September 1995).

PCB's are known to bioaccumulate (Koslowski and others, 1994), to cause reproductive failure in birds (Yamashita and others, 1993), and to have negative effects on communities of fish (Evans and others, 1990). Knowledge of the distribution and transport of PCB's in the environment is important for protecting human drinking water supplies, ensuring the chemical integrity of fish and other food products, and providing healthful habitats for fish, birds, and other animals.

PCB's have been identified as a contaminant of concern in the Milwaukee River, Wis. (Marti and Armstrong, 1990; fig. 1), resulting in issuance of a fish consumption advisory. The bed sediments of Cedar Creek, a tributary to the Milwaukee River, have high concentrations of PCB's. Results of the Cedar Creek Mass Balance Study (Westenbroek, 1993) indicated that Cedar Creek transported between 4 to 38 kilograms per year (kg/yr) of PCB's to the Milwaukee River during 1990 and 1991. The PCB's entered Cedar Creek through floor drains and in cooling waters that were discharged from

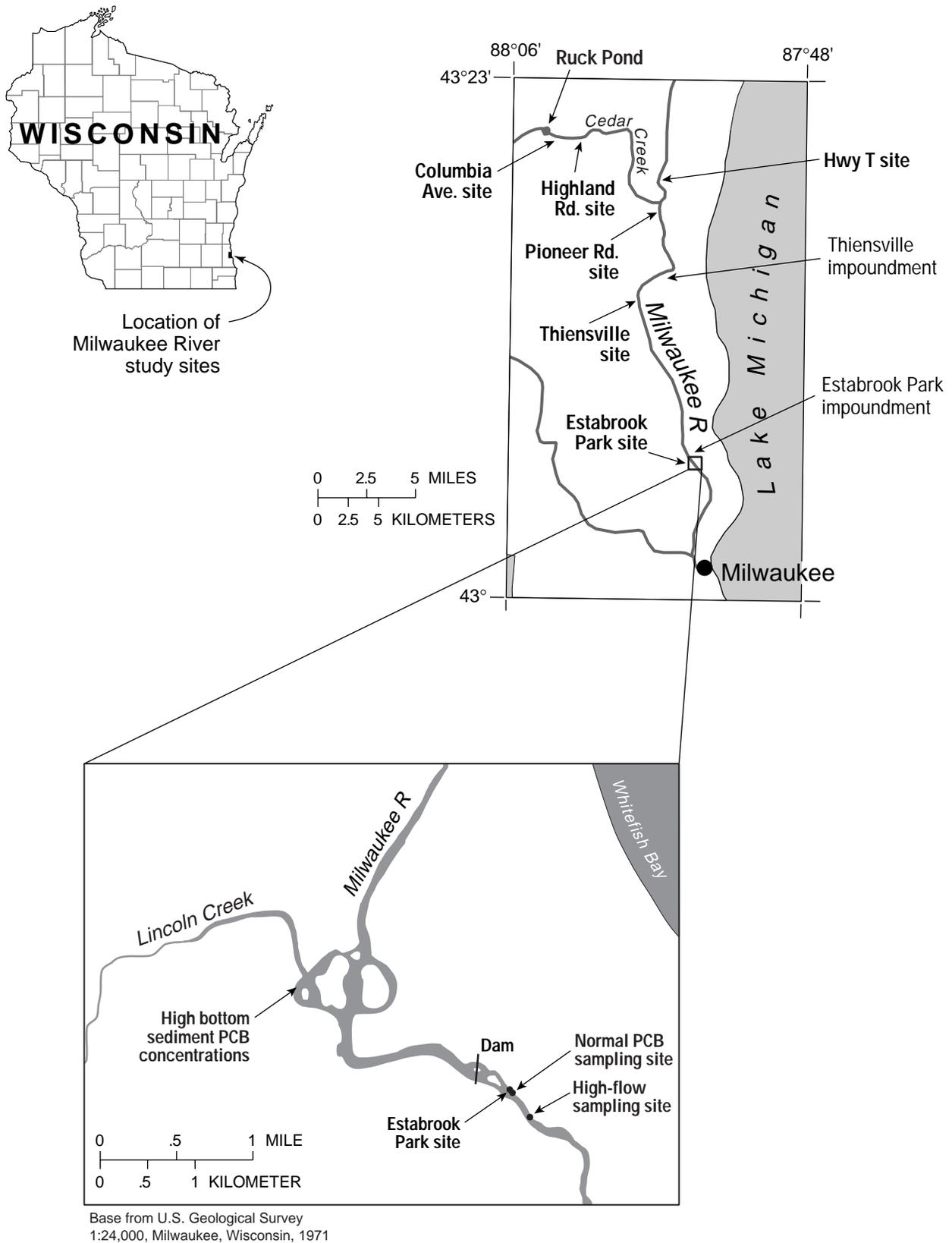


Figure 1. Location of Cedar Creek and Milwaukee River sampling sites.

Table 1. Summed PCB congener concentration in bottom sediment and accumulated PCB mass estimates resulting from the Wisconsin Department of Natural Resources bottom-sediment surveys
[From Westenbroek (1993). $\mu\text{g/g}$, micrograms per gram; kg, kilograms; --, no data]

Reach	Surficial sediment concentration ($\mu\text{g/g}$)	Maximum sediment concentration ($\mu\text{g/g}$)	Accumulated PCB mass (kg)
Cedar Creek			
Upstream from Columbia Ave. (10/7/94, postremediation)	8.3 to 280	280	Remediated (formerly 743)
Columbia Ave. to Highland Rd. (8/11/95–8/14/95)	8.3 to 64	190	568
Highland Rd. to Milwaukee River confluence	Not recently sampled. Mass estimate based on historical data.	--	118
Milwaukee River			
Confluence to Pioneer Rd.	Surveys indicate minimal soft sediment in this reach.	--	<10
Pioneer Rd. to Thiensville (10/26/93–10/29/93)	0.08	4.9	265
Thiensville to Trinity Creek (11/7/95)	<0.05 to 0.21	.21	--
Estabrook impoundment "hot spot" (9/25/95–9/28/95)	2.3 to 100	870	--
Estabrook impoundment (11/2/93)	0.26 to 3.3	380	5,276 (Thiensville to Estabrook)

several die-casting operations (Westenbroek, 1993). Results of a subsequent Wisconsin Department of Natural Resources survey of PCB contamination of Cedar Creek and Milwaukee River bottom sediments are summarized in table 1.

Although some of the PCB's at downstream sites may have originated from Cedar Creek, additional sources of PCB's may also contribute to the contamination of Milwaukee River water, sediments, and biota. Lincoln Creek, which joins the Milwaukee River upstream from Estabrook Park, may have been, or still is, an additional source of PCB's to the river. Additionally, river sediment-coring investigations done by the Wisconsin Department of Natural Resources located an area of PCB-contaminated sediments immediately downstream from the confluence of Lincoln Creek and the Estabrook impoundment (fig. 1).

In 1993, the U.S. Geological Survey (USGS), in cooperation with the Wisconsin Department of Natural Resources (WDNR) and the Milwaukee Metropolitan Sewage District, began this investigation to further understand the distribution and transport of PCB's and associated particulates in the Milwaukee River system. The data collection and analysis efforts were designed to support WDNR construction of a deterministic PCB transport model.

Purpose and Scope

This report presents results of a USGS, WDNR, and Milwaukee Metropolitan Sewage District (MMSD) cooperative investigation into the occurrence and transport of PCB's in the Milwaukee River system. Congener profiles in the operationally defined dissolved phase, suspended particles, and surficial bed sediments were determined. Total PCB congener loads and suspended-solid loads were computed at locations downstream from impoundments. Regression analysis on concentrations of summed PCB congeners (ΣPCB) as a function of total suspended solids, in addition to other environmental variables collected on a frequent basis, was used to compute the ΣPCB loads.

Environmental Setting and Hydrology

The Milwaukee River drains an area of approximately 850 mi^2 in southeastern Wisconsin (fig. 1). Mean annual discharge of the Milwaukee River from 80 years of record is 431 ft^3/s . Mean discharge measured during the study period was less than the annual average; 378 and 303 ft^3/s in 1994 and 1995, respectively. The Milwaukee River Basin comprises six major subbasins: the East-West Branch, North Branch, South Branch, Cedar Creek, the Menomonee River, and the

Kinickinnic River. Average annual precipitation is about 30 in., and two-thirds of the precipitation falls as rain during the growing season. Average annual snowfall is about 46 in., and average annual air temperature is 46°F (Wisconsin Department of Natural Resources, 1992).

The geology of the Milwaukee River Basin consists of unconsolidated, clay-rich glacial deposits resting on Silurian dolomite bedrock. Basin altitude ranges from about 1,360 ft above sea level in the northwest to about 580 ft above sea level at Milwaukee Harbor in the southeast. Surface drainage channels are generally well connected, and relatively few areas of the basin drain predominantly to ground water (Sullivan and others, 1995). The basin contains approximately 430 mi of perennial streams and 87 lakes and ponds with surface areas greater than 5 acres. The basin has long been predominantly urban and industrial in southern areas proximate to the city of Milwaukee (1990 population was about 636,000). Urban land, including residential areas and land used for transportation and utilities, occupies about 11 percent of the total basin area (Sullivan and others, 1995). About 75 percent of the basin is agricultural, about 8 percent is forested, about 5 percent is wetland, and less than 1 percent is barren.

Site Descriptions

Six sites (fig. 1) on Cedar Creek and on the Milwaukee River were sampled:

1. The Columbia Avenue dam site (USGS station 04086525) on Cedar Creek drains 121 mi² of the Milwaukee River Basin and is downstream from Ruck Pond impoundment, which was remediated in 1994. No monitoring equipment was onsite, and only a few samples were collected immediately downstream from the dam.
2. The Highland Road site (USGS station 04086528), 50 ft downstream from the Columbia impoundment on Cedar Creek, has a drainage area of 123 mi². This site was instrumented with a shore-based automated suspended-solids sampler and a continuous water-temperature probe. The sampler was fitted with a 3/8-in. propylene suction line and was set up to include purge and rinse cycles. Discharge data for Cedar Creek were collected downstream from this site at USGS station 04086500. The

Wire/Nail and Hamilton ponds are two Cedar Creek PCB-contaminated impoundments located between the Highland Road site and its confluence with the Milwaukee River. These sites, however, were not sampled as part of this investigation.

3. The Highway T site (USGS station 04086416) was on the Milwaukee River immediately upstream from the confluence of Cedar Creek and the Milwaukee River (fig. 1) and has a drainage area of approximately 479 mi². No equipment was installed at this site. Limited PCB samples were collected in the vicinity of the Highway T bridge to document PCB transport upstream from the Cedar Creek confluence with the Milwaukee River.
4. Milwaukee River flow at the Pioneer Road site (USGS station 04086600) originates from about 607 mi² of the basin. Samples were collected either about 60 ft downstream from the Pioneer Road bridge during base flow or from the bridge during high flow. The site was instrumented with an automated sampler activated by a stage sensor and with river-stage recorders for discharge computation. There was no impoundment at this site, so soft bed sediment suitable for sampling was collected from small, discontinuous pockets located mainly downstream from islands and along some sections of the bank.
5. The Thiensville site (USGS station 04086710) was downstream from Pioneer Road, a location representing discharge from about 643 mi² of the basin. Water samples were collected 50 ft upstream from the Highway 167 bridge at Thiensville during base flow or from the bridge during high flow. The site was instrumented with an automated sampler triggered by a stage sensor. Discharge was not measured at the site but rather was estimated from the measured discharge at the Pioneer site multiplied by the basin area ratio (1.06). Samples of soft bed sediment were collected from an impoundment upstream from the bridge.
6. The Estabrook Park site (USGS station 04087000) was in a Milwaukee County park, downstream from Thiensville, and about 6.6 mi upstream from the Milwaukee Harbor. Samples

during low to medium flow were collected approximately 2,000 ft downstream from the Port Washington Road bridge. At high flow, samples were collected from the downstream railroad bridge. Discharge data were collected continuously, and the site was instrumented with an automated sampler triggered by a stage sensor. Bed-sediment samples were collected from behind the dam and upstream from the water-sampling site.

Sampling and Analytical Methods

General methods of sample collection and field preparation are discussed in detail in Fitzgerald and Steuer (1997) and in House and others (1993). Water samples were collected by dipping 20-L stainless steel canisters through the water column at four locations across the creek or river. These samples were composited and processed as one 80-L sample. The particulate and operationally defined dissolved phases were separated onsite immediately after sample collection (particulate and operationally defined dissolved phase are defined for the purposes of this study by the filter pore size, 0.7 μm). Field filtering of the 80-L water samples involved a parallel stack of up to five 293-mm stainless steel filter plates with precombusted 0.7- μm glass fiber filters inserted between the plates. The filtrate was then pumped at a rate not exceeding 1-L/min through Amberlite XAD-2 resin columns to concentrate the operationally defined dissolved hydrophobic contaminants. The filters and XAD-2 resins were subsequently analyzed at the State Laboratory of Hygiene (SLOH) in Madison, Wis., by use of methods described in Fitzgerald and Steuer (1997).

Water samples analyzed for ancillary constituents such as particulate organic carbon (POC), dissolved organic carbon (DOC), chlorophyll *a*, chloride, volatile suspended solids (VSS), and total suspended solids (TSS) were collected in 1-L glass bottles submerged through the water column in the same manner and at the same locations as those used for PCB sampling. The four cross-section samples were composited in a teflon churn splitter (referred to as “CHURN samples”) to obtain the final representative sample (Ward and Harr, 1990). Subsequently, samples analyzed for particulate organic carbon (POC) and dissolved organic carbon (DOC) were processed through a stainless steel Gelman filter apparatus with a 0.45- μm silver filter. Chlorophyll

a samples were processed through a 5.0- μm mixed acetate and nitrate cellulose filter.

For comparison with results from this water-collection method—necessitated by the large water volume required for the PCB sample—a second suspended-solids sample was collected and analyzed separately. This suspended-solids sample was collected with a 470-mL glass bottle and plastic nozzle that was sequentially submerged at four equally spaced locations along a cross section, either manually at wadable sites or by use of a D-77 USGS sampler at nonwadable sites. Samples from the cross section (referred to as “equal-width-increment (EWI) samples”) were poured directly into the laboratory bottles themselves. No churn was used for splitting.

The automated suspended-solids samplers were used to collect point samples daily at 1200 hours and more frequently during storm events. When the river was frozen, sampling was reduced to once every 2 or 3 days at all sites and was often done manually with a 1-L plastic bottle. Additionally, the automated samplers were triggered at the time of EWI sample collection to assess the ability of the automated samples obtained at one point in the cross section to represent water quality in the entire cross section, as represented by the EWI samples. Automated and manual grab samples are referred to as “POINT samples.”

EWI samples collected for TSS determinations were placed in 1-L plastic bottles and chilled to 4°C during shipment to the SLOH. Automatically collected samples for TSS determination were removed from the automated sampler and kept chilled (4°C) during shipment to the MMSD. Samples sent to SLOH and MMSD were analyzed for TSS with the identical pipette method (State Laboratory of Hygiene, Madison, Wis., Method 340.1). A known volume of water was filtered through pre-weighed glass fiber filters, which were subsequently dried at 103–105°C for 1 hour, cooled, and reweighed. Based upon duplicate samples (appendixes 2a–2f), overall sampling precision (field and laboratory) was 6 percent.

Samples analyzed for PCB congeners and ancillary constituents were collected from June 1993 through August 1995. At Estabrook Park, 15 of 29 samples were collected when discharge was above the mean annual discharge of 431 ft³/s, and 24 of the samples were collected when the river was above the 50-percent exceedance discharge of 223 ft³/s. Sediment and PCB contaminant loading are greatest during high flow. Thus, to optimize the project data set for load estima-

tion, sampling was emphasized during high flow (Richards, 1994; Dolan and others, 1981).

All PCB samples were analyzed on a congener-specific basis by use of capillary column gas chromatography with electron capture detection (gas chromatograph with a 60-m DB5 column) at SLOH (Degenhardt, 1996). This method allows the determination of as many as 85 congeners (with 26 co-elutions). Details on quantitation, generation of response factors, surrogate standards, matrix spikes, retention time reference peaks, and internal standards are contained in Degenhardt (1996). The average recovery of surrogate and matrix spikes for all samples analyzed during the period coincident with the analysis of the samples from the study reported here can be found in table 1 of Fitzgerald and Steuer (1997). Congener concentrations were not corrected for percent recovery of either the surrogates or the matrix spikes. Detection limits, limits of quantification, IUPAC numbers, and congener descriptions used in sample analysis are reported in appendix 1.

Four samples of surficial bottom sediment (0–2 cm depth), one per season, were collected at the Pioneer, Thiensville, and Estabrook sites. Most samples were collected by means of an Ekman dredge, although some samples were collected with a simple hollow tube at the wadable site (Pioneer Road). Field and laboratory methods for bed-sediment constituents are described in detail in Fitzgerald and Steuer (1997).

The USGS computer program CLOAD was used to estimate TSS and PCB loads. CLOAD employs a flow-integration approach to estimate loads whereby concentration data are estimated by linear interpolation between existing data points and are subsequently multiplied by 15-minute discharge values (daily in winter) to obtain loads (Porterfield, 1972).

Field quality control consisted of analysis of field-equipment blanks and replicates. Congener distributions representative of the Highway T site (upstream control site), the Pioneer site (which had the lowest PCB concentration of the contaminated sites), and the two highest field-equipment blank samples are compared in figures 2a and 2b. Appendix 1 contains a complete listing of the plotted congeners. Numerous congeners (IUPAC nos. 5/8, 16/32, 28/31, 26, 33, 49, 44, 37/42, 41/64, 70/76, 66/95, 84/92, 101, 99, 87, 77/110, 149, 132/152) were detected in the field-equipment blanks but were not detected in the upstream-control-site samples. Therefore, contamination observed in the field blanks was most likely from the field-blank water and is not indicative of compromised samples.

Finally, overall sampling precision (including field and laboratory) based on five sets of duplicate samples of dissolved PCB's and particle-associated PCB's was 11 percent and 14 percent, respectively (1 standard deviation). A more detailed discussion on quality-assurance sample results can be found in Fitzgerald and Steuer (1997).

DISTRIBUTION AND TRANSPORT OF PCB'S AND ASSOCIATED PARTICULATES

PCB Congeners

Operationally defined dissolved and particle-associated PCB congener data from water-column and bed-sediment samples collected at the Columbia, Highland, Pioneer, Thiensville, and Estabrook sites are shown in figures 3a–3c. Congener data are represented as a percentage of the sums of all congeners. Data from samples collected at a given site were averaged together. PCB congener distributions in water and bed sediments were similar at the Highland, Pioneer, and Thiensville sites. In addition, the particle-associated PCB congener pattern appears nearly identical to the surficial-sediment core data, a relation that indicates interaction between the two media.

The congener pattern changes as one progresses downstream to the Estabrook site. The Estabrook congener distribution has a higher percentage of less chlorinated congeners than those observed at the upstream sites. This shift is especially noticeable in the suspended-particle-associated PCB and the bed-sediment distributions (figs. 3b and 3c). Unlike those for the upstream sites, the suspended-particle-associated PCB distribution at the Estabrook site is not solely reflective of the bed-sediment PCB profile. Rather, PCB distributions of suspended particles at Estabrook appear to be a mixture of those present in the Estabrook bed sediments and congeners transported from the upstream water column.

Historical records indicate the use of PCB Aroclor 1254 and 1260 at waste discharges into Cedar Creek and the Milwaukee River upstream from the Pioneer and Thiensville sites (Westenbroek, 1993). A comparison of PCB congener distributions of these two Aroclor mixtures with bed-sediment PCB distribution at Pioneer and Thiensville indicate marked similarities (fig. 3c). In contrast, bed-sediment PCB distributions at Estabrook more closely resemble a third Aroclor mixture (1242;

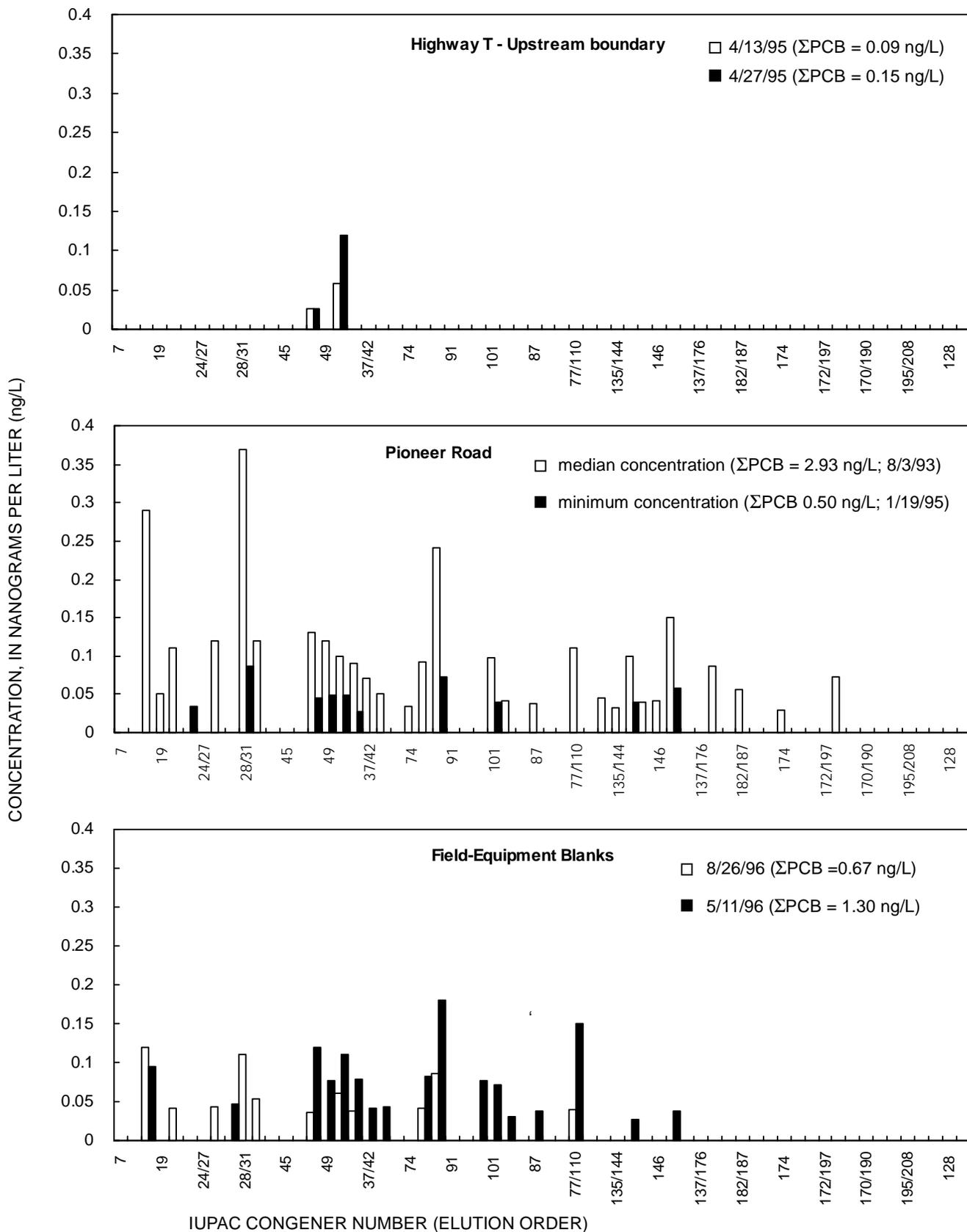


Figure 2a. Dissolved PCB congener distributions from the two highest field-equipment-blank concentrations and two Milwaukee River field sites. (“ Σ PCB” denotes summed PCB congeners.)

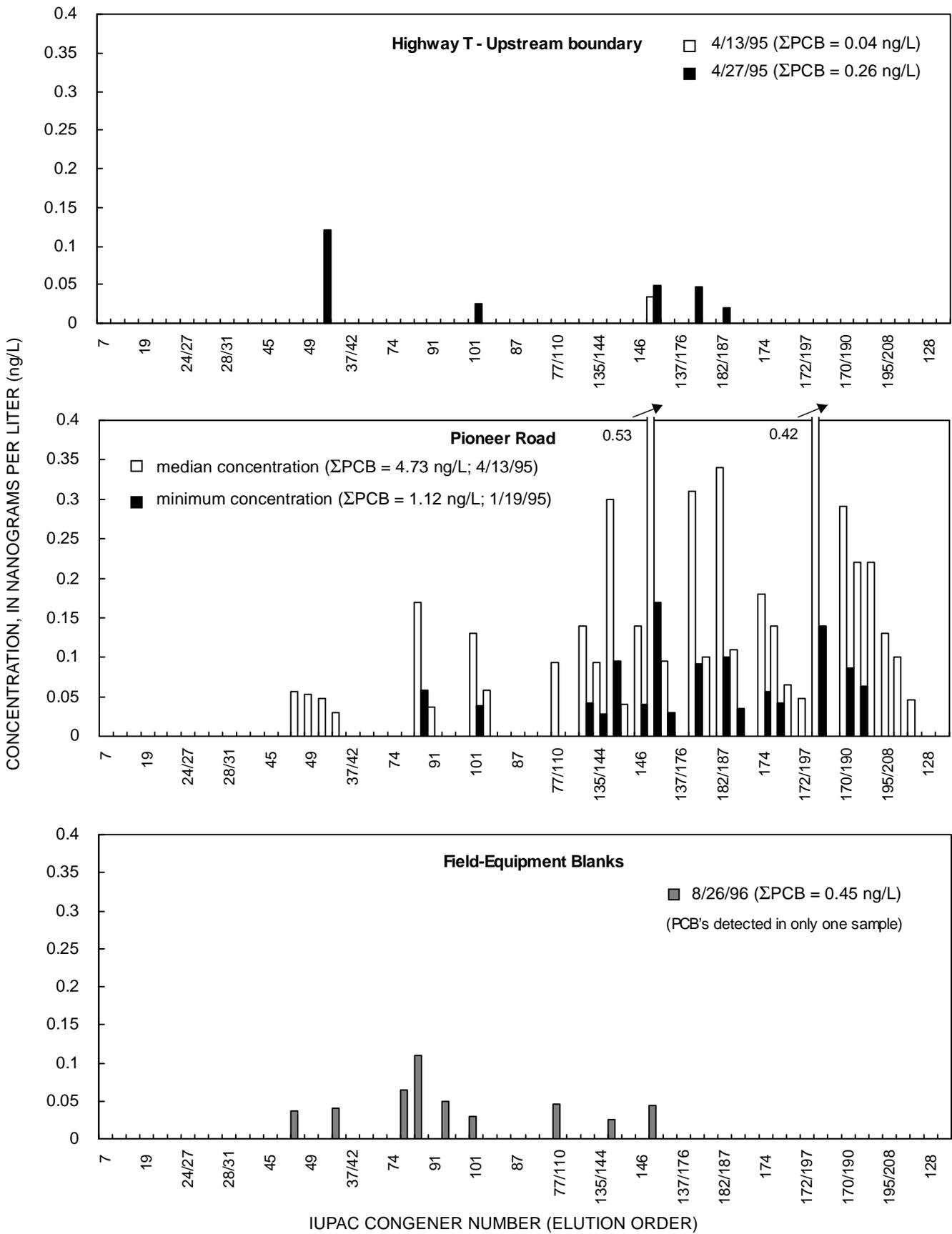


Figure 2b. Particulate PCB congener distributions from the two highest field-equipment-blank concentrations and two Milwaukee River field sites. (“ Σ PCB” denotes summed PCB congeners.)

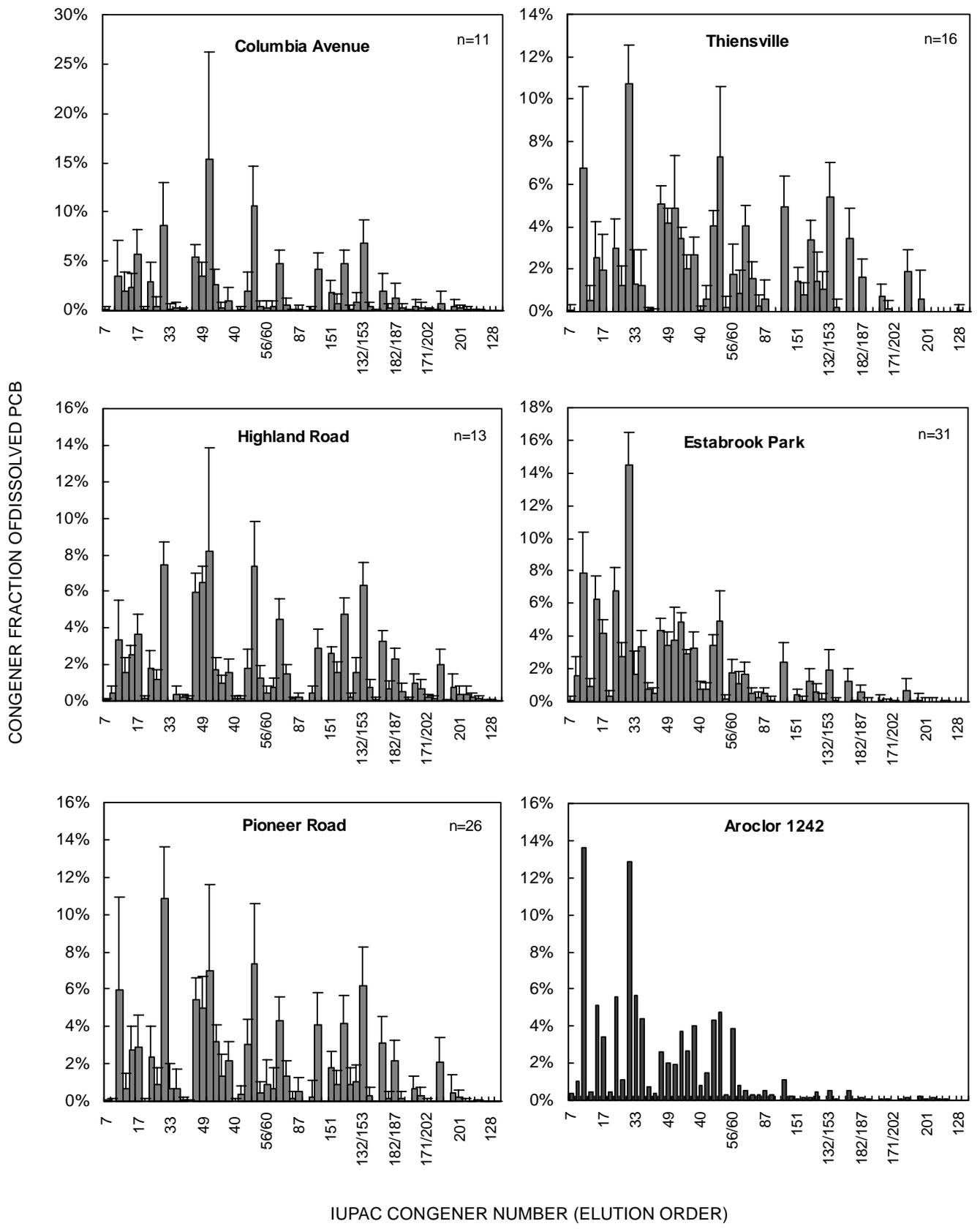


Figure 3a. Dissolved PCB congener distributions for Milwaukee River and Cedar Creek sites and one Aroclor mixture. (Error bars represent 1 standard deviation.)

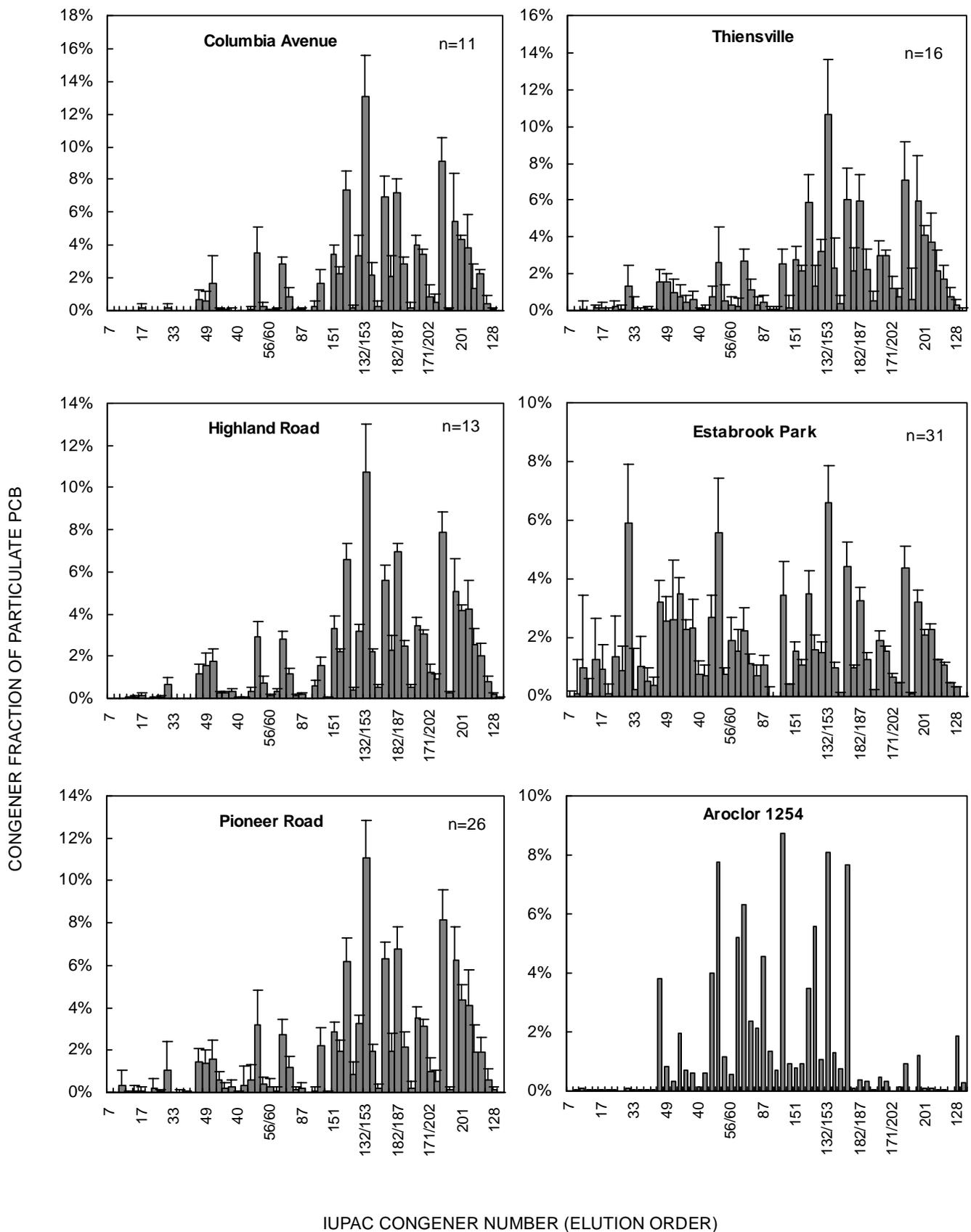


Figure 3b. Particulate PCB congener distributions for Milwaukee River and Cedar Creek sites and one Aroclor mixture. (Error bars represent 1 standard deviation.)

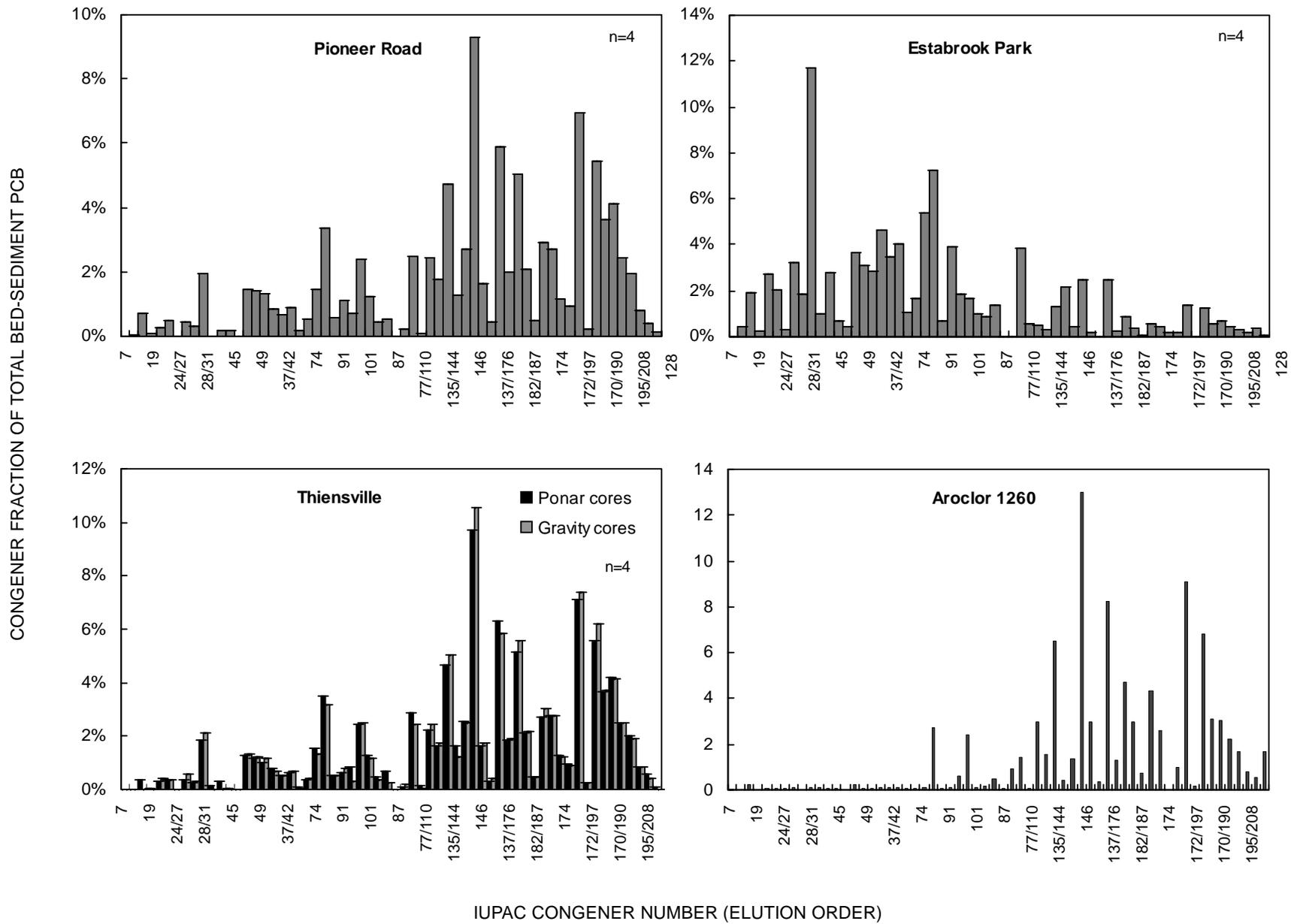


Figure 3c. Bed-sediment PCB congener distributions for Milwaukee River and Cedar Creek sites and one Aroclor mixture.

fig. 3a) with the addition of a relatively small percentage of some of the higher chlorinated congeners contained in Aroclor 1260 (fig. 3c). A possible source of Aroclor 1242 is the Lincoln Creek subbasin (fig. 1), which contains a mixture of industrial, commercial, and residential land use.

Phase Partitioning of PCB's

Physiochemical associations of PCB's in rivers are generally controlled by the interplay between the character (organic carbon content, surface area, mass) of sorbing phases (DOC, colloids, and POC) and the hydrophobicity of the PCB molecules themselves, usually approximated by the octanol-water partition coefficient (K_{OW}) (Karickhoff and others, 1979). A theoretical, thermodynamically based partitioning of PCB's between the truly dissolved phase, the DOC-bound phase (K_{DOC}), and the POC-bound phase (K_{POC}) can be computed as follows (assuming equilibrium conditions), solved here for K_{POC} (Karickhoff and others, 1979):

$$K_{POC} = C_{PAR} / [(C_{DIS} + C_{DOC})(POC) - (K_{DOC}/K_{POC})(DOC)(C_{PAR})], \quad (1)$$

where

- C_{PAR} is concentration of particle-associated PCB (mass per volume),
- C_{DIS} is concentration of "dissolved" PCB (mass per volume),
- C_{DOC} is concentration of DOC-associated PCB (mass per volume),
- POC is concentration of particle-associated organic carbon (mass per volume),
- DOC is concentration of dissolved organic carbon (mass per volume),
- K_{DOC} is partition coefficient for DOC-associated PCB (volume per mass).

For each sample, all term values in the above equation were measured except K_{DOC} and K_{POC} . These two partition coefficients cannot be determined from field measurements but must be computed from theory and other measured parameters, owing to the inability to accurately separate PCB's associated with the various phases. On the basis of a literature search, however, Bierman and others (1992) noted that the ratio between K_{POC} and K_{DOC} could be approximated as follows:

$$K_{POC}/K_{DOC} = 0.01,$$

where both unknowns have been defined previously. Therefore, this approximation reduces the problem to one equation and one unknown, allowing a unique solution. The K_{POC} value is based upon PCB partitioning to organic carbon; however, K_{POC} tends to have a relatively large error associated with the variability of the several terms in the equation. Another caveat is that although the PCB concentration of the operationally defined dissolved phase (C_{DIS}) is based on the mass of PCB's passing through a 0.7- μ m glass fiber filter, the DOC mass is determined by that which passes through a 0.45- μ m silver membrane filter. Thus, the mass of sorbing medium (DOC) is underestimated with respect to the operationally observed PCB concentration associated with DOC, resulting in an underestimate of the second denominator term (eq. 1) and therefore an underestimate of K_{POC} .

Alternately, an empirically determined, two-phase apparent distribution coefficient (K_D) can be computed from the measured parameters and is defined as follows:

$$K_D = C_{PAR} / (TSS \times C_{DIS}), \quad (2)$$

where all unknowns have been previously defined. As mentioned, the operationally defined dissolved phase was analyzed from the filtrate that passed through a 0.7- μ m glass fiber filter. Although the apparent K_D value is empirical and does not rise directly from partitioning theory, is mainly useful as a way to compare PCB distributions among several samples on a relative basis.

Computed apparent K_D and K_{POC} values, averaged from all data for each sampling site, are given in table 2. At all sites, K_D and K_{POC} for the summed PCB congeners was intermediate between those values for IUPAC congeners 28/31 (both trichlorobiphenyls) and 180 (a heptachlorobiphenyl). A negative K_{POC} resulted from the second term in the denominator in equation 1 being larger than the first, possibly a result of the assumed K_{DOC}/K_{POC} ratio of 0.01.

The apparent distribution and organic-carbon-normalized partition coefficients compare favorably between the Fox River site at De Pere, Wis., as computed in the Lower Fox River Model Study (Steuer and others, 1995) and the Milwaukee River sites. Although K_{POC} is often used in PCB transport modeling, K_{POC} was more variable than K_D in both the Lower Fox River Model study and this investigation. In the Fox River study, POC was determined by the difference between TOC and DOC; thus K_{POC} variability was thought to be

Table 2. Calculated log K_D and log K_{POC} values for selected PCB congeners and summed PCB congener concentrations at all sampling sites

[Σ PCB, summed PCB congeners; () indicates coefficient of variation; %, percent]

Site	Log K_D			Log K_{POC}		
	28/31	Σ PCB	180	28/31	Σ PCB	180
Milwaukee River Basin						
Columbia Ave.	4.5 (41%)	5.7 (62%)	6.1 (53%)	5.4 (45%)	6.8 (113%)	7.5 (118%)
Highland Rd.	4.8 (105%)	5.8 (117%)	6.4 (94%)	5.9 (100%)	7.5 (239%)	Negative
Pioneer Rd.	4.5 (73%)	5.2 (58%)	5.6 (58%)	5.7 (58%)	6.5 (67%)	7.1 (292%)
Thiensville	4.5 (72%)	5.2 (48%)	5.6 (47%)	5.7 (77%)	6.7 (141%)	6.3 (1,646%)
Estabrook Park	4.7 (78%)	5.0 (70%)	5.7 (36%)	6.1 (119%)	6.8 (209%)	Negative
Other studies—Fox River, Wis.						
Fox River at De Pere ¹	5.1	5.1	5.6	6.2	6.2	6.8

¹From Steuer and others (1995).

the result of that computation. However, K_{POC} values computed in the present study from directly measured POC concentrations also were more variable than the K_D values (table 2).

At all sites, the distribution of particle-associated PCB's is a substantially different distribution from that of the operationally defined dissolved phase (figs. 3a and 3b). The sediment/water partition coefficients (fig. 4) indicate that the more chlorinated congeners have a much greater affinity for particulate matter than the less chlorinated congeners. In some cases, such as IUPAC congener 7 (a less chlorinated congener) and congener 194 (a more chlorinated congener), estimated partition coefficients differ by an order of magnitude. At equilibrium or near-equilibrium conditions, the more chlorinated congeners have a greater affinity for particulate matter. Thus, partitioning could explain the differences in PCB distribution observed in the operationally defined dissolved phase and the particulate phase (figs. 3a and 3b).

Total Suspended Solids and Chlorophyll *a* Concentrations

PCB's and other hydrophobic, lipophilic compounds are typically found sorbed to riverine biotic material, sediments, and other solids. Thus, chlorophyll *a* (surrogate for algae) and TSS data were

collected at each site in addition to discharge data to facilitate interpretation of PCB concentrations and loads. Data from all sites indicate that the automated POINT sample TSS data, which were collected from a single location in the river, provided a reasonable approximation of the more representative EWI samples (fig. 5). Reasonable correlations of POINT and EWI data may result when the river being sampled is well mixed with respect to a constituent of interest, in this case, suspended solids. Occasionally, the POINT sample was collected manually rather than automatically, often during the winter when sample tubing was frozen. On two occasions at Thiensville (12/14/93 and 1/19/95) and once at Estabrook (8/31/94), the POINT sample yielded TSS concentrations that were much higher than the EWI or CHURN samples (appendixes 2e and 2f). These three samples are not included in figure 5. It is likely the manual sampling inadvertently collected resuspended bottom material. The river-discharge data or samples collected at the same time at other Milwaukee sites do not support the elevated TSS concentrations (appendix 2).

TSS, chlorophyll *a*, and discharge data from the Highland, Pioneer, Thiensville, and Estabrook sites (figs. 6a–6d) indicate that TSS concentrations during some intervals are not directly related to discharge. Although sediments and other solids, including detritus, are frequently mobilized during periods of snowmelt or storm discharge, biotic material can increase exponen-

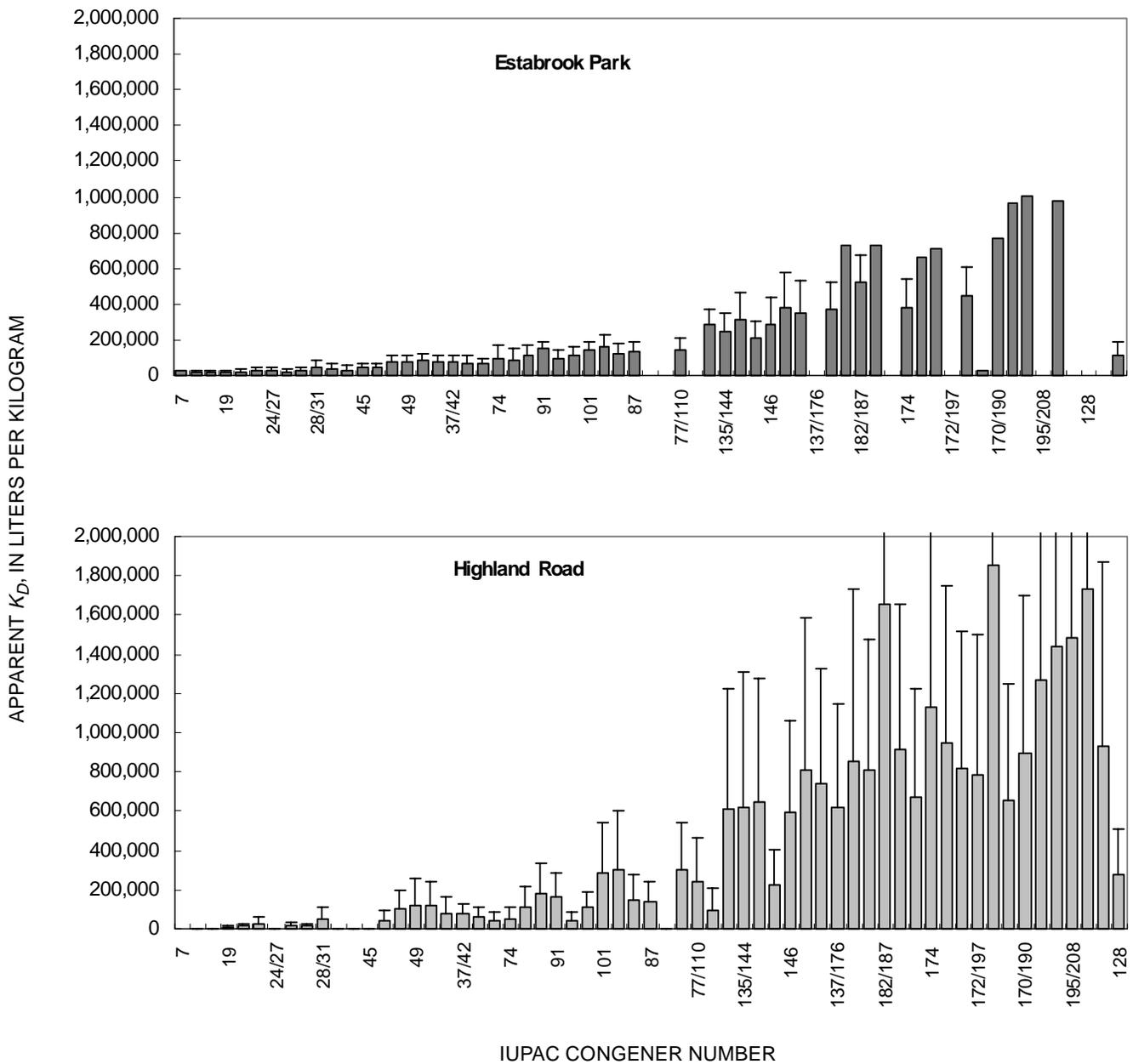


Figure 4. Apparent distribution coefficients (K_D) at two Milwaukee River Basin sites. (Error bars represent 1 standard deviation.)

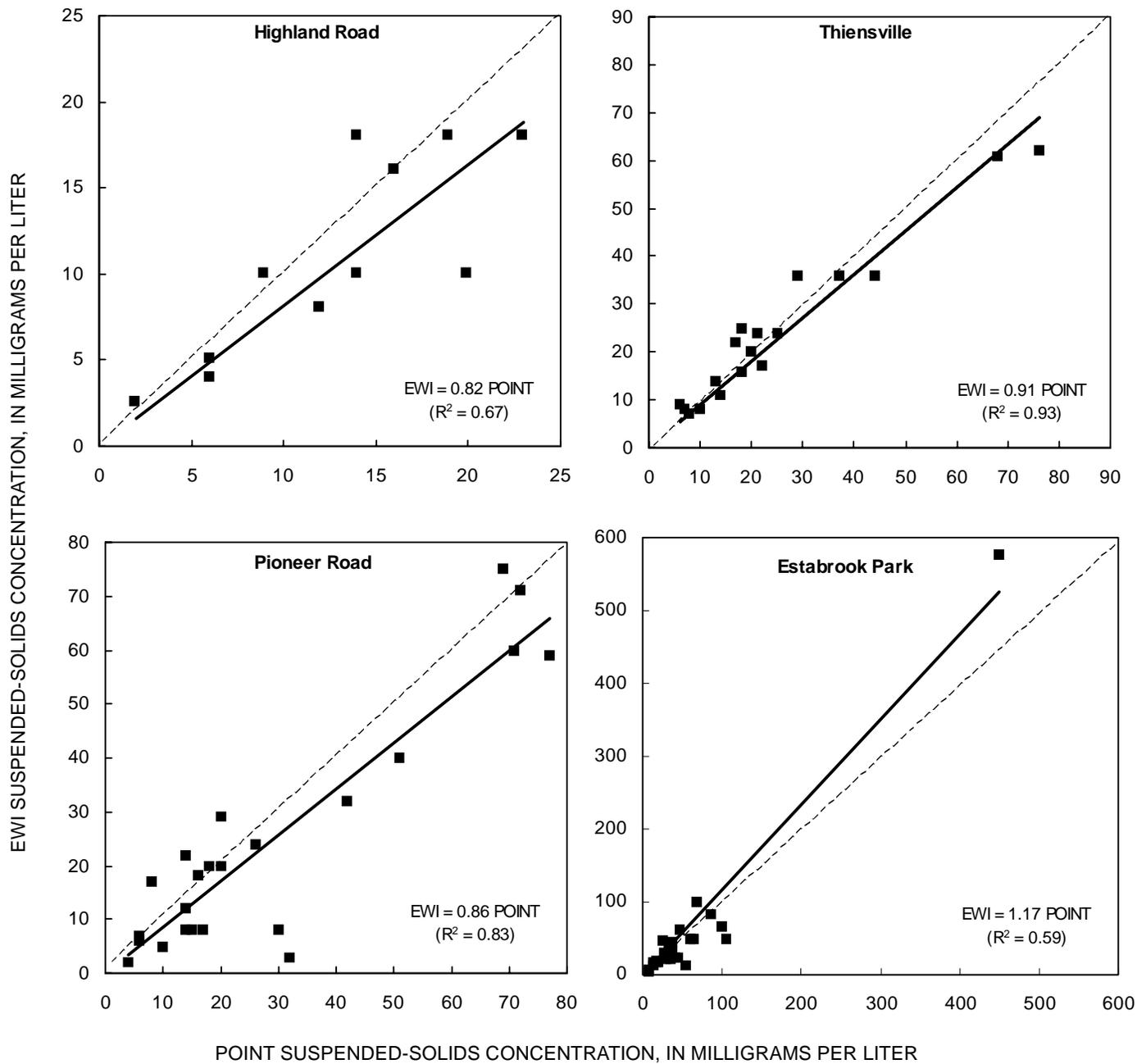


Figure 5. Correlation of point-sampled (POINT) and equal-width-increment (EWI) sampled suspended solids at four Milwaukee River and Cedar Creek sites.

tially with the availability of sunlight and resultant warmwater conditions. Therefore, factors in addition to discharge may be needed to represent suspended-solids transport and PCB transport in the Cedar Creek/Milwaukee River system. In general, concentrations of TSS and discharge increase sequentially from Highland Road to Estabrook Park. (Note the sequentially increasing y-axes scales on some of the graphs in figs. 6–9.)

At the Highland site, TSS concentrations did not exceed 40 mg/L except during late December 1994, when TSS concentrations exceeded 70 mg/L. This TSS spike was also observed at the downstream sites and may have been reflective of an algal bloom; no chlorophyll *a* data are available to confirm this. Some small TSS concentration increases correspond to the rising hydrograph limb (April through May 1995); but, in general, the impoundment did not generate high TSS concentrations. The overall cyclical TSS concentration pattern reflects the chlorophyll *a* (biotic growth) concentration data. This growth pattern is also observed at the three downstream sites.

At the Pioneer site, below the confluence of Cedar Creek and the Milwaukee River, TSS concentration increased greatly on the rising hydrograph limb during numerous events (fig. 7). Yet, during spring 1995, increased discharge did not generate high TSS concentrations at the Pioneer site. A late December 1994 increase in TSS similar to that noted at the Highland site (fig. 6) is readily observable in the Pioneer data (fig. 7). At Pioneer Road, Thiensville, and other sites downstream, however, the December 1994 increase that was so pronounced at the upstream Highland site is overshadowed by much larger solids concentrations associated with high-flow events and warm-weather conditions that occur annually.

The Thiensville site is immediately downstream from an impoundment, and TSS peaks increased slightly relative to those measured upstream at Pioneer Road. TSS and chlorophyll *a* concentrations are notably elevated during warm-weather periods of 1993 and 1994 (fig. 8). Elevated discharges in early spring of 1994 and 1995 were associated with low concentrations of TSS. This may have resulted from low availability of a flocculent, resuspendable bottom-sediment layer during that time of year or from reduced sediment inputs from the surrounding subbasin.

Estabrook Park, with its impervious urban basin contributions, is a hydraulically variable site compared to Thiensville and the other upstream sites. The rapid fluctuations in TSS concentration measured at

Estabrook necessitated use of a log scale for displaying the data (fig. 9). Although the Estabrook site is, like Thiensville, immediately downstream from an impoundment, Estabrook is also downstream from the urbanized Lincoln Creek tributary. Lincoln Creek drains a 9.6-mi² urban basin that includes industrial inputs and urban stormwater discharges. Estabrook had maximum chlorophyll *a* concentrations of greater than 250 mg/L (fig. 9), demonstrating the substantial contribution that biotic material can make to the TSS concentration during an algal growth period. Increased TSS concentrations are again observed on the rising hydrograph limb. As is the case with the two upstream sites, this response is not readily observed during the early spring periods.

Total Suspended Solids Load

Suspended-solids loads for the Highland, Pioneer, Thiensville, and Estabrook sites were estimated by the CLOAD procedure (table 3). Loads increased from Pioneer Road to Estabrook Park; however, as figure 10 and table 3 indicate, solids suspension and deposition are variable with time and river reach. For example, the cumulative TSS load at Thiensville was less than at Pioneer Road from about March through November 1994, an indication that material advected past the Pioneer site was being deposited in the Thiensville impoundment. By the end of the study period, in summer of 1995, the cumulative TSS load at Thiensville substantially exceeded loads advected at Pioneer Road, signifying net scour or substantial biotic growth or both in the Thiensville impoundment. Substantially larger TSS loads measured at Estabrook Park than at Thiensville resulted from sediment influx from the Lincoln Creek tributary and other urban sources, along with substantial biotic growth or scour in the Estabrook impoundment. During water year 1994, TSS input from Lincoln Creek was 2,300 tons (Corsi and others, 1997) upstream from the Estabrook site. Thus, more than 25 percent of the 8,100-ton TSS increase from Thiensville to Estabrook Park (table 3) can be attributed to Lincoln Creek input. A controlled dam release from the Estabrook impoundment on October 12, 1994, moved an estimated 103 tons of solids, which is represented as a short vertical segment of the Estabrook cumulative TSS load curve (fig. 10).

Comparison of discharge to TSS loads (fig. 10) also illustrates that although biotic material can substan-

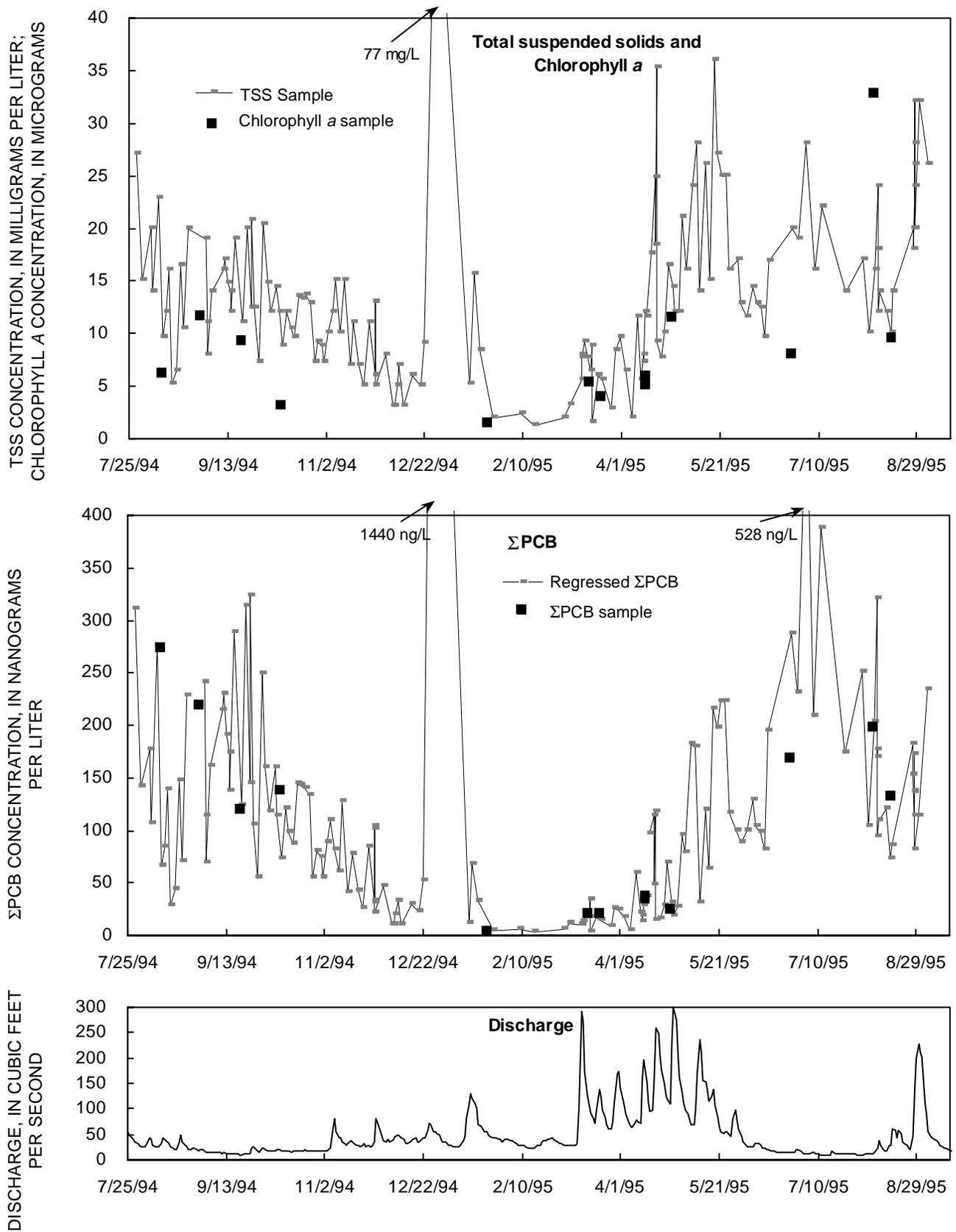


Figure 6. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Highland Road site on the Milwaukee River.

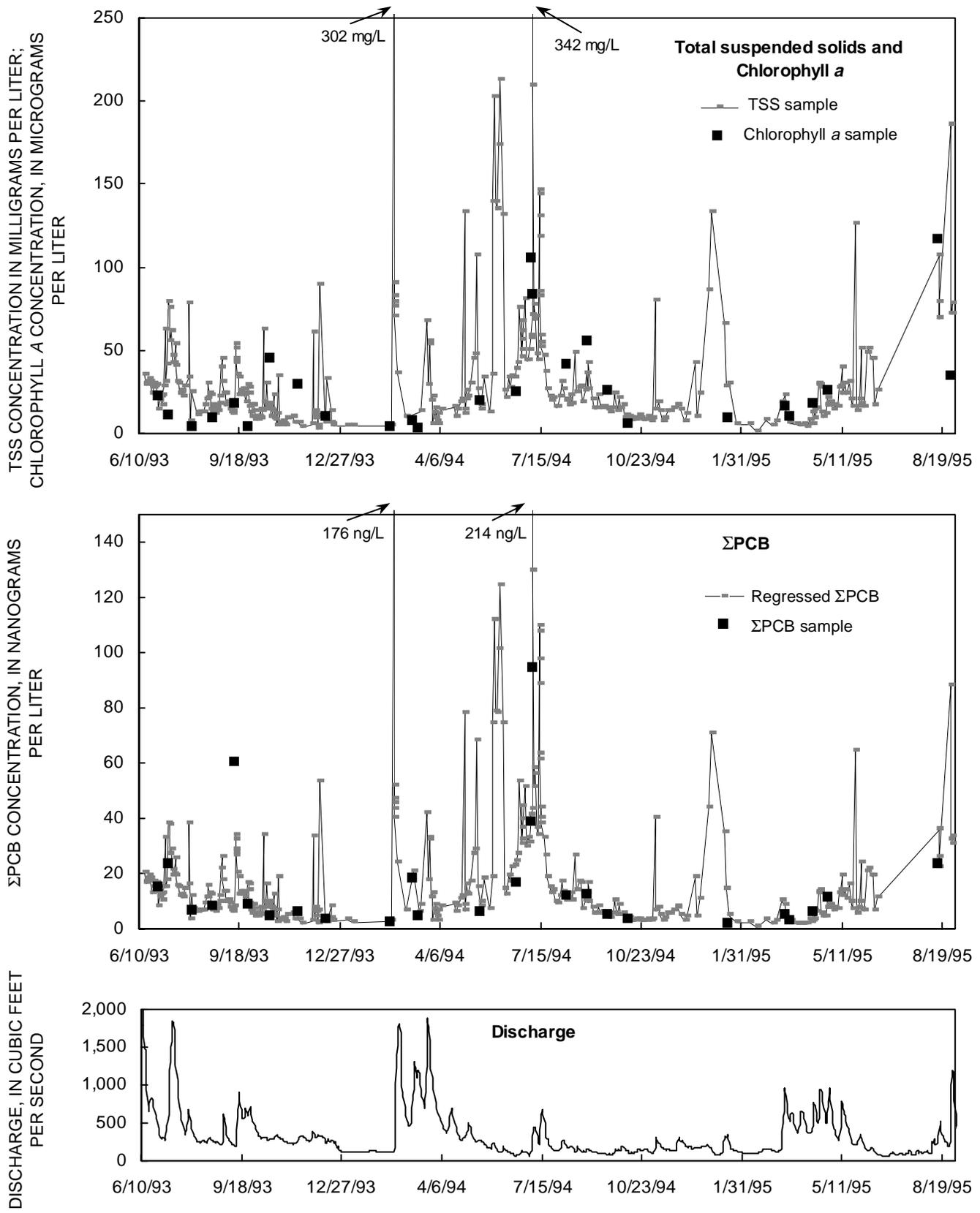


Figure 7. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Pioneer site on the Milwaukee River.

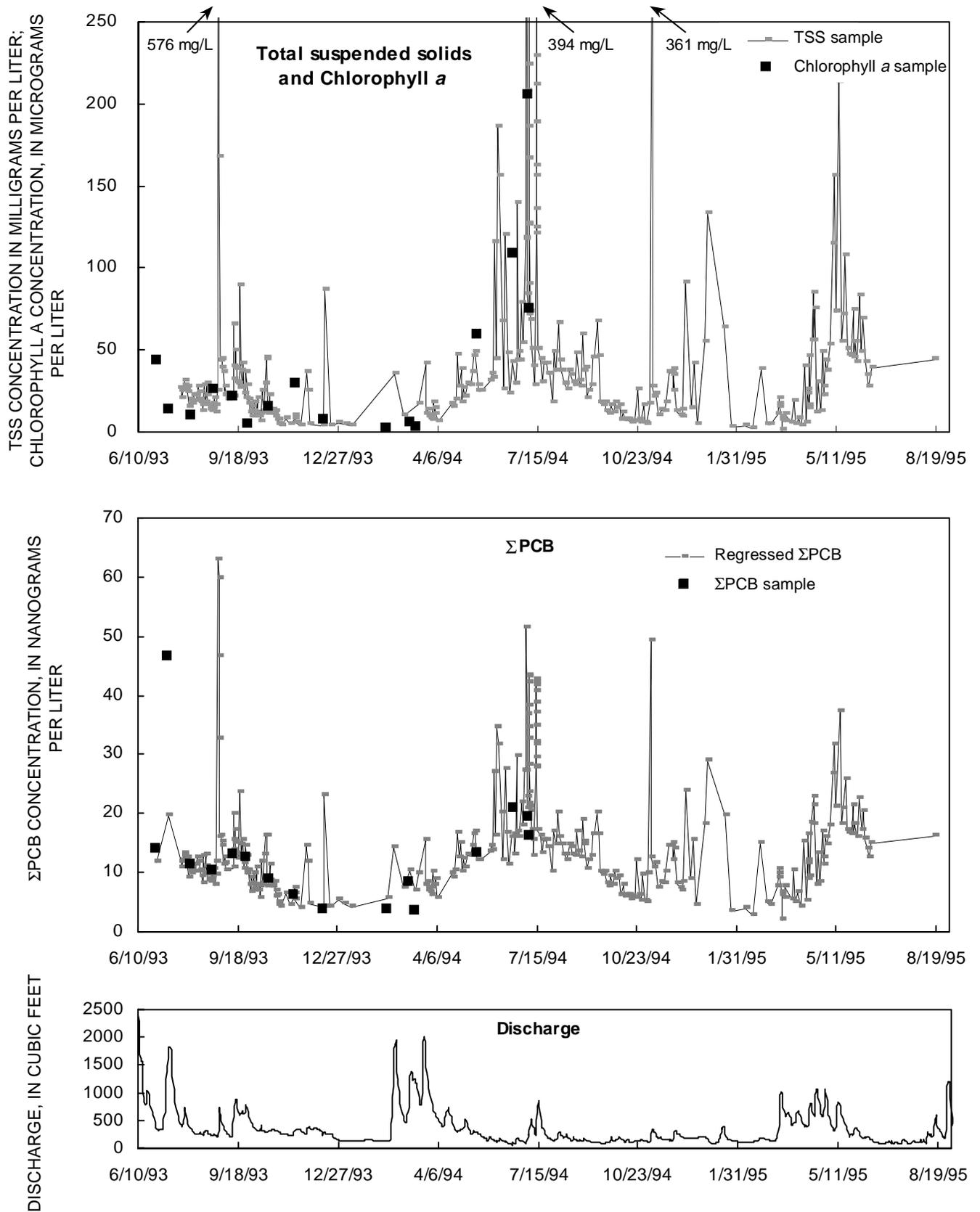


Figure 8. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Thiensville site on the Milwaukee River.

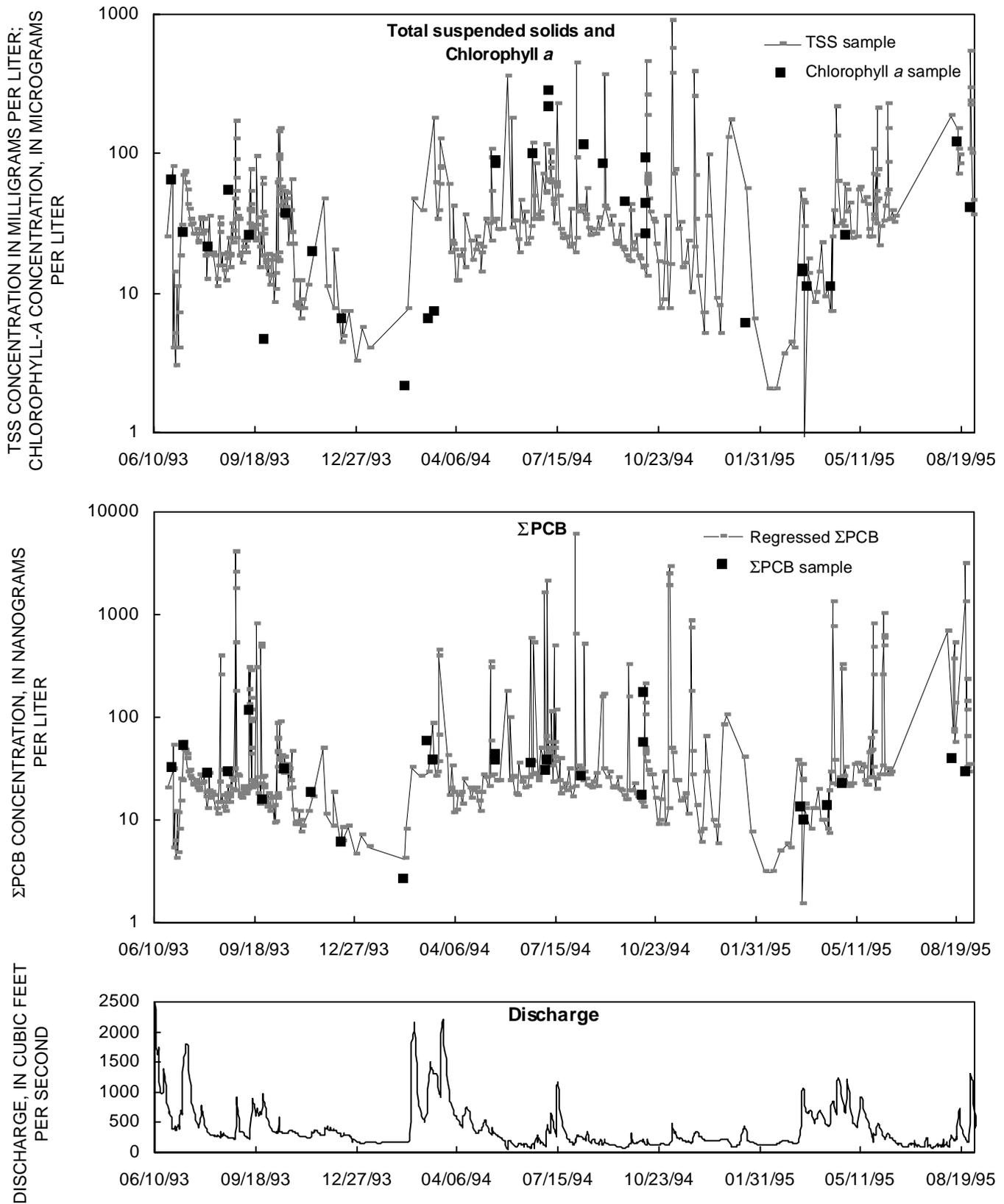


Figure 9. Total suspended solids (TSS), summed PCB congener (Σ PCB) concentration, and discharge data from the Estabrook Park site on the Milwaukee River.

Table 3. Total-suspended-solids loads computed for four Milwaukee River Basin sites

[The irregular load intervals are necessary to accommodate comparison with the Highland Road data, which were collected for a limited time interval; --, no data]

Site	Sampling interval (No. of samples)	Load (tons)			
		7/1/93–7/31/93 (1 month)	8/1/93–7/31/94 (1 year)	8/1/94–7/31/95 (1 year)	Water year 1994 10/1/93–9/30/94 (1 year)
Highland Road	7/29/94–9/4/95 (158)	--	--	630	--
Pioneer Road	6/16/93–8/29/95 (401)	2,800	9,600	4,400	8,700
Thiensville	7/22/93–8/17/95 (351)	3,000	9,100	8,200	7,700
Estabrook Park	6/22/93–8/3/95 (447)	2,800	16,800	11,200	15,800

tially increase TSS concentrations during times of low flow, most TSS is transported on the main stem of the Milwaukee River during high flow. In addition to the cumulative TSS load (fig. 10), TSS passing the Thiensville and Estabrook sites was analyzed on a reach basis (fig. 11) to illustrate the dynamic nature and complexity of TSS transport on the Milwaukee River. Intervals where the “Pioneer to Thiensville” line is positive indicates that solids loads were greater at Thiensville than upstream at Pioneer Road; however, in numerous cases, the line is negative, indicating deposition and accumulation of solids in the Thiensville impoundment. Similarly, a positive “Thiensville to Estabrook” line indicates greater solids transport at Estabrook Park than upstream at Thiensville, and a negative line indicates that solids are accumulating in the Estabrook impoundment.

Comparison of the two stream reaches produced some interesting results, such as during spring 1994 when sediments were being deposited at Thiensville (negative line) but being scoured at Estabrook Park (positive line). Net solids loading on the Thiensville to Estabrook reach is complicated by Lincoln Creek input. During this interval of positive net load (February and March 1994), 6,200 tons more TSS passed the Estabrook site than the Thiensville site, whereas input from Lincoln Creek was about 170 tons of TSS upstream from the Estabrook site (Corsi and others, 1997). Clearly, much of the solids passing the Estabrook site were resuspended from the bottom sediments upstream from the Estabrook Park. In contrast, during the end of the March to May 1995 event (which was much smaller than the spring of 1994 event), the opposite occurred: net load in the Pioneer to Thiensville

reach was positive (scour), whereas deposition occurred behind the Estabrook dam.

Concentrations and Loads of Transported PCB's in the Milwaukee River System

Data detailed in appendixes 2a–2f indicate that PCB concentration and load increase as one progresses down the Milwaukee River Basin. PCB samples from the Columbia site on Cedar Creek, immediately downstream from the remediated Ruck Pond impoundment, resulted in loads less than 3 grams per day (g/d) (appendix 2a). In contrast, PCB samples collected from the Highway T site on Cedar Creek, downstream from the contaminated Columbia impoundment, resulted in ΣPCB loads as high as 20 g/d.

At the Highway T site, 4 out of 5 PCB samples result in a ΣPCB load of less than 1 g/d. After Cedar Creek joins the Milwaukee River, downstream from Highway T, ΣPCB loads increased such that the median sampled summed PCB congener load at Estabrook was 26 g/d, and the maximum sampled load was 221 g/d.

At the four downstream sites, the fraction of PCB found in the particle phase ranged from 61 percent to 74 percent (median values; appendixes 2b, 2d, 2e, 2f). Thus, TSS formed the basis of the ΣPCB regression equations. All PCB congeners present in a sample were summed to obtain the reported ΣPCB concentrations for each sample.

Congener-specific PCB data have been published (Holmstrom and others, 1995, 1996, and 1997) and are stored in the USGS QWDATA data base. Concentrations of the operationally defined dissolved phase, particle-associated phase, and total ΣPCB's (both phases),

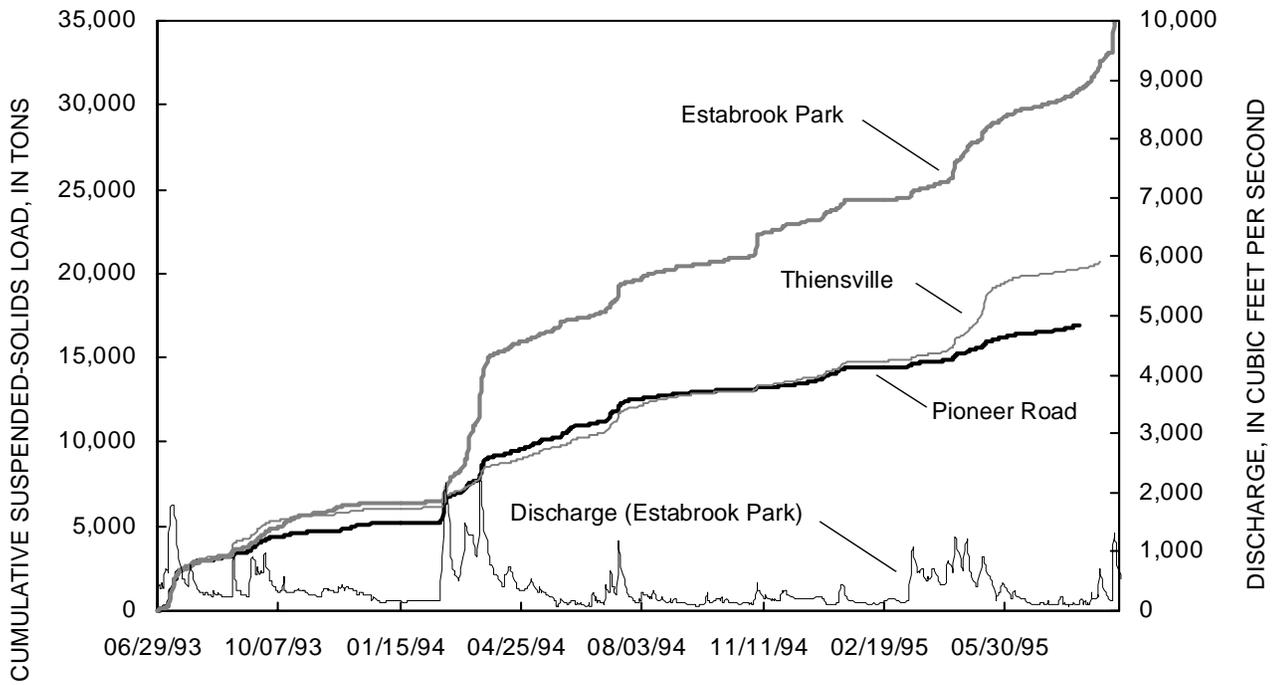


Figure 10. Cumulative suspended solids-loads at three Milwaukee River sites and discharge at the Estabrook site.

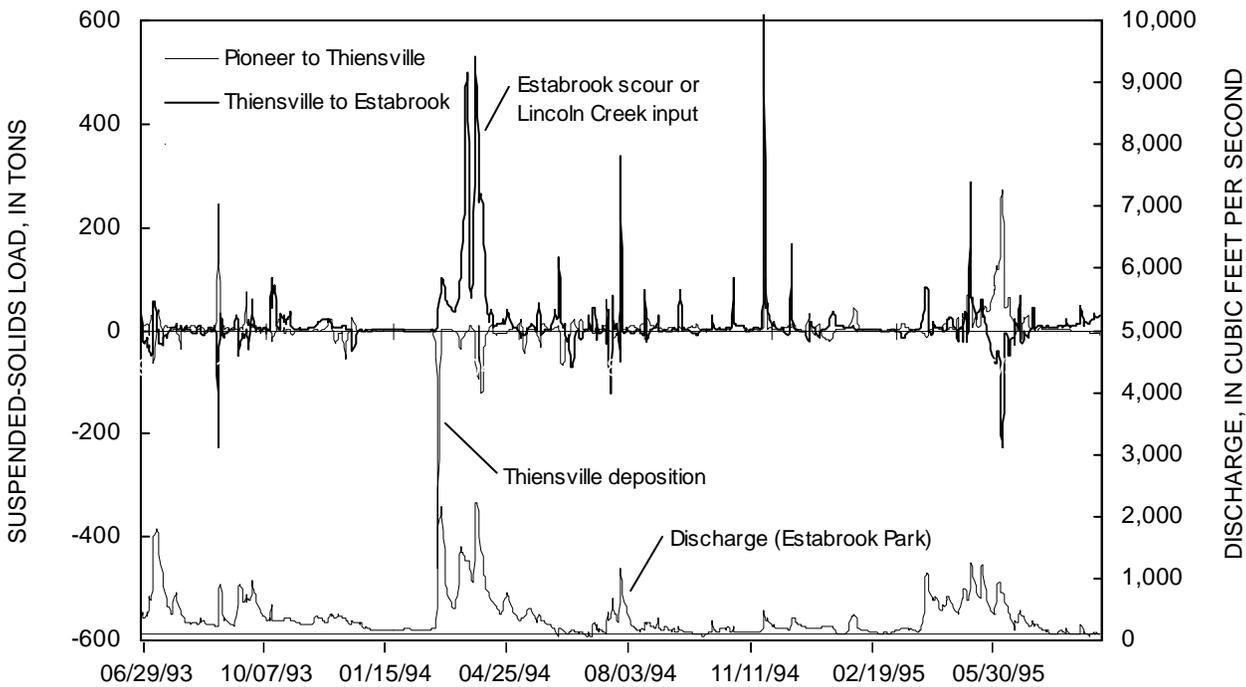


Figure 11. Net suspended-solids loads for two Milwaukee River reaches and Estabrook discharge.

Table 4. Summed PCB congener concentration regression relations and characteristics at Highland Road (Cedar Creek) and three Milwaukee River sites

[TSS, total suspended solids, in milligrams per liter; r^2 , correlation coefficient; SE, standard error; $\mu_{\log[\text{PCB}]}$, mean of the log (ΣPCB); %, percent;

$10^{\left(\frac{SE^2}{2}\right)}$ = bias correction factor]

Site	Regression equation	r^2	p-value	$1.96 \cdot \left(\frac{SE}{\mu_{\log[\text{PCB}]}}\right)$	$10^{\left(\frac{SE^2}{2}\right)}$
Highland Road	H ₁ : $\text{Log}(\Sigma\text{PCB}) = 1.56 \log X + 0.29$ $X = (-0.67 \text{Log } Q_c + 2) \text{TSS}$ Q_c is instantaneous Cedar Creek discharge in cubic feet per second, at the time of the TSS sample	0.93	1.0×10^{-7}	18.0%	1.03
Pioneer Road	P ₁ : $\text{Log}(\Sigma\text{PCB}) = 1.02 \log X - 0.05$ applied on or before August 24, 1994	.88	3.4×10^{-8}	30.0%	1.03
	P ₂ : $\text{Log}(\Sigma\text{PCB}) = 1.08 \log X - 0.26$ applied after August 24, 1994	.70	5.0×10^{-3}	54.9%	1.05
	$X = \left(\frac{\text{Daily Cedar Creek Discharge}}{\text{Daily Pioneer Discharge}}\right)^{0.3} \cdot \text{TSS}$				
Thiensville	T ₁ : $\text{Log}(\Sigma\text{PCB}) = 0.53 \log(\text{TSS}) + 0.34$.83	2.7×10^{-6}	21.2%	1.01
Estabrook Park	E ₁ : $\text{Log}(\Sigma\text{PCB}) = 0.78 \log X + 0.45$ $X = (0.006Q_L^2 - 0.02Q_L + 0.06) \text{TSS}$ Q_L is instantaneous Lincoln Creek discharge, in cubic feet per second	.85	8.9×10^{-12}	20.0%	1.02
	E ₂ : $\text{Log}(\Sigma\text{PCB}) = 0.81 \log \text{TSS} + 0.21$.74	8.0×10^{-9}	26.1%	1.04

along with the ancillary constituents are given in appendix 2.

PCB's and other hydrophobic compounds typically sorb to riverine biotic material, sediments, and other solids; thus, the ΣPCB regressions initially focused on the TSS variable. POINT TSS samples, instead of CHURN or EWI samples, were used in the ΣPCB loading regression analyses because of the greater data density and more complete event coverage afforded by the frequency of POINT sample collection. In addition to TSS, regression was used to examine ΣPCB concentration as a function of discharge, time of year, temperature, and precipitation. Depending on the site, some of these variables were used to transform the TSS variable. The site-specific environmental settings, impoundment hydrodynamics, surrounding subbasin and tributary inputs, and channel morphology required that the form of the regression equations be site specific (table 4). The dependent and independent variables were \log_{10} transformed to normalize the distributions; thus, it was necessary to apply the bias correction factor (table 4) as detailed in Gilroy and others (1998).

For the Highland site (fig. 6), a simple linear regression of $\log \Sigma\text{PCB}$ and $\log \text{TSS}$ resulted in a correlation coefficient (r^2) of 0.88. Without the log transformations of the variables, r^2 equaled 0.67. At this site, in addition to the positive ΣPCB -TSS correlation, ΣPCB was found to be negatively correlated with discharge (appendix 2b). This ΣPCB -discharge relation had the form of the transformation equation in table 4 with the slope (-0.67) and intercept (2) selected as to maximize r^2 . An example of the importance of Q_c transformation on TSS is on April 27, 1995, and August 17, 1995, when POINT TSS was 14 mg/L on both sample days but the discharge was 253 ft³/s and 63 ft³/s, respectively. On the high-flow day, April 27, 1995, the ΣPCB concentration was one-sixth of that on the low-flow day. Thus, the TSS variable was transformed (decreased) with increasing discharge (table 4).

At the Pioneer site (fig. 7), PCB-laden water from Cedar Creek is diluted by the relatively PCB-free Milwaukee River upstream (appendix 2c). The Cedar Creek/Milwaukee River flow ratio effectively transformed the TSS variable to reflect the decreased ΣPCB concentration during periods of low Cedar Creek dis-

charge relative to Milwaukee River discharge. For example, on July 7, 1994, and August 16, 1995, the TSS concentrations were nearly identical. However, the fraction of Milwaukee River flow that originated from Cedar Creek was nearly 3 times greater on July 7, 1994, resulting in a higher Σ PCB concentration.

On August 24, 1994, flow was diverted around the PCB-contaminated Ruck Pond impoundment on Cedar Creek to enable removal of contaminated sediment from Ruck Pond. Regression residuals—the difference between the regressed Σ PCB value and the sample Σ PCB data point—for the Pioneer site are shown in figure 12. If one regression equation is used for the entire Pioneer-site sampling period, 75 percent of the regression residuals after the Ruck Pond diversion are negative (fig. 12), signifying that the regression model overpredicted the data after August 24, 1994. If two regression equations are used, one before and one after the Ruck Pond flow diversion (remediation), the post-remediation residuals are less biased. Apparently Σ PCB concentration was at least partially affected by the Ruck Pond remediation; thus, the two regression equations were used to separate the data into before and after the diversion date (table 4).

At the Thiensville site (fig. 8), flow, temperature or precipitation transformation of TSS did not improve the linear correlation with Σ PCB; thus, the Σ PCB regression was based solely on TSS with no transformation. All PCB data were collected prior to the Ruck Pond flow diversion, thus, it was not possible to examine the Thiensville data in light of the Ruck Pond remediation.

At the Estabrook site, Lincoln Creek and the surrounding urban basin contribute significant discharge and suspended solids, as shown in figure 9. The substantial discharges may resuspend soft sediments at the Lincoln Creek confluence, an area in the Milwaukee River where strong eddies and distinct elevation changes of soft-sediment deposits have been observed (William Wawrzyn, Wisconsin Department of Natural Resources, oral commun., 1996). This is also an area of increased PCB concentrations in the bottom sediments (fig. 1; table 1). Transforming the TSS variable with Lincoln Creek instantaneous discharge (Q_L) appropriately increased the resulting PCB concentrations for the two PCB samples obtained during high Lincoln Creek inflow (appendix 2f) and improved the regression relation ($r^2 = 0.85$, table 4). Without the TSS variable transformation, the PCB regression equation had a lower linear correlation coefficient ($r^2 = 0.74$).

During the study period, Q_L rose to 2,500 ft³/s, much greater than the maximum discharge during which PCB samples were collected at the Estabrook site (95 ft³/s). Thus, it is unclear what the transformation relation should be when Q_L is greater than 95 ft³/s. For Q_L greater than 95 ft³/s, a linear extension ($X = 0.036Q - 0.32$ in equation E₁ in table 4) was used to estimate the PCB concentration. The complex physical setting upstream from Estabrook Park—including a large vertical PCB gradient in the bottom sediment in the vicinity of Lincoln Creek (fig. 1), significant sedimentation from urban inputs, and resuspension from a range of soft sediment deposits under specific flow—may require a deterministic model to obtain more accurate PCB loads at the Estabrook site.

The regression relation, regression statistics, and the log₁₀ bias correction factors are detailed in table 4. By comparing the POINT TSS concentrations (appendixes 2b–2f), which form the basis of the independent variable in the regression equations, to the full range of monitored TSS (figs. 6–9), it is apparent that the regression relations were based largely on the data range for which they are ultimately applied. The standard error multiplied by 1.96 and normalized by the dependent variable (log PCB), provides some indication of a confidence interval, although the actual 95-percent confidence interval is a function of the specific independent variable.

In general, over an extended period of time, total water-column PCB concentrations will decrease as PCB is transported out of the bottom sediments. The equations in table 4 do not contain time as an independent variable; thus, the regressions will not reflect this expected PCB concentration decrease. If these PCB regressions are compared to data collected in subsequent years, one would expect to see a negative trend in the residuals; the regression will be overpredicting the actual water-column concentrations. Limited data collection 5 to 7 years after this initial effort could be used to incorporate a time-decay function in the relation.

To compute Σ PCB loads, PCB concentrations computed from the frequent POINT TSS samples and the regression relations in table 4 were used in combination with 15-minute discharge data and the flow-integration method (CLOAD). This regression approach will be referred to as “RLOAD.”

Over the course of the investigation, it appeared that part of the Cedar Creek PCB load was deposited between the Highland and Pioneer sites; 1.9 kg more Σ PCB was advected past Highland Road than Pioneer

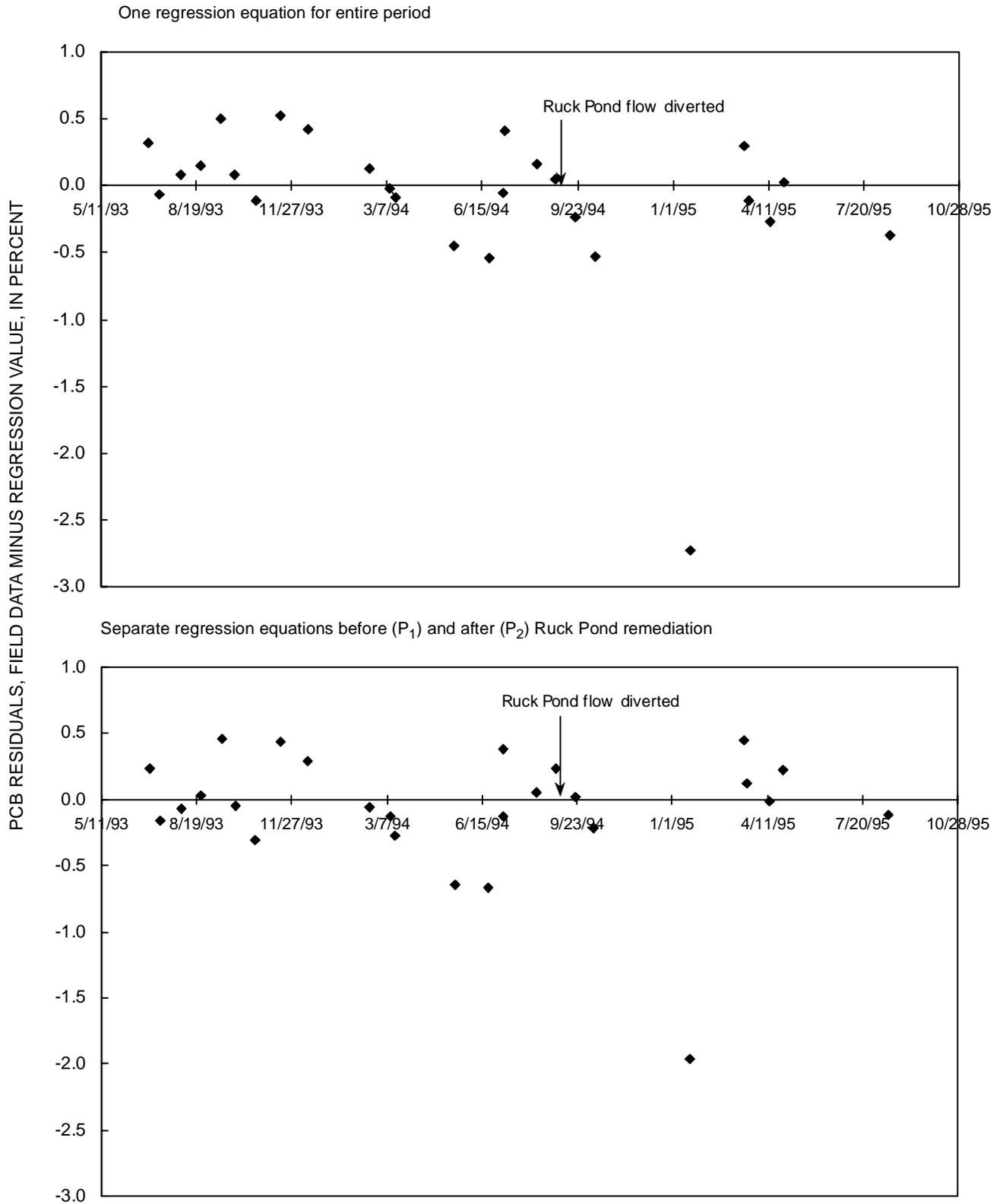


Figure 12. Pioneer PCB concentration regression residuals.

Table 5. Computed total loads for the Milwaukee River Basin sites using PCB regression relations (RLOAD)[Estabrook Park load computed with regression equation E₂; (), load values calculated with regression equation E₁; kg, kilogram; --, no data]

Site	PCB sampling interval (No. of samples)	Loads (kg)			
		7/1/93–7/31/93	8/1/93–7/31/94	8/1/94–7/31/95	Water year 1994
Highland Road	8/11/94–8/17/95 (13)	--	--	3.7	--
Pioneer Road	6/30/93–8/16/95 (26)	1.2	5.3	1.8	4.8
Thiensville	6/29/93–7/8/94 (16)	1.0	3.6	2.7	3.2
Estabrook Road	6/29/93–8/29/95 (27)	1.9 (1.8)	11.6 (20.3)	7.6 (16.3)	10.9 (17.5)

Road. In the Fox River system, volatilization losses were approximately 15 percent of advection (Steuer and others, 1995). Applying this rough approximation for volatilization loss (15 percent of 3.7 kg = 0.6 kg), it appeared that approximately 1.3 kg of PCB (3.7 - 1.8 - 0.6 = 1.3) may have been deposited upstream from Pioneer Road, possibly in the lower Cedar Creek impoundments (table 5).

Net annual Σ PCB loading in the Pioneer to Thiensville reach was inconsistent; one year it was less at Thiensville (by 1.7 kg), whereas the following year it was 0.9 kg greater at Thiensville. The Estabrook Park Σ PCB loads were computed using both regression relations. Estabrook Σ PCB advection was consistently greater than that at Thiensville (5 to 16 kg greater per year) an indication of Σ PCB flux from the Estabrook impoundment or surrounding watershed.

Cumulative Σ PCB loading as affected by time of year, discharge, and Estabrook dam releases is detailed in figure 13. Between June 29, 1993, and July 31, 1995, 38 kg of Σ PCB were advected past Estabrook (21 kg if one uses equation E₂, the regression that does not include the Lincoln Creek discharge transformation of TSS). The lowering of the Estabrook pool on October 12, 1994, released 51 g of Σ PCB (55 g if regression equation E₂ from table 4 is used).

For the purpose of load-computation comparison, Σ PCB loads were calculated by means of two additional approaches. In a second approach, the total integration method (CLOAD) was applied to the limited number of individual Σ PCB sample concentrations listed in appendix 2. These results will be referred to as SLOAD. The third load-computation approach, the Stratified Beale Ratio Estimator (SBRE), involved time-based strata defined by minimizing loading error over specific time intervals (Richards, 1994; Preston and others, 1989). The SBRE estimates both a load and an associated con-

fidence interval based on the root mean square error of the load computations. The RLOAD approach, which used the frequent POINT TSS data, in most instances resulted in larger loads than the SLOAD or SBRE methods that used solely the PCB concentration data. Intensive manual collection of PCB samples before and after event peaks was often impossible, whereas the automated TSS samplers did capture data during the peak load intervals. In one instance at the Estabrook site for the period June 29, 1993 to June 28, 1994, the regression approach based on TSS resulted in lower PCB loads than the SBRE approach did (table 6). Few PCB samples were collected during the low-TSS- and low-PCB-concentration winter period; thus, the SBRE loads encompassing this interval are probably too high.

SUMMARY

Concentrations of PCB congeners in the operationally dissolved, suspended-particle-associated, and surficial-bed-sediment (0–2 cm depth) phases at four sites on Cedar Creek and the Milwaukee River in Wisconsin were studied to determine the distribution and loads of total PCB's in the river. For three of the four sites, the PCB congener pattern in the particle-associated phase was similar to that in the bed sediment, indicating interaction between the two media. At the fourth site (Estabrook Park), the PCB congener distributions of suspended particles seemed to reflect a mixture originating from the Estabrook surficial bed sediments and suspended particles from the upstream sites. PCB distributions in the surficial bed sediments from all sites were generally recognizable as either one or both of PCB Aroclor 1242 and 1260. As expected, PCB distributions in the operationally defined dissolved phase generally showed higher abundances of the more soluble, less chlorinated congeners compared to both the suspended particles and surficial bed sediments. Variability in

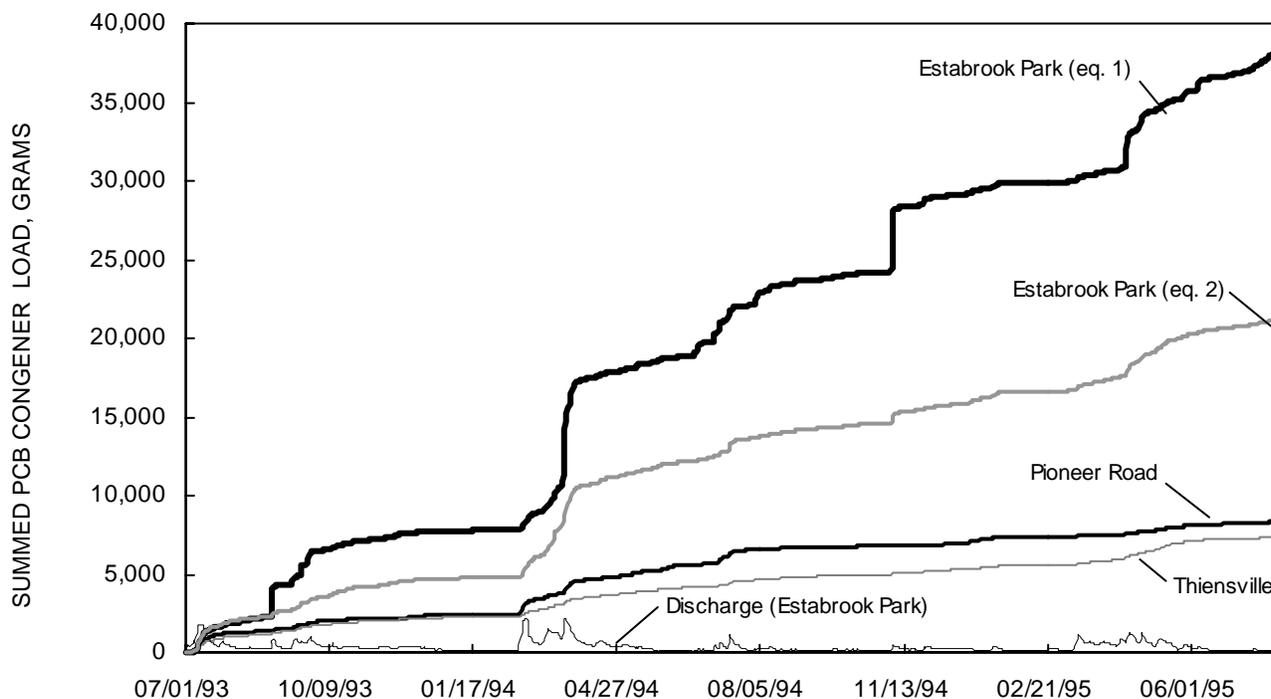


Figure 13. Cumulative summed PCB congener loads at three Milwaukee River sites and discharge at the Estabrook Park site.

computed distribution coefficients (K_D) was less than that for organic normalized carbon partition coefficients (K_{POC}). Combining congener-specific PCB data from the five sites, $\log K_D$ and $\log K_{POC}$ ranged from 5.0 to 5.8 and 6.5 to 7.5 units, respectively. Particle-associated PCB's exhibited two patterns: (1) a general increase in spring and summer associated with algal growth and (2) episodic increases associated with resuspension of bed sediments during storms. Calculated total suspended solids (TSS) and total PCB (Σ PCB) loads at each site were dependent on site-specific characteristics, including the tributary inflow and presence and operation of dams.

TSS loads during water year 1994 ranged from 8,700 tons at Pioneer to 15,800 tons at Estabrook. Regression relations based on single-point, automated sampler TSS measurements in addition to other environmental variables collected on a frequent basis were used to compute total Σ PCB concentrations. The regression-generated Σ PCB (total PCB concentration derived by summation of all dissolved and particulate congeners) concentrations were subsequently multiplied by 15-minute-discharge data to obtain loads. Σ PCB loads decreased from Highland (3.7 kg/yr) to Pioneer

(1.8 kg/yr), indicating PCB deposition between those sites. Computed loads of total Σ PCB's (operationally defined dissolved plus particle-associated phases) were an order of magnitude higher at the Estabrook site as compared to the three upstream sites and were likely due to a large reservoir of resuspendable PCB-laden sediment behind the dam. Uncertainty in the Estabrook Σ PCB loads is attributed to the limited PCB data collected during peak Lincoln Creek discharges, a period when PCB-laden bottom sediment may be resuspended in the confluence area. The lowering of the Estabrook impoundment in October 1994 released 0.05 kg of Σ PCB. A Σ PCB load comparison was done using two additional approaches: the Stratified Beale Ratio Estimator (SBRE) and the total-flow-integration method applied to individual sample concentrations (SLOAD). Results were comparable to Σ PCB loads based on regressed Σ PCB concentration values, but the SBRE and SLOAD commonly resulted in lower loads. This low bias was probably due to limited manual-sample collection during peak flows. This was not an issue with the regression approach that was based on automated TSS sampling.

Table 6. Computed summed PCB congener loads based on three computation approaches for the Milwaukee River Basin sites

[All loads in kilograms; SLOAD, integration method using sample PCB concentrations; RLOAD, integration method using regressed PCB values; SBRE, Stratified Beale Ratio Estimation; \pm , indicates 95 percent confidence interval]

Computation approach	Highland Rd. 8/8/94–8/7/95	Pioneer Rd. 6/30/93–6/29/94	Pioneer Rd. 7/1/94–6/30/95	Thiensville 6/29/93–6/28/94	Estabrook Pk. 6/29/93–6/28/94	Estabrook Pk. 6/30/94–6/29/95
SLOAD	2.0	3.8	2.4	4.2	13.2	6.4
RLOAD	3.7	5.9	2.5	4.2	¹ 19.8 ² 12.4	¹ 17.0 ² 8.3
SBRE	2.3 \pm 0.5	4.6 \pm 1.7	1.3 \pm 0.6	3.9 \pm 1.1	17.6 \pm 4.8	5.5 \pm 1.6

¹Using equation E₁ from table 4.

²Using equation E₂ from table 4.

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APPENDIXES 1–2

Appendix 1. PCB congeners found during laboratory analysis of water and sediments in the Milwaukee River Basin and their respective limits of detection and quantification in nanograms per liter

[From Degenhardt (1996). LOD; limit of detection, LOQ, limit of quantification; () indicates positions of chlorine substitution on biphenyl nucleus]

LOD	LOQ	Congener number and chlorine substitution position	LOD	LOQ	Congener number and chlorine substitution position
0.020	0.060	7 (2, 4)	0.035	0.11	85 (2, 2', 3, 4, 4')
.080	.27	6 (2, 3')	.030	.10	136 (2, 2', 3, 3', 6, 6')
.090	.30	5/8 (2, 3/2, 4')	.035	.11	77/110 (3, 3', 4, 4'/2, 3, 3', 4', 6)
.025	.070	19 (2, 2', 6)	.035	.11	82 (2, 2', 3, 3', 4)
.030	.090	18 (2, 2', 5)	.020	.070	151 (2, 2', 3, 5, 5', 6)
.030	.10	17 (2, 2', 4)	.025	.070	135/144 (2, 2', 3, 3', 5, 6'/2, 2', 3, 4, 5', 6)
.025	.070	24/27 (2, 3, 6/2, 3', 6)	.025	.070	149 (2, 2', 3, 4', 5', 6)
.035	.11	16/32 (2, 2', 3/2, 4', 6)	.030	.090	118 (2, 3', 4, 4', 5)
.035	.11	26 (2, 3', 5)	.030	.11	146 (2, 2', 3, 4', 5, 5')
.080	.27	28/31 (2, 4, 4'/2, 4', 5)	.030	.11	132/153 (2, 2', 3, 3', 4, 6'/2, 2', 4, 4', 5, 5')
.035	.11	33 (2', 3, 4)	.020	.070	141 (2, 2', 3, 4, 5, 5')
.055	.18	22 (2, 3, 4')	.030	.090	137/176 (2, 2', 3, 4, 4', 5/2, 2', 3, 3', 4, 6, 6')
.025	.070	45 (2, 2', 3, 6)	.035	.11	138/163 (2, 2', 3, 4, 4', 5'/2, 3, 3', 4', 5, 6)
.030	.090	46 (2, 2', 3, 6')	.040	.12	178 (2, 2', 3, 3', 5, 5', 6)
.025	.070	52 (2, 2', 5, 5)	.020	.070	182/187 (2, 2', 3, 4, 4', 5, 6'/2, 3, 4', 5, 5', 6)
.025	.070	49 (2, 2', 4, 5')	.035	.12	183 (2, 2', 3, 4, 4', 5', 6)
.035	.11	47/48 (2, 2', 4, 4'/2, 2', 4, 5)	.030	.11	185 (2, 2', 3, 4, 5, 5', 6)
.025	.070	44 (2, 2', 3, 5')	.025	.090	174 (2, 2', 3, 3', 4, 5, 6')
.035	.11	37/42 (3, 4, 4'/2, 2', 3, 4')	.030	.11	177 (2, 2', 3, 3', 4', 5, 6)
.040	.12	41/64/71 (2, 2', 3, 4/2, 3, 4', 6/2, 3', 4', 6)	.035	.11	171/202 (2, 2', 3, 3', 4, 4', 6/2, 2', 3, 3', 5, 5', 6, 6')
.030	.090	40 (2, 2', 3, 3')	.045	.14	172/197 (2, 2', 3, 3', 4, 5, 5'/2, 2', 3, 3', 4, 4', 6, 6')
.030	.090	74 (2, 4, 4', 5)	.030	.11	180 (2, 2', 3, 4, 4', 5, 5')
.040	.12	70/76 (2, 3', 4', 5/2', 3, 4, 5)	.020	.070	199 (2, 2', 3, 3', 4, 5, 6, 6')
.050	.16	66/95 (2, 3, 4, 4'/2, 2', 3, 5', 6)	.080	.27	170/190 (2, 2', 3, 3', 4, 4', 5/2, 3, 3', 4, 4', 5, 6)
.030	.090	91 (2, 2', 3', 4', 6)	.040	.14	201 (2, 2', 3, 3', 4, 5, 5', 6)
.050	.16	56/60 (2, 3, 3', 4'/2, 3, 4, 4')	.080	.27	196/203 (2, 2', 3, 3', 4, 4', 5, 6'/2, 2', 3, 4, 4', 5, 5', 6)
.050	.16	84/92 (2, 2', 3, 3', 6/2, 2', 3, 5, 5')	.080	.27	195/208 (2, 2', 3, 3', 4, 4', 5, 6/2, 2', 3, 3', 4, 5, 5', 6, 6')
.025	.070	101 (2, 2', 4, 5, 5')	.030	.11	194 (2, 2', 3, 3', 4, 4', 5, 5')
.025	.070	99 (2, 2', 4, 4', 5)	.040	.14	206 (2, 2', 3, 3', 4, 4', 5, 5', 6)
.030	.090	97 (2, 2', 3', 4, 5)	.035	.11	128 (2, 2', 3, 3', 4, 4')
.035	.11	87 (2, 2', 3, 4, 5')	.080	.27	167 (2, 3', 4, 4', 5, 5')

Appendix 2a. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Cedar Creek at Columbia Avenue (USGS station 04086525), 1994–95

[Q_c, Cedar Creek instantaneous streamflow at Cedarburg; ft³/s, cubic feet per second; μg/g, micrograms per gram; ng/L, nanograms per liter; mg/L, milligrams per liter; g/d, grams per day; %, percent; POINT, collected with point sampler; CHURN, processed from churn splitter; EWI, equal-width-increment sample; DOC, dissolved organic carbon; SOC, suspended organic carbon; FOC, fraction organic carbon; --, no data; <, less than; ΣPCB, summed congeners]

Date of sampling	Time of sampling	Q _c (ft ³ /s)	Total suspended solids				Carbon			ΣPCB				
			POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)	Chlorophyll <i>a</i> (μg/L)	SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate (μg/g)	Dissolved (ng/L)	Total (ng/L)	Load (g/day)
12/02/94	1430	39	--	3	6	1.60	0.50	9.0	16.7	1.55	0.52	0.97	2.5	0.2
1/12/95	1320	45	--	<5	<5	.87	.40	5.2	16.0	1.65	.66	.68	2.3	.3
1/24/95	1240	50	--	<5	<5	--	.50	8.4	20.0	1.94	.78	.84	2.8	.3
3/16/95	1730	102	--	4	4	7.10	.60	9.7	15.0	2.57	.64	4.7	7.2	1.8
3/22/95	1045	127	--	4	6	3.35	.70	11	17.5	2.23	.56	.67	2.9	.9
4/14/95	0715	163	--	8	8	10.7	.60	11	7.5	5.62	.70	1.4	7.0	2.8
4/27/95	1430	267	--	8	8	13.1	1.2	8.7	15.0	2.00	.25	.97	3.0	1.9
6/28/95	0700	15	--	8	8	5.41	1.1	7.9	13.8	31.91	3.99	17.1	49.0	1.8
8/08/95	1000	11	--	8	8	13.0	1.0	5.6	12.5	44.91	5.61	10.5	55.5	1.5
8/08/95	1001	11	--	10	9	11.8	1.3	5.5	13.0	31.77	3.18	11.5	43.1	1.2
8/17/95	1315	63	--	12	16	7.53	1.3	7.1	10.8	6.62	.55	2.9	9.5	1.5
Median		50	--	8	8	7.00	.70	8.4	15.0	2.57	.66	1.4	7.0	1.5

Appendix 2b. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Cedar Creek at Highland Road (USGS station 04086528), 1994-95

[Q_c, Cedar Creek instantaneous streamflow at Cedarburg; ft³/s, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter; μg/g, micrograms per gram; g/d, grams per day; DOC, dissolved organic carbon; SOC, suspended organic carbon; FOC, fraction organic carbon; POINT, collected with point sampler; CHURN, processed from churn splitter; EWI, equal-width-increment sample; %, percent; --, no data; <, less than; ΣPCB, summed PCB congeners]

Date of sampling	Time of sampling	Q _c (ft ³ /s)	Total suspended solids			Chlorophyll <i>a</i> (μg/L)	Carbon			ΣPCB				
			POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)		SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate (μg/g)	Dissolved (ng/L)	Total (ng/L)	Load (g/day)
8/11/94	0745	26	10	22	18	6.17	0.7	9.0	3.2	227.75	10.35	44.96	272.72	17.3
8/31/94	0800	19		18	18	11.6	1.2	6.6	6.7	173.83	9.66	43.74	217.56	10.1
9/21/94	1335	9.2	11	8	--	9.2	1.0	5.8	12	78.24	9.78	38.27	116.51	2.6
10/11/94	1020	19	9	8	10	3.09	.60	4.8	7.5	118.42	14.80	21.21	136.63	6.5
1/24/95	1030	50	2	<5	<5	1.43	.60	8.2	24	1.40	2.56	1.03	2.43	.3
3/16/95	1510	105	6	6	5	5.27	.80	9.4	13	15.50	2.58	4.60	20.10	5.2
3/22/95	0700	132	6	5	4	3.94	.60	11	12	18.56	3.71	1.23	19.79	6.4
4/14/95	0940	158	12	8	8	5.75	.70	11	8.8	29.91	3.74	6.07	35.98	13.9
4/14/95	0942	158	--	8	8	4.97	--	--	8.8	28.16	3.52	5.06	33.22	12.8
4/27/95	1220	253	14	12	10	11.4	.70	9.0	5.8	20.70	1.73	2.77	23.47	14.5
6/27/95	1530	14	20	8	10	7.99	1.2	8.6	15	118.48	14.81	48.81	167.29	5.7
8/8/95	1230	12	16	15	16	32.8	2.0	5.9	13	148.18	9.88	45.51	193.69	5.7
8/17/95	0845	63	14	18	18	9.50	1.8	5.8	10	107.52	5.97	23.35	130.87	20.2
Median		50	11	8	10	6.17	.70	8.6	10	78.24	5.97	21.21	116.51	6.5

Appendix 2c. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Highway T (USGS station 04086416), 1994-95

[Q_p, Milwaukee River instantaneous streamflow at Pioneer Road; ft³/s, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter; μg/g, micrograms per gram; g/d, grams per day; DOC, dissolved organic carbon; SOC, suspended organic carbon; FOC, fraction organic carbon; POINT, collected with point sampler; CHURN, processed from churn splitter; EWI, equal-width-interval sample; %, percent; --, no data; ΣPCB, summed PCB congeners]

Date of sampling	Time of sampling	Q _p (ft ³ /s)	Total suspended solids			Chlorophyll <i>a</i> (μg/L)	Carbon			ΣPCB				
			POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)		SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate (μg/g)	Dissolved (ng/L)	Total (ng/L)	Load (g/d)
4/13/95	1530	772	--	14	13	16.9	1.0	7.7	7.1	0.04	0.00	0.09	0.13	0.2
4/27/95	1700	879	--	20	18	25.3	1.5	9.5	7.5	.26	.01	.15	.41	.9
6/27/95	1140	57	--	32	26	165	3.7	9.2	11.6	1.94	.06	1.50	3.44	.5
8/8/95	1500	120	--	52	45	171	7.3	6.6	14.0	1.55	.03	1.25	2.80	.8
8/17/95	0745	560	--	60	64	85.0	4.0	9.0	6.7	1.66	.03	1.21	2.87	3.9
Median		560	--	32	26	85.0	3.7	9.0	7.5	1.55	.03	1.21	2.80	.8

Appendix 2d. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Pioneer Road (USGS station 04086600), 1994–95

[Q_p , Milwaukee River instantaneous streamflow at Pioneer Road; ft^3/s , cubic feet per second; ng/L , nanograms per liter; mg/L , milligrams per liter; $\mu\text{g/g}$, micrograms per gram; g/d , grams per day; Q_c/Q_p , Cedar Creek daily mean streamflow/Milwaukee River daily mean streamflow (at Pioneer Road); n, sample collected at noon; DOC, dissolved organic carbon; SOC, suspended organic carbon; FOC, fraction organic carbon; POINT, collected with point sampler; CHURN, processed from churn splitter; EWI, equal-width-increment sample; %, percent; --, no data; ΣPCB , summed PCB congeners]

Date of sampling	Time of sampling	Q_p (ft^3/s)	Total suspended solids				Carbon				ΣPCB				
			Q_c/Q_p	POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)	Chlorophyll <i>a</i> ($\mu\text{g/L}$)	SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate ($\mu\text{g/g}$)	Dissolved (ng/L)	Total (ng/L)	Load (g/d)
6/30/93	1315	285	0.19	20 ⁿ	22	20	21.6	1.1	13	5.0	8.97	0.41	6.06	15.03	10.5
7/11/93	1345	1,870	.11	55 ⁿ	62	--	10.3	4.6	14	7.4	17.10	.28	6.05	23.15	105.9
8/3/93	1000	300	.12	--	14	14	3.60	.5	12	3.6	3.48	.25	2.93	6.41	4.7
8/24/93	1515	250	.13	15 ⁿ	10	8	8.60	.6	8.9	6.0	3.89	.39	3.83	7.72	4.7
9/14/93	1520	646	.26	51	44	40	17.7	--	--	--	53.25	1.21	6.66	59.91	94.7
9/28/93	1415	614	.18	16	11	18	3.60	.4	14	3.6	5.13	.47	3.37	8.50	12.8
10/20/93	0915	290	.15	14	13	22	45.0	.8	9.2	6.2	2.33	.18	1.69	4.02	2.9
11/16/93	0745	322	.19	6	5	7	29.0	.8	7.8	16.0	3.23	.65	2.63	5.87	4.6
12/14/93	1445	265	.18	32	4	3	9.85	.3	8.1	7.5	1.43	.36	1.71	3.13	2.0
2/16/94	0745	110	.25	4	3	2	3.38	.5	4.6	16.7	1.17	.39	1.14	2.31	.6
3/10/94	1200	1,300	.27	--	32	31	7.27	2.6	9.7	8.1	16.70	.52	1.41	18.11	57.6
3/16/94	900	1,100	.26	--	9	6	2.47	.4	8.4	4.4	2.44	.27	1.97	4.41	11.9
5/17/94	1600	250	.16	17	8	8	19.5	1.1	9.2	13.8	3.47	.43	2.16	5.63	3.4
6/22/94	1400	67	.28	42	28	32	24.4	1.8	7.6	6.4	12.31	.44	3.86	16.17	2.6
7/7/94	1430	224	.22	71	59	60	105	3.9	6.8	6.6	32.76	.56	5.83	38.59	21.1
7/8/94	1515	410	.45	77	59	59	83	2.6	8.8	4.4	76.30	1.29	17.98	94.28	94.6
8/11/94	1050	169	.18	20	19	29	41.2	1.0	8.6	5.3	7.58	.40	4.15	11.73	4.8
8/31/94	0945	150	.13	26	26	24	55.4	1.9	6.3	7.3	7.33	.28	4.97	12.30	4.5
9/21/94	1150	112	.13	14	16	8	25.1	.8	6.0	5.0	2.90	.18	1.61	4.51	1.2
10/11/94	1150	99	.10	10	5	5	5.49	.3	6.0	6.0	1.16	.23	1.93	3.09	.7
1/19/95	1445	190	.19	30	10	8	8.89	1.3	10	13.0	1.12	.11	.50	1.62	.8
3/17/95	0740	774	.12	8	18	17	15.5	1.2	9.0	6.7	3.86	.21	.88	4.73	8.9
3/21/95	1430	626	.24	6	6	6	10.1	.6	8.8	10.0	1.82	.30	.84	2.66	4.1
4/13/95	1200	772	.26	14	12	12	17.9	1.0	9.0	8.3	4.73	.39	1.22	5.97	11.3
4/28/95	1420	945	.31	18	19	20	24.7	1.3	10	6.8	8.62	.72	2.25	10.87	25.1
8/16/95	1615	392	.08	69	79	75	116	7.3	8.2	9.2	20.79	.26	2.32	23.11	27.3
8/29/95	1730	1,320	.17	72	77	71	34.4	5.2	8.4	6.8	--	--	--	--	--
Median		300	.18	19	16	18	17.9	1.1	8.8	6.7	4.31	.39	2.29	7.06	4.8

Appendix 2e. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Thiensville (USGS station 04086710), 1994-95

[ft³/s, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter; µg/g, micrograms per gram; g/d, gram per day; Q_p, estimated discharge at Thiensville; n, sample collected at noon; DOC, dissolved organic carbon; SOC, suspended organic carbon; FOC, fraction organic carbon; POINT, collected with point sampler; CHURN, processed from churn splitter; EWI, equal-width-increment sample; %, percent; --, no data; <, less than; ΣPCB, summed PCB congeners]

Date of sampling	Time of sampling	Q _p (ft ³ /s)	Total suspended solids			Chlorophyll <i>a</i> (µg/L)	Carbon			ΣPCB				
			POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)		SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate (µg/g)	Dissolved (ng/L)	Total (ng/L)	Load (g/d)
6/29/93	1430	342	--	23	24	43.0	1.8	13	7.8	11.38	0.49	2.57	13.95	11.7
7/11/93	1140	1834	--	63	--	12.8	4.0	14	6.3	23.88	.38	22.63	46.51	208.6
8/3/93	1330	298	17 ⁿ	23	22	9.6	.8	12	3.5	8.94	.39	2.37	11.31	8.2
8/25/93	0745	249	20 ⁿ	16	20	25.3	.7	8.9	4.4	6.94	.43	3.38	10.32	6.3
9/14/93	1300	432	--	22	24	21.1	--	--	--	11.13	.51	1.91	13.04	13.8
9/28/93	1215	652	19	18	16	4.00	.4	13	2.2	8.78	.49	3.73	12.50	19.9
10/20/93	1140	301	22/13	12	14	14.7	.5	8.8	4.2	5.07	.42	3.80	8.86	6.5
11/15/93	1000	331	6	11	9	29.2	.8	7.2	7.3	3.93	.36	2.13	6.06	4.9
12/14/93	1250	291	86	3	3	6.65	.2	7.5	6.7	1.01	.34	2.66	3.67	2.6
2/15/94	1500	760	--	<2	2	2.23	.4	4.4	20.0	1.07	.53	2.58	3.64	6.8
3/10/94	1500	2605	--	20	19	5.34	--	--	--	7.25	.36	1.12	8.37	53.3
3/16/94	1200	1926	--	10	9	2.96	.5	7.6	5.0	1.94	.19	1.47	3.41	16.0
5/17/94	1400	257	25	24	24	59.2	2.2	9.6	9.2	10.57	.44	2.57	13.14	8.3
6/22/94	1145	74	--	42	45	108	3.8	8.3	9.0	18.03	.43	2.84	20.87	3.8
7/7/94	1245	232	76	59	62	205	4.9	7.2	8.3	16.38	.28	2.88	19.26	10.9
7/8/94	1315	452	68	60	61	75.1	2.3	8.0	3.8	12.42	.21	3.61	16.06	17.8
Median		336	20	21	19	17.9	.8	8.6	6.5	8.86	.41	2.62	11.91	9.6

Appendix 2f. Water column transport data for summed PCB congeners and related physical and water-quality characteristics at Milwaukee River at Estabrook Park (USGS station 04087000), 1994–95

[ft³/s, cubic feet per second; ng/L, nanograms per liter; mg/L, milligrams per liter; µg/g, micrograms per gram; g/d, grams per day; Q_E, Milwaukee daily mean streamflow at Estabrook; Q_L, Lincoln Creek instantaneous streamflow; TOC, total organic carbon; DOC, dissolved organic carbon; SOC, suspended organic carbon; FOC, fraction organic carbon; POINT, collected with point sampler; CHURN, processed from churn splitter; EW, equal-width-increment sample; %, percent; --, no data; ΣPCB, summed PCB congeners]

Date of sampling	Time of sampling	Q _E (ft ³ /s)	Total suspended solids				Chlorophyll a (µg/L)	Carbon			ΣPCB				
			(Q _L) (ft ³ /s)	POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)		SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate (µg/g)	Dissolved (ng/L)	Total (ng/L)	Load (g/day)
6/29/93	0930	400	3.8	79/4 ¹	26	24	64.0	2.1	13	8.1	20.77	0.80	11.36	32.12	31.4
7/11/93	0930	1750	6.3	72 ⁿ	70	--	27.0	3.4	13	4.9	37.67	.54	13.98	51.65	221.1
8/4/93	0900	305	4.1	35	21	21	20.9	1.2	12	5.7	16.38	.78	11.65	28.03	20.9
8/25/93	1100	248	3.5	19	17	18	53.2	1.1	8.3	6.5	16.74	.98	12.1	29.84	17.5
9/14/93	0945	511	95	76/37 ¹	33	32	25.5	--	--	--	101.32	3.07	11.36	112.68	140.9
9/28/93	0915	715	6.5	17	21	20	4.60	.5	12	2.4	12.21	.58	3.34	15.54	27.2
10/20/93	1400	316	3.4	46	59	61	36.2	1.5	8.9	2.5	22.65	.38	7.69	30.34	23.5
11/15/93	1400	360	5.0	--	17	20	19.7	1.0	7.2	5.9	12.91	.76	5.37	18.27	16.1
12/14/93	1010	321	3.1	7	8	6	6.39	.2	7.6	2.5	3.14	.39	2.73	5.87	4.6
2/15/94	1045	180	4.8	8	3	4	2.12	.3	4.6	10.0	1.34	.45	1.23	2.57	1.1
3/11/94	1000	1,400	5.2	--	43	45	6.36	--	--	--	49.10	1.14	8.32	57.42	196.6
3/16/94	1415	1,300	7.2	61	44	49	7.17	.8	7.9	1.8	30.10	.68	7.18	37.28	118.5
5/17/94	0900	268	3.6	28 ⁿ	30	30	83.6	1.2	9.3	4.0	29.88	1.00	12.89	42.77	28.0
5/17/94	1045	268	3.6	28 ⁿ	28	29	86.8	2.2	9.4	7.9	23.37	.83	13.87	37.24	24.4
6/22/94	0915	78	3.2	33	32	35	97.8	2.1	8.7	6.6	22.85	.71	11.49	34.34	6.6
7/7/94	0945	268	4.8	64	49	48	275	1.3	7.2	2.7	24.36	.50	5.68	30.04	19.7
7/8/94	1045	1,090	14	86	88	83	213	5.3	6.8	6.0	28.77	.33	8.01	36.77	98.1
8/11/94	1330	219	6.8	33	40	39	115	1.0	9.0	2.5	17.93	.45	8.09	26.02	13.9
8/31/94	1215	173	4.8	360	28	30	82.4	2.2	6.6	7.9	18.99	.68	14.89	33.88	14.3
9/21/94	0915	85	2.4	18	17	18	44.2	1.4	6.2	8.2	19.25	1.13	14.80	34.05	7.1
10/11/94	1445	124	3.4	13	14	13	25.8	1.0	6.1	7.1	9.64	.69	7.17	16.80	5.1
10/12/94	1000	530	2.8	450	436	576	90.8	7.8	6.6	1.8	160.43	.37	8.37	168.80	218.9
10/12/94	1315	191	3.2	68	99	100	43.3	2.3	6.4	2.3	46.94	.47	8.91	55.85	26.1
1/19/95	0930	220	4.0	55	13	12	6.03	1.1	7.2	8.5	4.88	.38	2.95	7.83	4.2
3/17/95	1045	858	3.4	29	28	22	14.6	2.0	8.8	7.1	10.25	.37	2.94	13.19	27.7
3/17/95	1050	858	3.4	44	28	24	13.9	1.6	9.1	5.7	13.75	.49	2.56	16.31	34.2
3/21/95	0845	647	6.1	14	21	18	10.8	.8	9.4	3.8	8.01	.38	1.83	9.84	15.6
4/13/95	0830	849	11	25	38	47	10.8	1.3	8.3	3.4	11.88	.31	1.58	13.46	27.9
4/28/95	0930	1,260	11	37	48	44	25.7	2.1	8.8	4.4	17.77	.37	4.45	22.22	68.5
8/16/95	1330	557	30	106	42	50	120	4.0	5.6	9.5	31.46	.75	7.36	38.82	52.9
8/29/95	1230	1,180	3.0	99	67	65	40.0	3.8	10	5.7	22.66	.34	5.76	28.42	82.0
Median		360	4.1	35	30	30	27.0	1.4	8.3	5.7	19.25	.54	7.69	30.04	26.1

¹Rapidly changing discharge, sample collected before and after PCB sample.