

Distribution and Transport of Polychlorinated Biphenyls and Associated Particulates in the Hayton Millpond, South Branch Manitowoc River, 1993–95

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

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 99–4101

Prepared in cooperation with the
WISCONSIN DEPARTMENT OF NATURAL RESOURCES

Middleton, Wisconsin
1999



U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

For additional information write to:

District Chief
U.S. Geological Survey
8505 Research Way
Middleton, WI 53562-3586

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225-0286

CONTENTS

Abstract	1
Introduction	1
Purpose and scope	2
Environmental setting and hydrology	2
Site descriptions	4
Sampling and analytical methods	4
Distribution and transport of PCB's and associated particulates	5
PCB congeners	5
Total suspended solids	9
Concentrations and loads of transported Σ PCB's in the Hayton Millpond system.....	9
Summary	14
References cited	15
Appendixes 1–2:	
1a. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics at South Branch Manitowoc River at Hayton Millpond outlet (USGS station 04085395), 1993–95	18
1b. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics at Pine Creek at Quarry Road (USGS station 040853936), 1995	19
1c. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics at Pine Creek at Charlesburg Road (USGS station 040853926), 1995	19
2. PCB congeners found during laboratory analysis of water and sediments in the Hayton Millpond Basin and their respective limits of detection and quantification in nanograms per liter.....	20

FIGURES

1. Map showing location of USGS sampling sites at Hayton Millpond, Quarry Road, and Charlesburg Road, and location of Wisconsin Department of Natural Resources sites (A, B) on Pine Creek, Jordan Creek, and Hayton Millpond	3
2a–c. Graphs showing:	
a. PCB congener distributions in the dissolved phase at Hayton Millpond and two sites on Pine Creek, east-central Wisconsin	6
b. PCB congener distributions in the particulate phase at Hayton Millpond and two sites on Pine Creek, east-central Wisconsin	7
c. PCB congener distributions in Hayton Millpond sediment cores, east-central Wisconsin, and congener composition of Aroclor 1254.....	8
3. Two-phase distribution coefficients for PCB congeners at the Hayton Millpond outlet, east-central Wisconsin	9
4. Correlation of total suspended solids resulting from two sampling methods used at the Hayton Millpond outlet, east-central Wisconsin	10
5. Discharge at Hayton Millpond outlet, east-central Wisconsin, and associated concentrations of total suspended solids, chlorophyll <i>a</i> , and total PCB.....	11
6. Cumulative PCB and suspended-solids loads at the Hayton Millpond outlet, east-central Wisconsin.....	12
7. PCB concentrations, estimated loading, and discharge on three sample days, Pine Creek and Hayton Millpond outlet, east-central Wisconsin, 1995.....	14

TABLES

1. Congener-summary PCB concentrations in bottom sediments from the Pine Creek and Hayton Millpond, east-central Wisconsin.....	2
2. Regression relations for total PCB concentration congener summation (Σ PCB) and selected congeners.....	12
3. Computed PCB loads at the Hayton Millpond outlet, east-central Wisconsin, resulting from three computational approaches.....	13

CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

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
millimeter	0.03937	inch
centimeter	.3937	inch
meter	3.281	foot
kilogram (kg)	2.205	pound
kilogram (kg)	.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:
$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32.$$

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), nanograms per liter (ng/L), or micrograms per gram (µg/g). 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. Micrograms per gram are metric units expressing the concentration of chemical constituents in solution as mass (micrograms) of constituent per unit mass (gram) of dry sample. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

ACKNOWLEDGMENTS

Technical Support

David E. Housner, Hydrologic Technician, U.S. Geological Survey, Middleton, Wis.
Halward (Nick) L. Hanson, Hydrologic Technician, U.S. Geological Survey, Middleton, Wis.
Judy A. Wierl, Hydraulic Engineer, U.S. Geological Survey, Middleton, Wis.
William R. Selbig, (Student) Hydrology, U.S. Geological Survey, Middleton, Wis.
Peter E. Hughes, Chief Supervisory Hydrologist, U.S. Geological Survey, Middleton, Wis.

Technical Reviewers

Robert P. Eganhouse, Research Chemist, U.S. Geological Survey, Reston, Va.
Dale J. Patterson (Deceased), Water Resources Engineer, Wisconsin Department of Natural Resources, Madison, Wis.
Mark L. Velleux, Water Resources Engineer, Wisconsin Department of Natural Resources, Madison, Wis.

Editorial and Graphics

Michael Eberle, Technical Publications Editor, U.S. Geological Survey, Columbus, Ohio
Janice A. Fuller, Editorial Assistant, U.S. Geological Survey, Middleton, Wis.
Susan Z. Jones, Editorial Assistant, U.S. Geological Survey, Middleton, Wis.
Gail A. Moede, Writer/Editor Student Trainee, U.S. Geological Survey, Middleton, Wis.
Aaron T. Konkol, Cartographic Assistant, U.S. Geological Survey, Middleton, Wis.

Distribution and Transport of Polychlorinated Biphenyls and Associated Particulates in the Hayton Millpond, South Branch Manitowoc River, Wisconsin, 1993–95

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

Abstract

The distribution and transport of polychlorinated biphenyl (PCB) congeners was determined at two sites on Pine Creek and at the Hayton Millpond on the South Branch of the Manitowoc River in Wisconsin during 1993–95. PCB congener compositions were analyzed in the operationally defined dissolved phase, suspended particulate phase, and surficial bed sediments (0–2 centimeters depth) several times throughout the sampling period. The relative abundances of PCB congeners in the suspended particles and in surficial bed sediments were generally similar to each other and to a known Aroclor mixture (1254). PCB congener composites in the operationally defined dissolved phase were higher in the less chlorinated congeners in keeping with their lower hydrophobicity and higher predicted solubility relative to the more chlorinated congeners. Suspended particle-associated PCB concentrations exhibited two patterns: (1) a cyclical variation in spring and summer associated with algal growth, and (2) episodic increases associated with resuspension of bed sediments during storms. Computed total suspended-solids (TSS) load at the millpond outlet was as high as 920 tons over a 3-month period (June 30–Sept. 30, 1993). Annual TSS loads for the following two years were lower, 610 and 500 tons, respectively. Total PCB concentrations in the water column varied at the millpond outlet, ranging from 34 to 302 nanograms per liter, whereas concentrations upstream on Pine Creek were as high as 563 nanograms per liter. In general, 70 percent of PCB's in the water column were associated with suspended particles. The total congener-summation PCB (Σ PCB) concentration regression equation incorporated the universal soil loss coefficient to represent erosion of assumedly

PCB-free sediment from fields upstream from the millpond. The Σ PCB load based on the regression relation was 3.4 kilograms during the 3-month high-flow interval (June 30–Sept. 30, 1993). Subsequent annual Σ PCB loads for the next two water years were 3.5 and 2.3 kilograms, respectively.

INTRODUCTION

Polychlorinated biphenyls (PCB's) were extensively used in the United States from 1929 until their manufacture was banned in 1977. PCB's are a class of compounds consisting of 209 individual congeners, which represent the set of chemical structures that can be formed by attaching from one to ten chlorine atoms to the available bonding sites on a biphenyl structure.

Various congener mixtures were formulated to provide optimal chemical and physical properties for specific uses and were marketed under names that included Aroclor and Askerel. It has been estimated that more than 1 million metric tons of PCB's have been produced worldwide (Schwarzenbach and others, 1993) for a wide variety of uses including lubricating and cutting oils, capacitor dielectrics, carbonless copy paper, transformer coolants, plasticizers, adhesives, and resins (Cairns and others, 1986). These PCB's may enter the environment from production, storage, and disposal sites and are a cause of concern because of deleterious effects associated with bioaccumulation (Yamashita and others, 1993; Koslowski and others, 1994; Rogers and Swain, 1983).

Research into contamination of sediment, water, and biota in the Lake Michigan basin has identified numerous source areas of PCB's. Rivers containing sediments that are contaminated with PCB's include: the Fox (House, 1995; Velleux and others, 1995; Steuer and others, 1995), the Sheboygan (David and others, 1994), and the Milwaukee (Steuer and others, 1999) in Wisconsin; the Grand Calumet in Indiana (Marti and Armstrong, 1990); and the Kalamazoo, Escanaba, and Manistique in Michigan (Marti and Armstrong, 1990).

Waukegan Harbor in Illinois has also been identified as being a source area of PCB contamination to Lake Michigan (Swackhamer and Armstrong, 1988). Atmospheric deposition of PCB's in the Lake Michigan basin has been an area of active research for many years (Sweet and others, 1993; Eisenreich and others, 1981).

Significant PCB contamination has been identified in the Hayton Millpond (hereafter referred to as the millpond), an impoundment on the South Branch of the Manitowoc River near Chilton, Wis., and in Pine Creek, a tributary to the millpond. The contaminated areas are upstream from the Killsnake State Wildlife Area in Calumet County, Wis., near the towns of Chilton, Hayton, and New Holstein (fig. 1). The millpond outlet flows to Lake Michigan by way of the Manitowoc River system.

Between 1987 and 1992, fish samples collected by Wisconsin Department of Natural Resources (WDNR) indicated elevated PCB concentrations in Hayton-area fish. The mean wet weight concentration of 16 $\mu\text{g/g}$ (range, 0.5 to 77 $\mu\text{g/g}$) was above the 1.9 $\mu\text{g/g}$ Division of Health level at which no fish should be eaten. The resulting "Do Not Eat" warning has been issued only one other time in Wisconsin. The lifetime additional cancer risk associated with Hayton-area fish exceeded 1 in 100 for all species collected; it was 1 in 35 for northern pike. Fish collected from the Manitowoc River upstream from the contaminated millpond area were virtually uncontaminated with respect to PCB; thus the probable PCB source was thought to be somewhere on Pine Creek (Wisconsin Department of Natural Resources, 1991). Despite the "Do Not Eat" warning, and the evidence for probable PCB source locations, the South Branch of the Manitowoc River, Millpond, and Pine Creek remain popular fishing spots.

During 1993–95, WDNR collected bottom sediments from Pine Creek and the millpond and found that the congener-summation PCB concentrations (ΣPCB)¹ averaged 45 $\mu\text{g/g}$ and ranged from <0.05 to >2,000 $\mu\text{g/g}$. The August 1995 sampling identified an area in northeast New Holstein as the probable source of PCB's to the Hayton Millpond. ΣPCB concentrations in sediment cores obtained upstream from the three dams

¹Specifically, ΣPCB refers to the sum of all PCB congeners detected in a given phase (dissolved, suspended particulate, or bed sediment).

in Chilton were all less than the minimum detection limit (0.05 $\mu\text{g/g}$).

Table 1. Congener-summary PCB concentrations in bottom sediments from the Pine Creek and Hayton Millpond, east-central Wisconsin
[Data collected by Wisconsin Department of Natural Resources. $\mu\text{g/g}$, micrograms per liter; kg, kilogram]

Site	PCB concentration range ($\mu\text{g/g}$)	PCB mass (kg)
Upstream from Jordan to Pine Creek confluence (A)	<.05–1,900	376
Confluence to Limekiln Road (B)	4.2–19	136
Limekiln Road to millpond entrance	0.5–15	11
Millpond	0.6–7.3	58

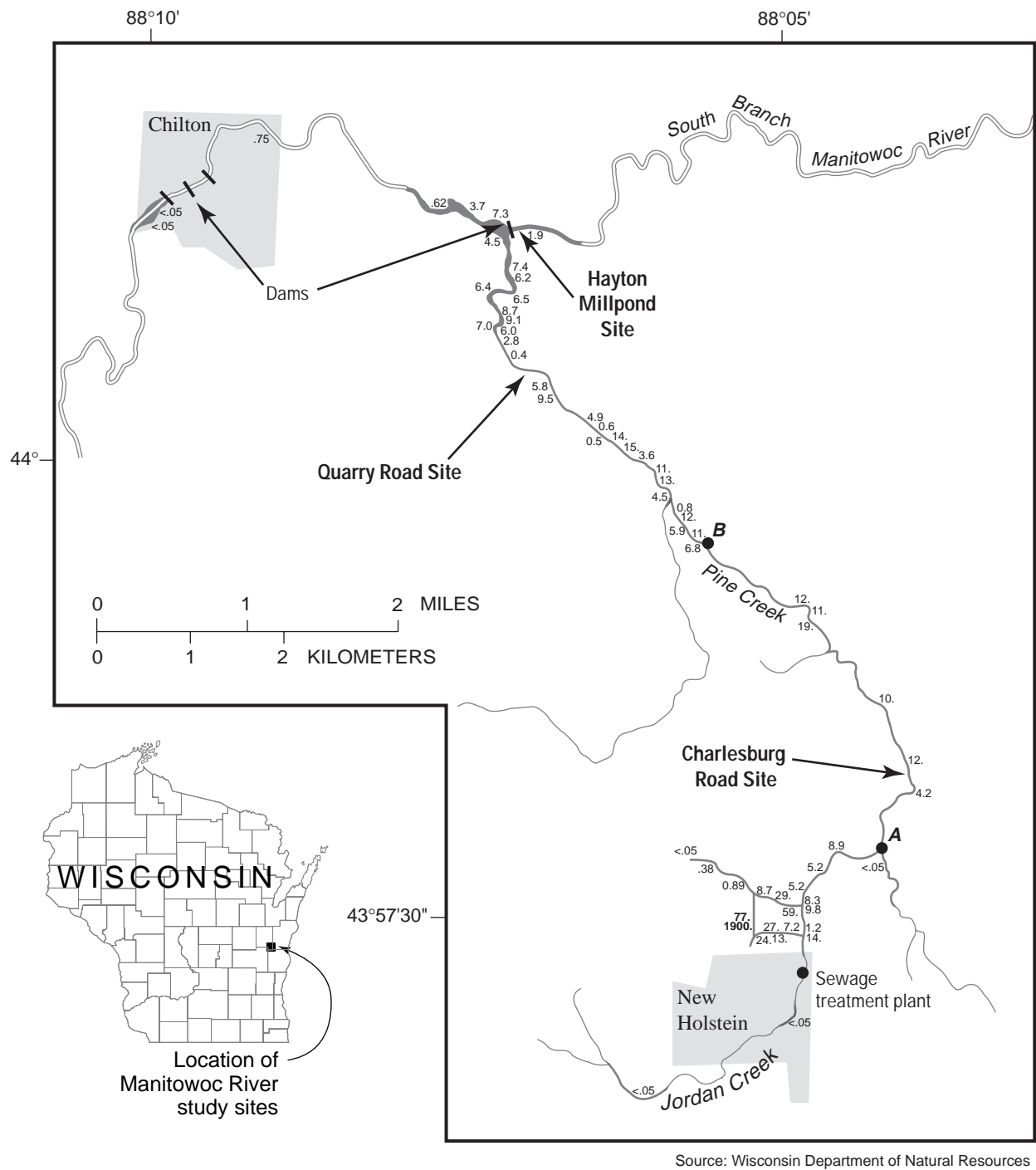
In 1993, the U.S. Geological Survey (USGS), in cooperation with the Wisconsin Department of Natural Resources (WDNR), began the investigation to further understand the distribution and transport of polychlorinated biphenyls and associated particles in Hayton Millpond. Results from this study will be used to assist WDNR in Hayton Millpond and Pine Creek remediation efforts.

Purpose and Scope

The purpose of this report is to present results of the USGS and WDNR cooperative investigation into the occurrence and transport of PCB's in the South Branch Manitowoc River near the Hayton Millpond. Congener profiles are compared for the operationally defined dissolved phases, suspended particulate phases, and surficial bed sediments. Congener-summation total PCB loads and suspended-solids loads presented in the report are based on data from the Pine Creek and Hayton Millpond sites, whereas a ΣPCB concentration regression relation, based on total suspended solids and rainfall data was used to compute the reported ΣPCB load for the millpond outlet.

Environmental Setting and Hydrology

The Manitowoc River Basin encompasses approximately 526 mi^2 and comprises five major watersheds, one of which is the 192 mi^2 South Branch Manitowoc River Watershed. The millpond outlet is 2 mi down-



Source: Wisconsin Department of Natural Resources

Figure 1. Location of USGS sampling sites at Hayton Millpond, Quarry Road, and Charlesburg Road, and location of Wisconsin Department of Natural Resources sites (A, B) on Pine Creek, Jordan Creek, and Hayton Millpond. (Concentrations of total PCB's in surficial bed sediments in parts per million (Aroclor 1254; dry weight basis) are noted at sampled locations.)

stream from Chilton, Wis. (fig. 1), and is part of the South Branch of Manitowoc River Basin. The 109-mi² watershed above the millpond outlet produces a mean annual discharge (3-year record) of 24 ft³/s. Annual mean discharge during the study period was 31 and 17 ft³/s during water years 1994 and 1995, respectively.

The New Holstein sewage treatment plant discharges to Jordan Creek, which joins Pine Creek just upstream from Charleston Road. Pine Creek discharges to the South Branch of the Manitowoc River at the millpond (fig. 1).

Agriculture is the predominant land use and 5 percent of this agricultural land is considered to have a high soil erosion potential. The South Branch of the Manitowoc River maintains a moderate stream gradient through most of Calumet County. The millpond is affected by sedimentation, algal blooms, and dense aquatic plant growth (Wisconsin Department of Natural Resources, 1991).

Site Descriptions

The three sites sampled during this investigation were the following (downstream to upstream):

1. South Branch of the Manitowoc River at the Hayton Millpond Outlet (USGS station 04085395): Water samples were collected approximately 100 ft downstream from the dam (fig. 1). An automated sampler, activated by a stage sensor, was installed at this site. Continuous temperature monitoring began in July 1994 and continued throughout the study period (June 30, 1993 to Sept. 11, 1995). Discharge has been measured continuously since 1993. Three seasonal bed-sediment samples (November 1993, February 1994, and May 1994) were collected from cross-sectional transects just upstream from the millpond dam (Fitzgerald and Steuer, 1997).
2. Pine Creek at Quarry Road (USGS station 040853936): From April 1995 to June 1995, three water samples were collected from this 31-mi², noninstrumented site located 1.8 mi upstream from the millpond site at the Quarry Road bridge. Pine Creek joins the South Branch of the Manitowoc River at the millpond (fig. 1).

3. Pine Creek at Charlesburg Road (USGS station 040853926): From April 1995 to June 1995, water samples were collected from this 5-mi² noninstrumented Charlesburg Road bridge site (fig. 1).

SAMPLING AND ANALYTICAL METHODS

General methods of sample collection and field preparation for subsequent PCB determinations are discussed in detail in Fitzgerald and Steuer (1997) and in House and others (1993). For this investigation, 80-L samples were collected by dipping 20-L stainless steel canisters through the water column at four locations across each creek or river. Specific water collection and processing details are provided in Steuer and others (1999).

Samples for ancillary water-quality characteristics such as sediment organic carbon (SOC), 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 for PCB sampling. Subsamples for five of the ancillary characteristics (TSS, VSS, chlorophyll *a*, SOC, DOC) were composited in a churn splitter to obtain the final representative sample (Ward and Harr, 1990). These samples are referred to as CHURN samples. Subsequently, samples to be analyzed for SOC content were processed through a stainless steel filter apparatus with a 0.45- μ m-pore-size filter. Chlorophyll *a* samples were processed through a 5.0- μ m-pore-size mixed acetate and nitrate cellulose filter.

For comparison with the TSS sample resulting from the 80-L sample approach (CHURN), 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 submerged at four locations along a stream cross section either manually (wadable sites) or in a D-77 USGS sampler (nonwadable sites). Samples from the cross section—referred to as “equal-width-increment” (EWI) samples—were composited in the sample bottles themselves; no churn was used.

The automated point sampler (POINT) at the millpond collected samples daily at 1200 hours and more often during storm events. When the millpond was frozen, sampling was reduced to once every 2 or 3 days. Additionally, the point samplers were triggered at the time of EWI sample collection to provide pairs of sam-

ples for comparison of TSS concentrations. Ideally, POINT TSS concentrations would be comparable to those in EWI samples, indicating that point samples capture a representative sample of the streamwater.

Three core samples of surficial bed sediment were collected in November 1993, February 1994, and May 1994 along one transect in the millpond impoundment. All samples were collected using either an Ekman dredge or gravity corer. Field and analytical methods for ancillary characteristics and bed sediments are described in detail in Fitzgerald and Steuer (1997).

Congener-specific PCB, TSS, and ancillary-characteristic samples were collected from June 1993 through September 1995; on 16 of the 22 PCB sample days, discharge was greater than $14 \text{ ft}^3/\text{s}$, the 50-percent exceedance discharge (Holmstrom and others, 1995). This emphasis on high-flow conditions optimized the project data set for load estimation given that increased sediment and PCB contaminant loads are expected during high flow (Dolan and others, 1981).

The USGS software program CLOAD was used to estimate suspended-solids and ΣPCB 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).

All PCB samples were analyzed on a congener-specific basis by use of capillary column gas chromatography with electron capture detection (HP 5890-II gas chromatograph with a 60-m DB5 column) at the State Laboratory of Hygiene (SLOH), Madison, Wis. (Degenhardt, 1996). This method can determine up to 85 congeners (with 26 co-elutions). Details on quantitation, generation of response factors, surrogate standards, matrix spikes, retention time reference peaks, and internal standards for PCB analyses are contained in Degenhardt (1996). The average recovery of these surrogates and matrix spikes for all samples analyzed during the period coincident with the analysis of the samples from the present study can be found in Fitzgerald and Steuer (1997). Concentrations of ΣPCB were not corrected for percent recovery of either the surrogates or matrix spikes. Detection limits, limits of quantification, IUPAC numbers, and congener descriptions used in sample analysis along with quality-control and field-equipment-blank results are reported in appendix 1 in Steuer and others (1999).

DISTRIBUTION AND TRANSPORT OF PCB'S AND ASSOCIATED PARTICULATES

PCB Congeners

PCB congeners in the operationally defined dissolved and particulate phases of water column and sediment core samples collected at Charlesburg Road, Quarry Road, and the millpond are presented as a percentage of the sum of all detected congeners (fig. 2). Appendix 2 contains a complete listing of the plotted congeners. All samples at a given site have been averaged together. The congener distributions appear to be similar between the three sites. In addition, the PCB congener pattern of suspended particles appears to be nearly identical to the millpond surficial bed sediment (compare figs. 2b and 2c); this similarity indicates interaction between the two media. There is also a similarity between these PCB congener suites and Aroclor 1254 (fig. 2c). The particulate-phase PCB compositions are substantially different from those of the dissolved phase at all sites (fig. 2).

PCB concentrations in the water column varied considerably. The total PCB concentration at the millpond outlet ranged from 34 to 302 ng/L; ΣPCB on suspended particles ranged from 0.3 to 10.7 $\mu\text{g/g}$ (appendix 1). This is contrasted to the three seasonal surficial bed-sediment samples from the millpond (0–2 cm) with the narrow range of 2.6 to 3.7 $\mu\text{g/g}$. Seventy-four percent (plus or minus 11 percent) of total water-column PCB's were associated with suspended particles (appendix 1a).

The two-phase distribution computation is described in Steuer and others (1999). The sediment/water distribution coefficients (K_d) in figure 3 indicates that the more chlorinated congeners have a much greater affinity for particulate matter than the less chlorinated congeners do. For example, distribution coefficients differ by more than an order of magnitude in some cases, such as between IUPAC congener 18 (a less chlorinated congener) and congener 180 (a more chlorinated congener). These differences in congener-partitioning characteristics explain some of the differences in the dissolved and particle-associated congener distributions illustrated in figure 2.

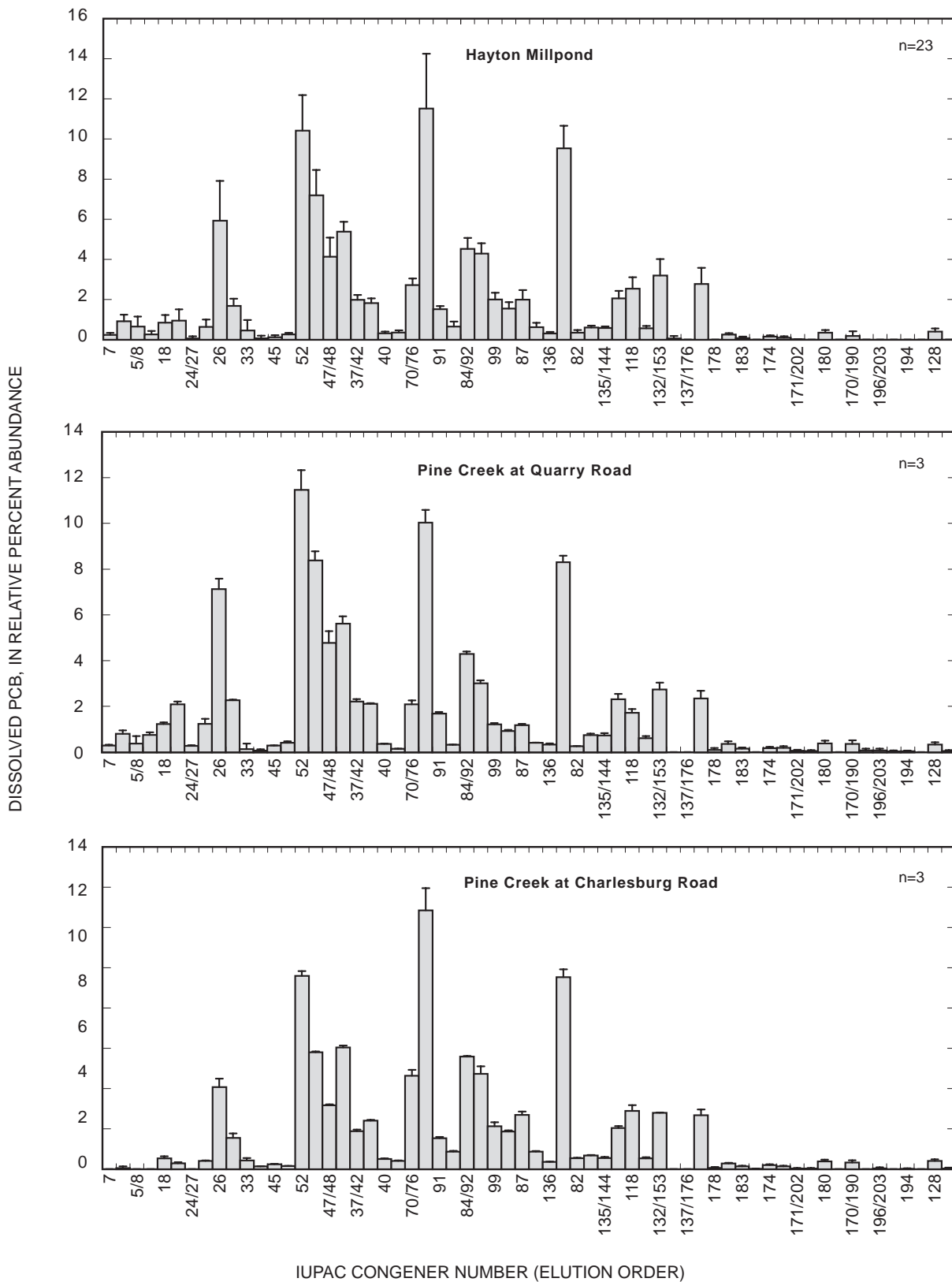


Figure 2a. PCB congener distributions in the dissolved phase at Hayton Millpond and two sites on Pine Creek, east-central Wisconsin. (Error bars represent 1 standard deviation.)

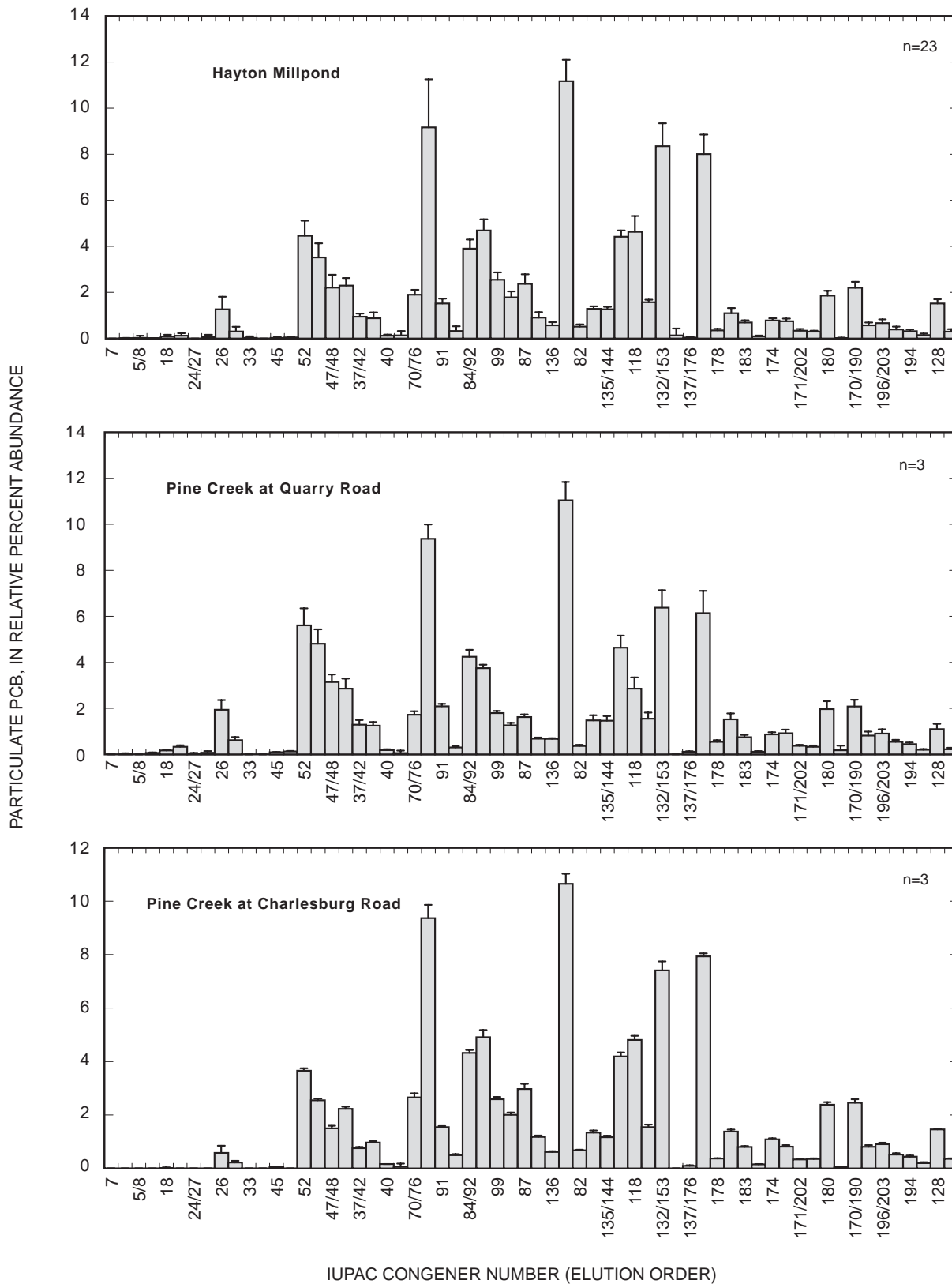


Figure 2b. PCB congener distributions in the particulate phase at Hayton Millpond and two sites on Pine Creek, east-central Wisconsin. (Error bars represent 1 standard deviation.)

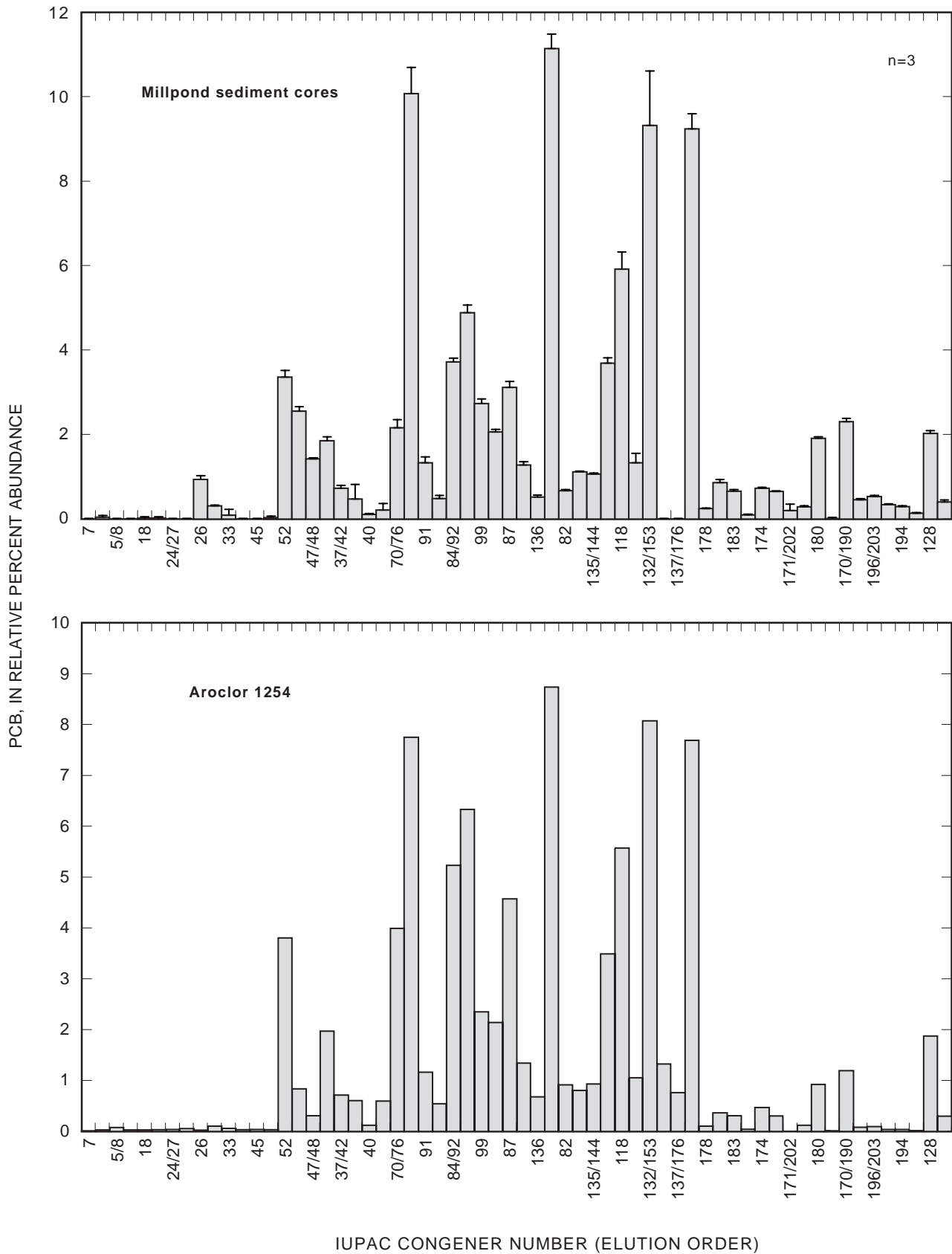


Figure 2c. PCB congener distributions in Hayton Millpond sediment cores, east-central Wisconsin, and congener composition of Aroclor 1254. (Error bars represent 1 standard deviation.)

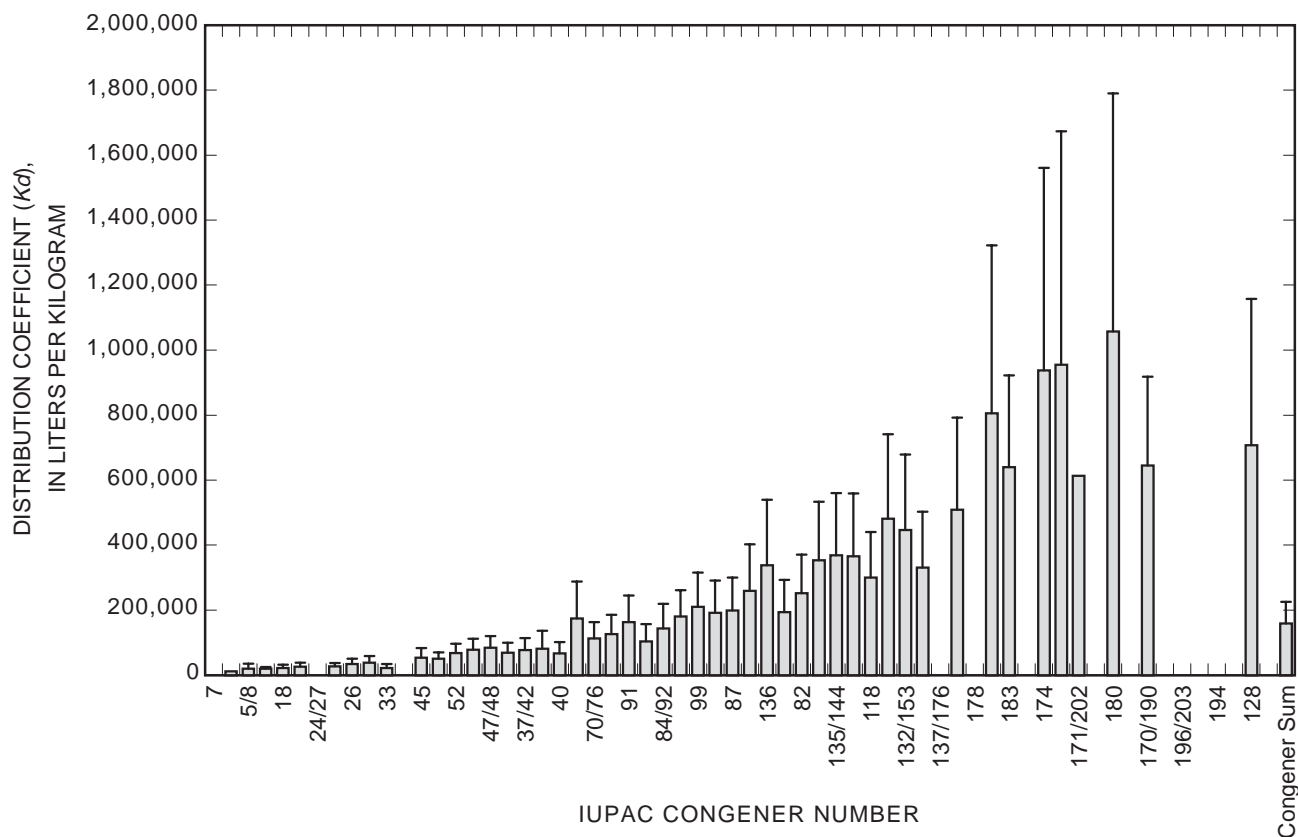


Figure 3. Two-phase distribution coefficients for PCB congeners at the Hayton Millpond outlet, east-central Wisconsin. (Error bars represent 1 standard deviation.)

Total Suspended Solids

The automated point TSS samples, which were collected from a single point in the river, provide a reasonable approximation of the EWI samples collected from the entire vertical and horizontal water column (fig. 4). Correlation between POINT and EWI data is strong when the sampled river is well mixed with respect to a constituent of interest; in this case, TSS. Turbulent flow below the millpond outlet dam—located just upstream from the monitoring site—may enhance water-column mixing. Additionally, agreement between the CHURN and EWI TSS data (appendix 1a) confirms that the PCB water-collection approach represented the entire water column.

TSS concentrations in the millpond outlet reflect both the rising limb of the hydrograph and the cyclical algal growth pattern represented by chlorophyll *a* concentrations (fig. 5).

Cumulative TSS load for the entire sampling period is displayed in figure 6 along with the discharge

hydrography for the millpond outlet. The annual suspended solids loads for water years 1994 and 1995 were similar, 610 tons and 500 tons, respectively. These loads, however, were about two-thirds of the 920-ton suspended-solids load that was computed for the last 3 months of water year 1993 (June 30, 1993–Sept. 29, 1993), a high-streamflow interval.

Concentrations and Loads of Transported Σ PCB's in the Hayton Millpond System

All PCB congeners present in a sample were summed to obtain congener-summation PCB concentrations (Σ PCB). Congener-specific PCB data have been published (Holmstrom and others, 1995, 1996, 1997) and are stored in the USGS QWDATA base. Concentrations of PCB's in the operationally defined dissolved and particulate phases and total PCB concentrations (dissolved and particulate), along with the ancillary constituents, are listed in appendix 1a.

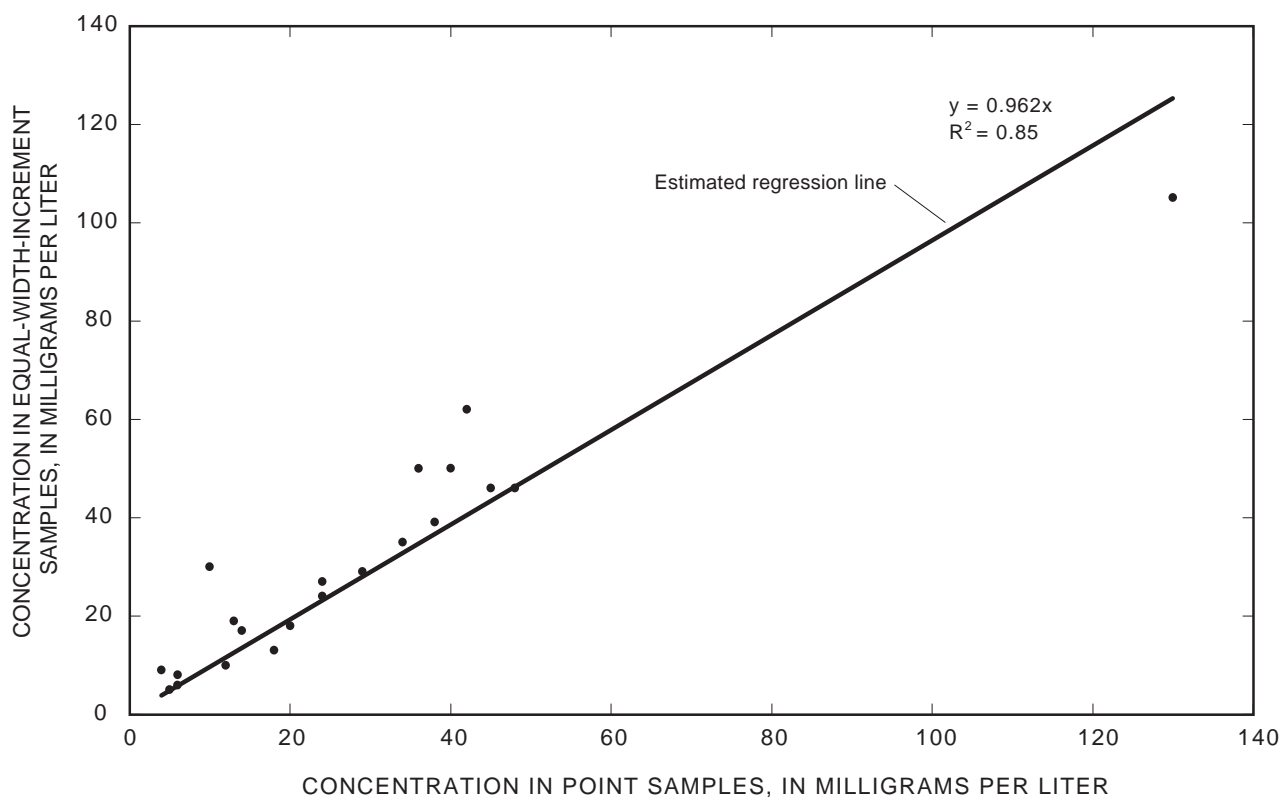


Figure 4. Correlation of total suspended solids resulting from two sampling methods at the Hayton Millpond outlet, east-central Wisconsin.

PCB's and other hydrophobic compounds typically sorb to riverine biotic material, sediments, and other solids; thus, the Σ PCB regressions initially focused on the TSS variable. POINT TSS samples were used in the Σ PCB load regression analyses because of the greater data density and potentially more accurate event coverage afforded by the frequency of automated sample collection. Regression efforts also examined PCB concentration as a function of discharge, time of year, temperature, and precipitation.

The concentrations of PCB's on suspended-solids particles (reported as micrograms per gram) are listed in appendix 1a. On five occasions, the particulate-phase PCB concentration dipped below 3.5 $\mu\text{g/g}$. For each of these occasions, precipitation had occurred within the previous two days. Cultivated fields in close proximity to reaches upstream from and adjacent to the millpond may supply a significant source of PCB-free sediment, resulting in a drop of particle-associated PCB. As a result, the Σ PCB regression was modified to include the universal soil loss coefficient (EI) (Wischmeier and Smith, 1978) in order to represent the tendency of

watershed soil erosion to transform (reduce) the TSS variable:

$$EI = [916 + 331 \cdot \log(I_{60})] \cdot I_{30}, \quad (1)$$

where

I_{30} is the 30-minute precipitation intensity² and I_{60} is the 60-minute precipitation intensity².

Revised regression relations incorporating EI are listed in table 2. The universal soil loss equation uses EI as an exponential function; in this study the coefficient and exponent on the summed EI's (day of sample and previous two days) were selected to maximize the r^2 value. For example, on July 6, 1993, an intense rain-storm produced an EI of 29.6 (appendix 1a). The millpond TSS concentration based on POINT samples was high (115 to 145 mg/L); yet, the particle-associated PCB decreased to 0.3 $\mu\text{g/g}$ (appendix 1a). A similar

²Precipitation intensities were computed from a rain gage on Otter Creek (USGS station 434907087573000) located 18 miles from the millpond.

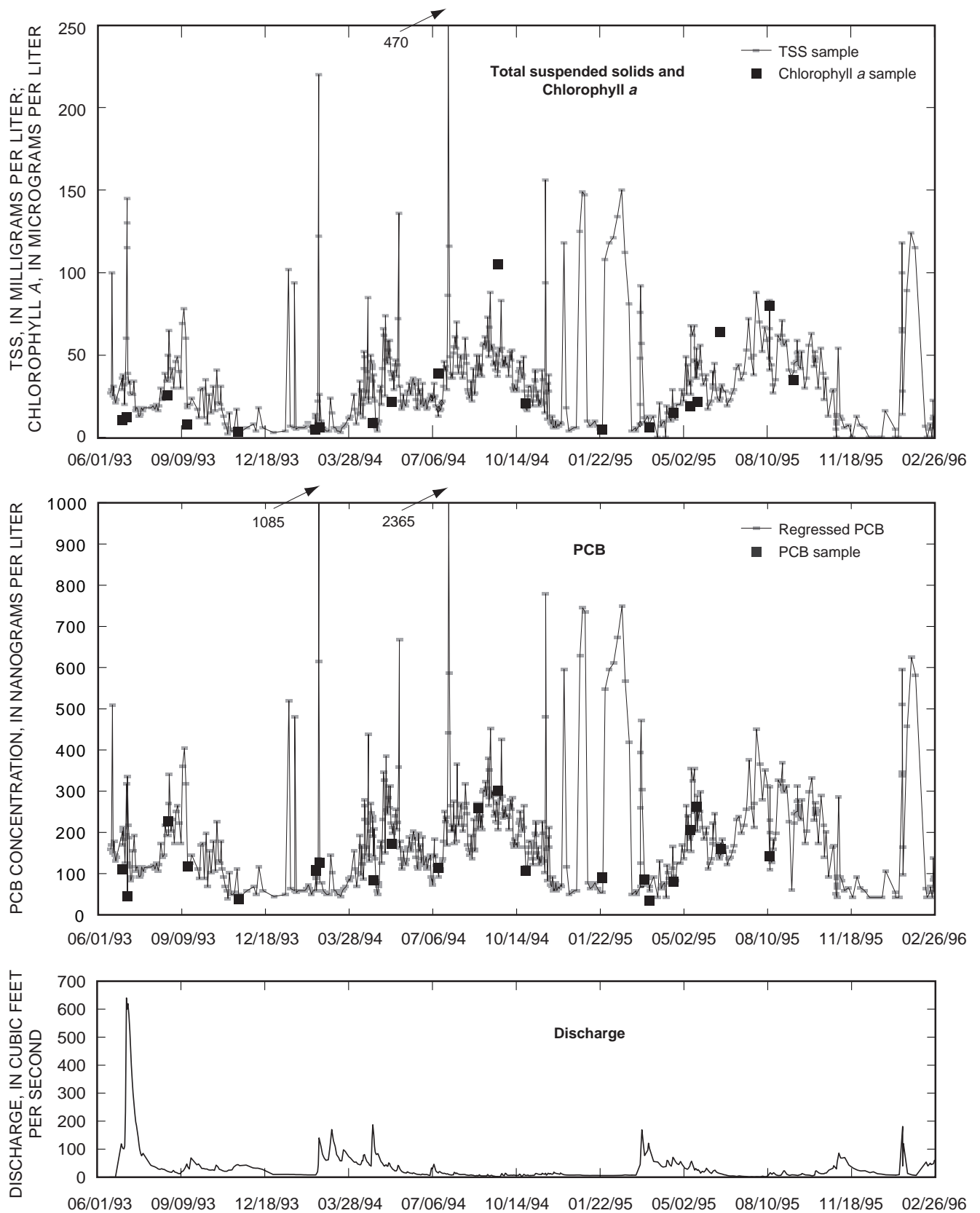


Figure 5. Discharge at Hayton Millpond outlet, east-central Wisconsin, and associated concentrations of total suspended solids (TSS), chlorophyll *a*, and total PCB.

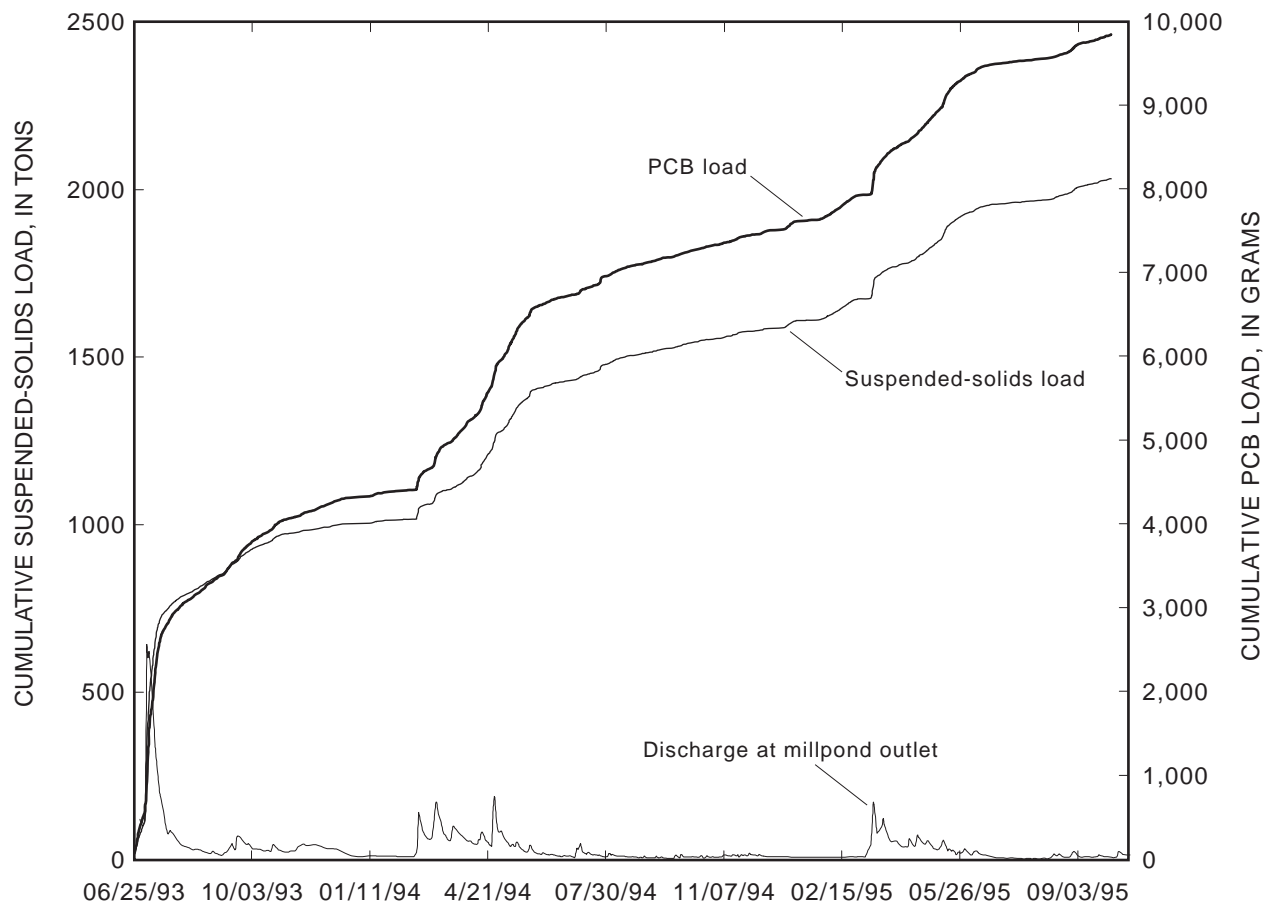


Figure 6. Cumulative PCB and suspended-solids loads at the Hayton Millpond outlet, east-central Wisconsin.

Table 2. Regression relations for total PCB concentration congener summation (ΣPCB) and selected congeners [r^2 , correlation coefficient; SE, standard error; μ_{PCB} , PCB mean; TSS, total suspended solids, in milligrams per liter; SL_2 , summation of universal soil loss coefficient for the day of the PCB sample and the previous two days; %, percent]

Regression relation	r^2	$1.96 \times SE / \mu_{PCB}$
(Equation 2) $\Sigma PCB = 480[TSS - (0.05 \cdot SL_2^{2.31})] + 29.8$	0.77	53%
(Equation 3) Congeners 77/110 = $0.53[TSS - (0.05 \cdot SL_2^{2.31})] + 2.78$.76	57%
(Equation 4) Congener 180 = $0.079[TSS - (0.05 \cdot SL_2^{2.31})] + 0.28$.80	53%

dilution of PCB-laden solids by clean solids was observed on August 13, 1995.

The WDNR has found PCB-laden sediment in the flood-plain area of Pine and Jordan Creeks (fig. 1). These contaminated flood-plain areas—many of which are grassland, woodland or pastureland—may not be as erodible as the more steeply sloped uncontaminated cultivated fields. An example of one such high-sloped cultivated field that may produce uncontaminated solids is immediately adjacent to the millpond. If land use of the contaminated flood plain areas changes (for example, if cultivated area increased), the soil erosion potential could increase and the above TSS transform (reduction) and resulting PCB regression relation may not be appropriate.

The linear regression was not as reliable if the TSS variable was transformed by discharge ($r^2=0.63$) instead of EI or not transformed at all ($r^2=0.24$). Σ PCB loads were computed by means of the regression relation (table 2, eq. 2), 15-minute discharge, and the flow-integration method (CLOAD) to obtain Σ PCB loads (fig. 6). This regression-based approach is referred to hereafter as “RLOAD.” Similar to TSS loads, the greatest PCB loads occurred during high flows.

The soil loss coefficient (EI) was also used in regressions for the co-eluting congeners 77/110 and congener 180 (table 2). The correlation coefficients are similar for both the congener-specific and congener-summation regressions. The 95-percent confidence interval was approximated by taking 1.96 times the normalized standard error (table 2); the actual interval width varies according to the independent variable.

For the purpose of comparing load-computation methods, Σ PCB loads were computed by means of two additional approaches (table 3). In the second approach, the flow-integration method was also used but computations involved individual-sample PCB concentrations rather than the regressed PCB concentrations. These results are referred to as “SLOAD.” A third approach, the Stratified Beale Ratio Estimator (SBRE), involved time-based strata defined by minimizing loading error over specific time intervals (Preston and others, 1989). The SBRE estimates both a load and associated confidence interval based on the root mean square error of the load computations. The integration method applied to individual-sample PCB concentration data (SLOAD) yielded lower loads than for regressed PCB concentration values (RLOAD) because manual PCB sample collection did not capture the transport peaks as well as the automated TSS sample collection did. Thus, the inten-

sive automated TSS sampling protocol (fig. 5) overcame a potential low that may result from the inability of manual operations to capture flow peaks.

Table 3. Computed PCB loads at the Hayton Millpond outlet, east-central Wisconsin, resulting from three computational approaches

[All loads in kilograms. () indicates a 95-percent confidence interval]

Interval (sampling interval)	3 months (6/30/93–9/30/93)	1 year (10/1/93–9/30/94)	1 year (10/1/94–9/30/95)
SLOAD	1.7	2.8	2.3
RLOAD	3.4	3.5	2.3
SBRE	1.4 (+/- 1.3)	2.8 (+/- 1.0)	1.8 (+/- 0.5)

In figure 7, Σ PCB concentrations are summarized for the three days when PCB samples were collected at the Pine Creek sites in conjunction with sampling at the millpond. Σ PCB concentrations increase from the Charlesburg Road site to the Quarry Road site, whereas Σ PCB concentrations decrease from the Quarry Road site to the millpond when Pine Creek inflow is diluted by streamflow from the relatively PCB-free upstream South Branch Manitowoc River (fig. 1).

Streamflow at the Pine Creek sites was not measured at the time of PCB sample collection; however, on five other occasions, streamflow was measured at Pine Creek sites in conjunction with sampling at the millpond outlet. From these measurements, approximate streamflow ratios for Quarry Road and Charlesburg Road are estimated at 0.41 ± 0.12 and 0.23 (one measurement) respectively, relative to the millpond outlet. The above approach, rather than basin-area ratios, was used to estimate streamflow because much of Pine Creek base flow may come from the New Holstein sewage treatment plant during times of low flow.

Multiplying the above streamflow estimates by the Σ PCB concentration data results in a consistent Σ PCB load increase from the Charlesburg Road to the Quarry Road site. This Σ PCB concentration and load increase from the Charlesburg Road site to the Quarry Road site is consistent with the observed increase in Σ PCB concentrations in surficial bed sediment in this same reach (fig. 1). This pattern indicates active interaction between the water column and bed sediments through processes such as resuspension, settling, and diffusion. Quarry Road to the millpond outlet is a much more hydrodynamically complex reach; this reach does not indicate a consistent Σ PCB loss or gain (fig. 7). On two of the three sample days, net Σ PCB transport through the Quarry Road to millpond outlet reach was negative

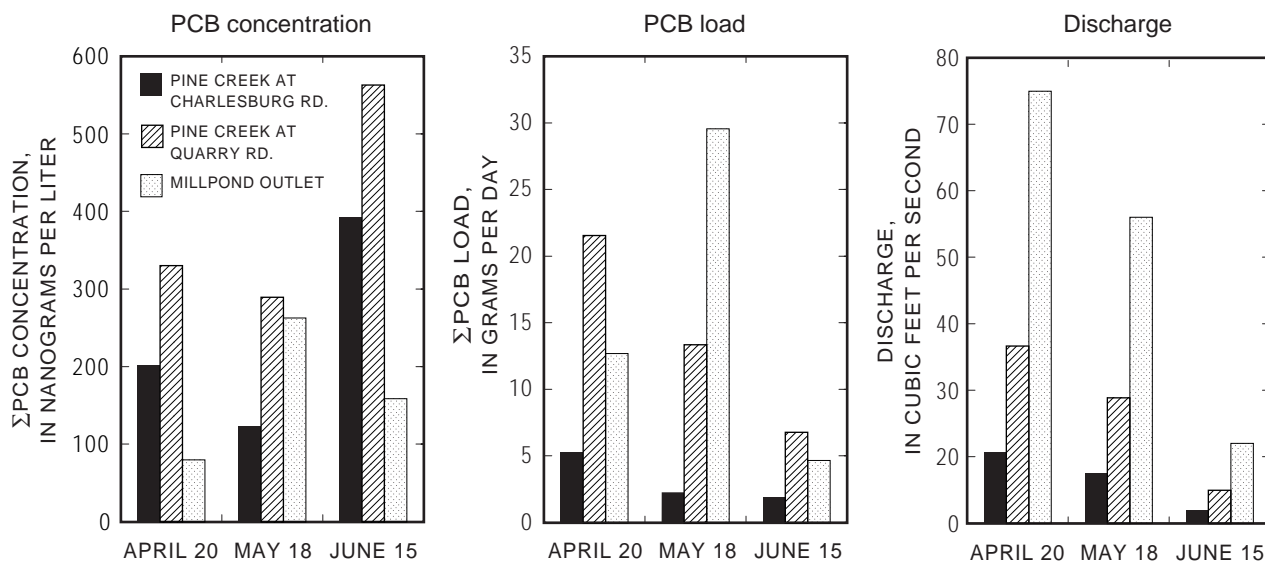


Figure 7. PCB concentrations, estimated loading, and discharge on three sample days, Pine Creek and Hayton Millpond outlet, east-central Wisconsin, 1995.

indicating ΣPCB deposition in the millpond. On May 18, 1995, however, there was positive net ΣPCB transport from the millpond. This positive net transport occurred near the peak of a chlorophyll *a* and TSS concentration cycle (fig. 5), and it may illustrate the importance of algal growth in the PCB transport dynamics.

SUMMARY

Concentrations of ΣPCB (the sum of all PCB congeners) in the water column operationally defined dissolved and particulate phases and in surficial bed sediment (0–2 cm depth) were determined at two sites on Pine Creek and at the Hayton Millpond in the South Branch of the Manitowoc River in Wisconsin to examine the distribution and loads of total PCB's in the river.

Total PCB concentrations in the water column varied considerably; at the millpond outlet, concentrations ranged from 34 to 302 ng/L. In general, 74 percent of the total water-column PCB was associated with suspended particles. PCB congener compositions appeared to be similar between the millpond outlet and the two upstream Pine Creek sites. In addition, the suspended-particle-associated PCB congener pattern appears to be nearly identical to that in the millpond surficial bed sediment; this similarly indicates interaction between the two media. There was also a similarity in these PCB congener suites to Aroclor 1254.

The apparent sediment/water distribution coefficients (K_d) varied by more than an order of magnitude over the range of congeners.

Computed total suspended-solids loads (TSS) at the millpond outlet were as high as 920 tons over a 3-month period (June 30–Sept. 30, 1993). Annual TSS loads for the following two water years were lower, 610 and 500 tons, respectively.

The ΣPCB concentration regression equation incorporated the universal soil loss coefficient to represent erosion of assumedly PCB-free sediment from fields upstream from the millpond. The ΣPCB load based on the regression relation was 3.4 kg during a 3-month high-flow interval (June 30–Sept. 30, 1993). Annual ΣPCB loads for the next two water years were 3.5 and 2.3 kg, respectively. Two alternative load-computation methods yielded similar but somewhat lower results.

Limited sampling at the two Pine Creek sites typically indicated higher ΣPCB concentrations than at the millpond outlet, some as high as 563 ng/L. Net ΣPCB loads between the Pine Creek sites and the millpond outlet did not show a consistent pattern, indicating that PCB-contaminated sediments are irregularly deposited and resuspended between Quarry Road and the millpond outlet.

REFERENCES CITED

- Cairns, T., Doose, G.M., Froberg, J.E., Jacobson, R.A., and Siegmund, E.G., 1986, Analytical chemistry of PCBs, *in* Ward, J.S., ed., PCBs and the environment: Boca Raton, Florida, CRC Press, v. 1, p. 2.
- David, M., Brondyk, L.M., and Sonzogni, W.C., 1994, Distribution of PCB congeners in Sheboygan River (Wisconsin) sediments: *Journal of Great Lakes Research*, v. 20, no. 3, p. 510–522.
- Degenhardt, D.E., 1996, Methods and quality control for the Organic Chemistry Unit of the Wisconsin State Laboratory of Hygiene: Madison, Wis., Wisconsin State Laboratory of Hygiene, 1,910 p.
- Dolan, D.M., Yui, A.K., and Geist, R.D., 1981, Evaluation of river load estimation methods for total phosphorus: *Journal of Great Lakes Research*, v. 7, no. 3, p. 207–214.
- Eisenreich, S.J., Looney, B.B., and Thornton, J.D., 1981, Airborne organic contaminants in the Great Lakes ecosystem: *Environmental Science and Technology*, v. 15, no. 1, p. 30–38.
- Fitzgerald, S.A., and Steuer, J.J., 1997, Polychlorinated biphenyls as probes of biogeochemical processes in rivers, *in* Eganhouse, R.P., ed. Molecular markers in environmental geochemistry: American Chemical Society Symposium Series 671, p. 382–397.
- Holmstrom, B.K. and others, 1995, Water resources data, Wisconsin, water year 1994: U.S. Geological Survey Water-Data Report WI-94-2, 388 p.
- _____, 1996, Water resources data, Wisconsin, water year 1995: U.S. Geological Survey Water-Data Report WI-95-1, 562 p.
- _____, 1997, Water resources data, Wisconsin, water year 1996: U.S. Geological Survey Water-Data Report WI-96-1, 464 p.
- House, L.B., 1995, Distribution and transport of polychlorinated biphenyls in Little Lake Butte Des Morts, Fox River, Wisconsin, April 1987–October 1988: U.S. Geological Survey Open-File Report 93-31, 43 p.
- House, L.B., Hughes, P.E., and Waschbusch, R.J., 1993, Concentrations and loads of polychlorinated biphenyls in major tributaries entering Green Bay, Lake Michigan, 1989–90: U.S. Geological Survey Open-File Report 93-132, 41 p.
- Koslowski, S.E., Metcalfe, C.D., Lazar, R., and Haffner, G.D., 1994, The distribution of 42 PCBs, including three coplanar congeners, in the food web of the western basin of Lake Erie: *Journal of Great Lake Research*, v. 20, p. 260–270.
- Marti, E. A., and Armstrong, D.E., 1990, Polychlorinated biphenyls in Lake Michigan tributaries: *Journal of Great Lakes Research*, v. 16, no. 3, p. 396–405.
- Porterfield, G., 1972, Computation of fluvial sediments discharge: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C3, 66 p.
- Preston, S.D., Bierman, V.J., Jr., and Silliman, S.E., 1989, An evaluation of methods for the estimation of tributary mass loads: *Water Resources Research*, v. 25, no. 6, p. 1379–1389.
- Rodgers, P.W., and Swain, W.R., 1983, Analysis of polychlorinated biphenyl (PCB) loading trends in Lake Michigan: *Journal of Great Lakes Research*, v. 9, no. 4, p. 548–558.
- Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M., 1993, *Environmental organic chemistry*: New York, New York, John Wiley and Sons, p. 36.
- Steuer, J., Jaeger, S., and Patterson, D., 1995, A deterministic PCB transport model for the lower Fox River between Lake Winnebago and DePere, Wisconsin: Wisconsin Department of Natural Resources, publication WR 389-95.
- Steuer, J.J., Fitzgerald, S.A., and Hall, D.W., 1999, Distribution and transport of polychlorinated biphenyls and associated particulates in the Milwaukee River system, Wisconsin, 1993–95: U.S. Geological Survey Water-Resources Investigations Report 99-4100, 37 p.
- Swackhamer, D.L., and Armstrong, D.E., 1988, Horizontal and vertical distribution of PCBs in southern Lake Michigan sediments and the effect of Waukegan Harbor as a point source: *Journal of Great Lakes Research*, v. 14, no. 3, p. 277–290.
- Sweet, C.W., Murphy, T.J., Bannasch, J.H., Kelsey, C.A., and Hong, J., 1993, Atmospheric deposition of PCBs into Green Bay: *Journal of Great Lakes Research*, v. 19, no. 1, p. 109–128.
- Velleux, M., Endicott, D., Steuer, J., Jaeger, S., and Patterson, D., 1995, Long-term simulation of PCB export from the Fox River to Green Bay: *Journal of Great Lakes Research*, v. 21, no. 3, p. 359–373.
- Ward, J.R. and Harr, C.A., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.
- Wischmeier, D.D. and Smith, D.D., 1978, Predicting rainfall erosion losses: U.S. Department of Agriculture Handbook 537, 58 p.
- Wisconsin Department of Natural Resources, 1991, Manitowoc River Basin water quality management plan: Report WR-282-91-REV, July 1991, 73 p.
- Yamashita, N., Tanabe, S., Ludwig, J.P., Kurita, H., Ludwig, M.E., and Tatsukawa, R., 1993, Embryonic abnormalities and organochlorine contamination in double-crested cormorants (*Phalacrocorax auritus*) and capian terns (*Hydroprogne caspia*) from the upper Great Lakes in 1988: *Environmental Pollution*, v. 79, p. 163–173.

APPENDIXES 1–2

Appendix 1a. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics at South Branch Manitowoc River at Hayton Millpond outlet (USGS station 04085395), 1993-95

[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; SL₂, modified universal soil loss coefficient summed for sample day and two previous days; 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; EWI, equal-width-increment sample; --, no data]

Date of sampling	Time of sampling	Instantaneous streamflow (ft ³ /s)	Total suspended solids				Carbon			ΣPCB				SL ₂	
			POINT (mg/L)	CHURN (mg/L)	EWI (mg/L)	Chlorophyll a (µg/L)	SOC (mg/L)	DOC (mg/L)	FOC (%)	Particulate (ng/L)	Particulate (µg/g)	Dissolved (ng/L)	Total (ng/L)		Load (g/d)
06/30/93	0745	123	¹ 29	36	29	10.7	0.4	17	1.1	92.1	2.6	18.3	110.4	33	0.2
07/06/93	1130	644	² 115/145	124	105	12.4	3.9	11	3.1	38.2	0.3	5.7	43.9	69	29.6
08/24/93	1000	22	³ 36	34	50	25.4	2.1	12	6.2	190.2	5.6	36.6	226.8	12	.7
09/16/93	1350	46	20	18	18	7.7	--	--	--	80.6	4.5	35.8	116.4	13	--
11/16/93	1120	45	4	4	9	3.15	.5	11	12.5	18.8	4.7	19.5	38.3	4	.1
02/16/94	1345	8	⁴ 6	12	8	4.83	.7	5.4	5.8	69.8	5.8	36.4	106.2	2	--
02/16/94	1500	8	⁴ 6	14	8	4.78	.5	5.3	3.6	73.4	5.2	35.3	108.7	2	--
02/21/94	1345	140	⁵ 10	26	30	5.88	2.0	13	7.7	100.1	3.9	26.1	126.2	43	.5
04/26/94	1015	193	24	24	24	8.60	1.2	13	5.0	55.4	2.3	27.7	83.1	39	3.1
05/18/94	1045	33	⁶ 38	39	39	21.1	1.9	13	4.9	145.8	3.7	26.7	172.5	14	--
07/13/94	0940	15	13	20	19	38.9	2.0	12	10.0	76.1	3.8	40.0	114.1	4	--
08/30/94	0945	3.8	⁷ 42	58	62	194	2.3	9.3	4.0	225.9	3.9	32.1	258.0	2	1.1
09/22/94	0955	2.5	40	71	50	105	4.4	8.5	6.2	264.7	3.7	36.9	301.6	2	--
10/25/94	1045	6.5	18	14	13	20.7	1.6	8.2	11.4	84.1	6.0	21.9	106.0	2	--
01/25/95	0830	5.8	5	5	--	4.72	.5	7.4	10.0	52.6	10.6	37.5	90.1	2	--
01/25/95	0835	5.8	5	5	5	4.24	.5	7.4	10.0	53.3	10.7	35.3	88.6	2	--
03/16/95	1000	76	12	10	10	--	--	--	--	60.5	6.0	25.1	85.6	16	--
03/22/95	1445	103	6	7	6	6.37	--	--	--	19.6	2.8	14.4	34.0	9	.8
04/20/95	1315	65	14	18	17	15.0	0.6	13	3.3	60.0	3.3	20.3	80.3	13	3.3
05/10/95	1100	50	34	35	35	18.9	2.1	12	6.0	167.1	4.9	38.6	205.7	25	.8
05/18/95	0915	46	⁸ 36/54	46	46	21.5	2.6	14	5.7	221.3	4.9	41.4	262.7	30	--
06/15/95	0920	12	24	30	27	63.9	1.9	5.9	6.3	121.8	4.1	36.8	158.6	5	--
08/13/95	2230	30	48	46	46	79.5	3.5	7.7	16.4	122.5	2.6	20.2	142.7	11	14.6
09/11/95	1715	7.6	⁹ 40	45	--	35.0	2.1	13	4.7	--	--	--	--	--	--
Median	--	32	22	25	26	15.0	1.9	11.0	6.0	80.6	4.1	32.1	110.4	11	--

¹Sample collected at 1400.

²Samples collected at 0000 and 1450.

³Sample collected at 1200.

⁴Estimated value based on 2/15/94 and 2/17/94 samples.

⁵Sample collected at 1145.

⁶Estimated value based on 5/17 and 5/19/94 samples.

⁷Sample collected at 1200.

⁸Rapidly changing streamflow, samples taken at 0830 and 1315.

⁹Sample collected at 1200.

Appendix 1b. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics at Pine Creek at Quarry Road (USGS station 040853936), 1995

[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_m, estimated daily streamflow based on streamflow ratio with Manitowoc River at Hayton Millpond outlet; 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; EWI, equal-width-increment sample]

Date of sampling	Time of sampling	Q _m (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/d)
04/20/95	1230	27	7	10	8	4.87	0.70	10	7	217.9	21.8	112.4	330.0	22
05/18/95	1200	19	6	5	5	5.14	.60	9.2	12	144.3	28.9	144.5	289.2	13
06/15/95	1020	5	26	28	22	14.7	1.6	12	5.7	388.8	13.9	174.8	562.9	7

Appendix 1c. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics at Pine Creek at Charlesburg Road (040853926), 1995

[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_m, estimated daily streamflow based on streamflow ratio with Manitowoc River at Hayton Millpond Outlet; 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; EWI, equal-width-increment sample; --, no data]

Date of sampling	Time of sampling	Q _m (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/d)
04/20/95	1015	11	--	6	4	3.92	0.60	11	10.0	153.6	25.6	46.7	200.3	5
05/18/95	1030	8	5	6	6	11.8	.70	9.4	11.7	69.3	11.5	53.7	123	2
06/15/95	1214	2	16	18	26	6.65	1	5.6	5.6	261.1	14.5	131.7	392.8	2

Appendix 2. PCB congeners found during laboratory analysis of water and sediments in the Hayton Millpond 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')