DISTRIBUTION AND TRANSPORT OF POLYCHLORINATED BIPHENYLS IN LITTLE LAKE BUTTE DES MORTS, FOX RIVER, WISCONSIN, APRIL 1987-OCTOBER 1988

By Leo B. House

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Multiply	By	To Obtain
acre	404.7	square meter
ounce	28.34	gram
pound (lb)	0.4535	kilogram
pound (lb)	453.5	gram
ton	907.2	kilogram
ton	0.9072	megagram
inch (in.)	25.4	millimeter
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square foot (ft^2)	0.0929	square meter
cubic foot (ft^3)	0.02832	cubic meter
cubic foot (ft^3)	28.32	liter
pound per cubic foot (lb/ft^3)	0.0160	kilogram per liter
gallon (gal)	3.785	liter
square mile (mi^2)	2.590	square kilometer
pound per square foot (lb/ft^2)	42,130	milligrams per square meter

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.

OTHER CONVERSIONS

acre	43,560	square foot
gram (g)	1×10^9	nanogram
kilogram (kg)	2.205	pound
megagram (Mg)	1×10^3	kilograms
gram (g)	1×10^6	microgram
gram (g)	1,000	milligram
milligram per kilogram (mg/kg)	1.0	microgram per gram
day (d)	86,400	second
meter (m)	1×10^6	micrometer
million gallon per day (Mgal/d)	133,680	cubic foot per day
million gallon per day (Mgal/d)	1.55	cubic foot per second
ton	2,000	pound

ABBREVIATED WATER-QUALITY UNITS

mg/L	milligrams per liter
µg/L	micrograms per liter
ng/L	nanograms per liter
mg/kg	milligrams per kilogram (dry weight)
µg/g	micrograms per gram (dry weight)
g/d	grams per day
kg/month	kilograms per month
$g/(m^3/s)$	grams per cubic meter per second (a discharge-normalized transport rate as used in this report)
$(mg/m^2)/d$	milligrams per square meter, per day (a flux rate from bottom sediments as used in this report)
Mg/d	megagrams per day (a rate of sediment transport as used in this report)

TRADE NAME DISCLAIMER: The use of trade or brand names in this report is for identification purposes only and does not constitute an endorsement by the U.S. Geological Survey.

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

$$°F = 1.8(°C) + 32$$

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Abstract

Polychlorinated biphenyls (PCB's) in the bottom sediment and water column of Little Lake Butte des Morts were studied by the Wisconsin Department of Natural Resources and the U.S. Geological Survey. The lake is a 8-kilometer-long impoundment of the Fox River between Lake Winnebago and Appleton, Wisconsin. Discharge of PCB's into the lake by paper mills and waste-treatment plants has resulted in their accumulation in the bottom sediment. The accumulation of PCB's in the sediment was estimated to be 1,100 kilograms in October 1987. The concentrations of PCB's in bottom-sediment core samples were as much as 190 micrograms per gram dry sediment. The congener distribution of the PCB's present in the lake most closely resembles that for the Aroclor 1242 PCB's mixture.

Thirty-two water samples were collected at the outlet of the lake to determine concentrations of PCB's. Concentrations of PCB's in the water column varied seasonally and ranged from 3.5 to 137 nanograms per liter. Concentrations of PCB's decrease in the winter and increases in the summer months. Concentrations of PCB's in the water column for particulates generally were 2.5 times that of dissolved PCB's. The suspended-solids concentrations ranged from 3 to 44 milligrams per liter.

Correlation analysis was used to identify the physical characteristics and water-quality characteristics having the highest degree of association with PCB's concentration in the water column. The highest correlation coefficients (r) for dissolved PCB's concentration were with water temperature (r=0.88) and particulate organic carbon concentration (r=0.72). The highest correlation coefficients for particulate PCB's concentration were with suspended-particulates concentration (r=0.77) and water temperature (r=0.70). Correlation coefficients for total PCB's (the sum of dissolved and particulate PCB's) concentration were similar to those for particulate PCB's concentration.

The mass of PCB's transported from the lake in streamflow during 1987-88 was calculated to be 110 kilograms annually. The PCB's transport rate decreased 50 percent from 1987 to 1988, for the period April through September. Transport of PCB's was greatest during April and May of each year. The average flux rate of PCB's into the water column from the bottom sediment in the lake was estimated to be 1.2 milligrams per square meter per day. The PCB's load seems to increase at river discharges greater than 212 cubic meters per second. This increase in PCB's load might be caused by resuspension of PCB's-contaminated bottom-sediment deposits. There was little variation in PCB's load at flows less than 170 cubic meters per second. The bottom sediments are a continuing source of PCB's to Little Lake Butte des Morts and the lower Fox River.

INTRODUCTION

The lower Fox River (fig. 1), between Lake Winnebago and Green Bay, is the most industrialized river basin in Wisconsin. Polychlorinated biphenyls (PCB's) in bottom sediment have been

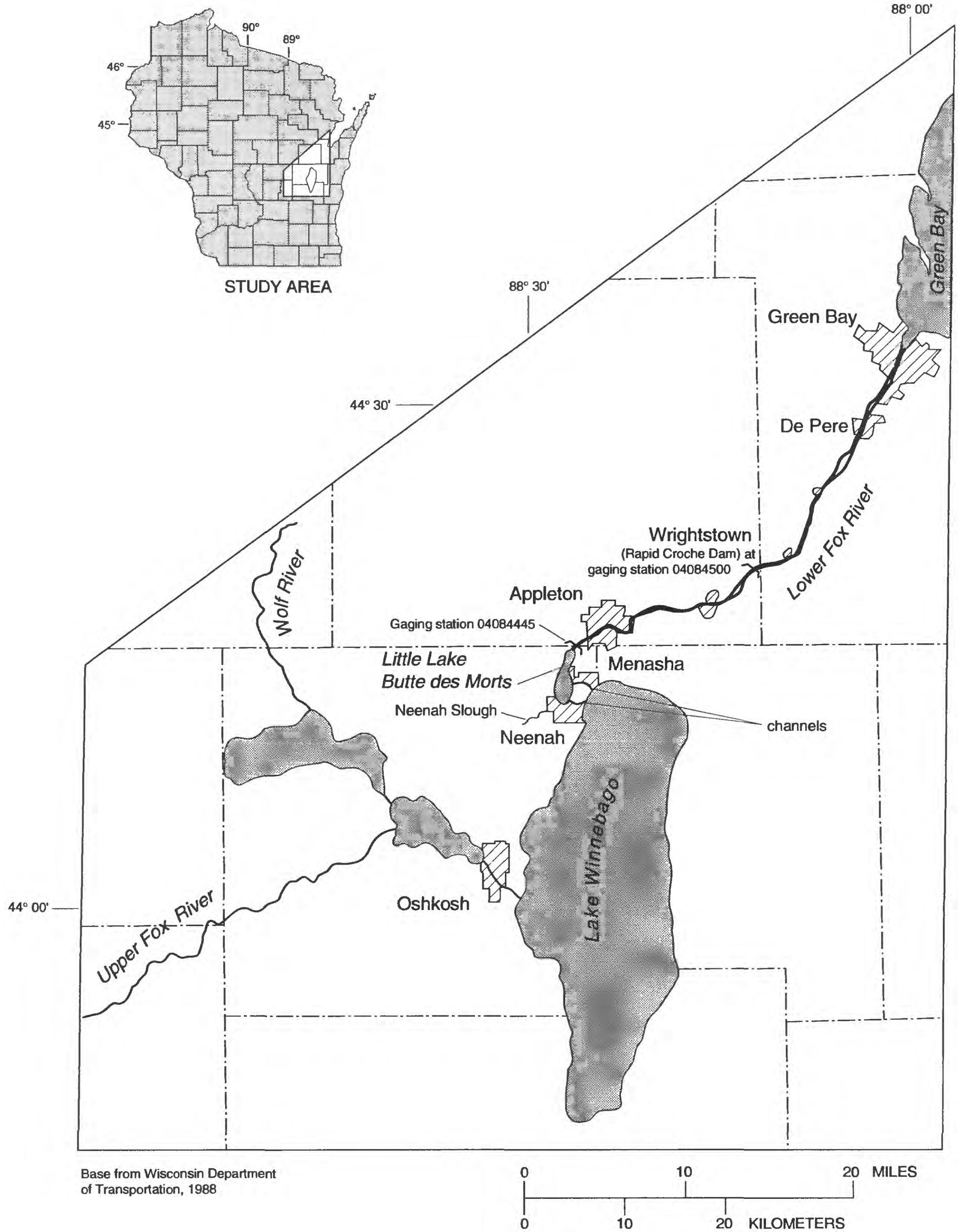

Figure 1. Location of study area, Little Lake Butte des Morts, lower Fox River, east-central Wisconsin.

identified and have been classified as "In-place Pollutants" by the Wisconsin Department of Natural Resources (WDNR) (Sheffy, 1980). A previous study of PCB's in Little Lake Butte des Morts found concentrations as much as 250 mg/kg in the bottom sediments of Little Lake Butte des Morts (Sullivan and others, 1983). In 1979, the WDNR issued a consumption advisory for fish taken from the river (Sheffy, 1980).

This cooperative study by the Wisconsin Department of Natural Resources (WDNR) and the U.S. Geological Survey (USGS) is the result of a recommendation in 1985 by the Governor's Task Force on Toxic Substances in Wisconsin that the lower Fox River bottom sediments be studied as a source of continuing pollution. The study was started in the fall of 1985 and continued through the spring of 1990. The Little Lake Butte des Morts area was selected as the initial site for study because of the known high concentration of PCB's in bottom sediments of the lake. The WDNR extracted cores of bottom sediment for determination of PCB's concentrations. The Wisconsin State Laboratory of Hygiene (WSLH) analyzed the cores for concentrations of PCB's.

Purpose and Scope

This report presents the results of an investigation of polychlorinated biphenyls in the bottom sediments and in the water column of Little Lake Butte des Morts. The scope of this report covers PCB's data collected from early April 1987 through early October 1988. This report includes a description of the pertinent hydrology and the physical setting of the lake. The report also includes an assessment of PCB's in the bottom sediments as of October 1987, and an analysis of advective transport of PCB's out of the lake during the 1987-88 data-collection period.

Acknowledgments

The author acknowledges Judith Crane for her contribution to this investigation. As a doctoral candidate in the Water Chemistry Department of the University of Wisconsin-Madison, Judith was responsible for the laboratory analysis of PCB's in water samples collected by the USGS. This involved the application and the evaluation of new techniques for determination of trace concentrations of PCB's. The method used for measurement of concentrations of PCB's in this investigation was developed by Edwin Marti (1984). William C. Sonzogni of the Water Chemistry Department of the University of Wisconsin-Madison supervised the analytical work. The Wisconsin State Laboratory of Hygiene, Organics Section, provided analysis of bottom-sediment cores. This work was also supervised by Dr. Sonzogni.

HYDROLOGIC SETTING

The hydrologic setting section of the study area is important to the interpretation of the PCB's concentration and transport data. This section of the report contains a description of the geographic location of the study area and includes documentation of the discharge, suspended-sediment transport, and water temperature in the Fox River before and during the investigation. A brief discussion of the sources of PCB's in the study area is also provided.

Location of Little Lake Buttes des Morts

Little Lake Butte des Morts is a 8-kilometer reach of the Fox River between the outlet of Lake Winnebago and the city of Appleton (fig. 1). The upstream end of the lake is bounded by dams controlling the elevation of Lake Winnebago's pool. These dams are in the cities of Neenah and Menasha, on what are known as the Neenah and the Menasha channels of the Fox River. The difference in elevation between Lake Winnebago and Little Lake Butte des Morts is about 3 meters. The navigation locks and canal are next to the Menasha channel. This canal provides access to Lake Winnebago for recreational boat traffic from May through October. Commercial barge traffic is no longer present on this reach of the Fox River. The downstream end of the study area is formed by the first dam at Appleton. This dam controls the pool elevation of Little Lake Butte des Morts.

Little Lake Butte des Morts (pl. 1) consists of three distinct zones. The most upstream zone lies between the Neenah and the Menasha channels and the Chicago and Northwestern railroad bridge.

This zone receives inflow from Lake Winnebago, the Neenah Slough, and several point discharges. The tributary of Neenah Slough enters Little Lake Butte des Morts near the landfill known as Arrow Head Park. The point discharges are from three paper mills and two sewage-treatment plants. Inflow from Lake Winnebago enters through the Neenah and the Menasha channels. Most of the inflow from the Neenah Slough is runoff from snowmelt or rainfall. This upstream zone of Little Lake Butte des Morts is about 4 ft deep, and its bottom is composed of sand and cobbles. The bottom of near-shore bay areas consists of soft clay and muck, and is the habitat of thick stands of macrophytes in the summer months. Industrial development is extensive along this zone's shoreline, particularly adjacent to the Neenah and the Menasha channels.

The middle zone of Little Lake Butte des Morts is bounded by the Chicago and Northwestern Railroad at the upstream end and by Stroebe Island downstream. Depths are 1.8 to 3.6 meters in the center of this zone. An excavated navigation channel extends from the Menasha locks to the center of the lake. Bottom material along the east edge of the zone consists of hard sand and cobble, and along the west edge, soft muck and clay. Bottom material in the deep areas tends to consist of soft organic muck. Inflow to the middle zone is from the Fox River upstream and from several small tributaries. One sewage-treatment plant and the Menasha locks discharge to this zone. The County Highway P bridge spans the zone at roughly its center. Residential development is extensive along the shoreline on the eastern edge of this zone and on Stroebe Island (pl. 1).

The downstream zone of Little Lake Butte des Morts begins at the downstream end of Stroebe Island and extends to the USGS streamflow gage at Lutz Park in Appleton. The width of the Fox River channel gradually narrows in this zone to about 180 m at Lutz Park. Depth generally ranges from 3.6 m at Lutz Park to 7.3 m near Stroebe Island. The channel bottom is primarily bedrock, except for an area of muck and clay near Stroebe Island just downstream from the mouth of Mud Creek. The channel is not dredged. The downstream zone includes several storm sewer outfalls. Inflow from Mud Creek is substantial only during snowmelt or storm runoff. Residential development, undeveloped shoreline, and parklands border the channel in this zone. The USGS streamflow gage (station number 04084445) is at the downstream end of the zone, at Lutz Park in Appleton.

Discharge

The drainage area of the Fox River is 15,200 km^2 at the outlet of Lake Winnebago, and is 15,400 km^2 at Appleton. The Neenah Slough and Mud Creek are the only significant tributaries entering Little Lake Butte des Morts. The drainage area of the Neenah Slough is 55.9 km^2 at the mouth, and that of Mud Creek is 65.0 km^2. The surface area of Little Lake Butte des Morts is about 5.7 km^2. Local inflow to the lake is not substantial when compared to inflow from Lake Winnebago.

A comparison of the long-term discharge of the lower Fox River (water years 1918-88)[1] with that of the study period (1986-88) is given in table 1. The USGS streamflow gage at the Rapid Croche Dam, station 04084500, is used for long-term comparison. The drainage area of the Fox River at Rapid Croche is 15,600 km^2, an area only 1 percent greater than at the Appleton gage site. A monthly mean discharge comparison is therefore meaningful.

Monthly mean discharge was above average during the last 3 months of water year 1986 (July-September 1986). A maximum daily discharge of 459 m^3/s was recorded at the Appleton gage site on September 25, 1986. This discharge was caused by intense basinwide rainstorms. The flow approximates the 5-year recurrence interval flood estimate of 490 m^3/s (Conger, 1981), for the Fox River at Rapid Croche Dam. The effect of these rainstorms, and the additional precipitation in October, carried over into the beginning of water year 1987. Another maximum daily discharge of 462 m^3/s was recorded on October 7 at Appleton. Discharge then decreased to near the long-term

[1]A water year (WY) is the period from October 1 through September 30 of the following year. The WY is identified by the ending year of this period. For example, the 1988 WY ends on September 30, 1988.

Table 1. Long-term discharge (water years 1918-88) and short-term discharge (water years 1986-88) of the lower Fox River [m^3/s, cubic meters per second; --, no data]

	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
Fox River at Rapid Croche, station 04084500, water years 1918-88, mean monthly discharge, in m^3/s												
Discharge	91.7	111	113	116	118	144	208	169	130	90.1	70.2	78.6
Standard deviation	67.0	64.5	41.5	38.2	34.6	63.5	113	89.1	65.2	44.4	36.3	54.5
Maximum	403	361	280	222	222	352	548	571	372	316	272	312
Minimum	20.6	35.2	44.2	40.6	50.0	45.2	45.0	35.7	31.1	27.8	21.6	20.1
(Mean annual discharge, 1918-88 = 120 m^3/s Standard deviation = 36.4 m^3/s)												
Fox River at Appleton, station 04084445, water years 1986-88, daily mean discharge, in m^3/s												
	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
1986 WATER YEAR DISCHARGE (No data collected before July 1986)												
Mean	--	--	--	--	--	--	--	--	--	132	110	252
Maximum	--	--	--	--	--	--	--	--	--	249	253	459
Minimum	--	--	--	--	--	--	--	--	--	94.0	71.6	68.0
1987 WATER YEAR DISCHARGE												
Mean	383	164	111	158	154	102	118	117	72.2	45.7	47.4	53.8
Maximum	462	286	142	215	186	116	229	214	170	51.8	66.8	85.5
Minimum	289	92.0	96.3	110	110	77.0	76.5	74.5	45.0	36.8	39.4	36.5
(1987 water year mean discharge = 127 m^3/s)												
1988 WATER YEAR DISCHARGE												
Mean	55.0	110	144	125	139	117	131	76.0	35.2	26.7	27.5	34.7
Maximum	83.3	152	175	181	161	175	219	103	47.6	29.3	34.3	75.9
Minimum	32.0	74.2	117	75.9	114	102	76.5	46.2	24.6	23.9	23.8	26.8
(1988 water year, mean discharge = 65.0 m^3/s)												

average in December. Discharge was slightly above average in January and February 1987, but was 42.5 m^3/s below the long-term average in March and more than 85.0 m^3/s below the long-term average in April.

Thus, by the time water sampling for PCB's began in April 1987, a flood had occurred that was followed by a decline in discharge to below-average levels. Discharge remained below average for the rest of water year 1987, although the annual average discharge (127 m^3/s) was slightly above the long-term average-annual discharge (120 m^3/s).

Water year 1988 was a year of drought for much of the Nation, including Wisconsin. Monthly mean discharge for the Fox River was substantially below average from May through August 1988. The monthly mean discharge for this period was lower than one standard deviation below the long-term mean. July and August flows were notably low. The minimum daily mean flow for this period was 23.8 m^3/s on August 17 at Appleton. The log-Pearson low-flow estimate for the 10-year recurrence interval, 7-day low-flow at Rapid Croche is 26.4 m^3/s. The monthly mean flows during July and August were only slightly (1.1 and 4.0 percent, respectively) above this 10-year low-flow value. Annual mean discharge for water year 1988 was 65.0 m^3/s, about one standard deviation (36.4 m^3/s) below the long-term mean-annual discharge. The monthly mean flow in July at Rapid Croche (29.1 m^3/s) was the second lowest flow on record for that month. Only July 1931 had a lower monthly mean flow (27.8 m^3/s).

In summary, discharge was near the 5-year flood magnitude before the collection of samples for the study. It declined on a monthly average basis to drought levels during the study.

Suspended-Sediment Transport

Most suspended sediment in Little Lake Butte des Morts is fine-grained material. More than 70 percent by weight is smaller than sand (0.062 mm diameter). The results of the particle-size analysis of water-column samples at the Appleton gage site are shown in table 2. Most of these samples were collected by use of a peristaltic pump installed at the gage. The pump intake was 15 m from shore, at a mid-depth of .76 m, in eddy-free current. The point samples are not always representative of the channel's cross-sectional average concentration. This is shown by the data for November 5 and 19, 1986. The cross-sectional average concentrations are for samples collected by use of the equal-width increment (EWI), a depth-integrating method described by Guy and Norman (1970).

Suspended-sediment concentration and the percentage of sand-sized material are greater for the EWI samples than for the point samples collected November 5 and 19, by use of the pump sampler. The differences narrowed as the discharge decreased from 255 m^3/s on November 5, to 113 m^3/s on November 19. This indicates that high discharges transport relatively more sand-sized particles than do low discharges.

Water samples were also collected to evaluate the inflow and outflow of suspended sediment from Little Lake Butte des Morts. These data are summarized in table 3. The suspended-sediment data were collected using the EWI method described by Guy and Norman (1970). Discharge and suspended-sediment concentrations were measured periodically in the Neenah and the Menasha channels (pl. 1). Suspended-sediment samples were collected daily at the outlet of the lake (the Appleton gage site). Lake storage volume is generally constant. Inflow to Little Lake Butte des Morts generally equals outflow on a daily basis. The hydraulic residence time generally ranges from less than 1 to several days. Hydraulic

Table 2. Analysis of suspended-sediment-particle size, Fox River at Appleton, Wisconsin [m^3/s, cubic meter per second; mm, millimeter; mg/L, milligram per liter; EWI, equal width increment sample; %, percent; >, greater than; <, less than]

Date of sampling	8-22-86	8-27-86	9-17-86	10-8-86
Type of sampling	Point	Point	Point	Point
Concentration (mg/L)	35	20	18	25
Sand, % (>.062 mm)	1.1	1.1	2.4	2.7
Fine, % (<.062 mm)	98.9	98.9	97.6	97.3
Discharge (m^3/s)	86.1	77.3	303	425
Date of sampling	11-5-86	11-5-86	11-19-86	11-19-86
Type of sampling	Point	EWI	Point	EWI
Concentration (mg/L)	17	26	19	23
Sand, % (>.062 mm)	1.0	29.3	1.3	14.3
Fine, % (<.062 mm)	99.0	70.7	98.7	85.7
Discharge (m^3/s)	255	255	113	113

Table 3. Suspended-sediment inflow and outflow, Little Lake Butte des Morts, Wisconsin
[Mg/d, megagrams per day; ft^3/s, cubic foot per second; d, day; °C, degrees Celsius]

Date of sampling	12-3-86	12-17-86	1-6-87	1-28-87	2-18-87
Sediment inflow (Mg/d)	288	74.7	65.1	30.0	30.9
Sediment outflow (Mg/d)	175	34.6	18.6	22.2	22.7
Inflow/outflow	1.6	2.2	3.5	1.4	1.4
Discharge (m^3/s)	148	108	153	172	146
Hydraulic residence time (d)	.66	.90	.64	.57	.67
Water temperature, °C	.6	.4	.8	.4	1.4
Date of sampling	3-17-87	4-16-87	4-30-87	5-26-87	7-22-88
Sediment inflow (Mg/d)	36.1	90.7	288	61.3	35.7
Sediment outflow (Mg/d)	36.0	295	486	125	112
Inflow/outflow	1.0	.31	.59	.49	.32
Discharge (m^3/s)	94.6	98.6	220	84.4	28.0
Hydraulic residence time (d)	1.0	.99	.44	1.2	3.5
Water temperature, °C	2.4	10.6	13.2	16.4	27.4

residence time is defined here as the lake volume divided by the rate of outflow. For Little Lake Butte des Morts, the relation is

$$QLAG = 97.4/Q \qquad (1)$$

where QLAG is the hydraulic residence time, in days; and

Q is the daily mean outflow at the Appleton gage site, in cubic meters per second.

The QLAG value can also be thought of as the "flushing time" for all water in the lake to be replaced by inflow. The hydraulic residence time is less than one day for the average long-term river discharge of 119 m^3/s (table 1). On the basis of this information, the lake is more like a slow riverine system than a typical lake. Therefore, the data and results of this study are best compared with other river studies and probably do not represent lacustrine environments.

The suspended-sediment inflow exceeds outflow for the data collected before April 1987. For the data collected in April 1987 and thereafter, the outflow of suspended sediment exceeds inflow by 68 percent or more. The change in the sediment inflow/outflow ratio after March 1987 is not explained by discharge or hydraulic residence time. However, the inflow/outflow ratio might be related to water temperature. The ratio drops below 1.0 (net sediment outflow) after the water temperature exceeds 2.4°C. This could be caused by a large contribution of suspended sediment associated with the runoff of snowmelt.

Local sediment inflow to the lake is also caused by storm runoff. The load of sediment on July 22 might be related to rainstorm activity. Rainfall on July 21 totaled 1.65 cm. This local rainfall could have caused washoff of shoreline sediment into Little Lake Butte des Morts and storm-sewer discharge into the lake. The storms could also have caused wave-induced erosion of shoreline. All these factors could cause the concentration of sediment at Appleton to increase. The increase in outflow of sediment during low flow periods could also be caused by biologic productivity. Algal production causes an increase in particulate matter outflow from the lake. This algal detritus is included in the measurement of suspended sediment. Other possible sources include point discharges from industry and wind-driven resuspension of bottom sediment.

Daily mean suspended-sediment concentration each month at the Appleton gage site are shown in table 4. The suspended-sediment concentration data are based on samples collected every 12 hours. Samples were collected with an automated pump sampler. Sixty EWI samples were collected during 1986-88 in order to adjust the pump-sampler concentrations to the cross-sectional average (Guy and Norman, 1970). Typically, an EWI measurement was made every 3 weeks and more frequently during rapidly changing discharge. The daily suspended-sediment concentration and load data are published in the USGS Water-Data Reports for Wisconsin (Holmstrom and others, 1988, 1989). The suspended-sediment load was calculated using methods described by Porterfield (1972).

The total annual sediment load during water year 1987 was 65,200 megagrams; the load was 65,000 megagrams in 1988. These loads were computed as the product of daily average discharge and the daily average suspended-sediment concentration. Monthly variations in the sediment load were considerable during water years 1987 and 1988. Annual average discharge for these two water years was 127 m^3/s and 65.0 m^3/s, respectively.

Water Temperature

Monthly mean water temperatures for water years 1987 and 1988 are also presented in table 4. Water temperature was monitored at the Appleton gage site by use of a thermistor probe coupled to a recording datalogger. The daily mean water temperature was computed as the average of the 15-minute-interval recordings, and monthly mean water temperature was computed as the average of the daily means.

The minimum monthly mean was 0.4°C in December 1986, and the maximum monthly mean was 25.7°C in July 1987. The maximum daily mean water temperature was 29.1°C on August 3, 1987.

Monthly mean water temperatures were less than 2.0°C during December through February of 1987 and 1988. Water temperature increased gradually in March, to range from 3.0 to 5.0°C, and then rapidly during April and May, to more than 20.0°C in summer. Water temperature decreased rapidly in October and November. The water temperature in winter (January-February) is less than 2.0°C.

Sources of Polychlorinated Biphenyls

PCB's manufactured in the United States were sold under the brand name Aroclor. An Aroclor is a mixture of various PCB's molecules having different molecular weights. Seven Aroclors were sold, and each was identified by a 4-digit number: 1221, 1232, 1242, 1248, 1254, 1260, and 1262. The first two digits (12) refers to the 12 carbon atoms in the biphenyl, and the last two digits represent the approximate percentage by weight of chlorine in that Aroclor. Each Aroclor was designed for specific industrial applications (Waid, 1986).

The unique chromatographic profile of each Aroclor allows the determination of the Aroclor that best represents the PCB's mixture in a sample of bottom sediment or water. Therefore, many mixtures of PCB's are reported as a specific Aroclor. The PCB's samples analyzed for this study most closely resemble Aroclor 1242. This Aroclor is associated with waste-process water from the recycling of paper (Carr and others, 1977).

The primary source of PCB's detected in water samples at the Appleton gage site is probably bottom sediment in Little Lake Butte des Morts. These PCB's are associated with past discharge of paper-mill wastes into the Fox River (Sullivan and others, 1983). Inflow from Lake Winnebago had PCB's concentrations of up to 4.2 ng/L. The Lake Winnebago outflow concentrations are consistent with atmospheric deposition to that lake (Crane, 1990).

PCB's may also enter the Fox River from urban stormwater. Concentrations of PCB's in storm runoff of as much as 7.9 μg/L (7,900 ng/L) and an average of 2.0 μg/L (2,000 ng/L) were reported in a study of industrial areas in Milwaukee, Wis. (U.S. Environmental Protection Agency, 1983). Runoff from Fox River industrial areas with PCB's concentrations of this magnitude could result in significant input to the river. The concentration of total PCB's in a water sample collected from the Neenah Slough on June 30, 1987, was

Table 4. Mean daily suspended-sediment concentration, sediment load, and water temperature, Fox River at Appleton, Wisconsin

[Fox River at Appleton, Station 04084445, water years 1986-88. Mean, maximum, and minimum daily average concentrations of suspended sediment, in milligrams per liter. Sed-load, suspended-sediment load, in megagrams (Mg) per month; Mg/d, megagrams per day; Discharge, monthly mean discharge, in cubic meters per second (m^3/s); Water temperature, in degrees Celsius; -, no data]

WATER YEAR 1986, SUSPENDED SEDIMENT

Month	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
Mean	--	--	--	--	--	--	--	--	--	30.6	25.2	22.6
Maximum	--	--	--	--	--	--	--	--	--	48.8	38.7	58.2
Minimum	--	--	--	--	--	--	--	--	--	17.6	18.0	14.2
Sed-load	--	--	--	--	--	--	--	--	--	11,280	8,077	15,610
Discharge (m^3/s)	--	--	--	--	--	--	--	--	--	132	110	252

WATER YEAR 1987, SUSPENDED SEDIMENT

Month	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
Mean	14.7	20.0	6.6	3.8	3.1	10.9	28.0	24.9	31.0	26.4	35.5	27.4
Maximum	26.2	91.4	14.7	9.8	6.4	29.6	48.0	39.0	46.7	39.3	104.0	39.4
Minimum	9.1	9.9	1.7	1.8	.8	3.3	9.8	12.6	24.3	18.2	18.8	18.4
Sed-load	15,270	8,677	2,018	1,628	1,159	3,008	8,241	7,716	6,035	3,236	4,507	3,728
	(Total annual load, 71,897 Mg; mean daily load, 197 Mg/d)											
Discharge (m^3/s)	383	164	111	158	154	102	118	117	72.2	45.7	47.4	53.8
Temperature												
Mean	[1]11.4	3.4	.4	.7	1.6	3.4	10.3	17.2	23.6	25.7	24.3	20.1
Maximum	14.2	10.4	.6	1.5	2.6	6.5	15.9	22.4	26.6	28.2	29.1	22.1
Minimum	10.3	.7	.3	.4	.4	.9	4.1	13.2	20.9	22.7	20.5	18.3

WATER YEAR 1988, SUSPENDED SEDIMENT

Month	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.
Mean	16.5	17.3	10.2	9.1	14.6	44.6	40.8	28.1	33.0	34.1	38.5	30.8
Maximum	41.0	40.0	18.0	24.0	59.0	128.0	100.0	47.0	49.0	50.0	54.0	97.0
Minimum	9.0	12.0	6.0	5.0	5.0	13.0	23.0	11.0	21.0	25.0	25.0	20.0
Sed-load	2,574	4,796	4,027	3,056	4,939	13,632	15,144	5,708	2,991	2,444	2,836	2,807
	(Total annual load, 71,598 Mg; mean daily load, 196 Mg/d)											
Discharge (m^3/s)	55.0	110	144	125	139	117	131	76.0	35.2	26.7	27.5	34.7
Temperature												
Mean	11.0	6.2	1.7	1.2	1.6	4.8	10.1	18.9	24.2	25.2	25.4	19.6
Maximum	17.1	11.2	3.4	2.1	2.8	7.4	12.2	24.2	26.8	27.2	28.7	22.5
Minimum	7.8	2.7	1.1	1.0	1.0	2.8	7.4	13.6	21.7	21.0	20.8	17.1

[1]Monthly average based on partial month starting October 8.

130 ng/L. This sample was collected after an intense thunderstorm over the Neenah industrial area. The concentration of total PCB's downstream at Appleton the same day was only 84 ng/L. Thus, industrial-area runoff may be a continuing source of PCB's to Little Lake Butte des Morts. The high concentration of total PCB's in the Neenah Slough may be caused by the proximity of the sample site to sediment-deposit area A (pl. 1). The concentration of PCB's in this deposit area is up to 190 μg/g. Wind and the effects of wave action from Little Lake Butte des Morts cause occasional upstream flow into the Neenah Slough. This deposit is probably the result of past discharge from the paper mill upstream on the Neenah Channel but could be the result of runoff from industrial areas next to the Neenah Slough.

Landfills adjacent to Little Lake Butte des Morts include Arrow Head Park and the site of the Menasha sewage-treatment plant. The Arrow Head Park landfill may contain a significant amount of PCB's (John Sullivan, Wisconsin Department of Natural Resources, oral commun., 1986). The buried PCB's may be slowly entering the river in ground-water flow. Ground-water samples collected from the landfill by the WDNR had concentrations of PCB's of up to 1.9 μg/L (1,900 ng/L) (Rick Stohl, Wisconsin Department of Natural Resources, oral commun., 1990).

There are several potential point-source discharges of PCB's into Little Lake Butte des Morts. Three paper mills and two sewage-treatment plants discharged water into the lake during the study period. Effluent samples were collected from each site about every three months by WDNR. The samples were analyzed with a detection limit of 0.2 μg/L (200 ng/L). No PCB's were detected in any of the samples.

These dischargers are not likely to be a significant source of PCB's. The combined discharge from all point sources near Little Lake Butte des Morts is about 22.8 Mgal/d (million gallons per day), or about 35.3 ft^3/s. If the average concentration of PCB's in effluent was 0.2 μg/L (200 ng/L), the PCB's load to the lake would be 17.2 g/d (grams per day). This load would be equivalent to a Fox River concentration at Appleton of 1.7 ng/L when the discharge is 119 m^3/s.

DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN BOTTOM SEDIMENT

Distribution of polychlorinated biphenyls in Little Lake Butte des Morts is associated with the distribution of soft-sediment deposits. Sullivan and others (1983) found that PCB's were associated with unconsolidated (soft) sediment deposits in Little Lake Butte des Morts. They reported PCB's concentrations of 1.0 to 250 μg/g dry weight in the bottom sediment. These deposits were found in embayments and in the deep areas of Little Lake Butte des Morts. Mapping of the soft-sediment deposits was followed by selection of sites for sediment coring. Total mass of PCB's associated with bottom sediment was computed by use of the sediment-core data. Methods, data, and computations are discussed in succeeding sections of this report.

Determination of Bottom-Sediment Mass

Mapping of the unconsolidated (soft) sediment within Little Lake Butte des Morts was necessary to ensure representative sampling of bottom sediment. A total of 48 cores were extracted for analysis. Cores were extracted only from areas of soft sediment where PCB's are most likely to accumulate. Areal extent and thickness of soft sediments were identified within Little Lake Butte des Morts by manually probing the bottom of the lake. The areas and depth of soft sediment were delineated on a scale-stable enlargement of the topographic maps of the lake. That map was then used to identify sites for extraction of cores. Thickness contours for 1, 2, 3, and greater than 3.5 ft of soft sediment were delineated on the map. The mass of sediment at a depth greater than 3.5 ft was not quantified for the study because there was no indication of detectable concentrations of PCB's below that depth. Six major areas of soft sediment were delineated as A, B, C, D, E1-E2, and F on plate 1.

Ten sediment cores (numbers 51 to 60 in squares shown on plate 1) were extracted for the determination of bulk density of bottom sediment. Bulk-density and particle-size data are presented in table 5. Bulk density (in kilograms per liter) was determined by dividing the dry weight of the sediment core by the volume of the coring tube at the maximum penetration depth. Depth of penetration

Table 5. Bulk density and particle size of bottom sediment, Little Lake Butte des Morts, Wisconsin, October 1987
[lb/ft^3, pound per cubic foot; kg/L, kilograms per liter; %, percent; m, meter; mm, millimeter; --, not applicable]

Sediment-deposit area	A	B	C	D	E1
Core site[1]	51	52	53	54	55
Bulk density, (kg/L)	.309	1.39	.358	1.57	.253
Size (mm) % smaller than					
16	100.0	100.0	100.0	99.0	--
8	98.6	91.0	99.9	96.2	100.0
4	95.9	77.8	99.4	92.7	99.4
2	93.7	68.4	99.1	87.6	99.0
1	91.0	63.4	98.9	82.7	98.4
.50	87.3	58.0	98.5	73.3	97.7
.25	78.2	52.3	98.0	53.3	94.8
.125	64.8	41.8	96.7	27.5	65.1
.062	52.2	37.2	94.1	22.0	27.6
Penetration, (m)	.76	.18	.76	.25	1.0
Type of material	Gray mud	Black sand and gravel, over red clay	.13 m of black mud over .23 m of red clay	Red clay mixed with black sand and shells	Dark-brown mud
Sediment-deposit area	E2	E2	E2	E2	E2
Core site[1]	56	57	58	59	60
Bulk density, (kg/L)	.253	.170	.071	.107	.277
Size (mm) % smaller than					
16	99.6	--	--	--	91.6
8	99.6	--	--	--	90.9
4	99.3	--	--	--	88.0
2	99.1	100.0	--	100.0	85.2
1	99.1	99.9	--	99.9	82.9
.50	98.7	99.8	100.0	99.8	78.6
.25	97.7	99.6	99.9	99.5	65.1
.125	96.4	98.5	99.6	99.4	49.0
.062	88.2	90.8	97.0	98.2	46.6
Penetration, (m)	.41	.91	1.22	.91	.30
Type of material	Brown mud	Dark-brown mud	Dark-brown thick mud	Dark-brown loose mud	Gray mud

[1]Core-site number refers to location shown on plate 1.

was determined from the residue line on the outside of the coring tube. The line was legible for all cores.

The bulk density of soft-sediment deposits ranged from 0.071 to 1.57 kg/L. The higher values are caused by the dense mixture of sand and clay in cores from the southern end of the lake. The mass of bottom sediment for each deposit area was determined by multiplying its volume by its average whole-core bulk density. The results of these calculations for each deposit are presented in table 6. The total mass of soft sediment for all the deposit areas is 478,000,000 kg, as computed by this method.

Table 6. Mass of soft-bottom sediment in Little Lake Butte des Morts, Wisconsin, October 1987
[m, meter; m x 10^3, thousand cubic meter; kg/L, kilograms per liter]

Depth of sediment (meter)	Sediment volume (m x 10^3)	Bulk density[1] (kg/L)	Mass of sediment (kilogram)
	Sediment-deposit area A		
0 to 0.30	40	.309	1.2×10^7
0.30 to 0.61	36	.309	1.1×10^7
0.61 to 0.91	30	.309	9.2×10^6
		Total mass of sediment =	3.3×10^7
	Sediment-deposit area B		
0 to 0.30	36	1.39	5.1×10^7
0.30 to 0.61	19	1.39	2.6×10^7
0.61 to 0.91	7.9	1.39	1.1×10^7
		Total mass of sediment =	8.8×10^7
	Sediment-deposit area C		
0 to 0.30	32	.358	1.2×10^7
0.30 to 0.61	26	.358	9.2×10^6
0.61 to 0.91	18	.358	6.3×10^6
		Total mass of sediment =	2.7×10^7
	Sediment-deposit area D		
0 to 0.30	61	.253	1.6×10^7
0.30 to 0.61	33	.253	8.5×10^6
0.61 to 0.91	13	.253	3.2×10^6
		Total mass of sediment =	2.7×10^7
	Sediment-deposit area E1		
0 to 0.30	110	.253	2.8×10^7
0.30 to 0.61	84	.253	2.1×10^7
0.61 to 0.91	59	.253	1.5×10^7
		Total mass of sediment =	6.4×10^7
	Sediment-deposit area E2		
0 to 0.30	440	.192	8.4×10^7
0.30 to 0.61	380	.192	7.3×10^7
0.61 to 0.91	330	.192	6.4×10^7
		Total mass of sediment =	2.2×10^8
	Sediment-deposit area F		
0 to 0.30	41	.170	7.0×10^6
0.30 to 0.61	32	.170	5.4×10^6
0.61 to 0.91	26	.170	4.3×10^6
		Total mass of sediment =	1.7×10^7
Total mass of sediment in Little Lake Butte des Morts is 4.8×10^8 kilograms.			

[1]Bulk density value used in calculations is based on a whole-core average and is not differentiated by depth of sediment. Mass was computed in pounds and converted to kilograms for reporting purposes.

Porosity was not computed for the sediment cores because the net weight of sediment samples was not determined. The specific density (gm/cm^3) was not determined for dry-weight sediment. Field notes indicate that specific density varied widely among cores, depending on location.

Concentration of Polychlorinated Biphenyls in Bottom Sediment

Forty-eight sediment cores were collected from Little Lake Butte des Morts in October 1987 for determination of solid phase (sediment) PCB's concentrations. Core locations and sample identification numbers are shown on plate 1. Cores were collected by personnel of the WDNR who used a stainless-steel, piston-coring unit supplied by the USGS. This corer was able to sample sediments within 1 meter of the sediment surface.

The length of core was measured at the time of sampling, and the type of material in the core was noted. The cores were divided into halves or thirds depending on the length of the core and type of material. The top section of each core was designated as section A; succeeding lower sections were designated B and C. Short cores less than .3 m (1 ft) were not subdivided and were designated as a single section. The PCB's concentration, in micrograms per gram of dry bottom sediment, was determined for each core section. These determinations were done by the WSLH by means of packed-column gas chromatography with an electron-capture detector. Total gross PCB's concentrations in the bottom-sediment samples were determined.

This analysis has a detection limit of 0.05 µg/g (Wisconsin State Laboratory of Hygiene, 1987). Details of the PCB's extraction and concentration methods are given in the Wisconsin State Laboratory of Hygiene (1987) reference. The concentrations (table 7) ranged from less than 0.05 to 190 µg/g; the highest concentration was found at site 4 of deposit-area A.

The PCB's concentrations at core site 1 indicate a relatively uniform distribution with depth, unlike data from the other 47 sites. Core site 1 is nearest to the mouth of the Neenah Slough. This distribution might be the result of continuing inflow and deposition of PCB's from the Neenah Slough watershed. Suspended sediment with a uniform PCB's concentration might be deposited near the mouth and undergo little subsequent resuspension.

The only evidence for burial of PCB's in the lake sediments is found in the data for core 15. Concentration of PCB's are higher at the bottom of the core than at the top. However, the discontinuous nature of the distribution indicates that an older PCB's deposit may have been covered by more recent deposition of PCB's. Burial in sediment does not appear to be the predominant fate of PCB's in the lake.

A 0.76 m thick sediment deposit at the gage site was completely removed by the river discharge in September 1986 (table 1). Sediment at virtually all deposit areas shown on plate 1 is subject to resuspension at higher river discharge or tributary inflow. This indicates that frequent resuspension of the surficial bottom sediments prevents any significant long-term burial of PCB's in the lake.

Direct comparison of the 1987 and past (Sullivan and others, 1983) concentrations of PCB's in bottom sediment of the lake might not be valid. Differences in PCB's concentration could be caused by core location or the length of core section used in the concentration analysis. However, the analytical method used to determine concentrations of PCB's were the same for the 1982, 1983, and 1987 samples (Wisconsin State Laboratory of Hygiene, 1987), and general comparison of the data supports the premise that concentrations of PCB's in the bottom sediment of Little Lake Butte des Morts are declining over a span of years. Concentrations of PCB's shown in table 8 are from cores taken from the embayment at the mouth of Neenah Slough (sediment-deposit area A, pl. 1). Sediments in this area have the highest concentration of PCB's within the lake and are not subject to high velocity currents of the Fox River.

Table 7. Concentration of polychlorinated biphenyls in bottom-sediment cores, Little Lake Butte des Morts, Wisconsin, October 1987

[Data are from Wisconsin State Laboratory of Hygiene; concentrations in micrograms per gram of dry sediment; <, less than; --, no sample section]

Site of core	1	2	3	4	5	6	7	8	9	10	11	12	13
Section A	29	35	60	190	160	0.58	4.0	0.72	2.4	--	--	--	--
B	31	<.05	.08	2.0	.47	.11	--	--	--	--	--	--	--
C	27	.06	<.05	.71	<.05	<.05	.06	--	.09	<.05	<.05	<.05	0.37
Depth of core penetration: (in meters)	.61	.46	.46	.61	.61	.46	.46	.15	.46	.30	.30	.25	.08
Site of core	14	15	16	17	18	19	20	21	22	23	24	25	26
Section A	.98	4.5	3.0	.12	.45	--	.96	.22	.38	.10	--	<.05	--
B	--	.50	--	<.05	.07	--	.08	<.05	--	<.05	--	<.05	--
C	.23	8.0	.30	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
Depth of core penetration: (in meters)	.30	.38	.30	.30	.30	.02	.38	.30	.21	.55	.09	.76	1.22
Site of core	27	28	29	30	31	32	33	34	35	36	37	38	39
Section A	2.1	.11	--	<.20	--	<.05	.41	4.2	.39	.96	<.05	.75	<.05
B	--	<.05	--	<.05	--	<.05	<.05	<.05	<.05	<.05	--	<.05	<.05
C	<.05	<.05	<.05	<.05	<.05	<.05	<.05	.06	<.05	<.05	<.05	<.05	<.05
Depth of core penetration: (in meters)	.25	.46	.91	.46	.06	.91	.38	.38	.25	.46	.30	.56	.91
Site of core	40	41	42	43	44	45	46	47	48	49		50	
Section A	1.3	<.05	<.05	<.05	--	<.1	<.05	<.05	.07	No sample possible, solid rock bottom		No sample possible, solid rock bottom	
B	.08	<.05	<.05	<.05	--	--	<.05	--	--				
C	<.05	<.05	<.05	<.05	<.05	<.05	<.05	--	--				
Depth of core penetration: (in meters)	.91	.76	.91	.91	.18	.30	.46	.25	.08				

Table 8. Concentration of polychlorinated biphenyls in bottom-sediment cores, Little Lake Butte des Morts, Wisconsin, 1982, 1983, and 1987

[Concentration in micrograms per gram; cores from soft sediment-deposit areas]

	1982 (3 cores)	1983 (7 cores)	1987 (5 cores)
Average concentration of PCB	176	125	95
Maximum concentration of PCB	250	246	190
Minimum concentration of PCB	48	25	17

Calculation of Mass of Polychlorinated Biphenyls in Soft-Bottom Sediment

The mass of PCB's in soft-bottom sediment was computed by use of bulk density, sediment-volume information, and concentrations of PCB's in cores. Mass of PCB's was determined for each area of soft-sediment deposit shown on plate 1.

Theissen polygons were developed to delineate the area represented by each sediment core. An average concentration in each 1-ft-depth interval of sediment was determined as the area-weighted average of the Theissen polygons within the area. Concentrations of less than 0.05 µg/g were assumed equal to 0.025 µg/g for computation. The mass of sediment in a deposit area was computed for each 1-ft-depth interval by use of the following equation:

$$SED_{mass} = \text{bulk density} \times \text{volume} \times (0.454) = \text{kilograms of sediment,} \qquad (2)$$

where bulk density is in pounds per cubic foot,
sediment volume is in cubic feet, and
the conversion factor 0.454 is in units of kilograms per pound.

The mass of PCB's associated with the bottom sediment for each 1-foot interval is computed by use of the mass of sediment given in table 6 and the following equation:

$$PCB's_{mass} = PCB's \times SED_{mass} \times 10^{-6} = \text{kilograms PCB's,} \qquad (3)$$

where PCB's concentration is in micrograms per gram,
SED_{mass} is sediment mass in kilograms, and
the conversion factor 10^{-6} is in units of grams per microgram.

The results of these calculations are given in table 9. The total mass of PCB's in bottom sediment of Little Lake Butte Des Morts as of October 1987 is estimated to be 1,100 kg by use of this method. Approximately 90 percent of the total mass of PCB's is in the deposit-area A. More than 80 percent of the total mass of PCB's in the bottom sediment are in the upper 0.3 meter of the deposit-area A. (The distribution of PCB's in bottom sediment is shown in figure 2.)

ADVECTIVE TRANSPORT OF POLYCHLORINATED BIPHENYLS

PCB's are being transported out of the lake by streamflow in dissolved and suspended particulate fractions. The dissolved fraction of PCB's was operationally defined as passing through a glass-fiber filter with a nominal pore size of 0.7 micrometers (see Appendix). A large part of this dissolved PCB's fraction is probably associated with colloidal particulate organic matter. PCB's are hydrophobic organic compounds that readily partition to organic particulate matter (Smith and others, 1988). Therefore, the dissolved PCB's concentrations referred to throughout this report are assumed to contain an undetermined amount of colloidal particulate PCB's. Bed-load transport of PCB's out of the lake is not significant. The bed load of sediment was too small to be measured or calculated with standard methods. The bottom of the Fox River channel at the gaging station is primarily bedrock. More than 70 percent of the sediment load consists of particles smaller than sand.

Collection and Analysis of Data on Transport of Polychlorinated Biphenyls

Samples of water for PCB's analysis were collected at the Lutz Park gage site in Appleton (pl. 1), located at the outlet of Little Lake Butte des Morts. Samples of water were also collected from both the Neenah and the Menasha channels, just upstream from the dams on each channel. These samples were collected to verify that inflow from Lake Winnebago was not a significant source of PCB's to the study area.

A large sample (about 16 L) of water was needed for analysis. This large sample volume was needed to analyze for PCB's in the range of 1 to 100 ng/L (nanograms per liter). A peristaltic pump equipped with teflon tubing was used to routinely collect these samples at the gage site. Depth-integrated, equal-discharge increment (EDI) water samples were also collected to determine if the discharge-weighted concentration of PCB's was equal to that in the pump samples. These EDI samples, which closely represent the cross-sectional average concentration of PCB's (Guy and Norman, 1970), were collected with a 1-L

Table 9. Mass of polychlorinated biphenyls in bottom sediment of Little Lake Butte des Morts, Wisconsin, October 1987
[kg, kilogram; PCB, polychlorinated biphenyls; mg/g, micrograms per gram; m, meter

Depth (m)	PCB's (µg/g)	Mass (kg)	Depth (m)	PCB's (µg/g)	Mass (kg)
Deposit-area A (5 cores)			Deposit-area B (3 cores)		
0.0 to 0.30	70	880	0.0 to 0.30	.08	4.1
0.30 to 0.61	3.7	40	0.30 to 0.61	.08	2.1
0.61 to 0.91	3.0	28	0.61 to 0.91	.08	.9
Mass of PCB in area A =		948	Mass of PCB in area B =		7.1
Deposit-area C (5 cores)			Deposit-area D (4 cores)		
0.0 to 0.30	1.1	12	0.0 to 0.30	1.44	22.4
0.30 to 0.61	.16	1.5	0.30 to 0.61	2.0	16.9
0.61 to 0.91	.16	1.0	0.61 to 0.91	2.0	6.4
Mass of PCB in area C =		15	Mass of PCB in area D =		46
Deposit-area E1 (7 cores)			Deposit-area E2 (22 cores)		
0.0 to 0.30	.096	2.7	0.0 to 0.30	.556	46.9
0.30 to 0.61	[1].025	.5	0.30 to 0.61	.031	2.3
0.61 to 0.91	[1].025	.4	0.61 to 0.91	.031	2.0
Mass of PCB in area E1 =		3.6	Mass of PCB in area E2 =		51
Deposit-area F (2 cores)			All deposit areas, (48 cores)		
0.0 to 0.30	.27	1.9	0.0 to 0.30 = 970 kg		
0.30 to 0.61	[1].025	.1	0.30 to 0.61 = 64 kg		
0.61 to 0.91	[1].025	.1	0.61 to 0.91 = 38 kg		
Mass of PCB in area F =		2.1	Total PCB mass of all areas is approximately 1,100 kilograms.		

[1]The PCB concentration is assumed to be one-half the detection limit.

glass bottle suspended in a weighted wire-basket sampler. The sampler was lowered into the water column to obtain a depth-integrated sample at each of three discharge centroids; six fillings of the bottle were obtained at each centroid. All water was composited into a 20-L stainless-steel pressure canister for transporting to the laboratory. Pumped samples were composited directly into the stainless-steel canister. Tests made for this study showed that PCB's were less prone to adhere to stainless steel than glass (Crane, 1990).

Concentrations of PCB's in the water samples were determined jointly by the Water Chemistry Department of the University of Wisconsin-Madison and the Wisconsin State Laboratory of Hygiene. All samples obtained for determination of PCB's concentration were filtered and extracted within 24 hours of collection. Analytical methods used were similar to those described by Marti and Armstrong (1990). A description of the analytical method is presented in the Appendix. This method had an 87-percent average recovery of PCB's for nine samples analyzed. The detection limit for total PCB's was determined to be 3.0 ng/L. The detection limits for dissolved and particulate PCB's fractions were 1.2 and 1.9 ng/L. Concentrations of less than 10 ng/L were reported to a tenth of a nanogram. The data relating to the transport of PCB's are summarized in table 10.

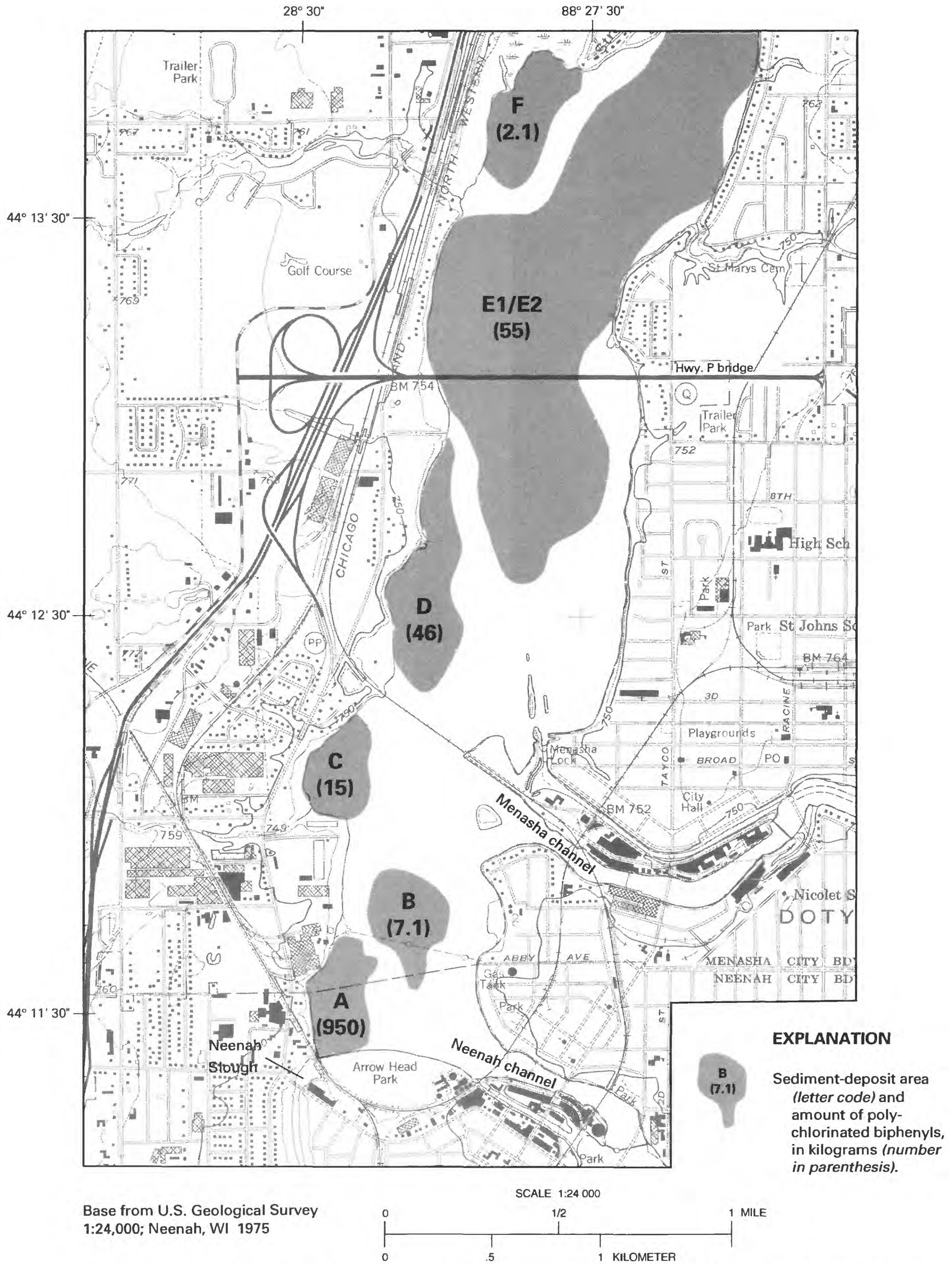

Figure 2. Distribution of polychlorinated biphenyls in Little Lake Butte des Morts, October 1987.

Table 10. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics, gage at Appleton, Wisconsin, and nearby sites in Little Lake Butte des Morts, 1987-88
[Data for Fox River at Appleton, USGS station number 04084445, unless otherwise indicated; m^3/s, cubic meters per second; °C, degrees Celsius; ng/L, nanogram per liter; mg/L; milligram per liter, mg/gm, microgram per gram; gm/d, gram per day; TOC, total organic carbon; DOC, dissolved organic carbon; POC, particulate organic carbon; FOC, fraction organic carbon; P-PCB's/Solids, particulate PCB's per gram suspended solids; T-PCB's, total PCB's; EDI, equal discharge increment sample; --, no data; <, less than; ≤, less than or equal to]

Date of sampling	Daily mean streamflow (m^3/s)	Temperature of water (°C)	Dissolved PCB (ng/L)	Particulate PCB (ng/L)	Suspended solids (mg/L)	TOC (mg/L)	DOC[1] (mg/L)	POC (mg/L)	FOC	P-PCB/ solids (mg/gm)	Total PCB (ng/L)	T-PCB load (gm/d)
4-07-87	83.8	7.8	15	49	[2]16.6	10	--	--	--	2.95	64	464
4-30-87	222	13.3	23	92	[2]27.5	9.2	--	--	--	3.34	115	2,210
5-26-87	82.1	16.4	16	50	[2]17.1	9.0	7.6	1.4	.08	2.92	66	468
Menasha Dam	--	--	<1.2	4.2	[2]8.4	8.9	7.8	1.1	--	--	4.2	--
Neenah Dam	--	--	<1.2	2.2	8.41	10	8.0	2.0	--	--	≤2.2	--
Neenah Slough[3]	--	--	2.5	28	--	7.6	5.9	1.7	--	--	28	--
6-30-87	45.0	23.4	27	57	[2]16.0	9.3	7.2	2.1	.13	3.56	84	327
Neenah Dam	--	--	<1.2	1.9	3.21	--	--	--	--	--	≤1.9	--
Neenah Slough[3]	--	--	20	110	[2]91	--	--	--	--	--	130	--
7-14-87	44.8	24.4	30	50	22.7	11	7.4	3.6	.16	2.20	80	310
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
7-28-87	44.8	26.6	30	66	20.0	12	8.1	3.9	.20	3.30	96	372
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
8-12-87	43.6	24.6	34	103	39.0	14	8.4	5.6	.14	2.64	137	517
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
8-25-87	46.4	22.6	20	62	36.4	14	8.2	5.8	.16	1.70	82	329
EDI	--	--	17	50	36.6	13	8.1	4.9	.13	1.36	67	269
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
9-08-87	38.0	21.8	22	55	33.1	14	9.3	4.7	.14	1.66	77	253
Menasha Dam	--	--	<1.2	<1.9	12.0	12	8.2	3.8	--	--	<3.0	--
9-22-87	61.2	18.4	22	48	22.0	11	7.5	3.5	.16	2.18	70	370
EDI	--	--	25	59	29.0	--	--	--	--	2.03	84	444
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
10-06-87	53.2	13.4	16	29	16.6	11	7.9	3.1	.19	1.75	45	207
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
10-20-87	34.8	11.4	13	24	10.6	9.6	7.9	1.7	.16	2.26	37	112
EDI	--	--	13	30	13.0	10	7.8	2.2	.17	2.31	43	130
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
11-03-87	77.9	10.4	8.9	36	21.1	11	8.1	2.9	.14	1.71	45	303
Menasha Dam:	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
11-17-87	89.5	8.7	22	105	39.4	9.3	7.0	2.3	.06	2.66	127	983
EDI	--	--	11	46	16.0	8.7	7.0	1.7	.11	2.88	57	441
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
12-01-87	153	3.4	4.4	12	12.5	9.2	7.4	1.8	.15	.96	16	212
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
12-17-87	137	1.1	2.4	5.2	9.3	--	--	--	--	.56	7.6	90.1
Neenah Dam	--	--	<1.2	5.8	--	--	--	--	--	--	≤7.0	--
1-05-88	107	1.1	1.4	2.1	3.8	7.4	6.4	1.0	.26	.55	3.5	32.5
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
Neenah Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
1-26-88	130	1.0	33	58	7.0	9.0	7.2	1.8	.26	8.29	91	1,020
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
3-15-88	118	3.3	9.2	12	3.3	8.3	6.8	1.5	.46	3.64	21	214
Menasha Dam	--	--	<1.2	2.6	--	--	--	--	--	--	≤3.8	--
Neenah Dam	--	--	<1.2	2.1	--	--	--	--	--	--	≤3.3	--
3-22-88	116	4.3	5.1	8.0	3.7	7.9	6.4	1.5	.40	2.16	13	130
Menasha Dam	--	--	<1.2	<1.9	--	--	--	--	--	--	<3.0	--
6-01-88	47.6	25.5	21	49	30.8	8.2	6.3	1.9	.06	1.59	70	288
Menasha Dam	--	--	<1.2	4.1	--	--	--	--	--	--	≤5.3	--

Table 10. Transport data for polychlorinated biphenyls and related physical and water-quality characteristics, gage at Appleton, Wisconsin, and nearby sites in Little Lake Butte des Morts, 1987-88--Continued

Date of sampling	Daily mean streamflow (m^3/s)	Temperature of water (°C)	Dissolved PCB (ng/L)	Particulate PCB (ng/L)	Suspended solids (mg/L)	TOC (mg/L)	DOC[1] (mg/L)	POC (mg/L)	FOC	P-PCB/ solids (mg/gm)	Total PCB (ng/L)	T-PCB load (gm/d)
6-21-88	33.4	25.9	25	48	21.6	11	8.2	2.8	.13	2.22	73	211
EDI	--	--	21	34	14.8	11	7.4	3.6	.24	2.30	55	159
Menasha Dam	--	--	<1.2	2.8	--	--	--	--	--	--	≤4.0	--
7-12-88	26.1	25.4	24	46	22.4	12	8.9	3.1	.14	2.05	70	158
EDI	--	--	29	75	24.9	11	7.8	3.2	.13	3.01	104	235
Menasha Dam	--	--	1.5	2.3	--	--	--	--	--	--	3.8	--
8-01-88	27.2	26.2	27	50	27.2	9.8	7.9	1.9	.07	1.84	77	181
EDI	--	--	28	70	43.9	13	7.7	5.3	.12	1.60	98	231
Menasha Dam	--	--	<1.2	2.6	--	--	--	--	--	--	≤3.8	--
8-24-88	27.7	24.0	20	62	[2]21.3	9.5	--	--	--	2.91	82	196
EDI	--	--	23	67	[2]26.0	12	--	--	--	2.58	90	216
Menasha Dam	--	--	<3.0	<3.0	--	--	--	--	--	--	<3.0	--
9-13-88	26.8	21.2	17	29	[2]15.1	11	7.9	3.1	.20	1.92	46	106
EDI	--	--	17	25	[2]12.8	11	8.9	2.1	.16	1.95	42	97.2
Menasha Dam	--	--	<3.0	4.0	--	--	--	--	--	--	4.0	--
10-03-88	72.4	17.2	9.0	31	[2]12.5	7.3	6.4	.9	.07	2.48	40	322
EDI	--	--	8.3	31	[2]23.5	7.8	6.7	1.1	.05	1.32	39	246
Menasha Dam	--	--	<3.0	<3.0	--	--	--	--	--	--	<3.0	--

[1]DOC concentration based on a 1.0-liter sample passed through a 0.45-micrometer glass fiber filter.
[2]Samples indicated are suspended-sediment concentrations determined by filtering a 0.5-L sample through a 1.6 micrometer glass fiber filter.
[3]Neenah Slough, USGS station number 04084419, tributary to Fox River downstream of the Neenah channel.

The data summary shown in table 10 includes both measured and computed data. Streamflow is the daily mean discharge for the Fox River at the Appleton gage site. PCB's samples were collected at discharges ranging from 26.1 to 222 m^3/s. The water temperature for sampled dates ranged from 1.1 to 26.6°C. The suspended-solids data in table 10 are based on either an analysis for suspended solids or suspended sediment. The suspended-solids data were determined as the average concentration value of duplicate or triplicate samples. The analysis for suspended solids employed a 50-mL sample volume passed through a 1.0-micrometer Nuclepore filter. The 50-mL sample is drawn with a pipette and does not include sand-sized particles. The suspended-sediment analysis uses a single, 500-mL sample passed through a 1.6 micrometer Whatman filter, and includes any sand particles in the water sample. The combined suspended solids and suspended-sediment concentration data are collectively referred to as "suspended particulates" in this report when no distinction is made between the analytical method used. The suspended-sediment data are denoted in footnote 1 in table 10. The difference between suspended solids and suspended-sediment concentrations in samples collected at the same time has been determined to be statistically different at the 95 percent confidence level; with the suspended solids generally showing higher concentrations. The USGS typically analyzes for suspended sediment, whereas sanitary or hygiene-oriented laboratories typically analyze for suspended solids.

Concentrations of particulate organic carbon (POC) were determined as the difference between total and dissolved organic carbon. The fraction of suspended sediment that is organic carbon (FOC), was computed by dividing the POC concentration by the suspended particulates concentration.

The concentration of PCB's per gram of dry suspended-particulate matter (SPM) was computed by dividing the concentration of particulate PCB's by the concentration of SPM. The result is expressed as micrograms of PCB's per gram of solids. These units are the same as those for the concentrations of PCB's in the bottom sediment shown in table 7. A comparison of these data with the concentrations of PCB's in the soft sediment indicates that the PCB's concentration on particles suspended in the water column is generally greater than in the bottom sediment. This is true except for a few of the high PCB's concentration deposit areas. The SPM has a higher organic carbon content than the bulk bottom sediment. Visual inspection of water samples reveals that much of the SPM consists of algal detritus. The PCB's per gram of SPM ranged from 0.55 to 8.3 mg/g.

Total concentration of PCB's were computed as the sum of the dissolved and the particulate fractions (table 10). The concentrations of PCB's in water samples collected by the point sampler and those collected from a boat using the EDI method were not significantly different.

A paired t-test statistical procedure was used to determine if there was a significant difference between the concentration of PCB's for samples collected by the two methods at the same time. The difference between the concentrations of PCB's obtained by the two methods was used as the test statistic. Analysis of the data indicated that the mean difference was not statistically different from zero at a 90-percent confidence level–that is, given the variability and the limited number of samples collected by the EDI method, one should not conclude that the concentration difference between the two methods of sampling is significant.

Most of the observed differences in PCB's concentrations are in the particulate PCB's fraction. Some of this difference can probably be attributed to the difference between cross-sectional average river transport and that near shore. There is no clear relation between the concentrations of PCB's in samples collected by EDI methods and those collected by the point sampler. The EDI values are used in plots and statistics in this report unless noted otherwise.

The PCB's data were tested to see if they fit a normal statistical distribution. In many statistical procedures, the data being analyzed are assumed to be normally distributed. If the data are not normally distributed, results can be questionable or invalid. The distribution of total concentrations of PCB's and log transformation of the values were tested for normality assumptions. The January 26, 1988 data were not used in the analysis because of their questionable and unexplained nature. The correlation-coefficient test of the probability plot involves computation of the correlation coefficient between the concentrations and their "normal scores." The "normal scores" are determined by dividing each concentration by the standard deviation of the sampled concentrations. If the data are normally distributed, the correlation coefficient will be close to 1–that is, the plot of the concentrations on probability paper would be approximately a straight line. For a sample size of 30 and a 95-percent confidence level, a correlation coefficient of 0.964 or greater is an indication of normality. The results of this correlation test for the data are as follows:

Total PCB's:	$r = 0.989$
Dissolved PCB's:	$r = .994$
Particulate PCB's:	$r = .971$
Log (Total PCB's):	$r = .915$

Thus, one can be 95 percent confident that total, dissolved, and particulate concentrations of PCB's are normally distributed. The log-normal distribution of concentrations is not as good an assumption for these data. Total, dissolved, and particulate concentrations of PCB's shown in table 10 are statistically described in table 11.

The summary statistics shown in table 11 are based on the water-column concentrations of PCB's at Appleton for 31 point-samples given in table 10 (the January 26, 1988 data were excluded as noted previously). The EDI samples were not used in computing these statistics. The "trimmed mean" is computed by discarding the highest and lowest 5 percent of the observations, and recalculating the mean. If the trimmed mean is significantly different from the sample mean, some of the outliers in the data set might not fit a normal distribution. If the median is significantly different from the sample mean, then the data distribution probably is skewed.

The differences between the sample mean and the trimmed mean, and the sample mean and median should not be considered significant unless it is greater than the standard error of the sample mean. These differences are not significant for the PCB's fractions or the total concentration of PCB's.

Total concentrations of PCB's in water samples from Little Lake Butte des Morts are plotted from April 1987 through October 1988 in figure 3.

Table 11. Summary statistics for total, dissolved, and particulate polychlorinated biphenyls concentrations, at gage at Appleton, Wisconsin
[ng/L, nanogram per liter]

	Maximum (ng/L)	Minimum (ng/L)	Sample mean	Standard error of mean	Sample median	Trimmed mean	Sample standard deviation
Total PCB	137	3.5	60.6	5.9	64.0	59.4	32.8
Dissolved PCB	34	1.4	16.9	1.5	16.0	16.9	8.6
Particulate PCB	105	2.1	43.8	4.6	48.0	42.3	25.6

(The 1/26/88 sample data were not included in the computation of these statistics.)

Concentration of PCB's are greatest in the summer and least in the winter. Total concentration obtained April 30, 1987, does not fit this general relation. The discrepancy might be caused by the discharge of 221.8 m^3/s. This discharge could have caused resuspension of PCB's-laden sediment. Total concentration obtained August 12, 1987, could be related to an unusually high particulate fraction of PCB's.

The PCB's data collected on January 26, 1988 (table 10) might be the result of a significant, but unknown, transport mechanism or process, or the result of an unusual condition under the lake's ice cover. The concentration is abnormally high for the winter. The chemist who analyzed the PCB's concentrations is confident that analytical error is not the cause (Crane, 1990). Two replicate samples collected on January 26 had similar concentrations. Contamination of the solvents used to extract the PCB's from the sample is a possible explanation. Resuspension of PCB's from the bottom sediment is an unlikely explanation because of the low (7 mg/L) suspended-sediment concentration in the samples collected that day, and the relatively normal river discharge. Air temperatures were substantially below freezing that week, so runoff from snowmelt cannot be the cause. There are no known significant point sources of PCB's into the lake; however, there may be unknown sources of PCB's. Because of the uncertain nature of the PCB's data, it was not used in the calculation computing the PCB's load for the Fox River at Appleton. The January 26 data was also not used in some of the statistical analysis presented in this report because the data probably were not representative of the predominant transport mechanisms in the lake.

The relation between particulate and dissolved fractions of PCB's is shown in figure 4. There is a strong positive correlation between the two fractions. Concentrations of particulate PCB's are about 2.5 times that of the dissolved, with a standard error of 13 ng/L. Concentration of particulate PCB's exceeds that of dissolved PCB's in all samples. The two outliers shown on the graph have higher than average suspended-particulates (SP) concentrations.

Relation of Fox River Discharge to Concentration and Load of Polychlorinated Biphenyls

The relation between daily discharge and both the dissolved and particulate concentrations of PCB's at the Appleton gage site is shown in figures 5 and 6. The PCB's concentrations tend to decrease as discharge increases up to about 170 m^3/s. This decrease is probably caused by the dilution of PCB's with increasing flow volume. At discharges greater than 212 m^3/s, the concentration of PCB's seem to increase, however, this interpretation is based on only one data point. In a study of PCB's transport in the Hudson River, Turk and Troutman (1981) found a similar relation of increasing concentration of PCB's with discharge that was based on more high-flow data points.

The trends shown in these figures are supportive of Turk and Troutman's (1981) findings. These figures illustrate possible trends only, and should not be used to predict concentration of PCB's. The trends conform to known physical transport mechanisms. For example, the particulate-PCB's concentration in the water column is expected to increase at very high discharge, as

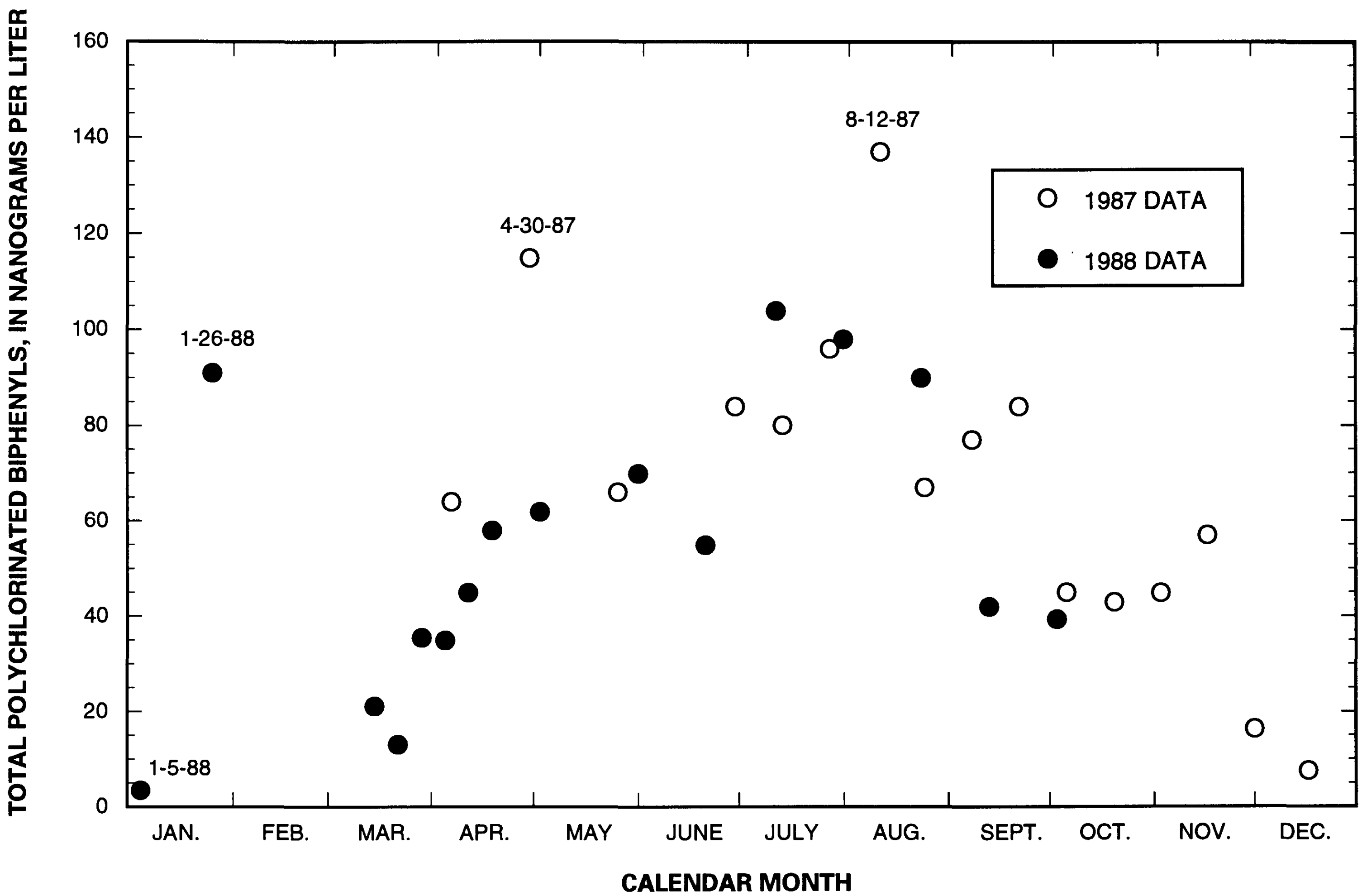

Figure 3. Seasonal relation of total polychlorinated biphenyls concentration, Little Lake Butte des Morts, Wisconsin. (Data from April 1987 through October 1988.)

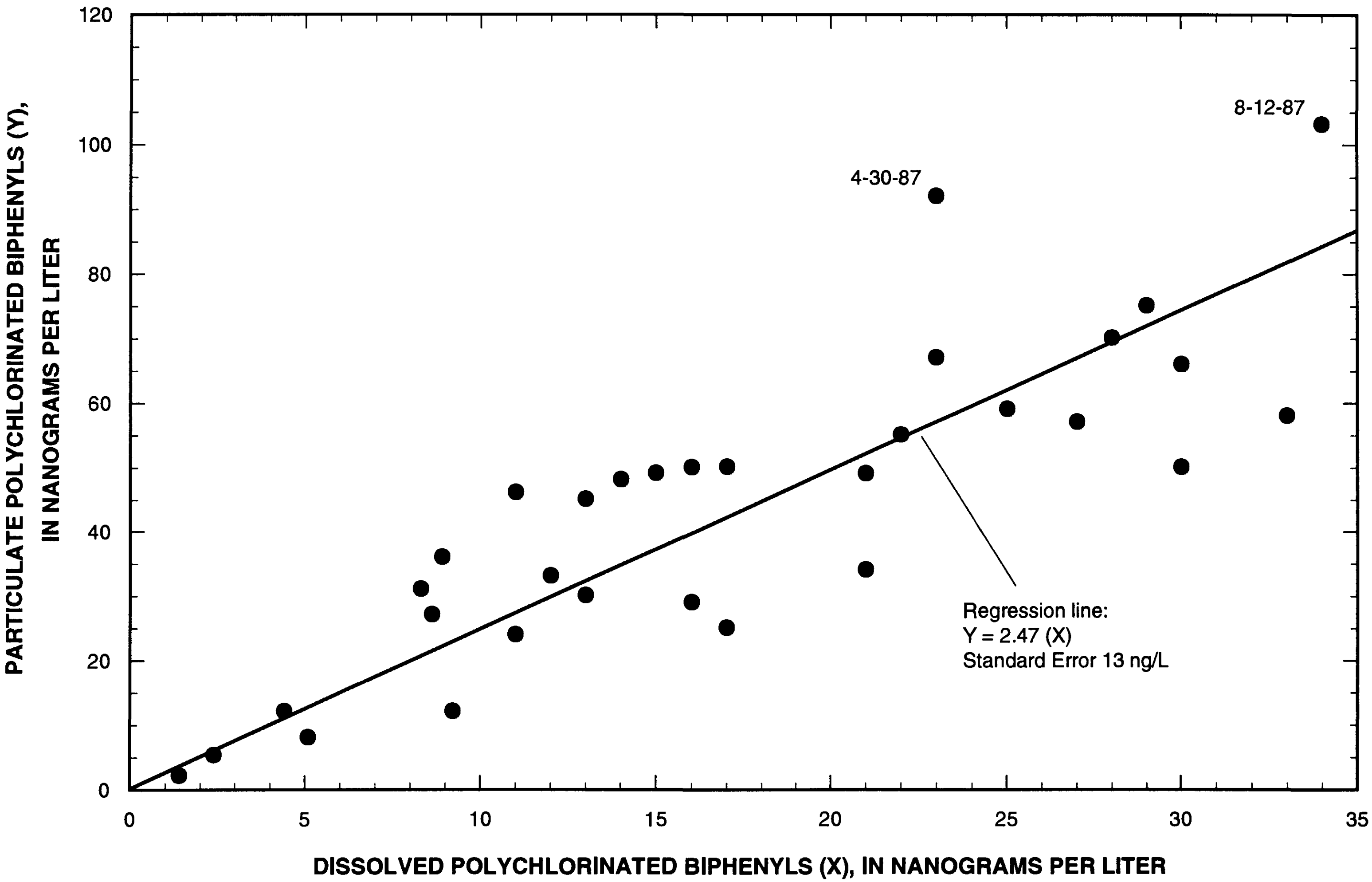

Figure 4. Relation between concentrations of dissolved (X) and particulate (Y) polychlorinated biphenyls, Little Lake Butte des Morts, Wisconsin, 1987-88.

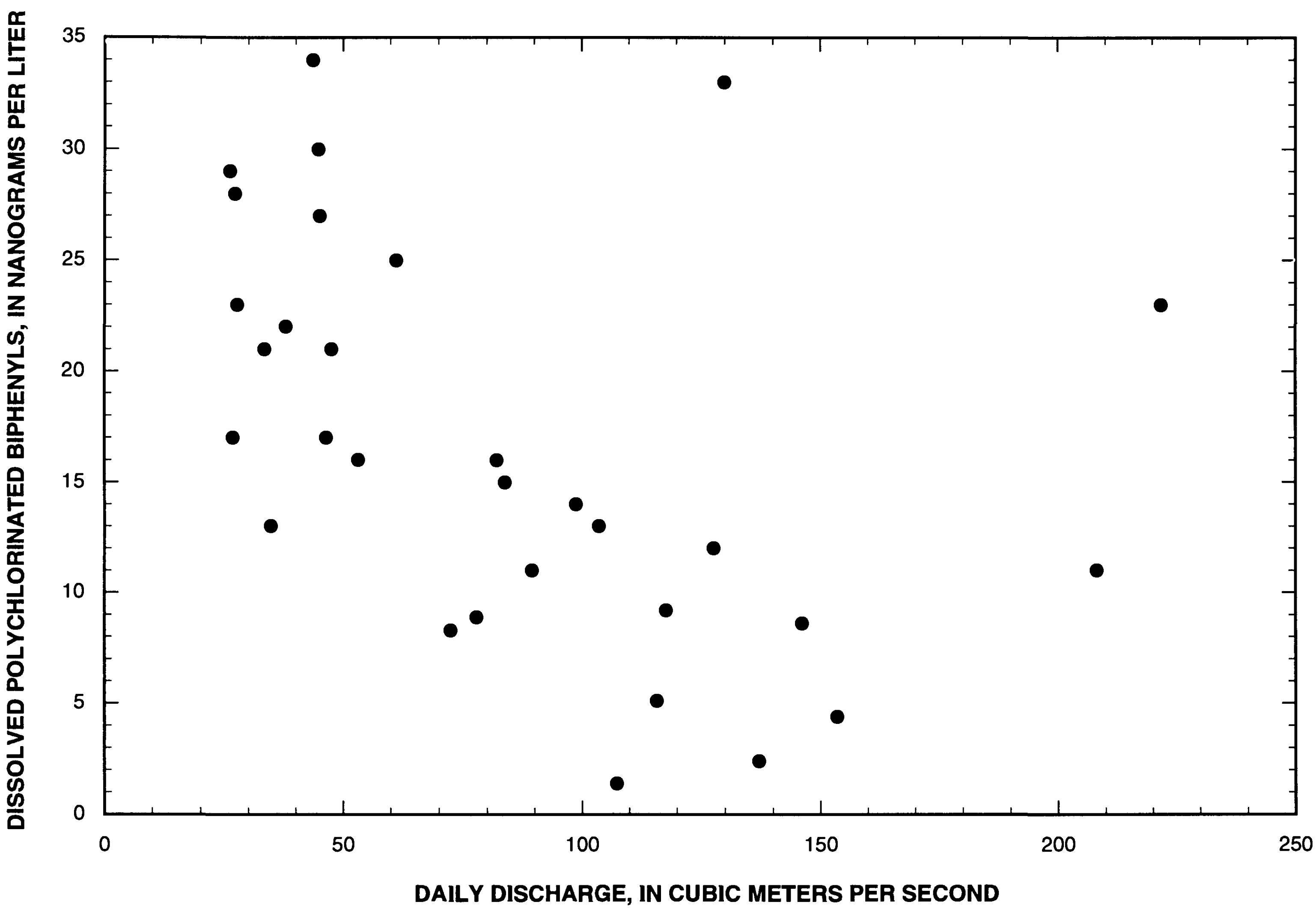

Figure 5. Relation between concentration of dissolved polychlorinated biphenyls and daily mean discharge, Fox River at Appleton, Wisconsin, 1987-88.

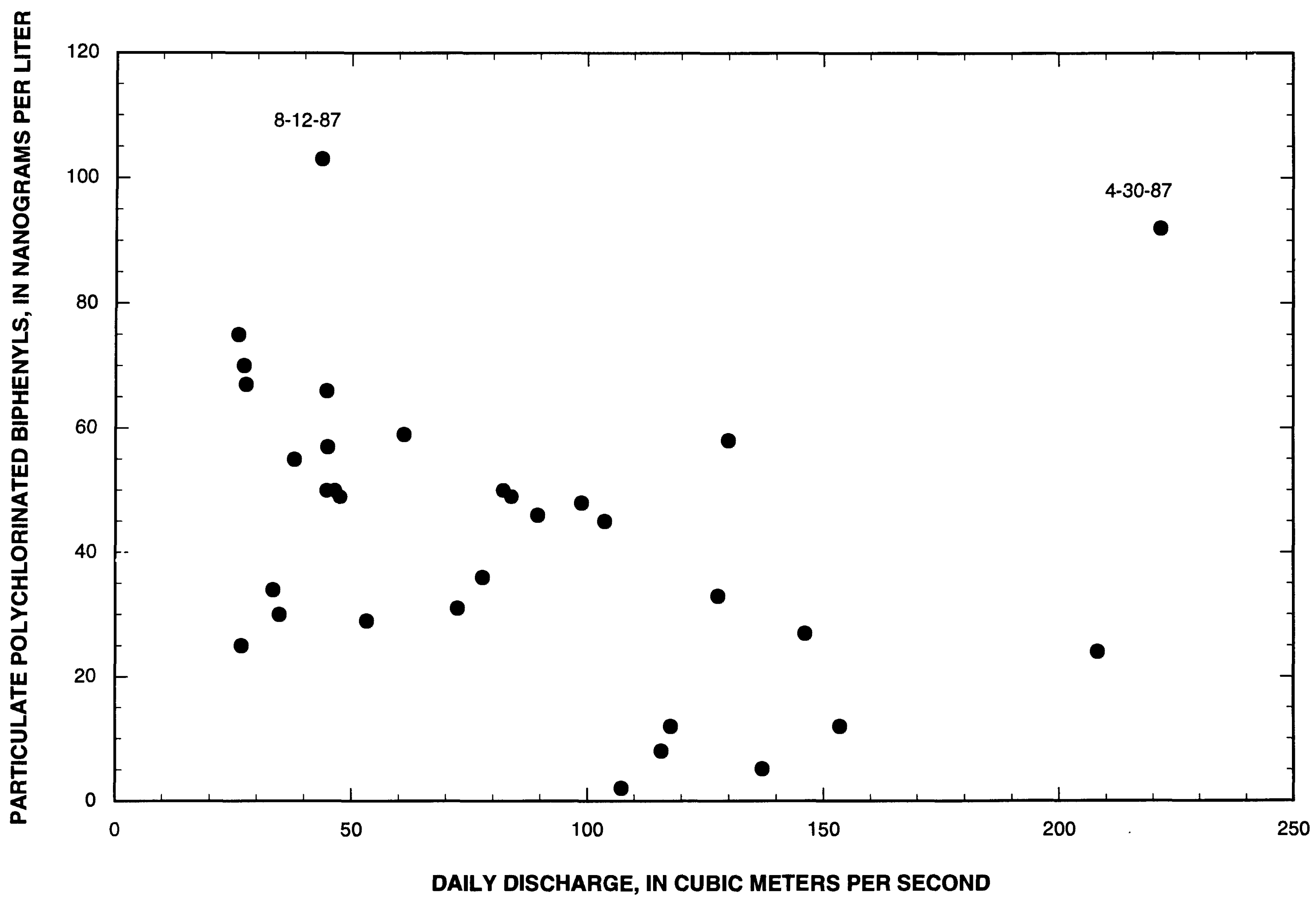

Figure 6. Relation between concentration of particulate polychlorinated biphenyls and daily mean discharge, Fox River at Appleton, Wisconsin, 1987-88.

particulate PCB's are resuspended from the streambed. The dissolved-PCB's concentrations are expected to be high at very low discharge as less flow volume is available to dilute the PCB's released from bottom sediments or discharged from point sources.

The relation between total PCB's concentration and total PCB's load and daily discharge is shown in figures 7 and 8. A trend for total PCB concentration similar to that for particulate PCB's concentrations is shown in figure 7. This similarity is expected as the particulate-PCB's fraction makes up an average 72 percent of the total PCB's concentration (table 11). The relation between total PCB's load and daily discharge is shown in figure 8. The PCB's load seems to increase significantly at discharges greater than about 212 m^3/s, however, this observation is again based on only one data point. The increased load could be caused by direct resuspension of PCB's-laden deposits. This can be caused by Fox River discharge or by tributary inflows such as from Neenah Slough. The data shown in figure 8 indicate that magnitude of the total PCB's load is relatively independent of Fox River discharge at flows less than 170 m^3/s. The daily total PCB's load at Appleton generally varies between 100 and 500 grams for flows of 28.3 to 142 m^3/s. This variability in PCB's load might be explained by the variability of organic carbon content in the water column.

Relation of Particulate Organic Carbon to Transport of Polychlorinated Biphenyls

The average total organic carbon (TOC) concentration found in this study of Little Lake Butte des Morts was 10.2 mg/L (1.9 standard deviation), and an average dissolved organic carbon (DOC) concentration of 7.6 mg/L (0.9 standard deviation). Particulate organic carbon (POC) concentrations for this study were computed as the difference between TOC and DOC. The analytical accuracy of individual TOC or DOC sample concentrations probably is within 1 mg/L (W.C. Songzoni, University of Wisconsin-Madison, oral commun., 1990). The average particulate organic carbon concentration was 2.6 mg/L (1.3 standard deviation). The average ratio of DOC to POC for individual samples was 3.5, whereas the DOC/POC ratio based on the average concentration was 2.9.

Wetzel (1975) states that DOC concentration in natural lakes is typically about ten times that of particulate organic carbon. Previous work by Birge and Juday (1926, 1934) on over 500 Wisconsin lakes found that the average DOC:POC ratio was about 11 to 1. They found the average DOC concentration was 15.2 mg/L, and the average POC concentration was 1.4 mg/L. Lower DOC concentrations and higher POC concentrations than the Birge and Juday averages were observed in Little Lake Butte des Morts. The lower DOC concentration in Little Lake Butte des Morts may be caused by the lower overall productivity of the river system compared to a lake.

The source of most DOC is biologic productivity. The dissolved fraction of organic carbon is operationally defined by the pore size of the filter used to separate the particulate fraction. DOC concentrations may, therefore, include a colloidal-articulate fraction that passes through the filter pores. The source of most particulate organic carbon in aquatic systems is organic detritus (primarily from dead algal cells) and living bacteria, phytoplankton, and zooplankton. Decomposing organic matter in the bottom sediment is known to release colloidal organic carbon particles (Wetzel and others, 1972). These organic colloids consist of biotic microparticles and extremely large organic macromolecules. The macromolecules are predominantly composed of high molecular weight fulvic and humic acid compounds. The colloidal fraction of DOC may be a key vector in the transport of PCB's from the bottom sediment into the water column. PCB's in both sediment and pore water might preferentially partition into the colloidal organic material and become suspended in streamflow. Recent research indicates that up to 90 percent of the dissolved PCB's fraction is actually associated with colloidal organic particulates (Anders Andren, University of Wisconsin-Madison, oral commun., 1990).

The rate of decomposition of the organic detritus in bottom sediments and the release of colloidal particles is affected by temperature. Decomposition generally occurs faster with warmer water

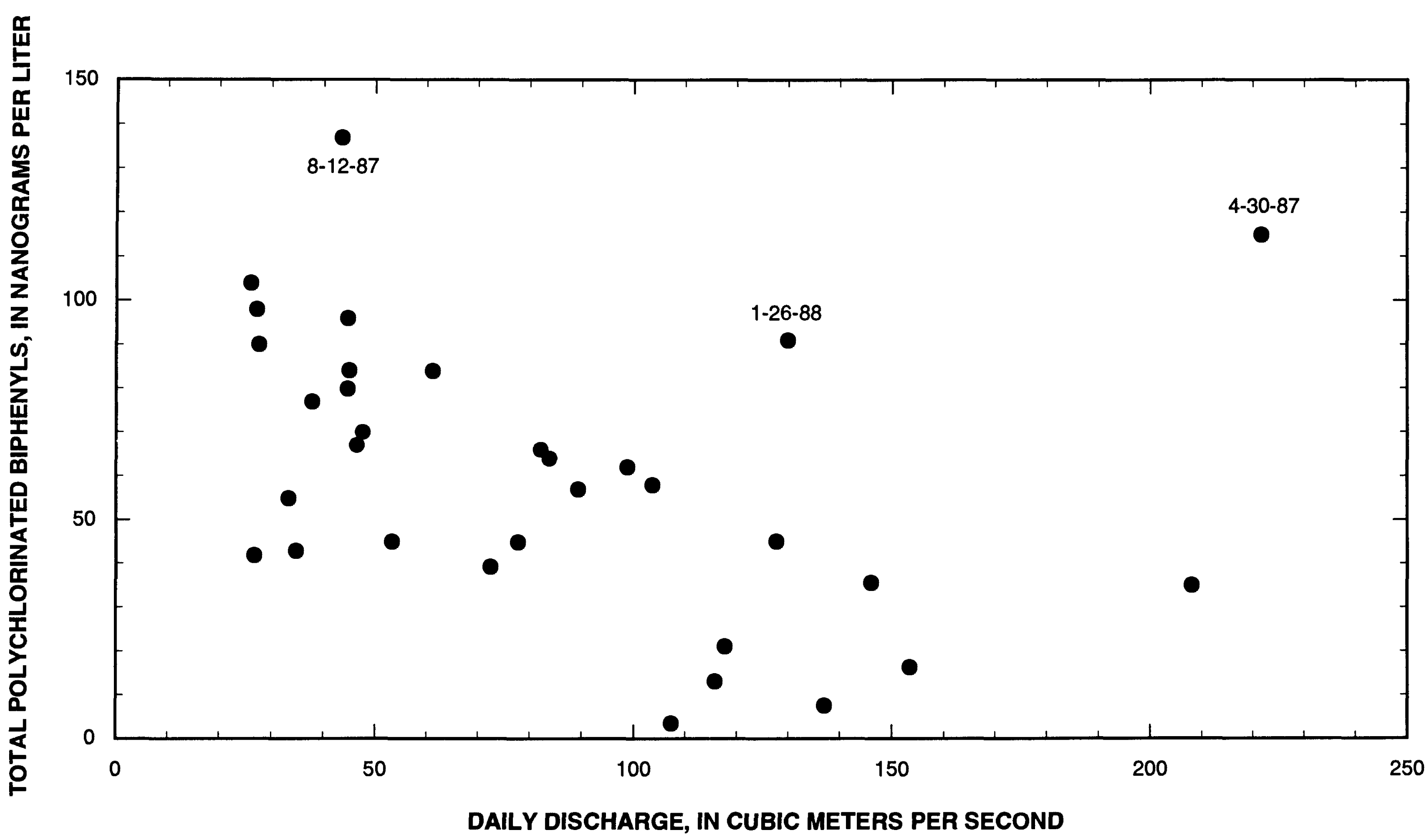

Figure 7. Relation between concentration of total polychlorinated biphenyls and daily mean discharge, Fox River at Appleton, Wisconsin, 1987-88.

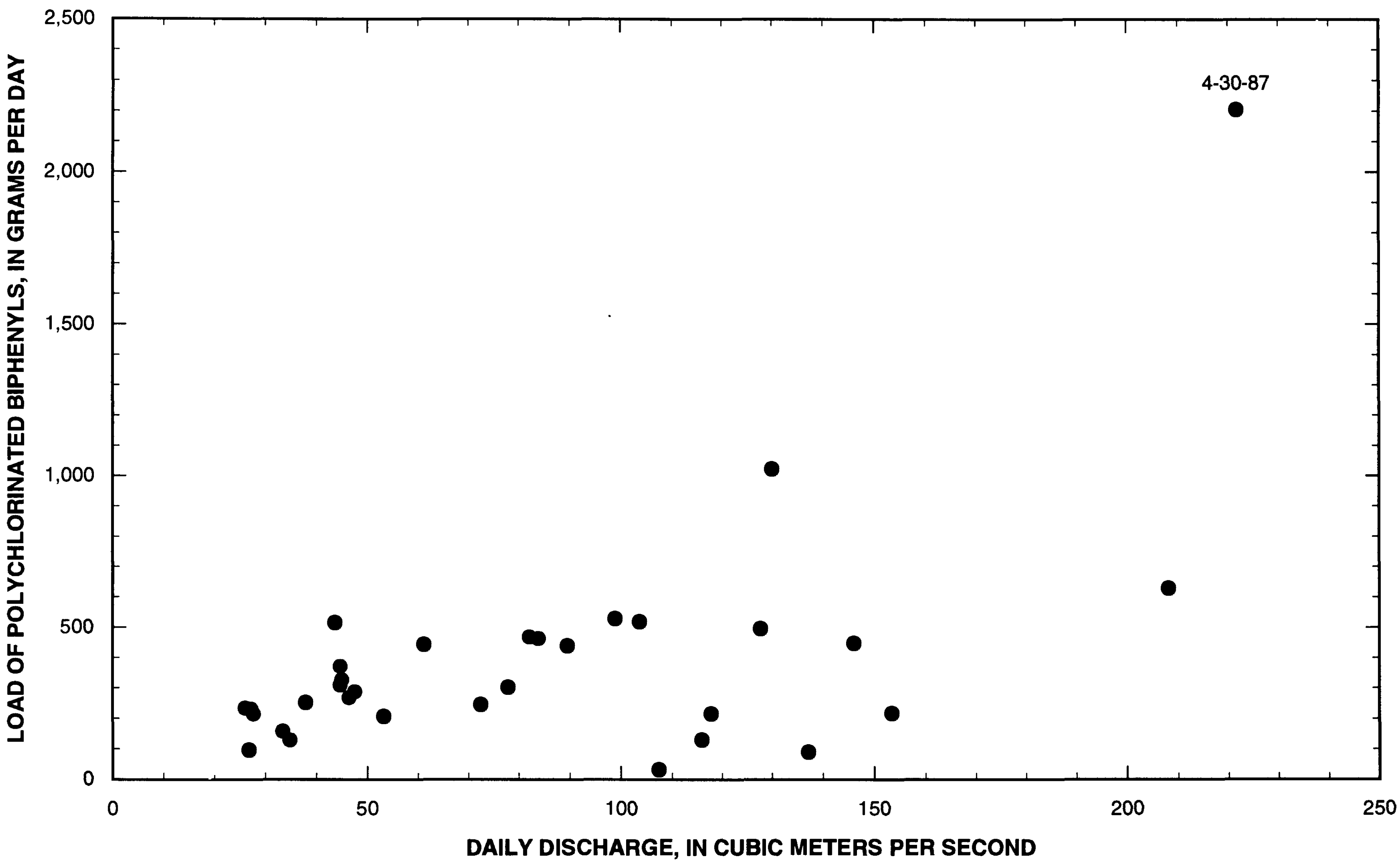

Figure 8. Relation between load of total polychlorinated biphenyls and daily mean discharge, Fox River at Appleton, Wisconsin, 1987-88.

temperatures. Studies have shown that POC concentrations generally increase during periods of warm water temperature, and when bottom sediments are disturbed or resuspended (Wetzel, 1975). POC concentrations were observed to decline in Little Lake Butte des Morts during the winter and early spring, possibly because of a reduction in-lake biologic productivity and the resultant decrease in production of algal detritus during the winter. The reduced winter and spring water temperatures also slow the rate of organic decomposition, with a resultant decrease in the production of colloidal material that is supplied to the water column. Ice cover over the lake may also reduce the disturbance of bottom sediments, and thereby reduce the supply of POC to the water column.

Correlation Analysis of Polychlorinated Biphenyl Concentration Data

Correlation (as used in this report) is a measure of the strength of a linear relation between two variables. Two variables with a perfectly linear (straight-line) relation would have a correlation coefficient (*r*) equal to one. Two totally noncorrelated variables would have a correlation coefficient close to zero. A negative correlation coefficient represents an inverse relation–that is, one variable decreases as the other increases. If two variables have a high correlation coefficient it does not prove a causative relation. The high correlation coefficient could mean that the two variables are related to a third unknown variable that is the causative factor. The reader should also be aware that the input data does not include all possible environmental factors and variables.

The data presented in table 10, excluding the data for January 26, 1988, were used in the correlation analysis. Results are presented in table 12. Only the correlation coefficients with an absolute value of 0.5 or greater are shown. All correlation coefficients shown were determined to be statistically significant at the 99-percent confidence level.

The physical and the water-quality characteristics presented in table 12 are defined as follows:

1. Discharge: daily average streamflow at the Appleton gage site.
2. Water temperature: daily average at the Appleton gage site.
3. Suspended solids: instantaneous sample, concurrent with PCB's sample.
4. Total organic carbon (TOC): determined from a 1-liter sample.
5. Dissolved organic carbon (DOC): determined from a 1-liter sample.
6. Particulate organic carbon (POC): computed as TOC minus DOC.
7. Lag time: previously defined as variable QLAG, hydraulic residence time.
8. Rainfall: computed as total accumulation within the past lag-time number of days; data from the Appleton airport located 6.1 km northeast of the Appleton gage.
9. Photoperiod: hours of daylight.
10. Windspeed: average daily windspeed; data from Appleton airport.
11. North wind: absolute value of north windspeed component; data from Appleton airport.
12. River stage: average daily stage at Appleton gage site.
13. Wind sum: sum of daily average windspeeds over past number of lag-time days; set equal to zero if surface on Little Lake Butte des Morts is frozen.

Variables that were highly correlated with PCB's concentrations were suspended particulates, water temperature, particulate organic carbon, and photoperiod. There is also a strong correlation (r=0.77) between photoperiod and water temperature. In general, the longer the day, the warmer the water. Water temperature and suspended particulates are not as strongly correlated (r=0.67). Concentrations of total and particulate organic carbon are also correlated with PCB's at a greater than 0.5 correlation coefficient. Dissolved organic carbon, wind, and river stage are not strongly correlated with the concentrations of PCB's. Wind-induced resuspension of bottom sediment was originally expected to be a significant factor in transport of PCB's, but this is not sup-

Table 12. Environmental variables correlated with concentrations of polychlorinated biphenyls
[Statistics based on 31 observations (1-26-88 data omitted); °C, degrees Celsius; mg/L, milligrams per liter; m^3/s, cubic meters per second; ng/L, nanogram per liter; d, day; PCB, polychlorinated biphenyls; <, less than]

Variable (unit of measure)	Mean value	Standard deviation	Minimum value	Maximum value
Discharge (m^3/s)	82.0	52.2	26.1	222
Water temperature (°C)	15.3	8.5	1.1	26.6
Suspended particulates (mg/L)	20.4	9.9	3.3	43.9
Total organic carbon (mg/L)	10.2	1.9	7.4	14.0
Dissolved organic carbon (mg/L)	7.6	.9	5.9	9.7
Particulate organic carbon (mg/L)	2.6	1.3	1.0	5.6
Hydraulic residence time (d)	1.7	1.0	.4	3.7
Rainfall (millimeters)	6.1	8.4	0	25.6
Photoperiod (hours)	13.0	2.4	8.2	16.2
Average windspeed (knots)	8.2	3.4	3.0	15.0
North wind (knots)	5.1	3.1	.5	11.5
River stage (meters)	1.68	.11	1.52	1.89
Wind summation (knots)	12.6	8.2	0	33

Variable (unit of measure)	Correlation coefficient (*r*) with: Total PCB	Dissolved PCB	Particulate PCB
Discharge (m^3/s)	<0.5	-0.55	<0.5
Water temperature (°C)[1]	.77	.88	.70
Suspended particulates (mg/L)[2]	.76	.66	.77
Total organic carbon (mg/L)	<.5	.66	.62
Dissolved organic carbon (mg/L)	<.5	<.5	<.5
Particulate organic carbon (mg/L)	.68	.72	.64
Hydraulic residence time (d)	.66	<.5	<.5
Rainfall (millimeters)	<.5	<.5	<.5
Photoperiod (hours)[3]	.69	.77	.64
Average windspeed (knots)	<.5	<.5	<.5
North wind (knots)	<.5	<.5	<.5
River stage (meters)	<.5	-.51	<.5
Wind summation (knots)	<.5	.51	<.5

[1]Cross-correlated with photoperiod, $r = 0.77$
[2]Cross-correlated with water tempature, $r = 0.67$.
[3]Cross-correlation with suspended solids less than r of 0.5.

ported by the statistics. Discharge is inversely correlated with dissolved concentrations of PCB's, probably because of the effects of dilution.

The results of the correlation analysis support the current theory and conceptual models of transport and partitioning of PCB's. PCB's are known to partition into the organic carbon fraction of suspended particulates (Witkowski and others, 1987). The release of colloidal organic carbon particles from decomposing detritus is proportional to water temperature. Quantifying the decomposition and release rates involved are beyond the scope of this investigation.

The lack of a strong correlation between DOC and dissolved PCB's was unexpected. Perhaps the abundance of dissolved organic carbon in the lower Fox River is so great that DOC is not a limiting factor. The Fox River is highly eutrophic, and the average concentration of DOC is 7.6 mg/L. Thurman (1986) notes that the concentration of DOC increases with algal production. Concentrations of DOC in the Fox River are virtually constant (7.6 mg/L average, standard deviation 0.9) throughout the year (table 12), likely reflecting a steady state of DOC production and decomposition.

A multivariate linear-regression analysis was used to examine the variables included in table 12. The PCB's concentrations were used as the dependent variable in the regression analysis. Separate equations were developed to predict total, dissolved, and particulate PCB's concentration. The regression equations were intended to predict PCB's concentrations from other data such as water temperature, photoperiod, suspended sediment, and discharge. The effort did not produce acceptable equations. The residuals of the regression showed increasing error with higher PCB's concentrations and were not uniformly distributed about the mean residual of zero. Transforming the data to log values did not improve the results. The use of a linear regression model to predict PCB's concentration was either not appropriate, or the independent variables used in the regression did not include all relevant factors. Subsequent efforts that relate the biotic solids concentration and chlorophyll-*a* concentration to PCB's concentration show more promise (Jeff Steuer, Wisconsin Department of Natural Resources, oral commun., 1992).

Computation of Monthly Loads of Polychlorinated Biphenyls

Daily and monthly loads of PCB's at the Appleton gage site were computed in units of grams per day and kilograms per month. Loads were calculated using an interpolated daily average concentration of PCB's. Straight-line interpolation of concentration values between water samples shown in table 10 was used. These daily concentrations were then multiplied by the corresponding daily average discharge to compute daily loads. The equation used is given as

$$L_{PCB} = C_{PCB} \times Q_{CFS} \times 0.08651, \qquad (4)$$

where L_{PCB} is PCB's load, in grams per day,

C_{PCB} is PCB's concentration, in nanograms per liter,

Q_{CFS} is daily average discharge, in cubic meters per second; and

0.08651 is the conversion factor to obtain grams per day units.

A summary of the monthly PCB's loads at Appleton is presented in table 13 and figure 9 for total, dissolved, and particulate PCB's. Monthly suspended-sediment loads at Appleton are also presented in table 13 and figure 10. The monthly mean discharge is presented in figure 11. The computed PCB's loads for the winter of 1988 were calculated without use of the January 26, 1988 sample data for reasons noted previously. Daily PCB's concentrations were estimated by interpolation for the period between January 5 and March 15 of 1988. The maximum PCB's loads occurred in April and May 1987. The maximum suspended-sediment loads occurred in March and April 1988. The maximum monthly total load of PCB's seems to follow one month after the maximum suspended-sediment load. The load of dissolved PCB's does not vary as much as the load of particulate PCB's. The monthly load of dissolved PCB's ranged from 1.1 to 7.1 kg, and the monthly load of particulate PCB's ranged from 2.4 to 21 kg.

Table 13. Monthly loads of polychlorinated biphenyls and suspended sediment, Fox River at Appleton, Wisconsin, April 1987 through September 1988
[Loads of dissolved and particulate PCB may not be equal to the total because of interpolation of concentration and round-off differences. PCB loads in kilograms; sediment load in megagrams; --, no data]

		Month											
		Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Total PCB	1987	--	--	--	27	27	14	11	13	10	6.7	11	3.5
	1988	1.7	3.5	6.5	16	13	5.8	6.9	6.6	4.1	--	--	--
	Mean	--	--	--	21	20	9.8	8.8	9.6	7.2	--	--	--
Dissolved	1987	--	--	--	5.8	6.0	3.9	3.6	3.3	3.1	2.0	2.4	1.1
	1988	0.7	1.5	2.3	4.0	3.3	2.0	2.0	1.8	1.3	--	--	--
	Mean	--	--	--	4.9	4.6	3.0	2.8	2.6	2.2	--	--	--
Particulate	1987	--	--	--	21	21	10	7.0	9.3	7.3	4.7	9.0	2.4
	1988	1.0	2.0	4.2	12	9.8	3.8	4.9	4.8	2.8	--	--	--
	Mean	--	--	--	16	16	6.9	6.0	7.0	5.0	--	--	--
Suspended sediment	1987	--	--	--	8,240	7,720	6,040	3,240	4,510	3,730	2,570	4,800	4,030
	1988	3,060	4,940	13,630	15,140	5,710	2,990	2,440	2,840	2,810	--	--	--

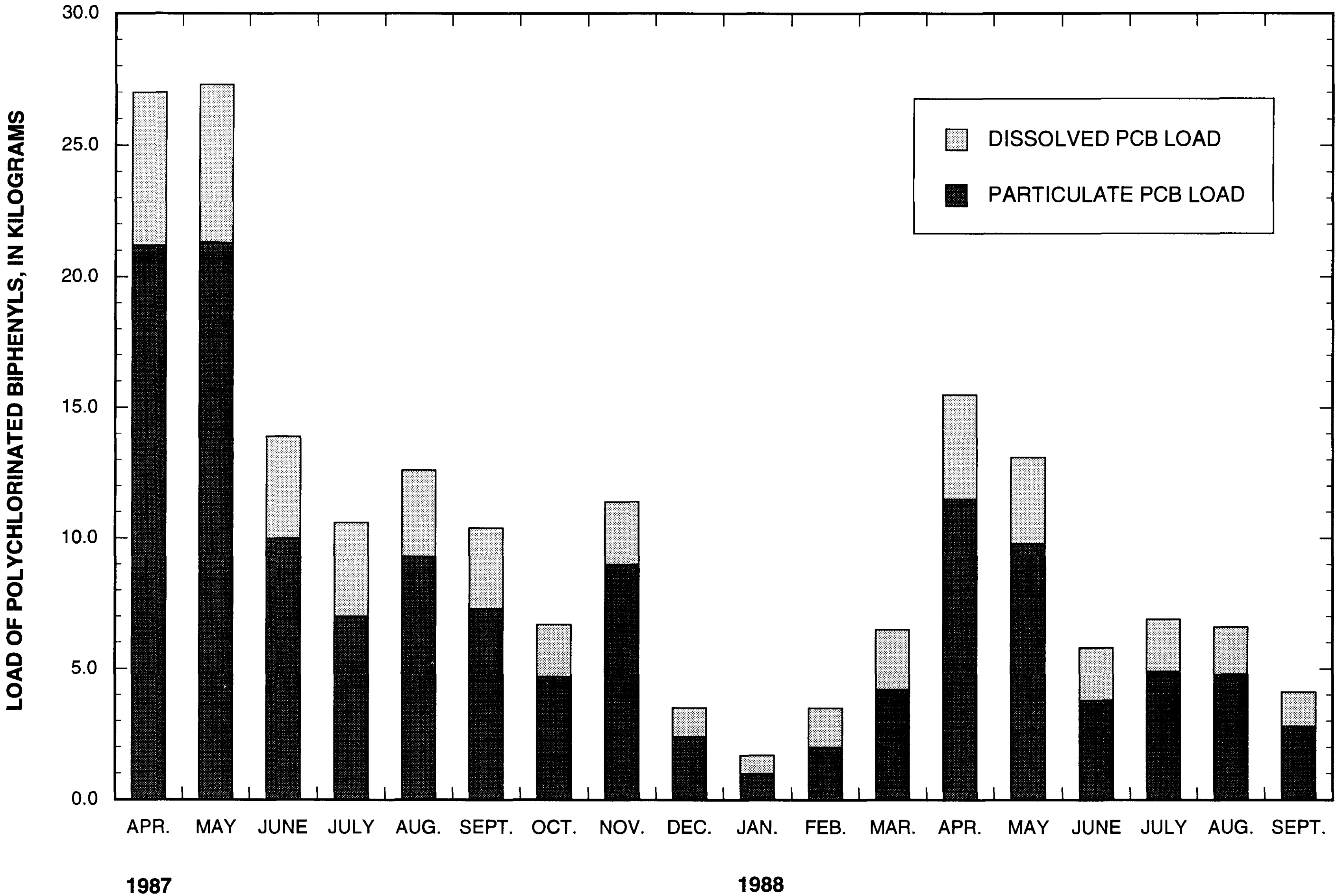

Figure 9. Monthly loads of total, dissolved, and particulate polychlorinated biphenyls (PCB), Fox River at Appleton, Wisconsin, April 1987-September 1988.

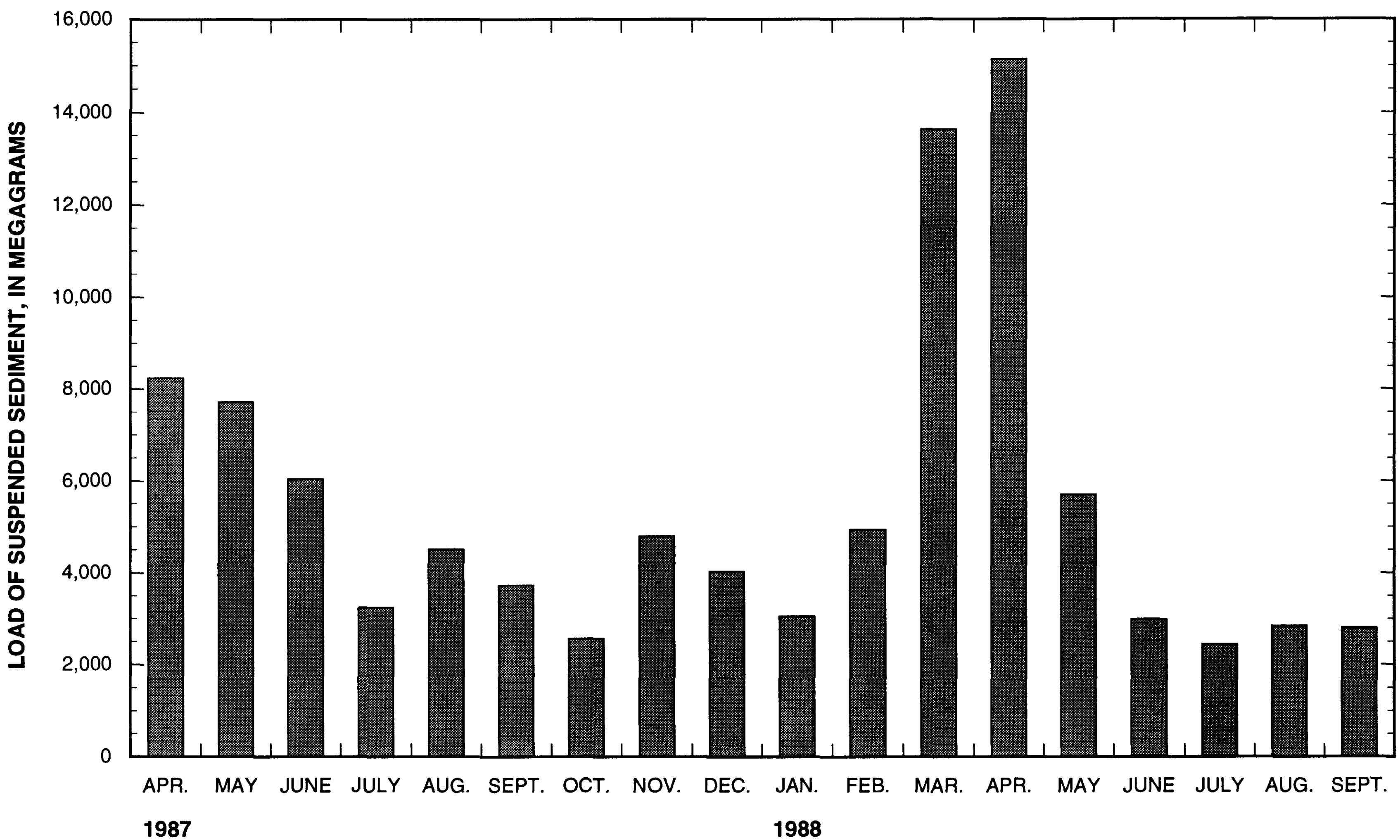

Figure 10. Monthly load of suspended sediment, Fox River at Appleton, Wisconsin, April 1987-September 1988.

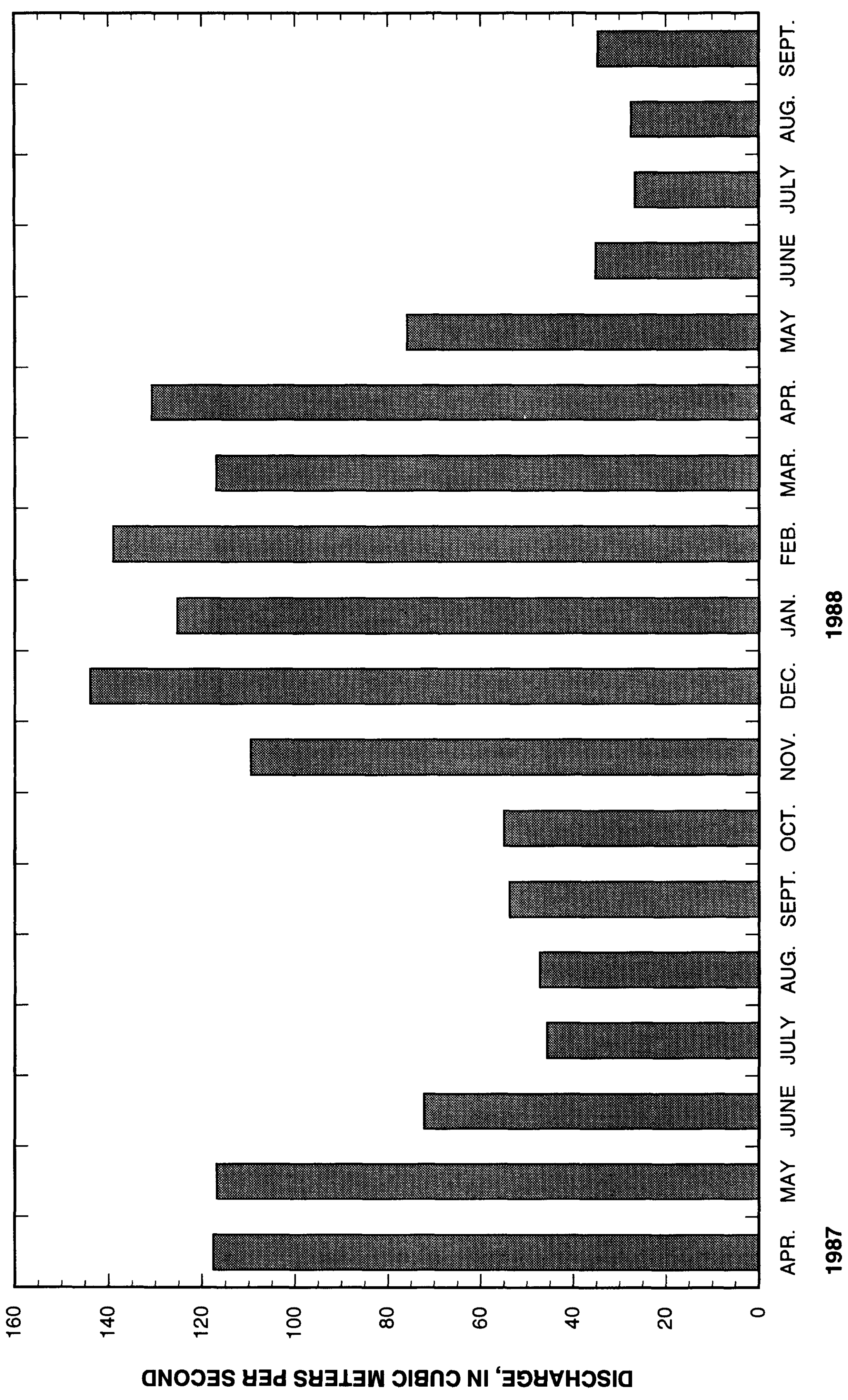

Figure 11. Monthly mean discharge, Fox River at Appleton, Wisconsin, April 1987- September 1988.

The average monthly loads of PCB's were 10.4 kg total, 2.8 kg dissolved, and 7.6 kg particulate during April 1987 through September 1988. The average annual loads of PCB's were 110 kg total, 30 kg dissolved, and 80 kg particulate, based on a water-year period. An average of 77 kg of total PCB's are transported from April through September.

The total load of PCB's transported in the April through September period declined 50 percent from 1987 to 1988. Load of total PCB's from April through September 1987 was 100 kg at the Appleton gage site. The load of total PCB's from April through September in 1988 was 52 kg. A large part of this reduction was caused by below-normal streamflow during the 1988 drought. The load of PCB's in 1988 also declined on a discharge-normalized basis. The discharge-normalized PCB's load was computed as the monthly load of PCB's divided by the monthly mean discharge. The load of PCB's normalized for discharge during the April through September period, was 1,340 g/(m^3/s) per month in 1987 and 953 g/(m^3/s) per month in 1988. Suspended-sediment load remained virtually unchanged at 1,098 and 1,052 megagrams for 1987 and 1988. The reduction in transport rates for PCB's from 1987 through 1988 might be caused by less resuspension of PCB's from deposit-area A (fig. 2). Discharge from the Neenah Slough is suspected of being the primary resuspension mechanism of this deposit and is highly dependent on storm runoff. Reduced runoff from industrial areas might also have resulted in less inflow of PCB's during 1988. The inflow of PCB's from Lake Winnebago (table 10, Neenah and Menasha channels) was not a factor in the change of PCB's transport at the Appleton gage site.

Computation of Polychlorinated Biphenyls Flux Rates in Bottom Sediment

High and low estimates of daily flux rates of PCB's from bottom sediment in Little Lake Butte des Morts are presented in table 14. These estimates are based on the assumption that bottom sediment is the sole source of PCB's in the water column. Flux rates are expressed in terms of milligrams of PCB's per square meter of bottom sediment per day. The flux is the result of several mechanisms that include flow-induced resuspension, bioturbation, and diffusion of PCB's in pore water out of the sediment. The actual flux rate is probably between the high and the low estimates. The high estimate is based on the assumption that all the load of PCB's at Appleton is derived from deposit-area A (table 9 and pl. 1). The surface area of this deposit is about 139,350 m^2. More than 90 percent of the lake's PCB's mass is in deposit-area A. The high estimate of PCB's flux is computed by dividing the indicated month's PCB's load (table 13) by the surface area of deposit-area A, and dividing again by an average of 30.4 days per month. This result is multiplied by 10^6 to get units of milligrams per square meter per day. The low estimate of PCB's flux is based on the assumption that PCB's enter the water equally from all areas of soft sediment within the lake. The total soft bottom-sediment surface area of the lake is 2.81 km^2. The equation used to compute the flux estimates reduces to

$$FLUX_{PCB} = LOAD_{PCB}/K, \qquad (5)$$

where $FLUX_{PCB}$ is daily average PCB's flux rate for month, in milligrams per square meter,

$LOAD_{PCB}$ is monthly average PCB's load, in kilograms, and

K is a conversion factor–4.236 for the high estimate, and 85.57 for the low estimate.

Estimates of the high PCB's flux range from 0.40 to 6.4 (mg/m^2)/d (milligrams per square meter per day); the flux rate was a maximum in May 1987. Estimates of the low PCB's flux range from 0.020 to 0.32; the rate was a minimum in January 1988. The average of all the estimates of high and low PCB's flux rates is 1.2 (mg/m^2)/d.

Loss of PCB's from Little Lake Butte des Morts by volatilization was not considered in the estimation of these flux rates from the bottom sediment. Loss by volatilization was expected to be small because of the relatively short hydraulic residence time in the lake, and the low estimated concentration of PCB's that are truly dissolved (not bound to colloidal organic material). Only the truly-dissolved PCB's are subject to volatilization. The annual vol-

Table 14. Flux rates of polychlorinated biphenyls in bottom sediment, Fox River at Appleton, Wisconsin, April 1987 through September 1988

	April	May	June	July	August	September
Average daily PCB flux [milligrams per square meter per day, (mg/m^2)/d]						
1987						
	April	May	June	July	August	September
High estimate	6.4	6.4	3.3	2.5	3.0	2.5
Low estimate	.32	.32	.16	.12	.15	.12
1987-88						
	April	May	June	July	August	September
High estimate	1.6	2.7	.83	.40	.83	1.5
Low estimate	.078	.13	.041	.020	.041	.076
1988						
	April	May	June	July	August	September
High estimate	1.3	3.1	1.4	1.6	1.6	.97
Low estimate	.065	.15	.068	.081	.077	.048
Average of all high and low flux rate estimates is 1.2 (mg/m^2)/d; standard deviation of 1.6 (mg/m^2)/d						

atilization of PCB's from the lake has been calculated to be at most 5 kg/yr (Jeff Steuer, Wisconsin Department of Natural Resources, oral commun., 1992).

SUMMARY AND CONCLUSIONS

Polychlorinated biphenyls in the bottom sediment and the water column of Little Lake Butte des Morts were studied from April 1987 through October 1988. The study area is a shallow reservoir pool of the Fox River between Lake Winnebago and Appleton, Wisconsin. An assessment was made of the total PCB's mass in the lake and of the PCB's transport out of the lake. Previous discharge of waste containing PCB's into the lake has resulted in bottom-sediment deposits that contain PCB's.

The summer of 1988 was a season of drought. Mean annual discharges of the Fox River at Appleton were 127 and 65.1 m^3/s in water years 1987 and 1988, respectively. Daily discharge ranged from a minimum of 23.8 m^3/s in August 1988 to a maximum of 229 ft^3/s in April 1987. Annual suspended-sediment transport out of Little Lake Butte des Morts was 65,200 megagrams in water year 1987 and 65,000 megagrams in water year 1988. Daily average water temperature ranged from 0.4°C to 29.1°C during the study period.

The amount of PCB's in bottom sediment of Little Lake Butte des Morts was estimated to be 1,100 kg as of October 1987. This estimate was determined from PCB's concentrations in 48 sediment core samples collected from the depositional areas of the lake. The maximum concentration of PCB's in the bottom sediment was 190 µg/g dry sediment. About 950 kilograms of PCB's were estimated to reside in a single area of less than 14,000 m^2. This deposit is probably the result of previous discharge from paper mills, runoff from industrial areas, or both.

Thirty-two water samples were collected at the outlet of the lake to determine the concentration of PCB's. The concentration of total PCB's in the water column ranged from 3.5 to 137 ng/L. Concentration of PCB's in particulates generally was 2.5 times that for the dissolved PCB's fraction.

A correlation analysis was done to determine the degree of association between selected environmental variables and concentrations of PCB's in the water column. The strongest correlations were between PCB's and water temperature, suspended sediment, and particulate organic carbon concentration. Multivariate linear-regression models were not adequate to predict PCB's concentrations from the data available.

The average annual load of total PCB's transported by streamflow from Little Lake Butte des Morts during 1987-88 was 110 kg. Peak loads occurred during April and May of each year. Monthly loads of PCB's during April 1987 through September 1988 ranged from 1.7 to 27 kg. The PCB's transport rate declined from 1,340 g/(m^3/s) per month in 1987 to 953 in 1988. The average flux rate of PCB's from bottom sediment was estimated to be 1.2 (mg/m^2)/d. Flux rates were computed assuming that the only source of PCB's to the study area was from bottom sediment, and that no substantial loss of PCB's from the lake was caused by volatilization.

The data from this study can be interpreted to show that the major controlling factor in PCB's transport under normal discharge conditions is the presence of POC (and the colloidal fraction of DOC) in the water column. Direct resuspension of sediment containing PCB's might occur at Fox River discharges greater than about 212 m^3/s. Scour of the PCB's deposit at the mouth of the Neenah Slough can occur during periods of local runoff. Although concentrations of suspended particulates and total PCB's are correlated, there are significant temporal differences between the occurrence of maximum PCB's and maximum suspended-sediment loads. Calculations of PCB's transport should not be based on suspended-sediment load alone.

Bottom sediments in Little Lake Butte des Morts are a continuing source of PCB's to the Fox River. Point-source discharges of PCB's to the lake are not significant. It is unlikely that all PCB's in the lake will be removed without remedial action, because the primary deposits of PCB's are not subject to scour by the Fox River.

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APPENDIX

METHODS OF ANALYSIS FOR POLYCHLORINATED BIPHENYLS IN THE WATER COLUMN

The following material is a condensed version of that given by Crane (1990).

Introduction

The analytic methods developed for this study were state-of-art at the time (1988). A series of experiments were made to refine the methodology for detecting low-level concentrations of PCB's (ng/L) in the water column. The general methodology closely followed that of Marti (1984), but improvements in the techniques were made with successive experiments.

Glassware Used and Cleaning Protocol

Glassware used included general laboratory glassware; columns (3 cm inside diameter x 17 cm long) for XAD-2 resin (Supelco Inc.); Snyder columns (3 bulb); micro-Snyder columns (1 bulb); concentration flasks; Kuderna-Danish (KD) flasks (250 and 500-mL); receiving vessels graduated in 0.1 mL units; separatory funnels; and chromatographic columns (20 x 325 mm). Sample vials included 1 mL gas chromatograph (GC) vials and 100 microliter GC automatic sampler vials.

All glassware was washed in detergent (Alconox), rinsed with tap water, and then rinsed three times with distilled water. Next, the glassware was covered with aluminum foil and combusted at 450 to 500°C for at least 4 hours.

PCB's Sample Filtration and Extraction

Water samples were transported from the field to the laboratory in a 20 L stainless steel pressure canister. The canisters were stored in a refrigerated locker at the lab until they could be extracted (generally within one day).

A combined filter head and resin column were used to separate PCB's into their respective particulate and dissolved fractions. The resin column was prepared by placing a glass wool plug in the bottom of the glass extraction column (3 cm x 17 cm) and clamping the Tygon drain tubing with a base clamp. A slurry of XAD-2 resin and acetone was added to fill the column with resin to 2 cm below the top joint. The column was capped with another plug of glass wool. The column was drained of acetone and attached to the water extraction apparatus using a stainless steel joint connector.

A 29.3 cm, microfiltration system GC50 grade, glass fiber filter was placed on the filtration head, wetted with distilled water, and secured. The PCB's field sample canister was attached to the filtration head by stainless steel tubing. The sample canister was pressurized to between 5 and 6 pounds per square inch with ultra-pure nitrogen to obtain a sample flow rate of about 200-mL/min. Thus, water passed sequentially through the filter, XAD-2 resin column, and into a carboy. The volume of the filtrate was measured and recorded. Filters were changed as needed to avoid reducing the effective pore size of the filter.

After PCB's extraction, the resin column was removed. The glass wool plug was removed and added to a Soxhlet. Next, the resin column was inverted over the Soxhlet, and acetone was added by pipet until the resin became loose enough to pour out. The column was rinsed with approximately 60-mL of acetone. Approximately 40-mL of hexane was added, followed by enough acetone/-hexane (60/40 mix), to make a total volume of about 300-mL.

Next, any particulate matter remaining in the sample canister was wiped out with a small piece of glass wool and added to the filter Soxhlet. The canister was then rinsed with three 50-mL aliquots of acetone/hexane (60/40). Next, the top part of the filter head was removed, and the filter was folded tightly and added to the Soxhlet. Three, 50-mL rinses of acetone/hexane (60/40) were added to the canister and siphoned through the filter head. All rinses were collected in a flask and added to the filter Soxhlet. Excess solvent left on the bottom of the filter head was removed with a disposable pipet. The inner part of the filter head was wiped with a small amount of glass wool to remove any particulate material.

The water phase in the filter sample Soxhlet WAS found to interfere with PCB's extraction. To solve this problem, the solvent from the filter Soxhlet was added to a separatory funnel and extracted two times with 50 mL-hexane followed by two minutes of vigorous shaking. Acetone was added if an emulsion formed in the separatory funnel. The top layer containing the hexane was transferred back to its original 500-mL round-bottom flask. Enough acetone was added to make the total volume approximately 300-mL.

PCB's samples were extracted in the Soxhlet apparatus for at least 16 hours. When Soxhlet extraction was completed, the solvent extracts for the filter and resin samples were transferred to different separatory funnels. The round-bottom flask was rinsed three times with 10-mL of hexane and the rinses were combined with the sample. Next, the hexane layer was transferred to a 500-mL Kuderna-Danish (KD) flask equipped with a three-bulb Snyder column. The solvent in the KD flasks was condensed down to approximately 10-mL in a steam bath. Next, 50-mL of hexane was added, and the sample was concentrated again to about 10-mL.

Isolation and Clean-up Using Alumina/Silica Gel Chromatography

Glass chromatographic (GC) columns (325 mm x 20 mm) with a 100-mL reservoir, coarse glass frit, and a teflon stopcock were used. About 1 cm of activated sodium sulfate followed by 1 cm of copper was added to the columns. The copper was used to remove sulfur from the samples.

Silica gel was previously activated at 150°C for at least 4 hours, and then added while warm to a 250-mL flask. The Silica gel was deactivated by adding distilled water from a pipet. The flask was sealed immediately and shaken vigorously until cool. Alumina was activated at 450°C for at least 4 hours and then allowed to cool to 150°C. The alumina was also added while warm to a 250-mL flask. The alumina was deactivated by adding distilled water from a pipet. The flask was sealed and shaken until cool. Both the Silica gel and alumina were allowed to stand at least two hours before use.

The chromatographic columns were then filled with about 13 cm of hexane to which a slurry of 8 grams of silica gel in hexane was added. Next, 9 grams of alumina were added and allowed to settle. The columns were topped with 1-2 cm of sodium sulfate. Excess solvent was drained from the column to lower the solvent level to the top of sodium sulfate. Three successive 20-mL rinses of hexane were added to the columns and drained the same way.

The filter and resin PCB's extracts, along with three hexane rinses (1 mL each), were eluted separately through the alumina/silica gel columns. Three 20-mL aliquots of hexane were used to elute the PCB's into their respective KD flask.

Next, the samples were concentrated in a steam bath to approximately 10 mL. The samples were removed from the steam bath, and 0.5 mL of iso-octane was added to each concentration flask. A one-bulb micro-Snyder column was attached for further solvent reduction to about 1.5 mL. The samples were reduced to a final volume of 1.0 mL using a gentle stream of ultra-pure nitrogen. The extract was transferred to a 1 mL GC vial and stored at 0°C, prior to GC analysis.

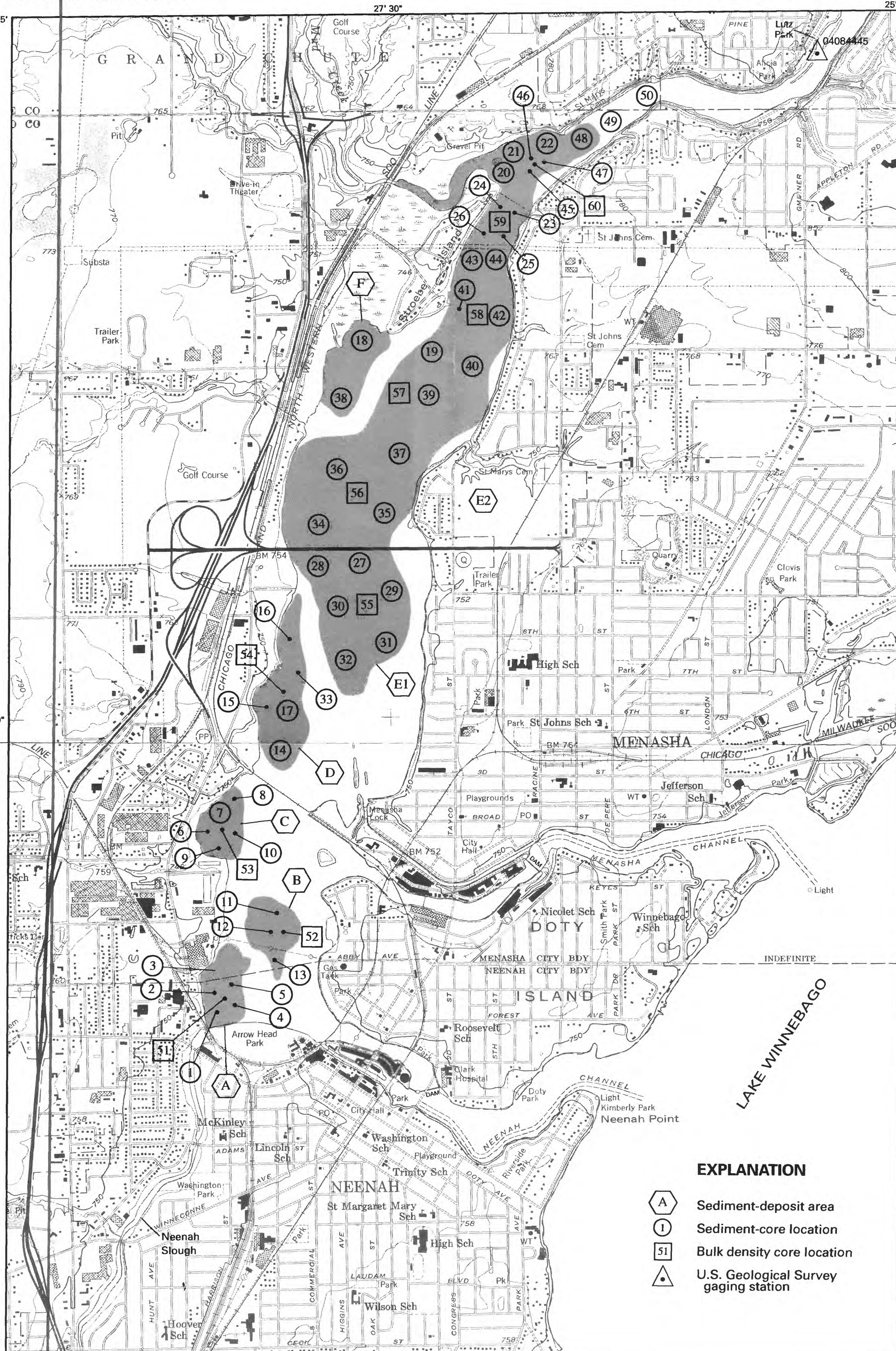
Gas chromatograph analysis for PCB's concentration was done using a Hewlett-Packard model 5830A gas chromatograph (GC) with a model 7671A automatic sampler. This GC used a model 18850A terminal integrator equipped with a 30-m fused-silica capillary column (J & W model db-5, 0.25 micrometer i.d.).

DATA ON PCB'S RECOVERY

A 16 L water sample was spiked with 1 mL acetone containing 723 ng of PCB's Aroclor 1242. The following recovery data was obtained using the method described in this appendix.

Date	Percent Recovery
4/30/87	88
5/26/87	99
6/30/87	101
7/14/87	86
7/28/87	83
8/12/87	78
9/08/87	82
9/22/87	80
10/06/87	92

House, L.B., 1993, Distribution and Transport of Polychlorinated Biphenyls in Little Lake Butte des Morts, Fox River, Wisconsin, April 1987-October 1988



Base from U.S. Geological Survey
1:24,000 Neenah, WI

SCALE 1:24,000

0 ½ 1 MILE

0 .5 1 KILOMETER

CONTOUR INTERVALS 10 FEET

NATIONAL GEODETIC VERTICAL DATUM OF 1929

Plate 1. Sediment-deposit areas and core-extraction sites, Little Lake Butte des Morts, Wisconsin, October 1987.