Technical Memorandum

Model Evaluation Workgroup Technical Memorandum 7a

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Prepared by

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Analysis of Bioaccumulation in the Fox River

Introduction

Evaluating the impact of different sediment management strategies on future polychlorinated biphenyl (PCB) concentrations in tissue of fish from the Lower Fox River, Wisconsin, requires that the relationship between PCB concentrations in fish and sediment be well understood. A directly proportional relationship between PCB concentrations in sediment and tissue is often presumed to exist, based on the chemical properties of PCB (i.e., its lipophilicity) and the assumption that chemical equilibrium is rapidly attained. However, several other factors may also affect the nature and strength of the relationship between PCB in sediment and fish. These factors include:

- Whether sediment is the major source of PCB to fish, either directly or indirectly
- Whether the exposure pathway is direct (e.g., dermal contact or incidental ingestion of sediment while feeding) or indirect (e.g., via a food chain)
- Whether biological processes (e.g., blood flow rate-limited uptake, active degradation) act to regulate fish body burdens of PCB.

A straightforward empirical evaluation of paired fish and sediment data can help determine whether these factors must be considered when predicting PCB concentrations in fish from PCB concentrations in sediment. Scatterplots of sediment and paired fish data can reveal the general form of any relationship, and regression analysis can be used to describe the relationship mathematically and to establish confidence limits for predictions. More direct relationships between fish and sediment are expected to be revealed by clearer trends in scatterplots, and by higher levels of statistical significance. Conversely, when relationships are weak or absent, trends should be difficult to discern in scatterplots and statistical significance will be low or absent. If statistically significant relationships can be identified, then the regression equation can be used as an empirical (as opposed to mechanistic) model of PCB bioaccumulation.

The fish species present in the Fox River have several different feeding strategies, corresponding to different trophic levels in the food web. Species at lower trophic levels (e.g., bottom feeders such as carp) are likely to have more direct exposure to PCBs in sediment than are species at higher trophic levels (e.g., primarily piscivorous fish such as pike). Therefore, because the exposure pathway from sediment to fish is less direct at higher trophic levels, the relationship between PCB concentrations in fish tissue and sediment may also be less clear (not statistically significant) at higher trophic levels.

Species-specific analysis of PCB concentrations in sediment and tissue is necessary to evaluate whether or not the trophic level has an impact on bioaccumulation.

To assess the applicability of empirical bioaccumulation models to fish in the Lower Fox River, fish and sediment data were examined to determine what relationships exist between PCBs in tissue and sediment. Pre-1998 and recent (1998) data were evaluated independently. Pre-1998 data were collected by a variety of investigations over approximately the last two decades, and have been compiled by Limno-Tech (LTI) into a single electronic database for this project. Most of these investigations sampled either sediment or tissue only; the fish species sampled varied between investigations, and sample collection and analysis methods may also have differed between investigations. For these reasons, the pre-1998 data are considered to be generally less suitable for bioaccumulation analyses than the 1998 data. The 1998 data were collected between June and August specifically to evaluate current ecological conditions and processes in the Fox River. Consistent methods were used to analyze the data, and therefore these data allow current bioaccumulation effects to be estimated.

Pre-1998 and recent data were compiled and summarized to generate sets of paired tissue and sediment PCB concentrations for different species, locations, and time periods, as appropriate to the data set. Scatterplots of these data were prepared, and regression analyses carried out. The relationships between fish length and tissue PCB concentration, and between PCB in sediment and benthic invertebrates, were also evaluated to further elucidate potential influences on PCB bioaccumulation. This document presents the results of these analyses.

Data Summarization

The two data sets—pre-1998 and recent—were summarized similarly. Measurements of total PCB in surface sediment were paired with measurements of total PCB in tissue based on proximity in space and time. Assessments of spatial proximity were based on the five different habitat zones, shown in Table 1, that have been identified in the Lower Fox River and Green Bay (Exponent 1998). Environmental conditions and potential PCB exposure are likely to be more uniform within any zone than between zones; thus, tissue and sediment data have been aggregated within each zone. Because fish are mobile, and because fish and sediment were ordinarily not collected at identical locations, it is not appropriate to associate each individual fish measurement within a zone with a single sediment measurement within the same zone. Thus, a single sediment PCB concentration was computed for each zone as the arithmetic average of all measurements of surface sediment within that zone. Similarly, a single fish tissue PCB concentration for each zone, species, and type of tissue (whole body or fillet) was computed as the arithmetic average.

Pre-1998 fish and sediment data were paired if they were collected within one year of each other. Recent (1998) fish and sediment data were all collected within a period of weeks, and so were not segregated by time period. Current sampling locations are shown in Figure 1.

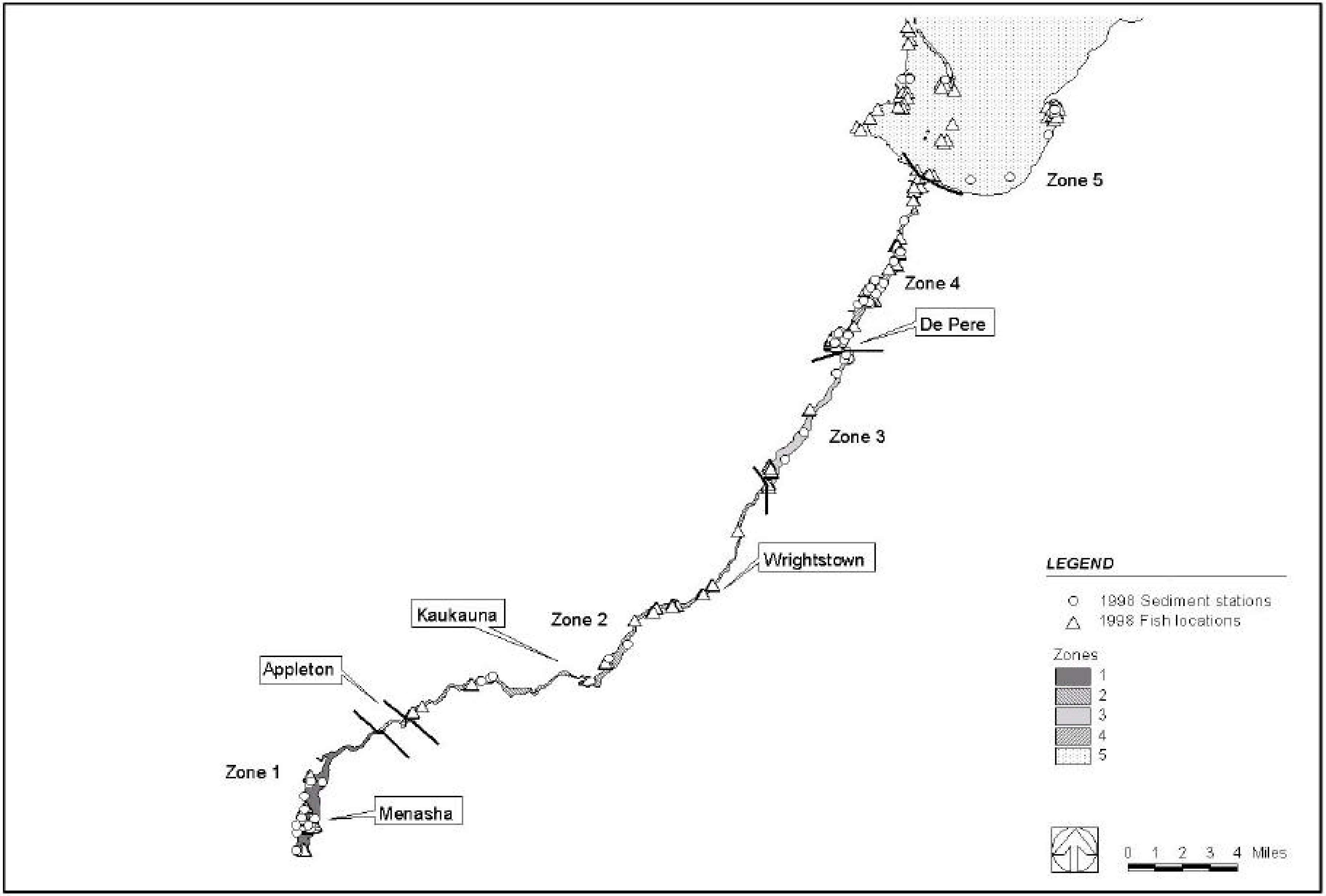

Figure 1. Sediment and fish sample locations sampled in 1998 in the Fox River project area by zone.

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Because of differences between historical investigations in the timing and location of fish and sediment samples, as well as of the fish species collected and of the measurement of total organic carbon (TOC) and lipid, individual species are not represented in very many zones or time periods. Consequently, pre-1998 data for all species were combined for analysis. The 1998 data set includes five fish species that were collected from all zones, and therefore the data were evaluated on a species-specific basis. Table 2 summarizes the 1998 data.

Because PCB is a nonpolar compound, it is expected to preferentially associate with TOC in the sediment and with lipid in tissue. The surface sediment PCB concentration in each sample was therefore standardized to TOC, and the tissue PCB concentration in each sample was standardized to lipid prior to summarization and analysis. (Non-standardized PCB concentrations were also summarized and analyzed.) Total PCB was computed as the sum of detected Aroclors.

Sediment and invertebrate PCB concentrations were also paired to interpret potential bioaccumulation relationships. Because sediment PCB concentrations were not measured at the exact locations of invertebrate collections, and because invertebrates do not range over an extensive area of the bottom as fish do, the PCB concentration for each invertebrate sample was paired with the average PCB concentration among all of the closest sediment samples. These data are shown in Table 3.

Table 1. Habitat Zones

Zone	Description
1	Little Lake Butte des Morts to Appleton
2	Appleton to Little Kaukauna Dam
3	Little Kaukauna Dam to DePere Dam
4	DePere Dam to the mouth of Green Bay
5	Green Bay

Table 2. Summary of 1998 fish and sediment data

Zone	Species	Fraction	Average sediment PCB (μg/kg dry)	Average tissue PCB (μg/kg wet)	Average sediment PCB (mg/kg TOC)	Average tissue PCB (mg/kg lipid)
1	Carp	Fillet	9800	2600	280	26
2	Carp	Fillet	9700	830	440	27
3	Carp	Fillet	640	1900	26	30
4	Carp	Fillet	690	5400	31	67
5	Carp	Fillet	220	2700	10	32
1	Northern pike	Fillet	9800	230	280	27

Zone	Species	Fraction	Average sediment PCB (µg/kg dry)	Average tissue PCB (µg/kg wet)	Average sediment PCB (mg/kg TOC)	Average tissue PCB (mg/kg lipid)
2	Northern pike	Fillet	9700	520	440	72
3	Northern pike	Fillet	640	440	26	560
4	Northern pike	Fillet	690	420	31	52
5	Northern pike	Fillet	220	420	10	43
1	Smallmouth bass	Fillet	9800	260	280	22
2	Smallmouth bass	Fillet	9700	240	440	23
3	Smallmouth bass	Fillet	640	120	26	11
4	Smallmouth bass	Fillet	690	390	31	33
5	Smallmouth bass	Fillet	220	420	10	34
1	Walleye	Fillet	9800	330	280	37
2	Walleye	Fillet	9700	630	440	50
3	Walleye	Fillet	640	780	26	28
4	Walleye	Fillet	690	590	31	40
5	Walleye	Fillet	220	2200	10	81
4	White sucker	Fillet	690	520	31	28
5	White sucker	Fillet	220	350	10	21
1	Yellow perch	Fillet	9800	110	280	20
2	Yellow perch	Fillet	9700	72	440	13
3	Yellow perch	Fillet	640	110	26	16
4	Yellow perch	Fillet	690	180	31	28
5	Yellow perch	Fillet	220	89	10	13
4	Alewife	Whole	690	2000	31	32
5	Alewife	Whole	220	670	10	11
1	Carp	Whole	9800	900	280	11
2	Carp	Whole	9700	1800	440	27
3	Carp	Whole	640	3600	26	40
4	Carp	Whole	690	4700	31	47
4	Carp	Whole	690	3900	31	43
5	Carp	Whole	220	1400	10	23
5	Carp	Whole	220	2500	10	17
1	Northern pike	Whole	9800	1500	280	79
2	Northern pike	Whole	9700	1300	440	44
3	Northern pike	Whole	640	3300	26	83

Zone	Species	Fraction	Average sediment PCB (μg/kg dry)	Average tissue PCB (μg/kg wet)	Average sediment PCB (mg/kg TOC)	Average tissue PCB (mg/kg lipid)
4	Northern pike	Whole	690	2600	31	85
5	Northern pike	Whole	220	370	10	24
1	Smallmouth bass	Whole	9800	2100	280	45
2	Smallmouth bass	Whole	9700	1000	440	25
3	Smallmouth bass	Whole	640	990	26	28
4	Smallmouth bass	Whole	690	1200	31	43
5	Smallmouth bass	Whole	220	1400	10	35
1	Walleye	Whole	9800	1000	280	20
2	Walleye	Whole	9700	2600	440	46
3	Walleye	Whole	640	2900	26	74
4	Walleye	Whole	690	5300	31	51
5	Walleye	Whole	220	2400	10	41
4	White sucker	Whole	690	1500	31	34
5	White sucker	Whole	220	540	10	36
1	Yellow perch	Whole	9800	360	280	10
2	Yellow perch	Whole	9700	630	440	20
3	Yellow perch	Whole	640	510	26	18
4	Yellow perch	Whole	690	1400	31	25
5	Yellow perch	Whole	220	390	10	12

Table 3. Paired invertebrate and sediment PCB data

Benthic Sample	Invertebrate PCB (μg/kg)	Invertebrate Lipid (%)	Standardized invertebrate PCB (mg/kg lipid)	Average sediment PCB (mg/kg)	Average sediment TOC (mg/kg)	Standardized sediment PCB (mg/kg TOC)
B00001	1200	0.55	220	15	4.4	340
B00002	60	0.8	7.5	0.23	3.6	6.4
B00003	200	0.76	26	0.74	1.9	39
B00004	140	0.46	30	1.1	1.6	69
B00008	60	0.49	12	0.18	2.1	8.6
B00009	48	0.61	7.9	0.16	2.1	7.6
B00010	71	0.33	22	0.39	1.3	30
B00011	47	0.61	7.7	0.047	2.1	2.2

Fish Bioaccumulation Analysis

Scatterplots of the pre-1998 data, for both fillets and whole fish, are shown in Figure 2. These plots represent multiple fish species, and show each individual tissue PCB concentration. Scatterplots of the 1998 data are shown in Figures 3 through 7. These figures show both the mean and range of PCB concentrations in fish tissue for each species. None of these data sets—pre-1998 or recent—exhibits a simple, direct relationship between PCB in sediment and fish. Linear regression analysis of these data indicates that there is no relationship: in all cases, the slope of the regression line is not significantly different from zero, indicating that PCB concentrations in fish tissue do not vary significantly in response to differences in PCB concentrations in sediment. This suggests that factors such as those listed on page 1 of this technical memorandum are influencing PCB bioaccumulation in the Lower Fox River.

Because the standardization procedure—dividing one measured quantity by another—ordinarily produces a result that has a greater variance than either of the original quantities, these analyses were repeated for the 1998 data using unstandardized PCB concentrations in sediment and tissue. Although the variance of the unstandardized PCB concentrations was lower than the variance of the standardized concentrations, no significant relationship between tissue PCB and sediment PCB was observed with these data either.

The absence of any apparent empirical relationship between PCB concentrations in fish and sediment indicates that the sediment PCB concentration alone is not an adequate predictor of fish PCB concentration. Any relationship must therefore be indirect, or affected by processes or characteristics other than just chemical concentrations. For example, tissue PCB concentrations may be affected by past exposures, multiple food web pathways, and active biodegradation. The 1998 data do not show that fish of different trophic levels (e.g., carp and pike) have clearly different responses to sediment PCBs, suggesting that factors such as physiological mechanisms in fish may be more important than food web dynamics in controlling PCB bioaccumulation.

Fish Length and PCB Bioaccumulation

The absence of a direct relationship between PCB concentrations in fish and sediment indicates that chemical equilibrium is not rapidly achieved. This implies that the instantaneous rate of PCB uptake (and loss) is limited, for example, by physiological characteristics of the fish or by delays imposed by transfer of PCB through the food chain. One expected result of a limitation of the instantaneous uptake rate is that because fish will continue to accumulate PCBs during a lengthy exposure, older fish are likely to contain higher concentrations than younger fish. Although the ages of fish collected in 1998 were not directly measured, their lengths were, and age and length are expected to be positively correlated. Therefore, to evaluate whether the absence of a direct relationship between PCB in fish and sediment might be the result of a limitation of the

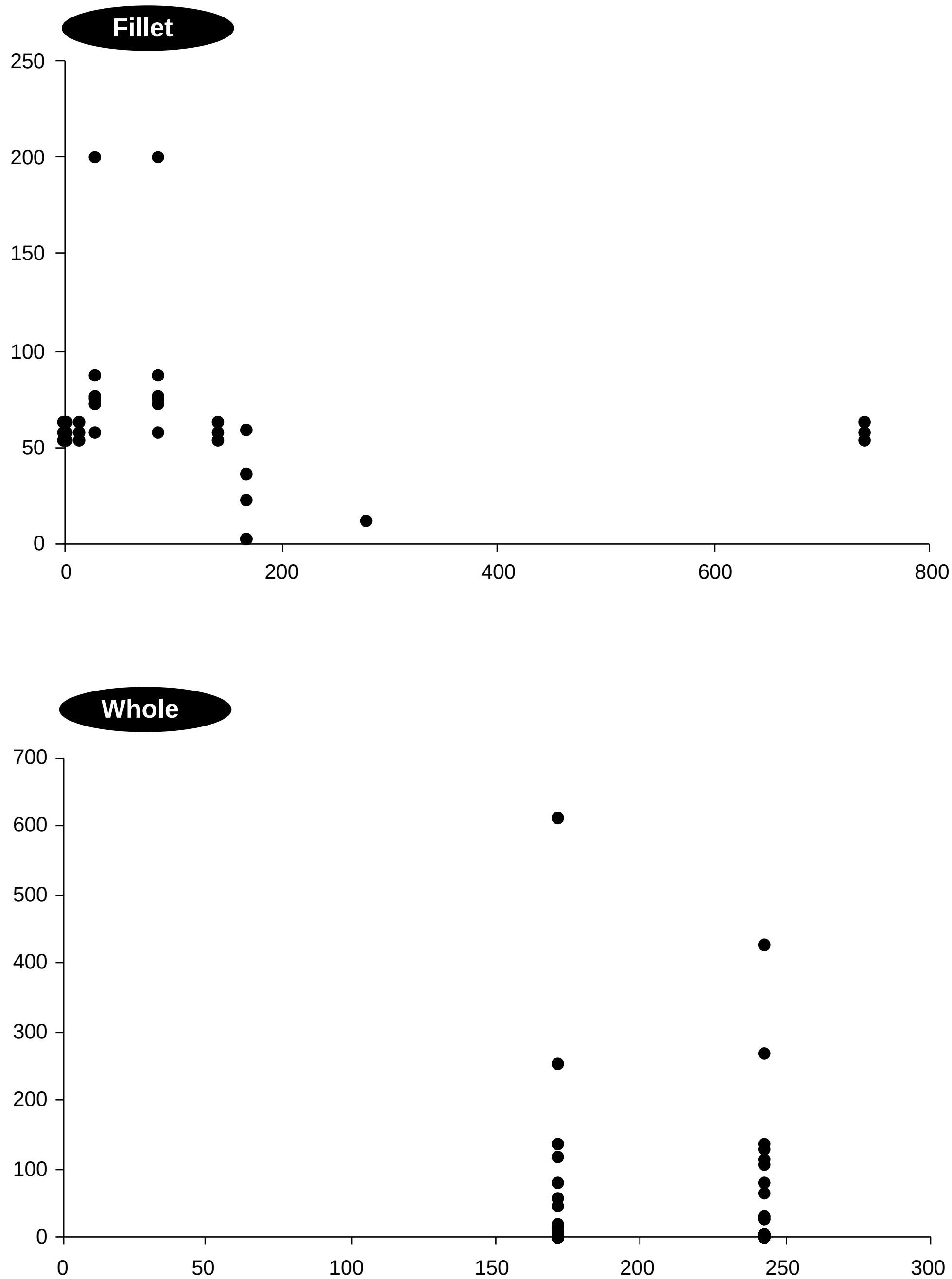

Figure 2. Relationship between total PCB in fish and sediment for historical data.

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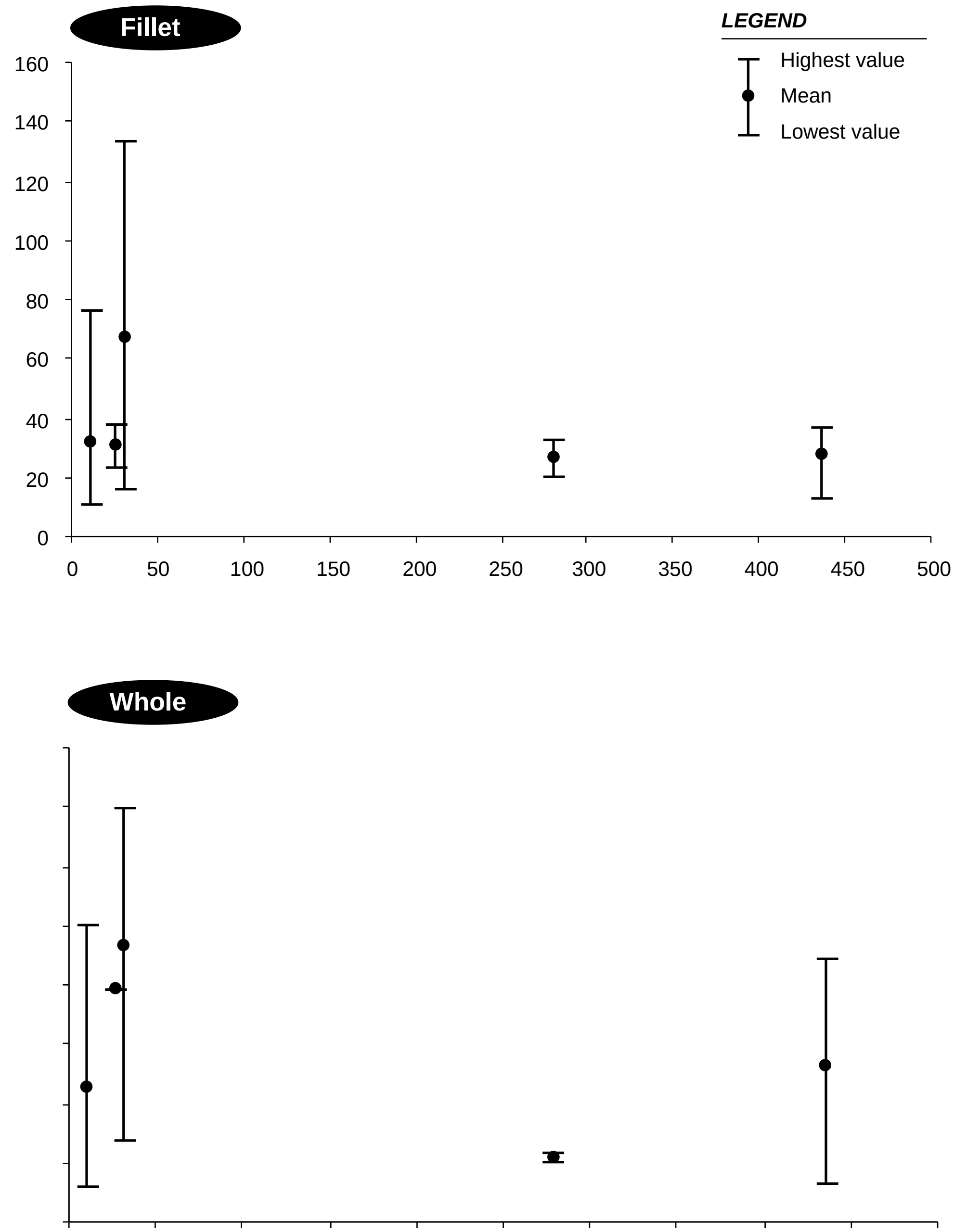

Figure 3. Relationship between total PCB in carp and sediment.

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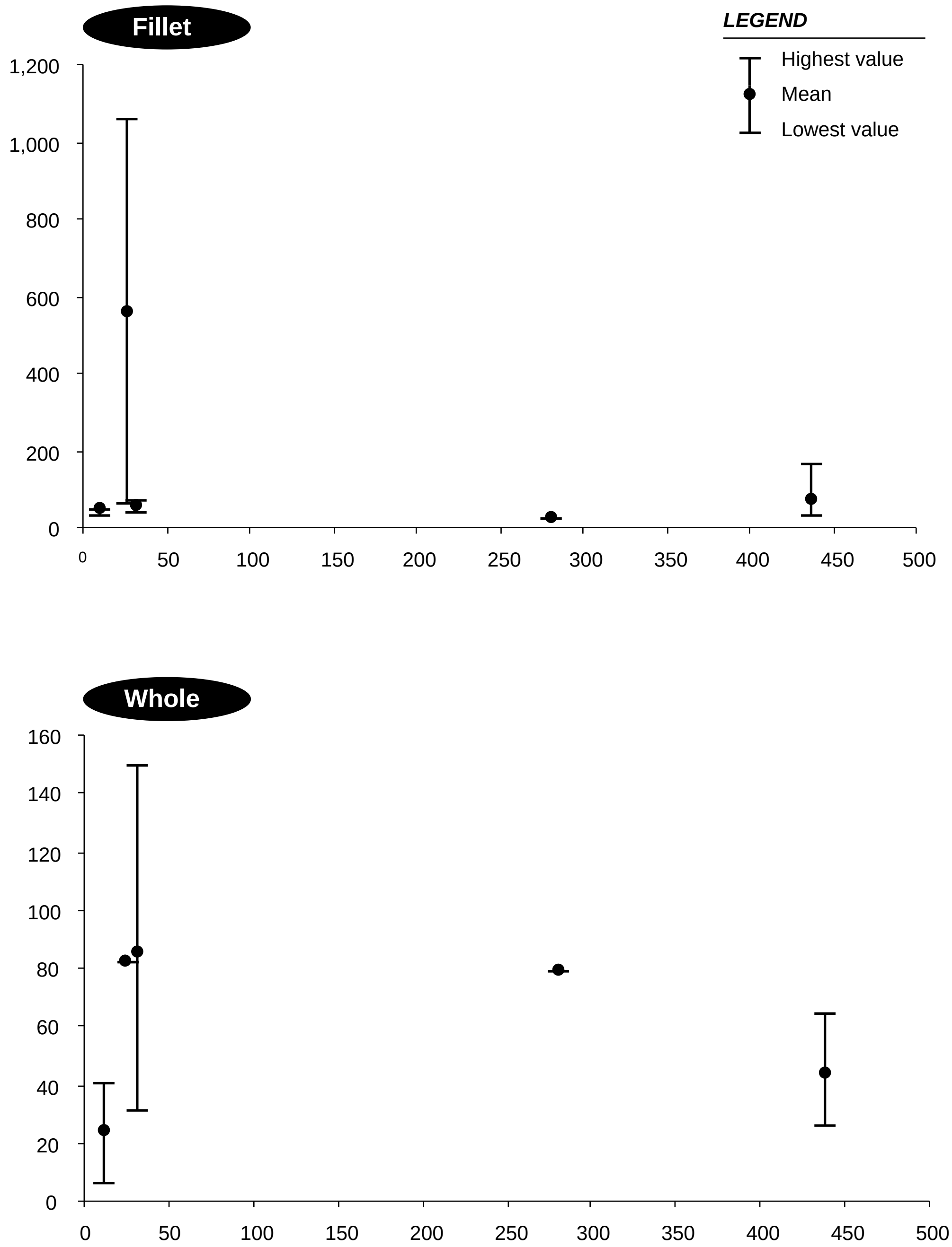

Figure 4. Relationship between total PCB in northern pike and sediment.

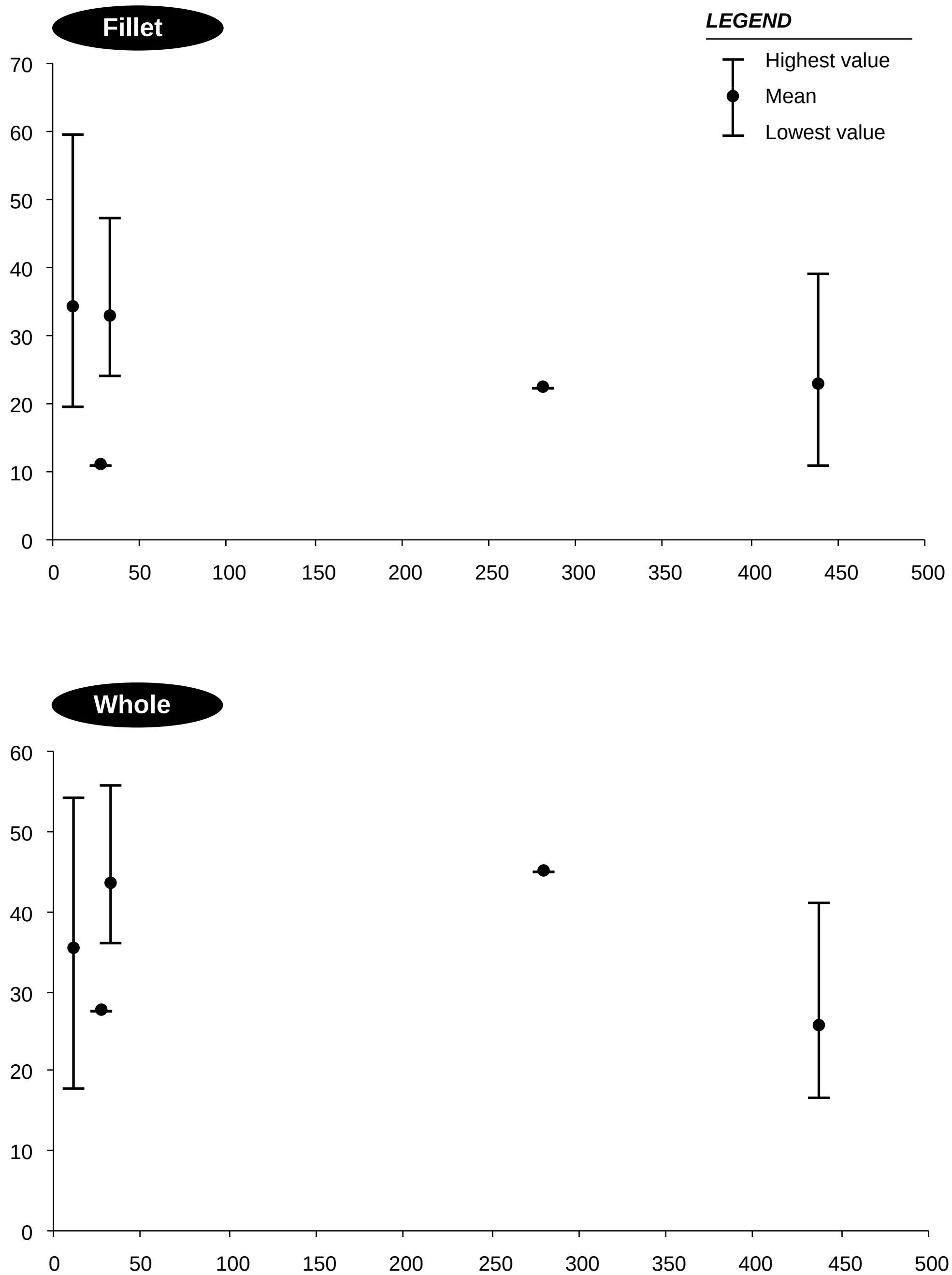

Figure 5. Relationship between total PCB in smallmouth bass and sediment.

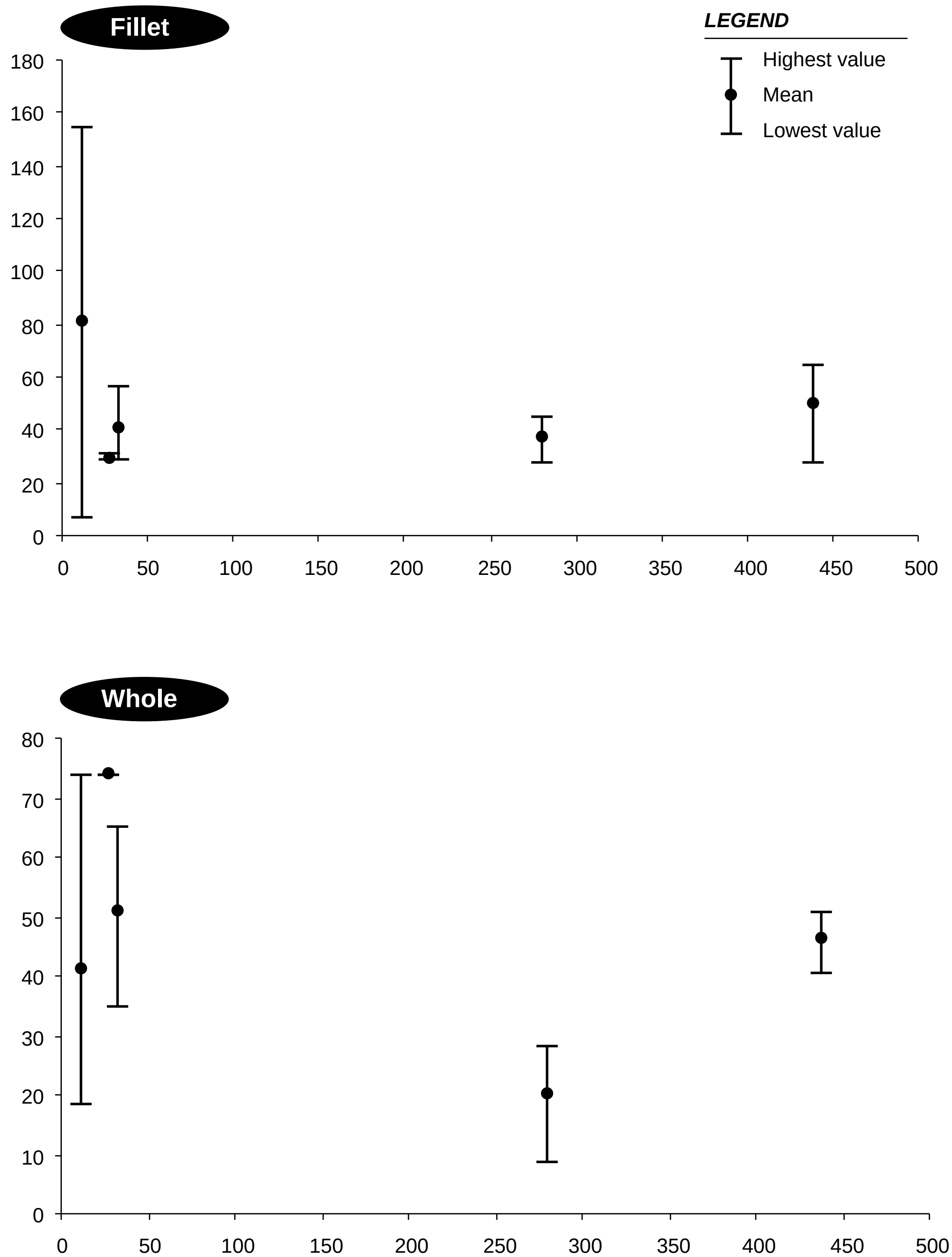

Figure 6. Relationship between total PCB in walleye and sediment.

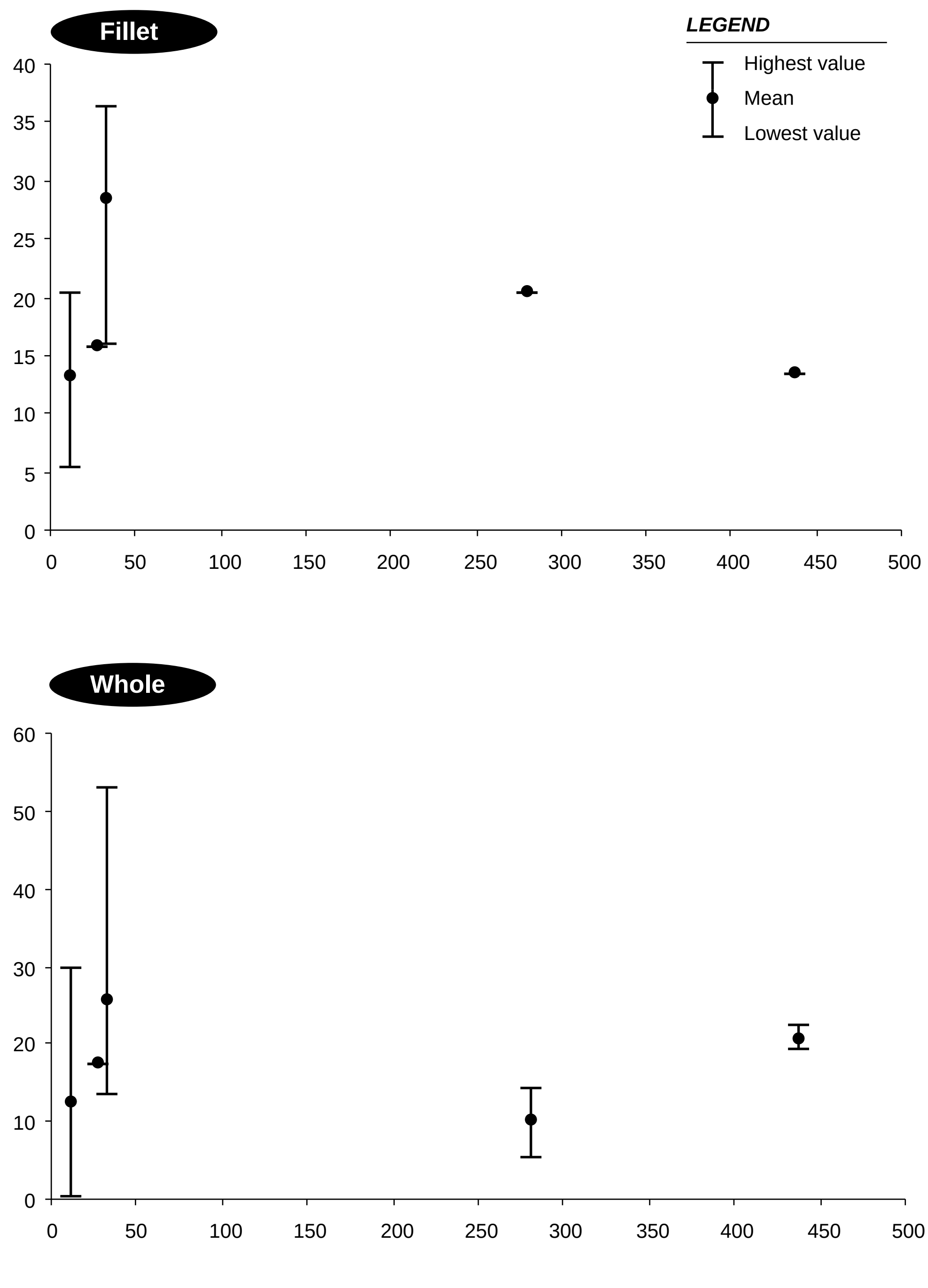

Figure 7. Relationship between total PCB in yellow perch and sediment.

instantaneous PCB uptake rate, PCB concentrations in fish were examined relative to fish length.

Figures 8 through 12 show the distribution of PCB concentrations in whole fish relative to fish length. An increase of PCB concentration with length (age) is seen for carp, walleye, yellow perch, and northern pike. The form of this increase varies from one species to another, with carp appearing to show the most rapid increase in PCB concentration with length, and northern pike the least rapid increase. These differences may be related to the position of these fish in the food chain, although species-specific variations in PCB affinity or degradation may also have an influence. No relationship between tissue PCB and length is seen for smallmouth bass, but the range of lengths for this species is relatively limited.

Similar relationships are seen when the PCB concentrations in fillet, rather than whole body, are viewed in relation to fish length. Standardization of PCB to lipid makes the relationships harder to discern because of the increased variation introduced by the standardization procedure.

The existence of a relationship between fish length and PCB concentration indicates that, although fish PCB concentrations are not directly related to sediment PCB concentrations, bioaccumulation is nevertheless occurring in a systematic fashion. This length/PCB relationship can be used to predict PCB concentrations in fish. However, accurate prediction of PCB bioaccumulation by fish will likely require modeling of exposure via the food chain throughout the lifetime of a fish.

Invertebrate Bioaccumulation Analysis

Because benthic invertebrates comprise a major component of aquatic food chains, the relationship between PCB concentrations in sediment and benthic invertebrates was examined.

A scatterplot of these data, as shown in Figure 13, shows a statistically significant relationship between PCB in invertebrate tissue and sediment. The form of this relationship is strongly controlled by the sample with the highest concentrations of PCB in both tissue and sediment. The equation of the line derived by least-squares linear regression is shown in Equation 1.

$$T = 2.1 + 0.63 \times S \qquad \text{Equation 1}$$

where:

T = total PCB concentration in invertebrates, mg/kg lipid

S = total PCB concentration in sediment, mg/kg TOC.

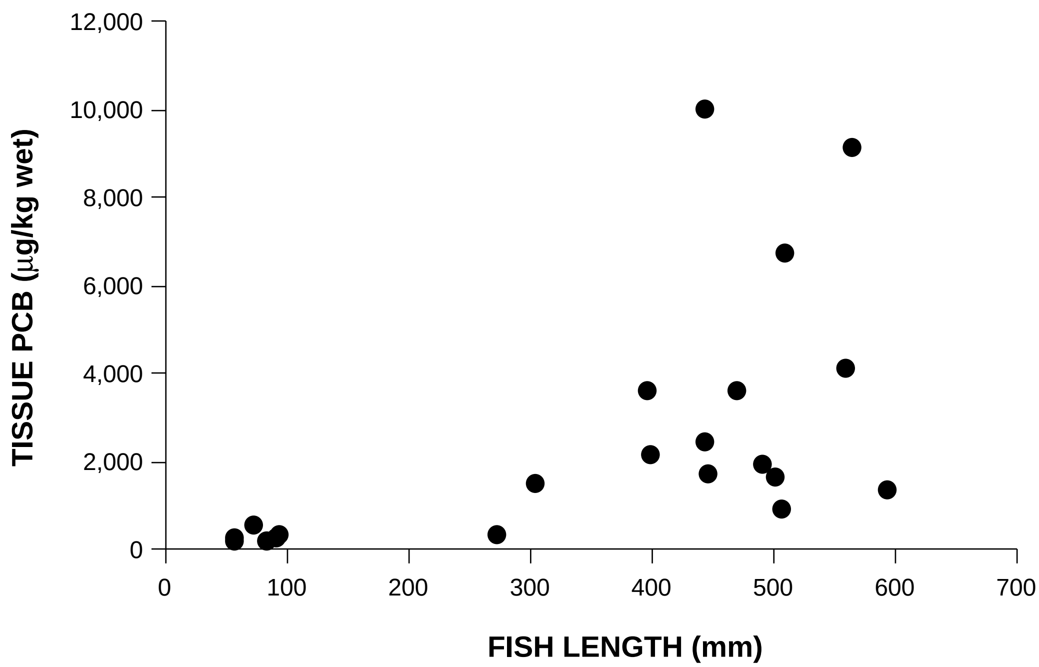

Figure 8. Whole-body PCB vs length for carp.

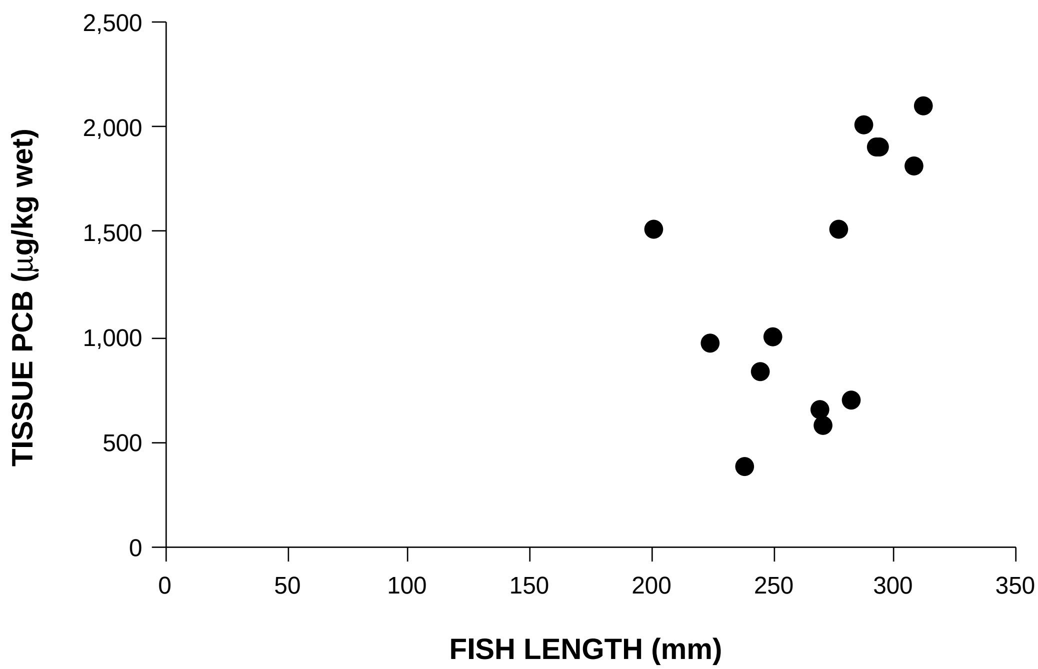

Figure 9. Whole-body PCB vs length for smallmouth bass.

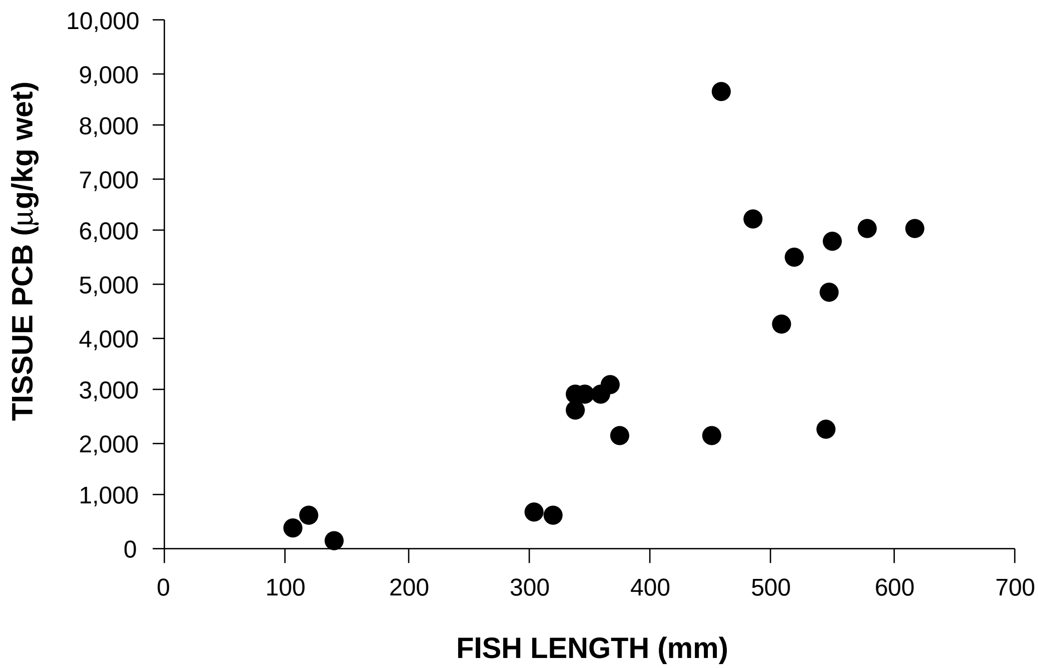

Figure 10. Whole-body PCB vs length for walleye.

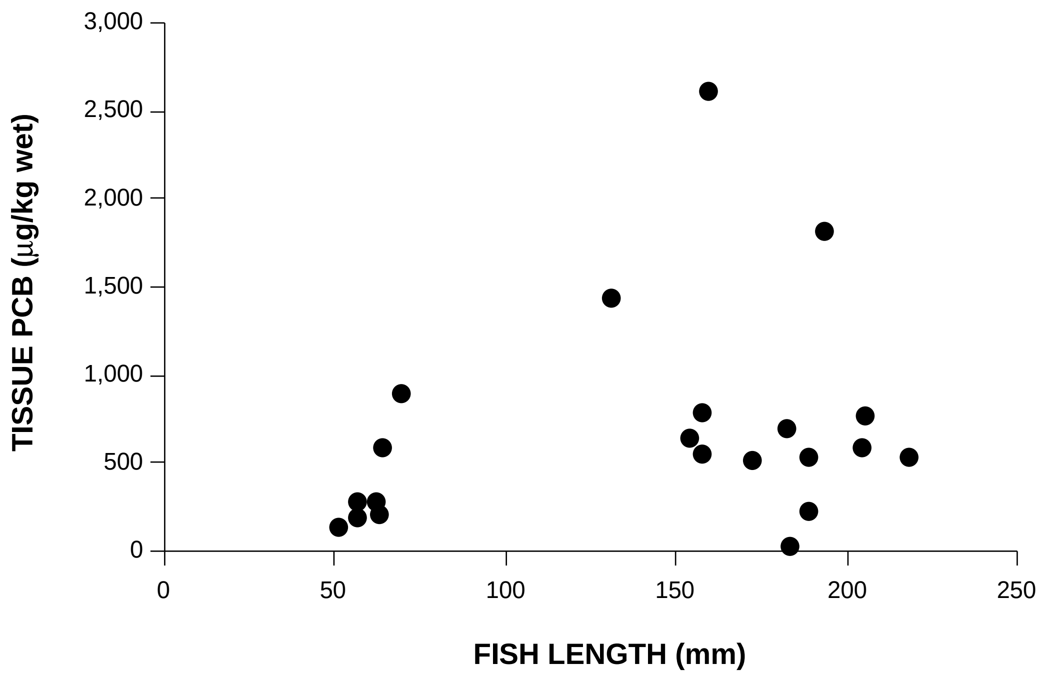

Figure 11. Whole-body PCB vs length for yellow perch.

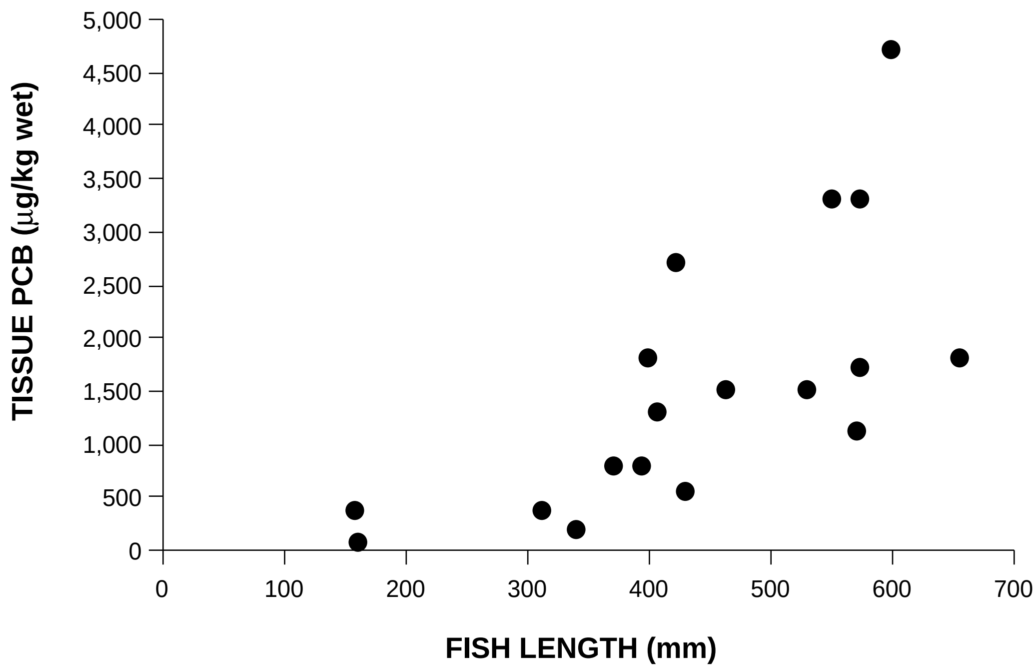

Figure 12. Whole-body PCB vs length for northern pike.

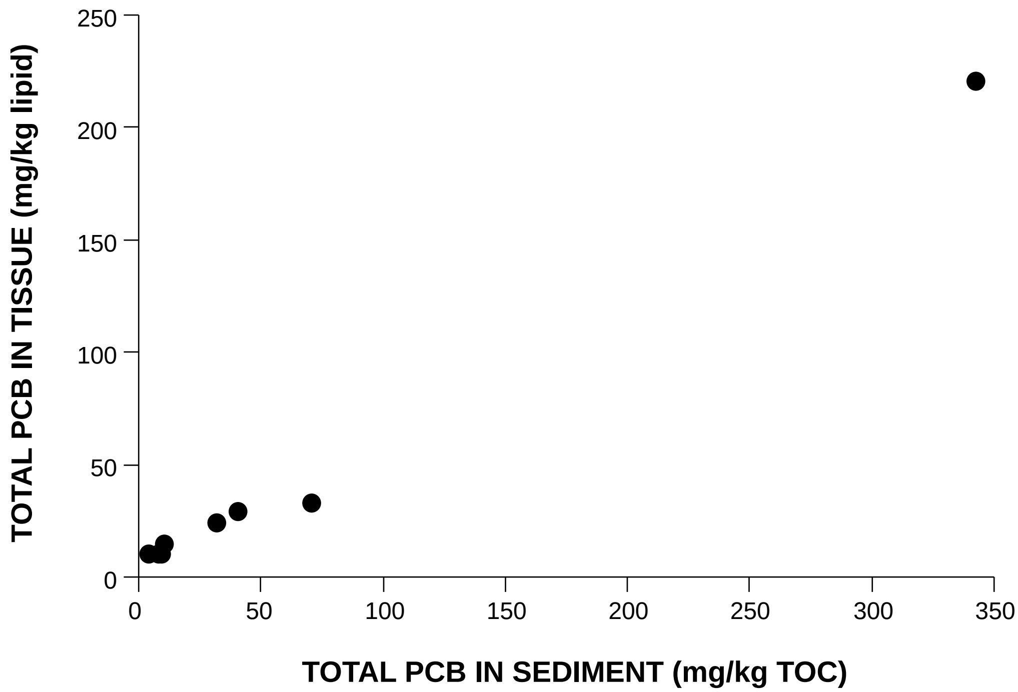

Figure 13. Total PCB in infauna and sediment.

The 95 percent confidence limits (–4.6 and 8.7) on intercept (2.1) include zero, so the slope of this line (0.63) can be used as a biota-sediment accumulation factor to predict PCB concentrations in invertebrates from PCB concentrations in sediment.

The existence of a statistically significant linear relationship indicates that benthic invertebrates are directly exposed to sediment PCBs. Thus, PCB concentrations in prey items at the base of the food web can be predicted based only on sediment PCB concentrations. Exposure to, and uptake of, PCBs by higher trophic level organisms can then be predicted by considering feeding preferences and physiological processes such as growth rate and assimilation efficiency.

Summary

Evaluations of pre-1998 and recent data show that total PCB concentrations in sediment and fish in the Fox River are not directly related to each other by any simple empirical function. Thus, tissue PCB concentrations cannot be accurately predicted from sediment PCB concentrations alone. However, total PCB concentrations in fish tissue are related to fish length, and total PCB concentrations in invertebrates are directly proportional to total PCB concentrations in sediment. The existence of a relationship between fish length and PCB concentration suggests that the rate of uptake by fish is limited by factors other than the local sediment PCB concentration. Other factors may also contribute to the apparent absence of a clear and direct relationship between PCB concentrations in fish and sediment. One of the most important of these is likely to be the exposure pathway. A limitation of the current analysis is that measurements of fish are associated with measurements of sediment collected from the same general location and time at which the fish were captured. However, pairing fish and sediment data in this way may not accurately represent exposure because of:

- Daily and seasonal movements of fish, so that conditions at the location of capture are not equivalent to those at the location of exposure
- Food web transfers that may result in higher trophic level fish being exposed to several dietary sources, each of which may in turn have had different exposures
- Temporal changes in sediment PCB concentrations that, in conjunction with a limited uptake rate, may result in a PCB body burden that reflects prior conditions more than conditions at the time of capture.

These factors are not accounted for using a proportional prediction model such as a biota-sediment accumulation factor (BSAF), but can be accounted for by explicitly modeling exposure pathways. Such a model should take into account spatial variability in the environment, the history of fish exposures, and the integrating effects of food web transfers of PCB. The relationship between PCBs in sediment and infauna, and the relationship between fish length and PCB concentration, can both be used to evaluate the exposure pathways responsible for PCB bioaccumulation by fish in the Lower Fox River.

Reference

Exponent. 1998. Habitat characterization for the Lower Fox River and Green Bay Assessment Area. Prepared for the Fox River Group and Wisconsin Department of Natural Resources. Exponent, Landover, MD.