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PCB concentrations in walleyes and their prey from the Saginaw River, Lake Huron: A comparison between 1990 and 2007

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ABSTRACT

Concentrations of polychlorinated biphenyls (PCBs) were measured in composited samples of walleyes *Sander vitreus* and their prey during 2005–2007 from Saginaw Bay, Lake Huron. There was a linear relationship between fish length and PCB concentrations in walleyes between 356 and 608 mm, but fish 680 mm had lesser concentrations than 608-mm fish. When fish 222–550 mm from 1990 were compared with those from 2007, there was a decrease of 1315 ng PCBs/g wet wt (ww). Concentrations of PCBs in gizzard shad *Dorosoma cepedianum* (190 ng PCBs/g ww) were three-fold less than fish collected in 1990 (516 ng PCBs/g ww). Round gobies *Neogobius melanostomus* collected from the Saginaw River had the greatest concentrations of PCBs (range: 200–350 ng PCBs/g ww) compared with other prey fishes (45–190 ng PCBs/g ww). Concentrations of PCBs in Saginaw River round gobies were three-fold greater than those from Saginaw Bay. Zooplankton from 1990 and 2008 contained 8.0 and 32 ng PCBs/g ww, respectively, while zebra mussels *Dreissena polymorpha* from 2008 contained 351 ng PCBs/g ww. Principal components analysis showed that PCB congeners differed between the largest walleyes and other fish. There are several possible explanations for lesser concentrations of PCBs observed in 2007. These include effects of dredging, changes in the food web related to round gobies, loss of alewife *Alosa pseudoharengus*, which was a major walleye prey item in 1990, and replacement by yellow perch *Perca flavescens*, or decreases in release of PCBs from sediments due to weathering, burial, or diffusion.

Introduction

The area comprised of Saginaw Bay and the Saginaw River, which is designated an International Joint Commission Area of Concern (AOC) due to contamination of sediments with persistent inorganic and organic pollutants (IJC, 1993), is also one of the shallow, fertile, and more productive areas in the Great Lakes for aquatic organisms. Being the terminus of the largest watershed in Michigan, the Saginaw River and Saginaw Bay receive urban and agricultural runoff, as well as domestic sewage and industrial effluents. Sediments are contaminated with metals and anthropogenic compounds, such as PCBs (polychlorinated biphenyls; Verbugge et al., 1995), which has led to fish consumption advisories for this river for species such as channel catfish *Ictalurus punctatus* and common carp *Cyprinus carpio* (Allan et al., 1991; MDPHs, 1993) and toxic effects in birds that feed on contaminated fish (Tillitt et al., 1992). The critical toxicity of PCBs has been attributed to several PCB congeners (Allan et al., 1991.). Similar contamination issues exist at other Great Lakes sites (Allan et al., 1991, Camazo et al., 1987), with most restrictions on fish consumption due to the presence of PCBs (Sonzogni et al., 1991), even though concentrations of most contaminants have been decreasing and some advisories have been relaxed (Bro et al., 1987; Foran and Vander Ploeg, 1989; Paneth, 1991).

The walleye *Sander vitreus* fishery of Saginaw Bay is considered to be world class by anglers (Fielder et al., 2007a,b) and commercial fishers harvest large quantities of other important species. In efforts to rehabilitate this area during 2000–2001, the mouth of the Saginaw River was dredged to remove accumulated toxic substances. This effort was part of the Natural Resources Damage Assessment remediation plan by the U. S. Fish and Wildlife Service, Michigan Department of Environmental Quality (MDEQ), and the U. S. Army Corps of Engineers to reduce the presence of PCBs and to a lesser extent other contaminants. A subsequent MDEQ sediment survey showed that concentrations of PCBs were less than the target

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level of 1 mg/kg wet weight (ww) (MDEQ, 2003). Loadings of contaminants to the river (Moll et al., 1995) and concentrations in forage fish and walleyes in this area were measured in 1990 (Giesy et al., 1997).

It was hypothesized that PCBs were transferred from the sediments to zooplankton and zebra mussels *Dreissena polymorpha* and then to forage fishes, such as the planktivorous gizzard shad *Dorosoma cepedianum,* alewives *Alosa pseduoharengus,* and the invasive molluskivore round goby *Neogobius melanostomus.* At different times, these three prey fish were common in the diet of walleyes between 1990 and 2008 (Fielder et al., 2007; D. Fielder, personal communication, Michigan Dept. of Natural Resources, Alpena, Michigan) and were thought to transfer contaminants to walleyes, which enter the river in fall-spring and spawn in spring (Jude, 1992). Since 1990, there have been changes in the food web (Fielder and Thomas, 2007), introduction of exotic species round gobies and zebra mussels (Jude et al., 1992, Nalepa and Fahnenstiel, 1995), and near disappearance from Lake Huron of alewives, major prey of walleyes (Fielder, 2007b). The Saginaw River was also dredged. Any or all of these changes could have altered transfer of PCBs to walleye. The objective of this study was to document changes in concentrations of PCBs in walleyes and other components in the food web during a dynamic period that included food web and ecosystem changes by comparing concentrations measured in 1990 (Giesy et al., 1997) with those measured during this study in 2007.

Methods

Study area

The Saginaw River watershed, which is approximately 15,695 km^2, is located in the east-central region of the lower peninsula of Michigan, and empties into Saginaw Bay, Lake Huron (Fig. 1). The Saginaw River is composed of four tributaries, the Flint, Shiawassee, Cass, and Tittabawassee Rivers (Moll et al., 1995). Fish and zooplankton were collected from the Tittabawassee and Saginaw Rivers and from Saginaw Bay proper.

Fish collection and sub-sampling

All fishes were collected during the period 2005–2007 from several locations in the Saginaw River-Tittabawassee River and Saginaw Bay (Fig. 1). Walleyes were collected to correspond spatially and temporally with samples collected in 1990 (Giesy et al. 1997) and were carefully selected to correspond with sizes collected, ignoring sexes, as was done in the earlier study. Walleyes in both studies had spawned prior to collection, thereby avoiding potential differences between sexes in contaminant levels due to presence of large amounts of fatty eggs (Madenjian et al. 2009). Walleyes of five sizes (Table 2) were collected. Small, medium, and large walleyes were collected on 1 May 2007 by electroshocking from the Tittabawassee River within 0.5 km of its

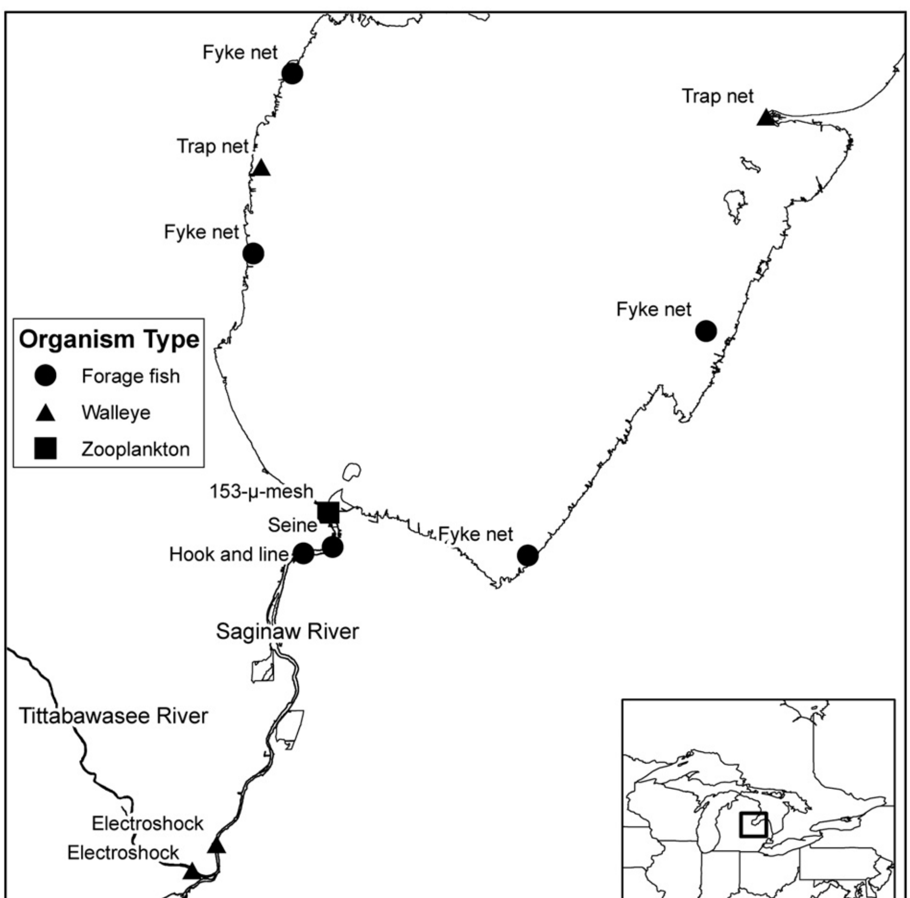

Fig. 1. Map of the Saginaw/Tittabawassee Rivers and Saginaw Bay, Lake Huron showing location in North American and sampling sites for various components of the food web sampled in 1990 and 2005–2008. Shown are: electroshocking sites (triangles in the Saginaw River) for walleyes, seine and hook and line site solid circles in the Saginaw River for round gobies, fyke net sites (solid circles in Saginaw Bay labeled fyke net) for forage fish, trap net sites (triangles in Saginaw Bay) for walleyes, and the zooplankton/zebra mussel site (square on Saginaw River mouth).

confluence with the Saginaw River and from the Saginaw River approximately 1 km down from the confluence of the Tittabawassee and Saginaw Rivers (Fig. 1). Water depths ranged from 1 to 3 m. Large and extremely large walleyes (mean = 608 and 680 mm, respectively) were collected by commercial fishers from two sites in Saginaw Bay, one near Pinconning, Michigan on the western side, and one on the eastern side near Sand Point off Bay Port, Michigan, 14 and 24 May 2007, respectively (Fig. 1). Gizzard shad were collected on 13 September 2007 using a seine in the Saginaw River near Essexville, Michigan (Fig. 1), while round gobies were collected by hook and line in the same areas where electroshocking was conducted and also near the Independence Bridge on the Saginaw River near the mouth of the river on 15 May 2007 (Fig. 1). Additional samples of potential forage fish (round gobies, bluntnose minnows *Pimephales notatus*, spottail shiner *Notropis hudsonius,* emerald shiners *Notropis atherinoides,* and banded killifish *Fundulus diaphanus*) were collected using fyke nets set in Saginaw Bay at four shallow wetland sites (Pinconning, Wigwam Bay, Quanticassee, and Sebewaing, Michigan, Fig. 1) during 18 July 2005. Fish were measured to the nearest mm total length, pooled, composited, and analyzed for PCBs (Table 1 lists mean fish size, sample sizes, and samples sizes for composites).

Lower food web collections

In order to establish linkages between accumulation of PCBs by gizzard shad and the lower food web, and to determine changes in PCB concentrations in zooplankton between 1990 and 2008, samples of zooplankton collected during 1990 and 2008 were analyzed as part of this study. These samples were collected in the Saginaw River at the river mouth on 30 August 1990 and 13 October 2008 by use of a 0.5-m diameter, 153-μ-mesh plankton net towed vertically 8 m in 9 m of water (Table 2, Fig. 1). Samples were preserved with 100% ethanol diluted to 50% by the sample volume.

Zebra mussels were collected because: (1) one large individual can filter 1 L (Reeders et al. 1989) or more (Fanslow et al., 1995, Horgan and Mills 1997) of water per day of algae and sediments, (2) they are dominant prey of large round gobies (French and Jude 2001), and (3) to make comparisons between concentrations measured during 1998 (Hanari et al. 2004) and 2008. During 13 October 2008, a large log floating in the river mouth in the same area where we collected zooplankton, was carried to shore, and a large quantity of zebra mussels removed and placed in a plastic bag on ice. They were transported to the laboratory, shells removed from two different size groups (<15 mm total length, and >15 mm total lengths), and PCBs were measured (see Quantification of PCBs).

Fish handling

Walleyes from each site were issued a numbered tag in the field, wrapped in contaminant-free aluminum foil shiny side out, kept on ice, and frozen in the laboratory. Five size groups (small, medium, large, very large, extremely large) were chosen based on availability of appropriate-sized walleyes that matched the size range of fish from the 1990 study (Table 2). Composites of fish were made for each size group with numbers ranging from two to six for composites and two to three for replicates. A fifth, composite size group (mean length = 680 mm—designated extremely large) was also included to determine if some of the largest walleyes in the system exhibited the same trends in concentrations of PCBs or had differing congener compositions. Since there were no corresponding fish of similar size collected in 1990, these fish were deleted from covariance analyses when size-PCBs relationships were analyzed from both periods.

Potential forage fish were separated by species, placed in aluminum foil, issued one number for identification, taken to the laboratory, and frozen. In the laboratory, fish were separated by appropriate size groups, weighed and measured as above, and issued additional numbers for each composite group. The numbers of fish included in the composite samples ranged from 2 to 18, while there were two to three replicates for each species measured (Table 1).

Laboratory procedures

Composite samples of whole fish of the desired size range (Table 1) were homogenized in a vertical, stainless-steel Hobart chopper that had been pre-cleaned with pesticide-free acetone and hexane prior to each sample. Between samples, the chopper was washed with a Liquinox–water solution, then rinsed with deionized, distilled water and methanol. Samples of ground fish were placed in glass jars with foil-lined covers and maintained frozen until analyzed.

Fish analysis procedures

Samples of composited, ground whole fish (20 g) were homogenized with sodium sulfate, spiked with surrogate standards, and extracted with methylene chloride and hexane (1:1, 400 mL) for 16 h in Soxhlets. All samples were spiked with two, non-Arochlor congeners (numbers 65 and 166; International Union of Pure and Applied Chemistry, Research Triangle Park, North Carolina, USA) as internal surrogate standards. After extraction, the solvent mixture was concentrated under nitrogen using a TurboVap II (Zymark) at 60 °C to 10 ml. A 1-mL aliquot of the extract was used for gravimetric

Table 1
Locations where fish, zooplankton, and zebra mussels were collected in the Tittabawassee and Saginaw Rivers and Saginaw Bay, Lake Huron during 2005–2008. BM = bluntnose minnow, BK = banded killifish, ES = emerald shiner, SP = spottail shiner, RG = round goby, E. Shocking = electroshocking, TN = trapnet. See Table 2 for mean total lengths of fishes.

Organism	Collection site	Date	Collection method
Small walleye	Tittabawassee/Saginaw River	7 May 2007	E. Shocking
Medium walleye	Tittabawassee/Saginaw River	7 May 2007	E. Shocking
Large walleye	Tittabawassee/Saginaw River	7 May 2007	E. Shocking
Very large walleye	Off Bayport & Pinconning, Michigan	14 and 24 May 2007	E. Shocking/TN
Extremely large walleye	Off Pinconning, Michigan	24 May 2007	TN
Gizzard shad	Saginaw River, Essexville, Michigan	13 September 2007	Seine
Round goby	Independence Bridge, Saginaw River	15 May 2007	Hook and line
BM,BK,ES,SP,RG	Off Pinconning, Michigan	18 July 2005	TN
BM,BK,ES,SP,RG	Wigwam Bay, Saginaw Bay	18 July 2005	TN
BM,BK,ES,SP,RG	Off Quanicassee, Michigan	18 July 2005	TN
BM,BK,ES,SP,RG	Off Sebewainig, Michigan	18 July 2005	TN
Zooplankton	Saginaw River mouth	30 August 1990	153-μ-mesh
		13 October 2008	153-μ-mesh
Zebra mussel	Saginaw River mouth	13 October 2008	By hand

Table 2
Fish, zooplankton, and zebra mussels collected from the Saginaw and Tittabawassee rivers (S/T) and Saginaw Bay (S. Bay), Lake Huron during 30 August 1990, 18 July 2005, 7–24 May 2007, and 13 October 2008. Shown are: N = number of replicates with number of fish composited (COMP) in parentheses, TL (SD) = total length in mm with standard deviation in parentheses. Also given is the lipid content (SD), and total PCBs. Pooled = pooled sample, rep = replicate.

Species	Size group	Location	Date	N (COMP)	Mean total length (mm) (SD)	Lipid (%)	Total PCBs (ng/g wet wt)
Walleye	Small	S/T River	7 May 2007	3 (6,5,5)	356(21)	4.8 (0.9)	460 (88)
Walleye	Medium	S/T River	7 May 2007	3 (5,5,4)	452 (21)	7.3 (1.3)	870 (94)
Walleye	Large	S/T River	7 May 2007	3 (4,4,4)	535 (27)	6.4 (2.4)	1,100 (123)
Walleye	Very Large	S. Bay	14 and 24 May 2007	3 (2,2,2)	608 (11)	4.4 (0.3)	1,900 (415)
Walleye	Extremely large	S. Bay	24 May 2007	2 (2,2)	680 (21)	4.9 (0.6)	1,200 (9)
Round goby	Small	S. River	15 May 2007	1 (9)	66 (2)	1	200
Round goby	Medium	S. River	15 May 2007	1 (18)	87 (4)	1	280
Round goby	Large	S. River	15 May 2007	1 (9)	102 (8)	1.1	350
Round goby pooled	ALL	S. River	15 May 2007	3 (9,18,9)	86 (14)	1 (0.1)	280 (74)
Gizzard shad	Small	S. River	13 September 2007	2 (2,2)	100 (12)	2.4 (0.1)	190 (19)
Round goby	Pooled-rep 1	S. Bay	18 July 2005	1 (40)	35 (5)	2.6	36
Round goby	Pooled-rep 2	S. Bay	18 July 2005	1 (22)	51 (3)	2.6	60
Round goby	Pooled-rep 3	S. Bay	18 July 2005	1 (19)	53 (4)	2.6	30
Round goby Pooled	ALL	S. Bay	18 July 2005	3 (40,22,19)	44 (1)	2.6 (0.02)	42 (16)
Bluntnose minnow	Small	S. Bay	18 July 2005	1 (61)	38 (7)	2.2	23
Bluntnose minnow	Large	S. Bay	18 July 2005	1 (29)	61 (5)	4	95
Bluntnose minnow	Pooled	S. Bay	18 July 2005	2 (61,29)	45 (12)	3.1 (1.3)	59 (51)
Emerald shiner	Medium	S. Bay	18 July 2005	2 (37,40)	46 (6)	1.6 (0.3)	51 (9)
Banded killifish	Medium	S. Bay	18 July 2005	2 (55,18)	38 (9)	1.3 (0.3)	28 (4)
Spottail shiner	Medium	S. Bay	18 July 2005	2 (30,32)	40 (3)	2.7 (0.4)	22 (2)
Zooplankton	All	S. River Mouth	30 Aug 1990	1	NA	NA	8
			13 Oct 2008	1	NA	NA	32
Zebra mussel	<15 mm	S. River Mouth	13 Oct 2008	1 (25)	NA	NA	286
	>15 mm			1 (25)	NA	NA	416

determination of lipids. A second 1-mL aliquot was passed through a column containing 10 g of 45% acidic silica gel (Kiesel gel, mesh size 230–400, Merck, Darmstadt, Germany) and a thin layer of sodium sulfate at the top. The column was cleaned with 150 mL of hexane prior to the transfer of sample extracts. Samples were then eluted with 200 mL of hexane and concentrated as above.

Quantification of PCBs

Identification and quantification of individual PCB congeners were accomplished at the Annis Water Research Institute, Grand Valley State University with an Agilent 6890 series, high-resolution, gas chromatograph coupled to a 5973 N quadrapole mass spectrometer. Separation of PCB congeners was achieved by use of a fused-silica, capillary column coated with DB-XLB (60-m × 0.25-mm i.d.) at 0.25 µm film thickness (J&W Scientific, Folsom, California). Column oven temperature was programmed from 80 to 160 °C at a rate of 40 °C/min and then to 170 °C at 10 °C/min, to 250 °C at 4 °C/min, and then to 296 °C at 8 °C/min with a final hold time of 10 min. Injector and transfer line temperatures were held at 260 and 250 °C, respectively. Hydrogen was used as the carrier gas and ^{13}C-decachlorobiphenyl was used as an internal standard. The mass spectrometer was operated in negative chemical ionization mode using methane as a reagent gas (Schmidt 1977). PCB congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster.

Reported PCB concentrations were not corrected for recoveries of surrogate standards. Since an internal standard method was used, all results were corrected for the internal standard. Results were not corrected for surrogate standards because they were added to the raw fish sample as model compounds to assess the performance of the extraction/clean up step. For analyses in this study, we used a ± 15% surrogate recovery control limit for the PCB method. The EPA methods for organochlorine pesticides and PCBs do not allow the correction of data for surrogate recoveries. Because surrogates are model compounds, actual recovery of the 70 congeners examined would be slightly different, making recovery correction somewhat arbitrary.

Procedural blanks were passed through the whole analytical procedure to check for interferences and laboratory contamination. The instrument was calibrated by use of individual congener standards from AccuStandard (New Haven, Connecticut, USA). Concentrations for each of 70 PCB congeners were determined. Calibration accuracy was based on the ability to analyze Arochlor standards and obtain predicted amounts and ratios obtained by Frame et al. (1996). Additional calibration verification was done using the West Coast Fish Studies standard supplied by AccuStandard. Appropriate quality control samples (blanks, matrix spikes, and duplicates) were analyzed to ensure precision and accuracy (USEPA, 1999). Spike recoveries ranged from 93% to 101%.

Statistical analyses

A covariance analysis was performed using SAS (SAS, 2007) to test for similar slopes and adjusted-mean concentrations of PCBs between walleye groups (357–608 mm) from 1990 compared with fish from 2007 ($N = 27$, $P = 0.05$: fish >608 mm were excluded). Levene's test (SAS) verified that there were no violations of the assumption of homogeneity of variance ($P > 0.05$, $P = 0.5688$). A principal components analysis principal components analysis (SAS 2007) was performed comparing the congener concentrations of PCBs among forage fishes and all sizes of walleyes. Data were standardized to a mean of zero and standard deviation of 1.0 and then the PCA was generated with a varimax rotation.

First-order kinetics calculations

Pseudo, first-order kinetics were used to describe the rate of decrease in PCB concentrations before and after dredging. The rate constant for the period before dredging was based on loadings of PCBs between 1971 and 1996 (Verbrugge et al. 1995). The rate after, including a period before and after dredging, was based on the change in concentrations of PCBs in YOY gizzard shad between 1990 and 2007. The rate constant for the decrease in concentrations in YOY gizzard shad was calculated by directly substituting the concentrations in the 2 years into Eq. (1). The equation was rearranged and concentrations from 1990 and

2007 inserted and the time set to 17 year and the value for k in year^{-1} (1990) was calculated.

$$C_{2007} = C_{1990}\left(e^{-kT}\right) \tag{1}$$

where:

C_{2007} the concentration in fish in 2007
C_{1990} concentration in fish in 1990
T time = 17 years
K pseudo, first-order rate constant in year^{-1}

Bioaccumulation factors

Bioaccumulation factors (concentration of PCBs in walleyes divided by mean concentration of PCBs in prey) were calculated for five size groups of walleyes. Four prey types (gizzard shad, round gobies from the Saginaw River and Saginaw Bay, and forage fish from Saginaw Bay) were used in calculations.

Results

PCBs

Mean concentrations of PCBs in composite samples of fish ranged from a minimum of 22 ng PCBs/g wet weight (ww) in spottail shiners to a maximum of 1,900 ng PCBs/g ww in large walleyes (Fig. 2, Table 2). Mean concentration of PCBs in composited samples of walleyes of the size usually taken by anglers (452–680 mm) was approximately 1300 ng PCBs/g ww with a range of 870 to 1900 ng PCBs/g ww (Table 2). Concentrations of PCBs were directly proportional to walleye length up to 608 mm (1900 ng PCBs/g ww), then concentrations of PCBs in the largest walleyes (680 mm–1,200 ng PCBs/g ww) were less.

Composited samples of young-of-the-year (YOY) gizzard shad, one of the primary prey of walleyes in Saginaw Bay from 1990 to 1996 (Fielder and Thomas, 2007), had a mean concentration of 190 ng PCBs/g ww, while emerald shiners, banded killifish, bluntnose minnows, and spottail shiners from Saginaw Bay contained lesser mean concentrations of PCBs with a range of 22 to 59 ng PCBs/g ww. Composited samples of spottail shiners and banded killifish both had the least concentrations among prey fish of approximately 25 ng PCBs/g ww.

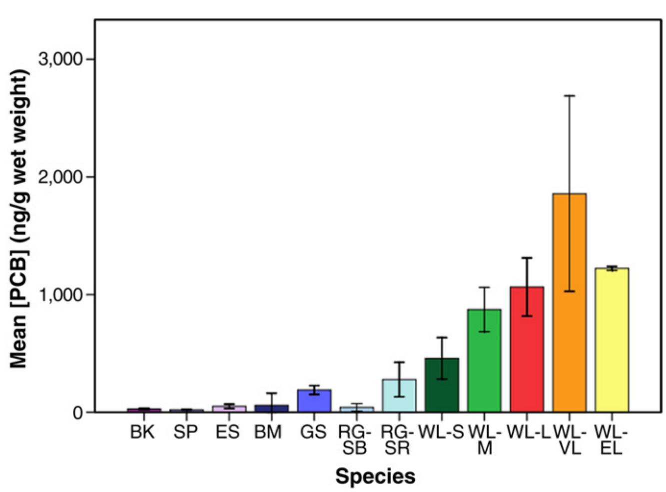

Fig. 2. Summary of the concentrations of PCBs (ng PCBs/g ww) in several fish species collected in the Saginaw River-Saginaw Bay complex, Lake Huron during 2005–2007. Definitions and mean length for the following composited groups are: WL-SM = small walleye 357 mm, WL-MED = medium walleye 452 mm, WL-L = large walleye 535 mm, WL-VL = very large walleye 608 mm, WL-EL = extremely large walleye 680 mm, GS = gizzard shad 100 mm, RG-SR = round gobies from Saginaw river 86 mm, RG-SB = round gobies from Saginaw Bay 44 mm, BK = banded killifish 38 mm, BM = bluntnose minnow 45 mm, SP = spottail shiner 40 mm, ES = emerald shiner 46 mm. Standard deviation bars (±2 SD) are given for each value. See Table 2 for additional information on these fish.

The round goby is a nonindigenous species that eats large numbers of zebra mussels when the fish are >50 mm (French and Jude, 2001) and, since their introduction in the 1990s (Jude et al., 1992), round gobies have been an important prey item of walleyes in Lake Erie (Bur et al., 2008; C. Knight, personal communication, Ohio Dept. of Natural Resources, Fairport, Ohio), the St. Clair River (Jude, 2001), and Saginaw Bay during 2005–2008 (Fielder and Thomas, 2007a). Concentrations of PCBs in round gobies collected on 15 May 2007 from the Saginaw River were the greatest among forage fish and linearly related to round goby lengths. Concentrations in round gobies collected in May 2007 ranged from 200 (composite sample: mean TL of 66 mm) to 350 ng PCBs/g ww (mean TL = 102 mm; Table 2). An additional sample of round gobies was collected from Saginaw Bay on 18 July 2005 and although these fish were somewhat smaller and collected during a different season than the Saginaw River fish, they were from the same region and are likely a valid comparison. The composited individuals from Saginaw Bay, which were approximately 44 mm, contained a mean concentration of PCBs of only 42 ng PCBs/g ww (Table 2), which was significantly ($t = 4.569$, $df = 2$, $P = 0.001$) less (about five fold) than concentrations in 66-mm round gobies from the Saginaw River.

On 30 August 1990, the mean concentration of PCBs in zooplankton from the Saginaw River (*Cyclops, Leptodora, Ceriodaphnia, Eucyclops, Diaphansoma, Daphnia galeata, D. retrocurva*, and *Eubosmina*) was 8.0 ng PCBs/g ww, while a comparable sample collected on 13 October 2008 contained 33 ng PCBs/g ww. Species composition for the 2008 sample was mostly *Eucyclops prinophorus, Bosmina longirostris*, and *Diaptomus oregonensis* with some *Ceriodaphnia, Daphnia parvula*, and *Holopedium gibberum*. The 1990 zooplankton sample contained 25% of the least concentrations found in any of the walleyes or forage fishes analyzed in this study. Composited samples of zebra mussels collected on 13 October 2008 contained 286 and 416 ng PCBs/g ww for samples <15 mm total length and >15 mm total length, respectively, for a mean of 351 ng PCBs/g ww (SD = 92).

Chlorinations and relative congener concentrations

Concentrations of individual PCB congeners were summarized by homolog group (number of chlorine atoms per PCB molecule) for composite samples of each of the fishes, zooplankton, and zebra mussels (Table 3). Of PCB congeners measured, congener No. 153/132 (two congeners with six chlorines that co-eluted) occurred at the greatest concentrations (data not shown) in walleyes. Concentrations of congener No. 205 were the least. When percent contribution of each homolog for each sample was examined, all samples showed a bell-shaped curve with maximum percentages occurring for the penta-homologs, with two exceptions. Zebra mussels and gizzard shad both had their peak percentages occurring with the tetra-homologs, shifting their distribution to the left (Table 3). There were a few subtle differences in distributions of homologs between round gobies from the Saginaw River and Saginaw Bay, since Saginaw River fish had greater percentages of tri-penta biphenyls than Saginaw Bay fish. Lastly, few differences in the distribution of percentages of homologs were observed among the other four forage fish species collected in Saginaw Bay.

Homolog patterns for zooplankton (Table 3) exhibited large differences between 1990 and 2008. Zooplankton from 2008 had 15.3% vs. 0% of trichlorobiphenyls and twice as much tetrachlorobiphenyls as was found in 1990 organisms. Zooplankton from 1990 had more penta-, hexa-, and septachlorobiphenyls than zooplankton from 2008. There were differences in patterns of relative concentrations of homologs in zebra mussels and zooplankton. Zebra mussels had greater

Table 3
Mean percent composition of each of the nine chlorination levels (di = dichlorobiphenyl hexachlorine, tri = trichlorobiphenyl hexachlorine, etc.) for PCB homologs found in composited food web components from the Saginaw and Tittabawassee Rivers and Saginaw Bay, Lake Huron during 2005–2008. RP = replicate, pooled = pooled samples, S. = Saginaw, Ext. = extremely. See Tables 1 and 2 for details on locations, gear used to collect samples, sample sizes, and concentrations of PCBs found in each sample.

Species	Size group/ year	% Di	% Tri	% Tetra	% Penta	% Sexta	% Septa	% Octa	% Nana	% Deca
Walleye	Small	2	8.5	22	31	22	11	2.7	0.42	0.28
Walleye	Medium	1.6	7.6	23	31	22	11	2.6	0.44	0.34
Walleye	Large	1.5	6.7	21	31	24	12	3	0.48	0.27
Walleye	Very Large	1.3	5.1	17	30	27	14	3.8	0.59	0.28
Walleye	Ext. large	1.7	6.4	20	30	22	14	4.5	0.87	0.57
Round goby—S. River	Small	3.4	19	33	22	13	6.4	1.7	0.29	0.22
Round goby—S. River	Medium	3.4	14	32	25	16	7.1	1.8	0.31	0.25
Round goby—S. River	Large	1.8	9.5	36	28	16	7	1.7	0.28	0.22
Round goby—S. River Pooled	All	3.2	8.1	14	35	25	11	2.8	0.50	0.37
Gizzard shad	Small	4.4	16	25	24	19	8.2	2.2	2	0.72
Round goby - S. Bay	Pooled-RP 1	4.3	6.8	16	32	25	12	3.1	0.61	0.53
Round goby—S. Bay	Pooled-RP 2	11	19	17	24	17	8.3	2.1	0.4	0.3
Round goby—S. Bay	Pooled-RP 3	2	16	11	33	24	10	2.6	0.5	0.44
Round goby—S. Bay pooled	All	6.7	18	14	29	21	9.3	2.4	0.45	0.37
Bluntnose minnow	Small	8.3	12	15	34	20	8	2	0.3	0.3
Bluntnose minnow	Large	2.8	7.5	15	33	25	12	3.3	0.62	0.38
Bluntnose minnow	Pooled	5.6	9.8	15	34	23	10	2.6	0.46	0.34
Emerald shiner	Medium	3	4.4	16	32	26	14	3.8	0.72	0.43
Banded killifish	Medium	3.4	7.7	6.4	32	31	15	3.6	0.47	0.55
Spottail shiner	Medium	3	4.4	16	32	26	14	3.8	0.72	0.43
Zooplankton	1990	0	0	11	46	28	13	1.2	0	0
Zooplankton	2008	0	15	24	38	15	5.8	1.4	0.15	0.18
Zebra mussels	2008	0	27	46	18	4.5	2.4	0.67	0.11	0.12

percentages of less-substituted congeners, such as tri- and tetrachlorobiphenyls vs. zooplankton, while zooplankton dominated zebra mussels with greater percentages of the penta, hexa, and septachlorobiphenyls (Table 3). Walleyes and their prey fish had lesser percentages of dichlorobiphenyls, while lower food web components had none. However, in general, lower food web components had greater percentages of the less-substituted homologs (tri-, tetra-, and penta-chlorophenyls), while fishes had greater percentages of the more chlorinated congeners (hexa-, septa-, octa-, and nanacholorbiphenyls).

Tetra-, penta-, and hexachlorobiphenyl homologs together composed 75% of the mass of all PCBs found in walleyes, while the tetra- through hepta-homolog groups composed 87% of the mass of all PCBs. Less-chlorinated homologs were prevalent in smaller walleyes, while more-chlorinated homologs were prevalent in larger sizes. The proportion of more-chlorinated homologs was greatest in the largest top predators, while less-chlorinated homologs were more prevalent in forage fishes. Proportions of tetra-chlorinated biphenyls were less in prey (15%) than those in walleyes (21%). There were also some differences (<3%) when homologs from prey were compared with those for walleyes: di- (3.7% prey vs. 1.6% walleye), tri- (9.4 vs. 6.9%), and penta-chlorinated byphenyls (33 vs. 31%). Finally, for the extremely large walleyes, there was a greater percentage of septa- to nana-substituted homologs when compared with forage fishes (Table 3).

A PCA analysis of congeners (Fig. 3) was performed to further explore differences among patterns of relative concentrations of congeners. The first principal component explained 90% of the variance. Factor 1 along the *x* axis represents increasing concentrations of chlorinated congeners (tetra- to deca-chlorinated biphenyls). A pattern of more chlorination was observed from small, to medium, to large, to very large walleyes, with the extremely large walleyes having a pattern that was intermediate between medium and large walleyes. Forage fishes contained a greater proportion of less-chlorinated biphenyls than did walleyes. Factor 2 (along the *y* axis), which explained 4% of the variation, represented the less-chlorinated congeners. The less-chlorinated congeners were more prevalent in round gobies from the Saginaw River than in round gobies and the other forage fishes collected from Saginaw Bay.

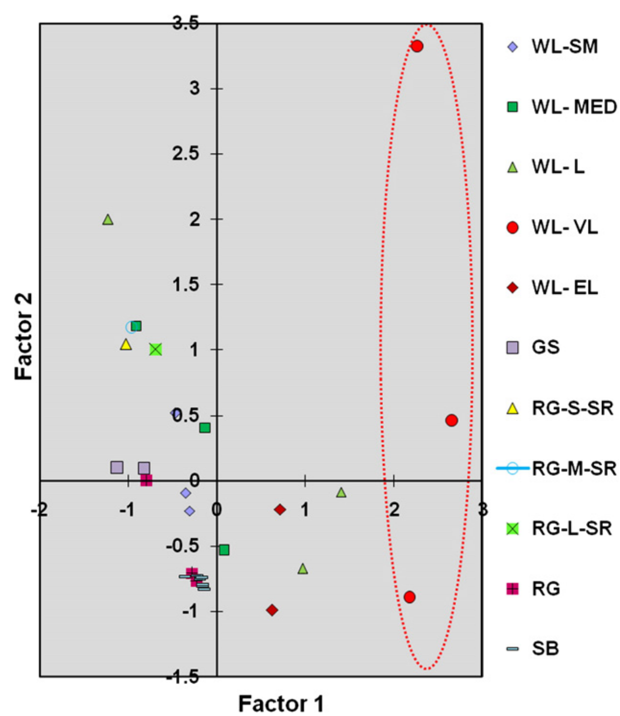

Fig. 3. Principal components analysis of the PCB congeners in forage fish and the various sizes of walleyes collected during 2007 from the Saginaw River and Saginaw Bay, Lake Huron. WL-SM = small walleye 357 mm, WL-MED = medium walleye 452 mm, WL-L = large walleye 535 mm, WL-VL = very large walleye 608 mm, WL-EL = extremely large walleye 680 mm, GS = gizzard shad, RG-S-SR = small round gobies from Saginaw river 66 mm, RG-M-SR = medium round gobies from Saginaw river 87 mm, RG-L-SR = large round gobies from Saginaw river 102 mm, RG = round gobies from Saginaw Bay 44 mm, SB = emerald shiners 46 mm, bluntnose minnows 45 mm, spottail shiners 40 mm, and banded killifish 38 mm from Saginaw Bay. See Table 2 for additional information on these fish.

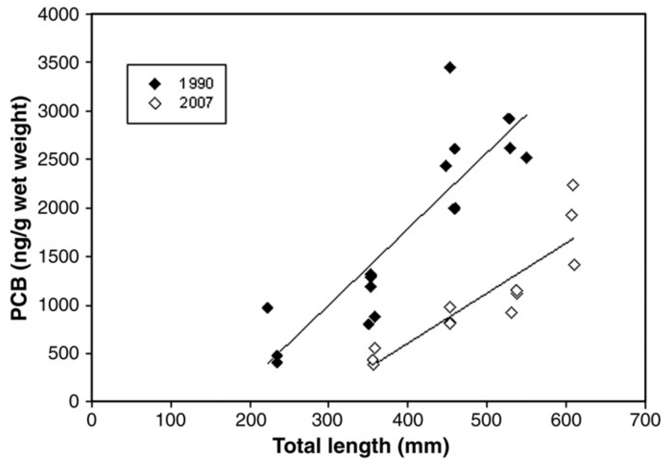

Fig. 4. Regression of walleye total length in mm (*X*) vs. PCB concentrations in ng PCBs/g ww (*Y*) for 1990 ($Y = 7.823X–1343$: $R^2 = 0.76$; data from Giesy et al. (1997)) and for 2007 ($Y = 5.163X–1457$: $R^2 = 0.80$; present study). Fish were collected from the Saginaw and Tittabawassee Rivers and Saginaw Bay, Lake Huron (see Tables 1 and 2 for additional details).

Comparisons between 1990 and 2007

The relationships between concentrations of PCBs in walleyes and their length had coefficient of determinations (R^2) of 0.76 and 0.80, respectively for 1990 (Giesy et al. 1997) and 2007 (Eqs. (2) and (3), respectively).

$$\text{PCBs (ng PCBs / g ww)} = 7.823^{*}\text{total length (mm)} - 1343 \quad (2)$$

$$\text{PCBs (ng PCBs / g ww)} = 5.163^{*}\text{total length (mm)} - 1457 \quad (3)$$

When these regressions were compared by use of ANCOVA ($P<0.0001$, $F = 42.79$, $df = 2$, $N = 27$), the mean concentration of PCBs during 2007 was found to be 1315 ng PCBs/g ww less than it was in 1990 (adjusted means: 2,015 vs. 700 ng PCBs/g ww for 1990 and 2007, respectively) (Fig. 4), which represents a 65% decrease. In both 1990 and 2007, concentrations of PCBs in composite samples of the largest walleyes collected were less than the next smaller size of walleyes: (1990: 539 mm–2686 ng PCBs/g ww and 627 mm–1769 ng PCBs/g ww vs. 2007: 608 mm–1900 ng PCBs/g ww and 680 mm–1200 ng PCBs/g ww). However, concentrations of PCBs in these largest walleyes in 2007 were still substantially less (by 569 ng PCBs/g) than they were in 1990. Concentrations of PCBs in composite samples of YOY gizzard shad and emerald shiners decreased from mean concentrations of 516 and 171 ng PCBs/g ww in 1990 to 190 and 51 ng PCBs/g ww in 2007, respectively. This decrease of approximately three-fold was significant (*t*-test, $P<0.001$).

The concentration of PCBs in zooplankton collected in 1990 was approximately four-fold less than zooplankton collected during 2008 (8 vs. 33 ng PCBs/g ww), but concentrations were still among the least measured in all types of samples collected in this study.

Pseudo, first-order kinetics

The pseudo, first-order rate constant for decrease in concentration of PCBs in YOY gizzard shad between 1990 (516 ng PCBs/g ww) and 2007 (190 ng PCBs/g ww) was 0.0588 year^{-1}. This is equivalent to a 6% decrease per year or a half time for decrease of 11.8 years.

Bioaccumulation factors

The range in bioaccumulation factors (BAFs) for five sizes of walleyes ranged from 2.4 to 9.8 for gizzard shad. Round gobies from the Saginaw River had lesser BAFs (1.6–6.7) than those from Saginaw Bay (11–44). Other forage fishes from Saginaw Bay had the greatest BAFs of 7.7–84.

Discussion

By collecting samples of the same sizes and species of fishes in 2007 as those collected by Giesy et al. (1997) in 1990, the degree of change that had occurred over the intervening 17-year period could be calculated. The observed decrease in concentrations of PCBs in walleyes and forage fishes may have been caused by any combination of dredging, reduction in inputs, other ongoing sedimentation processes, or modifications in the food web by newly introduced, nonindigenous species. In 2000–2001, the mouth of the Saginaw River was dredged to remove accumulated sediments contaminated with metals and organic compounds (MDEQ, 2003). The fact that concentrations of PCBs decreased 65% (based on covariance analysis) in walleyes from 1990 to 2007 is consistent with the results of other studies examining the effects dredging had on fish contaminants. In a companion study, Madenjian et al. (2009) showed that concentrations of PCBs in walleyes from the Tittabawassee River collected during 1996 prior to spawning were approximately 80% less in 2007. This decrease was corroborated by MDEQ (Bohr and Zbytowski, 2009) whole-fish walleye contaminant data from Saginaw Bay. Those researchers noted a substantial decrease in concentrations of PCBs at approximately the time of dredging. In other studies, concentrations of PCBs in Eurasian perch *Perca fluviatilis* (Bremle and Larsson, 1998) and DDT in shiner surfperch *Cymatogaster aggregata* (Weston et al., 2002) decreased following remedial dredging in a Swedish lake and San Francisco Bay, respectively. Walleyes that spend more time in the contaminated Tittabawassee and Saginaw Rivers, especially males (Fielder and Thomas, 2007), would be expected to ingest more PCBs through their diet than fish residing in Saginaw Bay or outer Lake Huron.

Round gobies and other prey fishes from Saginaw Bay during 2007 were considerably less contaminated than those from the Saginaw River and this trend was apparent in 1990 as well. During 1990, alewives from the Tittabawassee River had three-fold greater concentrations of PCBs (1218 ng/g ww) than those in Saginaw Bay (436 ng/g ww) (significantly different with $P = 0.045$ via *t*-test; Giesy et al., 1997). In addition, fish collected in Saginaw Bay contained greater concentrations of PCBs than did prey fish from Lake Huron proper (Madenjian et al., 1998).

Another contribution to the decrease in concentrations of PCBs in walleyes could be food web changes that were reflected in walleye diets in Saginaw Bay from 1990 to 2007. Diets of walleyes collected during 1990 from the Tittabawassee and Saginaw Rivers (Giesy et al., 1997) were mostly composed of alewives (62.5%, $N = 8$ fish that had eaten). During 1990–1996 walleyes from Saginaw Bay ate mostly gizzard shad, while during 1997–2003 alewife were the main prey consumed (Fielder and Thomas 2007a). From 2004 through 2008, yellow perch *Perca flavescens* and to a lesser extent, gizzard shad, were prominent prey, while round gobies began to be eaten during 2005–2007 (Fielder et al., 2007a; D. Fielder, personal communication, Michigan Department of Natural Resources, Alpena, Michigan). Therefore, it was hypothesized that changes in diet of walleyes as they shifted from more-contaminated clupeids and round gobies to less-contaminated yellow perch could change PCBs uptake in walleyes. In support of this observation, PCB concentrations of adult alewives (aroclors only) were almost three-fold greater than they were in adult yellow perch (skin on fillets) from Saginaw Bay in 1993 (Bohr and Zbytowski, 2009). In addition, from 1990 to 2007, concentrations of PCBs in other forage species, such as gizzard shad and emerald shiners from the Saginaw River, decreased almost three-fold. Concentrations in round gobies also decreased three-fold from 1998 to 2007. The decrease in concentrations of PCBs in walleyes (1315 ng PCBs/g ww) over the intervening 17 years (on average 77 ng PCBs/g ww per year) suggests that food web changes may have contributed to the decline in PCBs in walleyes. However, this cannot account for the decrease in

PCB concentrations in YOY walleye, which suggests that dredging likely reduced the available concentration of PCBs in the Saginaw River system.

To assess the potential role of dredging on the rate of decline in PCBs, pseudo, first-order rate constants were developed for the period before and after dredging. The rate constant for post dredging was determined to be 0.0588 year^{-1}, which is equivalent to about 6% per year. This has a half time for decrease of 11.8 years, which means that the concentration in walleyes would decrease 50% every 12 years. This information can be used in simulation models to predict future concentrations of PCBs in fish and assist in remedial-action decision making. The pseudo, first-order rate constant to describe the rate of change that was derived from PCB loadings between 1971 and 1996 was approximately 4% per year (kd = 0.036 year^{-1}; Verbrugge et al., 1995). Assuming these two estimates derived from two different parameters are equivalent, the rate of decline estimated between 1990 and 2007 is approximately 1.6-fold greater than the earlier estimate. One way to interpret this finding is that dredging in 2000–2001 accelerated declines in PCBs observed in walleyes (see Madenjian et al., 2009). However, changes in the food web may have also contributed to the observed decrease in PCB concentrations of larger walleyes.

Of the PCB congeners measured, congener No. 153/132 (with six chlorines) occurred in greatest concentrations at walleyes; this congener also composed a large percentage of the PCB congeners in salmonines in Lake Ontario (Oliver and Niimi, 1985). Lower food web components, especially zebra mussels, had greater percentages of the less-substituted PCBs (tri-, tetra-, and pentachlorobiphenyls). Zooplankton were intermediate, while fish had greater percentages of the greater-substituted homologs (hexa-, septa-, octa-, and nanacholorbiphenyls), a pattern also noted in the Lake Ontario food web (Oliver and Niimi, 1985). The less-substituted PCBs are more volatile and those organisms feeding closest to or on the sediments will more closely resemble the homolog patterns of the sediments than biota less associated with the sediments and higher on the food chain. Hence, benthic zebra mussels which filter water near sediments exhibited relatively great proportions of less-substituted PCBs, while zooplankton, which filter the pelagic water column of algae, had the next greatest proportions, followed by forage fish and top predators.

As walleyes grew larger, there was a small linear increase in the percentage that nana homologs composed and this apparent difference was also highlighted by the PCA and found in other studies (Oliver and Niimi, 1985). The PCA performed during this study showed a consistent pattern of increasing percentage of higher-chlorinated homologs along the *x* axis, from small, to medium, to large, to very large walleyes. The extremely large walleyes did not follow the pattern and were intermediate between medium and large walleyes. These extremely large walleyes in our samples were undoubtedly females, which leave after spawning and do not spend much time in the Saginaw/Tittabwassee Rivers as do males and smaller female walleyes. Evidence of this was our inability to capture any extremely large walleyes in the Saginaw River during our extensive electroshocking in May; we had to capture these fish in trap nets in Saginaw Bay. In addition, during both 1990 and 2007 these large fish had lesser concentrations of PCBs than did somewhat smaller walleyes. The reasons these fish may have had lower PCBs include: (1) these large females spend most of their time in Saginaw Bay (some migrate to other areas; Fielder and Thomas, 2007a) away from the more contaminated prey in the Saginaw River and recently have shifted diets to more yellow perch, which are less contaminated, and (2) because of their large size and gape width, these fish can feed on larger forage fish, which may not be available to smaller walleyes and could be less contaminated than prey consumed by smaller walleyes. These differences apparently also changed the composition of congeners bioaccumulated in these extremely large walleyes compared with smaller walleyes. A similar scenario was documented for Chinook salmon *Oncorhynchus tshawytscha* in Puget Sound, Washington (O'Neil and West, 2009). They attributed differences in PCB concentrations in salmon caught from two different areas to the amount of contamination in the area inhabited and to diets.

There is also a chemical-physical explanation for accumulation of more chlorinated congeners in larger fish. Rates of accumulation of these congeners would be expected to be enhanced over the less-chlorinated homologs, because enzyme-mediated systems in fish can metabolize less-chlorinated PCBs, while more-chlorinated congeners undergo little change (Ankley et al., 1992; Boon and Eijgenraam, 1988). In addition, less-chlorinated congeners would be expected to be nearer to steady state than the heavier, more-substituted congeners. Over time, as walleyes were exposed for longer periods and growth rate declined promoting less growth dilution, an increase in the relative proportion of more substituted PCB homologs would occur.

Patterns of PCB congeners displayed by the PCA analysis showed round gobies collected from the Saginaw River contained more less-chlorinated congeners than did round gobies (and other forage fish) from Saginaw Bay. This result suggests that food eaten by round gobies (benthos, especially zebra mussels) contained greater proportions of the less-chlorinated congeners, which reflects their closer association with contaminated sediments. These sediments generally have more, less-chlorinated congeners available for bioaccumulation than do the less-contaminated sediments in Saginaw Bay.

Zooplankton, along with other components of the Saginaw River food web, contained greater concentrations (15–32 ng/g ww) than found at other locations. For example, Houde et al. (2008) studied 17 lakes in Canada and the northeastern United States and found concentrations of PCBs in zooplankton ranged from 0.06 to 15 ng PCBs/g ww. During 2008, zooplankton contained greater concentrations of PCBs (as great as some Saginaw Bay forage fishes) and had a different homolog pattern than they did in 1990. Lakes with less plankton biomass have been reported to have greater concentrations of some organochlorine compounds (Taylor et al., 1991). This result suggests that plankton biomass in the river during 2008 was less than during 1990.

Because of poor recruitment of naturally produced walleye larvae, the walleye population in Saginaw Bay has been augmented by stocking (Fielder and Thomas, 2007, Fielder et al., 2007; Jude, 1992). In the early 2000s, however, there has been a dramatic reversal, with greater survival of naturally produced larvae, which has led to larger year classes being produced. This has been attributed by Fielder et al. (2007) to the near elimination of alewife from Lake Huron, which has led to reduced predation on larval emerald shiners (Schaeffer et al., 2008) and larval walleyes, which have both experienced increased recruitment. Larval fish predation by alewives was the factor thought to have led to the near extirpation of walleyes from Muskegon Lake, Lake Michigan in the 1960s (Schneider and Leach, 1977) and other species with pelagic larvae (Madenjian et al., 2002). Early mortality syndrome (thiamine deficiency due to eating alewives) does not appear to be a factor (Honeyfield et al., 2003). Since PCBs are known to affect hatching success (Matta et al., 1997) and PCBs have declined almost 65% from 1990 to 2007, it is possible that reduced concentrations of PCBs has also contributed to increased walleye recruitment in Saginaw Bay.

Concentrations of PCBs were magnified up to 10 times from gizzard shad and round gobies to walleyes. Gizzard shad were the main diet items of walleyes in Saginaw Bay during 1990–1996 and were very important during 2004–2008 (Fielder and Thomas 2007). Round gobies composed an important component of the diet during 2005–2007. Gizzard shad feed on zooplankton, algae, and detritus (Jude 1973) and round gobies feed on zebra and quagga *D. bugensis* mussels (French and Jude 2001) that filter algae and detritus from the river. Both fishes, especially round gobies, would be expected to accumulate PCBs through feeding on contaminated organisms and detrital particles from the Saginaw River (Kim, 2007; Kwon et al., 2006; Ng et al., 2008). Thus, these relatively great BAFs suggest that one of the main conduits of PCB transfer to walleyes is through consumption of contaminated gizzard shad and round gobies (prey with the greatest PCB concentrations), while pre-spawning and spawning walleyes reside in the river in fall and during the spring spawning season. Since males reside in the river longer, they would have greater accumulation rates for PCBs than females of comparable size as was found by Madenjian et al. (2009). A similar finding of more highly contaminated benthic invertebrates and fishes the closer they were to local sources of PCBs, while anadromous arctic charr *Salvelinus alpinus* showed little bioaccumulation, was found in a coastal area in Labrador (Kuzyk et al., 2005).

Evidence for fish in the Saginaw River containing greater concentrations of PCBs than most other areas of the Great Lakes and that these concentrations are due in part to bioaccumulation through the food chain comes from examination of round gobies. First, a composited sample of 66-mm (means size) round gobies collected during 2007 in the Saginaw River contained 200 ng PCBs/g ww, while 44-mm round gobies (although 33% smaller) from Saginaw Bay in 2005 contained 42 ng PCBs/g ww, an almost five-fold decrease in PCBs concentrations. Part of the reason for increased accumulation of PCBs in the Saginaw River is that diet of round gobies, especially large (>50 mm) ones, is composed of dreissenids (French and Jude, 2001), which can filter and sequester large quantities of toxic substances (Kwon et al., 2006; Morrison et al., 2000; Ng et al., 2008).

Second, in 1998 concentrations of PCBs were measured in round gobies from the Saginaw River (Hanari et al., 2004) prior to dredging in 2000–2001 from the same site as those collected in this study. Concentrations of PCBs in those round gobies (92–144 mm), which were slightly larger than those collected in 2007, ranged from 372 to 488 ng PCBs/g ww, which is approximately 1.5 times greater than those in round gobies (62–119 mm) collected in 2007 from the Saginaw River. This result suggests that concentrations of PCBs have decreased in the river since 1998 (pre-dredging); bioaccumulation rates in top predators also declined over this same period. This conclusion was corroborated with data from this study, Bohr and Zbytowski (2009) and Madenjian et al. (2009). In fact this decrease of 1.5 is essentially exactly the factor that was estimated to be attributable to the dredging, relative to first-order decreases due to dissipation and burial. However, composited zebra mussels from the same site in 1998 contained a mean concentration of 356 ng PCBs/g ww (Hanari et al., 2004), which showed little change from concentrations in 2008 samples. This finding shows that zebra mussels have the potential to accumulate relatively great concentrations of PCBs, which can then be transferred to round gobies.

Third, the study by Hanari et al. (2004) also examined PCBs in the Raisin River (an International Joint Commission Area of Concern and tributary to Lake Erie) in 1998 and found that the range of concentrations in 70- to 109-mm round gobies was 1990–4710 ng PCBs/g ww and that zebra mussels contained 814–2920 ng PCBs/g ww. This demonstrates that the zebra mussel-to-round goby trophic link can result in substantial transfer of PCBs to top predators, such as fishes, birds, mammals, and reptiles. In the St. Clair River, Hanari et al. (2004) found that contamination was less, as 77- to 133-mm round gobies contained 81–181 ng PCBs/g, which is closer to concentrations observed in Saginaw Bay round gobies, which contained 42 ng PCBs/g ww. Zebra mussels from the St. Clair River averaged 31 ng PCBs/g during 1999.

Concentrations of PCBs in round gobies and zebra mussels appeared to reflect available PCB concentrations in the ecosystem and represented changes over time, which suggests that they would be useful bioindicators to monitor changes in the overall contamination of AOCs (Richman and Somers, 2005) or these data could be used as endpoints in delisting of AOCs. Even though the relationship between round goby length and PCBs concentrations in this study was linear, there have been suggestions from other studies (Ng et al., 2008), that small round gobies, because they eat more benthos and eggs, sometimes have greater concentrations of PCBs than do larger round gobies that eat almost exclusively dreissenids (French and Jude, 2001). This linear relationship may be more prevalent in contaminated sites, where greater contamination overwhelms subtle differences with size observed in less contaminated sites. Hence, the bioindicator should use two to three sizes of round gobies to encompass this potential variation.

Concentrations of PCBs measured in fish from Saginaw Bay were greater than those reported for other locations in the Great Lakes (Williams et al., 1992). The mean concentration in composited, very large walleyes (608 mm) collected during 2007 was 1900 ng PCBs/g ww, which is less than the current concentration of 2000 ng PCBs/g ww that is required to trigger a fish consumption advisory (Foran and Vander Ploeg, 1989; Sonzogni and Swain, 1984; MDPH, 1993). One of the three composited replicates from these samples (2100 ng PCBs/g ww) did however exceed the guideline concentrations. However, data reported in this study may not be directly comparable to consumption guidelines, because they were determined in whole fish and guidelines are based on fillets. Nevertheless, concentrations of PCBs observed in these walleyes have been considered by some authors to be sufficient to warrant concern for a potential human health hazard (Bro et al., 1987; Cordle et al., 1982; Paneth, 1991).

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References

Ankley, G., Cook, P., Carlson, A., Call, D., Swenson, J., Cocoran, H., Hoke, R., 1992. Bioaccumulation of PCBs from sediments by oligochaetes and fishes: comparison of laboratory and field results. Can J Fish Aquat Sci 49, 2080–2085.

Allan, R.J., Ball, A., Cairns, V., Fox, G., Gilman, A., Peakall, A., Piekarz, D., Van Oosdam, J., Villeneuve, D., Williams, D., 1991. Toxic chemicals in the Great Lakes and associated effects. Environment. Dept. Fisheries & Oceans, Health & Welfare Canada, Canada. Vols I & II 758 pp.

Bohr, J., Zbytowski, J., 2009. Michigan fish contaminant monitoring program: 2008 Annual Report. MDEQ-WB Report # MI /DEQ/WB - 09/44, Lansing, Michigan.

Boon, J., Eijgenraam, F., 1988. The possible role of metabolism in determining patterns in PCB congeners in species from the Dutch Wadden Sea. Mar Environ Res 24, 3–8.

Bremle, G., Larsson, P., 1998. PCB concentration in fish in a river system after remediation of contaminated sediment. Environ Sci Technol 32, 3491–3495.

Bro, K.M., Sonzogni, W., Hanson, M., 1987. Relative cancer risks of chemical contaminants in the Great Lakes. Environ Manage 11, 495–505.

Bur, M.T., Stapanian, M.A., Bernhardt, G., Turner, M., 2008. Fall diets of red-breasted merganser (*Mergus serrator*) and walleye (*Sander vitreus*) in Sandusky Bay and adjacent waters of Western Lake Erie. Am Mid Nat 159, 147–161.

Camazo, J., Rice, C., Jude, D., Rossmann, R., 1987. Organic priority pollutants in nearshore fish from 14 tributaries to Lake Michigan. J Great Lakes Res 13, 296–309.

Cordle, F., Locke, R., Springer, J., 1982. Risk assessment in a federal regulatory agency: an assessment of risk associated with the human consumption of some species of fish contaminated with polychlorinated biphenyls (PCBs). Environ Perspect 45, 171–182.

Fanslow, D., Nalepa, T., Lang, G., 1995. Filtration rates of zebra mussels (*Dreissena polymorpha*) on natural seston from Saginaw Bay, Lake Huron. J Great Lakes Res 21, 489–500.

Fielder, D., Thomas, M., 2007. Fish population dynamics of Saginaw Bay, Lake Huron 1998–2004. Fisheries Research Report No. 2083 Michigan Department of Natural Resources. Ann Arbor, Michigan.

Fielder, D., Schaeffer, J., Thomas, M., 2007. Environmental and ecological conditions surrounding the production of large year classes of walleye (*Sander vitreus*) in Saginaw Bay, Lake Huron. J Great Lakes Res 33 (Suppl. 1), 118–132.
Foran, J.A., Vander Ploeg, D., 1989. Consumption advisories for sport fish in the Great Lakes Basin: jurisdictional inconsistencies. J Great Lakes Res 15 (3), 476–485.
Frame, G.M., Cochran, J., Boewadt, S.S., 1996. Complete PCB congener distributions for 17 Arochlor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener specific analysis. J High Resolut Chromatogr 19, 657–668.
French III, J.R., Jude, D., 2001. Diets and diet overlap of non-indigeneous gobies and small benthic native fishes co-inhabiting the St. Clair River, Michigan. J. Great Lakes Res 27, 300–311.
Giesy, J., Jude, D., Tillitt, D., Gale, R., Meadows, J., Zajieck, J., Petrman, P., Verbrugge, D., Sanderson, J., Schwartz, T., Tuchman, M., 1997. Polychlorinated-dibenzo-p-dioxins, -dibenzofurans, -biphenyls, and 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin equivalents in fishes from Saginaw Bay, Michigan. Environ Toxicol Chem 16, 713–724.
Hanari, N., Kannan, K., Horii, Y., Taniyasu, S., Yamashita, N., Jude, D., Berg, M., 2004. Polychlorinated naphthalenes and polychlorinated biphenyls in benthic organisms of a Great Lakes food chain. Arch Environ Contam Toxicol 47, 84–93.
Honeyfield, D., Vandergoot, C., Bettoli, P., Hinterkoft, J., Zajicek, J., 2003. Thiamine and fatty acid content of walleye tissue from three southern reservoirs. J Aquatic Animal Health 19, 84–93.
Horgan, M., Mills, E., 1997. Clearance rates and filtering activity of zebra mussels (*Dreissena polymorpha*): implications for freshwater lakes. Can J Fish Aquat Sci 54, 249–255.
Houde, M., Muir, D., Kidd, D., Guildford, S., Drouillard, K., Evans, M., Wang, X., Whittle, D., Haffner, D., Kling, H., 2008. Influence of lake characteristics on the biomagnification of persistent organic pollutants in lake trout food webs. Environ Toxicol Chem 27, 2169–2178.
International Joint Commission, 1993. IJC recommends United States, Canada phase out 11 toxics persistent in lakes. Environmental Report-BNA 24,1063. Windsor, ON, Canada.
Jude, D.J., 1973. Food habits of gizzard shad in Pool 19, Mississippi River. Trans Amer Fish Soc 102, 378–383.
Jude, D.J., 1992. Evidence for natural reproduction by stocked walleyes in the Saginaw River tributary system, Michigan. North Amer J Fish Manage 12, 386–395.
Jude, D.J., Reider, R., Smith, G., 1992. Establishment of Gobiidae in the Great Lakes basin. Can J Fish Aquat Sci 49, 416–421.
Jude, D.J., 2001. Round and Tubenose Gobies: 10 years with the latest Great Lakes phantom menace. Dreissena 11 (4), 1–14.
Kim, G.W., 2007. Trophic transfer of energy and polychlorinated biphenyls by native and exotic fish in Lake Erie. MS thesis, Ohio State University, Columbus, Ohio. 184 pp.
Kuzyk, Z.A., Stow, J.P., Burgess, N.M., Solomon, S.M., Reimer, K.J., 2005. PCBs in sediments and the coastal food web near a local contaminant source in Saglek Bay, Labrador. Sci Total Environ 351–352, 264–284.
Kwon, Tae-Dong, Fisher, S., Kim, G., Hwan, H., Jang-Eok., Kim, 2006. Trophic transfer and biotransformation of polychlorinated biphenyls in zebra mussel, round goby, and smallmouth bass in Lake Erie, USA. 2006. Environ Toxicol Chem 25 (4), 1068–1078.
Madenjian, C., Noguchi, G., Haas, R., Schrouder, K., 1998. Sexual difference in polychlorinated biphenyl accumulation rates of walleye (*Stizostedion vitreum*). Can. J. Fish. Aquat. Sci. 55, 1085–1092.
Madenjian, C., Jude, D., Rediske, R., O'Keefe, J., Noguchi, G., 2009. Gender difference in walleye PCB concentrations persists following remedial dredging. J Great Lakes Res 35, 347–352.
Madenjian, C., Fahnenstiel, G., Johengen, T., Nalepa, T., Vanderploeg, H., Fleischer, G., Schneeberger, P., Benjamin, D., Smith, E., Bence, J., Rutherford, E., Lavis, D., Robertson, J., Jude, D., Ebner, M., 2002. Dynamics of the Lake Michigan food web, 1970–2000. Can J Fish Aquat Sci 59, 736–753.
Matta, M., Cairncross, C., Kocan, R., 1997. Effect of a polychlorinated biphenyl metabolite on early life stage survival of two species of trout. Bull Environ Contam Toxicol 59, 146–151.
MDPH (Michigan Department of Public Health)., 1993. Contaminant trends in fish tissue. Status report. Michigan Department of Public Health Division of Health Risk Assessment, Lansing, MI.
MDEQ (Michigan Department of Environmental Quality), 2003. A sediment sampling survey of the Saginaw River, Bay County, Michigan. MDEQ Staff Report, 2–3 September, Lansing, Michigan.
Moll, R.A., Jude, D., Rossmann, R., Kantak, G., Barres, J., DeBoe, S., Giesy, J., Tuchman, M., 1995. Movement and loadings of inorganic contaminants through the lower Saginaw River. J Great Lakes Res 21, 17–34.
Morrison, H.A., Whittle, D., Haffner, G., 2000. The relative importance of species invasions and sediment disturbance in regulating chemical dynamics in western Lake Erie. Ecol Model 125, 279–294.
Nalepa, T., Fahnenstiel, G., 1995. *Driessena polymprpha* in the Saginaw Bay Lake Huron Ecosystem: overview and perspective. J Great Lakes Res 21, 4111–4416.
Ng, C., Berg, M., Jude, D., Janssen, J., Charlebois, P., Amaral, L., Gray, K., 2008. Chemical amplification in an invaded food web: seasonality and ontogeny in a high biomass, low-diversity ecosystem. Environ Toxicol Chem 27, 2186–2195.
Oliver, B.G., Niimi, A.J., 1985. Trophodynamic analysis of PCB congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. Environ Sci Technol 22, 388–397.
O'Neil, S., West, J., 2009. Marine distribution, life history traits, and the accumulation of polychlorinated biphenyls in Chinook salmon from Puget Sound, Washington. Trans Amer Fish Soc 138, 616–632.
Paneth, N., 1991. Human reproduction after eating PCB-contaminated fish. Hlth Environ Digest 5, 4–6.
Reeders, H.H., Bij deVaate, A., Slim, F.H., 1989. The filtration rate of *Dreissena polymorpha* (Bivalvia) in three Dutch lakes with reference to biological water quality management. Freshwater Biol 22, 133–141.
Richman, L., Somers, K., 2005. Can we use zebra and quagga mussels for biomonitoring contaminants in the Niagara River? Water Air Soil Pollut 167 (1–4), 155–178.
SAS (Statistical Analysis Software)., 2007. SAS Institute, Inc. 2007. Online Doc 9.1.2. Cary, NC.
Schaeffer, J., Warner, D., O'Brian, T., 2008. Resurgence of emerald shiner *Notropis atherinoides* in Lake Huron's main basin. J Great Lakes Res 43, 395–403.
Schmidt, L.J., 1997. Method for analysis of total PCBs and PCB congeners (full suite) and transnonachlor for gas chromatography/ negative chemical ionization single ion mass spectrophotometry, Vol II of Lake Michigan Mass Balance (LMMB) study methods compendium. Organic and mercury methods. EPA-905-R-97–012b. U.S Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL.
Schneider, J.C., Leach, J., 1977. Walleye (*Stizostedion vitreum vitreum*) fluctuations in the Great Lakes and possible causes 1800-1975. J Fish Res Board Can 34, 1878–1889.
Sonzogni, W., Maack, L., Gibson, T., Degenhardt, D., Anderson, H., Fiore, B., 1991. Polychlorinated biphenyl congeners in blood of Wisconsin sport fish consumers. Arch Environ Contam Toxicol 20 (1), 56–60.
Taylor, W., Carey, J., Lean, D., McQueen, D., 1991. Organochlorine concentrations in the plankton of lakes in southern Ontario and their relationship to plankton biomass. Can J Fish Aquat Sci 48, 1960–1966.
Tillitt, D.E., Ankley, G., Giesy, J., Ludwig, J., Kurita-Matsuba, H., Weseloh, D., Ross, P., Bishop, C., Sileo, L., Stromberg, K., Larson, J., Kubiak, T., 1992. Polychlorinated biphenyls residues and egg mortality in double-crested cormorants from the Great Lakes. Environ Toxicol Chem 11, 1281–1288.
USEPA, 1999. Method 1668, revision A: chlorinated biphenyl congeners in waters, soil, and tissue by HRGC/HRMS. United States Environmental Protection Agency, Washington, DC. EPA-821-R-00-002.
Verbrugge, D.A., Giesy, J., Mora, M., Williams, L., Crawford, R., Rossman, R., Moll, R., Tuchman, M., 1995. Concentrations of dissolved and particulate PCBs in water from the Saginaw River, Michigan. J Great Lakes Res 21, 219–233.
Weston, D.P., Jarman, W.M., Cabana, G., Bacon, C.E., Jacobson, L.A., 2002. An evaluation of the success of dredging as remediation at a DDT-contaminated site in San Francisco Bay, California, USA. Environ Toxicol Chem 21, 2216–2224.
Williams, L.L., Giesy, J., DeGalan, N., Verbrugge, D., Tillitt, D., Ankley, G., Welch, R., 1992. Prediction of concentrations of 2, 3, 7, 8-TCDD equivalents (TCDD-EQ) from total concentrations of PCBs in fish fillets. Environ Sci Technol 26, 1151–1159.