Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2018, 52, 4393−4401

pubs.acs.org/est

Distributions of PCB Congeners and Homologues in White Sucker and Coho Salmon from Lake Michigan

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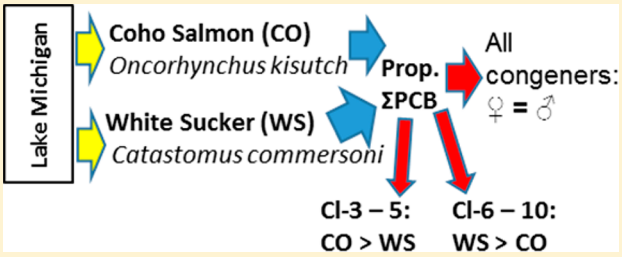
ABSTRACT: We tested the hypothesis of the proportion of higher chlorinated biphenyl (PCB) congeners increasing with increasing trophic level by comparing the respective PCB homologue distributions in an omnivore, white sucker (*Catostomus commersoni*), and a top predator, coho salmon (*Oncorhynchus kisutch*), from Lake Michigan. Adult females had the same congener and homologue proportions of total PCB concentration (ΣPCB) as adult males in both species. Hexachlorinated congeners comprised the largest proportion (32%) found in white sucker, followed by heptachlorinated (21%) and octochlorinated (18%) congeners. In contrast, pentachlorinated congeners comprised the largest proportion (33%) of ΣPCB found in coho salmon, followed by hexachlorinated (26%) and tetrachlorinated (24%) congeners. Coho salmon contained significantly higher proportions of tri-, tetra-, and pentachlorinated congeners, whereas white sucker contained significantly higher proportions of hexa- through decachlorinated congeners. Our results were opposite of the hypothesis of greater degree of PCB chlorination with increasing trophic level, and supported the contention that the PCB congener proportions in fish depends mainly on diet, and does not necessarily reflect the trophic level of the fish. Our results also supported the contention that diets do not vary between the sexes in most fish populations.



INTRODUCTION

The primary route of entry of polychlorinated biphenyls (PCBs) into the body of fishes is by food intake.[1−3] Further, biomagnification of total PCB concentration (ΣPCB) has been well documented.[4] In nearly all fish species studied, whole-body ΣPCB has been found to be between 17% and 43% higher in mature male than in mature female conspecifics.[3,5] This is due mainly to greater energy expenditure, which leads to greater food consumption, by males. Madenjian et al.[6] identified two mechanisms by which sexual differences in the PCB congener distributions of predator fish can arise: (1) a sexual difference in diet composition, or (2) the combined effects of a sexual difference in habitat utilization by the predator and a spatial gradient in the PCB congener distribution of the prey, such that the prey of the two sexes of the predator vary in PCB congener distribution. Thus, differential feeding by male and female fish at PCB "hot spots" can result in a sexual difference in congener distribution.[7,8] For example, old (age 14−21 years) male burbot (*Lota lota*) in Lake Erie had different PCB congener distributions than young (age 6−13 years) males, young females, and old females, probably due to old males feeding for longer periods at spawning sites that were PCB "hot spots."[8] In contrast, there were no differences between adult female and adult male burbot in their respective congener distributions in Great Slave Lake, a comparatively pristine system.[9] For most fish populations examined, however, the congener and homologue distributions for male and female conspecifics are the same, suggesting no difference in their respective diets.[3,5]

Several studies suggest that, overall, the degree of chlorination of PCBs found in organisms in aquatic food webs increases with trophic level.[10−14] Walters et al.[14] contended that this pattern also applies to fish at different trophic levels within a food web. In contrast, other studies revealed no significant differences in PCB congener distributions across fish species within a food web or no clear trend in degree of chlorination of PCB congeners with increasing trophic level of fish.[10,12,13] Given these mixed results, additional studies on differences in the PCB congener distributions across fish species of various trophic positions within the same food web are warranted.

White sucker (*Catostomus commersonii*) and coho salmon (*Oncorhynchus kisutch*) in Lake Michigan occupy low and high trophic levels, respectively.[15,16] Both species are consumed by humans in the Laurentian Great Lakes region.[17,18] Adult white

Received: January 11, 2018
Revised: February 23, 2018
Accepted: March 6, 2018
Published: March 14, 2018

DOI: 10.1021/acs.est.8b00186
Environ. Sci. Technol. 2018, 52, 4393−4401

suckers are omnivorous, feeding primarily on aquatic insects and their larvae (particularly chironomids), and benthic algae (including desmids and diatoms).[15,19] In Lake Michigan, adult white suckers feed mainly on chironomids and benthic algae (P. B. McIntyre, unpublished data). White sucker is a benthic species that is abundant and widely distributed across North America. It shows site fidelity to its spawning area, and exhibits fidelity to a home range at times of the year other than spawning time.[20] White sucker is considered to be a sentinel species for contaminated sediments in freshwater ecosystems.[20,21] Coho salmon is a top predator in the Lake Michigan food web, feeding predominately on alewife (*Alosa pseudoharengus*).[16,22−24]

Despite the vast difference in feeding habits between the two species, both adult white sucker and age-2 coho salmon can be captured in the shallow (<10 m deep) waters of the main basin of Lake Michigan during spring and fall months.[25,26] Most adult white suckers in Lake Michigan spawn in tributaries during April, but then return to the lake by May. A portion of the adult white sucker population continues to inhabit the shallow waters of Lake Michigan during the summer,[25] but some adult white suckers have been caught in waters as deep as 60 m in the main basin of Lake Michigan (C. P. Madenjian, unpublished data). During summer months, coho salmon are caught by anglers in Lake Michigan waters ranging from 15 to 75 m deep.[26]

In this work, we test two aspects of the PCB congener and homologue distributions in fish, using white sucker and coho salmon collected in Lake Michigan. First, we test for differences between adult males and females of both species for proportions of ΣPCB for individual congeners and homologues. If there is no differential habitat utilization or prey selection by males and females in either species, then there should be no intraspecific differences between the sexes for these proportions. Such results would support a growing body of evidence that the diets of both sexes of conspecifics, and the congener distributions they ingest, are the same.[3] Second, we test if the hypothesis[14] of increasing degree of PCB chlorination with trophic level is applicable to the omnivorous white sucker and the piscivorous coho salmon in Lake Michigan. If true, then the proportions of low-chlorinated congeners should be higher in white suckers and the proportions of high-chlorinated congeners should be higher in coho salmon.

MATERIALS AND METHODS

Field Methods. Details for capturing coho salmon are described in detail elsewhere.[24] In brief, 95 mature coho salmon were collected either with hook and line in Lake Michigan or at state-operated weirs in tributaries to Lake Michigan during 1995. Sex for each fish was determined in the field. Stomachs and a sample of scales from each fish were removed and examined in the laboratory. Fish were then individually wrapped in solvent-resistant aluminum foil, placed in a plastic bag, frozen, and then transported to the Great Lakes Science Center (GLSC) laboratory for further processing.

Details for capturing white suckers (N = 25 female, 26 male) are described in detail elsewhere.[21] In brief, spawning white suckers were collected with dip nets at the Kewaunee River (Wisconsin, U.S.A.), a tributary to Lake Michigan, on 19 April 2016. Sex for each fish was determined in the field. Otoliths were extracted and stomachs were removed from each fish. Fish were individually wrapped in plastic bags and frozen at −20 °C, and then transported to the GLSC laboratory for further processing.

Laboratory Methods. Age of each coho salmon was estimated by examining scales. In this study, we considered PCB data only for age-2 male (N = 60) and female (N = 35) coho salmon.[27] Age of each white sucker was estimated by examining thin sections of the otoliths,[28] and ranged from 4 to 24 years.[21]

Details for preparing coho salmon samples prior to PCB analyses are found elsewhere.[27] In brief, coho salmon were thawed and then composited into groups of five fish of the same sex, similar size, and similar time and location of capture. In total, 12 male and 7 female composites of five age-2 coho salmon were analyzed. Fish compositing was conducted according to the Lake Michigan Mass Balance project protocol.[29] Mean weight of the coho salmon was calculated for each composite. Each composite was homogenized using a commercial blender. About 50 g of the homogenate from each composite was placed in a contaminant free glass jar, sealed with a lid, and then frozen at −20 °C until time of extraction.

Details for preparing white sucker samples prior to PCB analyses are found elsewhere.[21] In brief, each of the frozen white suckers was partially thawed and then individually homogenized using appropriately sized blenders at the GLSC laboratory. For each fish, approximately 100 g of the whole-fish homogenate was placed in a contaminant-free glass jar, sealed with a lid, and stored at −20 °C. The frozen homogenates were transported to the University of Michigan School of Public Health for PCB and lipid determinations.

Methods for determining PCB congener concentrations in the homogenates have been described in detail elsewhere.[21,30−32] In brief, a 10-g sample of each homogenate was dried with 40 gof sodium sulfate and was extracted by repeated dichloromethane/hexane extractions. Lipids were removed following US Environmental Protection Agency's Method 1668B.[33] Analyte

Table 1. Mean Proportions of Total PCB for Eight Homologues Found in White Suckers (N = 51) in Five Age Categories[a]

	age range (years)						
no.	4−10	11−12	13−14	15−16	17−24		
Cl	(n = 11)	(n = 12)	(n = 10)	(n = 11)	(n = 7)	$F_{4,46}$	$p > F$
3	0.0002	0.0002	0.0002	0.0002	0.0002	0.31	0.87
4	0.0653	0.0655	0.0652	0.0652	0.0654	0.47	0.76
5	0.1551	0.1565	0.1557	0.1567	0.1568	0.99	0.42
6	0.3176	0.3174	0.3175	0.3166	0.3172	0.08	0.99
7	0.2051	0.2059	0.2079	0.2057	0.2059	0.66	0.62
8	0.1796	0.1775	0.1767	0.1796	0.1795	0.56	0.69
9	0.0756	0.0758	0.0753	0.0744	0.0738	0.61	0.66
10	0.0014	0.0013	0.0015	0.0015	0.0011	4.05	0.007

[a]For each homologue, an ANOVA was conducted to test for equal means in all age categories, with rejection at $p < 0.00625$ (= 0.05/8).

DOI: 10.1021/acs.est.8b00186
Environ. Sci. Technol. 2018, 52, 4393−4401

Table 2. Means and Standard Errors (SE) of Proportions of Total PCB Concentrations for 62 Congeners Found in 25 Adult Female and 26 Adult Male White Suckers[a]

congener	no.	females		males		
no(s)	Cl	mean	SE	mean	SE	*p*
28/31	3	0.00022	0.00000	0.00023	0.00000	0. 013
41/71	4	0.00910	0.00004	0.00911	0.00004	0.732
44	4	0.00259	0.00005	0.00260	0.00004	0.684
47/48	4	0.00441	0.00004	0.00440	0.00006	0.737
49	4	0.00206	0.00005	0.00201	0.00005	0.115
52	4	0.00444	0.00005	0.00443	0.00005	0.795
56/60	4	0.01950	0.00008	0.01946	0.00004	0.419
66	4	0.00562	0.00005	0.00564	0.00005	0.520
70/76	4	0.00816	0.00006	0.00819	0.00003	0.303
74	4	0.00265	0.00005	0.00264	0.00004	0.686
77	4	0.00024	0.00004	0.00023	0.00003	0.627
81/87	4/5	0.01331	0.00005	0.01322	0.00005	0.022
82	5	0.01030	0.00006	0.01025	0.00004	0.147
84/89/92	5	0.02271	0.00006	0.02271	0.00005	0.860
85	5	0.01937	0.00005	0.01927	0.00023	0.401
95	5	0.00188	0.00006	0.00185	0.00004	0.363
99	5	0.01371	0.00006	0.01373	0.00005	0.688
101	5	0.01599	0.00022	0.01621	0.00015	0.103
105	5	0.01815	0.00007	0.01815	0.00006	0.981
107	5	0.00105	0.00006	0.00102	0.00006	0.407
110	5	0.01254	0.00006	0.01255	0.00005	0.787
114	5	0.00131	0.00005	0.00119	0.00004	0.0007
118	5	0.01108	0.00005	0.01101	0.00012	0.332
123	5	0.00773	0.00005	0.00775	0.00003	0.438
126	5	0.01394	0.00019	0.01383	0.00020	0.458
128	6	0.01239	0.00013	0.01251	0.00013	0.223
131	6	0.00976	0.00005	0.00975	0.00004	0.859
132/153	6	0.09261	0.00044	0.09272	0.00032	0.708
134	6	0.01309	0.00005	0.01313	0.00003	0.136
135/144	6	0.01160	0.00005	0.01154	0.00005	0.124
137/176	6/7	0.03087	0.00048	0.03094	0.00041	0.835
138/163	6	0.07525	0.00049	0.07563	0.00041	0.244
141	6	0.01470	0.00005	0.01477	0.00005	0.076
146	6	0.02318	0.00037	0.02328	0.00038	0.718
149	6	0.01456	0.00006	0.01451	0.00005	0.190
151	6	0.01468	0.00004	0.01473	0.00005	0.202
156	6	0.00527	0.00017	0.00529	0.00023	0.911
157	6	0.00407	0.00009	0.00404	0.00015	0.707
167	6	0.00990	0.00001	0.00990	0.00002	0.884
170/190	7	0.01457	0.00045	0.01487	0.00046	0.363
171	7	0.00962	0.00006	0.00965	0.00023	0.808
172	7	0.00576	0.00020	0.00573	0.00032	0.914
173	7	0.00639	0.00009	0.00637	0.00025	0.881
174	7	0.01589	0.00057	0.01597	0.00041	0.835
175	7	0.01828	0.00038	0.01825	0.00035	0.907
177	7	0.00871	0.00004	0.00876	0.00025	0.699
180	7	0.05556	0.00038	0.05524	0.00038	0.248
182/187	7	0.01800	0.00002	0.01808	0.00027	0.560
183	7	0.01214	0.00013	0.01223	0.00017	0.430
185	7	0.01440	0.00002	0.01444	0.00006	0.302
191	7	0.00392	0.00007	0.00399	0.00018	0.433
193	7	0.00684	0.00029	0.00703	0.00029	0.344
194	8	0.04548	0.00054	0.04575	0.00053	0.488
197	8	0.05311	0.00045	0.05281	0.00043	0.346
199	8	0.04565	0.00051	0.04566	0.00038	0.978
200	8	0.01371	0.00041	0.01343	0.00037	0.319
202	8	0.01138	0.00054	0.01099	0.00017	0.189
205	8	0.01021	0.00058	0.00988	0.00044	0.381

DOI: 10.1021/acs.est.8b00186
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Table 2. continued

congener	no.	females		males		
no(s)	Cl	mean	SE	mean	SE	p
206	9	0.00622	0.00035	0.00600	0.00024	0.300
207	9	0.04814	0.00039	0.04837	0.00035	0.388
208	9	0.02064	0.00042	0.02070	0.00043	0.835
209	10	0.00141	0.00005	0.00138	0.00007	0.570

[a]Separate t-tests for equality of means were performed for each congener, with rejection value $p < 0.0008$ (= 0.05/62).

separation and quantification used an Agilent 5890/5973 GC/MS equipped with DB5-MS capillary column (30 m; inner diameter 0.25 mm; film thickness 0.25 μm, J&W Scientific, Folsom, CA, U.S.A.). All analyses were conducted in selected ion-monitoring mode using helium as the carrier gas, and methane was used as the mass spectrometer reagent gas. All injections were made in splitless mode. The column temperature started at 80 °C, held for 1 min, and then temperatures were increased by 20 °C/min to 150 °C, then increased by 2 °C/min to 250 °C, held for 4 min, increased by 30 °C/min to 300 °C, and finally held for 6 min. PCB congener concentrations were determined using electron capture negative chemical ionization (NCI). We calculated ΣPCB for each fish or composite as the sum of the concentrations of the PCB congeners found, and all PCB concentrations were reported on a wet weight basis. QA procedures were performed in parallel with analyses and included blanks (corn oil) and performance-check fish. Linearity, drift check, and spike-recovery analyses used a check fish. Drift checks used a repeated analysis of a standard and results were accepted only when these values varied by less than 10%. The acceptance criteria for linearity had to produce linearity plots with $r^2 > 0.999$. Spike recoveries ranged from of 88−95%. Surrogate recoveries of PCB congener 166 ranged from 76% to 103% for sucker extracts and 76−89% for coho salmon extracts. Detection limits for individual PCB congeners were calculated based on established protocol,[30,33] and ranged from 0.001 to 2.000 ng/g.[21] Congener numbering conformed to a widely used standard.[34]

Statistical Methods. For each fish (white sucker) and composite (coho salmon) sample, we calculated the proportion of ΣPCB measured for each congener identified. Co- and trieluting congeners were treated as single, individual congeners. In all, we identified 62 congeners in the white sucker samples and 80 congeners in the coho salmon samples, including co- and trieluters. Similarly, we calculated the proportion of ΣPCB measured for each of the eight homologues identified by summing the respective proportions of the trichlorobiphenyl through decachlorobiphenyl congeners for each sample. For two pairs of coeluting congeners, both members did not belong to the same homologue. To accommodate this uncertainty, we added one-half of the proportions of coeluting congeners 81/87 to the tetrachlorobiphenyl and pentachlorobiphenyl homologues (i.e., 0.0066 added for white sucker and 0.013 added for coho salmon), and one-half of the proportions of coeluting congeners 137/176 to the hexachlorobiphenyl and heptachlorobiphenyl homologues (i.e., 0.0152 added for white sucker and 0.00024 added for coho salmon).

We used ANOVAs to test null hypotheses of no change in PCB homologue proportions with age in white sucker. We grouped the 51 white suckers into five age categories (4−10, 11−12, 13−14, 15−16, and 17−24 years), created to make sample size of each category roughly the same. We performed eight ANOVAs, one for each PCB homologue found in white sucker, in which the dependent variable was the proportion of total PCB and the independent variables were the five age categories. For each homologue test, the rejection values were adjusted with a Bonferroni correction. Rejection of the null hypothesis occurred when $p < 0.00625$ (= 0.05/8).

Next, we used t-tests to test null hypotheses of no differences between males and females for their respective mean proportions of ΣPCB for each congener and homologue. Separate tests were conducted for each species. For each congener and homologue test, the rejection values were adjusted with a Bonferroni correction, reflecting the number of congeners and homologues identified. Rejection for each congener test occurred when $p < 0.0008$ (= 0.05/62) for white sucker and $p < 0.00063$ (= 0.05/80) for coho salmon, respectively. Similarly, for each homologue test rejection occurred when $p < 0.00625$ (= 0.05/8) for both species. For graphical purposes, the 95% confidence intervals for the mean proportions of ΣPCB of each homologue were calculated for males and females of each species.

Next, we combined the results of males and females in both species and used t-tests to test null hypotheses of no differences between white sucker and coho salmon with respect to their mean proportions of ΣPCB for each of the 8 homologues identified. Again, rejection for each homologue occurred when $p < 0.00625$. To better illustrate the differences between the two species with respect to their homologue distributions, we performed a principal components analysis, in which proportions of the eight homologues were treated as variables. For each fish, the second principal component was then plotted against the first principal component.

RESULTS AND DISCUSSION

For all eight homologues, we failed to reject the null hypothesis of no differences among the five age categories of white sucker for their respective mean proportions of total ΣPCB (Table 1). Although the dechlorinated homologue was nearly significant ($p = 0.007$), the p-value was still above the rejection level of 0.00625. Further, this homologue was represented by a single congener, which accounted for only about 0.14% of ΣPCB in white sucker. Thus, the mean proportions of each homologue did not change with age.

For the 62 congeners (including 12 pairs of coeluters and 1 trieluter) identified in white sucker samples, only the pentachlorinated congener 114 had a significant (t-tests, $p < 0.0008$) difference between females and males (Table 2). However, this congener represented only about 0.13% and 0.12% of the mean proportions of ΣPCB for females and males, respectively. We concluded, therefore, that the difference between the congener distributions of female and male white suckers was negligible. Similarly, there was no difference between female and male coho salmon for any of the 80 congeners (including 13 pairs of coeluters and 1 trieluter) detected (Table 3: t-tests, $p \geq 0.077$ in all cases).

Hexachlorinated congeners comprised the largest proportion (32%) of ΣPCB in white sucker, followed by heptachlorinated

DOI: 10.1021/acs.est.8b00186
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Table 3. Means and Standard Errors (SE) of Proportions of Total PCB Concentrations for 80 Congeners Found Composites, Each Containing 5 Fish, For Age-2 Female (N = 5 Composites) and Male (N = 12 Composites) Coho Salmon[a]

congener	no.	females		males		
no(s)	Cl	mean	SE	mean	SE	p
22	3	0.00189	0.00040	0.00162	0.00027	0.573
28/31	3	0.01429	0.00232	0.01244	0.00104	0.413
33	3	0.02160	0.00362	0.01970	0.00360	0.733
40	4	0.00595	0.00273	0.01205	0.00404	0.302
41/71	4	0.05269	0.01061	0.06856	0.00594	0.174
42	4	0.00238	0.00043	0.00339	0.00031	0.069
44	4	0.00907	0.00111	0.01130	0.00500	0.670
47/48	4	0.01534	0.00124	0.01456	0.00049	0.496
49	4	0.01325	0.00293	0.01178	0.00215	0.688
52	4	0.01442	0.00101	0.01417	0.00120	0.886
56/60	4	0.01303	0.00033	0.01281	0.00033	0.663
63	4	0.00361	0.00052	0.00319	0.00034	0.485
64	4	0.00403	0.00042	0.00417	0.00035	0.806
66	4	0.04272	0.00096	0.04244	0.00113	0.869
70/76	4	0.01779	0.00052	0.01772	0.00043	0.929
74	4	0.01180	0.00029	0.01175	0.00040	0.937
77	4	0.00217	0.00015	0.00201	0.00009	0.347
81/87	4/5	0.02850	0.00099	0.02643	0.00085	0.146
82	5	0.00179	0.00023	0.00239	0.00012	0.019
83	5	0.00402	0.00061	0.00404	0.00042	0.986
84/89/92	5	0.06822	0.00081	0.06741	0.00088	0.548
85	5	0.01882	0.00071	0.01653	0.00060	0.029
91	5	0.00648	0.00202	0.00653	0.00127	0.984
95	5	0.01641	0.00061	0.01639	0.00037	0.976
97	5	0.00979	0.00018	0.00976	0.00022	0.940
99	5	0.02576	0.00050	0.02512	0.00038	0.320
101	5	0.03857	0.00039	0.03831	0.00061	0.769
105	5	0.02276	0.00040	0.02296	0.00046	0.772
107	5	0.00729	0.00012	0.00739	0.00015	0.635
110	5	0.04525	0.00043	0.04418	0.00120	0.414
114	5	0.00492	0.00057	0.00457	0.00039	0.608
118	5	0.04457	0.00111	0.04379	0.00078	0.564
119	5	0.00174	0.00015	0.00165	0.00015	0.705
123	5	0.00035	0.00007	0.00034	0.00005	0.840
126	5	0.00036	0.00010	0.00033	0.00005	0.758
128	6	0.01218	0.00023	0.01160	0.00027	0.166
129	6	0.00051	0.00010	0.00047	0.00008	0.776
131	6	0.00265	0.00009	0.00223	0.00031	0.211
132/153	6	0.06724	0.00161	0.06518	0.00144	0.373
134	6	0.00132	0.00006	0.00119	0.00016	0.471
135/144	6	0.00691	0.00030	0.00739	0.00026	0.259
137/176	6/7	0.00045	0.00003	0.00049	0.00002	0.235
138/163	6	0.09691	0.00299	0.09220	0.00212	0.206
141	6	0.01209	0.00055	0.01301	0.00074	0.405
146	6	0.01862	0.00174	0.01585	0.00231	0.417
149	6	0.02480	0.00110	0.02134	0.00292	0.287
151	6	0.00682	0.00039	0.00725	0.00031	0.406
156	6	0.00399	0.00007	0.00368	0.00015	0.083
157	6	0.00201	0.00030	0.00204	0.00024	0.945
158	6	0.00787	0.00038	0.00753	0.00026	0.452
167	6	0.00626	0.00013	0.00590	0.00018	0.177
170/190	7	0.01196	0.00055	0.01057	0.00144	0.383
171	7	0.00261	0.00005	0.00266	0.00005	0.551
172	7	0.00531	0.00009	0.00540	0.00008	0.511
173	7	0.00007	0.00001	0.00010	0.00002	0.191
174	7	0.00731	0.00020	0.00766	0.00016	0.194
175	7	0.00124	0.00007	0.00121	0.00004	0.764
177	7	0.00878	0.00023	0.00914	0.00019	0.268

DOI: 10.1021/acs.est.8b00186
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Table 3. continued

congener	no.	females		males		
no(s)	Cl	mean	SE	mean	SE	*p*
178	7	0.00668	0.00030	0.00658	0.00018	0.762
180	8	0.02925	0.00069	0.03047	0.00070	0.266
182/187	7	0.01810	0.00096	0.01789	0.00064	0.854
183	7	0.00906	0.00046	0.00893	0.00025	0.793
185	7	0.00073	0.00002	0.00071	0.00001	0.649
189	7	0.00099	0.00014	0.00098	0.00008	0.942
191	7	0.00084	0.00010	0.00084	0.00006	0.967
193	7	0.00197	0.00011	0.00228	0.00015	0.160
194	8	0.00431	0.00028	0.00456	0.00012	0.349
195	8	0.00137	0.00009	0.00148	0.00003	0.310
196/203	8	0.01039	0.00073	0.01123	0.00025	0.308
197	8	0.00043	0.00002	0.00045	0.00001	0.221
198	8	0.00033	0.00002	0.00035	0.00001	0.184
199	8	0.00037	0.00002	0.00041	0.00001	0.177
200	8	0.00089	0.00004	0.00103	0.00006	0.140
201	8	0.01005	0.00061	0.01113	0.00026	0.077
202	8	0.00142	0.00004	0.00146	0.00003	0.430
205	8	0.00039	0.00005	0.00037	0.00003	0.753
206	9	0.00178	0.00007	0.00182	0.00003	0.633
207	9	0.00036	0.00003	0.00040	0.00001	0.274
208	9	0.00048	0.00004	0.00049	0.00003	0.889
209	10	0.00031	0.00002	0.00030	0.00001	0.854

[a]Separate *t*-tests for equality of means were performed for each congener, with rejection value $p < 0.00063$ (= 0.05/80).

(21%) and octochlorinated (18%) congeners (Figure 1, Table 4). In contrast, pentachlorinated congeners comprised the largest proportion (33%) of ΣPCB in coho salmon, followed by hexachlorinated (26%) and tetrachlorinated (24%) congeners. Values of *p* for the individual *t*-tests of differences between male and female white suckers for mean proportion of ΣPCB ranged from 0.013 for trichlorinated congeners to 0.88 for nanochlorinated congeners. Thus, none of the *t*-tests had a value of *p* less than the rejection value of 0.00625. These results indicated that there was no difference between male and female white suckers for the proportion of ΣPCB for any homologue. For coho salmon, values of *p* for the individual *t*-tests for the eight homologues ranged from 0.14 for octochlorinated congeners to 0.85 for the decachlorinated congener, indicating no difference between females and males for any homologue proportion. Collectively, these results justified our combining males and females for the between-species analyses of homologue proportions.

Coho salmon had significantly higher proportions of tri-, tetra-, and pentachlorinated congeners (Table 4, $p < 0.0001$).

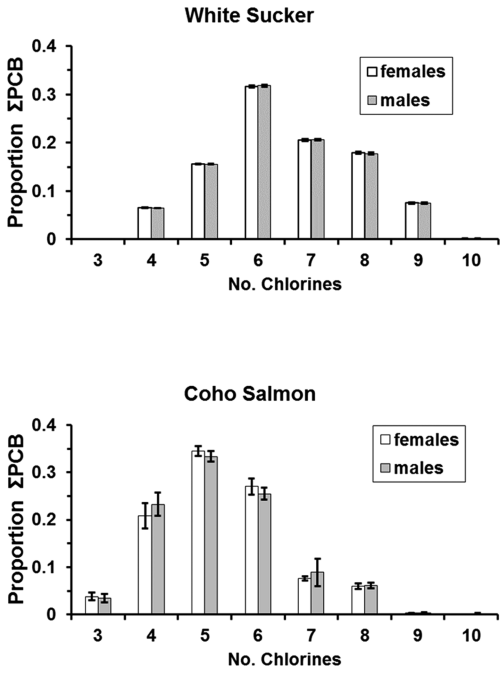

Figure 1. 95% confidence intervals of the proportions of total PCB concentrations (ΣPCB) found in each homologue group in adult white sucker (25 females, 26 males) and age-2 coho salmon (7 composites of 5 females, 12 composites of 5 males).

Table 4. Mean and Standard Errors (SE) of Proportions of Total PCBs in 19 Composites (12 Male, 7 Female) of 5 Age-2 Coho Salmon (CO) and 51 Individual (25 Female, 26 Male) Adult White Suckers (WS) for Homologue Groups 3−10[a]

no.	mean proportion (SE)			
Cl	coho salmon	white sucker	*p*	Conclusion
3	0.0352 (0.0026)	0.0002 (<0.0001)	<0.0001	CO > WS
4	0.2355 (0.0077)[b]	0.0653 (0.0007)[b]	<0.0001	CO > WS
5	0.3273 (0.0026)[b]	0.1561 (0.0003)[b]	<0.0001	CO > WS
6	0.2620 (0.0047)[c]	0.3173 (0.0045)[c]	<0.0001	WS > CO
7	0.0754 (0.0010)[c]	0.2061 (0.0042)[c]	<0.0001	WS > CO
8	0.0616 (0.0012)	0.1785 (0.0057)	<0.0001	WS > CO
9	0.0027 (0.0001)	0.0751 (0.0032)	<0.0001	WS > CO
10	0.0003 (<0.0001)	0.0014 (<0.0001)	<0.0001	WS > CO

[a]Sexes were pooled for both species. Separate *t*-tests of equal means were performed for each homologue group, with rejection value $p < 0.00625$ (= 0.05/8). [b]Includes one-half of the proportion of coeluting congeners 81 and 87 (i.e., 0.0066 added for white sucker and 0.013 added for coho salmon). [c]Includes one-half of the proportion of coeluting congeners 137 and 176 (i.e., 0.0152 added for white sucker and 0.00024 added for coho salmon). [d]Abbreviation: No. Cl = number of chlorines.

DOI: 10.1021/acs.est.8b00186
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In contrast, white sucker had significantly higher proportions of hexa- through decachlorinated congeners. The first two principle components accounted for 97.7% and 1.8%, respectively, of the total variance in the PCA. The two species exhibited clear separation when the second principle component was plotted against the first (Figure 2). The greater variance in coho salmon

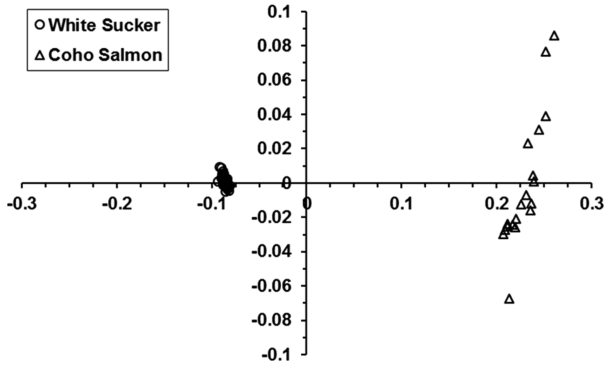

Figure 2. Principal component 2 (*y*-axis) versus principal component 1 (*x*-axis) for proportions of total PCB concentrations for tri- through decachlorinated congeners found in 51 individual adult white sucker (○) and 19 composites of five (95 total fish) age-2 coho salmon (Δ). The first two principal components accounted for 99.5% of the total variance.

in Figure 2 is likely due in part to much lower sample size (19 composites of 5 coho salmon versus 51 white suckers).[9]

The hypothesis of greater PCB chlorination in a higher trophic level,[14] represented by coho salmon, and less chlorination in a lower trophic level, represented by white sucker, was not supported by our data. In fact, our results were opposite. Increased PCB chlorination in higher trophic levels appears to be an oversimplification when applied to fishes in complex food webs such as in Lake Michigan. Although a previous study found higher proportions of low-chlorinated congeners in plankton and benthic macroinvertebrates than in fish in Lake Ontario, the homologue proportions in alewives, sculpin (*Cottus cognatus*), rainbow smelt (*Osmerus mordax*), and salmonids—species that occur in different trophic levels—were not different.[10]

Similarly, there was no clear trend in degree of chlorination for the respective homologue proportions found in alewives and coho salmon from Lake Michigan.[12] Another study involved a simple food chain (zebra mussels [*Dreissena polymorpha*], round goby [*Neogobius melanostomus*], and smallmouth bass [*Micropterus dolomieu*]) in Lake Erie.[13] Although the mussels contained greater proportions of the tri-, tetra-, and pentachlorinated congeners than the fish, the homologue distributions in round goby and smallmouth bass were not different. In still another study,[14] there was considerable overlap in proportions for homologues in fish from several trophic guilds in the stream system studied, and no rigorous statistical tests for degree of chlorination among fish guilds or confidence intervals about mean proportions of the homologues in the guilds are shown. Further, that study demonstrated that location within stream accounted for a large proportion (albeit less than trophic position) of the variance in congener proportion. Collectively, these results suggest that trends in PCB chlorination in aquatic food webs are less clear when applied to fish of different trophic levels.

It is unlikely that the differences between white sucker and coho salmon for their respective homologue proportions were due to the different years in which they were collected. PCBs were not manufactured in the U.S.A. after 1977, and ΣPCB in Great Lakes fish have subsequently declined.[35] Concentrations of total PCBs in skin-on fillets in Lake Michigan coho salmon declined by about 23.9% per year during 1977 and 1985, and then declined by 2.6% per year during 1985−2010.[36] However, the concentrations of individual congeners in lake trout (*Salvelinus namaycush*) from Lake Michigan declined at the same rate during 1979−1988[37] and during 1990−2017 (E. Murphy, US Environmental Protection Agency Great Lakes National Program Office, personal communication). Finally, our data indicate that homologue proportions were the same in white suckers age 4−24 years. Collectively, this indicates that the respective proportions of congeners, at least in some species in Lake Michigan, have remained fairly constant during the past 20−38 years.

PCB congener distribution did not vary significantly between the sexes of white sucker or coho salmon in Lake Michigan. Moreover, diet composition of female coho salmon does not significantly differ from diet composition of male coho salmon in Lake Michigan.[27] Thus, our results did not support a contention that habitat utilization varied between the sexes such that fish of one sex fed in an area influenced by a PCB "hot spot" in the sediments while fish of the other sex did not, for either species in Lake Michigan. A PCB "hot spot" effect has been documented for certain fish populations in Lakes Huron and Erie.[3,6−9]

For the salmonids in Lake Ontario, which included coho salmon, hexachlorinated congeners, followed by pentachlorinated congeners, had the highest proportions of ΣPCB.[10] The reverse occurred for the coho salmon from Lake Michigan in our study and elsewhere.[12] In both lakes, coho salmon feed primarily on alewives.[10,24] Perhaps the difference in coho salmon PCB congener distributions between the two lakes primarily reflects different congener mixtures in the point sources to Lake Ontario compared with those to Lake Michigan, as well as a difference in PCB congener distribution of the PCBs entering the lake via atmospheric deposition between the two lakes.[9]

Like all fish species examined so far,[3] male white sucker and coho salmon have higher whole-fish ΣPCB than their female conspecifics.[21,24] Total PCB concentrations of white sucker in this study was 202.8 ng/kg, with males having about 18% higher concentrations of ΣPCB than females.[24] The coho salmon used in this study, which were captured in 1995, contained an average ΣPCB of 1228.6 ng/kg, or about 6.1 times the PCB body burden as white sucker captured in 2017.[24] Assuming that the decrease in whole-body ΣPCB in Lake Michigan coho salmon continued to decline at 2.6% per year during 2010−2017,[36] the average whole-body ΣPCB in coho salmon would be 688.2 ng/kg in 2017, or about 3.4 times the current body burden of white sucker. Collectively, these results support the contention of biomagnification of ΣPCB in aquatic systems demonstrated elsewhere.[4,38,39]

Our results support a growing body of evidence that, for a given aquatic ecosystem, the PCB congener and homologue distributions in fish primarily depend on diet and not on trophic level. For most fish populations, PCB congener distributions apparently do not vary between the sexes, and coincidentally diet composition appears not to vary between the sexes in most cases.[3,5] We suggest additional research on homologue fates in food webs in aquatic ecosystems.

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DOI: 10.1021/acs.est.8b00186
Environ. Sci. Technol. 2018, 52, 4393−4401

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Tim Desorcie and Lynn Ogilvie assisted with homogenization of the fish. Patrick Kočovský, Ronald Hites, and three anonymous reviewers made helpful suggestions on previous drafts of this manuscript. Use of trade, product, or firm names does not imply endorsement by the United States Government.

■ REFERENCES

(1) Weininger, D. Accumulation of PCBs by lake trout in Lake Michigan. Ph.D. dissertation, University of Wisconsin, Madison, WI, 1978.
(2) Carlson, D. L.; Hites, R. A. Polychlorinated biphenyls in salmon and salmon feed: global differences and bioaccumulation. *Environ. Sci. Technol.* **2005**, *39*, 7389−7395.
(3) Madenjian, C. P.; Rediske, R. R.; Krabbenhoft, D. P.; Stapanian, M. A.; Chernyak, S. M.; O'Keefe, J. P. Sex differences in contaminant concentrations of fish: a synthesis. *Biol. Sex Differ.* **2016**, *7*, 42−57.
(4) Arnot, J.; Gobas, F. A. P. C. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ. Toxicol. Chem.* **2004**, *23*, 2343−2355.
(5) Madenjian, C. P. Sex effect on polychlorinated biphenyl concentrations in fish: a synthesis. *Fish Fish.* **2011**, *12*, 451−60.
(6) Madenjian, C. P.; Jude, D. J.; Rediske, R. R.; O'Keefe, J. P.; Noguchi, G. E. Gender difference in walleye PCB concentrations persists following remedial dredging. *J. Great Lakes Res.* **2009**, *35*, 347−352.
(7) Jude, D. J.; Rediske, R.; O'Keefe, J.; Hensler, S.; Giesy, J. P. PCB concentrations in walleyes and their prey from the Saginaw River, Lake Huron: A comparison between 1990 and 2007. *J. Great Lakes Res.* **2010**, *36*, 267−276.
(8) Stapanian, M. A.; Madenjian, C. P.; Rediske, R. R.; O'Keefe, J. P. Sexual differences in proportions of PCB congeners in burbot (*Lota lota*) from Lake Erie. *Chemosphere* **2013**, *93*, 1615−1623.
(9) Stapanian, M. A.; Madenjian, C. P.; Cott, P.; Rediske, R. R.; O'Keefe, J. P. Polychlorinated biphenyl congener distributions in burbot: evidence for a latitude effect. *Environ. Toxicol. Chem.* **2014**, *33*, 2448−2454.
(10) Oliver, B. G.; Niimi, A. J. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. *Environ. Sci. Technol.* **1988**, *22*, 388−397.
(11) Zaranko, D. T.; Griffiths, R. W.; Kaushik, N. K. Biomagnification of polychlorinated biphenyls through a riverine food web. *Environ. Toxicol. Chem.* **1997**, *16*, 1463−1471.
(12) Jackson, L. J.; Carpenter, S. R.; Manchester-Neesvig, J.; Stow, C. A. PCB Congeners in Lake Michigan Coho (*Oncorhynchus kisutch*) and Chinook (*Oncorhynchus tshawytscha*) Salmon. *Environ. Sci. Technol.* **2001**, *35*, 856−862.
(13) Kwon, T.-D.; Fisher, S. W.; Kim, G. W.; Hwang, H.; Kim, J.-E. Trophic transfer and Biotransformation of polychlorinated biphenyls in zebra mussel, round goby, and smallmouth bass in Lake Erie, USA. *Environ. Toxicol. Chem.* **2006**, *25*, 1068−1078.
(14) Walters, D. N.; Fritz, K. M.; Johnson, B. R.; Lazorchak, J. M.; McCormick, F. H. Influence of trophic position and spatial location on polychlorinated biphenyl (PCB) bioaccumulation in a stream food web. *Environ. Sci. Technol.* **2008**, *42*, 2316−2322.
(15) Becker, G. *Fishes of Wisconsin*; University of Wisconsin Press: Madison, WI, 1983.
(16) Savitz, J. Diets of Lake Michigan salmon and maximum size of alewife prey. *J. Freshwater Ecol.* **2009**, *24*, 563−566.
(17) Michigan Department of Natural Resources. *Michigan Suckers Are Popular with Spring Anglers*; Michigan Department of Natural Resources: Lansing, MI, 2012, http://www.michigan.gov/dnr/0,4570,7-153--275299--RSS,00.html.
(18) Michigan Department of Natural Resources. *Coho Salmon, Oncorhynchus kisutch*. Michigan Department of Natural Resources: Lansing, MI, 2017, http://www.michigan.gov/dnr/0,4570,7-153-10364_18958-45666,00.html.
(19) Saint-Jacques, N.; Harvey, H. H.; Jackson, D. A. Selective foraging in the white sucker (*Catostomus commersoni*). *Can. J. Zool.* **2000**, *78*, 1320−1331.
(20) Doherty, C. A.; Curry, R. A.; Munkittrick, K. R. Spatial and temporal movements of white sucker: implications for use as a sentinel species. *Trans. Am. Fish. Soc.* **2010**, *139*, 1818−1827.
(21) Madenjian, C. P.; Stevens, A. L.; Stapanian, M. A.; Batterman, S. A.; Chernyak, S. M.; Menczer, J. E.; McIntyre, P. B. Sex difference in PCB concentrations of a catostomid fish. *J. Environ. Analyt. Toxicol.* **2017**, *7*, 515.
(22) Stewart, D. J.; Kitchell, J. F.; Crowder, L. J. Forage fishes and their salmonid predators in Lake Michigan. *Trans. Am. Fish. Soc.* **1981**, *110*, 751−763.
(23) Madenjian, C. P.; Bunnell, D. B.; Warner, D. M.; Pothoven, S. A.; Fahnenstiel, G. L.; Nalepa, T. F.; Vanderploeg, H. A.; Tsehaye, I.; Claramunt, R. M.; Clark, R. D., Jr. Changes in the Lake Michigan food web following dreissenid mussel invasions: a synthesis. *J. Great Lakes Res.* **2015**, *41*, 217−231.
(24) Madenjian, C. P.; Elliott, R. F.; Schmidt, L. J.; Desorcie, T. J.; Hesselberg, R. J.; Quintal, R. T.; Begnoche, L. J.; Bouchard, P. M.; Holey, M. E. Net trophic transfer efficiency of PCBs to Lake Michigan coho salmon to their prey. *Environ. Sci. Technol.* **1998**, *32*, 3063−3067.
(25) Jude, D. J.; Tesar, F. J.; Tomlinson, J. C.; Miller, T. J.; Thurber, N. J.; Godun, G. G.; Dorr, J. A., III. *Inshore Lake Michigan fish populations near the D. C. Cook Nuclear Power Plant during Preoperational Years—1973, 1974*; Special Report No. 71; University of Michigan Great Lakes Research Division: Ann Arbor, MI, 1979.
(26) Elliott, R. F.; Holey, M. E. *A Description of the Diet of Lake Michigan Coho Salmon and Collections for Contaminant Analysis as Part of the 1994−1995 Lake Michigan Mass Balance Project*; Report No. 98−3; U.S. Fish and Wildlife Service: Green Bay, WI, 1998.
(27) Madenjian, C. P.; Schrank, C. S.; Begnoche, L. J.; Elliott, R. F.; Quintal, R. T. Sexual difference in PCB concentrations of coho salmon (*Oncorhynchus kisutch*). *Sci. Total Environ.* **2010**, *408*, 1719−1724.
(28) Edwards, W. H.; Stapanian, M. A.; Stoneman, A. T. An evaluation of precision in age e estimation of two treatments of otoliths from an aging burbot population. *J. Appl. Ichthyol.* **2011**, *27*, 43−48.
(29) Holey, M. E.; Elliott, R. F. *Quality Assurance Project Plan for Coho Sampling for Contaminant and Diet Analysis. Vol. I of Lake Michigan Mass Balance (LMMB) Study Methods Compendium. Sample Collection Techniques*. EPA-905-R-97-012a; U.S. Environmental Protection Agency Great Lakes National Program Office: Chicago, IL, 1997.
(30) Schmidt, L. J. *Analysis of Total PCBs and PCB Congeners and Trans-Nonachlor in Fish by Gas Chromatography/Negative Chemical Ionization Single Ion Mass Spectrometry. Lake Michigan Mass Balance Study (LMMB) Methods Compendium; Vol. 2: Organic and Mercury Sample Analysis Techniques*. EPA 905-R-97-012b; U. S. Environmental Protection Agency Great Lakes National Program Office: Chicago, IL, 1997.
(31) Schmidt, L. J. *Extraction and Lipid Separation of Fish Samples for Contaminant Analysis and Lipid Determination. Lake Michigan Mass Balance Study (LMMB) Methods Compendium; Vol. 2: Organic and Mercury Sample Analysis Techniques*. EPA 905-R-97-012b; U. S. Environmental Protection Agency Great Lakes National Program Office: Chicago, IL, 1997.
(32) Chernyak, S. M.; Rice, C. P.; Quintal, R. T.; Begnoche, L. J.; Hickey, J. P.; Vinyard, B. T.; et al. Time trends (1983−1999) for organochlorines and polybrominated diphenyl ethers in rainbow smelt (*Osmerus mordax*) from Lakes Michigan, Huron, and Superior, USA. *Environ. Toxicol. Chem.* **2005**, *24*, 1632−1641.
(33) U. S. Environmental Protection Agency. *Method 1668B: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and*

DOI: 10.1021/acs.est.8b00186
Environ. Sci. Technol. 2018, 52, 4393−4401

Tissue by HRGC/HRMS. EPA-821-R-08-020; U. S. Environmental Protection Agency Office of Water: Washington, DC, 2008.
(34) Ballschmiter, K.; Bacher, R.; Mennel, A.; Fischer, R.; Riehle, U.; Swerev, M. The determination of chlorinated biphenyls, chlorinated dibenzodioxins, and chlorinated dibenzofurans by GC-MS. *J. High Resolut. Chromatogr.* **1992**, *15*, 260−270.
(35) Hickey, J. P.; Batterman, S. A.; Chernyak, S. M. Trends of chlorinated organic contaminants in Great Lakes trout and walleye from 1970 to 1998. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 97−110.
(36) Rasmussen, P. W.; Schrank, C.; Williams, M. C. W. Trends of PCB concentrations in Lake Michigan coho and chinook salmon, 1975−2010. *J. Great Lakes Res.* **2014**, *40*, 748−754.
(37) Mac, M. J.; Schwartz, T. R.; Edsall, C. C.; Frank, A. M. Polychlorinated biphenyls in Great Lakes lake trout and their eggs: relations to survival and congener composition 1979−1988. *J. Great Lakes Res.* **1993**, *19*, 752−765.
(38) Suedel, B. C.; Boraczek, J. A.; Peddicord, R. K.; Clifford, P. A.; Dillon, T. M. Trophic transfer and biomagnification potential of contaminants in aquatic ecosystems. *Rev. Environ. Contam. Toxicol.* **1994**, *136*, 21−84.
(39) Alcock, R. E.; Boumphrey, R.; Malcolm, H. M.; Osborn, D.; Jones, K. C. Temporal and spatial trends in PCB congeners in UK gannet eggs. *Ambio* **2002**, *31*, 202−206.

DOI: 10.1021/acs.est.8b00186
Environ. Sci. Technol. 2018, 52, 4393−4401