Composition of Dioxin-like PCBs in Fish: An Application for Risk Assessment

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It is widely accepted that a congener-specific analysis of polychlorinated biphenyls (PCBs), rather than traditional Aroclor equivalent total PCB analysis, is required for risk assessment. This is based on the fact that environmental processes alter the original distribution of PCB congeners in Aroclors and that toxicity varies considerably among the congeners with dioxin-like PCBs (dl-PCBs) generally being among the most toxic. Using the largest known dl-PCB fish dataset, here we present a likely composition of dl-PCBs in fish. In contrast to common perception, we found that the dl-PCB composition is relatively constant (within approximately a factor of 2) regardless of fish species and total PCB level. The abundance of dl-PCBs expressed as a percentage of total PCB (25−75 quartile range) in fish is generally in the order of PCB-118 (3.0−6.2%) > PCB-105 (1.1−2.4%) > PCB-156 (0.39−0.75%) > PCB-167 (0.20−0.43%) > PCB-123 (0.11−0.26%) > PCB-157 (0.09−0.19%) ≈ PCB-114 (0.08−0.18%) > PCB-189 (0.045−0.094%) > PCB-77 (0.018−0.093%) > PCB-126 (0.015−0.036%) > PCB-81 (0.002−0.007%) ≈ PCB-169 (0.001−0.006%). The most toxic dl-PCB congeners PCB-126 and -169 contribute on average only 0.027 and 0.004% of total PCB, respectively. The statistically significant relationships presented between individual dl-PCB and total-PCB concentrations can be used as a practical tool to estimate dl-PCBs for risk assessment purposes. A comparison of the dl-PCB pattern presented here with other studies suggests that this dl-PCB composition is applicable to fish from North America and perhaps from other geographical regions throughout the world.

Introduction

Polychlorinated biphenyls (PCBs) are a class of organic compounds with 209 congeners having one to 10 chlorine atoms attached to a biphenyl. They were commercially produced as complex mixtures containing multiple isomers at different degrees of chlorination and were primarily marketed under the trade name Aroclor in North America. PCB mixtures have been used for a variety of applications largely based on their chemical stability and physical properties. Their stability is also responsible for their continued presence in the environment even decades after extensive regulatory actions and an effective ban on their production in the 1970s (*1*). Although the levels of PCBs in various environmental matrices have decreased dramatically since peaking in the 1970s (*1*−*3*), their current levels in fish are a major cause of fish consumption advisories in North America (*4*, *5*).

Environmental levels of PCBs are traditionally measured as total PCB based on Aroclor equivalent analysis, as opposed to congener-specific concentrations, due to analytical limitations and/or cost differentials (*6*). Many studies have shown that physical, chemical, and biological processes alter the distribution of PCB congeners in Aroclor after release into the environment (*7*−*9*). In addition, it is well-recognized that the potential for adverse effects varies considerably among PCB congeners (*10*). For these reasons, congener-specific PCB analysis is recommended for risk assessment purposes (*6*, *11*−*13*). Although the U.S. Environmental Protection Agency (U.S. EPA) has encouraged states to develop the capability to conduct congener-specific tissue analysis, the higher cost of the analysis has restrained most contaminant monitoring agencies to total PCB measurements with a limited number of fish samples being analyzed for congener-specific PCBs (*6*). In addition, even a congener-specific analysis does not normally determine environmentally relevant and toxicologically important low ppt levels of dioxin-like PCBs (dl-PCBs). Dioxin-like PCBs are a group of 12 PCBs that share a common toxic mechanism with the most toxic dioxin compound (i.e., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin or 2,3,7,8-TCDD) and generally are among the most toxic PCB congeners as they incur toxic effects at relatively lower concentrations than those of non-dl-PCBs (*9*, *13*). Environmental hazards associated with the dl-PCBs are generally assessed separately from the non-dl-PCBs. More complex and, in turn, costly dl-PCB-specific analytical methods (e.g., U.S. EPA method 1668a (*14*)) are available; however, such an analysis is not routinely performed due to budgetary limitations. Therefore, the true risk of dl-PCBs to human and ecosystem health may not be fully recognized.

Similarities in the composition of PCBs among fish species (*15*, *16*) and fish tissues (*15*, *17*, *18*) have been reported. These studies, however, lacked statistical significance due to the small sample size and limited number of fish species and aquatic systems considered. In addition, the saga of congener-specific selective enrichment from one environmental compartment to another and sporadic reports of inconsistencies of PCB composition in fish from relatively small sample sizes of limited fish species (e.g., ref *19*) have created a layer of perception that dl-PCB composition in fish cannot be generalized. Furthermore, the literature lacks a comparison of dl-PCB composition in various fish species on a large scale. As a result, the extent of applicability of similarities observed in the composition of dl-PCB in fish remains unclear.

The purpose of this paper is to investigate the composition of dl-PCBs and the relationship between levels of individual dl-PCBs and total PCB in fish. If the composition of dl-PCBs in fish is reasonably stable and the among-species differences for fish from a relatively wide geographic region with a variety of possible PCB sources are not statistically significant, a likely composition of dl-PCB in fish can be presented. Such a general pattern of dl-PCB will allow reasonable estimations of dl-PCB concentrations from relatively easily measured total PCB values. We first use what is likely the largest dl-PCB

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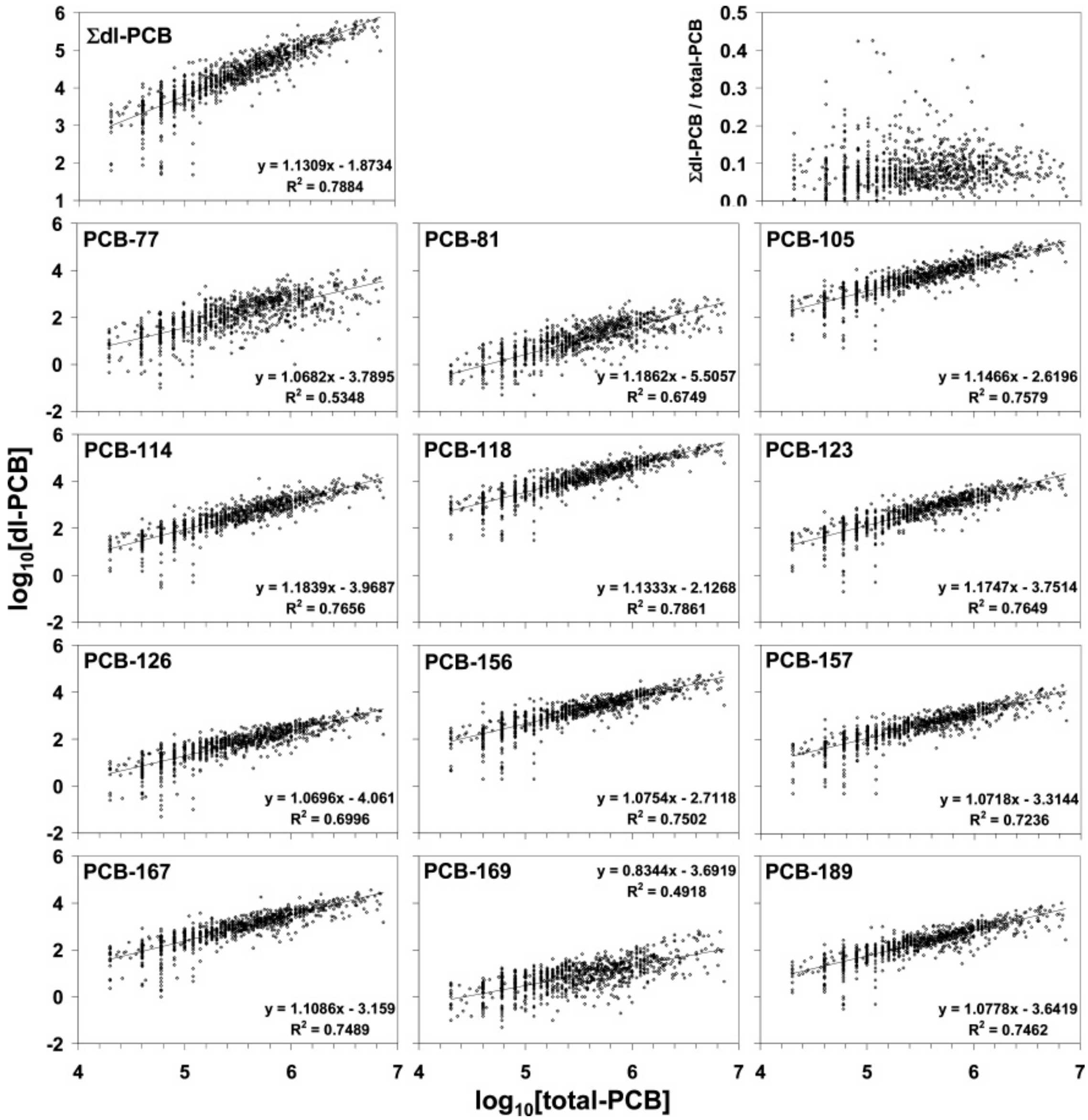

FIGURE 1. Log transformed concentration (pg/g wet wt) of ΣdI-PCBs and individual dI-PCB congeners as well as the fraction of ΣdI-PCBs in total PCB as a function of log transformed total PCB concentration (pg/g wet wt). The *y* refers to concentration of the dI-PCB congener being considered, and *x* refers to the total PCB concentration. The graphs are prepared for a sample size (*n*) of 912. Statistical significances (*P*) for all regressions are $<$0.001.

fish dataset in the world with a wide distribution of fish species, size, weight, sex, and PCB contamination level to examine if statistically significant regression models can be established between levels of individual dl-PCBs and total PCB in fish. The pattern of dl-PCB observed for this fish dataset is then compared with the patterns observed in other studies involving the same or different geographic regions and/or fish species.

Materials and Methods

Sample Collection. As part of the Sport Fish Contaminant Monitoring Program (SFCMP) of the Ontario Ministry of the Environment (MOE), Canada, in collaboration with the Ontario Ministry of Natural Resources (MNR), Canada, fish samples were collected from approximately 1700 locations in Ontario's inland lakes/rivers and the Great Lakes. The samples were analyzed for a variety of substances, and the data were used to provide consumption advice for sport fish (*4*) based on health protection guidelines provided by Health Canada. Fish were collected periodically during the late summer or early fall using gill nets and electro-fishing, stored frozen as whole fish, and shipped to MOE laboratories for chemical analysis, where they were sized, weighed, sexed, and filleted (skin-off) before analysis. The dataset generated by SFCMP of MOE includes total PCB and dl-PCB measurements in 912 skinless, boneless fillet samples of 22 different fish species (Supporting Information Table S1). These fish samples were collected from 1996 to 2004 from 80 locations across the province of Ontario, and they varied over a wide range in size, weight, and PCB concentrations (Supporting Information Table S2). The possible sources of PCB in the aquatic systems sampled also varied from atmospheric deposition to known recent and/or continuing point sources to a combination of atmospheric and point sources. The male to female distribution of the collected samples was almost even (51:49).

Extraction and Analysis. The analytical procedures used for total PCB and dl-PCB are described in detail elsewhere (*20*, *21*) and summarized next.

Total PCB. A 5 g sample of fish fillet was spiked with internal standards (decachlorobiphenyl and 1,3,5-tribromobenzene) and acid-digested overnight with hydrochloric acid. The acid digest was extracted with 25% (v/v) dichloromethane (DCM)/hexane. A 1 g equivalent was concentrated to 1 mL and cleaned using dry packed Florisil columns. The extract was split into two fractions: PCB and mirex (fraction 1) and organochlorine pesticides (fraction 2). Sample extracts were evaporated to 1 mL. Gas−liquid chromatography was used to determine total PCB concentrations using an HP 5890 Series-II gas chromatograph and Ni^{63} electron capture detector (ECD). The column (DB-17, 30 m, 0.53 mm i.d., 0.1 μm film thickness, J & W Scientific) head pressure was 3.5 psi, and the temperature program for fraction 1 was 80 °C for 1 min; 80−180 °C at 10 °C/min; 180−260 °C at 5 °C/min; and 260 °C for 6 min. Total PCB was determined using a 4:1 mixture of Aroclor 1254:1260 for quantification. This ratio of Aroclor best resembled the congener patterns detected for most fish samples. The chromatography was set up to resemble a historical separation obtained using packed analytical columns. For biological samples, typically 20−25 larger peaks were detected. Quantification was carried out using the summed area of the 23 largest peaks. For lower level samples, a minimum of 11 peaks was required for a positive identification.

Dioxin-like PCBs. A 5 g fish fillet was spiked with $^{13}C_{12}$-labeled surrogate standards for each of the 12 dl-PCBs, acid-digested overnight, followed by extraction with hexane and a three-stage column cleanup procedure (anhydrous sodium sulfate/sulfuric acid/silica, activated alumina, 5% Amoco PX21/activated silica (w/w)). The extract was split into two fractions: fraction A containing the mono-*ortho* PCBs -105, -114, -118, -123, -156, -157, -167, and -189 and fraction B containing the coplanar-PCBs -77, -81, -126, -169, and dioxins/furans (PCDDs/PCDFs). The fractions were analyzed in separate GC-HRMS runs. Analyses for dl-PCBs and PCDDs/PCDFs were performed on a Micromass Autospec HRMS at a resolving power of 10 000 with a Hewlett-Packard HP6890 gas chromatograph using a 40 m DB-5 column (0.18 mm i.d., 0.18 μm film thickness, J & W Scientific). The dl-PCB extracts were analyzed in splitless mode with He carrier gas at a linear velocity of 1.5 cm/s; injector temperature and transfer line temperature were maintained at 280 and 300 °C, respectively. The temperature program for fraction A was 150 °C for 1 min; 150−200 °C at 5 °C/min; 200−235 °C at 3 °C/min; 235 °C for 10 min; 235−300 °C at 12 °C/min; and 300 °C for 1 min. The temperature program for fraction B was 100 °C for 1 min; 100−200 °C at 30 °C/min; 200−235 °C at 3 °C/min; 235 °C for 10 min; 235−300 °C at 6 °C/min; and 300 °C for 12 min. All dl-PCB data were corrected for surrogate standard recoveries. Method blanks and spiked blank matrix samples were processed with each set of 10 field samples. The actual detection limit, which can be different from the method detection limit (MDL) depending on matrix effects in the sample, was calculated for every compound in every sample using MDL as a guide value for the expected detection limit. The MDLs are reported in Supporting Information Table S2.

Statistical Analysis. Congener concentrations below the detection levels were treated as half of the detection limit. To linearize relationships and stabilize variance, all data were log transformed before conducting a regression analysis. The regression models between dl-PCBs and total PCB concentrations were determined using SPSS (*37*).

Results and Discussion

We first examine the collective contribution of all 12 dl-PCBs to total PCB. The regression analysis showed a strong positive correlation ($R^2 = 0.788$; $P < 0.001$, $n = 912$) between Σdl-PCB and total PCB concentrations (Figure 1). The greater variation observed in the composition of dl-PCBs at lower levels of total PCB is presumably due to proportionally higher analytical errors at lower levels of PCBs. There is a constant, but flat, relationship between the fraction of total PCB that is Σdl-PCB and the total PCB (Figure 1). On average, dl-PCBs contribute about 8.5% (median 7.5%) to total PCB levels in fish with the variation in the contribution value being modest (25−75 quartiles 5.2−10.6%; results not shown). All dl-PCBs show strong positive relationships with total PCB (Figure 1) with, in most cases, total PCB levels explaining more than 70% variability in individual dl-PCB concentrations. These results are in agreement with a linear relationship observed between total PCB and dl-PCB related toxic equivalents (i.e., TEQ_{dl-PCB}) (*22*).

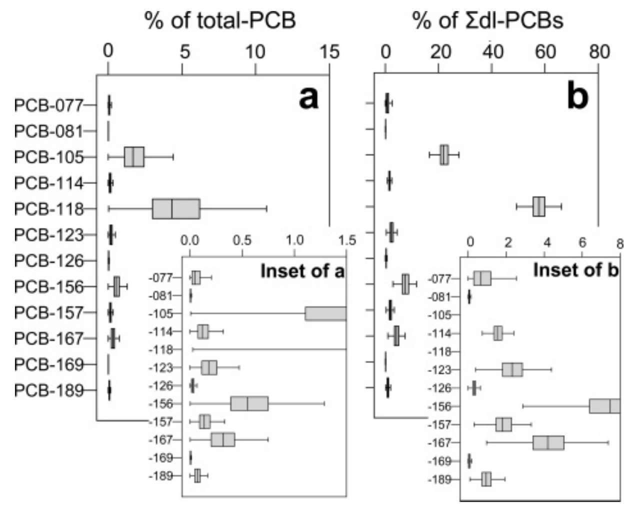

FIGURE 2. Percentage contribution of individual dl-PCB congeners to (a) total PCB and (b) Σdl-PCBs. These results are presented as box plots prepared using SPSS (*37*), in which the line within the box indicates the median, the box indicates the 25 and 75 quartile values, and the whiskers indicate the upper and lower values not classified as statistical outliers or extremes. The outliers and extremes were values more than 1.5 and 3 times the 25−75 interquartile range away from the closest end of the box, respectively. The graphs are prepared for a sample size (*n*) of 912.

Figure 2 presents the contribution of individual dl-PCB congeners to total PCB as well as to Σdl-PCBs. Two mono-*ortho* congeners PCB-118 and -105 are the most abundant dl-PCB congeners in fish. The average combined contributions of these congeners to total-PCB and Σdl-PCBs are about 7 and 80%, respectively (Figure 2 and Table 1). The abundance of dl-PCBs in fish is generally in the order of PCB-118 > -105 > -156 > -167 > -123 > -157 ≈ -114 > -189 > -77 > -126 > -81 ≈ -169. All non-*ortho* congeners (i.e., PCB-77, -81, -126, and -169) are the lowest dl-PCB contributors to total PCB levels in fish. The most toxic dl-PCB congeners, PCB-126 and -169 with toxic equivalency factors (TEF) of 0.1 and 0.03, respectively (*10*), contribute on average only 0.027% (median 0.024%; 25−75 quartiles 0.015−0.036%) and 0.004% (median 0.003%; 25−75 quartiles 0.001−0.006%) of total PCB, respectively. Although the observed percentage contributions of dl-PCBs to total PCB vary by 3−4 orders of magnitude, the 25−75 quartile values are generally within a factor of 2 (Table 1). The values for percentage contribution of individual dl-PCB to total PCB concentrations (Table 1) and the regression equations (Figure 1 and Supporting Information Table S3) can be used to estimate concentrations of each individual dl-PCB congener from a total PCB measurement in fish.

Sample Calculations. Illustrative estimated concentrations of all dl-PCBs from a total PCB measurement of 150 ng/g are summarized in Table 2. A sample calculation for PCB-118 is presented next.

From Figure 1:

$$\log[\text{PCB-118}] = 1.1333 \times \log[\text{total PCB}] - 2.1268;$$

therefore, for total PCB = 150 ng/g = 150 000 pg/g,

$$\log[\text{PCB-118}] = 3.738, \text{ and PCB-118} = 5464 \text{ pg/g}.$$

TABLE 1. Percentage Contribution of ΣdI-PCB and Individual dl-PCB to Total PCB Levels in Fish: Minimum, Maximum, Arithmetic Mean, Standard Deviations, Median, and 25−75 Quartile Values

congener	min	max	avg	SD	median	25 quartile	75 quartile
Σdl-PCB	0.04	42.5	8.5	5.35	7.5	5.2	10.6
PCB-077	0.0002	1.31	0.071	0.089	0.045	0.018	0.093
PCB-081	8.3×10^{-5}	0.05	0.005	0.01	0.004	0.002	0.007
PCB-105	0.008	13.75	1.92	1.31	1.67	1.11	2.43
PCB-114	0.0008	2.60	0.14	0.13	0.12	0.075	0.175
PCB-118	0.026	25.00	4.93	3.18	4.32	3.00	6.19
PCB-123	0.00067	1.79	0.20	0.15	0.18	0.11	0.26
PCB-126	0.0002	0.20	0.027	0.02	0.024	0.015	0.036
PCB-156	0.003	8.25	0.63	0.49	0.55	0.39	0.75
PCB-157	0.0008	1.73	0.15	0.11	0.14	0.091	0.19
PCB-167	0.003	3.46	0.34	0.25	0.32	0.20	0.43
PCB-169	5.1×10^{-5}	0.03	0.004	0.004	0.003	0.001	0.006
PCB-189	0.0004	0.83	0.077	0.058	0.068	0.045	0.094

TABLE 2. Estimated ΣdI-PCB (pg/g) and Individual dl-PCB Concentrations (pg/g) for Total PCB Measurement of 150 ng/g (or 150 000 pg/g)

	Using values from Table 1							using regressions from Figure 3 and Table S3		
	Min	max	avg	SD	median	25−75 quartiles		avg	95% confidence interval	
Σdl-PCB[a]	59.8	63803	12768	8031	11252	7826	15834	9529	3685	24641
PCB-077	0.1	1969	106	133	68	27	139	55	11	268
PCB-081	0.1	80	8	8	5	3	10	4	1	16
PCB-105	5.6	20625	2883	1963	2505	1662	3643	2075	746	5772
PCB-114	0.6	3900	214	201	174	113	263	144	50	413
PCB-118	38.8	37500	7395	4772	6475	4500	9286	5464	2113	14130
PCB-123	0.5	2679	307	227	266	167	384	214	75	610
PCB-126	0.1	300	41	27	36	23	54	30	10	91
PCB-156	2.5	12375	944	735	823	585	1125	712	262	1936
PCB-157	0.6	2588	230	170	204	136	284	172	60	493
PCB-167	2.5	5192	517	376	473	302	638	380	137	1054
PCB-169	0.0	43	6	6	4	2	9	4	1	16
PCB-189	0.6	1241	116	88	102	68	142	87	32	237
Σdl-PCB[b]	52	88490	12768	8705	11136	7588	15975	9341	3498	25035

[a] Σdl-PCB estimated from values presented in Table 1 and regression in Figure 1 and Table S3. [b] Sum of estimated concentrations of individual dl-PCBs.

An approximate 95% confidence interval for the estimated value can be estimated using standard error values for the coefficient and constant (Supporting Information Table S3), and 1.96 as a multiplier as follows (*23*):

$$\text{lower limit: } \log[\text{PCB-118}] = (1.133 - 1.96 \times 0.02) \times \log[\text{total PCB}] + (-2.127 - 1.96 \times 0.107)$$

$$\text{upper limit: } \log[\text{PCB-118}] = (1.133 + 1.96 \times 0.02) \times \log[\text{total PCB}] + (-2.127 + 1.96 \times 0.107)$$

Therefore, for total PCB = 150 000 pg/g, a 95% confidence interval for PCB-118 is 2113−14130 pg/g. Similarly, 90 and 99% confidence intervals can be calculated by replacing the multiplier 1.96 in the previous equations with 1.64 and 2.58, respectively (*23*).

Relatively simple calculations using total PCB = 150 000 pg/g and average (4.93%) and median (4.317%) values of PCB-118 as percentages of total PCB from Table 1 would have resulted in PCB-118 = 7395 and 6475 pg/g, respectively. A possible 25−75 quartile range of PCB-118 concentration estimated using values 3.00−6.19% from Table 1 is 4500−9286 pg/g.

dl-PCB in Various Fish Species. An analysis of the MOE data pooled for all fish species (Supporting Information Table S1) presented in Figures 1 and 2 suggests good correlations of dl-PCBs to total PCB. However, differences in the dl-PCB pattern among fish species are possible. In Supporting Information Figure S1, we present the contribution of each dl-PCB to total PCB for various fish species found in the MOE database. Overall, there was no statistically significant difference in the pattern among the fish species. Some atypical values were observed for burbot (*Lota lota*), northern pike (*Esox lucius*), and the *Percichthyidae* family species (i.e., white bass, *Morone chrysops*, and white perch, *M. americana*) for more than two dl-PCBs. However, such differences in the estimates for burbot and northern pike may be due to the small sample sizes (i.e., seven and three fish, respectively).

Evaluation. The dl-PCB composition presented here was prepared from a comprehensive MOE dataset ($n = 912$), which is likely the largest dl-PCB fish dataset in the world. However, the majority of the values were for predatory fish fillets collected over 10 years from various locations within only one province (i.e., Ontario, Canada). To determine the extent that the relationships we derived for the composition of dl-PCB in fish can be generalized to other geographical regions, we compare the dl-PCB composition found in the MOE dataset to other reported values from the literature.

We first compare the percentage contributions of dl-PCBs to total PCB (Figure 2a) with the contributions found in the freshwater fish contamination data recently collected by the U.S. EPA through a 4-year (2000−2003) national study known as the National Lake Fish Tissue Study (NLFTS) (*24*). The NLFTS dataset includes the quantification of PCB congeners in fish samples collected from 500 randomly selected lakes and reservoirs in the lower 48 states of the U.S. The U.S. EPA method 1668a (*14*) was employed to measure PCB congeners. The reported total PCB values in the NLFTS dataset are sum-

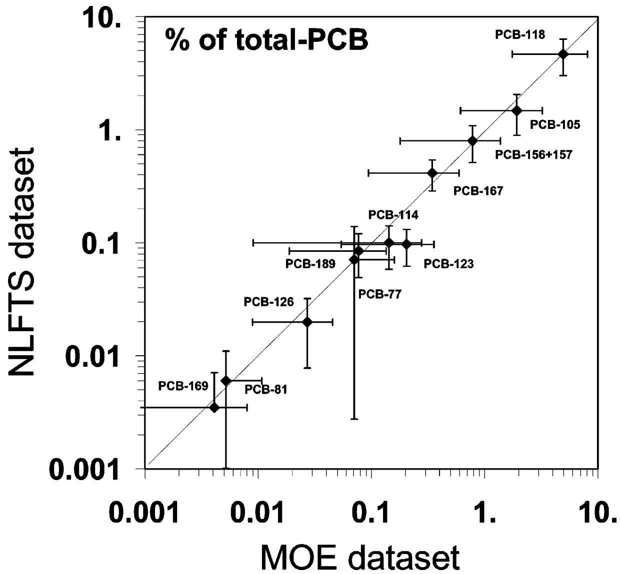

FIGURE 3. Comparison of percentage contribution of individual dl-PCB congener to total PCB calculated for the MOE dataset vs NLFTS dataset. The dotted line represents the perfect match. The whiskers are one standard deviation of the arithmetic mean values of the corresponding datasets. PCB-156 and -157 coeluted during the NLFTS analysis.

of-congener values and not the Aroclor equivalents as are often measured.

Since PCB-126 is toxicologically the most important dl-PCB congener due to the largest TEF and highest contribution to TEQ_{dl-PCB} among all dl-PCBs (*10*, *22*), for this evaluation, we created a dl-PCB subset of the NLFTS dataset using only those data points that had measured values of PCB-126 above the detection limit. The subset consisted of 55 skin-on fillet samples of 13 species of adult predator fish and 176 whole fish samples of 17 species of bottom-dwellers (Supporting Information Table S4). Each sample was a composite of −two to five fish of the same species and similar size from the same location. The length, weight, and total PCB ranged from approximately 18−85 cm (median 45 cm; 25−75 quartiles, 37−53 cm), 70−10 000 g (median 971 g; 25−75 quartiles, 618−1885 g), and 9−1266 ng/g wet wt (median 72 ng/g; 25−75 quartiles, 34−128 ng/g), respectively.

As shown in Figure 3, the NLFTS dl-PCB composition presented as a percentage of total PCB corresponds well with the composition shown for the MOE dataset (Figure 2a). The average percentage contribution values for eight dl-PCB congeners, PCB-77, -81, -118, -156 + 157, -167, -169, and -189, in the NLFTS dataset are within 20% of the corresponding average values in the MOE dataset. These congeners collectively account for on average 73% of the dl-PCB amount (Figure 2b). For the rest of the dl-PCBs, the NLFTS values are within 50% of the corresponding MOE values except for PCB-123, which differed by a factor of 2. All NLFTS average values, except for PCB-123, are also within the 25−75 quartile ranges for the MOE data (Table 1).

Lasrado et al. (*25*) analyzed dl-PCB data for a subset of 69 fish samples from the first year of the NLFTS and reported an average percentage contribution of dl-PCB congeners to total PCB. These values reported by Lasrado et al. (*25*) are within 15% of the corresponding average values for all 4 year NLFTS data and within 50% of the corresponding values for the MOE data (except for PCB-123, for which the values are within a factor of 2) (results not shown here). This comparison suggests that the composition of dl-PCB in the NLFTS dataset is consistent on a year-to-year basis.

Comparison of the MOE dl-PCB composition with other studies is summarized in Supporting Information Table S5 and is described here. Williams et al. (*26*) reported similar dl-PCB patterns in 17 samples of Lake Michigan chinook salmon (*Oncorhynchus tshawytscha*) collected in 1992. Koslowski et al. (*19*) analyzed two to five muscle and liver samples of carp (*Cyprinus carpio*), gizzard shad (*Dorosoma cepedianum*), silver bass (*Morone chrysops*), and smallmouth bass (*Micropterus dolomieui*), in addition to sediment, phytoplankton, and herring gull (*Larus argentatus*) eggs, collected from Lake Erie (Canada) and argued that measurements of total PCB might not be adequate to characterize the hazard associated with the distribution of each individual PCB congener in the Lake Erie food web. However, the contributions of measured PCB-77, -105, -118, -126, and -169 to total PCB in fish were, in most cases, within the observed ranges reported here for the MOE dataset.

Oliver and Niimi (*7*) analyzed whole-fish samples of slimy sculpin (*Cottus cognatus*), alewife (*Alosa pseudoharengus*), rainbow smelts (*Osmerus mordax*), coho salmon (*Oncorhynchus kisutch*), rainbow trout (*O. mykiss*), lake trout (*Salvelinus namaycush*), and brown trout (*Salmo trutta*) collected from Lake Ontario (Canada) from 1982 to 1986 and found similar contributions of PCB-105, -118, and -156 to total PCB.

Huestis et al. (*27*) analyzed archived samples of 4 year old whole lake trout (*S. namaycush*) collected annually from 1977 to 1993 from Lake Ontario (Canada). They also analyzed 3−9 year old Lake Ontario lake trout whole-fish samples collected in 1988. The dl-PCB composition reported for 22 sets of mean values from a total of 141 samples was generally within the 25−75 quartile ranges of the MOE dataset.

Bright et al. (*28*) found similar contributions of PCB-77 and -126 to total PCB in four-horn sculpin (*Myoxocephalus quadricornis*) collected from Cambridge Bay (NT, Canada) in 1992. In addition, the pattern was consistent between liver and whole-fish samples. The contributions of PCB-118 and -123 to total PCB found in 10 species of fish, namely, round goby (*Neogobius melanogaster*), greater sand eel (*Hyperoplus lanceolatus*), lesser sand eel (*Amodytes tobianus*), cod (*Gadus morhua*), lamprey (*Lamperta fluviatilis*), perch (*Perca fluviatilis*), pikeperch (*Stizostedion lucioperca*), flounder (*Platichhtys esus*), Baltic herring (*Clupea harengus*), and eelpout (*Zoarces viviparus*), collected from Gulf of Gdañsk (Baltic Sea) in 1992 were also within the observed ranges; however, the values were higher than 75% quartile values for the MOE dataset (*29*). Gerstenberger et al. (*30*) reported an unusually high (0.1−1.9%) contribution of PCB-81 to total-PCB in walleye (*Stizostedion vitreum*), siscowet (*Salvelinus namaycush siscowet*), carp (*Cyprinus carpio*), and whitefish (*Coregonus clupeaformis*) collected from Lake Superior (Canada) in 1991−92.

Guruge et al. (*31*) analyzed selected mono- and non-*ortho* PCBs (i.e., PCB-77, -105, -118, -126, -156, and -169) in ayu (*Plecoglosus altivelis*), bluegill (*Lepomis macrochirus*), and chub (*Opsariichthys uncirostris*) from Lake Biwa (Japan); in sea bass (*Lateolabrax japonicus*), mullet (*Mugil cephalus*), croaker (*Argyrosomus argentatus*), and gizzard shad (*Konosirus punctatus*) from Tokyo Bay (Japan); and mullet (*Nemyxus leuciscus*), common minnow (*Zacco platypus*), minnow (*Squalidus* sp.), fat minnow (*Moroco* sp.), catfish (*Silurus asotus*), carp (*C. carpo*), and silver curssian carp (*Carassius auratus langsdorfii*) from Tama River (Japan). The contributions of these dl-PCBs to total PCB were within the observed range and, in most cases, within or close to the 25−75 quartile ranges for the MOE dataset.

Total PCB concentrations were not explicitly mentioned in the studies published by Lundgren et al. (*32*) and Wan et al. (*16*). As such, we compared their reported contributions of dl-PCBs to Σdl-PCB with the composition for the MOE dataset shown in Figure 2b. Lundgren et al. (*32*) reported similar dl-PCB compositions, except slightly lower and higher contributions of PCB-118 and -156, respectively, for 11 samples of fourhorned sculpins (*Oncocottus quadricornis*) collected from five different coastal locations in the Gulf of Bothnia (northern Baltic Sea). For pooled samples of three for each of six fish species, weever (*Lateolabras japonicus*), catfish (*Chaeturichthys sitgmatias*), bartail flathead (*Platycephalus indicus*), white flower croaker (*Nibea albiflora*), wolfish (*Obontamblopus rubicundus*), and mullet (*Liza so-iuy*), collected from an isolated inner sea in the northeast region of China, Wan et al. (*16*) reported a very similar composition of dl-PCBs as shown here for the MOE data in Figure 2b.

The composition of dl-PCB in fish is presented after analyzing the largest known dataset of dl-PCB and total PCB in fish, which included 22 fish species of different trophic levels with wide ranges in size, weight, and PCB levels. The coefficients of determination for the regressions correlating individual dl-PCB to total PCB suggest that more than 70% of the variation in most dl-PCBs are explained by changes in total PCB levels. The 25−75 interquartile ranges of estimated dl-PCB concentrations from a total PCB measurement are expected to be generally within 2−3-fold. This level of precision can be viewed as reasonable given the possible measurement error of 12−90% for dl-PCBs and up to 35% for total PCB (*33*). In cases where more precise estimates are needed, complete congener-specific dl-PCB analysis of a representative number of samples or a composite sample can be used to provide a more reliable site-specific ratio of Σdl-PCB to total-PCB. Then, using the information presented Figure 2b, concentrations of dl-PCBs can be estimated. However, it is difficult to assess the expected improvement in the estimates through such a calibration of the dl-PCB fish composition for the environment in question because it may depend on many factors including sample size and variety of fish species in the system.

It should be noted that the dl-PCB composition presented as percentages of total PCB (Figure 2a) is based on the use of a 4:1 mixture of Aroclor 1254:1260 as a standard during the MOE total PCB analysis as described in the Materials and Methods. Use of a different Aroclor or mixture of Aroclors as the standard would have affected total PCB values and, thereby, the dl-PCB composition presented in Figure 2a. However, a very good agreement between the dl-PCB patterns in the Aroclor-based MOE dataset and sum-of-congener-based NLFTS subset (Figure 3) suggests that the dl-PCB composition presented in this paper should be reasonably valid for different types of total PCB measurements. As such, the composition should serve as a practical tool to estimate dl-PCB concentrations in fish until the cost barrier and analytical challenges involved in congener-specific dl-PCB analysis have been overcome.

Total PCB levels vary among fish tissues (*34−36*); however, similarities in the dl-PCB pattern among fish tissues suggest that corresponding dl-PCB concentrations can be estimated from any type of (e.g., skin-on or -off fillet, whole-fish) total PCB measurement. A very good match of the dl-PCB composition presented here with the composition in the national (U.S.) predator and bottom fish data for the 48 lower states of the U.S. suggests that the dl-PCB composition in fish is relatively constant and applicable at least in North America. Although sporadic cases of abnormal dl-PCB patterns in fish have been reported, a number of studies from other geographical regions have published dl-PCB fish data that translate into similar dl-PCB patterns as reported here. As a result of these similarities, we are optimistic that the dl-PCB pattern in fish is applicable, with reasonable accuracy of 2−3-fold, to fish from all over the world.

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Supporting Information Available

Names, scientific names, and scientific family names of the fish species considered in the Ontario MOE data (Table S1); details of fish size, weight, and measured PCB concentrations with MDL for the MOE dataset (Table S2); linear regressions of log transformed concentrations of Σdl-PCB and individual dl-PCB congener against the log transformed total PCB concentration (Table S3); names, scientific names, and scientific family names of the fish species considered in the U.S. EPA NLFTS subset of 231 samples utilized to compare dioxin-like PCB (dl-PCB) composition from the MOE dataset in Figure 3 (Table S4); comparison of the MOE dl-PCB composition with other published studies (Table S5); and percentage contribution of individual dl-PCB congeners to total PCB concentrations in various fish species considered in the MOE data (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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