

Congener-Based Aroclor Quantification and Speciation Techniques: A Comparison of the Strengths, Weaknesses, and Proper Use of Two Alternative Approaches

PAULA J. SATHER,[†]
JOHN W. NEWMAN,[‡] AND
MICHAEL G. IKONOMOU*,[†]

Department of Fisheries and Oceans, Institute of Ocean Sciences, Marine Environmental Quality Section, Sidney, British Columbia, Canada V8L 4B2, and Department of Entomology and Cancer Research Centre, University of California Davis, One Shields Avenue, Davis, California 95616

This paper compares two previously published methods, an Aroclor estimation method and a mixing model method, that relate Aroclor contamination to congener specific data in environmental samples. The Aroclor estimation method, which is consistent with U.S. EPA Method 8082, uses a limited set of congener specific data to estimate Aroclor contributions to the sample, while the mixing model method uses the full congener data to model sample compositions as linear combinations of Aroclors. The performance of these methods are compared, using 181 samples at a variety of trophic levels, in terms of (a) total PCB concentrations, (b) compositional modification levels from original Aroclors, and (c) determination of the Aroclor mixture or mixtures best describing the sample (Aroclor speciation). We find that the two methods agree in all three terms for samples of low trophic level, but disagree for samples of higher trophic levels. Most significantly, the comparison reveals systematic overestimation of total PCB content by the Aroclor estimation method for samples at high trophic levels. The implication is that Aroclor determinations using persistent congeners cannot reliably be used as surrogates for total PCB concentration. The strengths and weaknesses of each method are detailed.

Introduction

From the 1930s to the 1970s polychlorinated biphenyls (PCBs) were used in industry as dielectric fluids in capacitors and transformers and as hydraulic fluids and solvents. Worldwide production of PCBs (excluding the Soviet Union) between 1929 and 1989 is estimated to be 1.5 million ton (1). In North America, they were sold as mixtures under the trade name of Aroclor, with U.S. sales of Aroclors from 1957 to 1972 estimated at 324 thousand tonnes (2). Production was by bulk electrophilic substitution reactions which, together with steric effects, favor certain ring chlorine substitution patterns (4, 25-, 34-, 245-) and suppress or disfavor others (35-, 246-,

3, 26-, 235-, 345-) (3, 4). Variation in chlorine content determined the different mixtures from a low of 21 wt % (Aroclor 1221) to a high of 68 wt % (Aroclor 1268). Though the de novo synthesis of PCBs in the stack gas effluent of municipal waste incinerators has been established (5, 6), the primary source of PCBs to the environment has been through spillage or careless disposal of these industrial PCB mixtures. Once in the environment their stability, which made them so suitable for their industrial applications, has led to their environmental persistence and bioaccumulation.

The stability of PCBs has also led to the assumption that PCBs in environmental samples closely resemble those in Aroclors, which in turn justifies the quantification of PCBs as Aroclors rather than as individual congeners (7). However, congener specific analyses have also shown that PCB congener compositions in environmental samples often differ significantly from the original Aroclors. Hence, one can find in the literature claims both that environmental PCB congener patterns resemble Aroclors (8) and that they do not (9). As well, while congener specific methods for PCBs analysis are the gold standard of environmental PCB measurement, until legislation is updated quantitative assessments of Aroclor values will still be required. In the meantime procedures have been developed for the systematic characterization of environmental PCB congener profiles in terms of the Aroclor technical mixtures that were their source. However, a casual comparison of two of the most recent methods reveals significant differences in the output of these procedures. In an attempt to clarify and highlight these differences, we have systematically compared these two procedures with biotic samples at a variety of trophic levels to indicate the sources of bias and implications for the use of data from each. The first method, developed at the University of California, Santa Cruz (10), was a congener to an Aroclor conversion method using a limited number of congeners to estimate the most probable source of the detected congeners, while providing an estimate of total PCB content equivalent to that produced by EPA Method 8082. The second method was developed at the Institute of Ocean Sciences, Sidney, BC (11), to enable the use of all of the data from a full congener analysis for the determination of the Aroclor or mixture of Aroclors most similar to the detected PCB profile. Both methods also attempt to determine objectively the levels of compositional modification from original Aroclors. Specifically, we have compared the two methods with respect to (a) total PCB quantification, (b) estimation of the levels of compositional modification from the original Aroclors (called "weathering" in ref 10), though we did not attempt to distinguish modification that occurs in the ambient environment from that which occurs within the organism, and (c) the identification and quantification (normalized to 100%) of the Aroclor mixture(s) contributing to the sample's PCB compositional profile—in this paper called Aroclor speciation.

Methods and Materials

General. PCB congeners are referred to by a "BZ" number as defined by Ballschmitter et al. (12). Congener composition for Aroclors was taken from refs 13 and 14, and IUPAC numbering of congeners in these references was converted to Ballschmitter numbering (IUPAC 107, 108, 109, 199, 200, and 201 in refs 13 and 14 converted to BZ 108, 109, 107, 201, 199, and 200, respectively). Where necessary, congener weight percentages were added together to reflect coelutions on the DB5 column used in our laboratory. These coeluters are listed in their entirety in ref 11, but those specific to the Aroclor estimation method are 118/106, 160/163/164/138, 203/196,

* Corresponding author phone: (250)363-6804; fax: (250)363-6807; e-mail: IkonomouM@pac.dfo-mpo.gc.ca.

[†] Institute of Ocean Sciences.

[‡] University of California Davis.

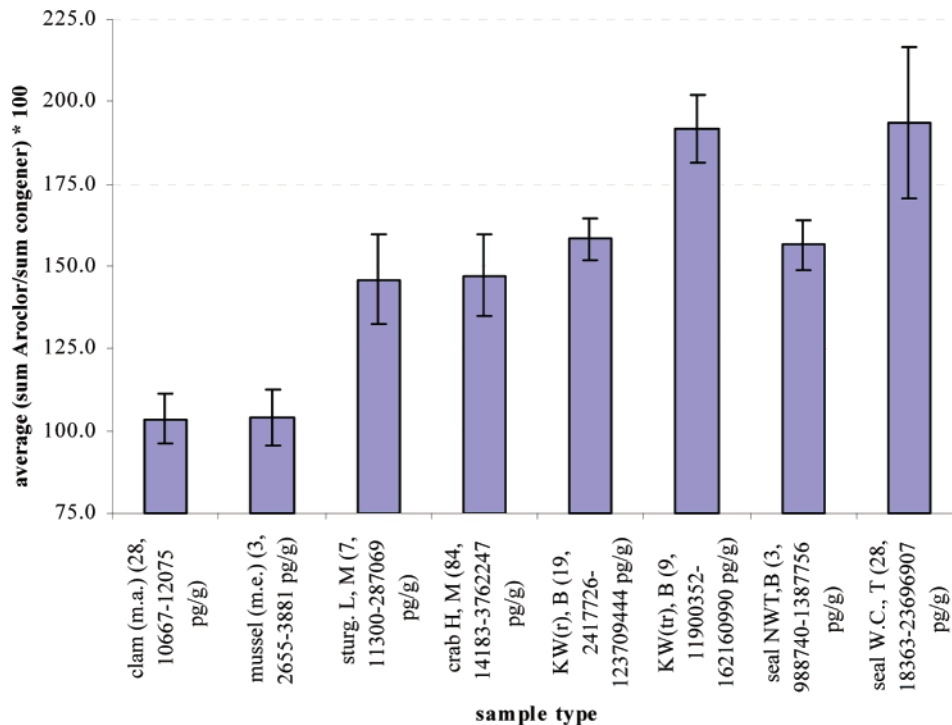


FIGURE 1. Comparison of total PCB quantitation. (sum Aroclors/sum congeners) \times 100. For all figures sample matrixes are as follows: m.e. = *mytilus edulis*; m.a. = *mya arenaria*; crab = Dungeness crab (*Cancer magister*); sturg. = sturgeon; KW = killer whale (*Orcinus orca*); seal NWT = ringed seal (*Phoca hispida*) Northwest Territories; seal W.C. = harbor seal West Coast; r = resident; tr = transient; H = hepatopancreas; M = muscle; L = liver; B = blubber; T = tissue includes blubber, heart, kidney, liver, muscle. Error bars are standard deviations; the number of samples is in brackets followed by the total PCB concentration range (sum of congeners).

TABLE 1. Composition as Weight Percentage of Quantitation Congeners and PCB 153 for Aroclors 1242, 1248, 1254, and 1260^{a,b}

congener	Aroclors				
	1242	1248	1254	1254(G4)	1260
18	9.24	4.58	0.09	0.25	0.07
28	6.08	3.36	0.06	0.19	0.05
31	6.34	4.53	0.11	0.28	0.05
99	0.39	1.45	3.55	3.02	0.03
118	0.69	2.18	12.27	7.35	0.48
128	0.04	0.13	1.52	1.42	0.4
138	0.15	0.5	6.19	7.35	7.18
194	0.00	0.03	0.01	0.01	1.62
195	0.00	0.01	0	0.00	0.77
203	0.00	0.03	0.01	0.02	1.75
201	0.00	0.05	0.01	0.01	1.75
153	0.14	0.52	4.47	6.06	11.04

^a The values are average weight percentages from up to 9 mass spectrometry system columns (labeled with GMF/MS or JWC/2 Col.) in Table 2 of ref 13 with the exception of lot G4 of Aroclor 1254 which was taken from ref 14. ^b Congeners 118, 138, 203, and 153 include coeluters 106, 160/163/164, 196, and 132, respectively.

and 132/153. For this discussion these coeluting groups will be referred to as 118, 138, 203, and 153, respectively. Microsoft Excel software was used for all calculations and verification of statistical work was done using PopTools, a freeware Excel add-in developed by Australian Greg Hood that uses the algorithms in TPMath by Dr. Jean DeBord.

Samples. The samples used for the comparison in this paper are the ones used in the original discussion of the mixing model method (11). One hundred eighty-one samples were analyzed by the IOS laboratory full congener PCB method. These samples include killer whale (*Orcinus orca*) blubber from both resident and transient animals, Dungeness crab (*Cancer magister*) muscle and hepatopancreas, sturgeon

liver and muscle, clam (*Mya arenaria*), and mussel (*Mytilus edulis*). The samples were collected from a variety of locations in British Columbia. In addition, harbor seal (*Phoca vitulina richardii*) tissues (blubber, muscle, liver, and kidney) from the Puntledge River on the West coast of British Columbia, and three blubber samples from arctic ringed seals (*Phoca hispida*) captured at Holman Island, Northwest Territories, are included.

Full Congener PCB Analysis. Details of the full congener PCB analysis have already been published (15–17) and are thus described only briefly here.

The full congener PCB analysis is an HRMS-based, internal standard, and independently validated method. Samples for analysis were homogenized, spiked with a representative suite of internal standards, and ground with Na₂SO₄. Extraction into 1:1 DCM/hexane and cleanup of the concentrated extract through gel permeation silica gel and alumina columns followed. Carbon fiber HPLC then separated the extract into three fractions. Fraction I contained the di-ortho-PCBs (DO); fraction II contained the mono-ortho-PCBs (MO); and fraction III contained the non-ortho-PCBs (NO). Each fraction was then spiked with recovery standards and analyzed by HRGC/HRMS on a DB-5 capillary column (60m \times 0.25 mm i.d., 0.1- μ m film). Each native congener or coeluting group of native congeners was quantitated against its appropriate surrogate using the internal standard method corrected to 100% recovery by the recovery standard. The full congener data set for 181 samples is very large and therefore has not been included in this paper. It is available on request from the corresponding author.

Mixing Model Analysis. The details of the mixing model have been described in detail (11) and are summarized here. A direct mixing model attempts to describe samples as a linear combination of sources. In this instance we want to describe the weight percentages of the individual congeners (weight percent composition) of a sample as a linear combination of the weight percent composition of three

TABLE 2. Composition as Weight Percentage of Quantitation Congeners and PCB 153 for Samples According to Sample Type^{a,b}

congener	samples							
	clam (m.a.) (28)	mussel (m.e.) (3)	sturg. L, M (7)	crab H, M (84)	KW(r), B (19)	KW(tr), B (9)	seal NWT,B (3)	seal W.C., T (28)
18	0.64 (0.67)	0.26 (0.02)	0.11 (0.08)	0.07 (0.05)	0.05 (0.04)	0.03 (0.02)	0.09 (0.10)	0.02 (0.01)
28	1.62 (0.97)	1.05 (0.08)	1.24 (0.82)	0.77 (1.05)	0.10 (0.11)	0.05 (0.05)	2.07 (0.30)	0.13 (0.07)
31	1.13 (0.68)	0.73 (0.09)	0.60 (0.42)	0.38 (0.70)	0.05 (0.04)	0.01 (0.00)	0.68 (0.26)	0.05 (0.04)
99	2.60 (0.42)	2.60 (0.44)	3.48 (0.76)	3.34 (0.80)	5.25 (1.57)	6.40 (1.59)	6.86 (0.86)	6.36 (1.76)
118	4.46 (1.20)	5.41 (0.88)	2.76 (1.02)	6.36 (2.58)	3.46 (1.69)	1.84 (0.47)	6.19 (0.51)	1.18 (0.53)
128	0.93 (0.28)	1.04 (0.24)	1.33 (0.18)	1.52 (0.38)	1.58 (0.26)	1.83 (0.36)	0.51 (0.26)	1.79 (0.51)
138	5.82 (1.49)	7.12 (0.70)	11.37 (1.31)	12.60 (1.67)	13.49 (1.43)	16.86 (2.40)	10.92 (1.47)	19.15 (2.94)
194	0.12 (0.10)	0.11 (0.02)	0.78 (0.70)	0.51 (0.33)	0.67 (0.47)	1.22 (0.65)	0.17 (0.07)	0.88 (0.39)
195	0.06 (0.05)	0.04 (0.01)	0.20 (0.16)	0.15 (0.10)	0.12 (0.09)	0.19 (0.08)	0.07 (0.01)	0.22 (0.08)
203	0.25 (0.12)	0.32 (0.15)	1.05 (0.88)	0.69 (0.38)	1.02 (0.78)	1.49 (0.75)	0.46 (0.11)	1.24 (0.59)
201	0.27 (0.11)	0.25 (0.15)	1.02 (0.83)	0.48 (0.31)	0.97 (0.92)	1.21 (0.70)	0.42 (0.14)	1.35 (0.57)
153	5.70 (1.50)	7.60 (0.60)	15.30 (2.10)	12.70 (3.60)	18.20 (2.00)	25.60 (2.90)	19.00 (4.20)	24.80 (8.20)

^a Values are average weight percentages with standard deviations in parentheses; the number of samples follows the sample type in parentheses.
^b Congeners 118, 138, 203, and 153 include coeluters 106, 160/163/164, 196, and 132, respectively.

TABLE 3. Relative Standard Deviations (Standard Deviation/Mean) × 100 for Aroclors 1254 and 1260 According to Sample Type

RSD	samples							
	clam (m.a.) (28)	mussel (m.e.) (3)	sturg. L, M (7)	crab H, M (84)	KW(r), B (19)	KW(tr), B (9)	seal NWT,B (3)	seal W.C., T (28)
1254	24 (24)	13 (4)	48 (10)	31 (17)	54 (13)	66 (4)	71 (13)	72 (8)
1260	50 (19)	53 (12)	33 (3)	37 (11)	47 (16)	43 (3)	53 (2)	43 (12)

^a Values are averages with standard deviations in parentheses; the number of samples follows the sample type in parentheses.

different Aroclors (1242, 1254, and 1260). Because there are many more congeners than Aroclors, there is no unique solution, so the best solution must be sought by minimizing the residual. Two methods of solution were described previously (11), an iterative method and the method of least-squares regression (LSR). Both provide values for Aroclor speciation and the residual sum of squares (RSS) value, which provides a relative measure of compositional modification. As described before, the methods produce a general agreement, and so for simplicity only the LSR results will be used in the following discussion.

Limited Congener Aroclor Estimation Method. The details of the analytical approach to Aroclor estimation using a limited congener set appear in Newman et al. (10). For the comparison described in this paper split samples were not run. Rather, the full congener data set for all 181 samples was reduced and re-processed according to the limited congener Aroclor estimation method as described in Newman et al. (10) with the exception that Aroclor to congener and congener to Aroclor conversion functions were not employed. Instead, weight percentages were used directly to convert congener to Aroclor amounts and Aroclor to congener amounts. The use of weight percentage conversions rather than experimentally determined conversion functions is justified by the use of an HRMS detector rather than an EC detector. The requirements for accurate PCB quantification using an EC detector have been detailed by Storr-Hansen (18). Quantification with an HRMS detector, with its high specificity in SIM mode, which all but eliminates interfering coelutions, and with its large linear range, is not so complex. It has been called the “detector of choice” (13) for this type of analysis.

Briefly, the Aroclor estimation calculations proceeded through a decision tree as follows:

The first decision, on the presence of Aroclor 1260, was based on the ratio of 118:203 in the sample vs in Aroclor 1254. The Aroclor 1254 ratio was multiplied by 0.5 to ensure the validity of the screen even if the 118 was preferentially degraded relative to 203. If the presence of Aroclor 1260 was indicated, then the amount of Aroclor 1260 was calculated

from each of the quantification congeners using the composition weight percentages. The values were averaged, and standard deviations (SDs) and relative standard deviations (RSDs or coefficients of variation) were calculated. Next, the same type of reasoning was applied to Aroclor 1248 using the 31:118 ratios. If the presence of Aroclor 1248 was indicated, the quantification congeners for Aroclor 1248 were first corrected for the presence of Aroclor 1260 and then used to calculate the amount of Aroclor 1248 in the sample.

At this point in Newman et al. (10) the presence of Aroclor 1260 is re-evaluated to catch false negatives for this Aroclor where the quantification congeners are less than the detection limits of the analytical method. In the samples examined for this paper all indicated the possible presence of Aroclor 1260 in the initial 118:203 ratio test. Therefore, the re-evaluation was unnecessary. Finally, the Aroclor 1254 quantification congeners were corrected for the presence of Aroclors 1260 and 1248 and then used to calculate the amount of Aroclor 1254 present. Values were averaged and SDs and RSDs were calculated.

The weathering estimates were then made using the PD153 method (percent difference of 153). This method uses PCB 153 because it is persistent in biota and abundantly present in the higher chlorinated Aroclors. For nonbiotic samples in which PCB 153 might not be persistent or for samples displaying a high abundance of lower chlorinated Aroclors and associated low levels of PCB 153, this method might not be appropriate. However, the prevalence of such samples is rare in California coastal and British Columbian samples, and therefore the method is broadly, if not universally, applicable. The weathering levels were estimated by calculating the theoretical concentration of PCB 153 based on the amount of each Aroclor calculated to be present, and subtracting the actual PCB 153 contribution according to the formula

$$PD153 = \left[\frac{(\text{PCB } 153_{\text{theory}} - \text{PCB } 153_{\text{actual}})}{\text{PCB } 153_{\text{actual}}} \right] \times 100 \quad (1)$$

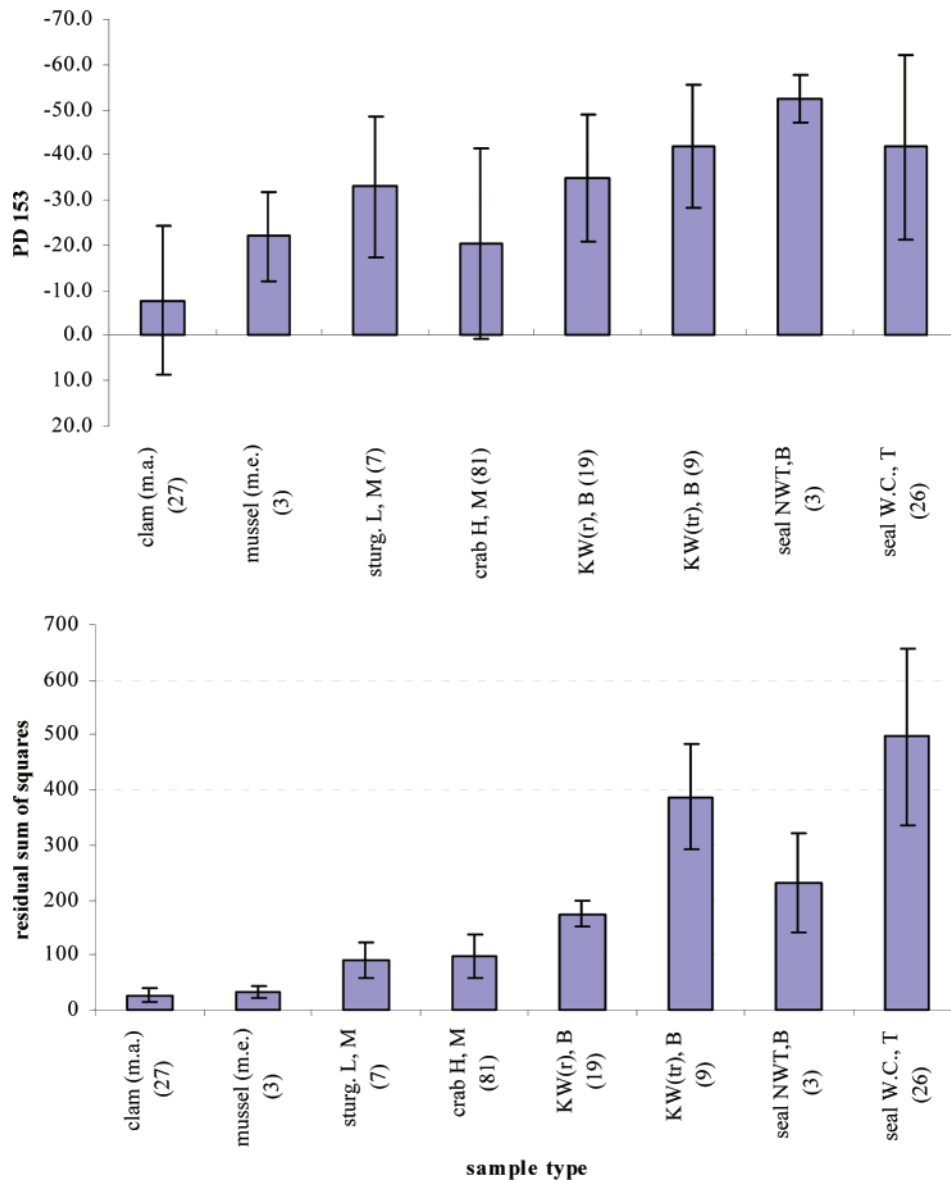


FIGURE 2. Measure of compositional modification from starting Aroclors according to sample type for the Aroclor estimation PD153 method (top, modification increases with decreasing PD153), and for the full congener mixing model method (bottom, modification increases with increasing RSS), and of 181 samples, 6 PD153 outliers have not been included in these averages (1 clam, 3 crab, and 2 seal).

Aroclor speciation is calculated by normalizing the Aroclor contributions to 100%.

Discussion

Quantification. The Aroclor estimation method approximates each Aroclor, with summation of these estimated Aroclors giving total Aroclor concentration, which one may be tempted to consider as a simple surrogate for the total PCB concentration in a sample. In contrast, the full congener method is a direct measure of all PCB congeners present, with summation of the measured PCB congeners giving a true measure of the total PCB concentration. Comparing the total PCB concentration as determined by these two methods, we find that the Aroclor estimation method overestimates total PCB concentration in most cases using the current sample set. When the samples are sorted by type, these overestimations become more systematic. As seen in Figure 1, total PCB concentrations in clam and mussel samples are estimated accurately with the sum of Aroclors approximately equalling the sum of congeners, suggesting that these methods will perform equivalently for low trophic level samples. Most other sample types at higher trophic levels

show an overestimation of total PCBs by the sum of Aroclor method compared to the measured sum of congeners. A maximum 2-fold or 100% error was observed in the highest trophic level samples. The low standard deviations show that these overestimations are not random. The crab samples, which include both muscle tissue and hepatopancreas tissue, demonstrate that the overestimations are not related to the total PCB value in the sample. The reasoning is that muscle tissue has much lower PCB concentrations than hepatopancreas tissue, but the overestimation ratios are indistinguishable between the tissue types.

Comparison of the relative quantities of quantification congeners in both the samples and in Aroclor standards reveals the source of these systematic overestimations. Table 1 shows the weight percentage of the quantification congeners for Aroclors 1248, 1254, and 1260 and for PCB 153 (the congener used to estimate weathering levels in the Aroclor estimation method). Table 2 shows the weight percentages of the quantification congeners for the samples according to sample type along with their standard deviations. First examining the Aroclor 1254 congeners, we see that, with the exception of the clam and mussel samples, congener

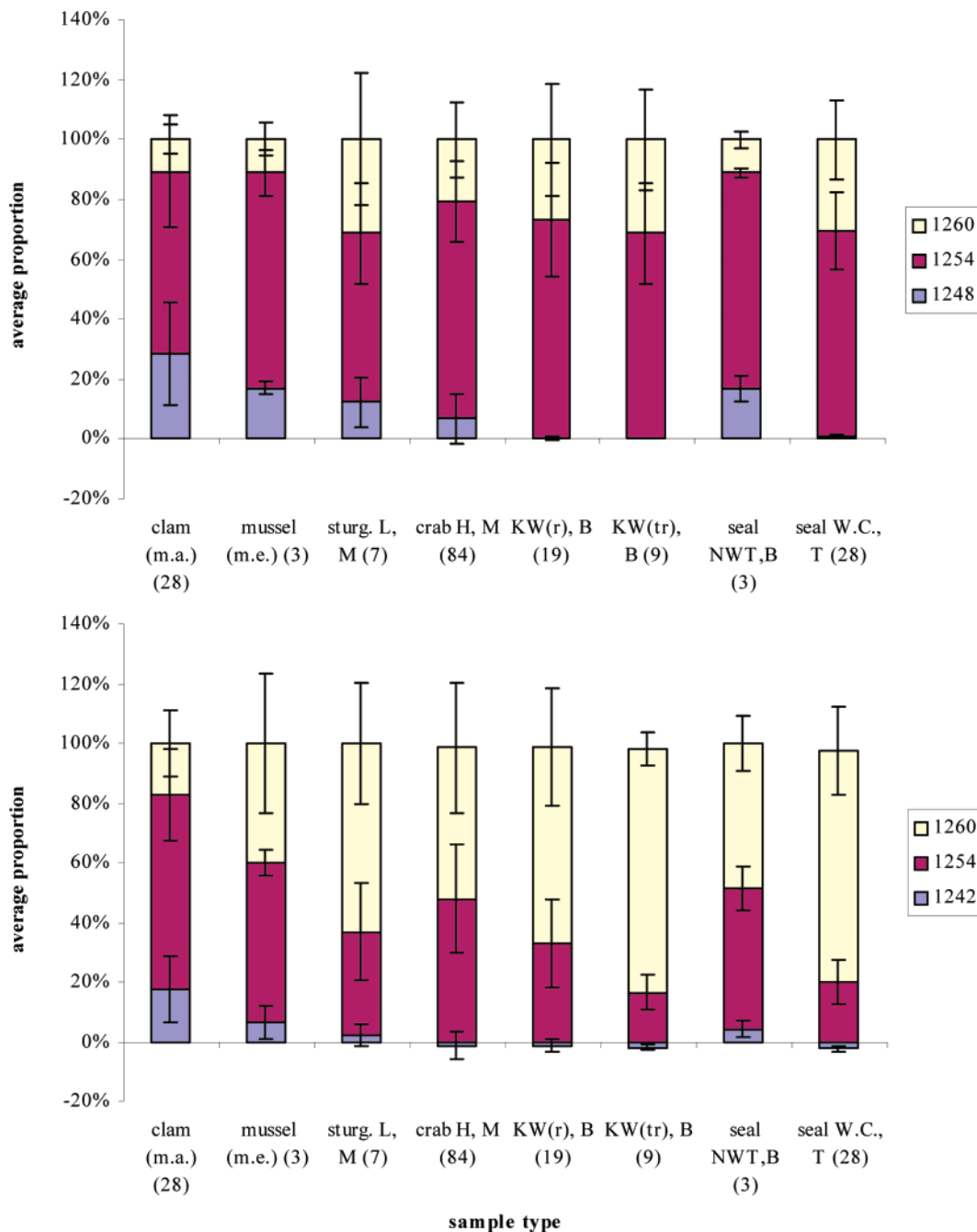


FIGURE 3. Aroclor speciation estimates according to sample type for the Aroclor estimation method (top) and for full congener mixing model method using normalized LSR values (bottom).

138 comprises over 11% and up to 19.15% of the total PCB concentration in the samples, while comprising only 6.19 or 7.23% of Aroclor 1254 and 7.18% of Aroclor 1260. Similarly, though not as dramatically, congener 99 ranges from 2.6% of the clam samples to 6.86% of NWT seal samples, while comprising only 3.02 or 3.55% of Aroclor 1254 and much less than that of the other Aroclors. Since the congener to Aroclor conversion is based on the concentration of the quantification congeners divided by their weight percentage in the Aroclor, any relative enrichment in the concentration of the quantification congeners will clearly result in very high estimates of Aroclor 1254 (see eq 2).

$$C_a = C_c / P_{ca} \quad (2)$$

where C_a is the concentration of Aroclor a in the sample, C_c is the concentration of congener c in the sample, and P_{ca} is the weight percentage of congener c in Aroclor a .

The other two congeners used for quantification of Aroclor 1254, 118, and 128 do not show such elevated compositions. However, their values are not low enough to average out the high estimations generated by congeners 99 and 138.

Comparison of the weight percentages in Aroclors and samples for Aroclors 1248 and 1260 do not show this type of dramatic overabundance. Thus, the high estimation of Aroclor 1254 explains most of the total PCB overestimation. Only in clam and mussel samples, where levels of congeners 99 and 138 are not higher than that in Aroclor 1254, does the Aroclor estimation method closely match the measured values for total PCBs. Therefore, Aroclor estimation using elevated or persistent congeners for quantification, including U.S. EPA 8082 data (10, 19, 20), leads to the systematic overestimation of total PCBs in compositionally modified biotic samples.

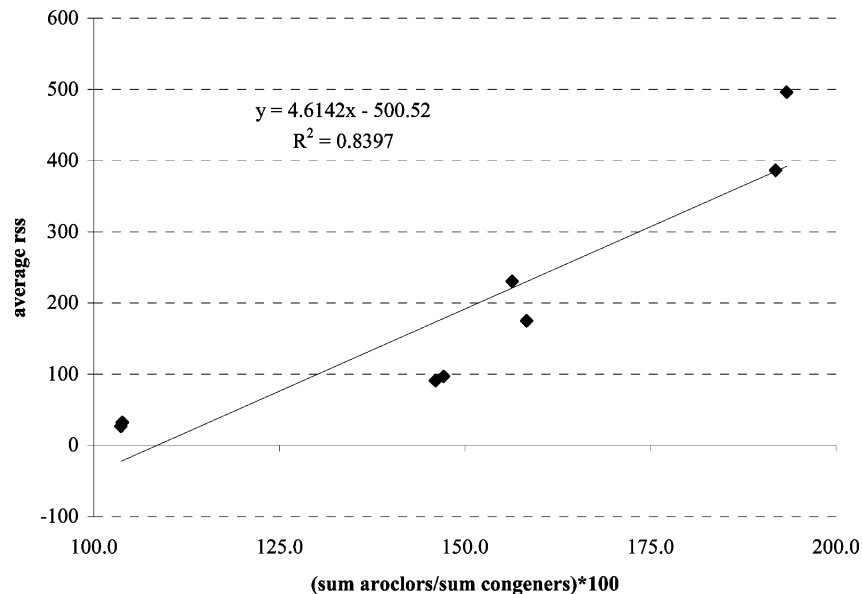


FIGURE 4. Regression of compositional modification measure by RSS from mixing model method (bottom Figure 2) on estimation of total PCB quantitation (sum Aroclor/sum congeners) \times 100 (Figure 1).

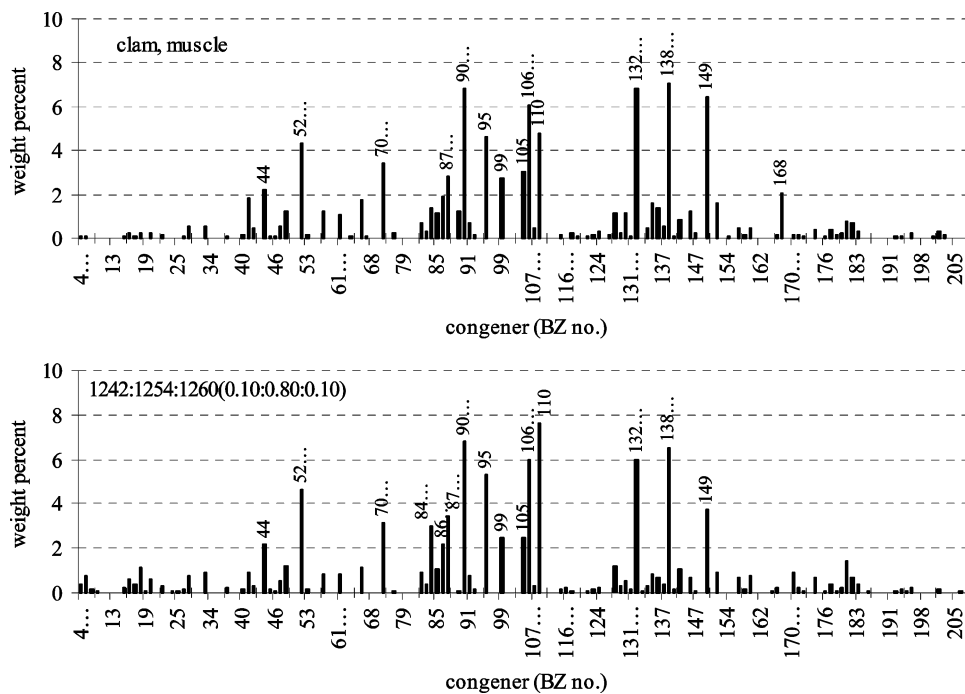


FIGURE 5. Congener composition expressed as percentage of total PCB concentration for a clam muscle sample (top, RSS = 24, PD153 = -11) and an approximate mixture of Aroclors (bottom, Aroclors 1242:1254:1260 (10:80:10)) by both mixing model method (actual Aroclors calculated 1248:1254:1260 (6:78:13)) and Aroclor estimation method (actual Aroclors calculated 1242:1254:1260 (10:80:9)). For Figures 5 and 6: congener order is by BZ number from 4 to 208 with coeluters identified by ellipses and placed at lowest congener position. Tick marks are every third congener with labels every sixth congener. Major peaks (>2%) are also labeled. Coeluters are as follows: 4/10; 5/8; 7/9; 16/32; 20/33; 24/27; 41/64/71; 42/59; 47/48/75; 52/73; 56/60; 61/74; 70/76; 83/109; 84/92; 86/97; 87/115; 90/101; 93/102; 106/118; 107/108; 116/117/125; 131/142; 132/153; 134/143; 135/144; 138/160/163/164; 139/140; 146/161; 170/190; 172/192; 174/181; 182/187; 196/203.

Relative Standard Deviations. Before continuation of the comparison between the two methods, some discussion of the relative standard deviations (RSDs) calculated by the Aroclor estimation method is in order. It was reported by Newman et al. (10) that the Aroclor estimation method was most accurate when the RSDs were less than 50% and that analytical results with RSDs > 50% should be reported with "appropriate qualifications" to indicate that the Aroclor values are poor descriptors of the underlying PCB concentrations. RSDs for Aroclors 1248, 1254, and 1260 were calculated for each of the 181 samples examined in this paper. Of these 181

samples, only 2 had RSD levels less than 50% for Aroclor 1248. An attempt to summarize the RSD levels for the other Aroclors is found in Table 3. From this table one can see that the least altered samples—clams, mussels, crabs, and sturgeon—have RSDs that are less than 50% on average. The exception of the RSDs for Aroclor 1260 in mussel samples reflects the extremely low concentrations of the Aroclor 1260 quantification congeners in the mussel samples. Samples that are more compositionally altered from the original Aroclors—the seals and killer whales—as expected show somewhat higher RSDs also. Still the average RSD for Aroclor

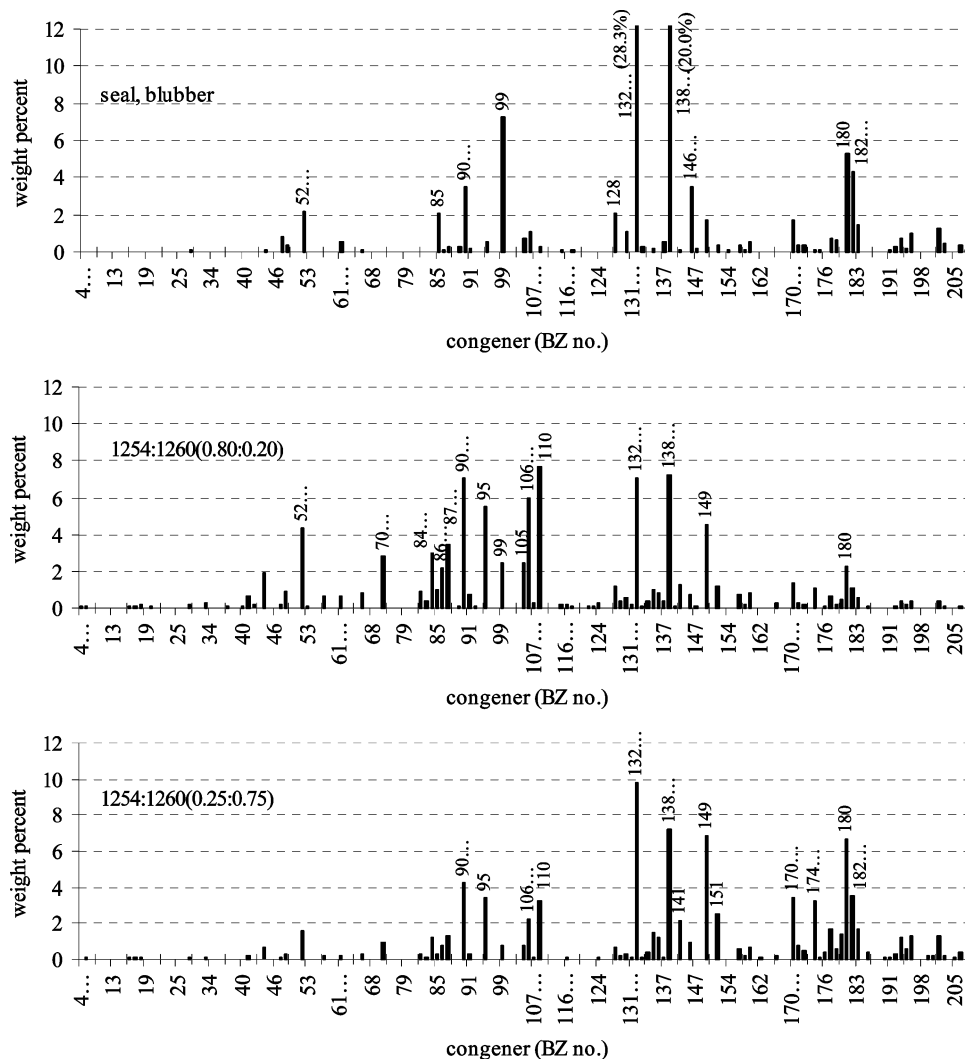


FIGURE 6. Congener composition expressed as percentage of total PCB concentration for a seal blubber sample (top) and approximate mixtures of Aroclors for this seal sample as determined by the Aroclor estimation method (center, actual Aroclors calculated 1248:1254:1260 (1:79:20), PD153 = -46) and by the mixing model method (bottom, actual Aroclors calculated 1242:1254:1260 (-3:38:102) and normalized to (-2:28:74), RSS = 401).

1260 is less than 50%, except for the NWT seals where it is 53%. In all seal and killer whale samples the RSDs for Aroclor 1254 average greater than 50%, which reflects the tremendous variation of the quantification congeners from starting compositions.

Compositional Modification. Figure 2 shows the level of compositional modification from original Aroclors according to sample type for both the Aroclor estimation method and the mixing model method. The two methods show general agreement in the increase in compositional modification with trophic level, though the mixing model shows greater differences in scale than the Aroclor estimation method. The methods similarly examine the differences between actual congener values and the theoretical Aroclor congener values. Their differences are in the number of congeners used for comparison—PCB 153 in the Aroclor estimation method versus all congeners in the mixing model—and also in the method of determining the theoretical speciation. The Aroclor estimation method first estimates Aroclor quantities so that any systematic errors are carried through the compositional modification determination. Specifically, when the amount of Aroclors with substantial proportions of PCB 153, like

Aroclors 1254 and 1260 (see Table 1), are overestimated by the Aroclor estimation method, the theoretical level of PCB 153 is also overestimated. The PD 153 method measures the difference between theoretical and actual levels of PCB 153 (see eq 1). Because the actual levels of PCB 153 are generally higher than the theoretical levels, inflation of the theoretical amounts decreases the difference between the two values and thus dampens the scale of compositional modification. In contrast, the mixing model calculations are independent of the total PCB sum of congener calculations and determine speciation and compositional modification together so as to minimize the latter. Minimization uses the sum of the squares of the difference between actual and theoretical values for all congeners, which has the effect of amplifying large differences and thus expanding the scale of compositional modification.

Aroclor Speciation. Figure 3 shows the normalized speciation of the samples by type according to the Aroclor estimation method and the mixing model method. The Aroclor estimation method uses the Aroclors 1248, 1254, and 1260, which are the Aroclors historically monitored by the California State Mussel Watch Program (10), while the mixing model method uses Aroclors 1242, 1254, and 1260 as they made up approximately 80% of Aroclor production in the

TABLE 4. Summary of Strengths and Weaknesses of Two Methods

Aroclor estimation method	Quantification	mixing model method
<ul style="list-style-type: none"> • consistent with guidelines defined by U.S. EPA 8082 • overestimates total PCBs for high trophic level biota 	<ul style="list-style-type: none"> • true measure for total PCBs 	
<p style="text-align: center;">Compositional Modification of Original Aroclors</p> <ul style="list-style-type: none"> • based only on PCB 153 • narrow scale and high variability • may not be appropriate for nonbiotic samples or lower chlorinated Aroclors 	<ul style="list-style-type: none"> • based on all congeners • broad scale shows trophic differences clearly 	
<ul style="list-style-type: none"> • based on persistent congeners • estimate of original source Aroclors 	<p style="text-align: center;">Aroclor Speciation</p> <ul style="list-style-type: none"> • based on all congeners • estimate of Aroclors as they appear in sample • bias toward Aroclor 1260 for high trophic level biota 	

United States between 1957 and 1975 (21). As has been discussed previously (11), Aroclor 1248 resembles a mixture of 67% Aroclor 1242 and 33% 1254. Given their compositional similarity, and given that neither Aroclor 1248 nor Aroclor 1242 form a significant part of the discussion, we have left them as is with no attempt to “convert” one to the other.

Some similarities are noticeable in the results from the two methods. First, the clam samples, which show the least compositional modification from original Aroclors, show agreement in Aroclor speciation between the two methods. This agreement in speciation coupled with the agreement in quantification (see Figure 1) demonstrates by two independent methods that some environmental samples bear a close relationship to mixtures of Aroclors as manufactured. Other relatively unmodified sample types—sturgeon and crab—do not show such close agreement in speciation because, as has already been discussed, PCBs 99 and 138 become enhanced relative to the original Aroclors, leading to high estimates for Aroclor 1254. Second, the most highly modified samples—killer whales and Puntledge River seals—show very little of the lighter Aroclors (1242 and 1248). Since the major portion of these Aroclors is comprised of congeners with four or fewer chlorines, 87.5% and 76%, respectively (13), the lack of these congeners in high trophic level samples may support the suggestion that trophic transfer efficiency is higher for PCBs with five or more chlorines than it is for PCBs with four or fewer chlorines (22). These findings are also consistent with the reported structure activity of relationship of chlorobiphenyl trophic transfer in marine organisms (23).

The major difference in the speciation results is the higher proportion of Aroclor 1260 in the mixing model results than in the Aroclor estimation results. Since the mixing model squares the difference between theoretical and actual values and minimizes the total, the speciation will be most influenced by congeners that are extremely enhanced or depleted with respect to Aroclors. The most obvious of these is PCB 153 (see Table 2), which, being present at 11% in Aroclor 1260 and only 5% in Aroclor 1254, pulls speciation toward Aroclor 1260. Though also enhanced, PCB 138 does not have the same effect on speciation because Aroclors 1254 and 1260 contain similar proportions of PCB 138.

While the mixing model seeks to determine the Aroclor mixture closest in composition to the sample using all the congeners, the Aroclor estimation method uses just a few congeners that are “routinely detected in near-detection-limit PCB profiles and have maximal compositional differences between the three Aroclor mixtures” (10). The first of these criteria ensures that the PCBs chosen are prominent Aroclor congeners; however, these are often among the more persistent congeners. If we assume that changes to PCB congener compositions are from the loss of PCBs, rather than from the rearrangement, loss, or addition of chlorine to existing PCBs, then the use of persistent PCBs for

quantification and speciation will tend to describe the source Aroclors rather than the actual PCB composition in the sample. Of course, in less compositionally modified samples these two measures are similar, and they diverge as a sample PCB composition becomes more modified from the source Aroclors. Figure 4 illustrates this connection by the significant correlation in the regression analysis between the overestimation of total PCBs by the Aroclor estimation method from Figure 1 and the measure of compositional modification by the mixing model method from Figure 2.

Figures 5 and 6 illustrate the extremes of agreement between the two methods. Figure 5 shows the PCB congener composition profile of a low trophic level clam sample and an approximate mixture of Aroclors (speciation) as determined by both methods. Inspection confirms how closely the compositional profile of the calculated Aroclor mixture matches the original sample. In addition, both methods indicate a low level of compositional modification, and the total Aroclor value agrees closely with the sum of congeners. In contrast, Figure 6 shows the PCB congener composition profile of a high trophic level seal sample. In this case the speciation results from the two methods differ significantly and are shown separately in the figure. The total Aroclor estimate is approximately twice the sum of congeners and compositional modification values from both methods are high.

While both of the data analysis methods examined in this paper connect congener specific data to Aroclor compositions, an understanding of the strengths and weaknesses of each may help the reader to decide how to proceed and which method best suits his or her needs. These strengths and weaknesses are summarized in Table 4.

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