Speciation and Quantitation of Aroclors Based on PCB Congener Data: Application to California Mussels and White Croaker†

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A procedure for speciation and quantitation of Aroclors in capillary gas–liquid chromatography electron capture detector (GC-ECD) chromatograms is described. Four pentachlorobiphenyls (IUPAC no. PCB-87, -110, -118, and -105) and three heptachlorobiphenyls (PCB-183, -180, and -170) are used as markers of Aroclor 1254 and Aroclor 1260, respectively. The Aroclor content of samples is estimated by comparing the congener composition with U.S. EPA Aroclor reference materials. In this study, the selected congener approach to Aroclor determination is applied to both California marine mussels (*Mytilus californianus* and *M. edulis*) and white croaker (*Genyonemus lineatus*) muscle. Both Aroclor 1254 and Aroclor 1260 were present in these species, and the congener patterns matched the Aroclor reference materials closely. In cases where reporting Aroclors is not appropriate, e.g., highly weathered samples, the method also provides PCB congener data.

INTRODUCTION

Recent reviews have outlined the practical difficulties in the determination of polychlorinated biphenyls (PCBs) in environmental and biological samples using packed-column, gas–liquid chromatography (GC) (Pellizzari et al., 1985; Alford-Stevens et al., 1985; Alford-Stevens, 1986; D'Elia et al., 1989). An experienced chemist can usually recognize Aroclor patterns on visible inspection of packed-column chromatograms, but the task is sometimes impossible due to (i) occurrence of more that one Aroclor mixture in the sample, (ii) environmental weathering of Aroclors by biological and nonbiological processes, and (iii) modification in patterns by incineration and/or chemical or physical treatment. These exceptions are frequently encountered in environmental toxicology and public health laboratories.

There have been major advances in GC technology in the past decade. High-resolution or capillary GC has benefited from developments in splitless and cold, on-column sample introduction devices, fused silica columns and chemically bonded stationary phases, microprocessor control of heated zones, and computerized data acquisition and processing. The linear dynamic range of the electron capture detector (ECD) has been greatly extended by use of modulated pulsed frequency operation (Pellizzari et al., 1985), and the reduced ECD cell volumes in new instruments are more compatible with the low gas flow rates associated with capillary GC.

Just 10 years ago the first capillary GC separations of Aroclor formulations appeared in the literature with research performed at laboratories drawing and coating their own glass capillary columns (Ballschmiter and Zell, 1980; Pellizzari et al., 1985). By 1984 all 209 PCB congeners had been synthesized and their chromatographic properties on an SE-54-coated, fused silica capillary studied (Mullin et al., 1984). Today PCB congener determinations for the major Aroclor components are well within the capabilities of most environmental laboratories owing to the availability of both chlorinated biphenyl reference standards and efficient, high-quality capillary columns.

Similar advancements in quantitative human health risk assessment of PCBs have placed new demands on chemists to lower detection limits and improve the accuracy of Aroclor identification. The U.S. Environmental Protection Agency (EPA) has determined that the positive evidence for carcinogenicity of Aroclor 1254 and Aroclor 1260 in animals, along with inadequate evidence in humans, establishes them as B2 or probable human carcinogens (U.S. Public Health Service, 1989). Where possible, Aroclor speciation is desirable because Aroclor mixtures vary considerably in their carcinogenic potency (Schaeffer et al., 1984). Low detection limits, ca. 50 μg/kg, are needed to estimate the risks of consuming contaminated food, even at the 10^{-5} lifetime excess cancer rate.

In evaluating the human health risks of consuming sportfish from California coastal waters, we recognized a need to improve existing Aroclor methods and to develop procedures that more fully utilize the enhanced separation and detection power of capillary gas chromatography (Draper, 1990). This study evaluates the feasibility of estimating Aroclor concentrations from PCB congener data for marine organisms collected from California coastal waters. The principal goal was to evaluate the use of multiple, selected PCB congeners as markers for two commercial PCB mixtures, Aroclor 1254 and Aroclor 1260. This approach may provide a straightforward and reliable alternative to use of computerized, multivariate statistical methods of pattern recognition in Aroclor speciation.

EXPERIMENTAL PROCEDURES

Apparatus. GC-ECD was used because of its availability, ease of operation, sensitivity, and superior analytical precision relative to GC–mass spectrometry (Alford-Stevens et al., 1986a,b). Extracts were separated on a 60 m × 0.32 mm, 0.25-μm phase DB-5 column (J&W Scientific, Folsom, CA). The instrument was a Hewlett-Packard Model 5890 with a ^{63}Ni ECD, a split–splitless inlet, and a Model 7673A autosampler/injector. A

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Table I. Typical Retention Times and Response Factors for Chlorinated Biphenyl Congeners

chlorobiphenyl structure	chlorobiphenyl IUPAC no.[a]	t_R	RRT[b]	RF[c]	RF-RSD[d]
2,3',4,5',6-penta	121	36.50	0.840	0.20	11
2,3,4,4'-tetra	60	38.40	0.884	0.23	18
2,2',4,5,5'-penta	101	39.43	0.908	0.34	12
2,2',3,4,5-penta	86	42.39	0.976	0.22	15
2,2',3,4,5'-penta	87	42.93	0.988	0.25	12
3,3',4,4'-tetra	77	44.27	1.019	0.52	18
2,2',4,4',5,6'-hexa	154	44.42	1.023	0.29	8.3
2,2',3,5,5',6-hexa	151	45.87	1.06	0.34	7.6
2,3',4,4',5-penta	118	47.59	1.10	0.34	12
2,2',3,4,5,6'-hexa	143	48.42	1.11	0.28	8.2
2,3,4,4',5-penta	114	48.88	1.13	0.22	9.1
2,2',4,4',5,5'-hexa	153	50.38	1.16	0.28	10
2,3,3',4,4'-penta	105	50.70	1.17	0.26	12
2,2',3,4,5,5'-hexa	141	51.84	1.19	0.24	8.3
2,2',3,4,4',5-hexa	137	52.61	1.21	0.24	9.2
2,2',3,4,4',5'-hexa	138	53.55	1.23	0.28	12
2,2',3,3',4,5-hexa	129	54.40	1.25	0.24	7.9
2,3,3',4,5,5'-hexa	159[e]	55.48	1.277	0.13	NA[f]
2,2',3,4,4',5,6'-hepta	182[e]	55.48	1.277	0.28	NA[f]
2,2',3,4',5,5',6-hepta	187[e]	55.50	1.278	0.35	NA[f]
2,2',3,4,4',5',6-hepta	183	56.04	1.29	0.34	8.5
2,2',3,3',4,4'-hexa	128	56.53	1.30	0.24	9.2
2,2',3,4,5,5',6-hepta	185	57.17	1.32	0.19	9.5
2,2',3,3',5,5',6,6'-octa	202[e]	59.04	1.359	0.30	NA[f]
2,2',3,3',4,4',6-hepta	171[e]	59.13	1.361	0.19	NA[f]
2,3,3',4,4',5-hexa	156	59.27	1.36	0.14	NA[f]
2,2',3,3',4,5,6-hepta	173	59.79	1.377	0.19	7.9
2,2',3,3',4,5',6,6'-octa	200	59.99	1.381	0.32	10
2,2',3,4,4',5,5'-hepta	180	61.39	1.41	0.25	14
2,3,3',4,4',5',6-hepta	191	62.22	1.43	0.20	8.0
2,2',3,3',4,4',5-hepta	170	65.22	1.50	0.24	15
2,2',3,3',4',5,5',6-octa	201	66.54	1.53	0.30	12
2,2',3,4,4',5,5',6-octa	203	67.28	1.549	0.16	NA[f]
2,2',3,3',4,4',5',6-octa	196	67.40	1.551	0.32	NA[f]
2,3,3',4,4',5,5'-hepta	189	69.59	1.60	0.16	11
2,2',3,3',4,5,5',6,6'-nona	208	71.90	1.655	0.19	NA[f]
2,2',3,3',4,4',5,6-octa	195	72.07	1.659	0.20	NA[f]
2,2',3,3',4,4',5,6,6'-nona	207	73.30	1.69	0.22	15
2,2',3,3',4,4',5,5'-octa	194	75.89	1.75	0.16	18
2,3,3',4,4',5,5',6-octa	205	76.86	1.77	0.16	14

[a] Structures and IUPAC numbering from Ballschmiter and Zell (1980). [b] Retention time relative to DDE. [c] Response factor, fg/peak area. [d] Response factor relative standard deviation for six-point calibration. [e] Not adequately resolved on 60 m × 0.32 mm (i.d.) DB-5 column for distinction. [f] Not available. For these congeners there was inadequate separation to determine response factors when analyzed simultaneously.

Table II. Typical Retention Times and Response Factors for Chlorinated Pesticides

structure	t_R	RRT[a]	RF[b]
t-chlordane	38.04	0.876	0.15
4,4'-DDMU	38.49	0.886	0.52
2,4'-DDE	39.07	0.900	0.29
c-chlordane	40.16	0.925	0.16
t-nonachlor	40.90	0.942	0.15
4,4'-DDMS	41.60	0.958	0.87
4,4'-DDE	43.43	1.000	0.26
2,4'-DDD	44.42	1.02	0.37
4,4'-DDD	48.66	1.120	0.42
2,4'-DDT	49.00	1.128	0.30
4,4'-DDT	53.10	1.22	0.37

[a] Retention time relative to DDE. [b] Response factor, fg/peak area.

Spectra Physics 4290 chromatography digitizer and a Spectra Physics Winner computerized data system were used for data acquisition and processing.

Instrument operating conditions were as follows: injector temperature, 225 °C; detector temperature, 325 °C; He carrier gas column head pressure, 20 psi; carrier gas flow rate, 2.4 mL/min; detector purge gas flow, 60 mL of argon–methane (95:5 v/v)/min; range, 2; attenuation, 3 (for a strip chart recorded). Splitless injection was used: split vent flow, 33 mL/min; septum purge, 2.7 mL/min; purge off time, 1.0 min.

The oven temperature program used was 80 °C for 2 min, +40 °C/min to 185 °C and hold for 25 min, +2 °C/min to 230 °C and hold for 25 min, +40 °C/min to 280 °C and hold for 5 min. This sequence afforded baseline separation of the 11 chlorinated pesticide analytes determined in this survey. Sample injection volume was 2.0 μL for a 1.0-mL final sample volume.

Reagents. Reference pesticide standards and Aroclor mixtures were provided by the U.S. EPA Repository for Toxic and Hazardous Materials, Environmental Monitoring and Support Laboratory (Cincinnati, OH). Chlorobiphenyl isomer mixtures were obtained from the National Research Council Canada (NRCC), Marine Analytical Chemistry Standards Program (Halifax, NS). Silica gel (230–400 mesh, S-0507) was purchased from Sigma Chemical Co. (St. Louis, MO). *n*-Hexane (85% *n*-hexane, N9262-03) was obtained from J. T. Baker (Phillipsburg, NJ). All other solvents were commercial and of residue grade.

Procedure. *Tissue Extraction.* Five grams of thawed tissue was combined with ~20 g of sodium sulfate and 60 mL of petroleum ether in a blender jar. The mixture was homogenized for 2 min with a Polytron apparatus and the solvent decanted and dried by percolating it through a funnel containing ~20 g of sodium sulfate in a paper cone. Tissue extraction was repeated with 3 additional volumes of petroleum ether, each time with 1 min of further homogenization. Alternatively, tissue extraction can be accomplished by using a mortar and pestle—the tissue is ground with ~20 g of dry sodium sulfate for 30 s prior to addition of the first 60 mL of solvent. The mixture is ground with the first volume of solvent for 5 min and for 2 min with subsequent volumes.

The tissue extract was reduced in volume on a rotary flash evaporatory and taken up in 10.0 mL of *n*-hexane. Eighty percent of the extract (8.0 mL) was transferred to a tarred Griffin beaker and evaporated to dryness at room temperature overnight. The oily residue was weighed to give the fat content.

Silica Column Cleanup. Sample extractions were fractionated on a silica gel column using a separation developed by Colorado State University Pesticide Laboratory (J. Tessari, 1989, personal communication). A 1 cm diameter glass chromatography column with a Teflon stopper and a reservoir (Kontes K-420280, Kontes, Vineland, NJ) was packed dry with 5.0 g of adsorbent which had been activated at 130 °C overnight. The packing was retained with a small plug of glass wool and topped with 1 cm of anhydrous sodium sulfate. The silica gel column was rinsed with 15 mL of *n*-hexane. Sample extracts were introduced in 2 mL of *n*-hexane, and the flask was rinsed with an additional 2 mL of solvent for quantitative transfer. When the sample had percolated into the adsorbent bed, an additional 35 mL of *n*-hexane was added to the reservoir. The first 15 mL eluting, containing highly nonpolar pesticides (Tessari, 1989), was discarded in this study, and the remaining hexane eluting (so-called F_3) was collected. Benzene (20 mL) was added to the column, and two additional 10-mL fractions, F_4 and F_5, were collected. F_3 contains PCBs and some 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene (DDE), while F_4 contains the majority of pesticides including 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) and its more polar isomers and metabolites and various cyclodiene insecticides. Fraction F_5 contains more polar pesticide residues (Tessari, 1989). Fractions F_3, F_4, and F_5 were each concentrated on a rotary flash evaporator, exchanged to isooctane, and reduced under a stream of dry nitrogen to 1.0 mL.

Prior to the analysis of samples, the silica column separation was evaluated. Aroclors eluted exclusively in F_3. Pesticides, ca. 94–99%, eluted in F_4 except for DDE, DDE (ortho, para isomer), and 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene (chlordane) (cis isomer) for which 13–18% eluted in F_3. The recoveries of Aroclor 1254 (n = 5) and Aroclor 1260 (n = 7) from spiked samples averaged 86 and 78%, respectively.

The U.S. FDA Florisil column separation (U.S. Department of Health and Human Services, 1977) with 0 and 6% diethyl ether in petroleum ether fractions was used to fractionate fish muscle extracts prior to GC analysis. Five-gram fish tissue samples were not defatted as the extract of only 1 g of tissue was applied to the column.

Quantitative Analysis. External calibration was used with one mixed pesticide standard containing 10–50 pg/μL in isooctane and two 100 pg/μL, single Aroclor mixtures, Aroclor 1254 and Aroclor 1260. The linearity of the detector was established

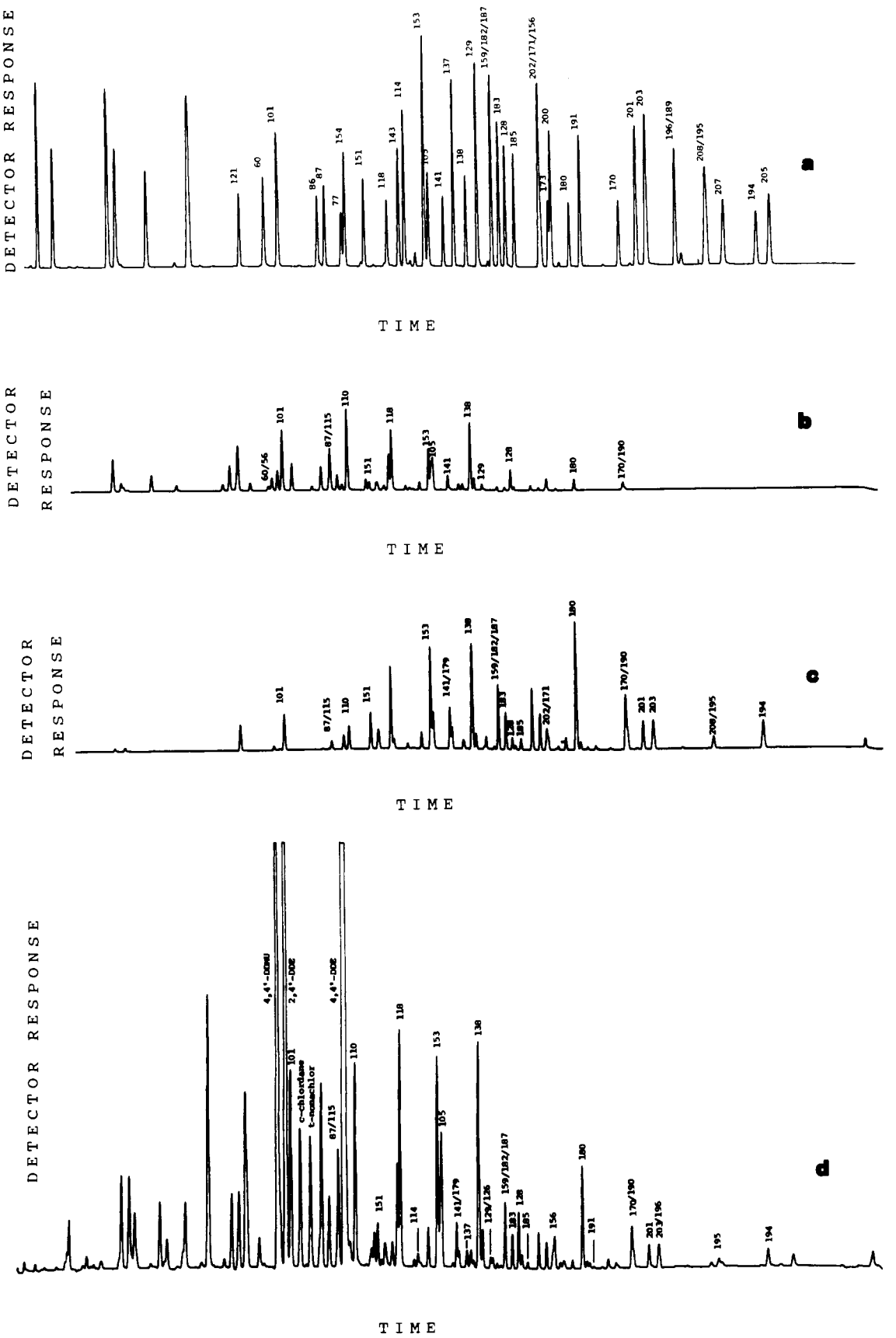

Figure 1. Capillary GC-ECD chromatograms: (a) mixed chlorobiphenyl calibration standard; (b) Aroclor 1254; (c) Aroclor 1260; (d) edible flesh of San Pedro Canyon white croaker (no 772), 0% Florisil fraction.

initially by six-point calibration; daily continuing calibration relied on a single point. Chlorobiphenyl isomer standards, four mixtures containing over 50 chlorobiphenyls, were diluted 1:99 (v/v) in isooctane, giving concentrations between 10 and 100 pg/μL prior to analysis. For this study the 40 chlorobiphenyls eluting between PCB-121 and PCB-205 were determined, although additional PCB congeners are contained in the NRCC mixtures. For multipoint calibration the mixtures were combined. PCB-77 coelutes with PCB-110, and as PCB-110 is the predominant congener in both commercial Aroclors (Schulz et al., 1989) and the environment, peaks corresponding to this retention time were reported as PCB-110. The sample component was first quantitated as PCB-77 and then multiplied by 0.58 on the basis of published relative response factors (Mullin et al.,

Table III. Chlorinated Biphenyl Isomers in U.S. EPA Aroclor 1254 and Aroclor 1260 Reference Standards

chlorobiphenyl IUPAC no.	chlorobiphenyl composition, wt %				composition factors	
	Aroclor 1254		Aroclor 1260		Aroclor 1254:chlorobiphenyl ratio	Aroclor 1260:chlorobiphenyl ratio
	mean	% RSD	mean	% RSD		
121	ND[a]		ND			
60 (56)[b]	0.44	19	ND			
101	13 (7.9)[c]	5.4	6.3 (5.0)[c]	16	7.7	16
86	ND		ND			
87 (115)[b]	6.2 (3.8)[c]	19	0.86	21	16	120
110	16 (5.8)[c]	21	3.3 (1.9)[c]	16	6.3	30
154	ND		ND			
151	1.5	14	5.2 (3.7)[c]	12	67	19
118	11 (6.4)[c]	44	ND		9.1	
143	ND		ND			
114	ND		ND			
153	5.3 (4.3)[c]	14	13 (11)[c]	15		
105	3.3	12	ND		30	
141 (179)[b]	1.5	22	3.3	17		
137	0.54	31	ND			
138	9.5 (3.2)[c]	12	13 (6.1)[c]	9.3		
129	0.67	26	ND			
183	0.49	5.4	5.5 (1.8)[c]	12	200	18
128	1.6	13	0.77	44		
185	ND		0.81	19		
156	1.0	16	ND			
173	ND		ND			
200 (157)[b]	ND		0.51	15		
180	0.93	15	11 (7.1)[c]	8.7	110	9.1
191	ND		ND			
170 (190)[b]	0.86	57	5.3 (3.9)[c]	12	120	19
201	ND		3.3	12		30
203 (196)[b]	ND		ND			
196	ND		ND			
189	ND		ND			
208	ND		ND			
195	ND		0.66	21		
207	ND		ND			
194	ND		1.3	29		
205	ND		ND			
s-PCB	73.8		74.1			

[a] Not detected. [b] These congeners also are Aroclor constituents (Eganhouse et al., 1989; Cooper et al., 1985) and cannot be resolved from the indicated chlorobiphenyl. [c] Multidimensional GC data (Schultz et al., 1989).

1984) to convert to PCB-110 concentration.

Procedure A for Estimating Aroclors. Two procedures were studied for estimating Aroclor content. The first approach is similar to conventional, packed-column procedures for Aroclor estimation and does not require chlorobiphenyl standards or determination of PCB congener concentrations. Five major peaks from each Aroclor mixture [Aroclor 1254, retention time relative to DDE (RRT), 0.832, 0.908, 0.925, 0.988, and 1.019; Aroclor 1260, RRT 1.28, 1.34, 1.41, 1.50, and 1.75] were used as markers. Response factors, e.g., [Aroclor]/marker peak area, were obtained for each. Areas of these marker peaks detected in sample chromatograms provide five estimates of the Aroclor concentration with the mean value being reported. The spread in these estimates, the relative standard deviation (RSD), provides a measure of how well the pattern matches the reference material. In other studies five additional peaks eluting between 15 and 31 min were used as Aroclor 1242 markers, and Aroclor estimates were confirmed on a second GC column, a 30-m DB-17 capillary (Draper, 1990).

Procedure B for Estimating Aroclors. The second approach investigated relies on an initial determination of PCB congener concentrations. Aroclor concentrations are then estimated from the known composition of Aroclor reference materials. Four pentachlorobiphenyls serve as markers for Aroclor 1254 (PCB-87, -110, -118, and -105), and three heptachlorobiphenyls are markers for Aroclor 1260 (PCB-183, -180, and -170). The IUPAC PCB numbering system of Ballschmiter and Zell (1980) is used throughout this paper. The congener concentration is multiplied by the predetermined composition factor, the [Aroclor]:[chlorobiphenyl] ratio, which is equivalent to the reciprocal of the weight percent for that congener in the Aroclor. As above, the mean value of the measure is reported, and the dispersion in these estimates is indicative of how well the sample pattern matches the reference material.

All residue levels in biological samples are reported on a fresh weight basis. Some of the parameters were summed to give the total concentration of related compounds, i.e., s-PCB is the sum of individual chlorobiphenyls, and s-Aroclor A is the sum of Aroclor mixtures determined by procedure A and so forth. For interpretation of pollutant patterns, the data were normalized by dividing the component by the sum of its relatives, e.g., [chlorobiphenyl]/[s-PCB]. Normalization of congener data to s-PCB (Duinker et al., 1988a,b) or a single congener, i.e., PCB-153 (Muir et al., 1988), is commonly used to facilitate interpretation and comparison of congener patterns.

Mussel Watch and White Croaker Specimens. Mussel samples were obtained through the California Mussel Watch program which is administered by the California Water Resources Control Board and the California Department of Fish and Game. The Mussel Watch program surveys toxic metal and synthetic organic pollutant levels in resident and transplanted California mussels (*Mytilus californianus*), resident Bay mussels (*Mytilus edulis*), and freshwater clams at coastal, bay, and estuarine stations throughout California (Hayes and Phillips, 1986). Samples were collected in the 1986–1987 season at the following stations: 303.4, Richmond Inner Harbor (Sante Fe Channel); 307.6, Oakland Back Harbor; 402.2, Monterey Bay (Parson's Slough); 506.3, Port Hueneme; 556, Marina del Rey; 601, Los Angeles Harbor (National Steel); 607.4, Long Beach Harbor; 662, Royal Palms reference station; 715, Anaheim Bay (Warner Avenue Bridge); 721 Newport Bay (entrance); 726.4, Newport Bay (Rhine Channel). Details of sampling and sample dissection procedures are reported elsewhere (Hayes and Phillips, 1986).

The use of marine mussels as indicator organisms for studying water quality has been reviewed (Goldberg, 1975; Goldberg et

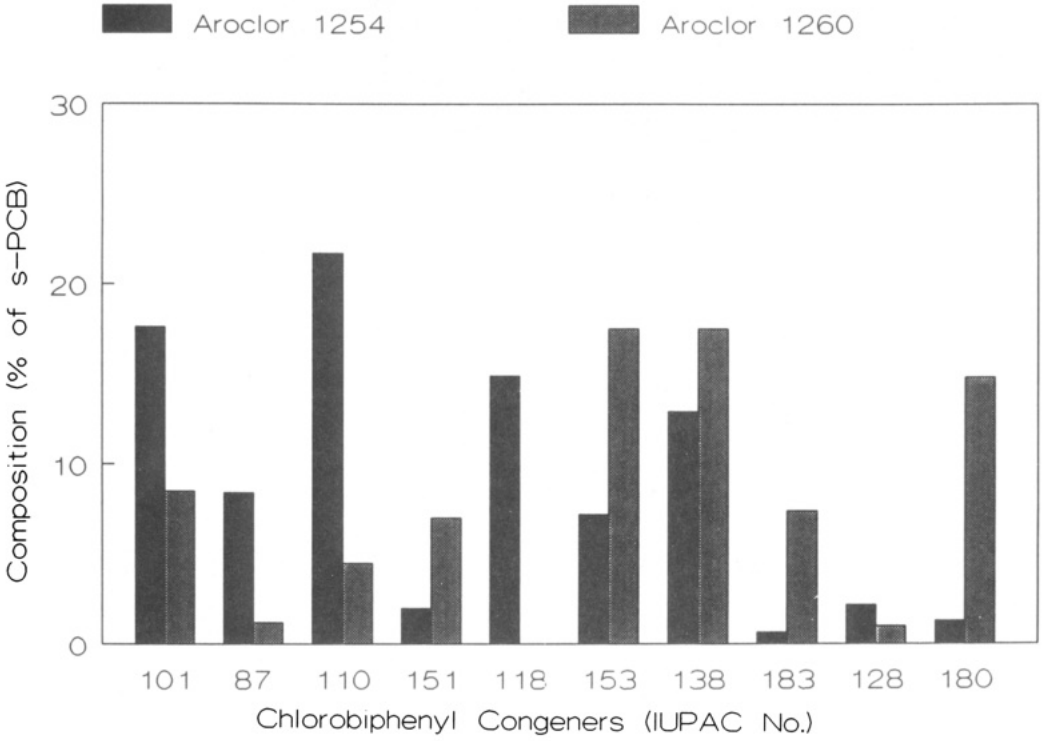

Figure 2. Apparent chlorobiphenyl composition of U.S. EPA Aroclor reference materials. Data are normalized and represent the individual chlorobiphenyl contribution to s-PCB.

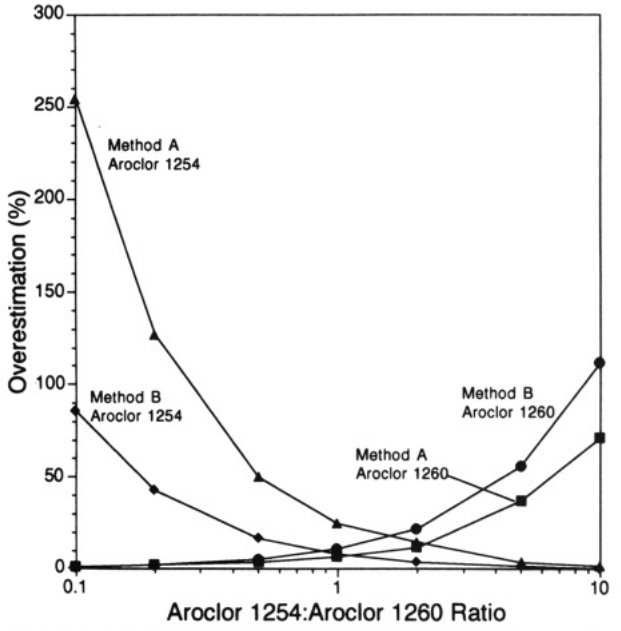

Figure 3. Predicted error in Aroclor determinations for various Aroclor 1254–Aroclor 1260 combinations using procedures A and B.

al., 1978; Farrington et al., 1983) and is now well established. Briefly, California mussels are transplanted from relatively pristine locations (Bodega Head, Trinidad Head, and Montana de Oro) to various coastal stations, where they are maintained for 4–6 months. This holding period allows the organisms to reach steady state with the surrounding water, a process completed in about 3 months for petroleum hydrocarbons and halogenated organics. All samples were transplanted California mussels except one resident Bay mussel (no. 721) and one resident California mussel (no. 662). The whole soft body including gonad tissue was dissected and frozen in solvent-rinsed glass jars with Teflon-lined closures before shipment to the laboratory.

The white croaker muscle was a composite consisting of fish of varying lengths, all harvested from the San Pedro Channel at Point Vicente. The composite was one of many samples collected and analyzed as part of a comprehensive survey of pollutants in sportfish from the Santa Monica Bay and surrounding southern California coastal waters (Draper, 1990).

RESULTS AND DISCUSSION

Gas Chromatography of Chlorobiphenyls and Chlorinated Pesticides. Both resolving power and precise retention time determination are required to identify PCB congeners by GC-ECD. The DB-5 column has a chemically bonded phase equivalent to SE-54, a coated phase widely used in the earlier high-resolution chromatography studies of Aroclors (Ballschmiter and Zell, 1984; Pellizzari et al., 1985). The DB-5 phase is commonly used in the most recent PCB studies (Cooper et al., 1985; Norstrom et al., 1988; Eganhouse et al., 1989), and the 60-m column has exceptional resolution, about 3500 theoretical plates/m according to manufacturer specifications.

Retention times were highly reproducible: for PCB-153 (t_R = 50.54 min) and PCB-201 (t_R = 66.75 min) t_R standard deviations were 0.013 (n = 6) and 0.018 (n = 4) min, respectively, over a 45-h period of instrument operation. Retention times for chlorobiphenyls exhibited a range of less than 2 s (eight replicates) during this time period: 35.86–35.89 (PCB-121), 38.78–38.81 (PCB-101), 52.98–53.01 (PCB-138), and 74.91–74.94 min (PCB-194). This precision accommodated narrow retention time windows, on the order of ±0.02 min (±1.1–1.5 SD), for optimum specificity.

Calibration of the instrument for congener analysis is time-consuming, particularly when the NRCC mixtures are not combined. In the present study a total of seven calibration standards were analyzed with each sample batch to allow quantitation of pesticides, Aroclors, and chlorobiphenyls by both Aroclor methods. With each chromatographic run exceeding 100 min, even one-point calibration required 12 h of instrument time. In practical application multipoint calibration requires combination of the four NRCC mixtures. To quantify Aroclors by procedure B, only seven congeners are required minimally, and these can be combined with pesticide standards. Retention times for 40 chlorobiphenyls and pesticides are summarized in Tables I and II.

Table IV. Chlorobiphenyls in California Mussel Watch Samples[a,b]

parameter	concn, μg/kg, for samples from station no.										
	303.4[c]	307.6	402.2	506.3	556	601	607.4	662	715	721	726.4
fat, wt %	NA[d]	1.18	1.59	2.26	0.87	1.26	1.33	1.49	1.34	1.88	1.64
PCB											
60	14	ND[e]	0.88	3.5	2.3	6.5	1.1	ND	0.64	0.51	ND
101	26	32	3.6	50	24	34	7.6	1.1	8.2	6.2	46
86	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1	ND
87	10	7.3	1.1	20	9.2	15	2.8	ND	2.4	1.6	18
110	30	27	2.8	89	42	61	12	1.2	12	8.2	78
151	4.7	10	0.83	11	3.2	7.4	1.5	ND	2.5	1.9	8.4
118	23	22	1.7	34	20	24	4.3	ND	3.0	2.5	39
114	ND	ND	ND	1.2	ND	0.34	ND	ND	ND	ND	1.2
153	14	35	1.4	38	15	24	5.9	1.1	7.6	2.8	23
105	6.8	ND	ND	16	7.7	10	ND	ND	ND	2.7	14
141	0.65	1.4	ND	2.6	0.34	0.59	ND	ND	ND	ND	0.59
137	0.39	0.42	ND	1.7	ND	0.36	ND	ND	ND	ND	0.37
138	22	37	2.4	57	15	23	6.7	1.3	11	5.2	21
129	ND	ND	ND	0.86	ND	ND	ND	ND	ND	ND	ND
159/182/187	2.9	9.2	0.53	8.6	2.5	6.3	1.6	0.43	2.0	0.66	4.7
183	2.0	5.2	0.37	4.6	1.7	4.4	0.96	ND	1.4	ND	2.6
128	3.2	3.8	0.23	11	2.7	4.5	0.94	ND	0.80	0.61	2.8
171/202	ND	4.1	ND	ND	ND	ND	ND	ND	0.81	ND	ND
156	ND	ND	ND	4.8	1.8	1.7	ND	ND	ND	ND	ND
200	ND	ND	ND	1.7	ND	0.67	ND	ND	ND	ND	ND
180	2.4	5.2	0.64	6.5	1.4	2.4	0.70	ND	1.1	ND	4.0
191	ND	ND	ND	3.0	0.73	0.64	ND	ND	ND	ND	ND
170	1.2	2.4	ND	4.6	0.39	0.81	ND	ND	1.2	ND	1.6
201	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.4
s-PCB	163	202	16.5	370	150	228	46.1	5.1	54.7	34.0	268

[a] PCB-121, -154, -143, -185, -173, -203, -196, -189, -208, -195, -207, -194, and -205 were not detected in mussel samples in this survey. [b] Only two chlorinated biphenyls were detected in the method blank, equivalent to 0.31 μg of PCB-138/kg and 0.41 μg of PCB-180/kg. The reported chlorobiphenyls were not corrected for the blank residue. [c] Sampling stations are identified under Experimental Procedures. [d] NA, not available; sample lost. [e] ND, not detected; instrument detection limits for individual chlorobiphenyls were in the 0.30–1.0 μg/kg range.

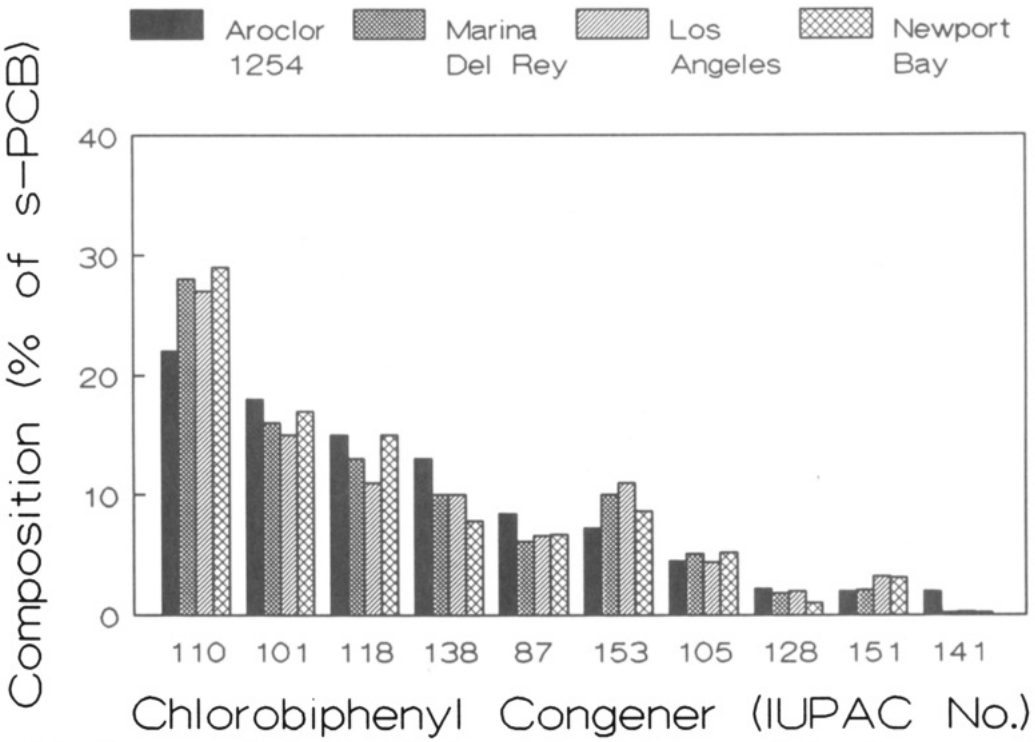

Figure 4. Chlorobiphenyl congener profiles for Mussel Watch samples from California inner harbors. Data are normalized to s-PCB.

With the 60-m DB-5 column a number of the PCB congeners were not separated (Table I). Chromatography of the four NRCC mixtures individually, however, allowed determination of response factors for most of the congeners. The chlorobiphenyl pairs identified by NRCC as difficult to resolve, PCB-86/-87, -202/-173, -171/-200, -201/-203, and -201/-196, were well separated by the 60-m capillary column. When the NRCC mixtures are combined, only 30 of the PCB congeners are completely resolved, limiting the response factor data obtained (Table I). A chromatogram of the mixed chlorobiphenyl standard is shown in Figure 1.

As expected, the chromatographic properties of chlorobiphenyls on the DB-5 column are very similar to those reported by Mullin and co-workers (Mullin et al., 1984) for a 50-m, wall-coated, SE-54 capillary. These investigators were able to resolve all but 11 congener pairs of the 209 isomers including the pairs PCB-202/-171 and PCB-

Table V. Corrected Aroclor Concentrations in California Mussels[a]

parameter	concn, μg/kg, for samples from station no.										
	303.4	307.6	402.2	506.3	556	601	607.4	662	715	721	726.4
					Procedure A						
Aroclor 1254	240	230	25	390(370)	190	280	65	ND	51	42	400
RSD	14	26	16	30	28	13	32		17	36	26
Aroclor 1260	32 (ND)	68 (11)	ND	270(170)	21 (ND)	44 (ND)	ND	ND	ND	ND	40 (ND)
RSD	40	67		84	90	120					55
s-Aroclor	240	241	25	540	190	280	65	ND	51	42	400
					Procedure B						
Aroclor 1254	190	160(150)	17	410(400)	200	290	53	ND	44 (42)	33	380
RSD	11	26	5.9	28	24	28	38		57	45	20
Aroclor 1260	27 (ND)	62 (44)	ND	76 (31)	17 (ND)	39 (ND)	ND	ND	19 (14)	ND	38 (ND)
RSD	29	44		20	71	90			48		23
s-Aroclor	190	194	17	431	200	290	53	ND	56	33	380

[a] Corrected values are indicated in parentheses. s-Aroclor is the sum of corrected Aroclor 1254 and Aroclor 1260.

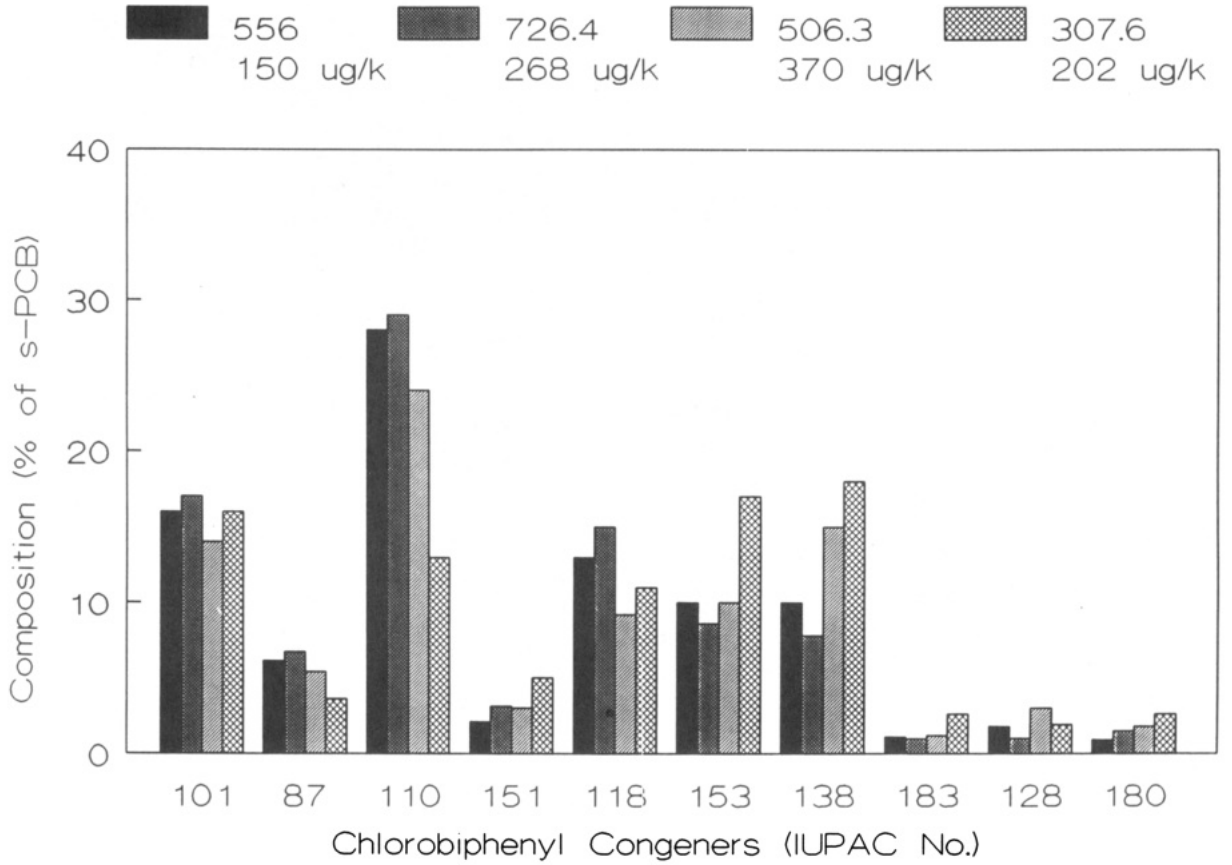

Figure 5. Chlorobiphenyl congeners in *Mytilus* species from California coastal waters. Data are normalized to s-PCB.

203/-196. In contrast with the present work, Mullin and co-workers were able to separate PCB-159/-182/-187 and -208/-195.

Detector linearity was demonstrated by multipoint calibration at six concentrations between 0.40 (PCB-173) and 90 pg/μL (PCB-101) (Table I). Over this range individual detector response factors had a mean RSD of 11% and none exceeded 18%—the typical criterion for linearity is a maximum RSD of 20%. Instrument detection limits were about 1 pg injected for each congener.

Chromatography of Pesticides and Metabolites. Eleven chlorinated pesticides, mostly metabolites of the insecticides DDT and 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane (DDD), were included as target analytes in this study (Table II). The ECD response factors for the cyclodienes, 1-*exo*,2-*endo*,3-*exo*,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (nonachlor) and chlordane isomers, are similar to the tetra- through nonachlorobiphenyls. The ECD response diminishes in the DDT metabolites as the number of chlorines drops [e.g., DDT > DDD > 2,2-bis(*p*-chlorophenyl)-1-chloroethane (DDMS) and DDT > DDD] and the amount of saturation increases [e.g., DDE > DDD and 2,2-bis(*p*-chlorophenyl)-1-chloroethylene (DDMU) > DDMS]. For the least "electron capturing" pesticide analyte the instrument detection limit is about 3 pg injected.

Identifying Congeners with a Nonspecific Detector. When an ECD is used, the identification of chlorobiphenyl congeners is based solely on retention time. Problems in resolving the isomers, even with capillary columns, may lead to misidentifications as indicated in Table III and thoroughly reviewed by Schulz and co-workers (Schulz et al., 1989). GC–MS studies of Aroclor mixtures (Muir et al., 1988; Eganhouse et al., 1989) have established the level of chlorination of major Aroclor peaks, eliminating many candidate structures. However, ambiguity remains in a number of the assignments as shown in Figure 1. In several instances the ECD response factors are similar, but in the cases of PCB-141/-179, -157/-200, and -170/-190 the response factors differ substantially with relative standard

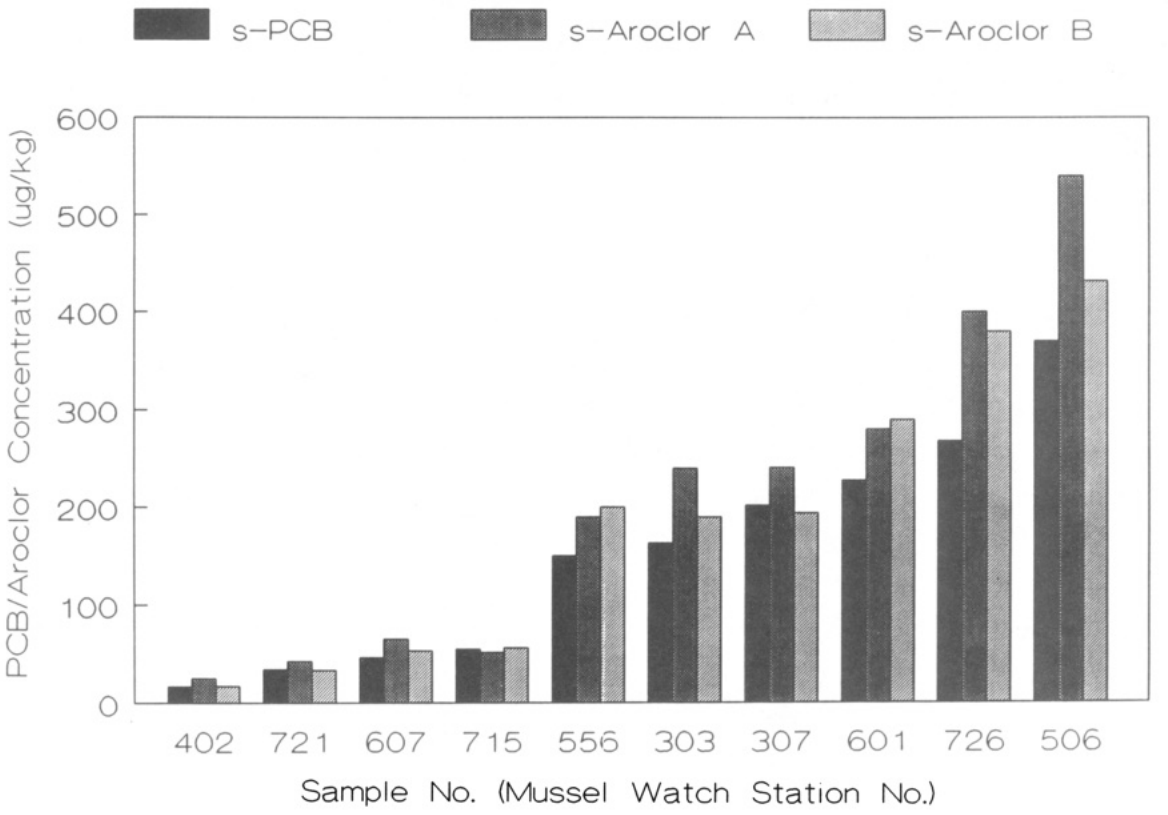

Figure 6. s-PCB, s-Aroclor A, and s-Aroclor B concentrations in California Mussel Watch samples.

differences of 50–110% (Mullin et al., 1984). Therefore, there may be considerable error in ECD quantitation of these congeners.

The chlorobiphenyl mixed standards contain 3,3′,4,4′-tetrachlorobiphenyl (PCB-77) which coelutes with 2,3,3′,4′,6-pentachlorobiphenyl (PCB-110) (Schulz et al., 1989). GC–MS and multidimensional GC-ECD have established unequivocally that the predominant congener in commercial Aroclors and biological samples is PCB-110 (Schulz et al., 1989). Therefore, the corresponding sample peak is first quantitated as PCB-77 and corrected by multiplying by 0.58 to obtain the PCB-110 concentration.

PCB Congeners in Aroclor Reference Materials. The congener content of two Aroclor mixtures, Aroclor 1254 and Aroclor 1260, was determined to obtain composition factors needed to determine Aroclors by procedure B. Aroclor 1254 was resolved into approximately 40 chromatographic peaks. The major components (>5 wt %) are PCB-101, -87, -110, -118, -153, and -138, which together account for over 61% of the mixture (Table III). Similarly, Aroclor 1260 is resolved into 37 peaks by capillary GC. The principal identified congeners in Aroclor 1260 are PCB-101, -110, -151, -153, -138, -183, -180, and -170, which together account for 63% of the formulation (Table III). With the NRCC chlorobiphenyl mixed standards, and excluding those that were not adequately resolved, it was possible to tentatively identify 74% by mass of either Aroclor 1254 or Aroclor 1260. Congener profiles are plotted in Figure 2.

Congener measurements in Aroclor mixtures were reproducible with RSDs less than 15% over a 3-month period (Table III). An exception was the determination of PCB-118 in Aroclor 1254, where there was inadequate resolution from other Aroclor constituents. The separation of PCB-153 from other congeners in both Aroclors was also a problem, but this did not affect its measurement precision. The composition data and factors summarized in Table III were used throughout the study for estimating Aroclor concentrations by procedure B.

Table VI. Chlorobiphenyls in San Pedro Channel White Croaker Muscle, No. CA772

chlorobiphenyl isomer	concn, μg/kg	RSD
101	120 ± 11	9.1
87	38 ± 3.5	9.2
110	72 ± 8.2	11
151	24 ± 2.3	9.6
118	161 ± 44	27
114	3.2 ± 0.29	9.1
153	72 ± 5.7	7.9
105	60 ± 6.0	10
141	18 ± 1.0	5.6
137	5.8 ± 0.62	11
138	105 ± 9.2	8.8
129	3.2 ± 0.40	13
183	14 ± 1.5	11
128	17 ± 2.0	12
185	1.5 ± 0.15	10
156	9.5 ± 0.57	6.0
180	39 ± 4.6	12
191	0.61 ± 0.091	15
170	23 ± 2.5	11
201	11 ± 1.3	12
203	6.8 ± 0.71	10
195	3.7 ± 0.30	8.1
194	6.9 ± 0.86	12

The accuracy of these determinations can be evaluated by comparing results of Tuinstra and co-workers (Tuinstra et al., 1983) and Buhler and co-workers (Buhler et al., 1988) and the recently published multidimensional GC data of Schulz and co-workers (Schulz et al., 1989). Partial agreement with literature values was found (Table III). Specifically, when data are compared to multidimensional GC data, probably the most accurate, relative percent differences for the major congeners of Aroclor 1254 and Aroclor 1260 average 60 and 46%, respectively. Aroclor batches are known to vary somewhat in chemical composition (Bush et al., 1989), but it is not known to what extent this contributed to the observed differences.

Investigators using two-dimensional GC or mass spectrometry have demonstrated the limitations of congener identification by retention time alone. Problems in the resolution of PCB-28, -52, -101, -138, and -153 have been reported (Roos et al., 1989; Duinker et al., 1988a,b). The NRCC chlorobiphenyl mixtures have some minor problems with purity, i.e., about 20% of the PCB-171 peak is PCB-202 and 20% of the PCB-195 peak is PCB-208 (W. D. Jamieson, 1990, personal communication). In addition, a non-chlorobiphenyl contaminant coelutes with PCB-189. The composition data presented in Table III represent apparent values, and they were not confirmed by chromatography on a second GC column or by multidimensional GC or spectroscopically.

Correcting Aroclor Concentrations. Congener markers were chosen on the basis of their abundance and unique association with a given Aroclor. The congener markers, however, are not specific. When one Aroclor mixture occurs in high concentration relative to another, the minor Aroclor is overestimated. Overestimation results from contributions of minor components from the major Aroclor mixture, a problem that is most severe when the two mixtures have similar chlorine content.

Quantitation errors for different Aroclor 1254/Aroclor 1260 mixtures were estimated by summing experimentally determined composition data. As seen in Figure 3, Aroclor 1260 is overestimated by 71 (procedure A) or 110% (procedure B) when the Aroclor 1254:Aroclor 1260 ratio is 10. Similarly, errors in estimating Aroclor 1254 are large when the ratio is less than 0.5. At a ratio of 0.1, over 72% of the measured Aroclor 1254 (procedure A) is contributed by Aroclor 1260. Such errors can be ignored, when the Aroclor concentrations are similar, or corrected by the following formulas, which were derived theoretically from Aroclor composition data:

procedure A

$$\text{corrtd [1254]} = \text{exptl [1254]} - (\text{exptl [1260]})(0.069)$$

$$\text{corrtd [1260]} = \text{exptl [1260]} - (\text{exptl [1254]})(0.25)$$

procedure B

$$\text{corrtd [1254]} = \text{exptl [1254]} - (\text{exptl [1260]})(0.085)$$

$$\text{corrtd [1260]} = \text{exptl [1260]} - (\text{exptl [1254]})(0.11)$$

The lack of specificity of the marker peaks and congeners may also result in a poor match of the observed patterns with the single Aroclor standards. With an Aroclor 1254: Aroclor 1260 ratio of 1.0, the chlorobiphenyl markers are expected to show a 5–11% RSD when compared to single Aroclor standards. At a 10:1 ratio, the Aroclor 1260 chlorobiphenyl markers are predicted to have a 21% RSD. For a 1:10 Aroclor 1254:Aroclor 1260 ratio, the pattern for Aroclor 1254 congeners is even more distorted (55% RSD). Two chlorobiphenyls, PCB-118 and PCB-105, are highly selective for Aroclor 1254. PCB-194, -195, -201, -200, and -185 appear to be specific for Aroclor 1260 (Table III), but these compounds were not chosen as Aroclor 1260 surrogates because of their low abundance in the reference material.

Chlorobiphenyls in California Marine Mussels. Chlorinated biphenyls were detected in mussel samples from each marine station (Table IV). The least contaminated organisms were resident California mussels from the Los Angeles/Long Beach Harbor reference station at Royal Palms (no. 662). This sample contained the major Aroclor 1254 isomers, PCB-101, -110, -153, and -138, at levels just above the instrument detection limits. Thirteen chlorobiphenyls were not detected in any of the marine samples (Table IV), and of these 10 were non-Aroclor PCBs and a further 3 were only minor Aroclor 1260 components, i.e., 0.66–1.3 wt %. These findings are not unexpected as PCBs sold in the United States since 1970 were almost exclusively (ca. 98%) Aroclor mixtures with 21–60% chlorine (U.S. Public Health Service, 1989).

s-PBC levels ranged from 5.1 μg/kg at the reference station to 370 μg/kg at Port Hueneme. Relatively high PCB levels were also found at Rhine Channel in Newport Bay, the National Steel station in Los Angeles, and Parson's Slough in Monterey Bay.

Are PCB Residues in Mussels Characteristic of Aroclors? A fundamental question in the analysis of PCBs in environmental and biological samples is the appropriateness of Aroclor measurement (Schwartz et al., 1987). Aroclors are composed of individual chlorobiphenyls, each with a different set of physicochemical properties and unique environmental fate. Moreover, these molecules respond uniquely to biological processes of absorption, metabolism, and excretion.

In the case of the PCB residues in Mussel Watch samples, the observed congener profiles correlate well with the U.S. EPA Aroclor reference material (Figure 4). The rank order of abundance and congener pattern is generally maintained. Minor enrichment of the PCB-110 and PCB-153 isomers appears to have occurred, but the pattern so closely resembles that of Aroclor 1254 that this designation is appropriate. This is true for each of the samples, which represent a wide geographic distribution of California coastal waters. In this case it is clear that environmental weathering has not significantly modified the Aroclor composition.

Estimating Aroclor by Procedure A. By procedure A Aroclor 1254 was detected at all sites except the Royal Palms reference station. All five marker peaks were detected in the samples, and the Aroclor 1254 pattern matched the U.S. EPA reference material well with a mean RSD of 24% (n = 10). The Aroclor 1254 concentrations ranged from 25 to 400 μg/kg (Table V).

Aroclor 1260 was a contaminant at only two stations (corrected data), and the highest Aroclor 1260 levels also were found at Port Hueneme. In both cases where Aroclor 1260 was present, all four of the marker peaks were detected. The Aroclor 1260 pattern did not fit the reference material as well, with RSDs averaging 83% (n = 10) due to the high relative concentration of Aroclor 1254 as discussed above. Corrections were sizable due to the high Aroclor ratios, and apparent Aroclor 1260 residues in the range 21–44 μg/kg were artifacts. Correction lowered the estimated levels by 37 (no. 506.3) and 83% (no. 307.6).

Estimating Aroclors by Procedure B. Instrument detection limits were slightly higher when procedure B was used, about 15 and 30 μg/kg for Aroclor 1254 and Aroclor 1260, respectively, due to the low abundance of the chlorobiphenyl markers in the Aroclor mixtures. Aroclor 1254 determined by procedure B was detected in the range 17–400 μg/kg. Here the distribution of chlorobiphenyl markers also matched the reference materials well (mean RSD 28%), although the fit for Aroclor 1254 was just as good by either estimation technique.

For the low apparent concentrations of Aroclor 1260 present, procedure B matched the single Aroclor pattern more closely than procedure A because of the greater specificity of the congener markers. The mean RSD was 42% (n = 8), about half that found when procedure A was used.

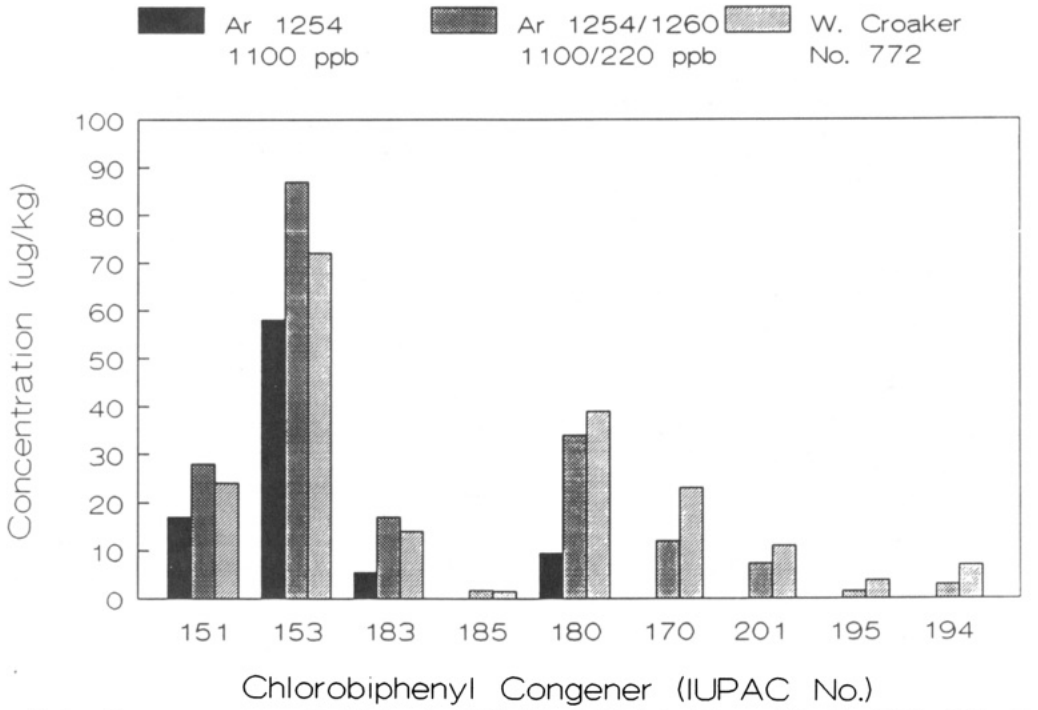

Figure 7. Chlorobiphenyl congener patterns in (a) Aroclor 1254, (b) a 5:1 (w/w) mixture of Aroclor 1254 and Aroclor 1260, and (c) San Pedro Canyon white croaker edible flesh.

As the contribution of Aroclor 1260 increases in the series 556, 726.4 < 506.3 < 307.6, the Aroclor 1254 markers, 2,2′,3,4,5′-penta- (PCB-87), 2,3,3′,4′,6-penta- (PCB-110), and 2,3′,4,4′,5-pentachlorobiphenyl (PCB-118) drop in relative abundance (Figure 5). The heptachlorobiphenyl markers of Aroclor 1260, PCB-137 and PCB-180, show a concomitant increase. PCB-153 and PCB-138, major hexachlorobiphenyls of Aroclor 1260, also become more prominent in the pattern, but they are not sufficiently selective to serve as surrogates for either Aroclor formulation (Table III).

Each of the PCB estimates provided similar results in this study (Figure 6). The same rank order was obtained with only a few exceptions for s-PCB, s-Aroclor A, and s-Aroclor B. Minor systematic differences are observed, however, and generally follow the order s-Aroclor A > s-Aroclor B > s-PCB. The sum parameter s-PCB, comprising only 15 chlorobiphenyls, provided a good approximation of the Aroclor content (Table IV).

Chlorinated Biphenyls and Aroclors in White Croaker. Samples of white croaker (*G. lineatus*) collected in the San Pedro Channel near Point Vincente were analyzed for several reasons. First, the samples are complex and have historically been highly contaminated with PCBs and other man-made chemicals. Municipal waters discharged at Whites Point outfall contaminated the local marine sediments with DDT, which originated at a manufacturing plant in Los Angeles (Goldberg et al., 1978). Second, the Aroclor residues in White Croaker muscle are expected to be more highly weathered than residues found in the Mussel Watch samples. Mussels and other bivalve mollusks have a comparatively limited enzymatic system for metabolizing xenobiotics (Farrington et al., 1983). Moreover, white croakers and other fish occupy a higher niche in the food web and the study samples were obtained from open ocean, not inner harbor, locations.

As expected, high levels of DDT were found in the sample. The chromatogram shown in Figure 1 represents the first Florisil fraction which contains DDE, 1-(*o*-chlorophenyl)-1-(*p*-chlorophenyl)-2,2-dichloroethylene (2,4′-DDE), and DDMU in addition to the chlorinated biphenyls. The second Florisil column fraction contained the more polar insecticide residues DDD and DDMS. The total DDT family residue in the edible portion was 10 mg/kg, and the fat content was 1.78%.

In spite of the complexity of the sample, the congener measurements were reproducible with RSDs in the range 6–15% (Table VI). The exception was PCB-118, which is poorly resolved from another sample component, most likely PCB-149 (Muir et al., 1988; Roos et al., 1989). The major chlorobiphenyl congeners present in San Pedro Channel white croaker muscle are PCB-101, -110, -118, -153, -105, -138, and -180, again major Aroclor 1254 and 1260 components. As with the Mussel Watch samples, many of the non-Aroclor chlorobiphenyls were absent, including PCB-121, -154, -143, -173, -196, -208, -207, and -205.

A corrected Aroclor 1254 content of 1100 μg/kg is estimated by procedure A, and the net Aroclor 1260 concentration is zero (e.g., −68 μg/kg). By procedure B, however, the sample is estimated to contain 1100 μg/kg Aroclor 1254 and 220 μg/kg Aroclor 1260, again after correction. Further examination of the predicted and observed congener distributions confirms the presence of Aroclor 1260 (Figure 7). Elevated concentrations of the Aroclor 1260 markers, PCB-183, -180, and -170, occur along with high levels of other Aroclor 1260 congeners including PCB-185, -201, -195, and -194. The congener-based estimate of Aroclor 1260 in white croaker therefore is more consistent with the available data.

CONCLUSION

The analytical methods detailed here have been successfully applied to the analysis of PCB congeners and Aroclors in a variety of marine samples including sturgeon edible flesh and striped bass livers. The techniques have also been used to measure pesticides and Aroclors in human milk, where Aroclor method detection limits of 6 μg/kg (whole milk) have been determined experimentally.

As has been previously established by the Mussel Watch program, Aroclors are widely distributed in California coastal waters and marine sediments with concentrations

varying widely from one inner harbor location to another. High-resolution GC, advantageous for quantitative analysis of halogenated pesticide residues in complex biological samples, provides various alternative approaches to PCB quantitation including s-Aroclor A, s-Aroclor B, and s-PCB. On the basis of PCB congener distributions in fish muscle, s-Aroclor B appears to be more accurate than s-Aroclor A in the analysis of biological residues. s-PCB is very similar to either Aroclor estimate and requires no pattern recognition or fitting. When Aroclor patterns have been seriously affected by environmental weathering or other processes (e.g., incineration or chemical treatment), the sum of measured congeners, s-PCB, should be reported.

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