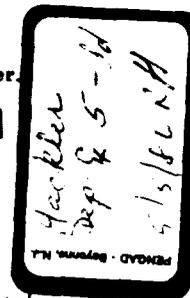


Interlaboratory Study on Determination of Polychlorinated Biphenyls in Environmentally Contaminated Sediments

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Three samples of sediments environmentally contaminated with polychlorinated biphenyls (PCBs) were analyzed by ten different laboratories using uniform calibration standards and standardized procedures for sample extraction, extract preparation, and chromatography. Six laboratories identified and measured PCBs as commercial Aroclor mixtures with electron capture (EC) detectors, and four used mass spectrometer (MS) detectors. All three sediments contained a mixture of Aroclors 1242 and 1254 but at different concentrations, approximately 0.2, 3 and 50 mg/kg, respectively. Despite written standardized procedures, procedural variations were introduced in some laboratories, and large differences in results were reported by participating laboratories. For EC data, the overall relative standard deviation of measurements of total Aroclor concentrations was 30%; for MS data deviation was 38%. The relatively complex calculations required to obtain Aroclor concentrations were an important source of data variability as well as being tedious and labor-intensive.

Concern about polychlorinated biphenyls (PCBs) as environmental pollutants began in 1966 when Jensen (1) discovered their presence in fish tissue from different parts of Sweden. This event occurred almost 40 years after PCBs became commercially available in the United States in 1929. Since 1966, PCBs have been the subject of many laboratory studies. An estimated (2) 6×10^8 kg of PCBs were produced between 1929 and 1977 in the United States. Although the manufacture, processing, distribution, and use of PCBs were severely restricted in the United States in 1979, the PCB problem has not ceased. Not only has careless handling of PCBs resulted in environmental contamination but also more than 3×10^8 kg of PCBs may still be in use as cooling liquids in electrical equipment (3).

The characteristic that makes PCBs such a problem is their stability and, therefore, persistence in the environment. This stability, however, has permitted frequent identification and measurement of PCBs as the original commercial formulation. Commercial PCB mixtures manufactured in the United States by the Monsanto Co. were called Aroclors. These are identified with four-digit numbers, the latter two digits indicating the weight percent of chlorine (e.g., Aroclor 1254 contains 54% chlorine). One exception, Aroclor 1016, does not follow this nomenclature rule. Aroclor 1016 is very similar to Aroclor 1242 in composition and contains about 40% chlorine.

The harbor at New Bedford, MA, is an example of PCB contamination that resulted from electrical capacitor manufacture in an era when industrial wastes were disposed by flushing them directly into the harbor or into the town sewage plant (2). Defective PCB-containing capacitors were disposed by dumping them into the town's landfill. To determine the extent of the PCB pollution problem, samples of sediments from New Bedford Harbor have been analyzed by many different laboratories during the past few years. Prior to this study, standardized procedures were not used. Instead, each laboratory produced data acquired with its favored procedure

for PCB extraction, enrichment, detection, and measurement.

The original purpose of this study was to determine the variability in results when several laboratories analyzed the same environmentally contaminated sediments with the same analytical procedures. As the study evolved, however, procedural variations among laboratories became apparent, and the goal became the assessment of the impact of procedural variations on analytical results.

Environmentally contaminated sediments were used for this study, because they present the real analytical challenge. Sediments fortified with PCBs in the laboratory may not truly represent environmentally contaminated sediments, because added PCBs may not be integrated into the sediment matrix. In addition, the variability of sediment characteristics can produce quite different matrix effects. Contaminated sediments from New Bedford Harbor were selected for this study, because available information permitted selection of sampling sites to collect three batches of samples containing PCBs at three different concentrations.

EXPERIMENTAL SECTION

Sample Collection and Homogenization. Sample I was collected from the inner harbor at a depth of about 2 m. It was finely divided dark silt with an apparent high organic content (i.e., "sticky black muck"). Sample II was collected outside the harbor at a depth of about 4.5 m. It was a sticky, sandy clay with a crust of cockle shells. (One analyst estimated 30% sand content with the remainder being a finely divided, dark silt.) Sample III, collected at a depth of approximately 1 m outside the harbor, was silty sand with some clam and scallop shells. After a known amount of 4,4'-dibromooctafluorobiphenyl (Ultra Scientific, Hope, RI) was added, each batch of wet sediment was thoroughly mixed to ensure homogeneity and divided into portions placed in 1-qt glass jars with screw caps lined with Teflon. Randomly selected aliquots were packed in ice and shipped to participating laboratories, where samples were refrigerated until used.

Analytical Materials. Samples were accompanied by standard solutions prepared by the Quality Assurance Branch (QAB), Environmental Monitoring and Support Laboratory, Cincinnati (EMSL-Cincinnati). Each of seven calibration solutions contained a commercial Aroclor (1221, 1232, 1016, 1242, 1248, 1254, or 1260) in methanol at a concentration of 5000 $\mu\text{g}/\text{mL}$, to be diluted as necessary. An eighth Aroclor solution was a quality control solution (composition unknown to participating laboratories) containing Aroclors 1016 and 1254 at concentrations of 24 and 31 $\mu\text{g}/\text{mL}$, respectively, in acetone. Solutions of 4,4'-dibromooctafluorobiphenyl and the internal standard, 4,4'-dibromobiphenyl (Ultra Scientific, Hope, RI), were prepared at concentrations of 1 $\mu\text{g}/\text{mL}$ in acetone, and each was sealed in a glass ampule.

Sample Extract Preparation. All participating laboratories were required to extract the samples with a Soxhlet procedure described below and were encouraged also to use a second extraction procedure that involved a high frequency dispersion (ultrasonic homogenizer). Written instructions were provided for these two extraction procedures, which are briefly described below. Details of the written procedures are available from the authors. In addition to the official Soxhlet procedure, one participating laboratory also used another Soxhlet extraction procedure. These will be distinguished as Soxhlet procedures A and B, with A designating the official study procedure.

Soxhlet Extraction, Procedure A. The entire wet sediment sample was transferred to a glass tray and spread evenly. Large sticks, stones, and shells were removed, and the sample was air-dried for 4 days. The sample was ground to uniform size with a mortar and pestle, and a 30-g aliquot was extracted for 16 h with 300 mL of 1:1 hexane/acetone. The extract was filtered through hexane-washed sodium sulfate and concentrated in a Kuderna-Danish apparatus.

Soxhlet Extraction, Procedure B. Duplicate 30-g aliquots of all three samples were extracted with 250 mL of 2-propanol in a Soxhlet apparatus. Because a wet sediment was used, a drying period was avoided. After a 16-h extraction with 2-propanol, a second 16-h extraction with 250 mL of dichloromethane was performed in the Soxhlet apparatus. Extracts were combined and added to a separatory funnel containing aqueous sodium sulfate solution. The dichloromethane phase was collected, and the aqueous phase was extracted with two additional 100-mL portions of dichloromethane. The three dichloromethane extracts were combined, filtered through sodium sulfate, and concentrated with a rotary evaporator.

Homogenizer Extraction. A 30-g aliquot of wet sediment sample was extracted with acetone while being ultrasonically disintegrated and homogenized. The acetone extract was added to a separatory funnel containing aqueous sodium sulfate solution, from which PCBs and other nonpolar materials were extracted with hexane. The hexane extract was concentrated in a Kuderna-Danish apparatus.

Removal of Interferences. All extracts were subjected to Florisil column chromatography and eluted with 6% ethyl ether in hexane. Sulfur was removed with a tetrabutylammonium sulfite reagent according to the procedure of Jensen et al. (4).

Electron Capture Determinations. A gas chromatograph (GC) equipped with a column packed with a methyl silicone liquid phase (SE-30 or OV-1) was used to separate sample extract components when an electron capture (EC) detector was used to identify and measure Aroclors. Aroclors were identified by visual comparison of sample extract chromatograms with Aroclor chromatograms. Two different measurement procedures were used; with both, Aroclor mixtures were used for calibration. In this report, one will be referred to as the Webb-McCall procedure and the other as comparison to Aroclor standard.

Webb-McCall Procedure (5). A known amount of each Aroclor standard was chromatographed by use of a methyl silicone packed column, and the area of each GC/EC peak was measured. Each laboratory calibrated detector response (ng of PCB/area) by using Webb-McCall data that provided weight percent information for each GC peak. Peaks were identified by whole numbers representing their retention times relative to a reference compound defined as 100. A sample extract was chromatographed under the same GC conditions, and the area of each peak in the resultant sample chromatogram was measured and multiplied by the appropriate calculated response factor. The sum of individual peak amounts was the total Aroclor amount, which was related to original sample weight or volume to obtain a concentration value.

Comparison to Aroclor Standard. One, a few, or all resolved GC peaks were selected to represent each Aroclor mixture, and a concentration calibration curve was determined by GC/EC analysis of standard solutions containing known amounts of each Aroclor. Either peak heights or peak areas were summed and converted to concentration units with the concentration calibration curve(s). The number of peaks used was highly variable (both within a laboratory and among all laboratories) depending on the particular extract components (i.e., presence or absence of interfering compounds) and on the analyst's judgment.

Mass Spectrometric Determinations. In all laboratories using a mass spectrometer (MS) as a detector, GC separations were performed with fused silica capillary columns coated with polydiphenyldimethylsiloxane (SE-54 or DB-5) and each MS was operated in the electron ionization mode. Both full-range mass spectra and selected ion monitoring data were acquired. Response factors for selected Aroclor components were calculated relative to the internal standard, 4,4'-dibromobiphenyl.

Two laboratories (no. 8 and no. 9) independently developed quite similar measurement procedures after sample extract components had been identified as either Aroclor 1016 or 1242 along with Aroclor 1254. Selected ion current profiles of ap-

propriate Aroclor standards indicated that areas of the two or three most intense ions in the molecular isotopic cluster of hexachlorobiphenyl components could be used to measure Aroclor 1254. Similarly, dichlorobiphenyl ions could be used to measure Aroclor 1242 or 1016, which could not be distinguished. One laboratory used one di- and three hexachlorobiphenyl GC peak areas; the other laboratory used three di- and five hexachlorobiphenyl GC peak areas.

A third laboratory (no. 7) prepared a solution containing a 50:50 (w/w) mixture of Aroclors 1242 and 1254 and devised a concentration measurement scheme involving two ions from the molecular isotopic cluster of di-, tri-, tetra-, penta-, and hexachlorobiphenyl components. The sum of di-, tri-, and half of tetrachlorobiphenyl ion areas was used to measure 1242; the remaining half of tetra- and all of penta- and hexachlorobiphenyl components were used to measure 1254. Tetrachlorobiphenyl peak areas were divided because analysis of individual Aroclors indicated approximately equal contribution by 1242 and 1254.

The fourth laboratory (no. 10) using MS measurements did not identify and measure extract components as Aroclor(s), because no particular Aroclor pattern could be distinguished. (Mixtures of Aroclor standards were not compared to sample components.) Literature values for weight percent composition of commercial Aroclor formulations were used to determine the amount of each isomer group in each Aroclor solution. Chromatographic peak areas of two major ions for each level of chlorination were summed to obtain a total area for that level of chlorination in each standard and sample extract. A response factor relative to the internal standard was calculated for each level of chlorination in each Aroclor. The mean response factor for each level of chlorination was used to determine PCB concentrations in sample extracts.

Evaluation of Sediment Homogeneity. Five aliquots of each of the three sediment samples were selected at random and extracted with Soxhlet procedure A. Extracts were analyzed with packed column GC/EC in the authors' laboratory by an experienced analyst who had no prior knowledge of the identity or concentration of PCB contaminants. For one sample, duplicate aliquots from the same bottle were extracted and analyzed. Aroclor concentrations were calculated with both described GC/EC measurement procedures (Webb-McCall and comparison to Aroclor standards). For comparison to Aroclor standards, a mixture of the two identified Aroclors was prepared, and selected peak heights in sample chromatograms were compared to those in the mixed Aroclor standard.

RESULTS AND DISCUSSION

Homogeneity Evaluation. Results of GC/EC analyses of randomly selected sample aliquots indicated that the samples were sufficiently homogeneous to proceed with the interlaboratory study (Table I). Because the three samples were environmentally contaminated sediments, true concentrations were unknown, and criteria for accuracy could not be specified. A mixture of Aroclors 1242 and 1254 was identified in all three samples. No interferences prevented accurate measurement of Aroclor 1254, but problems were encountered with GC/EC measurement of Aroclor 1242 in the two samples (II and III) containing Aroclor 1242 at concentrations of about 1 mg/kg or less.

All Aroclor 1242 concentrations calculated with the Webb-McCall procedure probably were lower than the actual amount of Aroclor 1242 present in sample extracts, because some Aroclor 1242 components could not be measured. The surrogate compound, 4,4'-dibromooctafluorobiphenyl, eluted in the Aroclor 1242 region of the chromatogram and prevented measurement of some PCB sample components. The surrogate compound had been added to each batch of sediment sample, before homogenization, to serve as an indicator of extraction efficiency. In some extracts, other sample components also interfered with measurements of Aroclor 1242 components.

With the Aroclor standard comparison procedure, Aroclor 1242 peaks without interferences could be selected except for

Table I. Results of Aroclor Determinations^a To Demonstrate Sediment Homogeneity

sample	n	Aroclor	calculated concentrations					
			Webb-McCall procedure			comparison to Aroclor stds		
			mean concn, ^b mg/kg	std dev, mg/kg	% RSD	mean concn, mg/kg	std dev, mg/kg	% RSD
I	5	1242	32	0.45	1.4	31	1.1	3.5
		1254	24	0.46	1.9	30	0.55	1.8
		total	56	0.45	0.8	60	0.89	1.5
II	5	1242	0.93	0.51	5.5	1.1	0.084	7.6
		1254	0.95	0.042	4.4	1.2	0.071	5.9
		total	1.9	0.084	4.4	2.3	0.15	6.5
III	7	1242	0.032	0.0051	16	- ^c	-	-
		1254	0.098	0.012	12	0.12	0.015	12
		total	0.13	0.017	13			

^aSingle laboratory, single analyst data; concentrations calculated with two different procedures using the same data. ^bInterference by surrogate compound and non-Aroclor sample components prevented measurement of some Aroclor 1242 components in all three samples. Reported values estimated to be 88%, 72%, and 14% of Aroclor 1242 present in samples I-III, respectively. ^cInterference by surrogate compound and non-Aroclor sample components; estimated minimum detectable concentration of 1 mg/kg.

sediment sample III, which contained the lowest concentration of PCBs. In that sample, the surrogate compound and sample components other than PCBs prevented measurement of Aroclor 1242. With that level of interferences, the minimum amount of Aroclor 1242 that could have been measured in that sample was estimated to be 1 mg/kg.

The relative standard deviation (RSD) of replicate concentration measurements (Table I) varied inversely with the value of the measured concentration. As mean total Aroclor concentrations ranged from 60 mg/kg to 0.13 mg/kg, RSD ranged from 1.5% to 13%, respectively. For measurements of either Aroclor 1242 or 1254, the RSD ranged from 1.4% to 16%. Although no historical statistical data were available to indicate the precision necessary to declare samples homogeneous, these intralaboratory data were judged to indicate acceptable sample homogeneity for the interlaboratory study.

Quality Control Solution. Accurate measurement of Aroclor concentrations in the quality control (QC) solution demonstrated only that detection and measurement aspects of the analyses were in control. Before analyzing sediment extracts, each participating laboratory analyzed the QC solution to identify and measure Aroclor components. Results were reported to the study coordinator. If results were within the previously established acceptance range, the laboratory proceeded with analyses of sediment sample extracts. If results were not within the acceptance range, the participant was so informed and was instructed to improve identification and measurement techniques before determining PCBs in sediment extracts.

The true value of total Aroclor concentration of 55 µg/mL in the quality control solution had been established by 52 analyses of the same solution in several laboratories. From those data, the acceptance range of 43-67 µg/mL for this study was statistically determined for a 95% confidence limit. Results reported by laboratories participating in this study ranged from 35 to 65 µg/mL with a mean of 53 µg/mL (RSD, 18.5%).

Only one participating laboratory reported QC solution concentration values that were outside acceptance limits. That laboratory was informed that their results indicated a serious problem with concentration measurements, and they were instructed to locate and correct the source of the problem before analyzing sample extracts. No other values for the QC solution were reported by that laboratory, but sample concentration measurements were later reported and are included among data reported here.

Study Variables. Efforts were made to minimize variability caused by participating laboratories using different

procedures. Written instructions for sample extraction, preparation, and analysis were included with each set of sediment samples. Laboratories were instructed to extract and analyze duplicate aliquots of each of the three sediment samples. Individual results were to be reported. Two laboratory reagent blanks were to be analyzed with each extraction procedure used.

Results of a study (6) to compare procedures to extract PCBs from environmentally contaminated lake sediment samples were the basis for selection of extraction procedures provided. A Soxhlet procedure that was found to be most efficient in that study was required of all participants. A homogenizer procedure that also was shown in that study to be efficient and convenient for sediment samples had several advocates among participating laboratories, who were encouraged to perform both extraction procedures.

Efforts to minimize study variables were not entirely successful. Varying priorities in participating laboratories negated plans to eliminate the sample storage time variable by having samples extracted at approximately the same time. In addition, the number of participating laboratories increased. Initially, eight laboratories were to participate in the study. Two were interested in analyzing extracts with GC/MS only, and six were prepared to use GC/MS techniques if extracts were not amenable to GC/EC techniques. After those six laboratories reported GC/EC results, more data were needed to allow comparison of GC/EC and GC/MS results. Two additional laboratories later extracted the samples and used GC/MS techniques to analyze the extracts. Some GC/MS analyses were not performed until 10 months after sample collection. Reanalysis of the sediment samples in the authors' laboratory did not, however, indicate any change in Aroclor composition during 5 months of storage.

All laboratories did extract aliquots of three apparently homogeneous, environmentally contaminated sediment samples, and they used the same standard solutions. No important deviations from specified extraction and chromatography (column and gas) procedures were reported, but variations in calibration and concentration measurement procedures were apparent. Some participants performing GC/EC analyses used the Webb-McCall measurement procedures, and others used the techniques referred to in this report as comparison to Aroclor standards. In addition, one laboratory reported Aroclor 1016 concentrations calculated with Webb-McCall procedures, although that Aroclor was not among Aroclors characterized by Webb and McCall.

A variety of comments, some contradictory, were received from participants. All reported that the data reduction process

Table II. Measured PCB Concentrations (mg/kg) in Duplicate Sediment Aliquots Extracted with Soxhlet Procedure A

lab no.	sample I			sample II			sample III		
	Aroclor 1242	Aroclor 1254	total PCBs	Aroclor 1242	Aroclor 1254	total PCBs	Aroclor 1242	Aroclor 1254	total PCBs
EC Data									
1	35	20	55	2.1 ^a	1.3	3.4	0.14 ^a	0.11	0.25
	34	20	54	2.1 ^a	1.4	3.5	0.16 ^a	0.14	0.30
2	15	5.8	21	1.5	0.53	2.1	0.19	0.02	0.21
	16	5.3	23	1.6	0.51	2.1	0.25	0.04	0.29
3	34	26	60	1.1	1.0	2.1	0.072	0.10	0.17
	33	25	58	1.2	1.1	2.3	0.068	0.094	0.16
4	40	19	59	1.3	0.80	2.1	0.20	0.080	0.28
	25	12	37	1.1	0.70	1.8	0.13	0.10	0.23
5	39	34	73	2.5	2.3	4.8		0.19	0.26 ^b
	39	34	72	2.7	2.2	4.9		0.18	0.25 ^b
6	17	45	62	0.87	2.0	2.9	0.084	0.20	0.28
	17	47	64	0.89	2.0	2.9	0.11	0.19	0.30
mean	29	24	53	1.6	1.3	2.9	0.12	0.12	0.25
SD	9.9	14	17	0.63	0.66	1.1	0.077	0.060	0.048
RSD, %	34	55	32	39	51	38	64	50	19
MS Data									
7	27	38	65	0.90	1.1	2.0	0.11	0.12	0.23
	26	37	63	1.0	1.5	2.5	0.12	0.13	0.25
8	11	27	38	0.90	2.2	3.1	0.08	0.11	0.19
	14	33	47	1.3	2.5	3.8	0.08	0.14	0.22
9	12	23	35	0.68	0.71	1.4	0.012	0.099	0.11
	6.8	30	37	0.27	0.83	1.1	0.050	0.058	0.11
10			57			2.7			0.076
			61			2.7			0.035
mean	16	31	50	0.84	1.3	2.4	0.075	0.11	0.15
SD	8.4	5.8	12	0.34	0.60	0.88	0.040	0.029	0.080
RSD, %	53	19	24	40	46	37	53	26	53
EC and MS Data									
mean	24	27	52	1.3	1.4	2.7	0.10	0.12	0.21
SD	18	18	20	18	18	20	18	18	20
RSD, %	46	44	29	50	48	37	69	42	37

^a Reported as Aroclor 1016. ^b A value of 0.07 mg/kg reported for Aroclor 1260 was included in this total.

was extremely labor intensive and time-consuming. Most laboratories reported some interference by coextracted sample components. These interferences varied among samples. Laboratories using GC/MS reported more interfering substances in sample I (the "sticky black muck" that appeared to be high in organic content). Total ion current profiles of full-range mass spectral data produced unresolved complex profiles ("broad humps") for sample I extracts. In some cases, Aroclor patterns could be discerned from extracted ion current profiles, but reanalysis with selected ion monitoring provided more conclusive evidence. Some discrepancies were noted among comments and observations of participating laboratories. Two reported that sulfur removal procedures were unnecessary because no sulfur interference was observed. Another laboratory reported that sulfur interfered with analyses although the specified sulfur removal procedure had been used.

Measured PCB Concentrations in Sediment Samples. Total Aroclor (or total PCB) concentrations were more precise than individual Aroclor 1242 or 1254 concentrations reported for samples extracted with the Soxhlet procedure A (the official study extraction procedure) and analyzed with either GC/EC or GC/MS (Table II). (When more than duplicate values for a sample aliquot were reported by a laboratory, only

the first two values obtained were used for results reported here.) For total Aroclor concentrations in Soxhlet procedure A extracts, the overall RSD was 34% (mean of RSDs of 29%, 37%, and 37% from Table II). For GC/EC data, the overall RSD was 30% and for GC/MS, 38%. GC/MS data followed the expected trend of increasing RSD with decreasing measured concentration (24% for mean concentration of 50 mg/kg, 37% for mean concentration of 2.4 mg/kg, and 53% for mean concentration of 0.15 mg/kg. GC/EC data, however, produced data with the lowest RSD for the sample containing the lowest concentration (0.25 mg/kg).

All GC/EC concentrations in Table II were measured with the Webb-McCall procedure or some variation of that procedure. Two laboratories used both measurement procedures (Webb-McCall and comparison to Aroclor standards) to calculate concentrations from the same GC/EC data. Those results (Table III) indicate that, in some laboratories, the particular procedure used for concentration calculations can be a very significant source of variability. Although laboratory 3 reported values with a mean relative difference (difference between values expressed as a percentage of the mean value) of 12% for the three samples, laboratory 2 reported values with a mean relative difference of 66% for the same samples. Laboratory 2 had reported unacceptable values for the QC

Table III. Mean Aroclor Concentrations Obtained with Two Different GC/EC Measurement Procedures

sample no.	lab no.	measurement procedure	n ^a	mean concentration, mg/kg (RSD)			RD, ^b % of total Aroclor	
				Aroclor 1242	Aroclor 1254	total Aroclor		
I	3	Webb-McCall	5	32 (2)	24 (2)	56 (2)	8.5	
		Aroclor std	5	31 (3)	30 (1)	61 (1)		
	2	Webb-McCall	4	15 (9)	6.5 (9)	22 (9)		60
		Aroclor std	4	24 (8)	17 (7)	41 (7)		
II	3	Webb-McCall	5	0.93 (6)	0.96 (5)	1.9 (4)	19	
		Aroclor std	5	1.1 (6)	1.2 (5)	2.3 (6)		
	2	Webb-McCall	4	1.5 (5)	0.50 (7)	2.0 (5)		61
		Aroclor std	4	2.4 (6)	1.3 (8)	3.7 (7)		
III	3	Webb-McCall	6	0.033 (15)	0.098 (12)	0.13 (13)	8.0	
		Aroclor std	6		0.12 (12)	0.12 (12)		
	2	Webb-McCall	3	0.19 (32)	0.03 (33)	0.22 (30)		78
		Aroclor std	3	0.38 (39)	0.12 (17)	0.50 (32)		

^an, number of measurements. ^bRD, relative difference; difference between two values expressed as a percentage of the mean.

Table IV. Measured PCB Concentrations (mg/kg) in Sediments Extracted with an Ultrasonic Homogenizer Procedure

lab/det	sample I			sample II			sample III		
	Aroclor 1242	Aroclor 1254	total PCBs	Aroclor 1242	Aroclor 1254	total PCBs	Aroclor 1242	Aroclor 1254	total PCBs
2/EC	15	6.1	21						
	16	7.1	23						
3/EC	29	23	52	0.92	0.89	1.8	0.071	0.092	0.16
	30	23	53	1.0	0.98	2.0	0.078	0.10	0.18
6/EC	4.2	10	14	0.57	1.2	1.8	0.074	0.16	0.23
	4.0	9.4	13	0.54	1.1	1.6	0.083	0.16	0.24
9/MS	1.5	7.4	8.9	0.22	0.42	0.64	0.034	0.40	0.43
	0.81	6.4	7.2	0.24	0.78	1.0	0.038	0.42	0.46
10/MS			57			2.1			0.15
			47			0.86			0.029
mean	13	12	30	0.58	0.90	1.5	0.063	0.22	0.23
SD	12	7.2	20	0.33	0.28	0.56	0.021	0.15	0.14
RSD, %	92	60	67	57	31	37	33	68	61

solution measured with the Webb-McCall procedure. These results indicate the importance of ensuring that measurement techniques produce acceptable results.

Impact of Different Extraction Procedures. Five laboratories reported data from sample aliquots extracted with an ultrasonic homogenizer (Table IV) as well as those extracted with the prescribed Soxhlet procedure (Table II). Comparison of concentrations measured with the same procedure in the same laboratory showed that some homogenizer extracts provided concentrations equivalent to Soxhlet concentrations, but many homogenizer extract values were lower than Soxhlet values. Laboratory 9, however, obtained considerably higher values for both homogenizer extracts of sample III, and laboratory 10 obtained a higher value for one homogenizer extract of sample III. More than one laboratory reported that the texture of sample I ("silty muck") was not as amenable to homogenizer extraction as was sample III, which was coarse and sandy.

The overall mean concentration of total Aroclor (0.23 mg/kg) measured in homogenizer extracts of sample III (Table IV) agreed well with the mean concentration (0.21 mg/kg) measured in Soxhlet extracts of sample III (Table II), but the RSD was 61% for homogenizer extracts and 37% for Soxhlet extracts. These data suggest that homogenizer extraction results may be very dependent on the particular homogenizer used. To produce results equivalent to those obtained with Soxhlet extraction procedures, the analyst must use equipment that is sufficiently powerful and in good operating condition.

No important differences were observed between concentrations measured in extracts obtained with Soxhlet proce-

Table V. Measured Aroclor Concentrations (mg/kg) in Sediment Samples Extracted with Soxhlet Procedures A and B

sample/aliquot	extraction procedure	Aroclor 1242	Aroclor 1254	total Aroclor
I/9A	A	27	38	65
	A	26	37	63
	B	27	38	65
	B	21	45	66
	mean	25	40	65
	SD	2.9	3.7	1.3
	RSD, %	12	9.2	2.0
II/2A	A	0.90	1.1	2.0
	A	1.0	1.5	2.5
	B	1.1	1.6	2.7
	B	0.8	1.4	2.2
	mean	0.95	1.4	2.4
	SD	0.13	0.22	0.31
	RSD, %	14	16	13
III/9A	A	0.11	0.12	0.23
	A	0.12	0.13	0.25
	B	0.10	0.17	0.27
	B	0.10	0.16	0.26
	mean	0.11	0.14	0.25
	SD	0.0096	0.024	0.017
	RSD, %	8.7	17	6.8

dures A and B used for these samples (Table V). The laboratory performing these comparative extractions, however, expressed a preference for Soxhlet procedure B, which is faster and involves fewer transfers and less glassware than Soxhlet

procedure A. In addition, procedure B eliminates the need for a 4-day drying period, during which the sample is subject to possible contamination. With procedure B, laboratory workers also avoid the potential hazard of handling dusty, dry powder.

Surrogate Compound Results. Reported concentrations of the surrogate compound, 4,4'-dibromooctafluorobiphenyl, were highly variable, ranging from not detected to approximately 116% of the amount added. Not only did the chosen surrogate compound not serve its intended purpose of indicating extraction efficiency but also it interfered with GC/EC measurement of sample PCB components. The surrogate concentration proved to be inappropriate for two of the three samples (too low in sample I and too high in sample III).

Interlaboratory variation in measured surrogate concentrations was much greater than intralaboratory variation. The RSDs of measured concentrations in all laboratories were 71%, 86%, and 52% for samples I-III, respectively, while the mean relative difference in 24 duplicate results was only 15%. This suggests that the surrogate compound was homogeneously distributed. Intralaboratory data indicated that the surrogate compound was successfully recovered from reagent blanks. For two Soxhlet blanks, an average recovery of 94% was reported; for two homogenizer blanks, average recovery was 96%. Efforts to correlate reported surrogate compound concentration with storage time before analysis revealed no apparent trends. Laboratories 4, 6, 9, and 10 had the most difficulty with detecting and measuring the surrogate; laboratories 4 and 6 were among the first to analyze extracts, while laboratories 9 and 10 analyzed them approximately 6 months later.

CONCLUSIONS

The use of uniform calibration materials and standardized procedures for sample extraction, extract preparation, and chromatography did not eliminate large differences in results obtained by different laboratories analyzing the same sediment samples. Inconsistent application of the relatively complex calculations required to obtain Arochlor concentrations is a significant source of variability, especially when a sample contains mixed Arochlors or interfering sample components. Generalized sample preparation and analyte enrichment procedures cannot handle all possible interferences. Although capillary column GC separations can obviate many interferences, the large amount of data significantly increases the time and effort required for computations, regardless of the detector used.

A new approach to PCB determinations is needed. In most environmental samples, the major concern is not the particular Arochlor present but the total level of PCB contamination. An additional important concern is the distribution of PCB congeners among the potentially more toxic and persistent isomer groups. The latter is very difficult to obtain with an EC detector but can be obtained relatively easily from the qualitative data provided by an MS detector. An analytical method combining a calibration procedure using individual PCB congeners, capillary column GC separation, MS detection, and automated data interpretation would provide more information and be more cost effective than procedures currently available for PCB determinations.

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