1989

PCB congener analysis with Hall electrolytic conductivity detection

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Order Number 9015930

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The College of William and Mary, 1989

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PCB CONGENER ANALYSIS WITH HALL ELECTROLYTIC CONDUCTIVITY DETECTION

A DISSERTATION

Presented to

The Faculty of the School of Marine Science

Virginia Institute of Marine Science

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Doctor of Philosophy

by

Robert D. Edstrom

1989

APPROVAL SHEET

This dissertation is submitted in partial fulfillment of

the requirements for the degree of

Doctor of Philosophy

Robert D. Edstrom

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DEDICATION

This work is dedicated to the Robert Edstrom family, Carl Edstrom family and Arnold Gansen family.

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ACKNOWLEDGMENTS

I wish to express my appreciation to my committee members for their patience and support during the development of this dissertation. Thanks to Dr. Craig Smith for his chemistry and computer programming expertise critical to the success of this methodology. I thank Dr. John Greaves and Ellen Harvey for the critical suggestions and stimulating conversations during the many phases of this dissertation. I also thank Harold Slone, Jimmy Greene and George Vadas for their technical support and sense of humor vital to the completion of this work. Thanks to the Council on the Environment of the state of Virginia for the financial support during the course of the Early Warning System project.

Finally, a special thanks to Dr. Robert Huggett for his willingness to take a chance on an undergraduate student, his patience, understanding and for giving me "all the rope" I needed during the last nine years.

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ABSTRACT

This work reports the development of an analytical methodology for the analysis of PCB congeners based on integrating relative retention data provided by other researchers. The retention data were transposed into a multiple retention marker system which provided good precision in the calculation of relative retention indices for PCB congener analysis. Analytical run times for the developed methodology were approximately one hour using a commercially available GC capillary column.

A Tracor Model 700A Hall Electrolytic Conductivity Detector (HECD) was employed in the GC detection of Aroclor standards and environmental samples. Responses by the HECD provided good sensitivity and were reasonably predictable. Ten response factors were calculated based on the molar chlorine content of each homolog group. Homolog distributions were determined for Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 along with binary and ternary mixtures of the same. These distributions were compared with distributions reported by other researchers using electron capture detection as well as chemical ionization mass spectrometric methodologies. Homolog distributions acquired by the HECD methodology showed good correlation with the previously mentioned methodologies.

The developed analytical methodology was used in the analysis of bluefish (Pomatomas saltatrix) and weakfish (Cynoscion regalis) collected from the York River, lower James River and lower Chesapeake Bay in Virginia. Total PCB concentrations were calculated and homolog distributions were constructed from the acquired data. Increases in total PCB concentrations were found in the analyzed fish samples during the fall of 1985 collected from the lower James River and lower Chesapeake Bay. Comparisons between the homolog distribution patterns in the fish samples with the previously mentioned Aroclor distribution patterns suggests a different source of PCBs for different areas.

Sediments, oysters (Crassostrea virginica) and brackish water clams (Rangia cuneata) collected from the tidal James River in 1986 were also analyzed. Total PCB concentrations and homolog distributions were calculated for all samples. Sediment total PCB concentrations were relatively constant over the sampling range except in the region of the turbidity maximum which were significantly higher. Total PCB concentrations in the Rangia from the region of the turbidity maximum were the highest of all the biota samples. Rangia homolog distribution patterns from this area were distinctly different from the sediment distribution patterns or the other Rangia distribution patterns in this segment of the river. Alteration of the endemic distribution pattern may be due to physical-chemical processes occurring within the turbidity maximum.

PCB Congener Analysis with Hall Electrolytic Conductivity Detection

CHAPTER I

GENERAL INTRODUCTION

History of PCBs

Polychlorinated biphenyls (PCBs) were produced in many areas of the world and marketed under trade names such as Aroclor (U.S.A.), Kanechlor (Japan), Sovol (U.S.S.R.), Pyralene (France), Phenoclor (Italy) and Clophen (West Germany). These products were used as petroleum additives, hydraulic fluids, heat transfer media and lubricants as well as other applications. The sales of Aroclors in the United States for 1970 alone was 36,287 tons of which Aroclor 1242 was the greatest at 22,680 tons (Cairns et al., 1986).

The identification of PCBs in fish and wildlife samples by Jensen in 1966 initiated a worldwide investigation to estimate the scope of the dissemination of these industrial chemicals into the environment. As a result, PCBs have been found to be present in fish from the North Atlantic (Ballschmiter, 1981c) and penguin eggs in the sub-antarctic (Ballschmiter, 1981b). Although production of PCBs has ceased in most countries, 800,000 tons of PCBs have been estimated as landstocked, either still in use or in storage areas (Tanabe and Tatsukawa, 1986). The dissemination of a portion of this material is inevitable.

Polychlorinated biphenyls were produced by the chlorination of biphenyl at high temperature in the presence of a catalyst such as ferric chloride. The mixture resulting form this reaction could

contain chlorinated biphenyls with one to ten chlorines. The Aroclors produced were 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262 and 1268. Aroclor number designations were assigned to provide information about the PCB mixture. The first pair of figures usually indicates the number of carbon atoms in the molecule (12) and the second pair indicate the chlorine content (e.g. 54%).

Theoretically, 209 PCB congeners of common origin and similar structure are possible from the chlorine substitution reaction. The number of congeners in each homolog group (membership defined by the number of chlorine atoms) are (Holden, 1986):

Mono-	3
Di-	12
Tri-	24
Tetra-	42
Penta-	46
Hexa-	42
Hepta-	24
Octa-	12
Nona-	3
Deca-	1

The accurate, precise and practical measurement of these individual PCB congeners in environmental samples is an ultimate goal which is now being approached.

History of PCB Analysis

Gas chromatography (GC) incorporating coated solid support packed columns with electron capture detectors (ECD) have been the instruments most frequently chosen for the analysis of these

chlorinated complex mixtures. ECDs are relatively inexpensive, easy to operate and provide high sensitivity to chlorinated compounds.

Gas chromatograms of environmental samples are often dissimilar to the standard Aroclors because of transformations which may occur due to differential partitioning, biologically degradation (Brown et al., 1984) or photolytic degradation (Mamantov 1985). The alteration of the peak pattern can confuse the identification of PCBs as Aroclors and result in erroneous quantification. Additionally, multiple Aroclors may be present in environmental samples which can make the discrimination of peak patterns more difficult. PCBs in environmental samples have most frequently been quantified by principal components of the PCB chromatographic pattern. This method compares the major peaks of an Aroclor standard chromatogram with the major peaks in the sample chromatogram. Calibration of the analytical instrument is based on the linear regression of the total peak areas or peak heights of the principal component peaks with increasing concentrations. The total response of these peaks in the sample is used to acquire a sample concentration with the understanding that the method may not be applicable in every instance (Sawyer, 1973a).

The United States Food and Drug Administration performed an interlaboratory study using individual peak quantification for total PCB concentrations (Sawyer, 1978a; Sawyer, 1978b). The method employed was to quantify each peak of the PCB pattern, then total the individual concentrations for a total PCB concentration. The results indicated that quantification of individual peaks provided more precise estimates of the total PCB concentration as opposed to total

response quantification. This study is significant because of the individual peak quantification method performed, which is a precursor to congener analysis.

Advances in PCB Analysis

Analysis of complex mixtures has been improved with the development and application of the GC capillary column. The utilization of capillary columns in the GC/ECD analysis of PCB congeners reduces the potential of misidentification of peaks when sample interferences are present. However, capillary columns do not preclude the coelution of non-chlorinated electron-capturing compounds with halogenated compounds. Erroneous information may be acquired when coeluting non-chlorinated compounds mask the responses of chlorinated compounds. Halogen selective GC detectors are sometimes chosen which provide increased confidence in peak identifications.

Some of the earliest work performed on the characterization of Aroclors was published by Sissons and Welti (1971). In later years, much effort was directed toward the identification of PCB congeners (Albro and Parker, 1979; Ballschmiter and Zell, 1980; Albro et al., 1981). A method of PCB congener nomenclature using International Union of Pure and Applied Chemistry (IUPAC) congener designations was reported by Ballschmiter (1980d) which provided a means of assigning standardized identities to the contents within chromatographic peaks (Table 1). In the following work, all congener numbers are IUPAC congener designations.

Table1. IUPAC Nomenclature for PCB Congener Identification.

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2'
5	2,3
6	2,3'
7	2,4
8	2,4'
9	2,5
10	2,6
11	3,3'
12	3,4
13	3,4'
14	3,5
15	4,4'
	Trichlorobiphenyls
16	2,2',3
17	2,2',4
18	2,2',5
19	2,2',6
20	2,3,3'
21	2,3,4
22	2,3,4'
23	2,3,5
24	2,3,6
25	2,3',4
26	2,3',5
27	2,3',6
28	2,4,4'
29	2,4,5
30	2,4,6
31	2,4',5
32	2,4',6
33	2',3,4
34	2',3,5
35	3,3',4
36	3,3',5
37	3,4,4'
38	3,4,5
39	3,4',5
	Tetrachlorobiphenyls
40	2,2',3,3'
41	2,2',3,4
42	2,2',3,4'
43	2,2',3,5
44	2,2',3,5'
45	2,2',3,6
46	2,2',3,6'
47	2,2',4,4'
48	2,2',4,5
49	2,2',4,5'
50	2,2',4,6
51	2,2',4,6'
52	2,2',5,5'
53	2,2',5,6'
54	2,2',6,6'
55	2,3,3',4
56	2,3,3',4'
57	2,3,3',5
58	2,3,3',5'
59	2,3,3',6
60	2,3,4,4'
61	2,3,4,5
62	2,3,4,6
63	2,3,4',5
64	2,3,4',6
65	2,3,5,6
66	2,3',4,4'
67	2,3',4,5
68	2,3',4,5'
69	2,3',4,6
70	2,3',4',5
71	2,3',4',6
72	2,3',5,5'
73	2,3',5',6
74	2,4,4',5
75	2,4,4',6
76	2',3,4,5
77	3,3',4,4'
78	3,3',4,5
79	3,3',4,5'
80	3,3',5,5'
81	3,4,4',5
	Pentachlorobiphenyls
82	2,2',3,3',4
83	2,2',3,3',5
84	2,2',3,3',6
85	2,2',3,4,4'
86	2,2',3,4,5
87	2,2',3,4,5'
88	2,2',3,4,6
89	2,2',3,4,6'
90	2,2',3,4',5
91	2,2',3,4',6
92	2,2',3,5,5'
93	2,2',3,5,6
94	2,2',3,5,6'
95	2,2',3,5',6
96	2,2',3,6,6'
97	2,2',3',4,5
98	2,2',3',4,6
99	2,2',4,4',5
100	2,2',4,4',6
101	2,2',4,5,5'
102	2,2',4,5,6'
103	2,2',4,5',6
104	2,2',4,6,6'
105	2,3,3',4,4'
106	2,3,3',4,5
107	2,3,3',4',5
108	2,3,3',4,5'
109	2,3,3',4,6
110	2,3,3',4',6
111	2,3,3',5,5'
112	2,3,3',5,6
113	2,3,3',5',6
114	2,3,4,4',5
115	2,3,4,4',6
116	2,3,4,5,6
117	2,3,4',5,6
118	2,3',4,4',5
119	2,3',4,4',6
120	2,3',4,5,5'
121	2,3',4,5',6
122	2',3,3',4,5
123	2',3,4,4',5
124	2',3,4,5,5'
125	2',3,4,5,6'
126	3,3',4,4',5
127	3,3',4,5,5'
	Hexachlorobiphenyls
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
130	2,2',3,3',4,5'
131	2,2',3,3',4,6
132	2,2',3,3',4,6'
133	2,2',3,3',5,5'
134	2,2',3,3',5,6
135	2,2',3,3',5,6'
136	2,2',3,3',6,6'
137	2,2',3,4,4',5
138	2,2',3,4,4',5'
139	2,2',3,4,4',6
140	2,2',3,4,4',6'
141	2,2',3,4,5,5'
142	2,2',3,4,5,6
143	2,2',3,4,5,6'
144	2,2',3,4,5',6
145	2,2',3,4,6,6'
146	2,2',3,4',5,5'
147	2,2',3,4',5,6
148	2,2',3,4',5,6'
149	2,2',3,4',5',6
150	2,2',3,4',6,6'
151	2,2',3,5,5',6
152	2,2',3,5,6,6'
153	2,2',4,4',5,5'
154	2,2',4,4',5,6'
155	2,2',4,4',6,6'
156	2,3,3',4,4',5
157	2,3,3',4,4',5'
158	2,3,3',4,4',6
159	2,3,3',4,5,5'
160	2,3,3',4,5,6
161	2,3,3',4,5',6
162	2,3,3',4',5,5'
163	2,3,3',4',5,6
164	2,3,3',4,5',6
165	2,3,3',5,5',6
166	2,3,4,4',5,6
167	2,3',4,4',5,5'
168	2,3',4,4',5',6
169	3,3',4,4',5,5'
	Heptachlorobiphenyls
170	2,2',3,3',4,4',5
171	2,2',3,3',4,4',6
172	2,2',3,3',4,5,5'
173	2,2',3,3',4,5,6
174	2,2',3,3',4,5,6'
175	2,2',3,3',4,5',6
176	2,2',3,3',4,6,6'
177	2,2',3,3',4',5,6
178	2,2',3,3',5,5',6
179	2,2',3,3',5,6,6'
180	2,2',3,4,4',5,5'
181	2,2',3,4,4',5,6
182	2,2',3,4,4',5,6'
183	2,2',3,4,4',5',6
184	2,2',3,4,4',6,6'
185	2,2',3,4,5,5',6
186	2,2',3,4,5,6,6'
187	2,2',3,4',5,5',6
188	2,2',3,4',5,6,6'
189	2,3,3',4,4',5,5'
190	2,3,3',4,4',5,6
191	2,3,3',4,4',5',6
192	2,3,3',4,5,5',6
193	2,3,3',4',5,5',6
	Octachlorobiphenyls
194	2,2',3,3',4,4',5,5'
195	2,2',3,3',4,4',5,6
196	2,2',3,3',4,4',5',6
197	2,2',3,3',4,4',6,6'
198	2,2',3,3',4,5,5',6
199	2,2',3,3',4,5,5,6'
200	2,2',3,3',4,5',6,6'
201	2,2',3,3',4',5,6',6
202	2,2',3,3',5,5',6,6'
203	2,2',3,4,4',5,5',6
204	2,2',3,4,4',5,6,6'
205	2,3,3',4,4',5,5',6
	Nonachlorobiphenyls
206	2,2',3,3',4,4',5,5',6
207	2,2',3,3',4,4',5,6,6'
208	2,2',3,3',4,5,5',6,6'
	Decachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'

The synthesis of all 209 congeners was performed recently. In 1984, valuable information was published by Mullin et al. (1984) which documented the synthesis and retention characteristics of all 209 PCB congeners on a commercially available GC capillary column. This work has facilitated the analysis of PCBs on an individual peak basis. It is now possible to analyze environmental samples for PCB congeners to acquire more accurate estimates of total PCB concentrations. Congener analysis will also provide information about the more toxic congeners.

The resolution of all 209 congeners on a single capillary column has not been performed. During a chromatographic run of an Aroclor standard, any one peak may consist of one or more congeners from the same or different homolog class. Ultimately, methodology providing the resolution of all congeners must be achieved. The identification and quantification of the more stressful PCB components in aquatic environments could then be performed. However, methodology for this advanced level of analysis is, at the present, in its early stages of development (Duinker et al., 1988; Schulz et al., 1989).

PCB Analysis-Detectors

The analysis of PCBs with gas chromatography has been performed using GC detectors with a wide range of sensitivities. PCBs have most frequently been analyzed with ECDs because of the high sensitivity often required for low environmental concentrations. ECDs are readily available from GC manufacturers and are relatively easy to operate. One additional advantage of the ECD is that it is not a destructive detector. This aspect of the ECD would permit a second detector to be

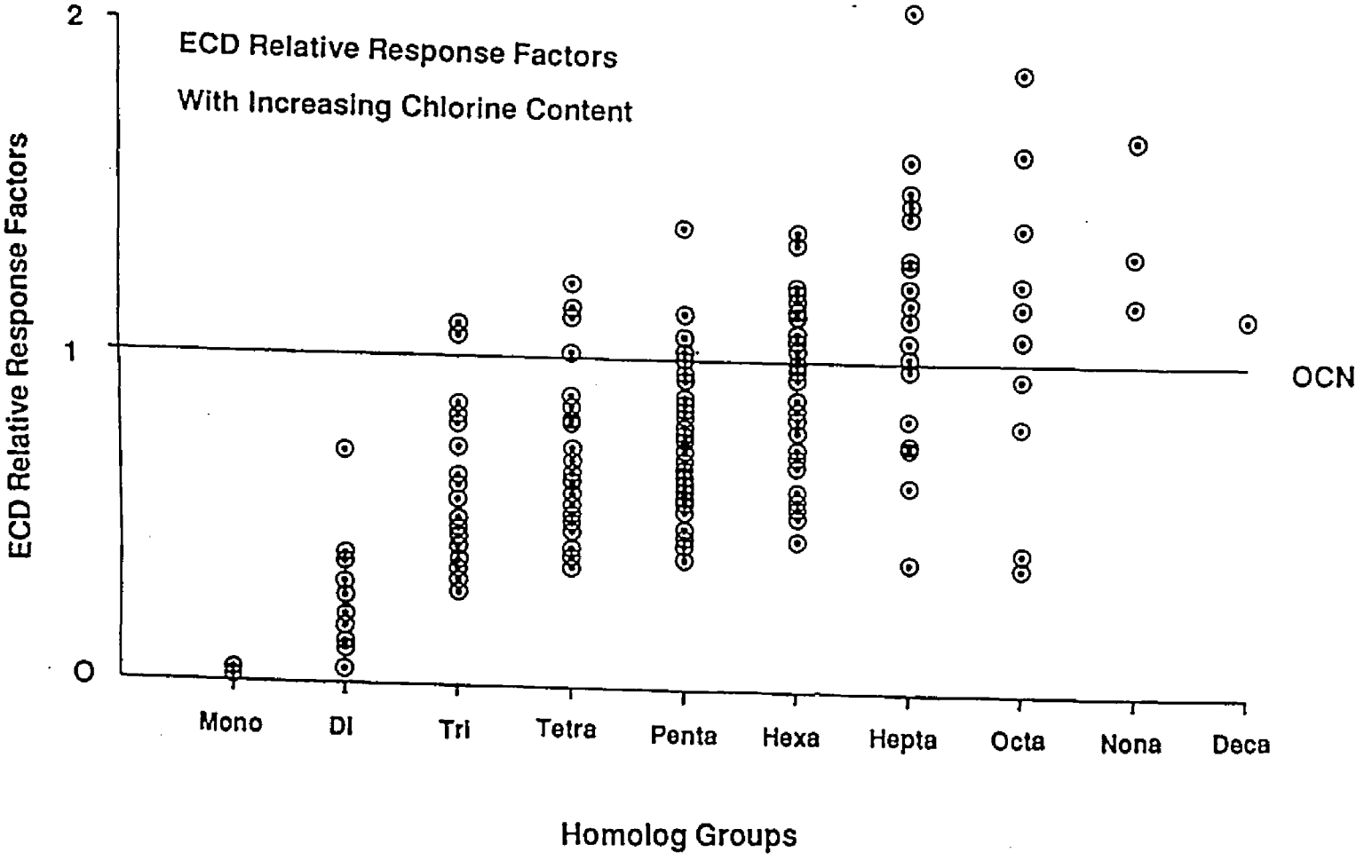
placed in series or detector effluents may be trapped for additional analysis.

Disadvantages of the detector are few, however they may be considered significant with respect to their impact on the quality of analysis. The ECD is not selective to halogenated compounds. ECD responses of anthropogenic and biogenic compounds containing double bonded oxygen, double bonded sulfur and nitrogen heterocycles can confuse the interpretation of a gas chromatogram. The inclusion of non-chlorinated species into the quantification of sample PCB concentrations will result in erroneous estimates of the absolute PCB concentration. Additionally, a non-halogenated compound coeluting with the compound of interest will also result in the over estimation of the sample concentration.

Another disadvantage of the ECD is the disproportionate response to PCBs within a homolog group. The ECD relative response factors of all 209 congeners have been provided by Mullin et al. (1984) based on the standard octachloronaphthalene. A plot of the reported relative response factors compiled according to homolog group is provided in Figure 1. Response factors within each group are highly variable in all homolog classes.

Gas chromatography with mass spectrometry (GC/MS) is often the preferred means of analysis for PCBs. Greater confidence in compound identifications may be acquired from the mass spectra of the analytes. Chemical ionization techniques can provide important information about the identity of chemicals in environmental samples. GC/MS with negative chemical ionization (NCI) attains sensitivities comparable to

Figure 1. ECD Relative Response Factors (Mullin et al., 1984) According to Chlorine Content.


ECD Relative Response Factors
With Increasing Chlorine Content
ECD Relative Response Factors
2
1
0
OCN
Mono
DI
Tri
Tetra
Penta
Hexa
Hepta
Octa
Nona
Deca
Homolog Groups

those of the ECD and provides greater abundances of molecular ions. Molecular weight as well as degree of chlorination data may be acquired using GC/MS with NCI.

A disadvantage of GC/MS instrumentation is the cost of analytical instruments capable of the various ionization techniques. GC/MS systems are often priced upwards from $100,000. The operation and maintenance of these systems can be costly in terms of required technical personnel support and materials.

An additional and seldom applied detector suitable for the analysis of PCBs is the Hall Electrolytic Conductivity Detector (HECD). The Hall detector can be operated in the halogen selective mode which is specific for halogenated compounds. Although the detector is not chlorine specific, it does reduce the potential of false responses by non-halogenated species and provides a clear selective response of halogenated compounds which coelute with non-halogenated compounds. This aspect of the detector can significantly simplify the interpretation of a chromatogram of an environmental sample.

PCB Analysis - Present State

Most of the environmental monitoring data at present has been reported as total PCB concentrations. Efforts by researchers are focused on the development of individual PCB congener analytical methodologies. Due to the newness of this technique, a paucity of PCB congener monitoring data exists. The major peaks in many environmental samples are often common peaks appearing in published

chromatograms (Ballschmiter, 1980d; Safe et al., 1983; Duinker et al., 1988). Some researchers have chosen to analyze or report the major peaks alone (Swackhamer et al., 1988; Maack and Sonzogni, 1988). Oliver and Niimi (1988) have constructed homolog distribution patterns for samples representative of the Lake Ontario food chain in attempts to discern pattern alterations at different trophic levels. This work is an example of the information which can be acquired from PCB congener analysis.

CHAPTER II

PCB Congener Analysis-Relative Retention System

INTRODUCTION

Industrially produced complex mixtures of halogenated compounds have been exemplified by the polychlorinated biphenyls (PCBs) but also include the polychlorinated terphenyls, halowaxes, toxaphene, chlordane and strobane. Many of these mixtures contain numerous chlorinated compounds distinguishable only by substitution position and degree of chlorination. Each of these mixtures presents difficulties in identification and quantification for the analytical chemist, even when high resolution capillary columns are employed.

Analysis of complex mixtures containing multiple residues can be facilitated by computer software during the identification of these compounds. Such is the case with PCB congener analysis. Computer software may be acquired which, when properly applied to data acquired from capillary gas chromatography (GC), provide accurate and precise identification of PCB congeners. Capillary gas chromatography columns are commercially produced with varying internal diameters, lengths and stationary phases. Stationary phases range from non-polar methyl silicones to polar cyano silicones. However, there is no commercially available capillary column which will resolve all PCB congeners.

Mullin et al. (1984) have characterized all 209 PCB congeners on a SE-54 (1% vinyl, 5% phenyl) 50 meter capillary column. The capillary column was temperature programmed at $1^{\circ}C$/ min. which resulted in an analytical run time exceeding two hours. A single retention marker, octachloronaphthalene, was used to calculate relative retention times. A single retention marker, however, will reflect perturbations in analytical conditions over the entire chromatographic process. The relative retention times provided allowed the determination of congener elution order as well as being indicators of congener coelution or resolution.

Since the resolution of all congeners is not possible, the discrimination of each chromatographic peak is essential. Congener analysis can be enhanced by precise retention indices of PCB peaks. An aid in the identification of congeners is the use of a relative retention index system. Kovats (1958) described the relationship between retention characteristics and structural features of a homologous series of compounds. Retention indices for chromatographic peaks between neighboring peaks were calculated by interpolation. This is advantageous when linear temperature programming is practiced to analyze a large range of molecular weight compounds. Temperature programming at different rates can have a significant effect on retention behavior and therefore, retention data. Major factors which introduce error into the precision of retention data are different batches of stationary phases, different silylating reagents or batches and active sites on column surfaces.

Lee et al., (1979) have demonstrated the precision which may be acquired by the use of a multiple retention marker methodology. These researchers characterized over 200 polyaromatic hydrocarbons with a 12 meter, SE-52 capillary column utilizing a single gradient temperature program. Four retention markers were employed to assign precise retention indices for each compound. A multiple retention marker system partitions the analytical run into approximately equal segments. The precision within these compartments will be greater than over an entire analysis.

The purpose of this study was to acquire relative retention indices for those congeners detected in Aroclor analytical standards, based on a multiple retention marker system. Additionally, this system should provide an analytical run time of approximately one hour and utilize a commercially produced capillary column.

MATERIALS AND METHODS

Instrumentation

The retention data for PCB congeners were obtained using a Varian 3300 gas chromatograph with a Tracor Model 700A Hall Electrolytic Conductivity detector (HECD, Tracor Instruments, Inc., Austin, Texas). The gas chromatograph was equipped with a J&W (J&W Scientific, Inc., Falsom, CA) SE-54, 0.25mm I.D. X 30 meter fused silica capillary column which contained a 0.25 um stationary phase coating. Two temperature programs were used which consisted of a single temperature gradient. The first program was an approximation of the temperature program reported by Mullin et al. (1984). Column conditions were

100°C hold for 2 min. then programmed at 1°C/ min. to 240°C. The second temperature program was the desired program for subsequent analyses of Aroclor standards and environmental samples. Column conditions for this program were 90°C hold for 4 min. then programmed at 4°C/ min. to 300°C.

Additional gas chromatograph operating conditions were: injector 310°C, detector base 310°C, reaction tube temp. 950°C, n-propanol electrolyte flow at 0.4 ml/min. The gases for analysis were ultra high purity (UHP) hydrogen as carrier gas (linear velocity = 45 cm/sec), UHP helium makeup gas (30 ml/min.) and UHP hydrogen reaction gas (100 ml/min.).

Analytical Standards

Aroclor standards were obtained from the United States Environmental Protection Agency Pesticides and Industrial Chemicals Repository, Research Triangle Park, North Carolina. Stock standard concentrations of individuals Aroclors were prepared at 5000 ug/ml with subsequent dilution to acquire working standard concentrations of 50 ug/ml. All stock and working standards were prepared with high purity Burdick & Jackson n-hexane purchased from Baxter Scientific, Inc. (Columbia, MD).

A composite standard consisting of seven Aroclors (1221, 1232, 1242, 1248, 1254, 1260 and 1262) in equal weight was prepared and designated PCB-7. The final concentration of this standard was 35.0 ug/ml. This standard was made to present all possible congeners detected in the Aroclors.

A second composite standard, PCB-3, consisting of Aroclors 1242, 1254 and 1260 in equal weight was prepared to a final concentration of 15.0 ug/ml. This composite represents three Aroclors which contain major peaks frequently detected in environmental samples.

Selected individual congener standards were purchased from Ultra Scientific, Inc. (Hope, Rhode Island) and prepared to a final concentration of 1.0 ug/ml.

Identification Methodology

Since the relative retention time data reported by Mullin et al. (1984) were the most complete information available, conversion of these data into a retention marker index system was performed. This provided retention indices traceable to the only existing complete set of PCB congener analytical standards.

Four retention markers and/or surrogates were coinjected with the congener standards and Aroclor standards for the calculation of each Congener Retention Index (CRI) or Hall Retention Index (HRI). The retention markers or surrogates and their assigned indices were : b-chloronaphthalene (1000), a-BHC/#8 (2000), o,p'-DDD/#154 (3000) and decachlorobiphenyl/ #209 (DCB, 4000). These retention markers provide an elution profile with three compartments of approximately equal duration.

The equation for calculating the CRI or HRI was:

$$\frac{RT\ X - RT\ A}{RT\ B - RT\ A} \times 1000 + C = CRI \text{ or } HRI$$

RT A = Retention time of marker eluting before congener X.

RT B = Retention time of marker eluting after congener X.

RT X = Retention time of congener X.

C = Retention index of marker eluting before congener X.

This equation is similar to that used by Kovats (1958) for interpolation of a peak between two neighboring peaks. The equation has been adapted to accommodate the four retention marker system.

Derivation of CRIs and HRIs

The relative retention time data from Mullin et al. (1984) were transposed into a relative retention index system using four retention markers. A flow chart showing the steps performed in the conversion method is shown in figure 2. In this method, two types of retention indices were used. CRIs were those indices (calculated or analytical) derived by using the surrogate (CRI) retention markers (#8/#154/#209). The congeners of specific interest included only those congeners which eluted between congeners #8 and #209. Analytical CRIs were obtained from the analyses of the appropriate standards to verify the accuracy of the transposed retention data. GC operating conditions were approximately those used by Mullin et al. (1984).

HRIs were indices (experimental or analytical) derived using the HRI retention markers (a-BHC/o,p'-DDD/DCB). Experimental HRIs were obtained from the analyses of the appropriate standards temperature programmed at $1^{o}C$/min. Analytical HRIs were obtained from the analyses of the same standards temperature programmed at $4^{o}C$/ min.

Figure 2. Derivation of Analytical HRIs from Relative Retention Time Data (Mullin et al., 1984).

DERIVATION OF ANALYTICAL HRIs

Relative Retention Times (Mullin et al., 1984)

↓

Calculated CRIs
(#8/#154/#209, 1°C/min)

↓

Analytical CRIs
(#8/#154/#209, 1°C/min)

↓

Experimental HRIs
(α– BHC/o,p'-DDD/DCB, 1°C/min)

↓

Analytical HRIs
(α - BHC/o,p'–DDD/DCB, 4°C/min)

The GC operating conditions for the analytical HRI data were those conditions desired for future analyses of environmental samples.

RESULTS AND DISCUSSION

Retention Indices of Major Components in Aroclors

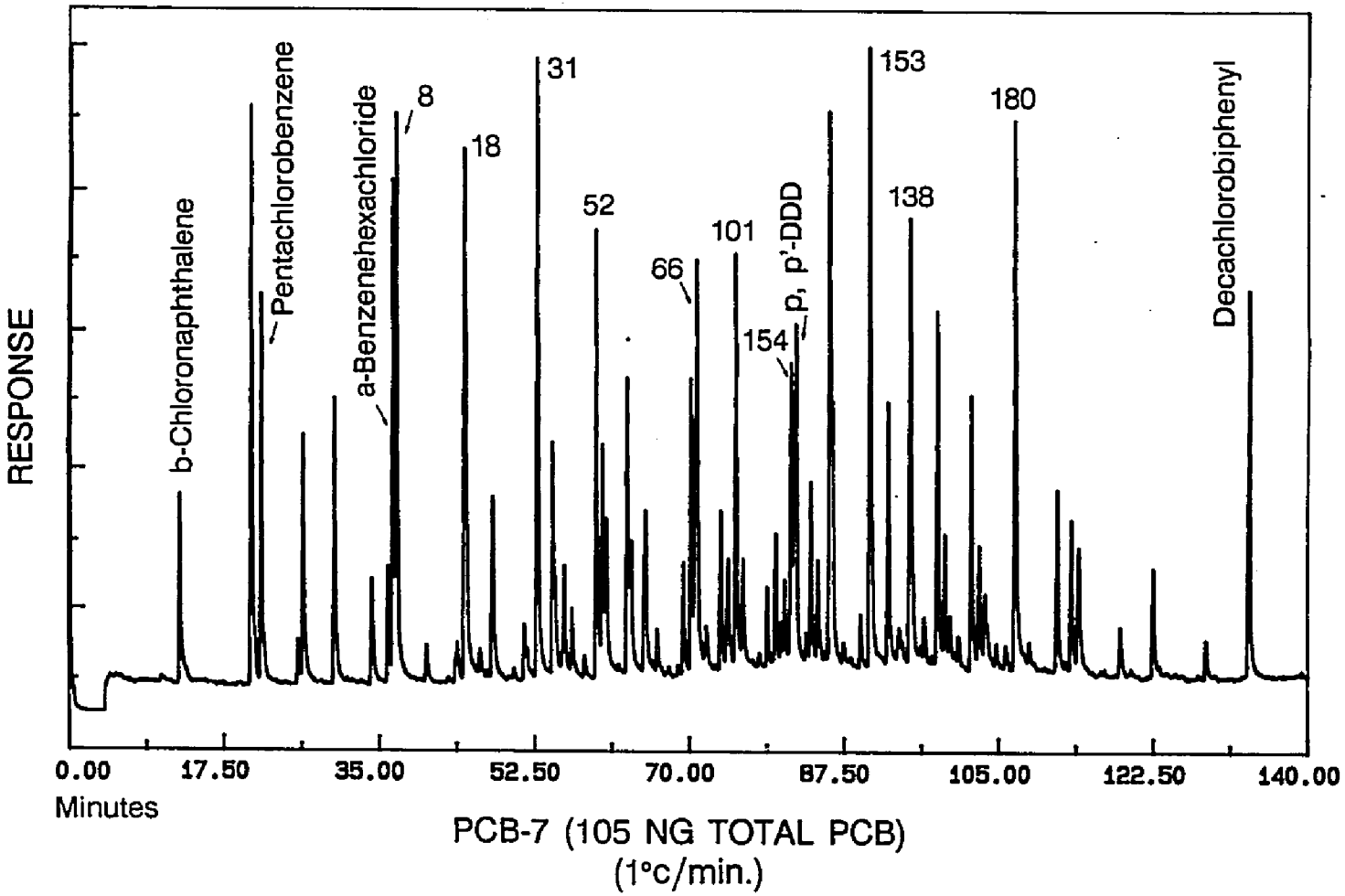
Most PCB congeners eluted between the 2000 and 4000 retention markers under both of the previously stated analytical conditions. Retention marker surrogates for the 2000, 3000 and 4000 retention markers consisted of congeners #8, #154 and #209 respectively. Each was chosen by its elution proximity to the Hall Retention Index (HRI) markers (a-BHC, o,p'-DDD and DCB) and to minimize differences between calculated and analytical indices.

Individual congener standards of the major peaks in the seven Aroclor composite, PCB-7, were chromatographed under the previously stated analytical conditions to reproduce retention data reported by Mullin et al. (1984). The selected individual congener standards were used to confirm the retention indices of specific congeners and to establish a basis for comparison of subsequent acquired retention data with data published.

A chromatogram of PCB-7 is shown in Figure 3 with HRI retention markers and CRI retention surrogates indicated. This chromatogram was run at $1^{\circ}C/$ min.

Table 2 lists major congeners in PCB-7 (IUPAC numbers in Figure 3). The calculated CRIs were acquired from a 50 meter column with an initial temperature of $100^{\circ}C$ (Mullin et al., 1984) and the analytical CRIs were acquired from a 30 meter column with an initial temperature

Figure 3. HECD Chromatogram of Aroclor Composite PCB-7 (1°C/min).



PCB-7 (105 NG TOTAL PCB)
(1°c/min.)

Table 2. Calculated and Analytical CRIs of Congener Standards Comprising Major Peaks in Aroclor Composite PCB-7. (Analytical Conditions: Temperature Program 1°C/ min.).

Congener #	Calc. CRI	Analytical CRI	Residuals
18	2167	2170	-3
31	2348	2352	-4
52	2497	2502	-5
66	2747	2751	-4
101	2850	2853	-3
153	3166	3167	-1
138	3254	3257	-3
180	3485	3487	-2

of 100°C. Again, the retention surrogates #8/#154/#209 were used to calculate the analytical CRIs. Residuals were calculated by the equation: Calculated CRI - Analytical CRI = Residual. The magnitudes of the residuals were considered to be indicators of the accuracy with which Mullin's retention data were reproduced. Inconsistencies between the two analytical systems would account for some of the deviation. The analytical run time to produce the analytical CRIs was 133 minutes which resulted in 21 retention index units per minute of run time (2.8 sec./ index unit) between congeners #8 and #209.

Table 3 repeats the analytical CRIs of the congener standards and lists the transposed experimental HRIs which are the retention indices of the congeners using a-BHC/o,p'-DDD/DCB as retention markers. Each data set was from the same chromatogram, only the retention markers were different.

Table 4 shows the retention indices from two chromatograms. However, both data sets were calculated using the a-BHC/o,p'-DDD/DCB retention index markers. The experimental HRI's were from a chromatogram temperature programmed at 1°C/ min. beginning at 100°C. The analytical HRI's were from a chromatogram temperature programmed at 4°C/ min. beginning at 90°C.

Residuals were calculated by the equation:
Experimental HRI - Analytical HRI = Residual. The magnitude of the residuals indicated that significant deviations occurred for congener indices below 2855.

Table 3. Analytical CRIs and Experimental HRIs of Congener Standards Comprising Major Peaks in Aroclor Composite PCB-7. (Analytical and Experimental Conditions: 1°C/min.).

CONGENER #	Analytical CRI	Experimental HRI
18	2170	2176
31	2352	2356
52	2502	2504
66	2751	2749
101	2853	2850
153	3167	3163
138	3257	3253
180	3487	3485

Table 4. Experimental and Analytical HRIs of Congener Standards Comprising Major Peaks in Aroclor Composite PCB-7. (Experimental GC Conditions: 1°C/min., Analytical GC Conditions: 4°C/ min.)

Congener #	Experimental HRI	Analytical HRI	Residuals
18	2176	2187	-11
31	2356	2374	-18
52	2504	2519	-15
66	2749	2762	-13
101	2850	2855	-5
153	3163	3161	+2
138	3253	3255	-2
180	3485	3483	+2

A comparison of the three tables shows that the largest differences occurred with the collection of the analytical HRI data. As was stated earlier, significant differences in retention data can occur between different temperature program rates. The decrease in initial temperature and faster program rate had a significant affect on the analytical HRIs.

Lee et al. (1979) have commented that the four retention markers must elute during the temperature program and that the first marker should elute 30°C to 40°C after the commencement of the temperature gradient. During the analytical HRI GC operating conditions, b-chloronaphthalene eluted about 18°C after the programmed 4°C/ min. gradient. An initial temperature of 90°C was required so that complete venting of the n-hexane solvent was performed. Incomplete venting of the solvent away from the detector will cause carbon fouling which reduces detector response and detection of closely eluting peaks. For this reason, an initial column temperature lower than 90°C was impractical. The 90°C initial temperature relative to the elution temperature of the early eluting congeners would account for some of the HRI deviation.

Determination of Congeners in Aroclors

The same method used to generate Tables 2, 3 and 4 was used to make congener designations for peak content in PCB-7. Where the higher temperature program rate was used, some of the peaks coeluted. This required an estimation of the major and minor components contained in some peaks.

Table 5 (analogous to Table 2) lists the calculated CRIs of each congener which eluted between congeners #8 and #209. Adjacent to the calculated CRIs are the analytical CRIs of the peaks which appear in a chromatogram of PCB-7. Both sets of CRIs were calculated using #8/#154/#209 as retention markers. The retention data from Mullin et al., (1984) indicated that 200 of the 209 possible congeners elute during this time period. Of the 200 theoretical congeners which elute during this window, 136 appeared in the chromatogram of PCB-7.

Table 6 is analogous to Table 3 for the Aroclor composite PCB-7. The experimental HRIs were calculated using the retention markers a-BHC/o,p'-DDD/DCB. Analytical CRIs and experimental HRIs were calculated from the same chromatogram ($1^{o}C$/ min.), the only difference was the retention markers employed in the calculation.

Figure 4 is a chromatogram of PCB-7 temperature programmed at $4^{o}C$/ min. The data acquired from this chromatogram were used to calculate analytical HRIs.

Table 7 is a compilation of experimental HRIs acquired by temperature programming at $1^{o}C$/ min. and the analytical HRIs acquired at $4^{o}C$/min. This table is analogous to Table 4, however, additional congener standards were run separately to aid in the discrimination of certain peaks. All congener standards are indicated with an asterisks. The analytical HRIs of all congener standards are indicated in parentheses. Thirty-one congener standards were run under the analytical HRI chromatographic conditions ($4^{o}C$/ min.). Residuals were calculated as in Table 4.

Table 5. Calculated and Analytical CRIs of Chromatographic Peaks in Aroclor Composite PCB-7. (+ = Not Observed, SRM = Surrogate Retention Marker).

	Congener #	Calc. CRI	Anal. CRI	CRI Res.
SRM Major Peak	8	2000	2000	
	14	2053	+	
	19	2073	2076	-3
	30	2107	+	
	11	2127	2131	-4
	12	2144	2148	-4
	13	2149	2153	-4
Major Peak	*18	2167	2170	-3
	15	2169	"	-3
	17	2172	2174	-2
	24	2203	+	
	27	2207	2210	-3
	16	2236	2242	-6
	32	2239	"	-3
	23	2276	+	
	34	2280	2282	-2
	54	2285	"	+3
	29	2291	2295	-4
	26	2316	2321	-5
	25	2323	2328	-5
	50	2343	+	
Major Peak	*31	2348	2354	-6
	28	2350	"	-6
	21	2379	+	
	33	2387	2392	-5
	20	2389	"	-3
	53	2394	2398	-4
	51	2409	2416	-7
	22	2416	2422	-6
	45	2435	2441	-6
	36	2446	+	
	46	2467	2472	-5
	39	2478	2483	-5
	69	2484	2483	+1
	73	2496	2502	-6
Major Peak	*52	2497	"	-5
	43	2506	+	
	38	2507	+	

Table 5 (continued)

	Congener #	Calc. CRI	Anal. CRI	CRI Res.
	49	2512	2517	-5
	47	2520	2527	-7
	75	2521	"	-6
	48	2524	2527	-3
	65	2529	"	-3
	62	2533	+	
	35	2548	2549	-1
	104	2553	2558	-5
	44	2574	2580	-6
	37	2582	2586	-4
	59	2582	2586	-4
	42	2585	2588	-3
	72	2617	2623	-6
	71	2618	"	-5
	41	2619	2626	-7
	64	2621	"	-5
	68	2633	+	
	96	2638	2640	-2
	40	2650	2656	-6
	103	2661	2665	-4
	57	2665	"	0
	100	2681	2685	-4
	67	2682	"	-3
	58	2696	2701	-5
	63	2703	2708	-5
	61,94	2714	2722	-8
	74	2717	"	-5
	70,76	2736	2740	-6
	98	2738	2740	-2
	102	2742	+	
	93	2744	2752	-8
	*66	2747	"	-5
Major Peak	80,95	2752	2756	-4
	88	2758	+	
	121	2767	+	
	91	2776	2780	-4
	55	2779	"	-1
	155	2808	2799	-9
	60,56	2811	2815	-4
	92,84	2830	2834	-4
	89	2840	+	

Table 5 (continued)

	Congener #	Calc. CRI	Anal. CRI	CRI Res.
Major Peak	90,101*	2850	2853	-3
	113	2863	+	
	99	2868	2871	-3
	79	2872	+	
	119,150	2893	2895	-2
	112	2898	+	
	109	2906	+	
	78	2909	2913	-4
	83	2910	"	-3
	152	2919	+	
	97	2930	2932	-2
	86	2932	"	-2
	116	2939	+	
	125	2942	+	
	145,81, 117	2944	+	
	115	2950	2954	-4
	87	2951	"	-3
	111	2953	"	-1
	85	2965	2968	-3
	148	2970	"	-2
	120,136	2974	2977	-3
	77	2985	+	
	110	2990	2992	-2
SRM	*154	3000	3000	
	82	3025	3027	-2
	151	3036	3037	-1
	135,144	3052	3052	0
	124	3057	+	
	147	3062	+	
	108,107	3067	3068	-1
	123	3074	+	
Major Peak	149	3078	3079	-1
	106	3080	"	+1
	118	3083	3084	-1
	139,140	3086	+	
	143	3106	3109	-3
	134	3108	"	-1
	114	3116	3117	-1
	142	3120	"	+3

Table 5 (continued)

	Congener #	Calc. CRI	Anal. CRI	CRI Res.
	131	3122	+	
	122,133	3126	3125	+1
	165,188	3138	3137	+1
	146	3146	3146	0
	161	3149	"	+3
	184	3161	+	
	132	3165	3166	-1
Major Peak	*153	3166	"	0
	105	3169	"	+3
	168	3173	+	
	127	3176	+	
	141	3206	3206	0
	179	3209	"	+3
	130	3225	+	
	176	3231	3231	0
	137	3236	3237	-1
	160,163	3252	+	
	164	3253	+	
Major Peak	*138	3254	3255	-1
	186	3257	3260	-3
	158	3260	"	0
	129	3278	3278	0
	126	3280	"	+2
	178	3286	3286	0
	166	3295	+	
	175	3304	3303	+1
Major Peak	182	3314	3314	0
	187,159	3315	"	+1
	183	3331	3330	+1
	162	3335	+	
	128	3340	3342	-2
	167	3353	3353	0
	185	3361	3361	0
	174,181	3390	3389	+1
	177	3406	3406	0
	171,202	3420	3419	+1
	156	3423	3424	-1
	173	3435	+	
	157	3442	3444	-2
	200	3446	"	-2

Table 5 (continued)

	Congener #	Calc. CRI	Anal. CRI	CRI Res.
	204	3450	+	
	192	3463	3465	-2
	172	3465	"	0
	197	3469	+	
Major Peak	*180	3485	3486	-1
	193	3494	+	
	191	3506	+	
	199	3517	3517	0
	169	3549	3550	-1
	170,190	3576	3578	-2
	198	3602	3596	-4
	201	3609	3609	0
	196,203	3624	3625	-1
	189	3673	3676	-3
	208	3716	3718	-2
	195	3717	"	-1
	207	3741	3741	0
	194	3789	3790	-1
	205	3802	3803	-1
	206	3905	3906	-1
SRM	*209	4000		4000

Table 6. Analytical CRIs and Experimental HRIs of Chromatographic Peaks in Aroclor Composite PCB-7. (+ = Not Observed, SRM = Surrogate Retention Marker).

Retention Std.	Congener #	Anal. CRI	Exp. HRI
a-BHC			2000
SRM Major Peak	8	2000	2009
	14	+	+
	19	2076	2084
	30	+	+
	11	2131	2138
	12	2148	2155
	13	2153	2160
Major Peak	*18	2170	2177
	15	"	"
	17	2174	2181
	24	+	+
	27	2210	2216
	16	2242	2247
	32	"	"
	23	+	+
	34	2282	2288
	54	"	"
	29	2295	2300
	26	2321	2326
	25	2328	2332
	50	+	+
Major Peak	*31	2354	2358
	28	"	"
	21	+	+
	33	2392	2395
	20	"	"
	53	2398	2398
	51	2416	2416
	22	2422	2422
	45	2441	2444
	36	+	+
	46	2472	2475
	39	2483	2485
	69	"	"
	73	2502	2504

Table 6 (continued)

Retention Std.	Congener #	Anal. CRI	Exp. HRI
Major Peak	*52	"	"
	43	+	+
	38	+	+
	49	2517	2519
	47	2527	2527
	75	"	"
	48	"	"
	65	+	+
	62	+	+
	35	+	+
	104	2558	2559
	44	2580	2580
	37	2586	2588
	59	"	"
	42	2588	2590
	72	2623	2624
	71	"	"
	41	2626	2626
	64	"	"
	68	+	+
	96	2640	2640
	40	2656	2656
	103	2665	2664
	57	"	"
	100	2685	2685
	67	"	"
	58	2701	2701
	63	2708	2707
	61,94	2722	2721
	74	"	"
	70,76	2740	2738
	98	"	"
	102	+	+
	93	2752	2752
	*66	"	"
Major Peak	80,95	2756	2754
	88	+	+
	121	+	+
	91	2780	2777
	55	"	"

Table 6 (continued)

Retention Std.	Congener #	Anal. CRI	Exp. HRI
	155	2799	2797
	60,56	2815	2813
	92,84	2834	2831
	89	+	+
Major Peak	90,101*	2853	2850
	113	+	+
	99	2871	2868
	79	+	+
	119,150	2895	2891
	112	+	+
	109	+	+
	78	2913	2909
	83	"	"
	152	+	+
	97	2932	2928
	86	"	"
	116	+	+
	125	+	+
	145.81,117	+	+
	115	2954	2949
	87	"	"
	111	"	"
	85	2968	2963
	148	"	"
	120,136	2977	2972
	77	+	+
	110	2992	2987
SRM	*154	3000	2995
o,p'-DDD			3000
	82	3027	3023
	151	3037	3033
	135,144	3052	3048
	124	+	+
	147	+	+
	108,107	3068	3064
	123	+	+
Major Peak	149	3079	3075
	106	"	"

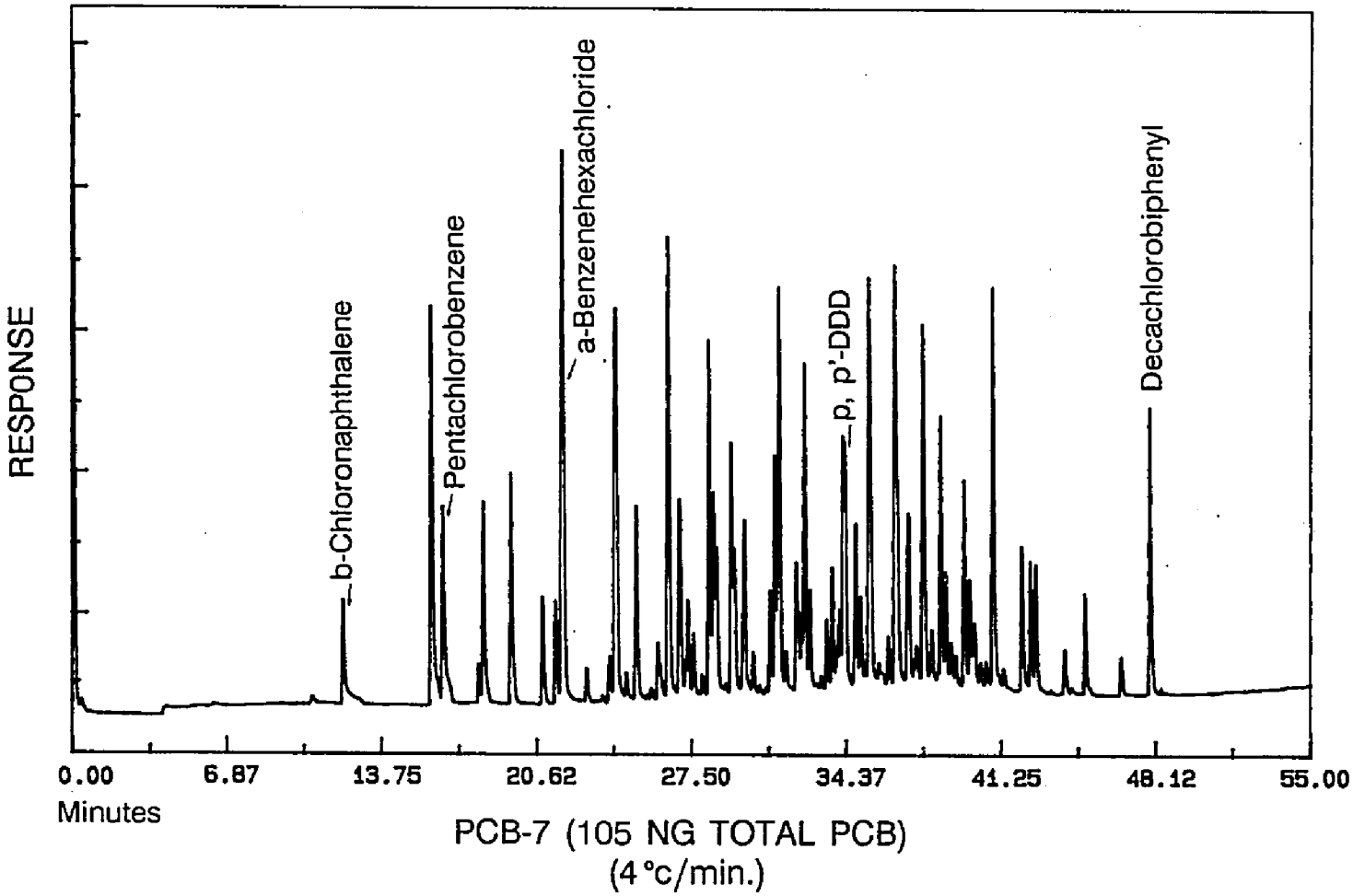
Table 6 (continued)

Retention Std.	Congener #	Anal. CRI	Exp. HRI
	118	3084	3080
	139,140	+	+
	143	3109	3105
	134	"	"
	114	3117	3113
	142	"	"
	131	+	+
	122,133	3125	3121
	165,188	3137	3133
	146	3146	3143
	161	"	"
	184	+	+
	132	3166	3162
Major Peak	*153	"	"
	105	"	"
	168	+	+
	127	+	+
	141	3206	3203
	179	"	"
	130	+	+
	176	3231	3228
	137	3236	3234
	160,163	+	+
	164	+	+
Major Peak	*138	3255	3252
	186	3260	3257
	158	"	"
	129	3278	3275
	126	"	"
	178	3286	3282
	166	+	+
	175	3303	3300
Major Peak	182	3314	3311
	187,159	"	"
	183	3330	3327
	162	+	+
	128	3342	3339
	167	3353	3350
	185	3361	3358

Table 6 (continued)

Retention Std.	Congener #	Anal. CRI	Exp. HRI
	174,181	3389	3386
	177	3406	3403
	171,202	3419	3417
	156	3424	3421
	173	+	+
	157	3444	3442
	200	"	"
	204	+	+
	192	3465	3463
	172	"	"
	197	+	+
Major Peak	*180	3486	3483
	193	+	+
	191	+	+
	199	3517	3515
	169	3550	3548
	170,190	3578	3576
	198	3596	3594
	201	3609	3608
	196,203	3625	3624
	189	3676	3674
	208	3718	3717
	195	"	"
	207	3741	3740
	194	3790	3789
	205	3803	3802
	206	3906	3906
SRM/DCB	*209	4000	4000

Figure 4. HECD Chromatogram of Aroclor Composite PCB-7 (4°C/min).



PCB-7 (105 NG TOTAL PCB)
(4 °c/min.)

Table 7. Experimental and Analytical HRIs of Chromtographic Peaks in Aroclor Composite PCB-7. (+ = Not Observed, SRM = Surrogate Retention Marker).

Retention Std.	Congener #	Exp. HRI	Anal. HRI	Congener Std. HRI	CRI Res.
a-BHC		2000	2000		
SRM Major Peak	8	2009	2000		+9
	14	+	+		
	19	2084	2086		-2
	30	+	+		
	*11	2138	2143	(2140)	-5
	12	2155	2168		-13
	13	2160	"		-8
Major Peak	*18	2177	2184	(2187)	-7
	15	"	"		"
	17	2181	2189		-8
	24	+	+		
	27	2216	2227		-11
	16	2247	2261		-14
	32	"	"		"
	23	+	+		
	34	2288	2301		-13
	54	"	"		"
	*29	2300	2315	(2316)	-15
	26	2326	2338		-12
	25	2332	2345		-13
	*50	+	+	(2361)	
Major Peak	*31	2358	2374	(2374)	-16
	28	"	"		"
	21	+	+		
	*33	2395	2414	(2414)	-19
	20	"	"		"
	53	2398	"		
	51	2416	2444		-28
	22	2422	"		-22
	45	2444	2464		-20
	36	+	+		
	46	2475	2495		-20
	39	2485	"		-10
	69	"	"		"
	73	2504	2519		-15
Major Peak	*52	"	"	(2519)	"
	43	+	+		

Table 7 (continued)

Retention Std.	Congener #	Exp. HRI	Anal. HRI	Congener Std. HRI	CRI Res.
	38	+	+		
	*49	2519	2534	(2536)	-15
	*47	2527	2546	(2548)	-19
	75	"	"		"
	48	"	"		"
	65	+	+		
	62	+	+		
	35	+	+		
	104	2559	2578		-19
	*44	2580	2597	(2601)	-17
	37	2588	2608		-20
	59	"	"		"
	42	2590	"		-18
	72	2624	+		
	71	"	+		
	41	2626	2644		-18
	64	"	"		"
	68	+	+		
	96	2640	2659		-19
	*40	2656	2674	(2675)	-18
	103	2664	2699		-25
	57	"	"		"
	100	2685	+		
	67	"	+		
	58	2701	+		
	63	2707	2721		-14
	61,94	2721	2735		-14
	74	"	"		"
	*70,76	2738	2751	(2752)	-13
	98	"	"		"
	102	+	+		
	93	2752	2766		-14
	*66	"	"	(2762)	"
Major Peak	80,95	2754	+		
	*88	+	+	(2771)	
	*121	+	+	(2777)	
	91	2777	2791		-14
	55	"	"		"
	155	2797	2827		-30
	*60,56	2813	"	(2827)	-14

Table 7 (continued)

Retention Std.	Congener #	Exp. HRI	Anal. HRI	Congener Std. HRI	CRI Res.
	92,84	2831	+		
	89	+	+		
Major Peak	90,101*	2850	2857	(2855)	-7
	113	+	+		
	99	2868	2876		-8
	79	+	+		
	119,150	2891	2899		-8
	112	+	+		
	109	+	+		
	78	2909	2917		-8
	83	"	"		"
	152	+	+		
	97	2928	2936		-8
	86	"	"		"
	116	+	+		
	125	+	+		
	145,81,117	+	+		
	115	2949	2956		-7
	87	"	"		"
	111	"	"		"
	85	2963	2971		-8
	148	"	"		"
	120,136*	2972	2980	(2979)	-8
	*77	+	+	(2989)	
	110	2987	2993		-6
SRM	*154	2995	3000	(3000)	-5
o,p'-DDD		3000	3000		
	82	3023	3036		-13
	151	3033	"		-3
	135,144	3048	3052		-4
	124	+	+		
	147	+	+		
	108,107	3064	3067		-3
	123	+	+		
Major Peak	149	3075	3078		-3
	106	"	"		"
	118	3080	"		+2
	139,140	+	+		
	143	3105	3112		-7
	134	"	"		"

Table 7 (continued)

Retention Std.	Congener #	Exp. HRI	Anal. HRI	Congener Std. HRI	CRI Res.
	146	3143	3142		+1
	114	3113	+		
	142	"	"		"
	131	+	+		
	122,133	3121	3120		+1
	165,188	3133	+		
	146	3143	3142		+1
	161		"		"
	184	+	+		
	132	3162	3163		-1
Major Peak	*153	"	"	(3161)	"
	*105	"	"	(3167)	
	168	+	+		
	127	+	+		
	141	3203	3208		-5
	179	"	"		"
	130	+	+		
	176	3228	3235		-7
	137	3234	"		-1
	160,163	+	+		
	164	+	+		
Major Peak	*138	3252	3255	(3255)	-3
	186	3257	+		
	*158	"	+	(3263)	
	129	3275	3284		-9
	126	"	"		"
	178	3282	"		-2
	166	+	+		
	175	3300	3302		-2
Major Peak	182	3311	3312		-1
	187,159	"	"		"
	183	3327	3329		-2
	162	+	+		
	128	3339	3346		-7
	*167	3350	"	(3353)	+4
	*185	3358	3363	(3362)	-5
	174,181	3386	3390		-4
	177	3403	3408		-5
	171,202	3417	3422		-5

Table 7 (continued)

Retention Std.	Congener #	Exp. HRI	Anal. HRI	Congener Std. HRI	CRI Res.
	156	3421	"		-1
	173	+	+		
	192	3463	3462		+1
	172	"	"		"
	197	+	+		
Major Peak	*180	3483	3483	(3483)	0
	193	+	+		
	191	+	+		
	199	3515	3521		-6
	*169	3548	+	(3557)	
	170,190	3576	3580		-4
	198	3594	3595		-1
	201	3608	3608		0
	196,203	3624	3625		-1
	189	3674	3675		-1
	208	3717	3721		-4
	195	"	"		"
	*207	3740	3742		-2
	194	3789	3787	(3788)	+2
	205	3802	3801		+1
	206	3906	3905	(3905)	+1
SRM/DCB	*209	4000	4000		

Experimental and analytical HRIs were calculated using the a-BHC/o,p'-DDD/DCB retention markers. Figure 5 is a plot of the experimental HRIs on the horizontal axis and the analytical HRIs on the vertical axis. Good agreement was found between these two sets of retention data with minor deviations at the lower index numbers.

There were 78 analytical HRIs between the 2000 and 4000 retention markers which accounted for 136 congeners. The total of all analytical HRIs between the 1000 and 4000 retention markers was 86, accounting for 145 congeners.

Table 8 lists the complete set of retention indices resulting from the calculation of analytical HRIs for the entire range of PCB congener peaks which appear in PCB-7. The table was compiled in the order of elution from the SE-54 capillary column. A shorter run time of 48 min. resulted in 77 retention index units / min. (0.8 sec./ index unit) between the a-BHC and DCB retention markers.

A recent publication by Schulz et al. (1989) reports the congener contents of Aroclors 1016, 1242, 1254 and 1260 using Multi-Dimensional Gas Chromatography with Electron-Capture Detection (MDGC/ECD). This analytical technique employes two capillary columns with different stationary phases to resolve all 209 PCB congeners. The congeners reported by Schulz et al. (1989) were compared with the congeners listed in Table 7 and good agreement was noted except for minor peaks (<1.0% total congener contribution).

Figure 5. Plot of Analytical HRIs with Respect to Experimental HRIs of Peaks in Aroclor Composite PCB-7.

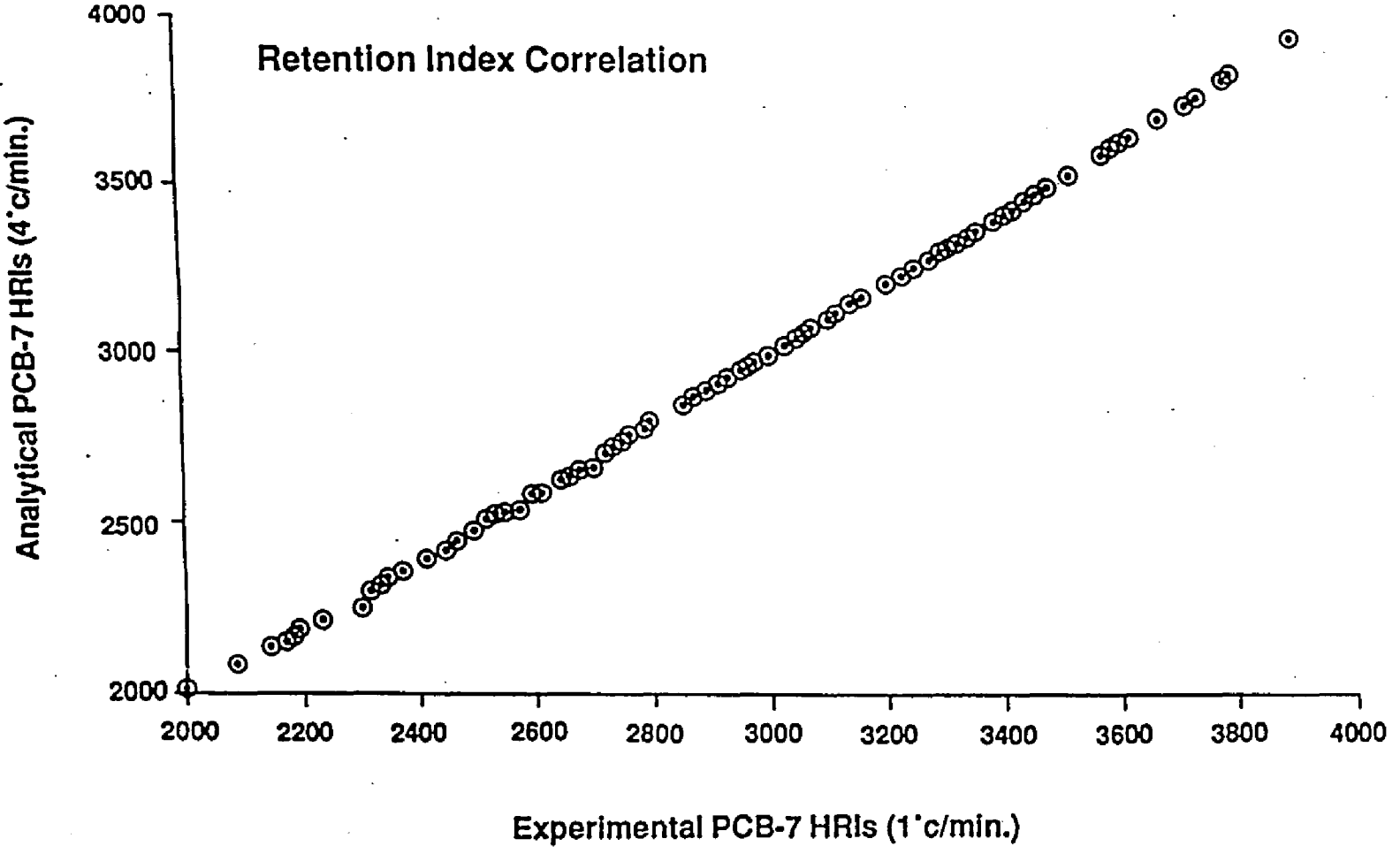

Retention Index Correlation
Analytical PCB-7 HRIs (4°c/min.)
Experimental PCB-7 HRIs (1°c/min.)
4000
3500
3000
2500
2000
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000

Table 8. Analytical HRIs of Chromatographic Peaks in Aroclor Composite PCB-7.

Congener/Ret. Std.	HRI
b-CHLORONAPHTHALENE	1000
1	1405
2	1620
3	1643
4,10	1770
7,9	1913
6	1973
a-BHC	2000
8,5	2000
19	2086
11	2143
12,13	2168
18,15	2184
17	2189
27	2227
16,32	2261
34,54	2301
29	2315
26	2338
25	2345
31,28	2374
33,20,53	2414
51,22	2444
45	2464
46,39,69	2495
73,52	2519
49	2534
47,74,48	2546
104	2578
44	2597
37,59,42	2608
41,64	2644
96	2659
40	2674
103,57	2699
63	2721
61,94,74	2735
70,76,98	2751
93,66	2766
91,55	2791
155,60,56	2827
90,101	2857
99	2876
119,150	2899
78,83	2917

Table 8 (continued)

```
    97,86              2936
    115,87,111         2956
    85,148             2971
    120,136            2980
    110                2993
o,p'-DDD/154           3000
    82,151             3036
    135,144            3052
    108,107            3067
    149,106            3078
    118                3084
    143,134            3112
    122,133            3120
    146,161            3142
    132,153            3163
    105                3167
    141,179            3208
    176,137            3235
    138                3255
    129,126,178        3284
    175                3302
    182,187,159        3312
    183                3329
    128,167            3346
    185                3363
    174,181            3390
    177                3408
    171,202,156        3422
    157,200            3445
    192,172            3462
    180                3483
    199                3521
    170,190            3580
    198                3595
    201                3608
    196,203            3625
    189                3675
    208,195            3721
    207                3742
    194                3787
    205                3801
    206                3905
    209    DCB         4000
```

Precision of Retention Data

Table 8 is the foundation upon which all subsequent peak identifications were made. The precision of retention indices was demonstrated by Lee et al. (1979) with a multiple retention marker system. Lee found the precision of polyaromatic hydrocarbons indices with this system was ± 0.25 index units based on retention increments of 100. This value would then be ± 2.5 index units based on retention increments of 1000. Retention index precision is valuable if the limit of resolution is also known.

Retention indices in this study were calculated to the whole integer. A review of closely eluting peaks in the chromatogram of PCB-7, run at $1^{\circ}C$/ min., indicated a limit of resolution of 3-4 index units. PCB-7 run at $4^{\circ}C$/ min. indicated a limit of resolution of 6-7 index units. It was, therefore, considered unnecessary to calculate indices to less than a whole integer.

The Aroclor composite, PCB-3, consisting of Aroclors 1242, 1254 and 1260 in equal weight was analyzed once each day for ten non-consecutive days. This was performed to determine the variability of the retention data over an extended period of time. The major congeners from Tables 2, 3 and 4 were detected in each analysis and for each congener the standard deviations over the twelve days was less than or equal to ± 1 retention unit. Table 9 lists the analytical HRIs of the major congeners for each of the ten days and the standard deviations of the HRIs over that period.

Table 9. Analytical HRIs of Major Peaks in PCB-3 During Ten Non-Consecutive Days (Standard Deviation less than ± 1 Retention Index Unit).

Day	1	2	3	4	5
CONGENER #					
18	2188	2188	2189	2188	2188
31	2376	2376	2377	2376	2377
52	2519	2520	2520	2519	2520
66	2767	2767	2767	2766	2767
101	2857	2857	2857	2856	2857
153	3162	3163	3162	3163	3162
138	3255	3255	3255	3255	3255
180	3484	3484	3483	3484	3483

Day	6	7	8	9	10	std. deviation
CONGENER #						
18	2188	2188	2188	2188	2188	0.3
31	2376	2377	2376	2376	2376	0.5
52	2520	2520	2519	2520	2520	0.5
66	2767	2767	2767	2767	2767	0.3
101	2857	2857	2857	2857	2857	0.3
153	3162	3162	3162	3162	3163	0.5
138	3255	3255	3255	3255	3255	0
180	3483	3483	3483	3483	3483	0.5

CHAPTER III

PCB CONGENER ANALYSIS-DETECTION

INTRODUCTION

Hall Electrolytic Conductivity Detector (HECD)

The Hall detector has been used for the analysis of purgeable halocarbons and, to a lesser degree, PCB analysis of environmental samples. Federal agencies such as the U.S. Environmental Protection Agency and the U.S. Food and Drug Administration recognize GC/HECD as acceptable instrumentation for the analysis of chlorinated compounds.

The principals for operation of the Hall detector are simple and straight forward. Compounds eluting from a capillary column are transferred into a nickel reaction tube which is flushed with hydrogen. The reaction tube is heated to 950^{o}C or greater. All compounds entering the reaction tube are pyrolyzed to the basic elements and catalytically reduced.

The reduced pyrolytic products are transferred to the electrolytic conductivity cell. Electrolyte is pumped from a reservoir to the cell block were pyrolytic products and electrolyte are mixed in the gas-liquid contactor. Dissociations of the acidic hydrogenhalides increases the conductance of the cell current and a response is recorded on a chart recorder.

Investigations into the pyrolytic efficiency of the HECD have been performed by Ramus and Thomas (1985) of Oregon State University. The pyrolytic efficiency of the Hall detector reactor was studied by interfacing the reactor/reaction tube assembly with a mass spectrometer and monitoring the mass of the parent compound at different reactor temperatures. Twelve standards were tested including one Aroclor. A reactor temperature of 950^{o}C was determined as a minimum setting for complete pyrolysis. This information is fundamental to the application of the Hall detector for predicting responses of compounds when analyzing multiple residues in environmental samples.

Lopez-Avila and Northcutt (1982) have reported that the response of the Hall detector is roughly proportional to the organic chlorine content of a compound. The responses of chloroanilines were moderately similar for the same chlorine content. Chloronitroaniline responses were more consistent and predictable for compounds containing one and two chlorines. The reactor temperature during these experiments was, however, less than the optimum temperature for complete pyrolysis as shown by Ramus and Thomas (1985). This would result in response factors applicable at the specified reactor temperature.

The purpose of the following study was to investigate the responses of the Hall detector to the different PCB homolog classes and develop methodology for the accurate quantification of PCB congeners. This method would then be used to determine homolog

distributions of standard Aroclors which could be compared with distributions reported by other researchers.

MATERIALS AND METHODS

Standards

Aroclor standards were acquired from the U.S. Environmental Protection Agency Pesticides and Industrial Chemicals Repository, Research Triangle Park, North Carolina. The Aroclors included 1016, 1221, 1232, 1242, 1248, 1254, 1260 and 1262. Stock standards of each were prepared at 5000 ug/ml with subsequent dilution to 50 ug/ml for working standards. All standards were made with Burdick & Jackson n-hexane.

Three Aroclor composites equal by weight were made and consisted of Aroclors 1242/1254, Aroclors 1254/1260 and Aroclors 1242/1254/1260. The total PCB concentrations of these standards were 50 ug/ml, 50 ug/ml and 30 ug/ml respectively.

Selected individual tetrachloro- and hexachloro- congener standards were purchased from Ultra Scientific, Inc. A standard with five tetrachlorobiphenyls (IUPAC numbers 40, 50, 54, 70, and 77) and a standard with five hexachlorobiphenyls (IUPAC numbers 138, 153, 154, 158 and 167) were prepared such that each congener in each standard was at a final concentration of 1.0 ug/ml.

A DCMA standard or Dry Color Manufacturers Association standard was also purchased from Ultra Scientific, Inc. This solution contained ten congeners (IUPAC numbers 1, 11, 29, 47, 121, 136, 185, 194, 206 and 209) each possessing a different number of chlorines and

present in different concentrations. A 1:10 dilution was performed to acquire the working standard.

Instrumentation

Detector modifications were necessary to reduce the dead volume between the capillary column and the conductivity cells, thereby preserving the peak shape of the compounds which eluted from the column. A capillary column detector adapter from Alltech Associates (Deerfield, IL) was installed after silver soldering the accompanying tee to the adapter tube. The reaction tube was 1/16" O.D. x 0.020" I.D. nickel 200 tubing acquired from Alltech Associates. The teflon transfer tube was 1.5 mm O.D. x 0.3 mm I.D. teflon tubing purchased from Supelco, Inc. (Bellefonte, PA).

The small diameter nickel and teflon tubing effectively reduced the dead volume between the end of the capillary column and the conductivity cell such that a path of reasonably unform internal diameter was achieved.

Identification and Quantification

Identification and quantification was performed by a Hewlett-Packard 3354 Laboratory Data System. Four retention markers were coinjected with the congener standards and Aroclors for the calculation of each Hall Retention Index (HRI). The method of identification of congeners was described previously. The retention markers and their assigned indices were b-chloronaphthalene (1000), a-BHC (2000), o,p'-DDD (3000) and decachlorobiphenyl (4000).

A response standard, pentachlorobenzene (PtCB), was coinjected with the standards to normalize the response of each congener to the response standard. Ten normalization factors were calculated for the ten homolog classes. These factors were calculated as follows:

$$\frac{\dfrac{\text{X g/mole Cl in congener y}}{\text{X g/mole of congener y}}}{\dfrac{\text{177 g/mole Cl in ptCB}}{\text{250 g/mole ptCB}}} = \text{Normalization Factor}$$

The normalization factors used for mono- through decachlorobiphenyl were 0.26, 0.45, 0.58, 0.68, 0.77, 0.83, 0.89, 0.93, 0.97 and 1.00.

The chlorine content of PCB chromatographic peaks can be determined by isotope ratios of the molecular ions with chemical ionization mass spectrometry (CI/MS). Onuska, Kominar and Terry (1983) have determined the chlorine content of the chromatographic peaks in a mixture of Aroclors 1242, 1254 and 1260 using this technique. The capillary column and carrier gas were the same as in this study although the GC temperature program was slightly different. Integration of this information with retention data provided the estimation of the chlorine content of chromatographic peaks for subsequent response factor assignments (Table 10).

The quantification of a congener identified in a standard was calculated as follows:

$$\frac{\dfrac{\text{Area cts congener y}}{\text{Area cts ptCB per 1 ng}}}{\text{Normalization factor for congener y}} = \text{ng of congener y}$$

Table 10. Analytical HRIs of Chromatographic Peaks in Aroclors 1221, 1232, 1242, 1248, 1254, 1260 and 1262 with Chlorine Content and Response Factor Assignments. (R.F. = Response factor).

Congener/Ret. Std.	HRI	Chlorine #	R.F.
b-CHLORONAPHTHALENE	1000		
1	1405	1	0.26
2	1620	1	0.26
3	1643	1	0.26
4,10	1770	2	0.45
7,9	1913	2	0.45
6	1973	2	0.45
a-BHC	2000		
8,5	2000	2	0.45
19	2086	3	0.58
11	2143	2	0.45
12,13	2168	2	0.45
18,15	2184	3	0.58
17	2189	3	0.58
27	2227	3	0.58
16,32	2261	3	0.58
34,54	2301	3	0.58
29	2315	3	0.58
26	2338	3	0.58
25	2345	3	0.58
31,28	2374	3	0.58
33,20,53	2414	3	0.58
51,22	2444	3	0.58
45	2464	4	0.68
46,39,69	2495	4	0.68
73,52	2519	4	0.68
49	2534	4	0.68
47,74,48	2546	4	0.68
104	2578	5	0.77
44	2597	4	0.68
37,59,42	2608	4	0.68
41,64	2644	4	0.68
96	2659	5	0.77
40	2674	4	0.68
103,57	2699	5	0.77
63	2721	4	0.68
61,94,74	2735	4	0.68
70,76,98	2751	4	0.68
93,66	2766	4	0.68

Table 10 (continued)

Congener/Ret. Std.	HRI	Chlorine #	R.F.
91,55	2791	5	0.77
155,60,56	2827	4	0.68
90,101	2857	5	0.77
99	2876	5	0.77
119,150	2899	5	0.77
78,83	2917	5	0.77
97,86	2936	5	0.77
115,87,111	2956	5	0.77
85,148	2971	5	0.77
120,136	2980	6	0.83
110	2993	5	0.77
o,p'-DDD/154	3000		
82,151	3036	6	0.83
135,144	3052	6	0.83
108,107	3067	5	0.77
149,106	3078	6	0.83
118	3084	5	0.77
143,134	3112	6	0.83
122,133	3120	5	0.77
146,161	3142	6	0.83
132,153	3163	6	0.83
105	3167	5	0.77
141,179	3208	6	0.83
176,137	3235	7	0.89
138	3255	6	0.83
129,126,178	3284	7	0.89
175	3302	7	0.89
182,187,159	3312	7	0.89
183	3329	7	0.89
128,167	3346	6	0.83
185	3363	7	0.89
174,181	3390	7	0.89
177	3408	7	0.89
171,202,156	3422	7	0.89
157,200	3445	8	0.93
192,172	3462	7	0.89
180	3483	7	0.89
199	3521	8	0.93
170,190	3580	7	0.89
198	3595	8	0.93
201	3608	8	0.93

Table 10 (continued)

Congener/Ret. Std.	HRI	Chlorine #	R.F.
196,203	3625	8	0.93
189	3675	7	0.89
208,195	3721	9	0.97
207	3742	9	0.97
194	3787	8	0.93
205	3801	8	0.93
206	3905	9	0.97
209 DCB	4000	10	1.00

RESULTS AND DISCUSSION

Assumptions

At the onset of the method development, two assumptions were made about the function of the Hall detector.

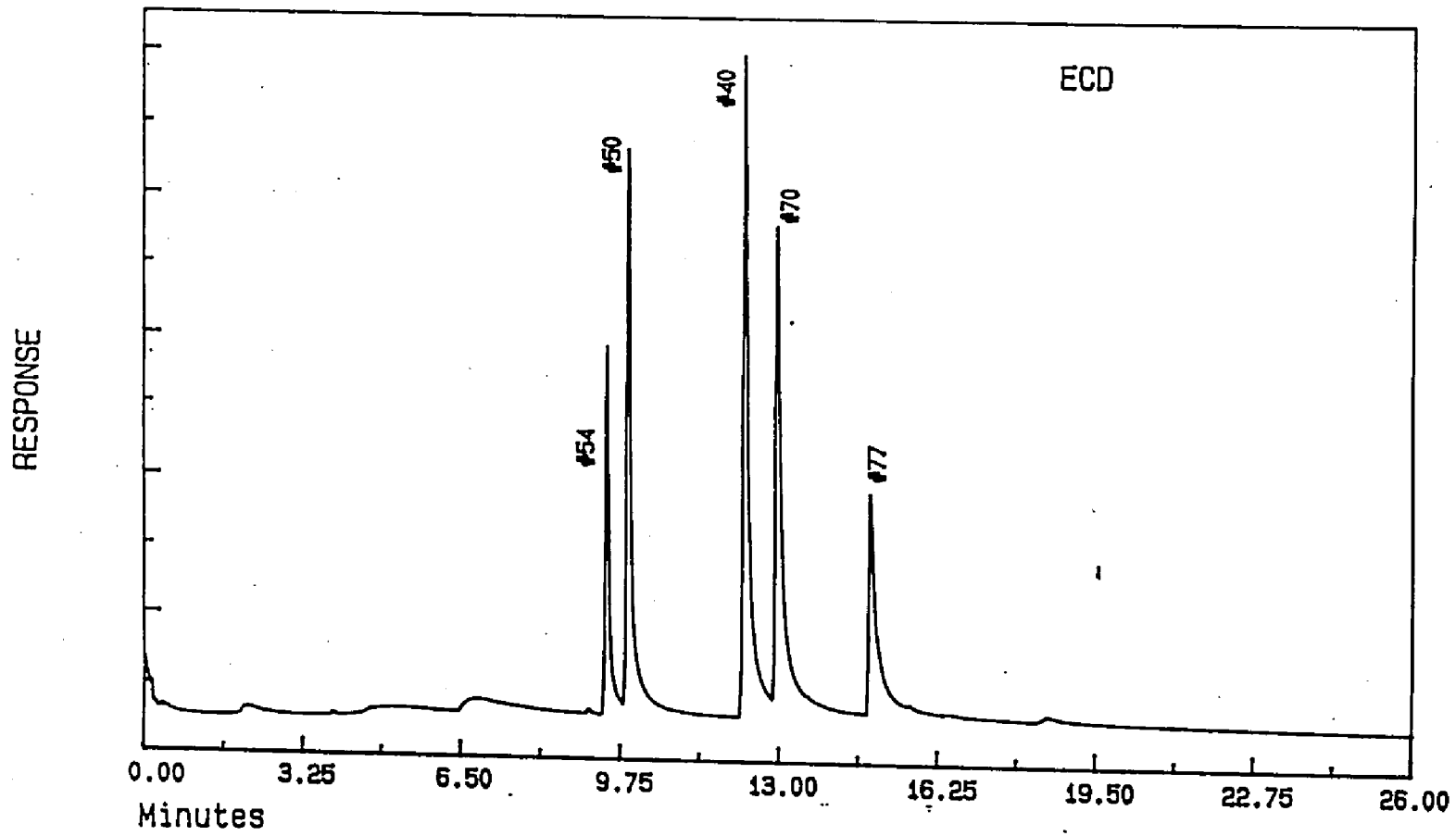
The first assumption was that the mass transfer efficiency of the PCBs in the GC injection port to the capillary column was equivalent within and among homolog groups for any given standard injected. Selective mass transfer of congeners could bias the distribution patterns of Aroclor standards.

Also, the pyrolytic and catalytic reduction efficiencies were assumed to be equivalent within homolog groups during each analysis.

ECD Response-PCB Congeners

As was mentioned earlier, one of the characteristics of the ECD is the disproportionate response between congeners with the same degree of chlorination. The ECD homolog group response is variable over a wide range and requires the use of specific response factors for each congener. Figure 6 is a chromatogram of five tetrachlorobiphenyls using an ECD (IUPAC congener numbers adjacent to each peak). The responses were different even though the weights of the materials injected were equal, 2.0 ng each.

Figure 6. ECD Chromatogram of Five Tetrachlorobiphenyls (IUPAC Congener Numbers).



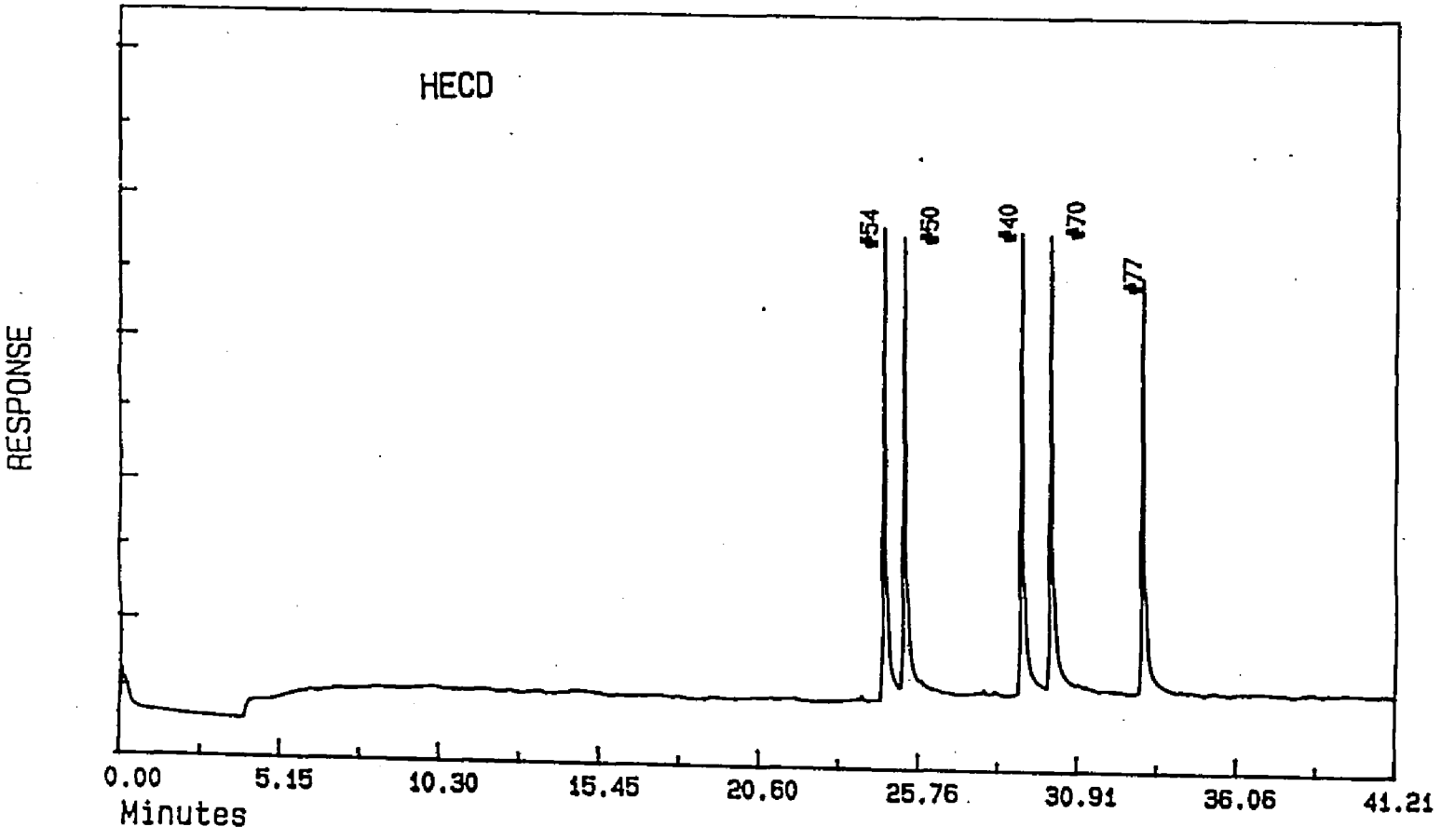
FIVE TETRACHLOROBIPHENYLS 2.0NG EA.

HECD Response-PCB Congeners

The Hall detector by contrast will respond similarly to congeners within a homolog class. Figure 7 is a chromatogram of five tetrachlorobiphenyls with the Hall detector. As can be seen, responses are nearly equal for an equivalent weight of material. (IUPAC congener numbers are indicated adjacent to each peak). The responses in this chromatogram indicated that the pyrolytic and catalytic efficiencies within a homolog group were nearly equal. Since pyrolytic efficiencies have been shown to be 100% at 950^{o}C or greater, catalytic efficiencies must have been the remaining variables. It was not necessary to determine the degree of catalytic efficiency, only that efficiencies within a homolog group were equal.

Figures 6 and 7 demonstrate one important aspect about chromatograms obtained by ECD as opposed to chromatograms obtained by HECD. Major components in Aroclors appear as major peaks in a chromatogram with HECD because of the response to percent molar chlorine content relationship. ECD responses to congeners are dependent on the electron affinity of each chlorine atom for slow electrons, which is irrespective of chlorine content. This means that a major peak on a ECD chromatogram may not be a major component in a complex mixture. Therefore, the responses in an ECD chromatogram may not always be indicative of the major components in a standard or sample. This is supported by the relative response factors of PCB congeners reported by Mullin et al. (1984). Any one relative response

Figure 7. HECD Chromatogram of Five Tetrachlorobiphenyls (IUPAC Congener Numbers).



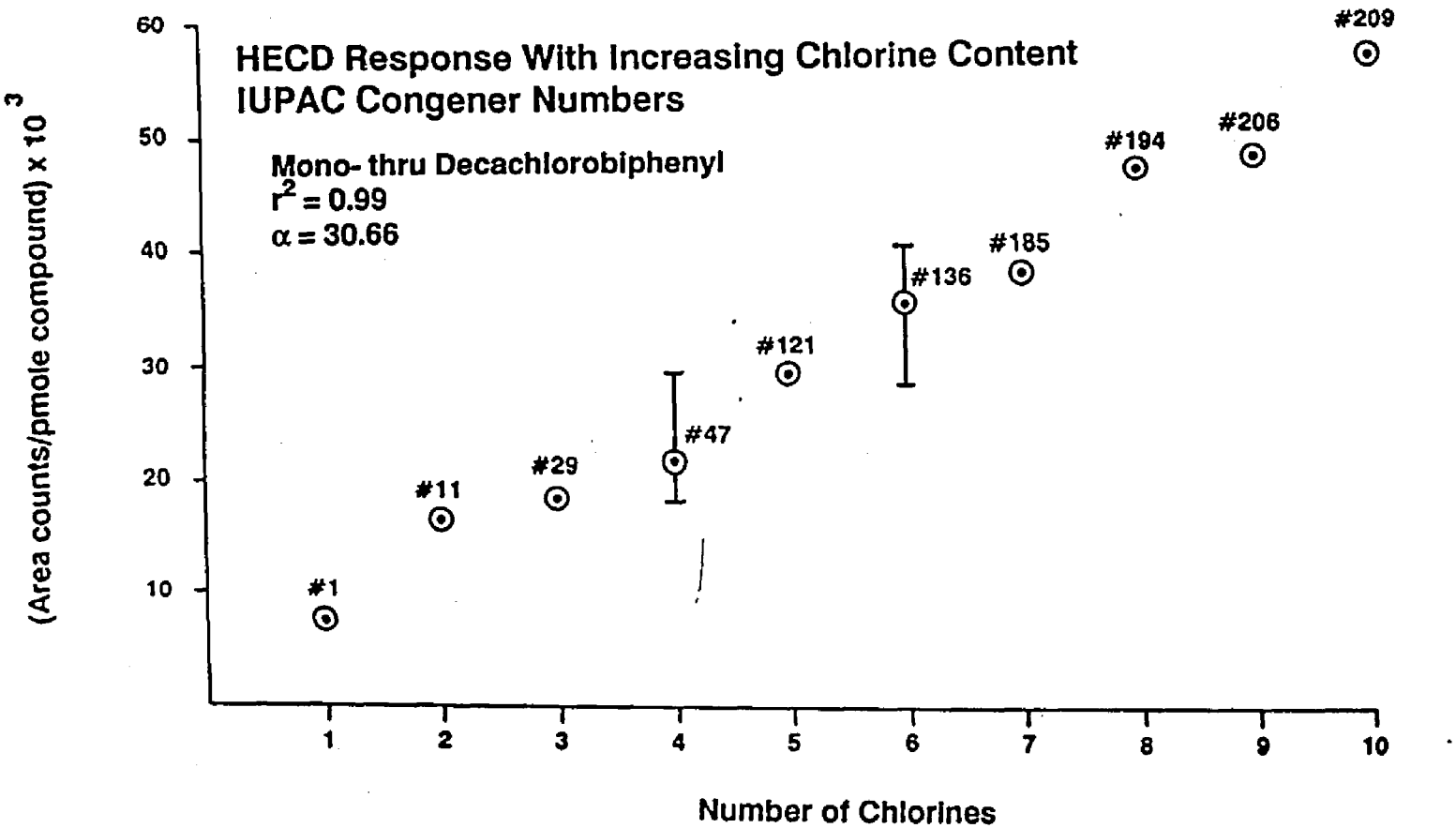
FIVE TETRACHLOROBIPHENYLS 1.0NG EACH

factor may be similar to those for congeners in as many as six other homolog groups. This is not the case with the Hall detector.

The response of the HECD to congeners of increasing chlorine content is linear. A graph (Figure 8) of the HECD responses from congeners containing one through ten chlorines provided a correlation of 0.99. Vertical axis values were calculated by dividing the area counts of each congener peak by the number of picmoles of compound injected. The horizontal axis indicates the chlorine content of the congener. A DCMA standard was injected to obtain these data. IUPAC congener numbers of each compound are provided for the same. Weights of the injected congeners ranged from 0.2 ng for decachlorobiphenyl to 4.0 ng for monochlorobiphenyl. The range of responses from multiple injections of five tetrachlorobiphenyls and five hexachlorobiphenyls are indicated by the bars in their respectable positions. Coefficients of variation were 14.1% and 11.2% for the tetrachloro- and hexachlorobiphenyls respectively.

It is apparent from this graph that the assumption of equal mass transfer within and among homolog groups in the GC injection port to the capillary column was reasonable.

Figure 8. HECD Response of Representative Homolog Group Congeners with Respect to Chlorine Content.


HECD Response With Increasing Chlorine Content
IUPAC Congener Numbers
Mono- thru Decachlorobiphenyl
$r^2 = 0.99$
$\alpha = 30.66$
(Area counts/pmole compound) x 10^3
60
50
40
30
20
10
#1
#11
#29
#47
#121
#136
#185
#194
#206
#209
1
2
3
4
5
6
7
8
9
10
Number of Chlorines

Homolog Distributions-Aroclor Standards

Analysis of eight individual Aroclor standards described earlier provided the homolog distributions listed in Table 11. The homolog distributions generated by the Hall detector methods and by Onuska et al. (1985) using GC/ECD and GC/MS are reported in weight percent composition. Pearson correlation analysis was performed to estimate the intensity of linear relationships which may exist between pairs of data sets. Correlation coefficients (r) from the comparison of the two methods are provided at the bottom of each pair of data sets. All correlation coefficients were equal to or greater than 0.92 indicating that the weight percent contributions were similar for both methods. Deviations in the weight percent values may be due to differences between batches of Aroclors, methods of quantification and limits of resolution for each capillary column.

Table 12 is a compilation of homolog distributions of Aroclor composites acquired from the Hall detector method of analysis and the same provided by Onuska et al. (1985). Correlation coefficients are provided at the bottom of each pair of data sets. All r values were equal to or greater than 0.95 indicating that the distributions were similar.

Individual Peak Quantification-Aroclor Standards

Weight percent contribution data for individual peaks in Aroclor standards have been published by two groups of researchers. Capel et

Table 11. Homolog Distributions of Eight Aroclors

Homolog Group	AR1221		AR1232		AR1016	
	Hall	Onuska	Hall	Onuska	Hall	Onuska
Mono-	74.8	59.6	36.1	31.4	0.6	3.0
Di-	19.2	36.4	11.8	25.6	9.8	19.2
Tri-	4.9	3.6	30.5	26.4	57.5	53.1
Tetra-	0.5	0.5	17.9	14.1	31.4	23.1
Penta-	0.2	0.3	3.0	1.2	0.7	1.0
Hexa-	0.3	0.5	0.5	0.6	---	0.4
Hepta-	<0.1	0.2	0.1	0.4	---	0.1
Octa-	---	0.1	<0.1	0.2	---	0.1
Nona-	---	---	---	0.1	---	---
	r = 0.94		r = 0.92		r = 0.97	

Homolog Group	AR1242		AR1248		AR1254	
	Hall	Onuska	Hall	Onuska	Hall	Onuska
Mono-	1.1	---	0.9	---	---	---
Di-	9.3	17.5	1.3	1.0	0.2	---
Tri-	46.8	44.7	29.1	28.3	0.1	0.3
Tetra-	37.6	29.9	53.6	54.6	8.6	15.0
Penta-	4.1	6.1	8.1	11.4	46.6	44.1
Hexa-	1.1	0.8	6.1	2.6	34.4	35.1
Hepta-	---	0.7	0.6	1.4	9.6	4.6
Octa-	---	0.2	0.2	0.6	0.5	0.8
Nona-	---	0.1	<0.1	0.1	---	0.1
	r = 0.98		r = 0.99		r = 0.98	

Homolog Group	AR1260		AR1262	
	Hall	Onuska	Hall	Onuska
Mono-	---	---	---	N. R.
Di-	0.1	0.3	---	N. R.
Tri-	0.4	0.6	---	N. R.
Tetra-	2.2	0.7	---	N. R.
Penta-	10.1	8.0	---	N. R.
Hexa-	32.1	42.0	21.2	N. R.
Hepta-	39.0	35.6	47.8	N. R.
Octa-	11.6	11.8	17.7	N. R.
Nona-	1.4	0.9	2.9	N. R.
	r = 0.95			

N. R. = Not Reported.

Table 12. Homolog Distributions of Binary and Ternary Mixtures of Aroclors 1242, 1254 and 1260.

Homolog Group	AR1242/1254		AR1254/1260	
	Hall	Onuska	Hall	Onuska
Mono-	---	--	---	---
Di-	7.5	8.8	---	0.2
Tri-	24.9	22.5	---	0.4
Tetra-	21.9	22.4	5.6	7.8
Penta-	30.2	25.1	36.5	26.0
Hexa-	13.4	18.0	33.1	38.6
Hepta-	2.1	2.6	20.9	20.1
Octa-	---	0.5	3.5	6.3
Nona-	---	0.1	0.5	0.5
	r = 0.98		r = 0.95	

Homolog Group	AR1242/1254/1260	
	Hall	Onuska
Mono-	---	---
Di-	1.7	5.9
Tri-	16.0	15.2
Tetra-	17.3	15.2
Penta-	17.9	19.4
Hexa-	26.8	26.0
Hepta-	17.2	13.6
Octa-	2.7	4.2
Nona-	0.5	0.4
	r = 0.97	

al. (1985) used GC/ECD and GC/MS to quantify several major and minor components of Aroclors 1242, 1254 and 1260. Schulz et al. (1989) have developed a multidimensional gas chromatography technique incorporating multiple capillary columns to reportedly resolve all 209 congeners. Weight percent contributions of individual congeners present in Aroclors 1242, 1254 and 1260, as well as other PCB formulations, were calculated. Electron capture detection was used exclusively by Schulz et al. (1989).

Tables 13, 14 and 15 list the weight percent contributions of selected peaks in Aroclors 1242, 1254 and 1260 respectively, from the Hall detector, Capel et al. (1985) and Schulz et al. (1989). The weight percent values acquired from the Hall detector were similar to those reported by Capel et al. (1985) and/or Schulz et al. (1989). HECD values represent the contribution of the entire peak relative to the major component. Where HECD peaks include multiple components, the appropriate components reported by Capel et al. (1985) or Schulz et al. (1989) were added together to represent one peak.

The HECD weight percent contributions in Table 14 are mean values of five analyses from 50 ng injections of Aroclor 1254. Standard deviations of the peak contributions are provided next to the appropriate peak and were less than 1.0% in each case. The HECD contributions of congeners 149 and 118 are listed separately since both components were resolved. Values from Capel et al. (1985) and Schulz et al. (1989) were reported as one peak and the same are

Table 13. Weight Percent Contributions of Selected Peaks in Aroclor 1242 by HECD, Capel et al. (1985) and Schulz et al (1989).

Congener(s)	HECD	Capel et al.	Schulz et al.
4,10	4.30	1.37	3.21
15,18	5.06	9.38	7.79
17	9.79	4.27	2.88
16,32	6.59	5.77	2.89
28,31	13.57	11.74 (a)	11.11
20,33,53	6.84	7.32	5.72
22,51	3.38	1.79	3.64
52,73	3.21	4.54	4.04
47,48,75	3.97	1.75	1.87
37,42,59	4.90	2.88	1.44
41,64	4.22	4.62	3.50
66,93	4.56	4.22	4.53 (b)

(a) = Reported Values Combined.
(b) = Reported as Congeners 66,95.

Table 14. Weight Percent Contributions of Selected Peaks in Aroclor 1254 by HECD, Capel et al. (1985) and Schulz et al. (1989) (Five Replicate Analyses with HECD.)

Congener(s)	HECD (Mean)	Std. Dev. (n = 5)	Capel et al.	Schulz et al.
52,73	3.73	0.47	3.34	5.18
66,93	7.56	0.78	6.10	6.61 (b)
90,101	7.73	0.30	8.42	8.87
99,113	5.05	0.43	4.56	3.60
87,111,115	3.82	0.17	3.32	4.08
110	5.69	0.14	10.32	5.85
149	2.40	0.08	(c)	(c)
118	8.76	0.21	(c)	(c)
118,149			11.50	8.60
132,153	2.69	0.22	3.14	6.24
138	7.87	0.75	9.11	3.20
128,167	2.38	0.41	1.66	2.28 (a)

(a) = Reported values combined.
(b) = Reported as congeners 66,95.
(c) = Reported as one peak (118,149).

Table 15. Weight Percent Contributions of Selected Peaks in Aroclor 1260 by HECD, Capel et al. (1985) and Schulz et al. (1989).

Congener(s)	HECD	Capel et al.	Schulz et al.
66,93	2.02	3.48	3.04 (b)
90,101	2.28	4.04	5.58
82,151	2.35	7.05 (a)	3.67
149	7.81	0.00	7.83
132,153	10.27	1.32	14.49
141,179	5.05	4.53 (a)	4.35
138	7.44	8.33	6.13
159,182,187	4.65	2.56	3.97
174,181	4.13	2.55	3.85
177	2.56	1.61	2.21
180	9.83	6.50	7.12
170,190	4.03	4.77	4.70

(a) = Reported values combined.
(b) = Reported as congeners 66,95.

provided in Table 14. The combined HECD contributions for congeners 149 and 118 were similar to those determined by Capel et al. (1985) and Schulz et al. (1989).

Chemometrics: SIMCA Suitability

In the preceding tables, correlation analysis was used to compare the acquired homolog distributions with distributions reported by Onuska et al. (1985). This was chosen to estimate the applicability of the results from the Hall detector method to principal components model. The model under consideration was the SIMCA model which is an acronym for Soft Independent Method of Class Analogy (Onuska et al., 1985). This model has been described and tested by several researchers (Stalling et al., 1987a; Stalling et al., 1985b; Onuska et al., 1985, Dunn et al., 1985) although not all used PCB congener data.

The steps in pattern recognition as described by Dunn et al. (1985) are shown in Figure 9.

A crude but analogous approach was used in testing these homolog distributions. First, training sets of known classification were collected comprising the Aroclor and Aroclor composite distributions. This is in step 1.

Next, distances were calculated or in this case, correlation coefficients for the training sets from the test sets. The test sets were the distributions reported by Onuska et al. (1985) and in later discussions will be the environmental samples. This is step 2.

Figure 9. Steps in Pattern Recognition Described by Dunn, et al. (1985).

CHEMOMETRICS: SIMCA
(Soft Independent Method of Class Analogy)

1. Establish training sets.
2. Derive classification rules.
3. Select features.
4. Refine classification rules.
5. Classify unknowns.
6. Review results graphically.

Steps 3 and 4 were computer manipulations of GC data.

Finally, classification of the unknowns or sample chromatographic peaks is performed, based on the strength of the distance relationships. This is step 5.

This crude method of comparison was dependent on the sample homolog distributions possessing unaltered patterns as compared to the standard Aroclors. When alteration of the Aroclor patterns were encountered, the comparisons failed indicating that a more powerful means of data manipulation (i.e. individual peak comparisons) would be required.

With the SIMCA programs, Theta values would be calculated based on the principle components nearest neighbor(s) or training set(s) closest to the test set. Beta values would also be calculated which represent the variable loading of the nearest neighbor(s). Three dimensional plotting of the principal components permit viewing of the training and test sets data structures. This is step 6.

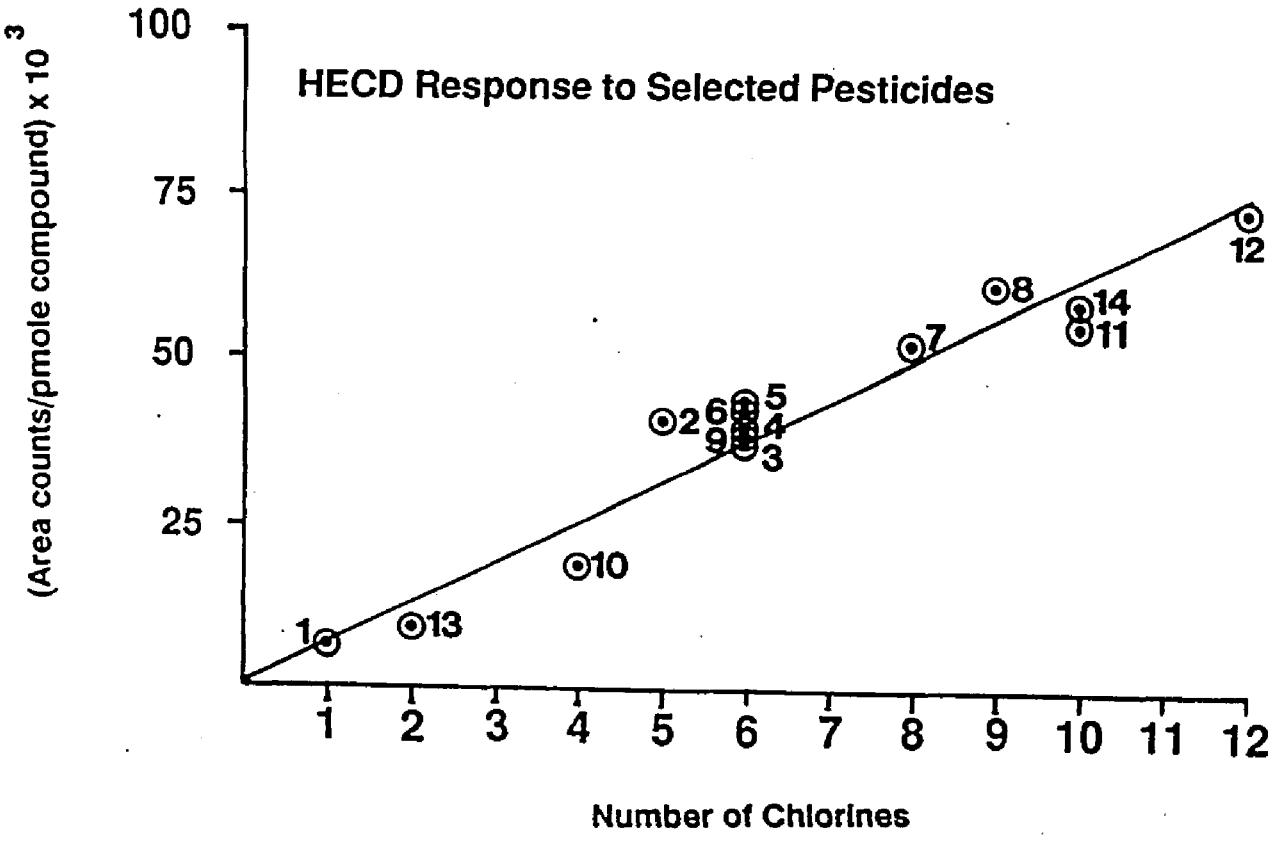
Pattern recognition programs such as this can provide more accurate and more rapid estimations of the Aroclor contributions in environmental samples. However, data manipulation programs should be flexible to accommodate homolog distribution data as well as individual congener data for those situations where highly altered distribution patterns are encountered.

ADDENDUM: HALL DETECTOR RESPONSE TO NON-PCB MATERIALS

HECD Response-Pesticides

The Hall detector should respond similarly to other chlorinated hydrocarbons containing only carbon, hydrogen and chlorine. Compounds with atoms in addition to these, such as oxygen, may respond slightly differently when the percent content of these atoms is high. The response may be different because the Hall detector is sensitive to oxygen. Oxygen present in a chlorinated compound could have a positive or negative affect on response. When the content is low however, the linearity of response may not be adversely affected. Figure 10 is a graph of the responses of fourteen compounds, 1.0 - 2.0 ng of each, with respect to chlorine content. The vertical axis is the area counts per picomole of compound and the horizontal axis is the number of chlorines in the compound. A correlation coefficient of 0.97 was acquired from these data even though the structures of many of these compounds are dissimilar. Compounds 7, 9 and 11 contained one oxygen each and compound 13 contained three oxygens. However, the responses of each do not deviate significantly from linearity. The compounds injected and the number of chlorines and oxygens for each were:

Figure 10. Linear Response of HECD to Selected Chlorinated Pesticides with Respect to Chlorine Content.

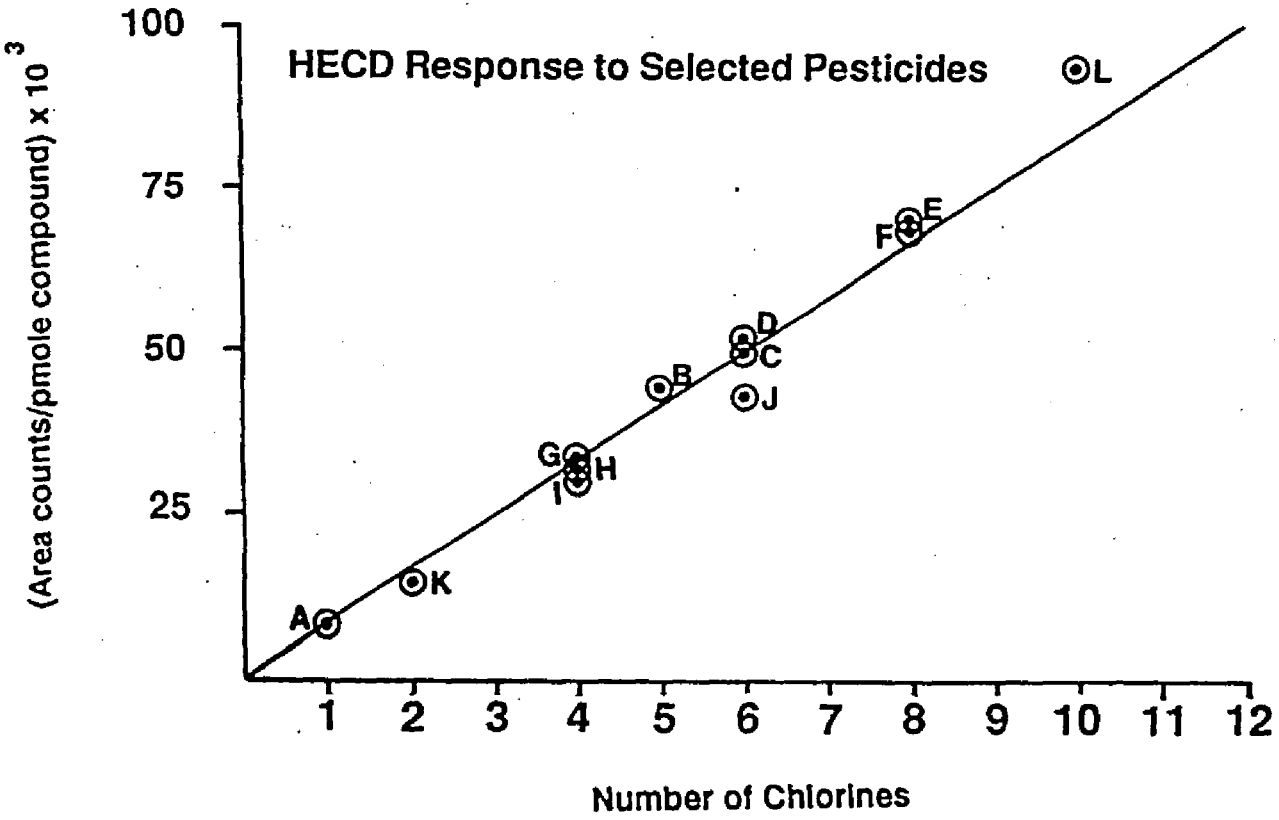

HECD Response to Selected Pesticides
(Area counts/pmole compound) x 10 3
100
75
50
25
1
2
3
4
5
6
7
8
9
10
11
12
Number of Chlorines
1
13
10
2
6
9
5
4
3
7
8
14
11
12

	Compound	Chlorines	Oxygens
1	b-Chloronaphthalene	1	0
2	Pentachlorobenzene	5	0
3	a-Benzenehexachloride	6	0
4	g-Benzenehexachloride	6	0
5	a-Chlordene	6	0
6	g-Chlordene	6	0
7	Oxychlordane	8	1
8	t-Nonachlor	9	0
9	Dieldrin	6	1
10	o,p'-DDD	4	0
11	Kepone	10	1
12	Mirex	12	0
13	t-Permethrin	2	3
14	Decachlorobiphenyl	10	0

Figure 11 is a similar graph of twelve compounds (1.0 - 2.0 ng each), eight of which were different than those shown in figure 10. Again, linearity with respect to chlorine content is acquired. The correlation coefficient of these data was 0.99 and chemical structures of many of these compounds were also dissimilar. Compound J contained one oxygen and compound K contained three oxygens, but their responses did not deviate from linearity. The compounds injected with the chlorine and oxygen content of each were:

	Compound	Chlorines	Oxygens
A	b-Chloronaphthalene	1	0
B	Pentachlorobenzene	5	0
C	a-Benzenehexachloride	6	0
D	Aldrin	6	0
E	g-Chlordane	8	0
F	a-Chlordane	8	0
G	p,p'-DDE	4	0
H	o,p'-DDD	4	0
I	Tetrachloroquaterphenyl	4	0
J	Endrin Ketone	6	1
K	c-Permethrin	2	3
L	Decachlorobiphenyl	10	0

Figure 11. Linear HECD Response to Selected Chlorinated Pesticides with Respect to Chlorine Content.


HECD Response to Selected Pesticides
L
(Area counts/pmole compound) x 10 3
100
75
50
25
A
K
G
H
I
B
D
C
J
F
E
1
2
3
4
5
6
7
8
9
10
11
12
Number of Chlorines

HECD Response-Slope of Response Curve

One point which is obvious from Figures 10 and 11 is the different slopes of the lines for each graph. As with many GC detectors the response acquired from the detector will often change from day-to-day and even from run-to-run. The data from these two graphs were collected on two different days, hence the different slopes because of the changing condition of the nickel reaction tube as well as other factors.

Pentachlorobenzene was described as a response standard in earlier discussions to acquire homolog distribution patterns. As can be seen in these two figures, the response of pentachlorbenzene describes the slope of the response curve to a reasonable approximation. In this manner, the response of pentachlorobenzene for each analytical run sets the slope of the response curve for all eluting compounds. Other compounds could also be used as a response standard, but the degree of chlorination should be five or greater so that its response is a sensitive indicator of the slope of the response curve.

The predictability and linearity of Hall detector response to chlorinated hydrocarbons provided two simple and easy internal checks which can be performed on a run-to-run basis. Equivalent response by Pentachlorobenzene and Decachlorobiphenyl from equivalent weights of material was described earlier. This permits a rapid means of comparing detector responses near the beginning of the analytical run with detector response near the end of an analytical run. From this determination, the consistency of detector response during each analysis can be estimated.

Secondly, linearity of detector response during each analysis can be checked using the responses of the relative retention markers. A plot of the area counts per picmole of compound injected with respect to chlorine content should result in a linear response curve from each analysis. Reduced responses at the high chlorine range of the response curve can be indicative of excessive carbon fouling in the reaction tube or other instrument problems.

Analysis of Mixtures with Unknown Structures-Technical Chlordane

Chlordane is a pesticide which was used in such applications as control of ants and cockroaches where DDT provided inadequate control, and for the treatment of homes against termites. It was produced by the Diels-Alder addition reaction of cyclopentadiene and hexachlorocyclopentadiene with further chlorination of the intermediate product, chlordene. This resulted in a mixture of which a-chlordane (cis), g-chlordane (trans), a-chlordene (cis), g-chlordene (trans), heptachlor, t-nonachlor (trans) and c-nonachlor (cis) are major components (Brooks, 1974).

These major components contained six, seven, eight and nine chlorines and comprised 80% of the formulation. Higher chlorination analogues of unknown structure are suspected of being present, some of which may contain up to thirteen chlorines. A total of 100 compounds may be present in technical chlordane for which identifications have not been confirmed.

Complex mixtures such as this can be analyzed with GC/HECD if the molecular weight and degree of chlorination of the major constituents

in chromatographic peaks are known. Ramus et al. (1984) have reported that it is possible to analyze compounds of unknown structure in the absence of analytical standards when this information is available. Since the Hall detector response in this method is based on the molar chlorine content, structural knowledge of the compound of interest is desirable but not required for reasonable analysis. Molecular weight and chlorine content data may be acquired from GC/MS with negative chemical ionization of the chromatographic peak(s) of interest.

Figures 10 and 11 (shown previously) show the responses of five of the six major components of technical chlordane. These responses do not deviate from the linearity of the response curves and indicate that other compounds of the same basic carbon structure but different by degrees of chlorination should also conform to the linear response curve.

Gas chromatography with NCI mass spectrometry was performed on a technical chlordane standard to determine the molecular weights and degree of chlorination of selected peaks. Table 16 lists the HRIs, molecular weights and chlorine numbers of some of the components in the technical standard. This information can be used to acquire accurate total chlordane concentrations in environmental samples.

Other complex mixtures which may be analyzed in this manner are toxaphene (polychlorinated camphenes), strobane (polyclorinated terpenes), PCTs (polyclorinated terphenyls), PCQs (polychlorinated quaterphenyls) and halowaxes (polyclorinated naphthalenes) as well as the congeners of the chlorinated dibenzofurans and dibenzodioxins.

Table 16. HRIs, Molecular Weight and Chlorine Content of Major Peaks in Technical Chlordane.

HRI	MW	ID	CL #
1828	216		4
2054	248		5
2071	248		5
2353	298		5
2433	370	Heptachlor	7
2460	336	Chlordene	6
2578	372		7
2586	338		7
2613	370		8
2685	394		8
2693	406	Chlordane	8
2701	372		7
2720	372		7
2739	336	Chlordene	6
2805	372		7
2825	406	Chlordane	8
2851	406	Chlordane	8
2883	406	Chlordane	8
2900	440	Nonachlor	9
2927	406	Chlordane	8
2959	406	Chlordane	8
3012	406	Chlordane	8
3089	406	Chlordane	8
3128	440	Nonachlor	9
3136	440	Nonachlor	9
3158	440	Nonachlor	9

CHAPTER IV

PCP CONGENER ANALYSIS-WEAKFISH AND BLUEFISH

INTRODUCTION

Chlorinated hydrocarbons have been found to be ubiquitous contaminants in many species of aquatic life on a global scale (Ballschmiter and Zell, 1980; Zell and Ballschmiter, 1980a, Zell and Ballschmiter, 1980b; Ballschmiter et al., 1981a; Ballschmiter et al., 1981b; Ballschmiter et al., 1983; Oliver and Niimi, 1988). Of the chlorinated hydrocarbons, the polychlorinated biphenyls are some of the most commonly detected. Among the varieties of aquatic life found to be contaminated are finfish, which are of significant economic importance in many areas of the United States.

In 1984, the Council on the Environment of the state of Virginia awarded a contract to the Virginia Institute of Marine Science to survey chlorinated hydrocarbons, including PCBs, in Virginia's seafood. The purpose of this survey was to establish baseline information about chlorinated hydrocarbon concentrations to provide a database for future comparison and to determine the public exposure to chlorinated hydrocarbons.

Various species of seafood were collected from wholesale distributors along the lower Chesapeake Bay, York River and Rappahannock River. Wholesale distributors were chosen to be the

suppliers of the seafood so that an estimate of the public exposure to chlorinated hydrocarbons from this food source could be made. The selection of specific distributors was made on the proximity of the supplier to the desired source. Additionally, attempts were made during each sampling to verify the source of the seafood being purchased; however, the information may not have been reliable.

A ban on commercial fishing in the James River due to contamination of the pesticide Kepone prevented the purchase of fish from local distributors. A sampling of fish from this River was important to the survey because of heavy industrialization along the lower portions of the river. Also, different species of fish will migrate in and out of the James River during various times of the year. To accommodate this, fish from the James River were provided by the Virginia State Water Control Board.

The results presented here were obtained from analyses of bluefish (Pomatomas saltatrix) and weakfish (Cynoscion regalis) samples collected in 1985 from the lower James River, lower Chesapeake Bay and York River as part of this project.

MATERIALS AND METHODS

Sample Preparation

Ten grams of edible tissue were chopped to a fine consistency and desiccated with a 4:1 mixture of anhydrous sodium sulfate and amorphous precipitated silica. The ratio of tissue to desiccant was one part tissue to three parts desiccant. The resulting mixture was stirred and then frozen. After freezing, the mixture was allowed to

thaw and then was blended with a Hamilton-Beech blender to form a homogeneous powder. The resulting powder was Soxhlet extracted with 1:1 ethyl ether/petroleum ether for 12 hours. Each raw extract was evaporated on a hot plate to 10 mls and transferred to a 11 mm x 300 mm chromatography column containing 3.0 g Florisil and 3.0 g anhydrous sodium sulfate. The column was eluted with 30 ml of n-hexane followed by 30 ml of 15% methylene chloride in n-hexane such that non-polar compounds were fractionated from more polar compounds. These solutions were each evaporated to a final volume of 0.5 ml under a gentle stream of nitrogen. The non-polar fraction was analyzed for PCBs using the instrumentation and operating conditions as well as the identification and quantification methodology described previously. Sample spike recoveries which estimate the extraction and sample preparation efficiencies were found to be 90% $\pm$ 5%.

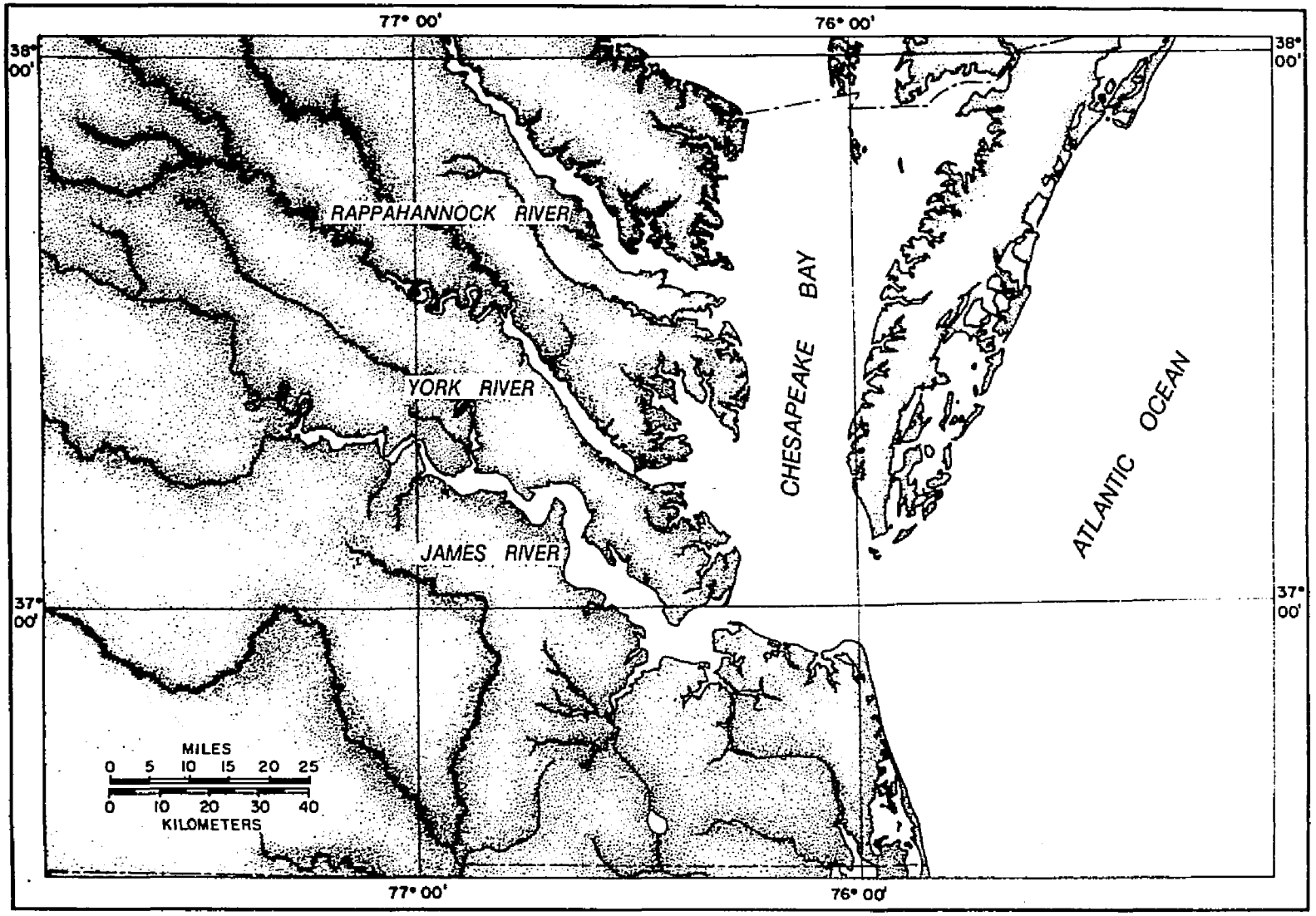
RESULTS AND DISCUSSION

Total PCB Concentrations

Fifty-nine weakfish and bluefish samples were obtained between June and December of 1985 and analyzed for PCBs. The sources of the fish were the lower James River, lower Chesapeake Bay and York River (Figure 12).

Moderate levels of PCBs (less than 1.0 ppm, ppm = parts per million) were found in the weakfish samples from the York River. This was not surprising because of the limited industrial activity along the river. Weakfish collected from the lower James River in October and bluefish collected from the lower James River and lower Chesapeake

Figure 12. Map of Chesapeake Bay with Associated Rivers.


77° 00'
76° 00'
38° 00'
37° 00'
RAPPAHANNOCK RIVER
YORK RIVER
JAMES RIVER
CHESAPEAKE BAY
ATLANTIC OCEAN
MILES
0 5 10 15 20 25
0 10 20 30 40
KILOMETERS

Bay in October and December of 1985 contained significant levels of PCBs (greater than 2.0 ppm, Figures 13, 14). Significant levels were considered to be total PCB concentrations equal to or greater than the U. S. Food and Drug Administration 2.0 ppm (wet weight) action level for finfish. The large range of concentrations for these fish was probably due to the combining of fish populations at this time of year and small sample size.

Twenty percent (2 of 10) of the bluefish and 33% (3 of 9) of the weakfish samples collected in October from the lower James River were >2.0 ppm. The average fish weight was 863 gms and 1,090 gms respectively.

Twelve percent (1 of 8) of the bluefish samples taken from the lower Chesapeake Bay in October were >2.0 ppm. The average fish weight was 1,907 gms.

Bluefish samples from the lower Chesapeake Bay in December of 1985 contained the highest levels of PCBs. Eighty-three percent (5 of 6) of the bluefish samples contained in excess of 2.0 ppm total PCBs. The average fish weight was 1,180 gms.

Homolog Distribution Patterns-Lower James River and Lower Chesapeake Bay Bluefish and Weakfish

Detailed analysis of the PCB composition in the samples of bluefish and weakfish from the lower James River in October indicated that Cl-3 thru Cl-7 biphenyls comprised 95.1% and 95.6% respectively of the total PCB concentrations (Table 17, Figures 15, 16). The composition of the PCBs in the bluefish and weakfish samples from the

Figure 13. Plot of Total PCB Concentrations in Weakfish from the York River, Lower James River and Lower Chesapeake Bay.

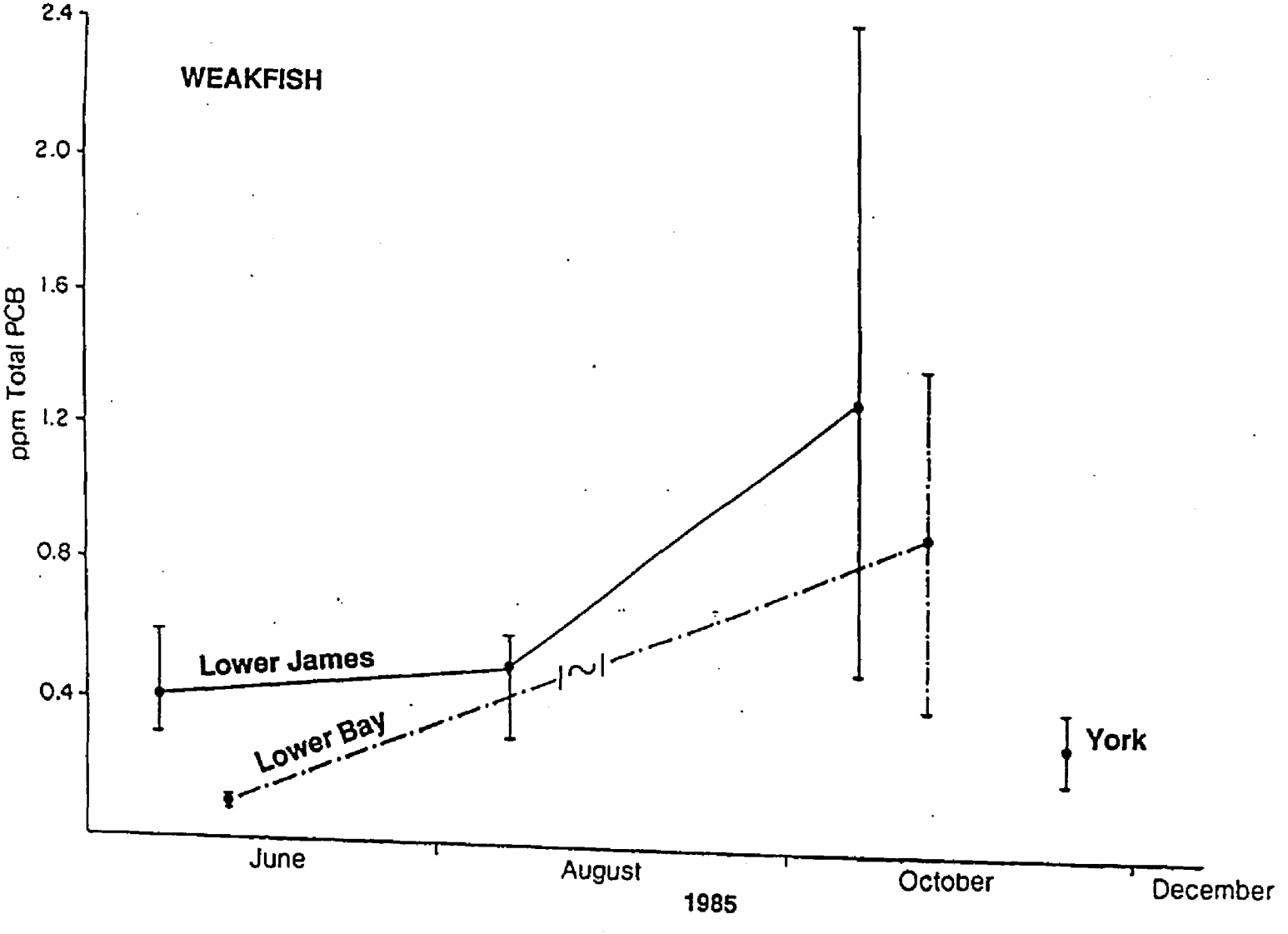

WEAKFISH
2.4
2.0
1.6
1.2
0.8
0.4
ppm Total PCB
Lower James
Lower Bay
York
June
August
October
December
1985

Figure 14. Plot of Total PCB Concentrations in Bluefish from the Lower James River and Lower Chesapeake Bay.

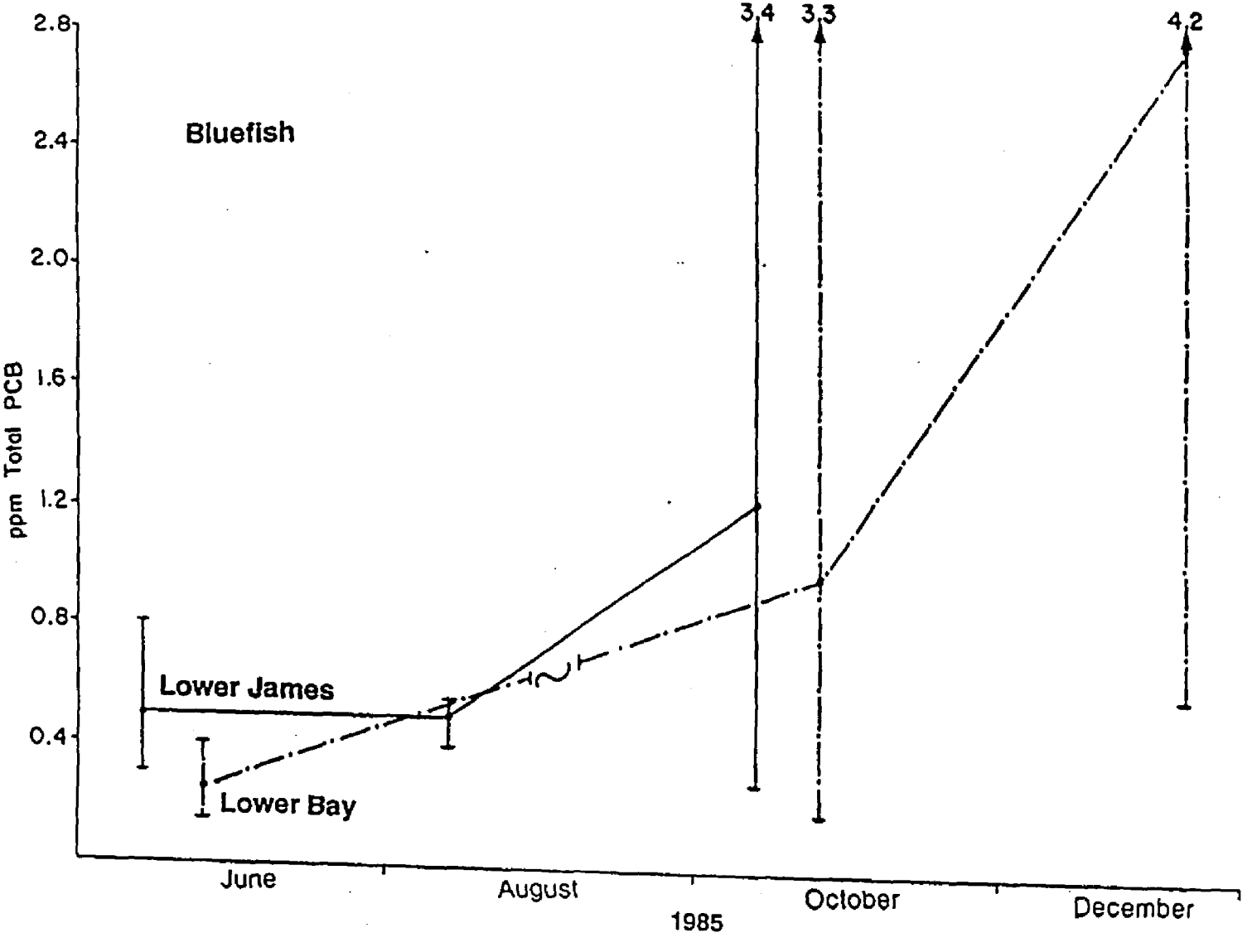

Bluefish
ppm Total PCB
2.8
2.4
2.0
1.6
1.2
0.8
0.4
3.4
3.3
4.2
Lower James
Lower Bay
June
August
October
December
1985

Table 17. Mean Values of Percent Homolog Group Distribution Relative to Total PCB in Weakfish and Bluefish.

Sample	Homolog Group 1	2	3	4	5	6	7	8	9	ΣPCB
October										
Lower James River										
Weakfish	0.3	1.3	6.3	13.5	27.0	35.9	12.9	2.2	0.6	1.3
Bluefish	0.2	0.5	5.0	11.7	23.4	39.6	15.4	2.4	0.7	1.4
Lower Chesapeake Bay										
Weakfish	0.4	1.1	11.3	18.6	23.7	31.6	10.1	1.3	0.4	0.9
Bluefish	0.7	0.3	11.3	25.3	25.7	23.2	8.3	1.5	0.8	1.0
York River										
Weakfish	0.6	1.3	18.4	25.6	26.6	18.5	3.9	0.8	0.4	0.3
December										
Lower Chesapeake Bay										
Bluefish	0.2	2.4	8.4	15.1	23.8	32.4	11.9	2.4	2.1	2.7

ΣPCB = Total PCB in ug/gm wet weight

Figure 15. Graph of Homolog Distributions in Bluefish from the Lower James River in October.

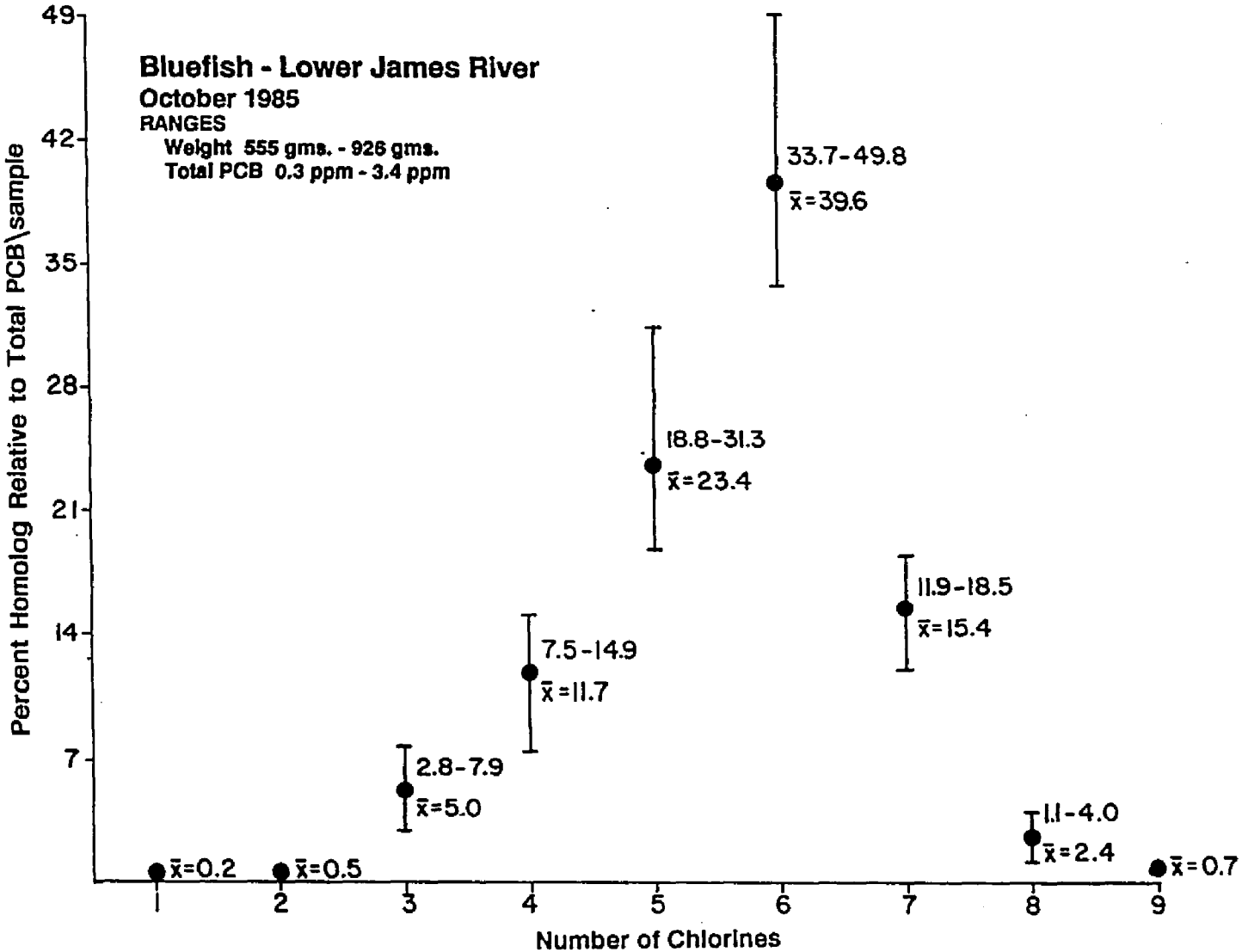
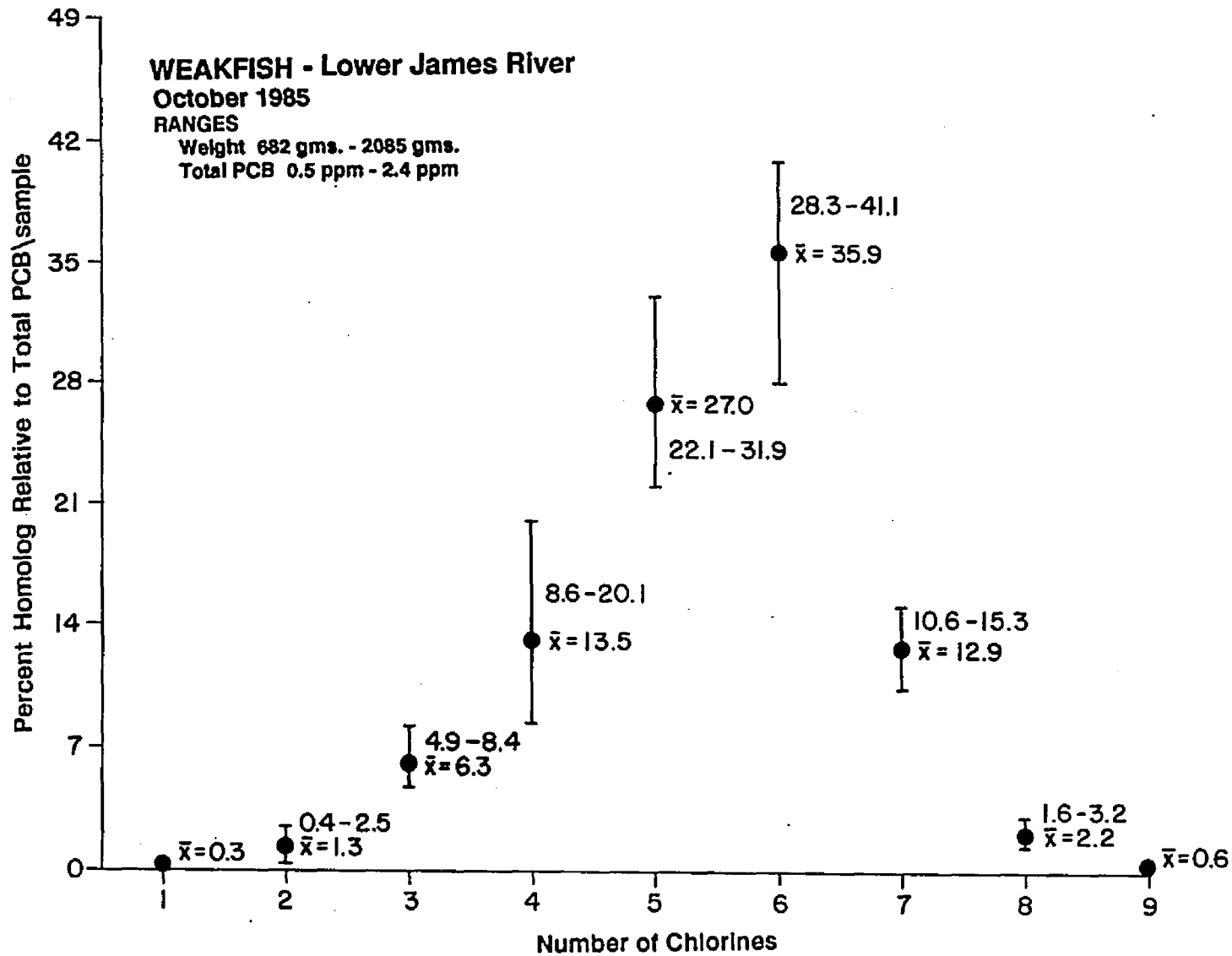

Bluefish - Lower James River
October 1985
RANGES
Weight 555 gms. - 926 gms.
Total PCB 0.3 ppm - 3.4 ppm
Percent Homolog Relative to Total PCB\sample
49
42
35
28
21
14
7
33.7-49.8
x̄=39.6
18.8-31.3
x̄=23.4
11.9-18.5
x̄=15.4
7.5-14.9
x̄=11.7
2.8-7.9
x̄=5.0
1.1-4.0
x̄=2.4
x̄=0.2
x̄=0.5
x̄=0.7
1
2
3
4
5
6
7
8
9
Number of Chlorines

Figure 16. Graph of Homolog Distributions in Weakfish from the Lower James River in October.


WEAKFISH - Lower James River
October 1985
RANGES
Weight 682 gms. - 2085 gms.
Total PCB 0.5 ppm - 2.4 ppm
Percent Homolog Relative to Total PCB\sample
49
42
35
28
21
14
7
0
1
2
3
4
5
6
7
8
9
Number of Chlorines
x̄=0.3
0.4-2.5
x̄=1.3
4.9-8.4
x̄=6.3
8.6-20.1
x̄=13.5
x̄=27.0
22.1-31.9
28.3-41.1
x̄=35.9
10.6-15.3
x̄=12.9
1.6-3.2
x̄=2.2
x̄=0.6

lower Bay in October (Figures 17, 18) and the bluefish from December (Figure 19) were 93.8%, 95.3% and 91.6% Cl-3 thru Cl-7 biphenyls respectively.

A similarity existed between the distribution patterns of Aroclors 1254/1260 with the samples from the lower James River. Correlation analysis of the mean percentages of lower James River weakfish distribution patterns with the distribution patterns from an equal mixture of Aroclors 1254 and 1260 resulted in a correlation coefficient of 0.95 and is illustrated in Figure 20. The clear bars represent the mean values of the percent congener of each homolog class relative to the total PCB concentrations in weakfish samples from the Lower James River. The striped bars indicate the percent congener of each homolog group relative to the total PCB concentration in an equal weight composite of Aroclors 1254 and 1260.

It is apparent from this graph that there were also lower molecular weight congeners present in these samples indicating a possible contribution of a lower chlorine content Aroclor. Bluefish samples from the lower James River during this time period showed nearly identical distribution patterns to the weakfish samples.

These homolog distribution patterns were found to be consistent between samples, regardless of the total PCB concentrations present. Inspection of the individual sample homolog patterns with respect to total PCB concentration did not indicate a pattern/concentration dependence. Both the highest and lowest concentrations were found in samples with patterns similar to Aroclors 1254/1260.

Figure 17. Graph of Homolog Distributions in Bluefish from the Lower Chesapeake Bay in October.

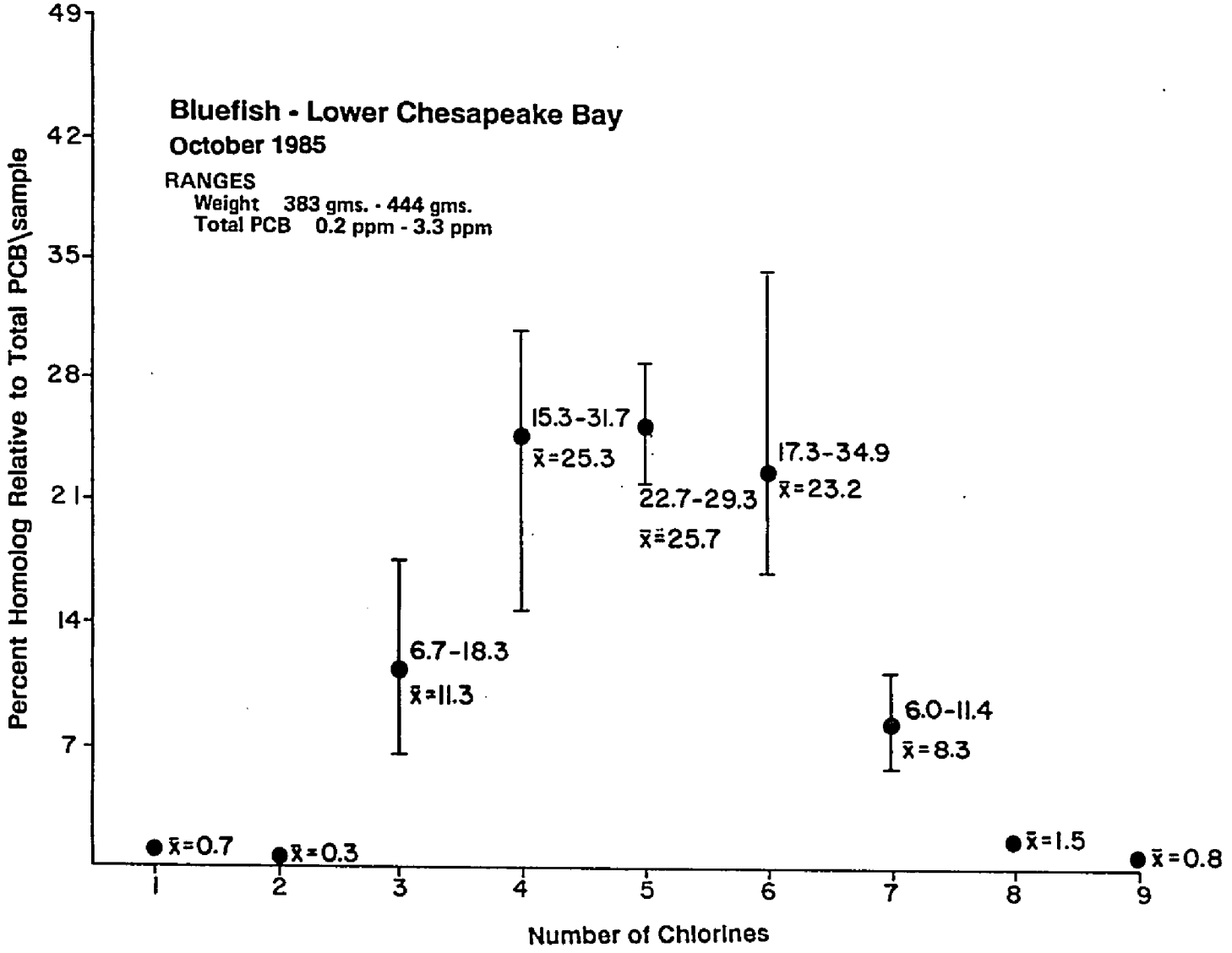

Bluefish - Lower Chesapeake Bay
October 1985
RANGES
Weight 383 gms. - 444 gms.
Total PCB 0.2 ppm - 3.3 ppm
Percent Homolog Relative to Total PCB\sample
49
42
35
28
21
14
7
x̄=0.7
x̄=0.3
6.7-18.3
x̄=11.3
15.3-31.7
x̄=25.3
22.7-29.3
x̄=25.7
17.3-34.9
x̄=23.2
6.0-11.4
x̄=8.3
x̄=1.5
x̄=0.8
1
2
3
4
5
6
7
8
9
Number of Chlorines

Figure 18. Graph of Homolog Distributions in Weakfish from the Lower Chesapeake Bay in October.

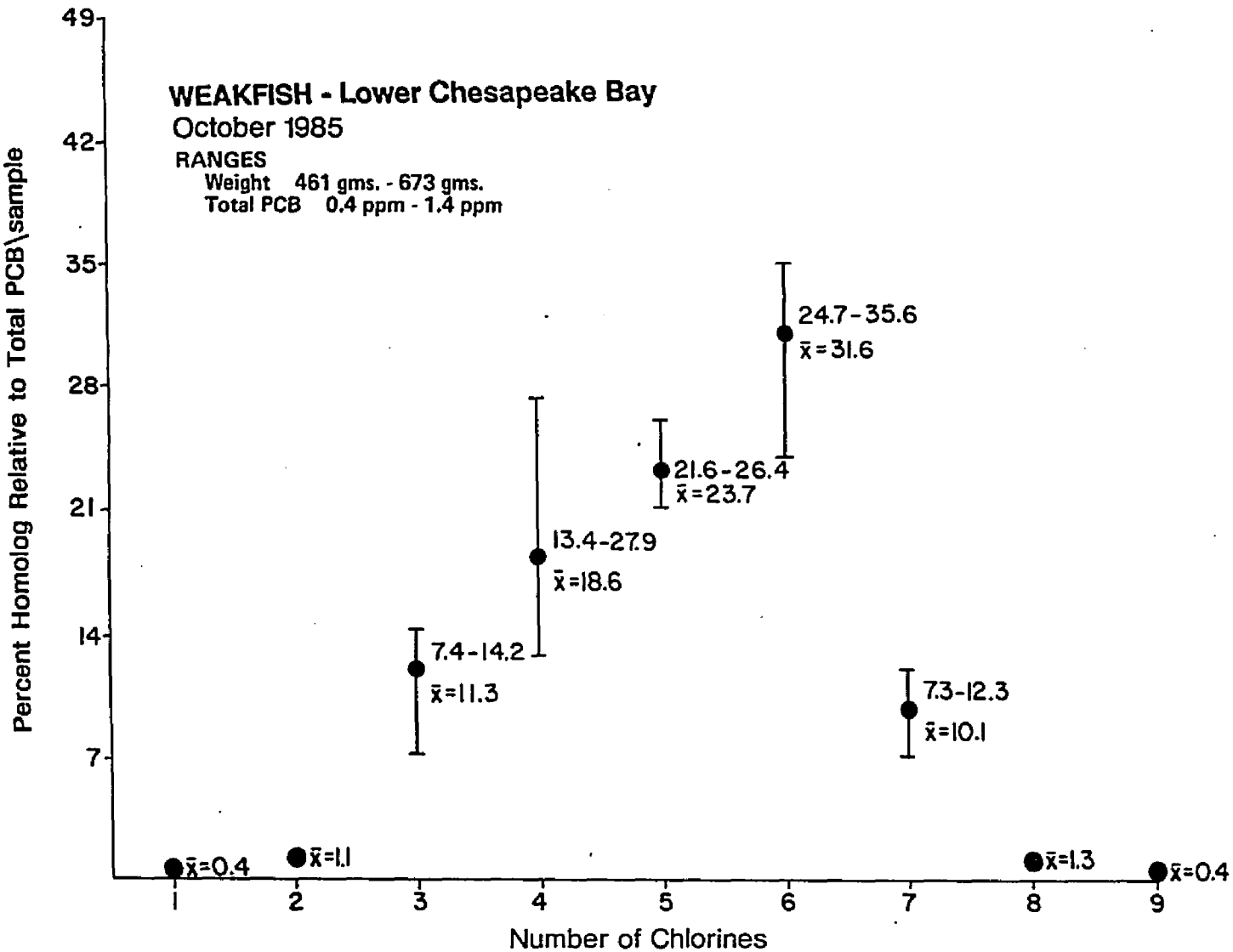

WEAKFISH - Lower Chesapeake Bay
October 1985
RANGES
Weight 461 gms. - 673 gms.
Total PCB 0.4 ppm - 1.4 ppm
Percent Homolog Relative to Total PCB\sample
49
42
35
28
21
14
7
24.7-35.6
x̄=31.6
21.6-26.4
x̄=23.7
13.4-27.9
x̄=18.6
7.4-14.2
x̄=11.3
7.3-12.3
x̄=10.1
x̄=0.4
x̄=1.1
x̄=1.3
x̄=0.4
1
2
3
4
5
6
7
8
9
Number of Chlorines

Figure 19. Graph of Homolog Distributions in Bluefish from the Lower Chesapeake Bay in December.

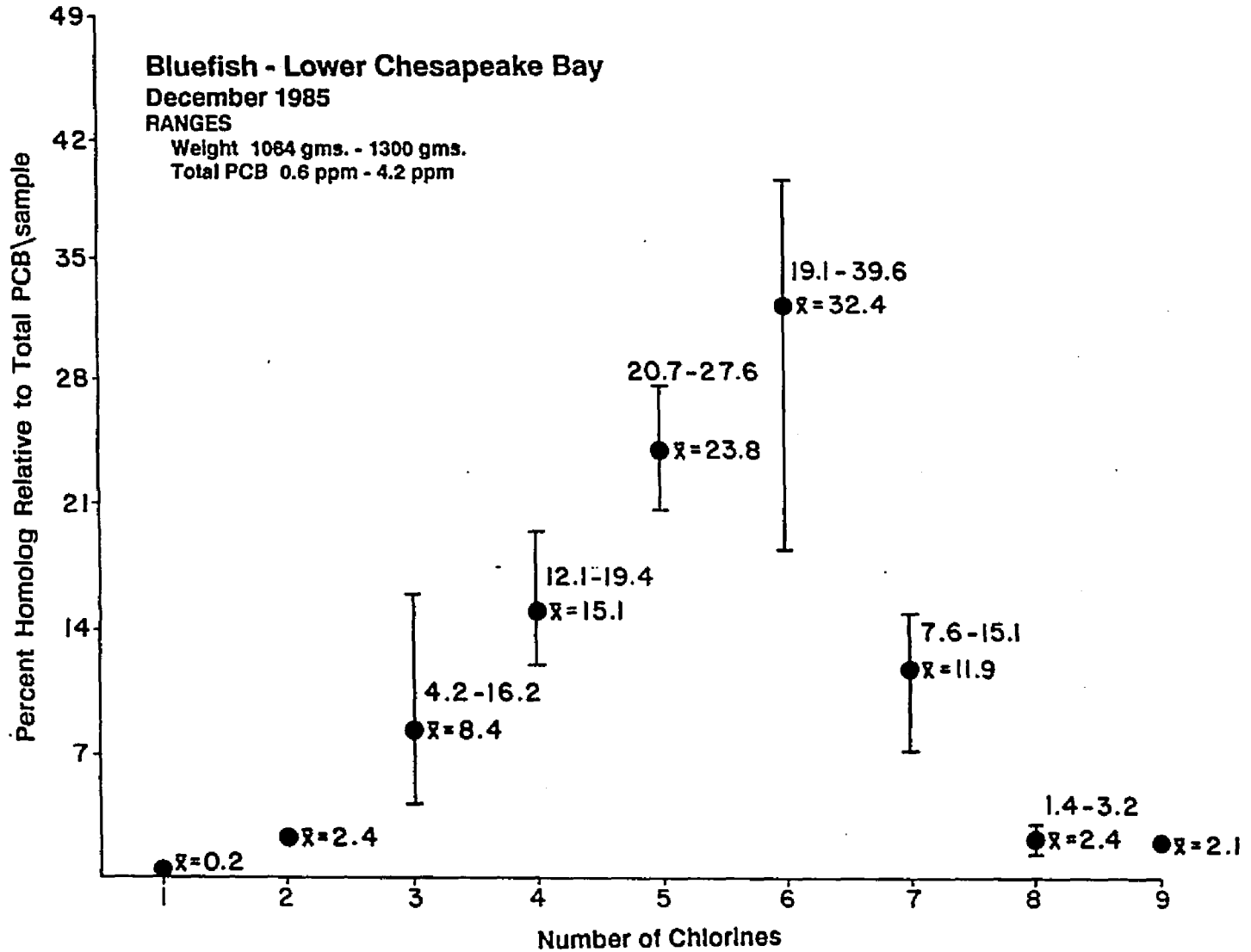
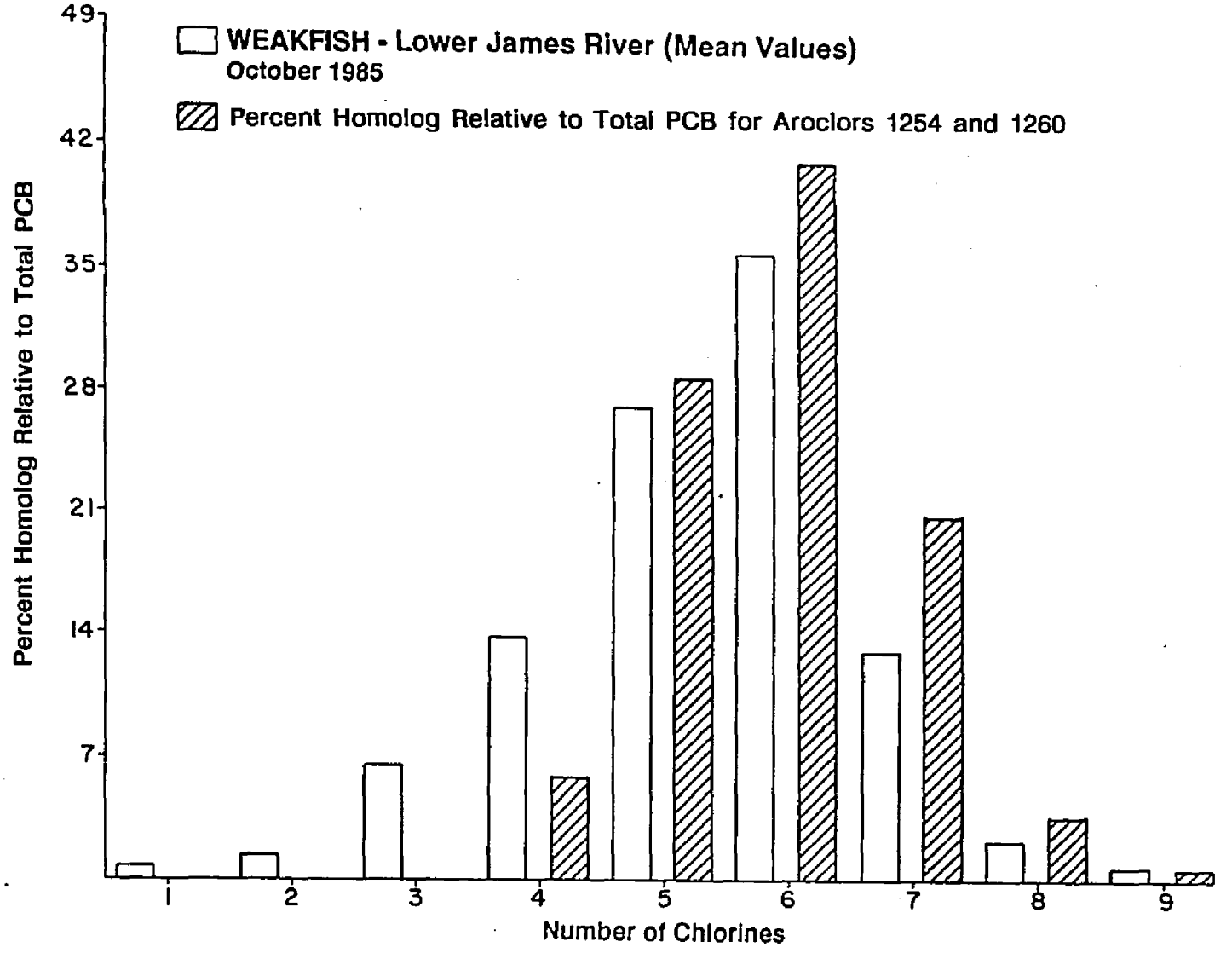

Bluefish - Lower Chesapeake Bay
December 1985
RANGES
Weight 1084 gms. - 1300 gms.
Total PCB 0.6 ppm - 4.2 ppm
Percent Homolog Relative to Total PCB\sample
49
42
35
28
21
14
7
19.1 - 39.6
x̄ = 32.4
20.7 - 27.6
x̄ = 23.8
12.1 - 19.4
x̄ = 15.1
4.2 - 16.2
x̄ = 8.4
7.6 - 15.1
x̄ = 11.9
1.4 - 3.2
x̄ = 2.4
x̄ = 0.2
x̄ = 2.4
x̄ = 2.1
1
2
3
4
5
6
7
8
9
Number of Chlorines

Figure 20. Graph of Homolog Distributions in Weakfish from the Lower James River in October and Aroclors 1254/1260.


WEAKFISH - Lower James River (Mean Values)
October 1985
Percent Homolog Relative to Total PCB for Aroclors 1254 and 1260
Percent Homolog Relative to Total PCB
49
42
35
28
21
14
7
1
2
3
4
5
6
7
8
9
Number of Chlorines

The similarity between the distribution patterns in bluefish and weakfish samples from the lower James River in October (Figures 15, 16) and the same species from the lower Chesapeake Bay in October (Figures 17, 18) also indicate that the fish from the lower James River, as well areas, were probably migrating into the lower Bay. A combining of fish populations from other areas may be one explanation for the large variation in congener composition and total PCB concentrations in the lower Bay in October.

A comparison of individual bluefish samples from the lower Bay in October revealed that three of the eight samples contained composition patterns more similar to Aroclor 1242/1254 while the remaining five contained patterns more similar to Aroclors 1254/1260 (Table 18). A differentiation was not found in the weakfish samples. The total PCB concentrations listed in this table suggest an association of high concentrations with the source of the Aroclors 1254/1260 pattern. Data from the lower James River samples do not indicate a pattern/concentration dependence.

Oliver and Niimi (1988) have reported homolog distributions for various species of fish collected from Lake Ontario localities. Distribution patterns were not significantly different between species of fish which included sculpins, alewives, smelt and salmonids (coho salmon, rainbow trout, lake trout and brown trout). Pentachloro-biphenyls dominated the homolog patterns in these samples with hexachloro compounds showing a secondary dominance. The total PCB concentrations in the salmonids were over four times greater than in the small smelt. Clearly from these data, a pattern/concentration

Table 18. Percent Homolog Distributions of Individual Bluefish from the Lower Chesapeake Bay in October.

	Homolog Group									
Wt. AR1254/1260	1	2	3	4	5	6	7	8	9	ΣPCB
394 gm		0.1	6.7	15.3	29.3	34.9	11.4	1.4	0.8	0.8
930 gm		3.2	7.4	17.0	25.5	33.2	11.1	1.6	0.5	1.2
960 gm	0.4	2.4	10.8	17.3	26.0	31.3	9.1	1.7	1.0	0.6
1885 gm	0.2	6.4	13.1	24.6	26.8	33.7	7.0	2.0	1.7	3.3
1470 gm		0.6	4.0	10.1	22.0	34.9	16.7	4.3	3.6	1.2
AR1242/1254										
389 gm	1.1	0.7	8.9	28.9	25.1	17.3	7.6	1.7	0.6	0.2
444 gm	1.0	--	18.3	31.7	22.7	17.5	6.0	1.5	1.0	0.3
905 gm		3.5	9.8	23.1	29.1	23.7	7.7	1.6	1.4	0.2

Σ PCB = ug/gm wet weight.

dependence was not indicated. A dependence of homolog pattern with the total PCB concentration in environmental samples was not indicated by data from Oliver and Niimi (1988) or data from this study.

Homolog Distribution Patterns-York River Weakfish

Weakfish samples from the York River collected during the same month contained distribution patterns discernibly different from the James River fish. The congener distribution patterns of the York River weakfish contained PCBs with predominantly three through six chlorines. Eighty-nine percent of the PCB contamination in these samples was attributed to this range of chlorine content (Figure 21). The contribution of congeners with chlorines greater than six was less than seven percent.

Correlation analysis of the mean percentages of these distribution patterns with the distribution pattern from an equal weight mixture of Aroclors 1242 and 1254 provided a correlation of 0.94 and is displayed in Figure 22. The clear bars indicate the mean values of the percent congener of each homolog group relative to the total PCB concentrations in the York River weakfish. The striped bars indicate the percent congener of each homolog class relative to the total PCB concentration in an equal weight mixture of Aroclors 1242 and 1254.

A discernible difference existed between the distribution patterns of the James River fish and the York River fish. Lower James River distribution patterns were distinctly lower in Cl-3 and Cl-4 biphenyls than the York River distribution patterns. This may

Figure 21. Graph of Homolog Distributions in Weakfish from the York River in October.

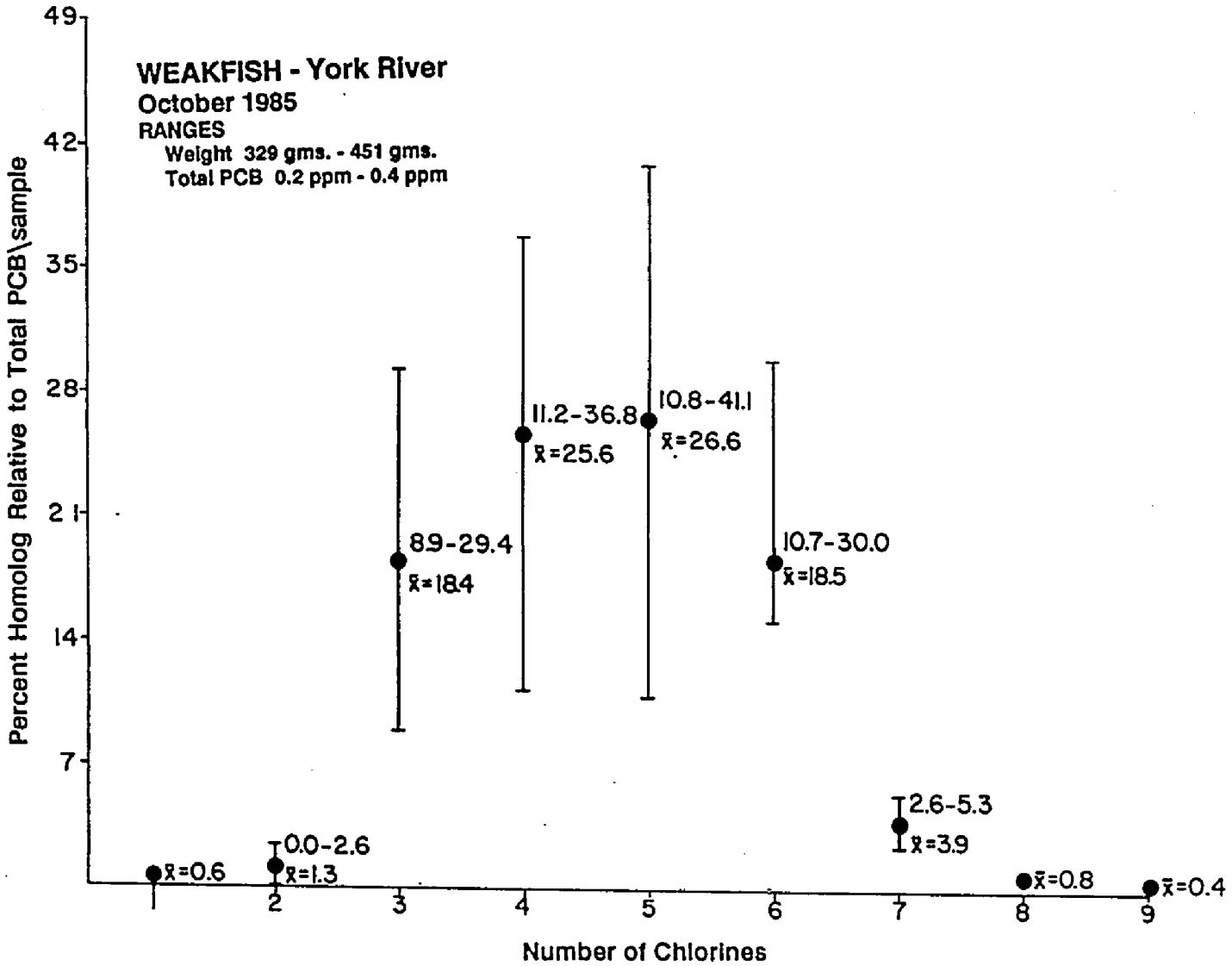
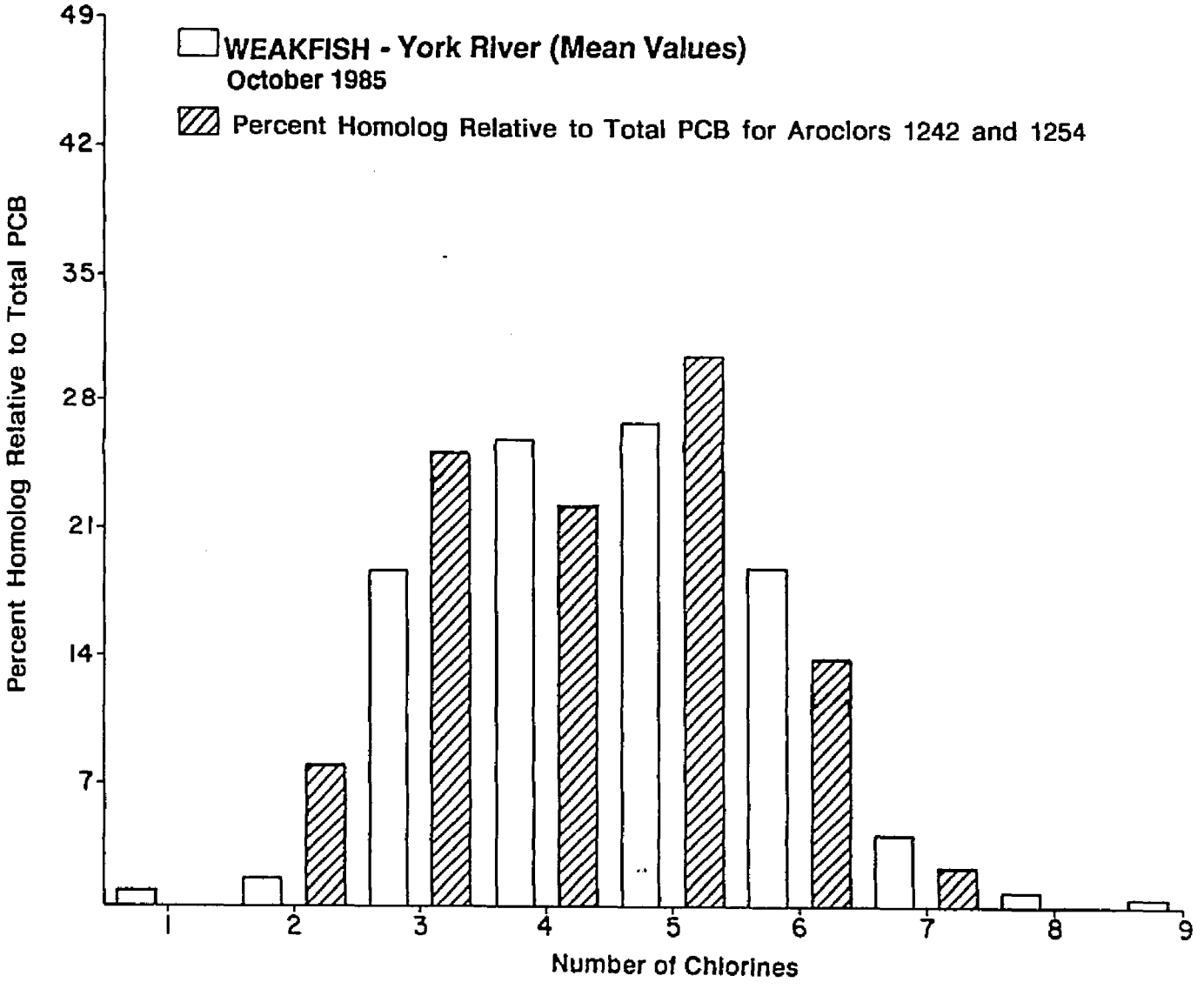

WEAKFISH - York River
October 1985
RANGES
Weight 329 gms. - 451 gms.
Total PCB 0.2 ppm - 0.4 ppm
Percent Homolog Relative to Total PCB\sample
49
42
35
28
21
14
7
0.0-2.6
x̄=1.3
x̄=0.6
8.9-29.4
x̄=18.4
11.2-36.8
x̄=25.6
10.8-41.1
x̄=26.6
10.7-30.0
x̄=18.5
2.6-5.3
x̄=3.9
x̄=0.8
x̄=0.4
2
3
4
5
6
7
8
9
Number of Chlorines

Figure 22. Graph of Homolog Distributions in Weakfish from the York River and Aroclors 1242/1254.


WEAKFISH - York River (Mean Values)
October 1985
Percent Homolog Relative to Total PCB for Aroclors 1242 and 1254
Percent Homolog Relative to Total PCB
49
42
35
28
21
14
7
1
2
3
4
5
6
7
8
9
Number of Chlorines

indicate a different source of PCBs for lower James River samples than for the York River samples.

December Samples-Lower Chesapeake Bay Bluefish

The distribution patterns of PCBs in bluefish from the lower Chesapeake Bay collected in December were similar to the patterns of bluefish and weakfish from the lower James River collected in October. Five of the six bluefish samples showed homolog patterns similar to Aroclors 1254/1260 where hexachlorobiphenyls were the dominant homolog group. The remaining sample pattern was similar to Aroclors 1242/1254.

Bluefish are not usually found in the lower Chesapeake Bay during December. Additionally, fish migrating into the James River characteristically acquire a detectable concentration of the pesticide, Kepone. Lower Chesapeake Bay fish, had they resided in the James River, should have had measured levels of Kepone in their tissues. Kepone analysis of the December bluefish revealed no traces of Kepone to a detection limit of 0.1 ppm. This suggests that the December bluefish may have migrated into the bay from elsewhere or may have been caught off shore after migrating south along the Atlantic coast.

Since the bluefish from December probably obtained their PCB contamination while residing in a different area than where they were caught, it is interesting to reconsider the similarity of congener compositions between the December bluefish and fish from the lower James River.

CHAPTER V

PCB CONGENER ANALYSIS-SEDIMENTS AND BIVALVES

INTRODUCTION

Environmental monitoring literature is replete with total PCB data found in the biotic and abiotic compartments of freshwater and marine aquatic environments. Significantly less information is available with respect to congener analysis because reliable chromatographic retention data based on analytical standard compounds have only recently been published (Mullin et al., 1984). The dissemination of this important information has stimulated efforts by several researchers to develop PCB congener analytical methodologies for environmental monitoring (Capel et al., 1985; Maack and Sonzogni, 1988; Oliver and Niimi, 1988; Niimi and Oliver, 1989; Schulz et al., 1989) and modelling. Several models have been developed to explain and predict the fate and distribution of hydrophobic compounds after entering various aquatic habitats (Pavlou and Dexter, 1979; Thomann and Di Toro, 1983; Di Toro, 1985; Mackay et al., 1985a; Mackay et al., 1985b; Mackay et al., 1986).

The construction of homolog distribution patterns for PCBs in environmental samples has become one technique of data manipulation which potentially can provide additional information about the partitioning processes which occur in aquatic environments. The

contribution of each homolog class to a total PCB concentration in water or sediment may be different depending on physical-chemical processes in the physical compartments (Oliver and Niimi, 1988). Similarly, distribution patterns may be different among trophic levels in the biotic compartments or within aquatic organisms (Weigelt, 1986; Oliver and Niimi, 1988; Duinker et al., 1988). Baseline information about the total PCB concentrations and homolog distribution patterns of the biotic and abiotic compartments in aquatic environments may be helpful in estimating the stresses within a system.

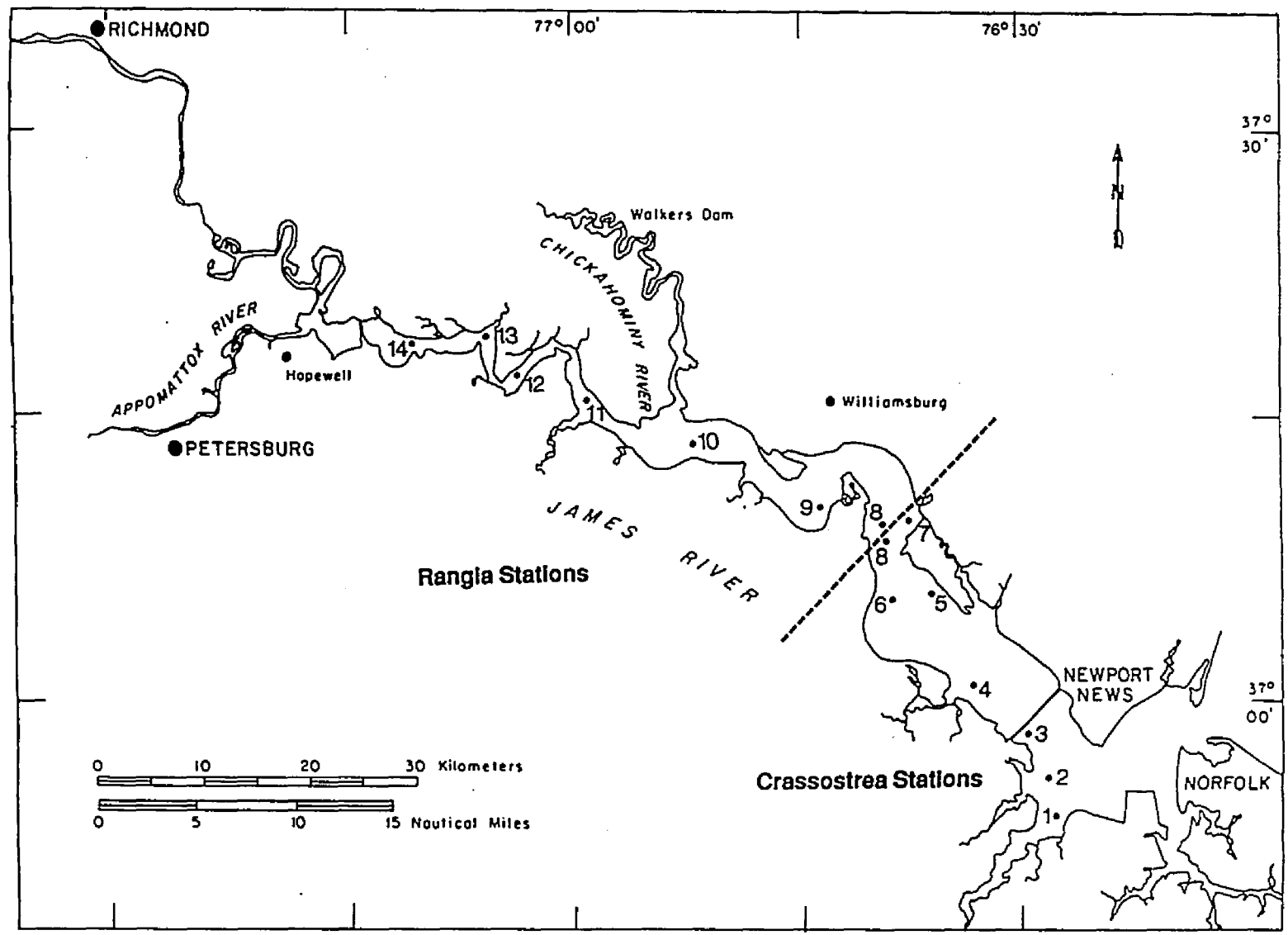
The purpose of the work reported here was to determine total PCB concentrations and homolog distributions in the sediments, oysters (Crassostrea virginica) and brackish water clams (Rangia cuneata) from the James River. Subsequently, estimations of the differences and similarities between the acquired total PCB concentrations, constructed patterns and sample locations of sediments and bivalves would be performed.

MATERIALS AND METHODS

Sample Collection

All samples were collected in October of 1986. Sampling stations were located from approximately 15 KM to 115 KM upstream from the mouth of the James River (Figure 23). The sediment samples represent the top 2 cm of the sediment bed and were collected with a Ponar surface grab. Bivalve samples were collected with a clam dredge or oyster dredge.

Figure 23. Map of James River with Sampling Stations 1 through 14.


RICHMOND
77° 00'
76° 30'
37° 30'
37° 00'
N
Walkers Dam
CHICKAHOMINY RIVER
APPOMATTOX RIVER
Hopewell
PETERSBURG
Williamsburg
JAMES RIVER
Rangia Stations
Crassostrea Stations
NEWPORT NEWS
NORFOLK
1
2
3
4
5
6
7
8
8
9
10
11
12
13
14
0 10 20 30 Kilometers
0 5 10 15 Nautical Miles

Sample Preparation

All samples were freeze-dried prior to soxhlet extraction with methylene chloride. Composite bivalve samples, consisting of 5-8 specimens each, were prepared to provide sufficient material for analysis. Extracted sediment material ranged from 50 to 150 grams (dry weight) and extracted bivalve tissue ranged from 1.3 to 2.2 grams (dry weight). Sample extracts were fractionated to remove high molecular weight biogenic material with gel permeation chromatography on Biobeads SX-8 with further fractionation by performance liquid chromatography. Detailed information on the sample preparation can be found in Bieri et al. (1986).

Analytical Protocol

PCB concentrations in these samples were assumed to be minimum values because spike recovery data which estimates the extraction efficiencies and losses due to sample preparation were not available.

Identification and quantification methodology as well as analytical instrumentation and operating conditions were consistent with the same described previously. Homolog distribution patterns were calculated as weight percent compositions of the total PCB concentrations.

RESULTS AND DISCUSSION

Sediments

The results of PCB congener analysis in sediments from the James River during the fall of 1986 indicated relatively constant total PCB concentrations at most sampling stations along the length of the river (Figure 24, Table 19). Two sampling stations showed a distinctly higher PCB concentration when compared to the remaining stations. Stations 10 and 11 (75 and 85 km, respectively, upstream from the mouth) were about twice the total PCB concentrations of the next highest station, however their homolog distribution patterns were not appreciably different from stations bracketing this area or from each other.

A comparison of the PCB congener homolog patterns of the sediments showed the Cl-6 biphenyls to dominate at all stations. The stations downstream from 100km (stations 1-12) had a homolog pattern dominated by Cl-6 biphenyls with the Cl-4, Cl-5 and Cl-7 biphenyls comprising the majority of the remaining total PCB concentration. Upstream from 100km (stations 13 and 14), the two remaining stations provided distributions reduced in PCBs containing seven chlorines or greater (10.3%).

Biota

The total PCB concentrations in oysters were low through most of the sampling range in the James River (Figure 25, Table 20). A mean total PCB concentration for all samples was calculated to be 173.9 ng/gm dry/weight. Samples from station 8 showed the highest

Figure 24. Total PCB Concentrations in Sediment from the Tidal James River.

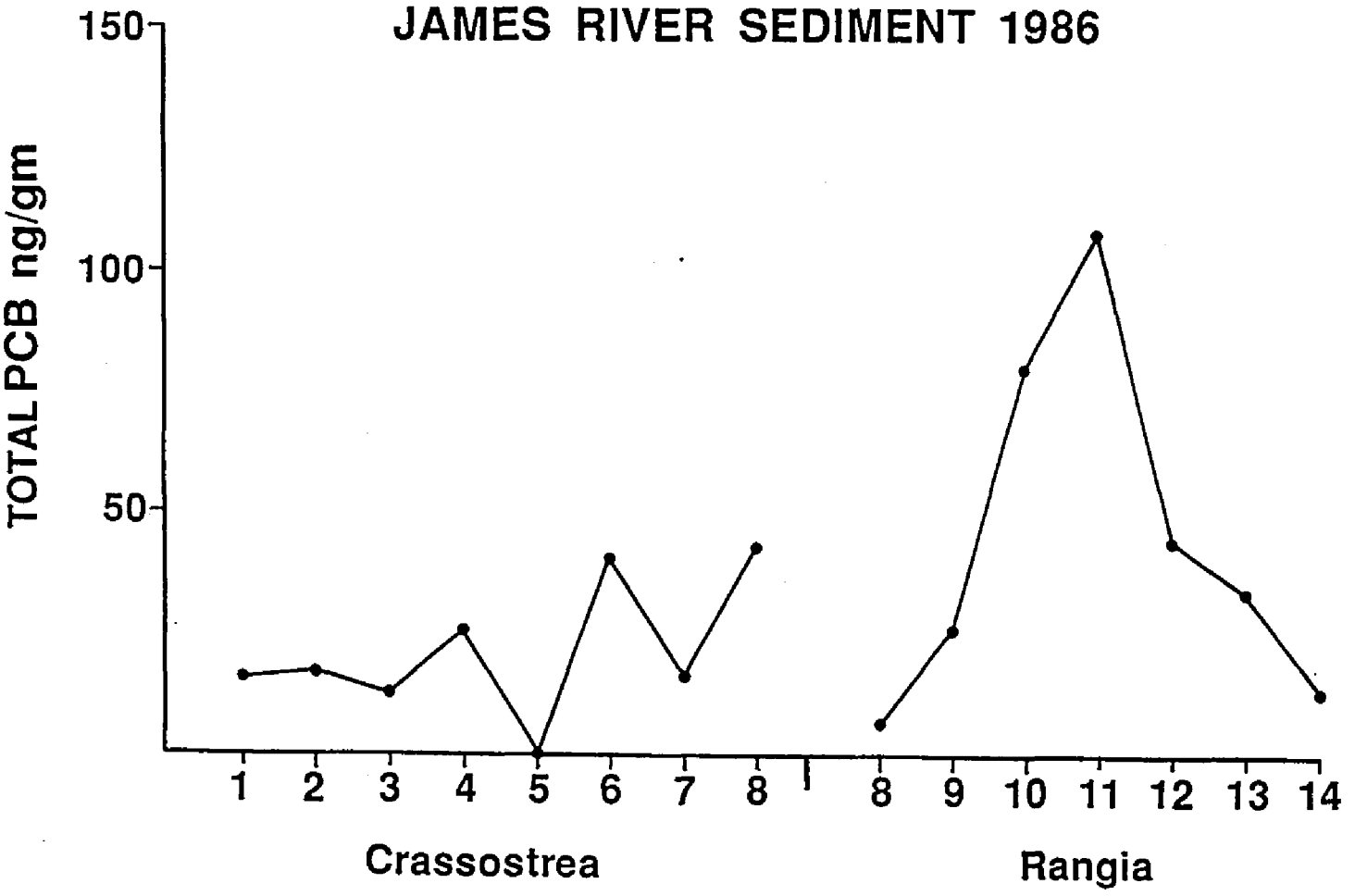

JAMES RIVER SEDIMENT 1986
TOTAL PCB ng/gm
150
100
50
1
2
3
4
5
6
7
8
8
9
10
11
12
13
14
Crassostrea
Rangia

Table 19. Percent Homolog Distributions and Total PCB Concentrations in Sediments from the Tidal James River.

Homolog Group	*Crassostrea* Stations 1	2	3	4	5	6	7	8
Mono-	-	-	-	-	-	-	-	0.4
Di-	1.0	-	0.9	0.4	-	0.2	1.4	1.5
Tri-	2.4	1.6	2.4	5.6	-	6.6	2.1	3.3
Tetra-	13.4	12.4	10.7	11.7	23.8	15.4	9.7	8.2
Penta	19.7	20.5	21.3	26.6	33.6	26.0	14.0	13.3
Hexa-	41.2	48.0	46.1	34.1	38.5	35.0	46.7	44.9
Hepta-	14.3	15.7	12.6	15.6	--	12.9	19.0	21.0
Octa-	3.2	1.4	4.0	4.2	--	2.8	4.5	6.1
Nona-	0.8	0.3	1.9	1.8	4.0	1.0	2.6	1.6
Σ PCB	15.7	17.5	12.6	25.5	0.5	40.7	16.3	42.8

Homolog Group	8	9	*Rangia* Stations 10	11	12	13	14
Mono-	--	--	--	--	--	--	--
Di-	4.2	3.8	0.7	0.8	1.9	2.5	5.2
Tri-	2.4	3.3	7.8	6.9	4.2	5.4	5.3
Tetra-	11.3	11.0	9.5	8.1	9.4	17.5	12.7
Penta-	15.1	13.7	15.8	18.0	18.4	27.2	28.1
Hexa-	44.1	46.1	47.3	38.7	45.1	36.9	36.8
Hepta-	17.3	15.4	14.2	19.4	15.3	8.5	8.8
Octa-	4.3	4.2	3.6	4.2	3.9	1.3	0.7
Nona-	2.4	2.4	1.0	0.8	1.8	0.5	0.4
Σ PCB	6.5	25.8	79.6	107.5	43.2	32.8	12.4

Σ PCB: Total PCB concentrations in ng/gm dry weight.

Figure 25. Plot of Total PCB Concentrations in Crassostrea and Rangia from the Tidal James River.

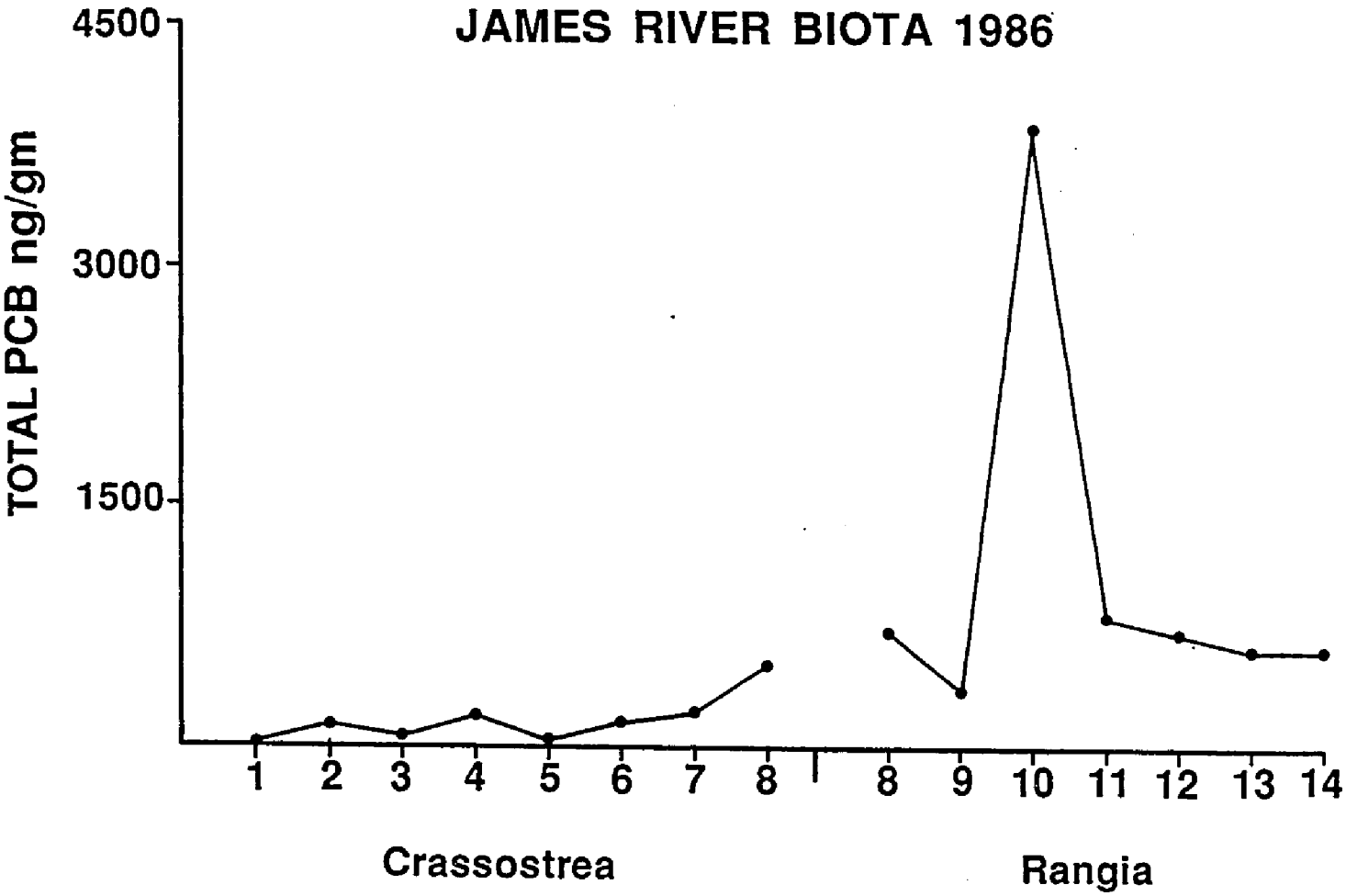

JAMES RIVER BIOTA 1986
TOTAL PCB ng/gm
4500
3000
1500
1
2
3
4
5
6
7
8
8
9
10
11
12
13
14
Crassostrea
Rangia

Table 20. Percent Homolog Distributions and Total PCB Concentrations in Crassostrea and Rangia from the Tidal James River.

Homolog Group	Crassostrea Stations 1	2	3	4	5	6	7	8
Mono-	-	-	-	-	-	-	-	-
Di-	-	-	-	-	-	-	-	-
Tri-	27.0	19.1	6.7	8.1	14.8	-	2.1	6.0
Tetra-	4.0	18.4	16.4	15.9	30.7	15.4	10.6	10.3
Penta-	18.9	27.8	32.4	33.2	23.8	38.1	35.8	33.9
Hexa-	45.3	28.2	37.2	34.7	18.8	32.7	41.9	34.5
Hepta-	4.8	5.5	7.3	8.1	4.4	12.2	9.0	13.5
Octa-	---	---	---	--	7.4	1.6	0.6	0.4
Nona-	---	1.1	---	--	--	--	--	--
Σ PCB	46.7	124.7	79.6	200.5	47.0	152.8	218.4	521.2

Homolog Group	Rangia Stations 8	9	10	11	12	13	14
Mono-	-	-	0.5	--	--	--	--
Di-	-	-	2.4	--	0.7	--	0.6
Tri-	1.7	4.4	19.4	2.4	5.0	3.1	2.9
Tetra-	8.9	11.8	35.2	10.5	8.0	14.1	11.9
Penta-	18.9	42.3	33.7	20.4	26.0	26.2	29.3
Hexa-	39.5	30.2	7.7	37.3	33.0	34.1	35.2
Hepta-	24.4	11.2	1.0	21.9	20.5	17.7	17.1
Octa-	5.0	--	--	5.1	5.6	3.4	2.2
Nona-	1.6	--	0.1	2.3	1.2	1.3	0.8
Σ PCB	731.5	378.1	3848.0	837.8	716.2	602.6	616.9

Σ PCB: Total PCB concentrations in ng/gm dry weight.

concentration of PCBs. This station was the furthest upstream of the oyster sampling stations in the James River. The PCB homolog patterns in the oysters were variable. Three of the eight oyster stations were dominated by Cl-6 biphenyls, however Cl-5 and Cl-6 compounds were the more abundant congeners at most of the sampling stations.

The total PCB concentrations in Rangia samples were similar at all stations except station 10 which was 3848.0 ng/gm dry weight (Figure 25, Table 20). The mean concentration of total PCB for all Rangia stations except station 10 was 647.2 ng/g (dry wt.). Congener homolog patterns in the Rangia samples were variable. In general, the homolog patterns at the stations upstream from station 10 were similar. The sample patterns were dominated by Cl-6 biphenyls with Cl-4, Cl-5 and Cl-7 biphenyls comprising the majority of the remaining total PCB concentrations.

The distribution patterns in Rangia samples at stations 9 and 10 were different from each other and their corresponding sediment patterns. Station 8, the Rangia station furthest downstream, was dominated by Cl-6 biphenyls and station 9 was dominated by Cl-5 biphenyls. The Rangia sample at station 10 was dominated by Cl-4 and Cl-5 biphenyls in nearly equal proportions and was the highest in total PCB concentration. These three stations exhibited a progressive decrease in hexa-, hepta-, octa- and nonachlorobiphenyls with increasing distance upstream. Station 8 biota contained a similar pattern to station 11 indicating a recovery of the endemic pattern in this segment of the river.

Sediment and Biota Comparisons-Correlation Analysis

A comparison of oyster PCB homolog patterns with the corresponding sediment PCB homolog patterns at each station did not show a consistent correlation. Correlation analysis of the homolog distributions in the oyster samples with distributions in the sediments provided the correlation coefficients listed on table 21. Three of the eight stations (1, 3 and 7) dominated by Cl-6 biphenyls in the sediment pattern reflected the same dominance in the biota. Good correlation (0.95) was found between the patterns in the sediment and oysters at one station, station 4. This station was dominated by Cl-5 and Cl-6 biphenyls in both sample types and comprised over 60% of the total PCB concentrations.

By contrast, a comparison of Rangia PCB homolog patterns with the corresponding sediment PCB homolog patterns showed good similarity. Five of the seven stations (8, 11-14) where the sediments were dominated by Cl-6 biphenyls reflected the same dominance in the biota. Correlation analysis of the sediment PCB distributions with those in the clam samples provided the correlation coefficients in table 21. Good correlation (>0.95) resulted at all stations except stations 9 and 10.

Comparisons between homolog patterns of bluefish and weakfish from the James River with an equal weight mixture of Aroclors 1254/1260 were described in the previous chapter. Table 21 lists correlation coefficients from correlation analysis of the respective sediment and bivalve samples with the same Aroclor mixture homolog pattern. Correlation analysis of sediments with this Aroclor mixture

Table 21. Sediment and Bivalve Correlations (r).

Crassostrea Station	1	2	3	4	5	6	7	8
Sed/Biota	0.76	0.64	0.20	0.95	0.73	0.83	0.83	0.80
Sed/54,60	0.95	0.95	0.94	0.97	0.71	0.94	0.92	0.92
Biota/ 54,60	0.66	0.63	0.87	0.86	0.29	0.87	0.93	0.94

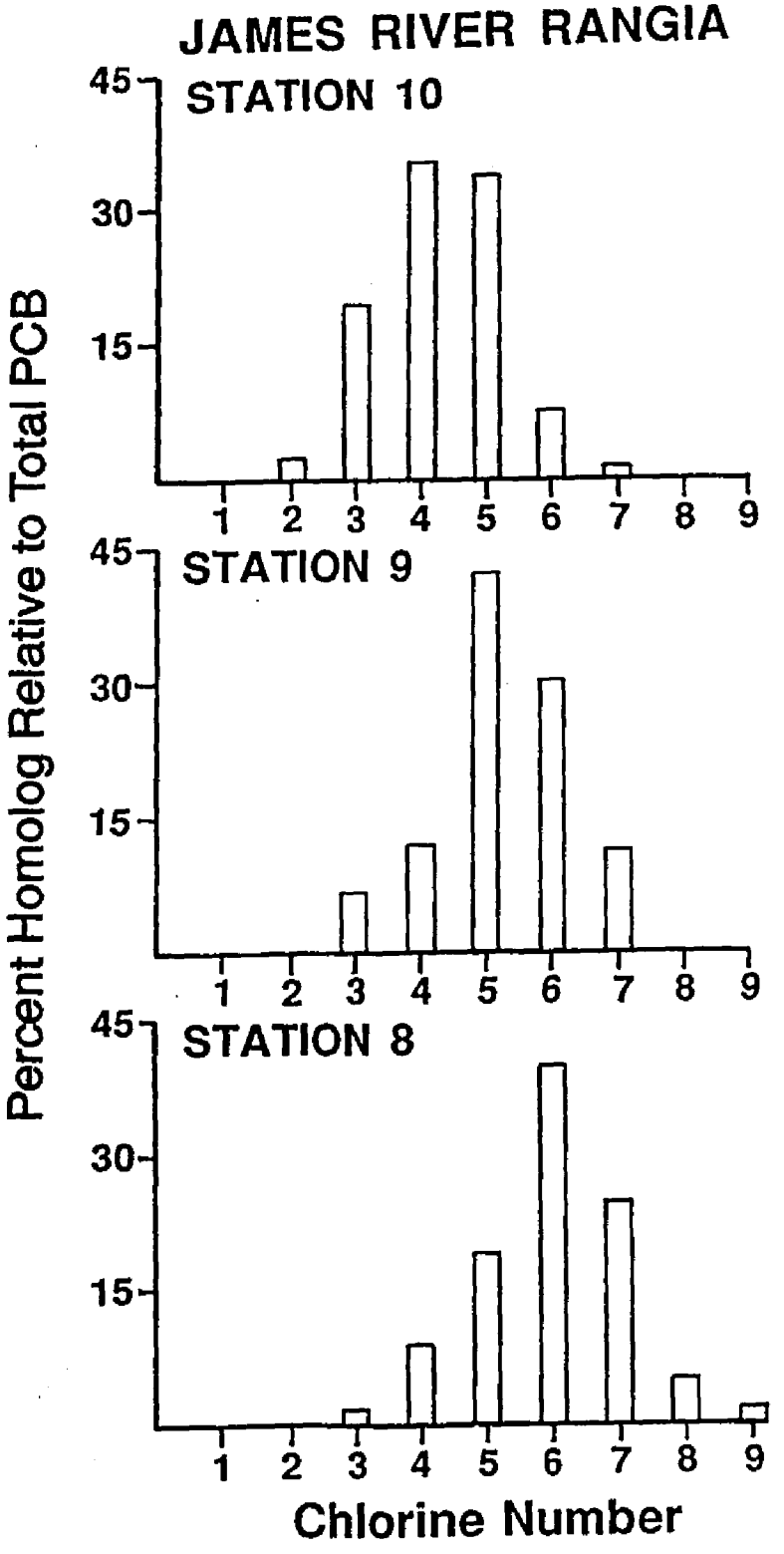
Rangia Station	8	9	10	11	12	13	14
Sed/Biota	0.96	0.65	0.17	0.98	0.95	0.95	0.96
Sed/54,60	0.92	0.90	0.90	0.96	0.94	0.89	0.92
Biota/ 54,60	0.96	0.85	0.22	0.98	0.99	0.97	0.98

provided correlation coefficients greater than or equal to 0.89 at all stations except station 5. The same was performed with the biota homolog patterns and resulted in greater variation of correlation coefficients. Two of the Crassostrea stations and five of the Rangia stations resulted in correlation coefficients greater than or equal to 0.93.

As was stated earlier, the sediment distribution patterns in the Rangia segment of the river were similar. This was in contrast to the biota patterns at stations 9 and 10 which contained increasingly lower molecular weight material (Figure 26) with distance upstream. A comparison between stations 9 and 10 showed nearly identical sediment distribution patterns ($r = 0.99$), while the biota distribution patterns were discernibly different from each other ($r = 0.56$). The biota PCB pattern for station 9 was dominated by Cl-5 biphenyls and was similar to the homolog distributions in Aroclor 1254 ($r = 0.99$). Station 10 was dominated by an almost equal proportion of Cl-4 and Cl-5 biphenyls and was dissimilar to all Aroclor homolog distributions or any combinations of the same.

Station 9 and 10 are in the region of the turbidity maximum in the tidal James River (Nichols and Trotman, 1977). The scouring of the river bottom by the salt wedge resuspends sediments which are then transported into the water column along the saltwater/freshwater interface. Sorption and desorption of chlorinated hydrocarbons to suspended sediments have been shown to be suspended sediment concentration dependent (Voice et al., 1983). Additionally, saline water is high in ionic elements which are available to complex with

Figure 26. Graph of Homolog Distributions in Rangia at Stations 8, 9 and 10 from the Tidal James River.


JAMES RIVER RANGIA
STATION 10
STATION 9
STATION 8
45
30
15
1 2 3 4 5 6 7 8 9
Percent Homolog Relative to Total PCB
Chlorine Number

humic and fulvic acids forming macromolecular complexes. These complexes can potentially bind certain chlorinated hydrocarbons (Hassett and Milicic, 1985), thus removing them from solution. Physico-chemical processes such as these could alter an Aroclor distribution pattern or the endemic distribution pattern in the various biotic or abiotic compartments of a river.

CHAPTER VI

CONCLUSIONS

The analytical methodology presented for the determination of total PCB concentrations and homolog distribution patterns provided a relatively rapid analytical run time of one hour per sample. Distribution patterns of Aroclor standards were comparable to the same reported by other researchers. The Hall detector provided good sensitivity with a more predictable response based on the molar chlorine content of a compound. This was in distinct contrast to the response of the electron capture detector within a homolog group. Although the electron capture detector is ultimately more sensitive, the selectivity of the Hall detector can be an aid when analyzing samples which generally contain halogenated and non-halogenated residues. One additional consideration for choosing the Hall detector for routine PCB analysis is that the GC/Hall detector system is less expensive to acquire and operate than GC/MS instrumentation.

The analysis of blue fish and weakfish samples from the lower Chesapeake Bay and lower James River included some fish with levels of total PCB concentrations greater than 2.0 ppm during the fall of 1985. Weakfish from the York River did not contain comparable concentrations during this time period. A comparison of homolog distribution patterns from these samples suggests a different source of contamination for the York River samples than for the James River

samples. The differentiation of distribution patterns in bluefish from the lower Chesapeake Bay in October of 1985 was probably a result of the combining of bluefish populations from various areas during the fall migration southward.

Sediment samples from the tidal James River contained homolog distribution patterns which were relatively consistent throughout the sampling range. The highest total PCB concentrations were in the area of the turbidity maximum. Distribution patterns in oyster samples were highly variable and relatively low in total PCB concentrations. Most of the Rangia samples, by contrast, contained distribution patterns which were comparable to each other and to the corresponding sediment homolog pattern. Homolog patterns in Rangia collected at two sampling stations within the region of the turbidity maximum were decidedly different from the other Rangia homolog patterns. Sample patterns in these samples were deficient in the higher chlorinated congeners. Physical-chemical partitioning processes in this segment of the river may be responsible for the alteration of the homolog distribution patterns in these samples.

THOUGHTS FOR FUTURE RESEARCH

The following suggestions are provided for further development of the initiated analytical methodology to achieve a comprehensive chlorinated hydrocarbon programs:

1. It is important to develop methodology for the resolution of all 209 PCB congeners which can be employed in a cost effective manner. This may require the use of more than one GC capillary column, simultaneously, each with a different stationary phase coating and multiple GC detectors.

2. The construction of ortho, meta and para substitution distribution patterns could provide additional information about the partitioning of PCB congeners between the biotic and abiotic compartments of aquatic environments.

3. Additional monitoring of PCB congener partitioning within the region of the turbidity maximum in other estuaries should be initiated. Subsequent comparisons between similar types of estuaries may provide information to better understand the fate and transport of PCB congeners with respect to homolog class and the more toxic compounds.

4. Analytical methodology for the analysis of other complex mixtures should be developed. These would include innovative sample preparation techniques to separate these mixtures from each other to minimize interferences.

5. The integration of these analytical methodologies with a sophisticated principal components pattern recognition model would provide a powerful and comprehensive chlorinated hydrocarbon monitoring program. Data acquired from these methodologies could be manipulated with the presently available Chemometrics SIMCA series of programs and be of significant benefit.

APPENDIX

OPERATION OF THE TRACOR MODEL 700A HALL ELECTROLYTIC CONDUCTIVITY DETECTOR

The operation of the Hall detector can be a frustrating experience for even the most accomplished GC analyst. Since the detector has, historically, not been used for PCB congener analysis; this author would like to offer some suggestions to anyone considering using the HECD.

Provided below are ten suggestions about preferred equipment and troubleshooting aspects of the Model 700A Hall detector.

1. All gases must be ULTRA HIGH PURITY. Gases suitable for GC/MS analysis will be good for GC/HECD analysis.

2. Stainless steel tubing, valves and fittings which have been solvent rinsed with high purity methanol, acetone and hexane.

3. Stainless steel diaphragm pressure regulators and flow regulators.

4. Once in operation the nickel reaction tube will be the most frequent problem. If peak shape or response are poor, change reaction tube first. Should a new reaction tube prove ineffectual, check for leaks. Joints which frequently form leaks can be silver soldered thus eliminating future problems.

5. The coarse zeroing adjustment should be in the full counter-clock position. This is the OFF position. The fine zeroing adjustment should be in the full clockwise position. This is also the OFF position. All chart recorder zeroing can be accomplished with recorder adjustments. If adjustment of the coarse zeroing control is needed to bring the detector signal on scale, the system has probably been contaminated by the gases or a component in the gas delivery lines.

6. If the detector provides no response to analytical standards when a new reaction tube has been installed, check to be sure that the reaction tube is not stainless steel. Nickel tubing is magnetic while good quality stainless steel is not.

7. Peak response as well as detectable peak resolution is dependent on the condition of the reaction tube. Carbon fouling can reduce the quality of a chromatogram which will appear as a column in poor

condition. It is best to change reaction tube before suspecting a poor column.

8. Cleaning of the reactor base, conductivity cell or regeneration of the ion exchange column should be required only once or twice per year.

9. Reactor operating temperature and the quality of sample preparation will determine the frequency of reaction tube replacement. Nickel tubing purchased from a chromatography products supplier is inexpensive when purchased in continuous lengths.

10. It is highly recommended, by this author, that sample preparation for HECD analysis should be performed with the same rigorous procedures as for ECD analysis. The benefits of analysis by the Hall detector are not from the apparent reduced analytical costs by the omition of steps in sample preparation, but rather in the analytical confidence gained with selective halogen detection.

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