## John G. Haggard

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August 11, 1994

Mr. Douglas J. Tomchuk
Remedial Project Manager
U. S. Environmental Protection Agency

Emergency \& Remedial Response Div.
26 Federal Plaza - Room 747
New York, Ny 10278
Dear Mr. Tomchuk:

## RE: STRIPED BASS FISH CONSUMPTION ADVISORY - STATE OF DELAWARE

As you are aware, the Institute for Evaluating Health Risk (IEHR) has reported on the result of a reevaluation of a number of historical laboratory studies of PCB carcinogenic effects in rats. The reassessed data underscore that there are major differences in carcinogenic potential based on the degree of chlorination of the PCB mixture. While the results from studies of mixtures with $60 \%$ chlorination consistently report a high incidence of liver tumors, studies in rats which were fed mixtures with $54 \%$ or $42 \%$ chlorination did not detect statistically significant elevations of liver tumors. The General Electric Company (GE) has requested that as a result of the IEHR findings, the regulatory agencies involved in the Hudson River project not treat all PCB as if they had a chlorination level of $60 \%$, when in fact the majority of PCB's found in Hudson River fish, water and sediment are much less chlorinated. The preponderance of lower chlorinated PCBs is not unique to the Hudson River, since nationwide it is estimated only $12 \%$ of all PCB formulations sold had a chlorination level of $60 \%$.

While, the U. S. EPA and New York State agencies have not yet adopted this new scientific information, it has been utilized by the State of Delaware. Enclosed for your information is a health advisory for striped bass in the Delaware Estuary issued by the Delaware Department of Natural Resources and Environmental Control. A key finding of the assessment performed by the Department is given on page 26 of the enclosed report and states:

[^0]

GE again requests that this approach be adopted for assessing health risks due to consumption of fish from the Hudson River. Please let me know if you would like any additional information related to this issue.


Engineering Project Manager

Enclosure

June 9, 1994
Vol. 24, No. 169

For Further Information, Contact: David Small (DNREC), (302) 739-4509

Dr. Leroy Hathcock (DHSS),
(302) 739-5617

## STATE ISSUES HEALTH ADVISORY ON DELAWARE ESTUARY FISH

The Delaware Department of Natural Resources and Environmental Control (DNREC) and the Department of Health and Social Services (DHSS) today issued a public health advisory on the consumption of several fish species from the Delaware River and Bay.

The advisory comes as the result of intensive study of contaminants in fish tissues and is being issued due to the detection of elevated levels of polychlorinated biphenyls (PCBs) in the fish.

Specifically, the advisory recommends no consumption of recreational-size striped bass ( 28 -inches and larger), channel catfish, white catfish and white perch taken from the Delaware River between the Pennsylvania - Delaware line and the Chesapeake and Delaware Canal.

Limited consumption is being recommended for striped bass, channel and white catfish caught in the area from the Chesapeake and Delaware Canal to the mouth of Delaware Bay. Fishermen, their friends and families who may consume these species of fish from below the Chesapeake and Delaware Canal are advised to limit their consumption to five, eight-ounce meals per year. Consumption by children is advised to be limited to three, four-ounce meals per year.

The reason the advisory is more restrictive north of the Canal is because the type of PCBs found in the fish from that area represent a greater human health risk.

The federal Superfund program and the State Hazardous Substance Cleanup Program are investigating several potential sources of PCB contamination. According to scientists, the presence of PCBs now being detected in the river and bay reflect, in part, past disposal practices. Overall, the health of the Delaware Estuary has improved significantly during the past 20 years.

The advisory is a precautionary measure and is based on a projected health risk to fishermen, their friends and families who may consume fish from the river and bay over a long period of time. For instance, scientists project the lifetime cancer risk to people who consume recreational size striped bass taken from the river between the Chesapeake and Delaware Canal and the Pennsylvania line is 1 -in- 36,000 assuming as little as one 8 -ounce meal per year. Risk for people consuming one 8 -ounce meal per week of these same fish increases the risk to 1 - in- 670 .

Continued, ...

# S'TATE OF DELAWARE FISH CONSUMPTION ADVISORY AREAS FOR THE DELAWARE ESTUARY 



Hnated?

Toxics such as PCBs and other contaminants such as heavy metals often end up in our waterways from a variety of sources - abandoned hazardous waste dumping areas or from sewage treatment harges. Many of these conrarninants can remain in the environment for years and end up in the bottom sediments of our waterways. Many fish feed off the bottom and ingest these contaminants directly; others eat smaller organisms which contain contaminants. The higher the level of organism in the food chain, the greater the concentration of contaminants.

What contaminant is of great. est concern in fish caught in the Delaware River and Bay?

PCBs, or polychlorinated biphenyls, are the contaminants of :atest concern in several species sh found in the Delaware 1...er and Bay. This family of chemicals are chlorine-based
compounds which were once widely used as coolants, especially in electrical transformers. Their manufacture and use, to a large extent, is now prohibited in this country.

X nich fish have been shown to be contaminated?

In the testing performed by the Delaware Department of Natural Resources and Environmental Control (DNREC), the highest average concentrations of PCBs have been found in catfish. However, tests also have shown levels of concern in striped bass and white perch taken from the Delaware River.

What is the State doing about

Staff with DNREC and the Department of Health and Social Services have issued advice to fishermen, their friends and families on the consumption of fish caught in the Delaware River and

Bay. Staff with DNREC are also investigating potential sources of contamination.

$\square$an I eat the fish?

The State is recommending that striped bass, white perch, and channel or white catfish caught in the area from the C\&D Canal to the Pennsylvania line not be consumed. The advisory also recommends that people limit their consumption of striped bass, channel and white catfish caught in the area from the C\&D Canal south to the mouth of the Delaware Bay to five, eight-ounce meals per year and that children limit their consumption to three. four- ounce meals per year.

Whhat are the health risks associated with eating contaminated fish?

PCBs are a cancer-causing agent in laboratory animals, although tests on humans have proved inconclusive. PCBs also can cause neuro-
and cisorders of the immune sistem. If the advisory is followed, however, the risks of developing cancer from eating fish are a lot Less than from being in an automoe accident or developing cancer: from smoking cigarettes.
ization, higher sediment concentrations and lower dilution are all believed to contribute to this finding. Therefore, fish which spend more time in that area are likely to accumulate higher levels of contaminants.

Are there other things I can do to manage my risks?

Yes, measures include:

1. Follow advisories issued by the state.
2. Eat smaller fish, as long as they are of legal size.
3. Dress and clean fin by skinning
letting the fat drip away while cooking.

Wmation?

Call the Department of Natural Resources and Environmental Control, Office of Information an Education at 739-4506 or the Department of Health and Social Services, Division of Public Health at 739-5617.


## ommon Risks

## Cancer Risks

## Average Lifetime Risk

All Cancers ..... 1 in 3
Lung Cancer ..... 1 in 12
Eating 8 ounce Striped Bass per week from Delaware river over 30 years ..... 1 in 690
Diagnostic X-Ray ..... 1 in 7,100
Eating 8 Ounce Charcoal Broiled Steak per week ..... 1 in 48,000
Drinking Water EPA Limit for Trichloroethylene ..... 1 in 6,700,000
Other Risks
Motor Vehicle Accident ..... 1 in 56
Accident at home ..... 1 in 120
Police killed in line of Duty ..... 1 in 150
Electrocution ..... 1 in 2,500

## Fact Sheet

## TEE <br> , <br> EALTH ADVISORIES

 ON FISH CONSUMPTIONFishing is an important activity in Delaware's inland and coastal waters and provides wholesome, relaxing recreation. In addition, fish are a good source of protein and can decrease your chances of Trt disease. Unfortunately, . . tain fish taken from some locations in Delaware waters contain toxic chemicals which may be harmful to your health.

The amounts of these chemicals found in Delaware fish are not known to cause immediate sickness, but they can collect in the body over time and may affect your health or that of your children.

Fish may absorb and concentrate certain toxic chemicals if they are present in their environment. Even when present in water in extremely small amounts, pollutants such as PCBs tend to accumulate in fish sue over time.


To help protect public health, the Department of Natural Resources and Environmental Control (DNREC) and the Department of Health and Social Services (DHSS) have joined forces to collect and analyze fish tissue regularly and consider appropriate actions to protect public health.

Action levels have been established for various pollutants. These levels are used to establish health advisories based on pollutant levels within fish. The action level which has been established by DNREC and DHSS is based on a risk of one additional case of cancer per population of 100,000 people. This level is consistent with the State's Hazardous Substance Cleanup Program.

The assumption of one additional case of cancer per 100,000 population is based on the premise that the population is consuming fish over a long period of time (30 years).

How can anglers manage their health risks?

1. Adhering to health advisories issued by the state.
2. Eating smaller representatives of the species as long as they are of legal size.
3. Dressing and cooking the fish in a manner which reduces contaminants such as:

- Removing all the skin.
- Slicing off the belly flap of meat along the bottom of the .fish.

TTim away fatty tissue along the back just under the dorsal (back) fins.

- Cutting away the v-shaped wedge of fat along the lateral line on each side of the fish.
- Baking or broiling the trimmed fish on a rack or grill so some of the remaining fat drips away.
- Discarding any drippings and not eating or retusing them.

For details call DNREC at 739-4506


## FINAL REPORT

State: Delaware
Project No.: AFC-5
Grant No.: NA26FAO148-01
Project Title: Delaware Estuary Striped Bass Monitoring Job 2. PCB Levels in Delaware Estuary Striped Bass
Period Covered: March 1, 1992 - February 28, 1993
Prepared by: Richard W. Greene and Roy W. Miller
Date:
April 18, 1994

This project was partially funded through a grant from:
UNITED STATES DEPARTMENT OF COMMERCE

National Oceanic and Atmospheric Administration
National Marine Fisheries Service
Northeast Region
Management Division
State - Federal Relations Branch


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## ACKIOWLEDGEMENTS

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The work described in this report was funded by a grant provided by the U. S. Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service.

The Delaware Fish Contamination Committee, which is composed of representatives from the Delaware Department of Health and Social Services (DHSS) and the Delaware Department of Natural Resources and Environmental Control (DNREC), has reviewed this document and has recommended its release.

## 1. INTRODUCTION

### 1.1 BACKGROUND

In 1988, the Delaware River Basin Commission (DRBC) reported that channel catfish and white perch from the Delaware Estuary contained polychlorinated biphenyls (PCBs) and chlorinated pesticides [DRBC, 1988]. Sampling conducted in 1986 and 1987 revealed that nine out of ten channel catfish composites taken from an area bounded by Burlington Island (north of Philadelphia) down to the Schuykill River exceeded the U.S. Food and Drug Administration (FDA) action level of 2 parts per million (ppm) in edible muscle tissue. White perch taken from the same vicinity contained $P C B$ levels ranging from 0.1 ppm up to 1.4 ppm in edible muscle tissue, with a mean over the entire area of 0.92 ppm .

In response to the DRBC findings, the Commonwealth of Pennsylvania issued a health advisory that recommended that the public curtail its consumption of channel catfish from the Estuary [PADER, 1988]. As a precautionary measure, they also advised against consumption of all bottom-dwelling fish species. The State of New Jersey followed suit in 1989, advising the public not to consume channel catfish from the Estuary [NJDEPE, 1989]. Pennsylvania has since reaffirmed their advice on channel catfish and also added American eel and white perch explicitely to their advisory [PADER, 1990]. The Pennsylvania advisory covers an area from Yardley, PA (across the River from Trenton, N.J.) down to the PA/DE border. The New Jersey advisory covers the same general area but begins approximately 15 miles downstream of Yardley. The official demarcation of the New Jersey advisory is the Interstate 276 Eighway Bridge near Burlington-Bristol down to Birch Creek, which is opposite the PA/DE border. Although the advisories issued by the two states were slightly different in terms of the species covered and exact areal coverage, both states cited PCB levels in excess of or approaching the FDA action level as the principal basis for their respective actions. Pennsylvania also cited elevated chlordane levels as an additional concern.

While sufficient information was available to permit Pennsylvania and New Jersey officials to issue advisories in their respective jurisdictions, no comparable information was available for waters below the PA/DE border that would allow Delaware managers the opportunity to evaluate the need for an advisory. Several fish contamination studies were conducted between 1989 and 1993 to help fill this data gap. In 1989, the U.S. Environmental Protection Agency (EPA) collected fish contaminant data from 10 locations throughout the Delaware Estuary, 3 of which were below the state line. The results of
that effort confirmed the previous work reported by the DRBC for areas above the state line and indicated that channel and white catfish below the state line were also contaminated with PCBs and chlorinated pesticides [EPA, 199la]. Sampling for white perch was limited to a single site (Chester Island), and the PCB concentration detected, 0.86 ppm , was consistent with the levels previously reported by the DRBC.

In addition to adding to the fish contaminant database for the Estuary, another significant observation came out of the EPA study. Namely, they reported a shift in PCB "signature" in the fish between those in the Philadelphia/Camden region versus those from the Chester/wilmington area southward. More specifically, the chromatographic pattern in the fish from Lumberville to the mouth of Schuylkill River was predominated by Aroclor 1254 with a lesser amount of Aroclor 1260. At and downstream of Chester, the pattern was reversed, with Aroclor 1260 representing the larger fraction. This observation provides potential insights regarding the fate and transport of PCBs in the Delaware Estuary and also provides clues as to potential sources. Furthermore, the different chromatographic patterns remind us that PCBs in the environment are in fact complex mixtures which are not exactly like Aroclor 1254, Aroclor 1260, or any other commercial PCB formulation.

Another significant data collection effort conducted during the same time period as the EPA study was a study performed by the U.S. Fish and Wildlife Service [USFWS, 1991]. Their study involved the collection of striped bass, channel catfish, white perch, and blue crab, all from locations in the Estuary below the PA/DE state line. There were two important features of their study. First, all samples were analyzed as whole body composites. Second, more sophisticated analytical techniques were employed to characterize the PCB content of the samples than had been utilized in previous fish contamination studies in the Estuary. The USFWS study not only provided further evidence of fish contamination in the Estuary, their study also yielded data on striped bass, which is arguably one of the key biological resources in the Estuary. Levels of PCBs detected in whole body striped bass samples taken from the Wilmington and Port Penn stations ranged from 2.2 ppm to 6.4 ppm , well in excess of the FDA tolerance level. However, recognizing that contaminant levels in whole body samples are not representative of levels found in the edible muscle tissue, the USFWS recommended that a separate study of PCB contamination in the edible portion of striped bass be conducted.

As a follow up to the USFWS's recomendation, and in response to mounting concerns over fish contamination in the Delaware Estuary in general, the Delaware Department of Natural Resources and Environmental Control (DNREC) conducted a pilot study of PCB contamination in the edible tissue of striped bass during 1991
and 1992 [DNREC, 1992]. That study was limited to striped bass between 20 and 24 inches in length which had been taken off the Cherry Island Flats. The Cherry Island Flats, located adjacent to Wilmington, Delaware, are believed to be an important spawning area for striped bass in the Estuary [Weisberg and Burton, 1989]. A special feature of the pilot study was a methods comparison between the traditional Aroclor method of determining PCB content (EPA Method 608, GC/ECD) and a more sophisticated technique (EPA Method 680, GC/MS) similar to the method used by the USFWS which provided results in terms of total chlorobiphenyl (i.e. total PCB) content. The two methods used in the pilot study independently confirmed the presence of PCBs in the edible muscle tissue of striped bass. The more sophisticated analytical technique, however, yielded total PCB levels which were approximately twice those reported as total Arochlors. The mean concentration using the Aroclor method was 0.66 ppm and the mean concentration using Method 680 was 1.4 ppm . Discussions with other researchers regarding our findings revealed they have observed similar discrepencies between Aroclor content and total PCB [Battelle Memorial Institute, 1990].

Based on the results and experience gained in the pilot study, DNREC proceeded to a full-scale investigation during 1992 and 1993 to define the nature, extent, and magnitude of the striped bass contamination problem. This report discusses the specific objectives, methods, findings, and conclusions of the fuil-scale study. The results of this study were first reported in preliminary form at the U.S. EPA's National Technical Workshop "PCBs in Fish Tissue" in May of 1993 [EPA, 1993a]. The results have since been discussed with managers and scientists from the Pennsylvania Department of Environmental Resoures (PADER), New Jersey Department of Environmental Protection and Energy (NJDEPE), Delaware River Basin Commission (DRBC), and Maryland Department of the Environment (MDE).

### 1.2 OBJECTIVES

There were three primary objectives to this study:

1. Characterize the PCB and chlorinated pesticide content in striped bass from the Delaware Estuary using the best analytical methods currently available;
2. Determine if there are significant differences in PCB and pesticide content between recreational size striped bass and commercial size striped bass taken from two separate geographic regions of the Estuary; and
3. Assess the human health risk to recreational and subsistence anglers who consume striped bass from the Delaware Estuary in support of Delaware's Toxics in Biota Program.

### 1.3 REPORT ORGANIZATION

Following a discussion of background information and objectives in Chapter 1 , the materials and methods used in the study are presented in Chapter 2. Included in Chapter 2 are discussions on field collection, sample preparation, target analytes, analytical methods, and data reduction (including statistical treatment of the data and risk assessment methodologies). Also included in Chapter 2 is an overview of PCB chemistry. Chapter. 3 presents the analytical results of the study as well as the findings of the risk analysis. In Chapter 4, we revisit the study objectives and discuss several salient issues regarding fish contamination and risk assessment in an effort to place the striped bass study into perspective. Finally, Chapter 5 presents a brief summary and concluding remarks.

## 2. MATERIALS AND METHODS

### 2.1 FIELD COLLECTION

Two size categories and two geographic areas were selected for study. The two size categories included striped bass of a size considered legal in Delaware's comercial fishery (those between 18 and 28 inches total length, TL) and those legal for recreational harvest (minimum size 28 inches TL). The two geographic areas chosen for study included the mid-Delaware Bay and the Delaware River striped bass spawning grounds in the vicinity of the Cherry Island Flats. FIGURE 2-1 shows the two areas targeted for study within the overall geographic setting of the Delaware River Basin. The two size classes and two locations constitue a $2 \times 2$ study design in which eight categories can be considered: recreational size fish from mid-Delaware Bay; commercial size fish from mid-Delaware Bay; recreational size fish from the Delaware River spawning grounds; commercial size fish from the Delaware River spawning grounds; all fish (recreational + commercial size) from the spawning grounds; all fish (recreational + comercial size) from mid-Delawaré Bay; all recreational size fish; and all coumercial size fish. These eight categories represent the populations upon which inferences were drawn in this study. These categories are referred to throughout this report as BAYREC, BAYCOM, SGREC, SGCOM, SG, BAY, REC, and COM, respectively. The first four categories are referred to as the primary study categories. TABLE 2-1 summarizes the sizes and locations investigated.

TABLE 2-1 Size Categories and Sample Locations

|  |  |  |
| :---: | :---: | :---: |
|  | > 28 inches | > 28 inches |
|  | 18-28 inches | 18-28 inches |



Figure 2-1 --Locanion of the Delaware River Basin

The goal of the study was to collect twenty-five (25) striped bass from each of the four primary categories, for a total of one hundred (100) fish. Under the study design, the 100 fish were to be grouped in a "5 of $5^{\prime \prime}$ replicate-composite fashion to produce 20 samples. In other words, each group of 25 fish from a particular category was to be divided into 5 composite samples, each composite consisting of equal mass aliquotes taken from 5 individual fish. Such a strategy is recognized as an effective means of balancing information needs with budgetary constraints [EPA, 1993b; Rhode, 1976; Paasivirta and Paukku, 1989; and Mack and Robinson, 1985]. The principal advantage of compositing is that it reduces the number of samples that need to be analyzed. The reduction in the number of samples analyzed does not, however, result in a concomitant reduction of precision for population estimates (such as the PCB content in recreational size striped bass from the Delaware Bay, for instance). The main drawback of using compositing is that differences in chemical concentration between individuals in the population is lost. However, this information is not considered important in the context of conventional risk assessment which relies upon mean concentrations in a given fish species.

As shown in TABLE 2-2, our goal of collecting 100 fish was not met. Seventy-nine (79) fish were actually secured. Fortynine striped bass ( 25 commercial size and 24 recreational size) were obtained as by-catch from commercial shad fishermen working gill nets in mid-Delaware Bay du-ing the months of February and March of 1992. The remaining thirty stripers ( 25 commercial size and 5 recreational size) were obtained from the spawning grounds by Delaware Division of Fish and Wildlife personnel using gill nets during April and May of 1992.

TABLE 2-2 Number and Location of Fish Retained


Although the optimum number of total fish was not obtained, it was still possible to produce 20 samples. Not all 20 samples however, contained 5 fish each. Five, 5-fish composites were produced from the commercial size fish from mid-Delaware Bay as well as for the comercial size fish from the spawning grounds. Four, 5-fish composites and one 4-fish composite were prepared from the recreational size fish taken from mid-Delaware Bay. The remaining five recreational size striped bass from the spawning grounds were treated as individual samples. A decision was made by fisheries personnel not to sacrifice 20 additional recreational size fish from the spawning grounds because of potential adverse impact to the spawning stock.

All fish were transported from the field to the Department of Natural Resources and Environmental Control's laboratory in Dover, Delaware for initial processing.

### 2.2 SAMPLE PREPARATIOR

Upon receipt frem the field, all specimens were first weighed and measured and then assigned a sample identification number. APPENDIX A presents the sample identification number assigned to each sample, where the sample was collected, and the number of fish contained in each sample. After assigning sample numbers, the fish were then scaled and the fillet portions from both sides were cut away for further processing. Skin was left on the fillets to mimick the manner in which most people are believed to prepare striped bass for consumption. No deliberate attempt was made to cut away meat from the belly flap, lateral line, or dorsal line. The fillet portions from a single fish were then combined and passed through a tissue grinder until a homogenous mass was produced. Forty (40) grams of tissue was subsampled from the mass. The above procedure was performed on each fish from a particular sample. For purposes of compositing, the 40 gram aliquotes were thoroughly mixed together to produce a single sample. This procedure was performed until a total of 20 samples were produced. All samples were placed in ciean amber jars, labelled, and stored at -20 degrees Centigrade until ready for shipment to a contract laboratory.

All cutting tools, cutting surfaces, pans and other instruments used to process the samples, including internal surfaces of the tissue grinder, were cleaned prior to and after each fish was processed.

The samples were packed on dry ice and shipped to the Midwest Research Institute (MRI) in Kansas City, Missouri on July 30, 1992. MRI received the samples frozen and in good condition on July 31, 1992.

### 2.3 TARGET ANALYTES

The tendency for PCBs and chlorinated pesticides to accumulate in fish and fish-eating animals such as raptors, wading birds, and humans have placed them into a class of contaminants broadly referred to as bioaccumulative pollutants. In addition to PCBs and chlorinated pesticides, the bioaccumulative pollutants also include the dioxins and furans as well as certain metals such as lead and mercury. Because of budgetary limitations, this study did not consider the entire class of bioaccumulative pollutants. Rather, resources were targeted to known problem pollutants in the Delaware Estuary, with special emphasis on state-of-the art analytical techniques for PCBs.

Target analytes selected for this study included the PCB homologs (Cll - Cl10), forty-seven (47) specific PCB congeners, the chlorinated pesticides DDT, DDD, DDE, chlordane, and dieldrin, and extractable lipids. TABLE 2-3 lists the specific analytes considered in this study. The PCB congeners selected include the non-ortho, mono-ortho, and di-ortho substituted PCBs [EPA, 1991b]; congeners reported as major constituents in Aroclor mixtures [Schulz, 1989]; and congeners typically detected in humans that consume a high amount of fish [MRI, 1992].

The list of PCB congeners presented in TABLE 2-3 was developed by DNREC in early 1992 based upon information that was reviewed at that time. Subsequent review of the literature has led DNREC to expand its list of target PCB congeners to 63 [DNREC, 1994a]. This point is made simply to demonstrate the rapidly evolving nature of this type of work. To DNREC's knowledge, the congener-specific and homolog-specific analyses described in this report serve as the most complete characterization of PCBs to date for environmental samples taken from the Delaware Estuary. Future analyses using the expanded congener list will further advance the state of knowledge. Because the primary focus of this study is on PCBs, a brief review of PCB chemistry is provided at this point to help the reader understand PCB terminology, as well as the discussion of PCB methods and results that will follow later in this report.

Polychlorinated biphenyls are a class of synthetic organic compounds formed through the progressive chlorination of biphenyl. The basic structure of the biphenyl molecule is shown in FIGURE 2-2, along with the other target analytes included in this study. Positions 2 through 6 and $2^{\prime}$ through $6^{\prime}$ of the biphenyl molecule are ordinarily occupied by hydrogen atoms. In the synthesis of PCBs, these hydrogen atoms are successively substituted for chlorine atoms to yield a variety of compounds of different overall chlorine content and different physical, chemical, and toxicological properties.

## TABLE 2-3 Target Analytes

## 

A. HOMOLOGS

Monochlorobiphenyl Dichlorobiphenyl Trichlorobiphenyl Tetrachlorobiphenyl Pentachlorobiphenyl

Hexachlorobiphenyl Heptachlorobiphenyl Octachlorobiphenyl Nonachlorobiphenyl Decachlorobiphenyl
B. CONGENERS (listed by iJPAC number")

PCB1
PCB3
PCB4
PCB7
PCB18
PCB2 8
PCB4 4
PCB5
PCB74
PCB77
PCB78
PCB79

PCB80
PCB8 1
PCB87
PCB99
PCB101
PCB105
PCB114
PCB118
PCB1<3
PCB126
PCB127
PCB128

PCB137
PCB138
PCB153
PCB156
PCB157
PCB158
PCB166
PCB167
PCB168
PCB169
PCB170
PCB180

PCB183
PCB185
PCB187
PCB189
PCB190
PCB191
PCB194
PCB199
PCB205
PCB207
PCB209

## 

$0, p^{\prime}$ and $p, p^{\prime}$ DDT
$0, P^{\prime}$ and $P, P^{\prime}$ DDD
$0, p^{\prime}$ and $p, p^{\prime}$ DDE
alpha and gamma Chlordane Dieldrin
oyisish

Extractable Lipids

- Appendix B defines specific PCB congeners by IUPAC number.


## TARGET ANALYTES

## CHEMICAL STRUCTURE



PCBs


DDT


CHLORDANE


DDD


DIELDRIN


DDE


#### Abstract

If all combinations of chlorine positioning and saturation are considered, a total of 209 different PCB molecules are theoretically possible. Each unique chlorine substitution pattern leads to what is known as a PCB congener. The International Union of Pure and Applied Chemistry (IUPAC) has assigned individual numbers from 1 to 209 to uniquely identify each of the possible PCB congeners. APPENDIX B lists the IUPAC numbers for all 209 of the congeners. Of these 209 congeners, the ones that are of greatest interest are those that can assume a coplanar structure to some degree. A coplanar condition occurs when the two benzene rings that comprise the biphenyl molecule lie more or less in the same geometric plane, thereby producing molecules that are structurally (and toxicologically) similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin [Safe, 1984]. The degree of coplanar conformation depends upon whether there is zero, one, or two chlorine atoms occupying the ortho (furthest inside) positions on the biphenyl molecule. coplanarity is greatest for the non-ortho PCBs substituted in bott para (outside) positions and one or more of the meta positions and weakest for the diortho PCBs. APPENDIX C shows the chemical structure of the coplanar PCB congeners. As will be discussed later in this report, the dioxin-like health effects of PCBs appear to depend upon the amount and type of coplanar PCB present. The final point to be made about PCB congeners is that the analytical methods used to identify and quantitate them have only become available over the last decade. Characterizing PCBs in terms of individual congener content is without question the most complex (and expensive) way to describe PCBs, but it is also the most accurate.


The second most detailed way to describe PCBs is in terms of the so-called homolog content. A PCB homolog refers to a group of congeners with the same number of chlorine atoms, irrespective of chlorine positioning. PCB homologs also are referred to as isomer groups or simply as chlorobiphenyl groups. As an example of a PCB homolog group, the tetrachlorobiphenyl group (tetra-CB or Cl4 group, for short) includes all congeners with four chlorine atoms. Similarly, heptachlorobiphenyl refers to the group of congeners with seven chlorine atoms. Because there are ten possible positions where chlorine could attach to the biphenyl molecule, there are ten possible PCB homolog groups. By convention, the PCB homologs are referred to as mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and decachlorobiphenyl.

Commercially produced PCBs are not composed of a single congener, nor a single homolog group. Rather, they consist of a complex mixture of congeners from several homolog groups. For instance, Arochlor 1260, the trade name given to a PCB product previosly manufactured by the Monsanto Company, contains a mixture of congeners from the tri-, tetra-, penta-, hexa-, hepta, octa-, nona-, and decachlorobiphenyl groups in varying
proportions. Under the manufacturer's naming scheme, the first two digits signify that there are 12 carbon atoms in the product, and the second two digits signify that the product contains approximately 60 percent chlorine by weight.

When released to the environment, commercial PCB mixtures undergo degradation processes which alter the original congener distribution. Depending upon the extent of breakdown, environmental PCB mixtures may, and often do, differ considerably from the commercial Aroclor mixtures from which they were derived. Unfortunately, degradation does not appear to render commercial PCB mixtures less toxic. Several researchers have reported selective retention and accumulation of the coplanar dioxin-like PCB congeners as one moves up the food chain [Oliver and Niimi, 1988; Rubiak et al., 1989]. These findings provide additional reason to use congener-specific methods to characterize pCBs in the environment. The traditional analytical approach of visually matching the chromatographic pattern of the environmental sample to that of an Aroclor standard is now recognized as the least accurate of the available techniques, and under many situations, can result in significant errors [AlfordStevens et al., 1986; Schwartz et al., i987].

### 2.4 ANALYTICAL METHODS

APPENDIX D contains a complete description of the analytical methods used in the study. APPENDIX D reproduces, in its entirety, the final laboratory report submitted by the contract lab. A few of the details from the report are presented here for continuity.

The analytical approach included high resolution gas chromatography/low resolution mass spectrometry (ERGC/LRMS) of all twenty samples for the chlorinated pesticides and for PCB congeners other than the non-ortho substituted congeners. Four of the twenty samples, one from each of the primary study categories (SGREC/SGCOM/BAYREC/BAYCOM) were also analyzed for the non-ortho substituted PCB congeners using high resolution gas chromatography/high resolution mass spectrometry (GRGC/HRMS). The analytical methods and detection levels actually achieved are summarized in TABLE 2-4.

TABLE 2-4 Analytical Methods and Detection Limits

| aysuryer | 3:2:x:00 | Desteccison mumy |
| :---: | :---: | :---: |
| Mono-ortho PCBs, Di-ortho PCBs, and Pesticides | HRGC/LRMS <br> SW 846 Method 3640 | 1-10 ppb |
| Non-ortho PCBs | ERGC/LRMS <br> SW 846 Method 8290 | 2 pptr |

The samples selested for non-ortho PCB analysis included samples R02SG, C04SG, R03B, and CO1B. Each of these samples was randomly selected from their respective categories. Budgetary constraints prevented analysis of all twenty samples for the nonortho PCBs. In addition to the specific PCB congener work, total PCBs also were determined based on the sum of the chromatographic peaks detected for mono through deca PCB homologs.

Quality control measures included ongoing instrument calibration, method blanks, control spikes, duplicate matrix spikes, and percent recoveries for carbon-13 internal quantitation standards and surrogate standards. The interested reader is directed to APPENDIX D for further details concerning quality control. Based upon the results of the quality control efforts, overall laboratory performance was excellent. No major analytical problems were encountered.

### 2.5 DATA REDUCTIOX

A number of statistical and other mathematical calculations were performed to help sumarize and compare the data. The techniques used for these calculations are presented in the sections that follow.

### 2.5.1 Statistical Treatment

The general statistical approach involved first determining whether the data upon which inference was to be drawn could reasonably be described as a normal or lognormal distribution.

Because the number of samples was less than 50, the Shapiro-wilk "W" Test was used for this purpose [Gilbert, 1987]. Equality of variance also was tested as a prerequisite of using parametric statistics. This was done using Bartlett's Test [Zar, 1984]. In general, most of the data could not meet the prerequisites needed to justify use of parametric statistics. Consequently, nonparametric statistical methods were chosen to test for significance of results.

The Kruskal-Wallis one-way analysis of variance was used to determine whether length, total PCB, percent chlorination, DDT, DDD, DDE, and chlordane concentrations among the four principal study categories (SGREC/SGCOM/BAYREC/BAYCOM) were statistically different. The test considers both the distribution and median of each category being compared and uses the null hypothesis that the four categories are from the same population. Results are presented as an $H$ statistic and a probability (P) that the categories satisfy the null hypothesis. In the actual performance of the test, the calculated value of $P$ is compared to a critical level oe significance, which we took for all cases to be 0.05 . If the calculated $P$ value was less than the critical level, then at least one of the four categories was statistically different from the others. Conversely, if the calculated $p$ was greater than 0.05 , then the categories were not significantly different. In this latter case, the data from all four categories were pooled together to produce a single representative mean concentration that was later used in risk assessment calculations. Finally, when testing for significant differences between any two categories, the Mann-Whitney U Test was used. Again, a critical level of 0.05 was used to test significance of results. Calculated $P$ values less than 0.05 were used to indicate that the two categories were significantly different. Kruskal Wallis and Mann-Whitney tests were performed with the aid of Minitab statistical software [Minitab, 1988]. The results of these tests are presented in Chapter 3 of this report.

### 2.5.2 Polychlorinated Biphenyls

Characterizing PCBs in terms of congener and homolog content generates large data sets. For the 20 samples analyzed in this study alone, over 1000 PCB results were produced, not counting quality control results. To reduce these results to a managable size, and to provide important insights into underlying characteristics, several calculations were performed on the raw PCB data. Calculations were performed to determine total PCB, chlorobiphenyl distribution, overall level of chlorination, total coplanar PCB, and toxicity equivalents. The equations used for these calculations are presented below.

Total PCB is simply the sum of mono- through decachlorobiphenyl as indicated in equation 1. This equation was
used to compute total PCB for all twenty striped bass samples. The resulting twenty values were further collapsed by displaying the minimum, maximum and mean concentrations for the four study categories on a single graph.

TOTAL PCB $=\sum_{i=1}^{10}(C H L O R O B I P H E N Y L)_{i}$

It is noted $e t$ this point that if a particular homolog was not detected in the sample, its value was assumed to be zero. Although the effect of this assumption technically has the potential to bias the total PCB values downward from their true values, any such bias will be negligible because the detection levels used in this study were extremely low in comparison to the homolog concentrations that were actually detected. This same treatment of "non-detects" was used for all other analytes considered in the study.

After an estimate of total PCB was obtained from equation 1, it was possible to determine the chlorobiphenyl distribution in the samples by dividing the concentration of each homolog group by total PCB and expressing the result as a percentage. This is shown in equation 2 .

$$
\begin{equation*}
\underset{\text { \% CHLOROBIPHENYL } i}{\text { IN SAMPLE } j}=\frac{\text { CONC. OF CB i IN SAMPLE } j}{T O T A L P C B ~ I N ~ S A M P L E ~} j x ~ 1.00 \tag{2}
\end{equation*}
$$

Because each sample contains PCBs from 10 separate homolog groups, equation 2 yields ten separate values for each sample. Each value represents the relative contribution of the particular homolog to the total PCB content in the sample. The sum of the ten values for eac: sample will equal 100\%. The equation above was used to deternine the chlorobiphenyl distribution for all twenty striped bass samples.

Finally, the overall level of chlorination in the sample was computed by a two-step process. First, the percent of each homolog in the sample (from equation 2 above) was multiplied by its corresponding mass fraction of chlorine. This produces 10 partial sums. These partial sums are added together to yield the desired estimate for level of chlorination. Equation 3 is a concise mathematical statement of this two-step process.

$$
\begin{gather*}
\text { LEVEL OF CHLORINATION }  \tag{3}\\
\text { IN SAMPLE } j
\end{gather*} \sum_{i=1}^{10} A_{i} \times B_{i}
$$

, where $A_{i}$ and $B_{i}$ are defined as follows:

$$
\begin{equation*}
A_{i}=\frac{\text { CHLOROBIPHENYL }}{\text { IN SAMPLE } j}=\frac{\text { CONC. OF CB } i \text { IN SAMPLE } j}{\text { TOTAL PCB IN SAMPLE } j} \times 100 \tag{4}
\end{equation*}
$$

$$
\begin{equation*}
B_{i}=\frac{\text { MASS FRACTION OF }}{\text { CHLORINE IN CB }} \text { i }=\frac{i \times M . W \cdot O F C H L O R I N E}{M . W \cdot O F C B_{i}} \tag{5}
\end{equation*}
$$

In equation 3, " $A_{i}$ " is identical to equation 2 and values of "B" are tabulated in TABLE 2-5. The chlorine mass fractions listed in TABLE 2-5 are based upon a molecular weight of 12 for carbon, 1 for hydrogen, and 35.45 for chlorine.

TABIE 2-5 Molecular Weight of PCB Homologs and Their Corresponding Chlorine Mass Fractions

| pcs zonowog | forerthat | Honscumar | wass maction of chlorimb |
| :---: | :---: | :---: | :---: |
| Mono | $\mathrm{C}_{12} \mathrm{H}, \mathrm{Cl}$ | 188.65 | 0.1879 |
| Di | $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{Cl}{ }_{2}$ | 223.10 | 0.3177 |
| Tri | $\mathrm{C}_{12}^{12} \mathrm{H}^{8} \mathrm{Cl}^{2}$ | 257.54 | 0.4130 |
| Tetra | $\mathrm{C}_{12}^{12} \mathrm{H}_{6} \mathrm{Cl}_{4}{ }^{3}$ | 291.99 | 0.4856 |
| Penta | $\mathrm{C}_{12} \mathrm{H}_{5} \mathrm{Cl}_{5}$ | 326.43 | 0.5430 |
| Hexa | $\mathrm{C}_{12}^{12} \mathrm{~B}^{18} \mathrm{Cl}_{6}{ }^{5}$ | 360.88 | 0.5893 |
| Hepta | $\mathrm{C}_{12}^{12} \mathrm{H}^{2} \mathrm{Cl}^{6}$ | 395.32 | 0.6277 |
| Octa | $\mathrm{C}_{12}{ }^{12} \mathrm{H}^{3} \mathrm{Cl}_{1}$ | 429.77 | 0.6598 |
| Nona | $\mathrm{C}_{12} \mathrm{FECl}^{1}$ | 464.21 498.63 | 0.6873 0.7108 |
| Deca | $\mathrm{C}_{12} \mathrm{Cl}_{10}$ | 498.63 | 0.7108 |

Equation 3 was used to compute the overall level of chlorination in all twenty striped bass samples. The results of these calculations are tabulated in chapter 3 along with a summary chart which displays the minimum, maximum, and mean level of chlorination for the four primary study categories. As will be discussed later in this report, certain health effects of PCBs appear to depend upon the degree of chlorination. Hence, it is important to consider this characteristic when the data are to be used in a human health risk assessment. We turn now to calculations performed on the PCB congener data.

Total coplanar PCB is the sum of the non-ortho, mono-ortho, and di-ortho coplanar PCB congeners in the sample. The congeners included in this sum are those shown in APPENDIX C. Because the full complement of coplanar PCBs were only measured in samples R02SG, C04SG, R03B, and C01B, total coplanar PCB could only be computed for those four samples. The percentage of the total coplanar PCB in the non-ortho, mono-ortho, and di-ortho groups was also computed for these four samples as simple quotients. Finally, linear regression was used to determine the degree of correlation between total PCB and total coplanar PCB in the four samples.

The final calculation performed to help characterize the PCB content of the samples was the so-called toxicity equivalents. Again, this is a congener-specific calculation involving just the coplanar PCBs. As such, these calculations were limited to the
four samples mentioned above. Computationally, a toxicity equivalent (T.E.) is the product of a congener concentration and a toxicity equivalence factor, or TEF for short. If more than one congener is present which has a toxicity equivalence factor, then the toxicity equivalents for all such congeners are added as indicated in the equation below.

$$
T . E .=\sum_{i=1}^{n}(T E F)_{i} \times(\text { CONC })_{i}
$$

A TEF represents the toxic respons of the PCB congener relative to that of $2,3,7,8$-tetrachloredibenzo-p-dioxin. A fundamental premise for the development of TEFs is that coplanar PCB congeners are like diokin in that they appear to elicit their responses through a common, receptor-mediated mechanism dependent upon the structure of the molecule [EPA, 1991b]. The biochemical response typically used to assign TEFs is the degree of induction of the liver enzyme aryl hydrocarbon hydroxylase (AAB). Under this scheme, dioxin is the most potent and is assigned a TEF of 1.0. TEFs for the inciividual coplanar PCBs are then assigned values less than 1.0 based on their lower potency. Insofar as dioxins and furans were not included as target analytes in Delaware's striped bass study, the toxicity equivalents computed in this report are likely to underestimate the total toxicity equivalents in the striped bass (assuming some level of dioxins and furans are in fact present in the fish). The TEFs used in this report for coplanar PCBs were developed by Stephen Safe from Texas A \& M University [Safe, 1990]. TABLE 2-6 lists these TEFs.

TABLE 2-6 Toxicity Equivalent Factors For Coplanar PBs

## CONGENER

ruse
serf
a) Non-ortho

| $3,3,, 4,4$, | 77 | 0.01 |
| :--- | ---: | :--- |
| $3,4,4,5$ | 81 | not available |
| $3,3,4,4,5$ | 126 | 0.1 |
| $3,3,4,4,5,5$, | 169 | 0.05 |

b) Mono-ortho
8 Specific Congeners
$105,114,118,123$
$156,157,167,189$
c) Di-ortho

| 13 Specific | $128,137,138,153$ | 0.00002 |
| :--- | :--- | :--- |
| Congeners | $158,166,168,170$ |  |
|  | $180,190,191,194$ |  |
|  | 205 |  |

### 2.5.3 Chlorinated Pesticides

DDT, DDD, and DDE each have two possible isomeric forms depending upon the location of the chlorines on the base structure. These two forms are referred to as the $0, p^{\prime}$ and $p, p^{\prime}$ isomers. For purposes of presenting results in chapter 3, these two forms were summed together. Therefore, reference to DDT is understood to represent the sum of $0, p^{\prime}$ DDT and $p, p^{\prime}$ DDT. Similarly, reference to DDD and DDE refer to o, $P^{\prime}$ DDD and $p, p^{\prime}$ DDD, and $0, p^{\prime}$ DDE and $p, p^{\prime}$ DDE, respectively. By extension, total DDT represents the sum of both forms of DDT, both forms of DDD, and both forms of DDE.

$$
\begin{equation*}
\text { TOTAL } D D T=D D T+D D D+D D E \tag{7}
\end{equation*}
$$

Calculations to sumarize the chlorinated pesticide data included: mean DDT, mean DDD, mean DDE, and mean total DDT content by size class and location; and percent DDT, DDD, and DDE to total DDT in all samples combined. The results of these calculations are tabulated and displayed in various forms in chapter 3.

### 2.6 HUNAN HEALTH RISK ASSESSMENT

In conducting a risk assessment for chemically contaminated fish, we sought to answer the following basic questions:

1. What contaminants are present in the fish and at what concentrations?
2. What type of health effects are associated with exposure to these contaminants?
3. How potent are the contaminants?
4. Who might consume the fish and how much do they consume?
5. What is the magnitude of health risks posed?

This section of the report describes the methods and materials that were used to answer these questions for the case of striped bass contamination in the Delaware Estuary. In short, risk assessment was the principal tool used. The specific procedures used follow current EPA guidance [EPA, 1986a; EPA, 1986b; EPA, 1988; EPA, 1989a; EPA, 1989b; and EPA, 1993b] and other published sources [Dourson and Clark, 1990].

Risk assessment, as first proposed by the National Academy of Sciences [NAS, 1983], and refined over the years, is an orderly way of investigating and projecting future outcomes associated with "risky" situations. More formally, risk assessment is a scientifically-based procedure used to estimate the probability of adverse health effects under particular exposure conditions. As described by the NAS, risk assessment consists of four separate steps:

1. HAZARD IDENTIFICATION;
2. DOSE-RESPONSE EVALUATION;
3. EXPOSURE ASSESSMENT; AND
4. RISK CEARACTERIZATION.

Each of the above four steps are discussed below within a general context and within the specific context of striped bass contamination in the Delaware Estuary.

### 2.6.1 Hazard Identification

Hazard identification is the qualitative determination of whether a substance causes or is likely to cause an increased incidence or severity of illness in the human population. This qualitative determination is based upon epidemiological evidence which links human exposure to actual observed illness in the human population as well as on results of laboratory tests conducted on experimental animals. These two primary forms of information are also supplemented by data on chemical structure, physical properties, and other assays.

Due to the general paucity of and difficulty in obtaining good epidemioloc: data linking chemical exposure to illness in humans, the most sommon form of data used to support the hazard identification $s$ iep comes from laboratory tests on experimental animals. Typicaily, these experiments involve the administration of high doses of a chemical agent to mice or other rodencs over periods of months to years. Occasionally, higher mamals such as primates are used. The primary objective of such experiments is to determine if continuous exposure to the chemical causes adverse health effects, what those healch effects are, and what the nature of the dose-response curve is. The discussion that follows summarizes the literature that was compiled concerning the health hazards associated with exposure to PCBs, DDT, and chlordane. Dieldrin is eliminated from further discussion because it was only detected in one of the twenty striped bass samples and that concentration was extremely low.

### 2.6.1.1 Polychlorinated Biphenyls

For purposes of this report, the health hazards of PCBs are broken down into three general categories: cancer, chronic systemic toxicity (including immunotoxicity), and developmental toxicity. These effects will be addressed in order.

PCB mixtures containing $60 \%$ chlorine by weight are clearly carcinogenic to laboratory animals [ATSDR, 1993]. Hepatocellular carcinomas have been reported in three strains of rats and two strains of mice which were fed Aroclor 1260 [EPA, 1994]. Studies of lower chlorinated Aroclors (e.g. Aroclor 1242 and 1254) have not demonstrated significant increases of either benign or malignant tumors [IERR, 1991]. The U.S. EPA nevertheless considers Aroclor 1250 to be representative of all PCBs, and hence, classifies a: PCBs as probable (B2) human carcinogens [EPA, 1994]. Although several studies have reported statistically higher rates of liver (and biliary) cancer in humans exposed in occupational settings, existing epidemiological
data are considered inadequate to classify PCBs as known (A) human carcinogens due to the existence of confounding factors or lack of exposure quantification [EPA, 1994].

With regard to chronic systemic toxicity, studies using laboratory animals have shown that PCBs affect numerous organ systems, including the cardiovascular, GI, hematological, musculoskeletal, hepatic, renal, dermal, immunological, neurological, and reproductive systems [ATSDR, 1993]. These effects have been observed in bioassays involving both higherchlorinated and lower-chlorinated Aroclor mixtures. Based on the existing data, ATSDR believes the immunosuppressive effects are the most sensitive endpoint of those examined to date. These effects are believed to be mediated by the coplanar PCB congeners [Safe, 1990]. Human data on the immunosuppressive effects of PCBs as well as other chronic systemic health effects are sparse and generally inconclusive.

Finally, PCB mixtures have been shown to cause developmental effects in experimental animals [ATSDR, 1993]. Nearobehavioral effects, including abnormal motor coordination and compromised learning, appear to be a critical endpoint for developimental toxicity. It has been shown that human offspring can be exposed to PCBs via mothers milk and through transplacental transfer [ATSDR, 1993]. An epidemiological study in Michigan showed persistent motor and cognitive deficits in children subject to prenatal exposure to PCBs (as measured from cord blood levels). The study is believed to be inconclusive, however, due to the presence of several possible confounding factors [EPA, 1993c].

### 2.6.1.2 DDT and Motabolites

As was the case for PCBs, the health effects associated with exposure to DDT fall into three categories: cancer, immunotoxicity, and developmental toxicity.

DDT, DDD, and DDE are all classified as probable (B2) human carcinogens. Liver tumors are cited in 24 of 25 animal assays conducted on these compounds [EPA, 1994]. With regard to human data, occupational studies of workers exposed to DDT are of insufficient duration to assess carcinogenicity. However, elevated leukemia incidence was noted in two of those studies [EPA, 1994]. A more recent study involving the analysis of fatty tissue from the breast of 20 women with malignant breast tumors and 20 women with benign breast tumors revealed significantly higher levels of DDT, DDE, and PCBs in the group with malignanciès, suggesting a possible association [Falck, 1992]. In a related study, breast cancer was found to be strongly associated with DDE in serum [Wolff et al, 1993].

Immunological effects have been observed in animals exposed to DDT [ATSDR, 1992]. Effects include atrophy of the thymus,
decreased number of mast cells, and decreased germinal centers of the spleen.

DDT has been shown to cause developmental toxicity in several species of experimental animals [ATSDR, 1992]. Observed effects include decreased fetal brain, kidney, and body weights [ATSDR, 1992]; abnormal gonad development and decreased fertility in offspring [Hayes, 1982]; increased offspring mortality [EPA, 1994]; and structural/functional alterations in the brain and attendant behavioral effects [ATSDR, 1992]. Of the foregoing effects, neurobehavioral effects appear to be the most sensitive indicator of developmental toxicity [ATSDR, 1992]. Information on the developmental effects of DDT to unborn children exposed in utero or those exposed via mothers milk was not identified in the literature.

### 2.6.1.3 Chlordane

Chlordane is classified by the EPA as a pwobable (B2) human carcinogen. Liver cancer was identiried in four etrains of mice of both sexes and in male rats [EPA, 1994]. No sinudies were located which show an association between chlordane exposure and cancer in humans. ATSDR does, however, note that multiple neurological effects (including gran-mal seizures and altered EEG results) have been reported in humans under acute and chronic exposures to chlordane [ATSDR, 1990]. With regard to more subtle systemic health effects, little information appears to be available. EPA cites one study in which liver atrophy developed in female rats which were fed chlordane. Information on developmental effects of chlordane also appear to be lacking. However, chlordane is known to bioaccumulate in human tissue, and consequently, exposure occurring prior to pregnancy can contribute to maternal body burden and may result in exposure to the developing fetus, newborn, and infant [ATSDR, 1990].

### 2.6.2 Dose-Response Evaluation

The purpose of the dose-response evaluation is to determine the relationship between the amount of a chemical administered (deliberately, in the case of experimental animals, or accidentally, in the case of a human population) and an observed health effect in the exposed group. The manner in which the dose-response data are interpreted depends upon the toxicological endpoint being considered and whether the dose-response data were generated from human exposure data or from assays conducted on experimental animals. If the endpoint is cancer and sufficient dose-response data exists for a human population, a "best fit" line is drawn through the data and the slope is taken as a measure of the chemical's cancer potency.

In the case of animal carcinogenicity data, the high doses necessary to elicit a tumor response must be extrapolated back to
the low dose region to be of practical use in evaluating the exposures typically experienced by the human population. This low dose extrapolation is performed using a mathematical model, typically the linearized multistage model. As noted in Johannsen [Johannsen, 1990], the linearized multistage model was originally proposed by Crump and others as a generalization of the ArmitageDoll multistage model of carcinogenesis. The linearized multistage model assumes that cancer results from a series of interactions between the carcinogenic agent and DNA, with the rate of interaction being linearly related at low dose [EPA, 1989a]. An important feature of this model is that it predicts some finite risk of cancer even at the lowest conceivable doses. Taken to the limit, the model assumes that risk is only zero if exposure is zero. The underlying hypothesis, therefore, is that cancer is a non-threshold phenomenon.

As in the case of human carcinogenicity data, the slope of the dose-response curve from an animal assay is an indication of the cancer potency of the chemical. In this case however, the upper 95th percent confidence limit on the slope in the low dose range, as computed through the multistage procedure, is used. This value is refered to alternatively as the cancer potency slope, slope factor, or simply $q_{1}^{*}$ for short. Quantitatively, the slope factor represents the excess cancer risk per unit of exposure. As such, the units of $q_{3}$ are the inverse of those of exposure. For instance, if the units of exposure are expressed as mg of pollutant ingested per body weight of the individual exposed per time (e.g. mg/kg/d), then the units of $\mathrm{q}_{1}{ }^{*}$ will be $1 /(\mathrm{mg} / \mathrm{kg} / \mathrm{d})$. Cancer potency slopes used for the contaminants considered in the striped bass study will be discussed below. First, however, a brief discussion is presented on how doseresponse data for non-cancer endpoints is characterized.

In contrast to carcinogenic hazard, non-cancer hazards assume that toxic effects only occur after exposure exceeds some threshold level. In other words, up to some particular level of exposure, the body's natural defense mechanisms are able to ensure that a toxic effect is not likely to occur. The so-called Reference Dose (RfD) is used as an estimate of the exposure that is assumed not to be associated with significant risk of noncancer toxicity. More formally, the RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime [Dourson and Clark, 1990]. The units of RfD are the same as the units of dose, mg of contaminant per body weight of human receptor per day (mg/kg/d). Operationally, the RfD is obtained by dividing either the highest dose of the chemical that did not produce a toxic effect in experimental studies (i.e. the No Observed Adverse Effect Level or NOAEL), or the lowest dose that did produce a toxic effect (i.e. the Lowest Observed Adverse Effect Level or LOAEL), by the product of an
uncertainty factor and a modifying factor. The uncertainty factor accounts for differences in sensitivity to toxic effects within and between species, as well as differences in toxic effects between chronic and subchronic exposures. The modifying factor reflects the confidence in the quality of the animal assay data in predicting health effects in humans.

The principal sources of information that were consulted for potency slopes and reference doses were the U. S. EPA's Integrated Risk Information System [EPA, 1994] and the U. S. Department of Health \& Human Services'(DEBS) Toxicological Profiles. The Integrated Risk Information System (IRIS) is an electronic database maintained by the U.S. EPA which contains chronic human health risk information on hazard identification and dose-response. The toxicological profiles contain similar information and are available in hardcopy format from DHES' Agency for Toxic Substances and Disease Registry (ATSDR) in Atlanta, Georgia. The following sections identify and briefly discuss the potency slopes and RfDs used in the striped bass risk assessment.

### 2.6.2.1 Polychlorinated Biphenyls

IRIS lists a cancer slope factor of 7.7 per $\mathrm{mg} / \mathrm{kg} / \mathrm{d}$ based on the Aroclor 1260 rat feeding study conducted by Norback and Weltman [Norback and Weltman, 1985]. This slope factor was calculated considering malignant liver tumors and neoplastic nodules combined. EPA has stated that it believes the 7.7 slopi factor to be accurate within a factor of 2 for environmental PCB samples with a level of chlorination close to 60 of [EPA, 1993a]. At the same time, EPA believes that the 7.7 slope factor may be as much as two orders of magnitude too stringent for environmental PCB samples of lesser chlorination. The Institute for Evaluating Eealth Risks goes one step further by noting that cancer assays in lower chlorinated Aroclors (e.g. Aroclor 1242 and 1254) do not demonstrate significant increase of either benign or malignant tumors [IEHR, 1991]. The IEHR's reevaluation is particularly compelling because it relied upon consistent diagnosis of liver patholgy using current criteria and nomenclature.

Based on the forgoing, a slope factor of 7.7 was applied to all striped bass samples having an overall level of chlorination of approximately $60 \%$. Striped bass samples with lesser chlorination were not assumed to represent a cancer hazard.

With regard to chronic systemic toxicity of PCBs, immunological effects were taken as the sensitive endpoint. Based on the results of a 55 -month monkey study, ATSDR estimates that a dose of $2 \times 10^{-5} \mathrm{mg} / \mathrm{kg} / \mathrm{d}$ is likely to be without appreciable risk of adverse immunological effects in humans [ATSDR, 1993]. This value was used in the risk assessment
regardless of the level of chlorination in the striped bass samples.

The RfD used in this study for neurodevelopmental toxicity was $8 \times 10^{-5} \mathrm{mg} / \mathrm{kg} / \mathrm{d}$. This value was derived by applying a factor of 10 each for inter and intraspecies variability to a NOAEL of $0.008 \mathrm{mg} / \mathrm{kg} / \mathrm{d}$ for neurological effects in the offspring of rhesus monkeys [Levin et al, 1988]. The RfD used in this study is slightly less conservative than the RfD of $5 \times 10^{-5}$ proposed for use in the Great Lakes states for their fish advisory program.

### 2.6.2.2 DDT and Metabolites

IRIS lists slope factors of $0.34,0.24$, and 0.34 per $\mathrm{mg} / \mathrm{kg} / \mathrm{d}$ for DDT, DDD, and DDE, respectively. EPA, however, recommends that a single slope factor of 0.34 be applied to the sum of DDT, DDD, and DDE [EPA, 1993b]. The single slope factor was used in the striped bass zisk assessment.

With respect to immological effects, ATSDR estimates that human dose should be less than $1.8 \times 10^{-3} \mathrm{mg} / \mathrm{kg} / \mathrm{d}$ to avoid such risk [ATSDR, 1992]. ATSDR also estimates that human dose should be less than $5 \times 10^{-5} \mathrm{mg} / \mathrm{kg} / \mathrm{d}$ to avoid risk of neurobehavioral effects [ATSDR, 1992]. Both of these reference doses were considered in the striped bass risk assessment.

### 2.6.2.3 Chlordane

IRIS lists a cancer slope factor of 1.3 per $\mathrm{mg} / \mathrm{kg} / \mathrm{d}$ for chlordane. This value is the geometric mean of the slope factors calculated from four separate data sets [EPA, 1994]. IRIS also lists an RfD of $6 \times 10^{-5} \mathrm{mg} / \mathrm{kg} / \mathrm{d}$ based on a study which found liver atrophy in female rats. EPA places low confidence in this RfD, however, due to the lack of corroborating evidence in a second mammalian species and the insensitive endpoint in the primary study. Finally, ATSDR provides a guarded estimate of a developmental exposure limit for chlordane [ATSDR, 1990]. A value of $1 \times 10^{-4} \mathrm{mg} / \mathrm{kg} / \mathrm{d}$ is given with the proviso that it be used with caution because it is based on a LOEL as opposed to a NOAEL.

### 2.6.2.4 Summary of Cancer Potency and Reference Doses

TABLE 2-7 provides a concise sumary of the potency slopes and reference doses used in the striped bass risk assessment.

### 2.6.3 Exposure Assessment

Exposure assessment is the estimation of the amount of a substance ingested, inhaled, or absorbed by a target population. In the current study, we are interested in obtaining an estimate

*Applied to PCB Mixtures with Level of Chlorination Approximately Equal to 60\%.
unintentionally ingested by recreational and subsistence anglers who consume striped bass from the Delaware Estuary. The methods used to obtain this estimate are described below.

First, an estimate of the lifetime average daily exposure rate (IADE) was computed from equation 8:

$$
\begin{equation*}
\left(\frac{L A D E}{(\mathrm{mg} / \mathrm{d})}=\frac{C \times M S \times M F \times E D \times(100-R F) / 100}{L T}\right. \tag{8}
\end{equation*}
$$

> where, the following variables are defined: $$
\begin{aligned} C= & \text { concentration of the contaminant in the } \\ & \text { edible portion of the fish, (mg/kg or ppm) } \\ M S= & \text { meal size in ounces } x 0.02835, ~(\mathrm{~kg} / \mathrm{meal}) \\ M F= & \text { number of meals consumed per year divided } \\ & \text { by } 365 \text { days per year, (meals/d) } \\ E D= & \text { duration over which exposure is assumed to } \\ & \text { occur, (Yrs) } \\ L T= & \text { lifetime duration, (Yrs) } \\ R F= & \text { percent reduction in contaminant concentration } \\ & \text { in the fish due to trimming and cooking losses, ( } \% \text { ) }\end{aligned}
$$

In the above equation, the average concentration in the fish was used under the assumption that, over a lifetime, a consumer of striped bass from the Delaware Estuary will eat some stripers that are more contaminated than the mean and some that are less contaminated than the mean, but, that on a time weighted basis, his or her exposure will be a stronger function of the mean concentration in the fish than an upper quartile. The other assumption implicit to this approach is that the mean concentration will remain relatively constant over time. For a potential lifetime of 75 years or longer, the validity of this assumption should be explored.

There are some data on long-term trends in PCB concentrations in fish from systems like the Hudson River and the Great Lakes which suggest significant declines in pollutant levels over the last two decades. In the Great Lakes, at least, the levels of PCBs appear to be leveling off [EPA, 1993a]. Unfortunately, there are no comparable long-term data on striped bass or other species from the Delaware Estuary which would allow us to
extrapolate potential declines in future PCB concentrations based upon historic trends. Even if such long-term trend data were available, the fact that pollutants like PCBs and chlorinated pesticides are extremely persistent, and that these pollutants continue to be loaded into the Delaware Estuary, argues against assuming a declining function of pollutant concentration for purposes of risk assessment.

The product of meal size and meal frequency in the previous equation provides an estimate of fish ingestion in mass per unit of time. For purposes of this report, a standard meal size of 8 ounces was assumed for adults, while the meal size for children was assumed to be 4 ounces. Furthermore, to reflect the fact that some people may consume considerable quantities of striped bass from the Delaware Estuary, while others may consume only an occasional meal, a range of plausible meal frequency values were assumed. Specifically, the following four meal frequencies were considered: one meal per year, two meals per year, one meal per month, and one meal per week. The first two values might be thought of as the meal frequency associated with a fisherman who vacations along the Delaware coast and has a successful fishing trip. The third scenario may be thought of as the recreational angler who goes fishing on the weekends during the striped bass season and has a moderately successful catch rate. The last scenario could correspond to a high-end consumption rate for a recreational angler, or alternatively, to the consumption rate of a subsistence fisherman. Using a range of values as just described not only provides an indication of how sensitive exposure and risk are to the amount of fish consumed, it also makes the findings of the risk assessment ultimately easier to explain.

Exposure duration reflects the length of time an individual is expected to be exposed to a particular toxic agent from a given source (e.g. PCBs in striped bass from the Delaware Estuary). Information on exposure duration is typically derived from population mobility data. Because the population is quite mobile, exposure duration will vary from individual to individual, and from household to household. However, for purposes of risk assessment, exposure duration is typically assigned a value which reflects a reasonable worst-case of residence time. Consistent with that practice, the exposure duration used in this study was taken as the 90 th percentile value for the number of years adults reside in a given household. This value was computed by the EPA to be approximately 30 years [EPA, 1989b] and is based upon a survey conducted by the U.S. Bureau of the Census in 1983. The 90 th percentile value contrasts with a median (i.e. 50th percentile) value derived from the same study of roughly 9 years. An analysis using even more recent information suggests the average residence time for all U.S. households is closer to 4.6 years, and that the mean for the northeast region is roughly 7.4 years [Israeli and Nelson, 1992].

This report nevertheless uses a 30 -year exposure duration for adult receptors. Although this value may seem unreasonably conservative, especially in light of the more recent figures, the fact is that this value will underestimate exposure for those people who spend their entire lives in the same region, even if they do change their principal place of residence. In the case of a child receptor, exposure was assumed to occur over the entire first 6 years of life.

Based upon current data, the average life expectancy of the entire U.S. population is 74.7 years [EPA, 1989b]. For purposes of this report, a life expectancy of 75 years has been assumed. This value aggregates males and females, blacks, whites, and others.

The final variable which appears in the above equation is RF, which is the percent reduction in contaminant concentration in the fish due to trimming and cooking losses. Based on recent studies conducted on Great Lakes ish, typical losses of PCBs and chlorinated pesticides resulting from proper trimoing and cooking may be around one-third (e.g. 33\%), and in some cases, as high as 50\% [Zabik et al 1993]. These figures, however, assume that the angler has followed trimong advise carefully and that the oils in the fish are allowed to drip away during cooking. Although it is indeed important to provide advise to anglers on how they might reduce theix risk through proper trimming and cooking, there is little guarantee that they will follow that advise. For this reason, the reduction factor assumed in this risk assessment was zero. This causes the reduction factor quotient in the above equation to default to a value of 1 , which has no influence on the estimate of IADE.

After computing lifetime average daily exposure (IADE), an estimate of lifetime average daily dose (IADD) was obtained using equation 9 below.

$$
\begin{equation*}
\underset{q g / \mathrm{kg} / \mathrm{d})}{L A D D}=\frac{L A D E \times A F}{B W} \tag{9}
\end{equation*}
$$

, where the following additional variables are introduced:
$A F=$ gastrointestinal absorption factor
BW = average body weight of the exposed population, (kg)

The gastrointestinal absorption factor is a value between 0 and 1 which reflects any known or expected differences between the efficiency at which the contaminant of interest is absorbed by bioassay animals verses humans. No quantitative information was located on gastointestinal absorption efficiency in animals versus humans. Consequently, a value of 1 was used. This assumes that the efficiency of absorption is the same for humans and bioassay animals.

The other variable in the above equation which must be specified is body weight. Body weight is an important factor because it influences dose inversely. In other words, if a large person and a small person are both exposed to an identical amount of given pollutant, the smaller person will experience a larger dose. This concept has been taken into account in this assessment by specifying three separate receptor groups, each of which has its own characteristic weight. The three groups include adults of average weight, women of child-bearing age, and children between the ages of 0 and 6 years old. The mean body weight of all adults between the ages of 18 and 75, men and women combined, is 71.8 kilograms, or roughly 158 pounds [EPA, 1989b]. The average body weight of women of chid-bearing age is 63.6 kilograms, or approximately 140 pounds [EPA,1989b]. This average includes all women between the ages of 18 and 45. Finally, the average weight of boys and girls combined between the ages of 0 and 6 years old is 14.5 kilograms, or 40 pounds [EPA, 1989b]. For this study, nominal weights of $70 \mathrm{~kg}, 64 \mathrm{~kg}$, and 14.5 kg were assumed for the three groups.

A summary of the various exposure factors discussed in this section appear in TABLE 2-8.

### 2.6.4 Risk Characterization

Risk characterization is the integration of the previous three steps (hazard identification, dose-response evaluation, and exposure assessment) to produce a concise description of the nature and magnitude of potential harm to the public. The risk characterization also identifies the major assumptions, scientific judgements, and, to the extent possible, estimates the uncertainties embodied in the assessment [EPA, 1986a]. A necessary step in defining the magnitude of potential harm is to calculate the cancer risk (in the case of carcinogens) and the hazard index (in the case of non-cancer endpoints). The techniques that were used to compute cancer risk and hazard index as well as related risk characteristics are presented below.

### 2.6.4.1 Carcinogenic Effects

Excess lifetime cancer risk was computed as the product of the lifetime average daily dose (LADD) and the cancer potency

slope $\left(q_{2}{ }^{*}\right)$ as shown in equation 10 below. Because $q_{1}{ }^{*}$ is an upper bound estimate of the low-dose slope as determined through the multistage procedure, the equation below will yield estimates of risk that are conservative, representing a plausible upper limit for the cancer risk at the assumed exposure. Consequently, it is unlikely that the "true" or "actual" risk associated with a given exposure is higher than the risk predicted using this model.

$$
\begin{equation*}
R I S K=L A D D \times q_{1}^{*} \tag{10}
\end{equation*}
$$

As discussed previously, LADD has units of $\mathrm{mg} / \mathrm{kg} / \mathrm{d}$ and $\mathrm{q}_{1}{ }^{*}$ has units of $1 /(m g / \mathrm{kg} / \mathrm{d})$. The product of these two values (i.e. risk) is therefore unitless. Risk, in fact, can assume any real value between 0 and 1. A risk of 0 corresponds to the absence of exposure, and a risk of 1 corresponds to certainty that exposure will result in a health effect. Most risk projections, of course, fall somewhere in between 0 and 1 and their meaning must therefore be interpreted within a probabilistic domain. Risk, by definition, is the probability of injury, disease, or death under specific circumstances.

By convention, excess lifetime cancer risks derived from the above equation are typically expressed in scientific notation. For example, a computed risk of 0.00004 is written as $4 \times 10^{-5}$. Alternatively, this same risk could be expressed as a lifetime rate. This is obtained simply by taking the reciprocal of the computed excess risk. For instance, a lifetime risk of $4 \times 10^{-5}$ is the same as 1 additional cancer in 25,000 individuals over a 75 yr period (i.e. $1 / 0.00004=25,000$ ). Similarly, $1 \times 10^{-6}$ is the well-known 1 in a million cancer risk. Finally, risk values can be expressed as a standard rate per 100,000 individuals. Extending our original example, 1 in 25,000 could be written as 4 in 100,000. Risk projections presented in this report utilize the first two methods.

The final point to be made about the above equation is that it is written in terms of "excess" risk because risks associated with exposure to environmental contaminants are added to, or in "excess" of, cancer risks associated with all other exposures linked to cancer (e.g. tobacco smoking).

Equation 10 applies to the case where a person is consuming fish which contains a single pollutant. The more common situation, and Eie one which we must consider in the case of the striped bass, is that the person is simultaneously exposed to multiple pollutants in the fish. It is unknown whether the risk associated with multiple pollutants is greater than, less than,
or equal to the sum of the risks for each pollutant taken individually. As a working hypothesis, simple additivity of risk was assumed as shown in equation 11 . This equation, which is consistent with federal guidelines [EPA, 1986b], states that aggregate lifetime cancer risk is obtained by computing the risk associated with each pollutant individually and then adding those risks together. This assumption is reasonable in the case of simultaneous exposure to PCBs, DDT/DDD/DDE, and chlordane because all are linked to the same type of cancer, namely, liver cancer.

$$
\begin{align*}
& \text { AGGREGATE LIFETIME }=\sum_{i=1}^{n}(L I F E T I M E \text { CANCER RISK })_{i} \\
& \quad \text { CANCER RISK }
\end{align*}
$$

Knowing the aggregate cancer risk from the equation above and cancer risk associated with each chemical individually, the proportion of risk attributable to each chemical is easily computed as follows:
$\begin{aligned} & \text { \% OF AGGREGATE RISK } \\ & \text { DUE TO CHEMICAL } i\end{aligned}=\frac{\text { CANCER RISK FOR CHEMICAL } i}{\text { AGGREGATE CANCER RISK }} \times 100$

The above equations were used in conjunction with the cancer potency slopes and exposure factors previously presented to estimate lifetime cancer risk associated with consuming striped bass from the Delaware Estuary. For purposes of the cancer risk assessment, two receptor groups were considered: average adults and children. The results of the cancer risk projections, along with a concise statement of assumptions and uncertainties, are presented in chapter 3 of this report.

### 2.6.4.2 Non-carcinogenic Effects

The magnitude of non-cancer health effects is determined by taking the ratio of the estimated exposure dose to the RfD for the chemical of interest. This ratio is referred to as the Hazard Index. Hazard indices greater than 1 indicate that a potential non-cancer hazard exists. Hazard indices less than 1 are expected to be without appreciable risk of adverse effects.

For chronic systemic toxicity, the hazard index was computed using equation 13 .

$$
\begin{equation*}
H . I .=\frac{L A D D}{R f D} \tag{13}
\end{equation*}
$$

This equation was used along with the reference doses and exposure factors presented previously to assess the likelihood of immonological effects to the average adult population and women of child-bearing age due to PCBs and DDT/DDD/DDE in the striped bass. The equation was also used to assess potential liver damage in those same receptor groups as a result of chlordane exposure.

Similar to the approach used for cancer effects, an aggregate nazard index for chronic systemic health effects was also computed alon, with the proportion of the hazard index attributable to each chemical in the mixture. The governing equations appear below.

$$
\begin{aligned}
& \text { AGGREGATE } \\
& H A Z A R D \text { INDEX }
\end{aligned}=\sum_{i=1}^{n}(H A Z A R D I N D E X)_{i}
$$



The approach taken to compute the hazard index for developmental effects was slightly different than that used for chronic systemic effects. For developmental effects, an average daily exposure rate was used rather than a lifetime average daily exposure rate. Computationally, this modification involved eliminating exposure duration and lifetime duration from equation 8 prior to computing the hazard index. Defining DOSE as the average daily exposure rate, the hazard index for developmental toxicity was computed using equation 16 .

$$
\begin{equation*}
H . I .=\frac{D O S E}{R f D} \tag{16}
\end{equation*}
$$

This equation was used to assess the potential for neurodevelopmental effects in children by assuming a child could be exposed either directly from consuming the contaminated fish or indirectly from transfer from the mother (in utero or through breast milk). These two possibilities required the consideration of both the child as a receptor and women of child-bearing age as a potential vector.

Following the methods described previously, an aggregate hazard index for neurodevelopment toxicity was computed and the proportion of the aggregate index attributable to PCBs, DDT/DDD/DDE, and chlordane was determined.

All results of the risk assessment described in this section appear in chapter 3.

## 3. RESULTS

The results presented in this chapter fall into three general areas. First, information concerning the lengths and weights of the striped bass samples is presented. Second, the results of the chemical analyses and statistical comparisons are discussed. And finally, the results of the risk assessment are presented.

### 3.1 LENGETS AND WEIGHTS

TABLE 3-1 lists the lengths and weights of the striped bass samples. The lengths of the four primary study categories (SGREC/SGSOM/BAYREC/BAYCOM) were compared for significant differences using the Kruskal-Wallis test as described earlier. As expected, at least one of the 4 categories proved $t$, be significantly different ( $P=0.001$ ). Two sample Mann-Whitney tests also showed that commercial size fish were significantly smaller than the recreational size fish ( $\mathrm{P}=0.0002$ ), also as expected. Among recreational size fish, the mean lengths were not significantly different between Bay and Spawning Ground samples ( $\mathrm{P}=0.144$ ) . Finally, although the median length of commercial size fish on the spawning grounds ( 553 mm total length) was nominally smaller than the median length of commercial size fish from the Bay ( 618 mm ), this difference was not significant ( $P=0.06$ ) for a critical level of 0.05 .

### 3.2 CHEMICAI CHARACTERIZATIOA

All of the raw data generated by the laboratory are presented in APPENDIX D. Table 8 of APPENDIX D lists the concentrations of mono-ortho, di-ortho and other targeted PCB congeners as well as the concentrations of chlorinated pesticides. Values presented in Table 8 are in units of ng/g (ppb) wet weight. Table 9 of APPENDIX $D$ presents the concentrations of mono through deca PCB homologs. Those values are also listed in units of $\mathrm{ng} / \mathrm{g}$ wet weight. Finally, Table 10 of APPENDIX D lists the concentrations of the non-ortho substituted PCB congeners detected in samples R02SG, C04SG, R03B, and C01B. Units associated with Table 10 are $\mathrm{pg} / \mathrm{g}$ (pptr) wet weight.

TABLE 3-1 Lengths and Weights of Striped Bass*


- See Appendix A for sample ID codes


### 3.2.1 Total PCB, Percent Chlorination, and Chlorinated Pesticides

Using the techniques described in the previous chapter, the following values were computed from the raw data: total PCB content; percent chlorination; $0, p^{\prime}$ DDT + $p, p^{\prime}$ DDT; $0, p^{\prime}$ DDD + p, ${ }^{\prime}$ ' DDD; $0, p^{\prime}$ DDE + p, $P^{\prime}$ DDE; total DDT; and alpha plus gamma chlordane. The results of those calculations are sumarized in TABLE 3-2. FIGURES 3-1 through 3-5 provide a graphical representation of the results for the 4 primary study categories (SGREC/SGCOM/BAYREC/BAYCOM). FIGURE 3-6 shows a similar chart for lipid variation among the primary categories. The number at the top of the bar in the figures is the maximum value for the given category. The value below the bar is the minimum for the category. The solid bar is the arithmatic mean.

The values in TABLE 3-2 were used as the basis for statistical comparisons between the various study categories. As shown in TABLE 3-3, there were no statistically significant differences between categories in the case of total PCB, DDT, DDE, and total DDT. In contrast, 7 of the 9 statistical comparisons performed on percent chlorination revealed significant differences among and between categories. The Kruskal Wallis test on the four primary categories indicated that at least one of the four categories was different ( $P=0.002$ ). Pairwise comparisons between any two of the four primary categories revealed that the level of chlorination in the recreational size striped bass from the spawning grounds was statististically greater than the level of chlorination in the commercial size fish from the spawning grounds ( $\mathrm{P}=0.012$ ), the recreational size fish from the Bay ( $\mathrm{P}=0.012$ ), and the commercial size fish from the Bay ( $\mathrm{P}=0.012$ ). Furthermore, a comparison of the level of chlorination in all striped bass from the spawning grounds versus all striped bass from the Bay showed that those on the spawning grounds carried a higher degree of chlorination ( $\mathrm{P}=0.0006$ ). Additional evidence that the level of chlorination in fish taken off the spawning grounds is elevated is that commercial size striped bass from the spawning ground had a statistically higher level of chlorination than either recreational size fish from the Bay ( $\mathrm{P}=0.022$ ) or comercial size fish from the Bay ( $\mathrm{P}=0.037$ ).

TABLE 3-3 indicates that three other comparisons showed significant differences. First, the concentration of DDD in recreational size fish taken as a group was significantly lower than DDD in commercial size fish taken as a group ( $\mathrm{P}=0.026$ ). Chlordane in recreational and commercial size fish combined from the spawning grounds was higher than both sizes combined from the Bay ( $\mathrm{P}=0.038$ ). Finally, the concentration of chlordane in commercial size striped bass from the spawning grounds was higher than that in recreational size stripers from the Bay ( $P=0.022$ ).

TABLE 3-2 Summary of PCB and Chlorinated Pesticide Concentrations in Striped Bass From the Delaware Estuary ( $\mathrm{ng} / \mathrm{g}$ wet weight)


TABLE 3-3 Significance Levels* (p) for Statistical Comparisons Between Study Categories


## 'Significance levels less than 0.05 indicate that the groups being compared are

 significantly different.
## VARIATION IN TOTAL PCB CONTENT BY SIZE CLASS AND LOCATION



## VARIATION IN PERCENT CHLORINATION BY SIZE CLASS AND LOCATION



## MEAN DDT/DDD/DDE CONTENT BY LOCATION AND SIZE CLASS


$\square_{\text {DDT }}$
$\square$ DDD
$\square \mathrm{DDE}$
■total

## VARIATION IN TOTAL DDT BY SIZE CLASS AND LOCATION



## VARIATION IN CHLORDANE CONTENT BY SIZE CLASS AND LOCATION



## VARIATION IN LIPID CONTENT BY SIZE CLASS AND LOCATION



The three differences just noted have little practical importance to the overall findings of the study. However, the differences in percent chlorination described above are important because they impact the human health risk assessment in a critical way. Specifically, results of the statistical analyses demonstrate that the level of chlorination is higher in the fish from the spawning ground area than in the Bay, and in particular, is highest for recreational size fish from the spawning grounds. Furthermore, the level of chlorination in the recreational size fish from the spawning grounds is very close to 60\%, thereby providing a reasonable basis to use the cancer potency developed for Aroclor 1260 in those samples.

To provide some insight into why the level of chlorination was higher in the fish from the spawning grounds versus the Bay, consider FIGURE 3-7 and FIGURE 3-8. These two figures depict the chlorobiphenyl distributions in two typical samples, C04B and R04SG, respectively. It can be seen from both distributions, which were computed from equation 2 in Chapter 2, that the majority of the weight contribution comes from tetrachlorobiphenyl through heptachlorobiphenyl. Note, however, that the distribution for the Bay sample is skewed towards the left (mono through penta) while the distribution for the recreational size fish from the spawning ground is skewed to the right (hexa through deca). This difference in chlorobiphenyl distribution explains the apparent differences in overall level of chlorination discussed above. Reasons why the chlorobiphenyl distributions themselves differ is a more complex matter which will be discussed in general terms in Chapter 4. Information on the chlorobiphenyl distribution of all twenty samples is available upon request.

Because there were no significant differences in total PCB, total DDT, or chlordane content among the 4 primary study categories, the data were pooled to yield grand means for purposes of the human health risk assessment. The mean PCB content from this study considering all 20 samples was 901.6 ppb (. 9016 ppm$)$. Mean total DDT content was 340.9 ppb ( 0.341 ppm ), and mean chlordane content was $21 \mathrm{ppb}(0.021 \mathrm{ppm})$. When the PCB data from DNREC's 1992 pilot study were also considered, a representative mean concentration of approximately 1000 ppb ( 1 ppm) was obtained. The mean contaminant concentrations and their $95 \%$ confidence limits are shown in TABLE 3-4.
) CHLOROBIPHENYL DISTRIBUTION SAMPLE C4B


FIGURE 3-7

## CHLOROBIPHENYL DISTRIBUTION SAMPLE R4SG



## TABLE 3-4 Mean Concentrations in Striped Bass



As an aside, DDE represented 70.8 of total DDT, DDD represented $27 \%$, and parent DDT represented 2.2 \%. However, as explained in Chapter 2, these analytes were not treated differently from a toxicological perspective, and consequently, total DDT was used in the risk assessment.

### 3.3.2 Polychlorinated Biphenyl Congeners

Congeners which were detected in all samples included IUPAC 52, 74, 77, 80, 81, 87, 99, 101, 105, 118, 126, 127, 138/158, 153, 167, 169, 170/190, 180, 183, and 187. In addition, IUPAC 168 was detected in all but one sample. PCB congeners which were not detected in any of the samples included IUPAC $1,3,4,7$, 114, 123, 137, 166, 189, 191, and 205. Congeners which were infrequently detected included IUPAC 128, 157, and 185 (1 detection each); IUPAC 200 ( 2 detections); and IUPAC 18 and 207 (3 detections).

Of the congeners detected in all samples, IUPAC 153 and the coeluting pair $138 / 158$ were most abundant, each generally ranging between 50 and 150 ppb , or roughly $10 \%$ of total PCB each. Of the non-ortho substituted congeners, IUPAC 77 exhibited the highest concentration in all 4 samples, followed by IUPAC 126, 169, and finally, 81. This same ordering of coplanar PCBs has been reported by others in the literature [Tanabe et al., 1987]. The concentration of IUPAC 77 in the striped bass samples ranged from a low of 246 pptr in the recreational size fish from the spawning ground to a high of 500 pptr in the commercial size fish from the Bay. Congener 126 ranged from 111 pptr in the commercial size fish from the spawning ground to 168 in the comercial size fish from the Bay. Congeners 169 and 81 were both detected in the low parts per trillion, congener 169 ranging from approximately 8 pptr to 11 pptr and congener 81 ranging from roughly 5 pptr to 11 pptr.

The concentrations of non-ortho, mono-ortho, and di-ortho substituted PCB congeners detected in samples R02SG, C04SG, R03B, and CO1B appear in TABLE 3-5. Also in that table is a breakdown of the percentage of non-ortho, mono-ortho, and di-ortho substituted congeners to total coplanar PCBs in the four samples. Note that the fraction of total coplanar PCB which is non-ortho substituted is quite small, ranging between 0.1 and 0.4 percent. In contrast, di-ortho substituted congeners make up the bulk of the total coplanar PCB content at approximately $75 \%$, while monoorthos represent roughly 25\%. TABLE $3-5$ also provides an estimate of the percentage of total PCB which is coplanar. A simple linear regression between total PCB and total coplanar PCB for the four samples yielded the relationship below, which has an $r^{2}$ value of 0.983 .

$$
[T O T A L P C B]=0.218+2.15 \times[T O T E L \text { COPLANAR PCB }]
$$

A plot of the above equation appears as FIGURE 3-9. Extrapolation of this equation to other PCB contamination situations is not advisable because of the small sample size used to develop the equation anc because it is based specifically on data for striped bass from the Delaware Estuary.

TABLE 3-6 presents the toxicity equivalents (T.E.) computed from the coplanar PCB congener data and the toxicity equivalence factors (TEFs) introduced in Chapter 2. Toxicity equivalents due soley to coplanar PCB congeners range from 61 pptr in sample R03B up to 95.2 pptr in sample R02SG. The mean T.E. level for the 4 samples was $73.7 \mathrm{pptr}(0.0000737 \mathrm{ppm})$. The average percent contribution of non-ortho, mono-ortho, and di-ortho substituted PCB congeners to total toxicity equivalents is roughly 25\%, 70\%, and 5\%, respectively. Therefore, although non-ortho substituted PCB congeners represented only 0.1 to $0.4 \%$ of the total coplanar PCB content on a concentration basis, they represented approximately 25 \% of the total toxicity equivalents. The opposite was true for the di-ortho substituted congeners. On a concentration basis, that group contributed roughly 75 \% of the total coplanar PCBs, yet, in terms of toxicity equivalents, they only represented $5 \%$. The findings discussed above are presented graphically in FIGURES 3-10 and 3-11.

### 3.3 RISR ASSESSMERTI

The contaminants of concern in this study have been shown to cause a variety of adverse health effects in laboratory animals when administred at high doses. Observed effects include liver cancer, immunotoxicity, and neurobehavioral deficits. The

TABLE 3-5 Concentrations of Non-ortho, Mono-ortho, and Di-ortho Substituted PCBs in Striped Bass from the Delaware Estuary and Comparison to Total PCB Concentrations (ng/g wet weight)

| rupac mumber | $\begin{aligned} & \text { shipiz } \\ & \text { rozse } \end{aligned}$ | $\begin{aligned} & \text { sispir } \\ & \text { acouse } \end{aligned}$ | $\begin{aligned} & \text { Suypry: } \\ & \text { natus. } \end{aligned}$ | $\begin{aligned} & \text { Snypise } \\ & \text { cons } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| a) Non-ortho |  |  |  |  |
| 77 | 0.246 | 0.262 | 0.306 | 0.5 |
| 81 | 0.00607 | 0.00471 | 0.00802 | 0.0109 |
| 126 | 0.159 | 0.111 | 0.146 | 0.168 |
| 169 | 0.0112 | 0.00798 | 0.0107 | 0.00942 |
| b) Mono-ortho |  |  |  |  |
| 114 | ND | ND | ND | ND |
| 118 | 40.2 | 28.0 | 25.6 | 31.8 |
| 123 | ND | ND | ND | ND |
| 156 | 8.55 | 5.22 | 3.39 | 3.8 |
| 157 | ND | ND | ND | ND |
| 167 | 9.64 | 5.82 | 3.85 | 4.64 |
| 189 | ND | ND | ND | ND |
| c) Di-ortho |  |  |  |  |
| 137 | ND | ND | ND | ND |
| 138/158 | 132.0 | 73.0 | 45.8 | 54.7 |
| 153 | 134.0 | 70.3 | 41.5 | 52.0 |
| 166 | ND | ND | ND | ND |
| 168 | 8.05 | 6.65 | 3.94 | 4.13 |
| 170/190 | 20.6 | 11.0 | ND | ND |
| 180 | 54.5 | 26.8 | 14.0 | 14.6 |
| 191 | ND | ND | ND | ND |
| 194 | 7.19 | ND | ND | ND |
| 205 | ND | ND | ND | ND |
| Total <br> Coplanitemser | $\text { \#\# } 4 \%$ | ऑ23, | $\$ 46$ | $\frac{\pi}{4}$ |
| \% Non-ortho | 0.1 | 0.2 | 0.3 | 0.4 |
| \% Mono-ortho | 16.2 | 20.2 | 27.8 | 27.7 |
| \% Di-ortho | 83.7 | 79.6 | 71.9 | 71.9 |
| Totall PCA | \#, \#3 | \#\#\# | $5$ | $525$ |
| \% Coplanar | 37.5 | 32.3 | 28.2 | 33.2 |

## REGRESSION OF TOTAL PCB AND TOTAL COPLANAR PCB




TABLE 3-6 Toxic Equivalents (T.E.) of AHH-Active PCB Congeners
in striped Bass From the Delaware Estuary


## TOXIC EQUIVALENTS OF AHH-ACTIVE PCBs



## CONTRIBUTION OF COPLANAR PCBs TO TOXICITY EQUIVALENTS


evidence of similar health effects in humans is only suggestive at present. Similar effects in humans under low dose exposures is, however, biologically plausible. This point serves as the fundamental underpinning of the risk projections presented in the sections to follow. For convenience, the risk assessment results have been separated into cancer effects versus non-cancer effects.

### 3.3.1 Cancer

TABLE 3-7 presents the lifetime cancer risks associated with consuming striped bass from the Delaware Estuary. The values presented reflect the aggregate risks associated with the presence of PCBs, DDT/DDD/DDE, and chlordane in the fish. Because the risks in the table were derived using the linearized multistage model, they should be viewed as upper-bound estimates under the exposure conditions considered. In other words, the true risks are not likely to be higher for the exposures considered. The true risks may be lower and may in fact be zero when one considers that the link between exposure to PCBs, DDT/DDD/DDE, and chlordane and cancer in humans is presently equivocal.

The fact that the risk estimates in TABLE 3-7 are upperbounds should not be interpreted to mean that they are worst-case estimates. They are not. Worst case estimates would be produced by using maximum detected contaminant concentrations in the fish; assuming that human exposure occurs over an entire lifetime rather than 30 years; and for this particular case, by assuming that all PCBs are as potent as Aroclor 1260. One could further elevate the risks over those shown in TABLE 3-7 by considering the PCB congener data collected in this study within the context of 2,3,7,8-TCDD toxicity equivalents and the cancer potency of dioxin. This latter point was demonstrated by Greene and Miller at the U.S. EPA's National Workshop on PCBs in Fish [EPA, 1993a]. In the final analysis, the risk estimates appearing in TABLE 3-7 were developed based upon the belief of the authors that the methods upon which they were derived are not unnecessarily conservative nor unwittingly permissive.

To facilitate interpretation of the risk estimates appearing in TABLE 3-7, please refer to FIGURES 3-12, 3-13, and 3-14. Note that the verticle axis of the figures is on a logarithmic scale and that a reference risk level of $1-i n-100,000$ (i.e. $10^{-5}$ ) has been drawn in to provide a benchmark commonly used in environmental risk management. The $10^{-5}$ level is not intended to imply that risks below that level are universally "acceptable" or that those above that level are always "unacceptable". The $10^{-5}$ risk level is shown on the figures to provide some sense of the magnitude of the risk.

TABLE 3-7 Lifetime Cancer Risk Associated With Consuming Striped Bass From the Delaware Estuary


## CANCER RISK PROJECTIONS RECREATIONAL SIZE STRIPERS FROM THE SPAWNING GROUND VERSUS ALL OTHER CATEGORIES

## RISK





## CANCER RISK PROJECTIONS STRIPED BASS - SGCOM, BAYREC, AND BAYCOM

 RISK

The first thing to notice about the series of figures is that the risk associated with consuming recreational size striped bass from the spawning ground is much higher than the risk associated with consuming striped bass from the Bay or from consuming comercial size striped bass from the spawning ground. Quantitatively, the risk associated with consuming the recreational size striped bass from the spawning ground is roughly 100x the risk associated with the other categories. This disparity is due to the assumption made in this report that only PCB mixtures with a level of chlorination close to $60 \%$ represent a cancer hazard to humans. As shown earlier, the recreational size fish from the spawning ground was the only category that met this criterion. Interestingly enough, if the PCB potency in the other categories was not zero (as assumed), but rather, two orders of magnitude less than the potency of Aroclor 1260 (as EPA has suggested might be the case for lower chlorinated PCBs), then the risk estimates for the Bay fish and the commercial size fish from the spawning ground would still be in the correct range.

The second thing to notice from the figures is the actual magnitude of the the cancer risks posed. FIGURE 3-13 shows that the lifetime cancer risk to adults and children who consume recreational size striped bass from the spawning ground is in excess of 1 -in-100,000 assuming a consumption rate of as little as 1 meal per year. At a top end consumption rate of 1 meal per week, risks to these receptor groups increase to in excess of 1-in-1000. In contrast, FIGURE 3-14, which applies to categories other than recreational size fish from the spawning ground, demonstrates that adults and children would have to consume 1 meal per week of striped bass from the Bay or 1 meal per week of commercial size fish from the spawning ground for their risk to even marginally exceed 1-in-100,000.

Note from both FIGURE 3-13 and 3-14 that risks are slightly higher for the adult than the child. The reasons for this are that children were assumed to eat smaller portions than their adult counterparts, and the exposure duration for the child was taken as 6 years as opposed to the 30 years assumed for adults. The mitigating effects of smaller meal size and shorter exposure duration for chidren were only partially offset by the smaller body weight of children.

The final point to be made concerning the cancer risk assessment relates to the relative contributions of PCB, DDT/DDD/DDE, and chlordane to aggregate risk. As can be seen in FIGURE 3-15, over ninety-eight percent (98.2\%) of the aggregate risk associated with consuming recreational size striped bass from the spawning ground is due to PCBs. DDT/DDD/DDE and chlordane contribute the balance of the risk for this group at 1.5\% and 0.3\%, respectively. The relative contribution in the fish from the Bay as well as the comercial size fish from the spawning ground is quite different. Roughly eighty-two percent

## PROPORTION OF AGGREGATE CANCER RISK ATTRIBUTABLE TO PCBs, DDT/DDD/DDE, AND CHLORDANE



SGREC
OTHERS
(81.9\%) of the risk associated with consuming those fish is due to DDT/DDD/DDE. Chlordane contributed approximately eighteen percent (18.18).

### 3.3.2 Mon-Cancer

TABLE 3-8 summarizes the hazard indices computed for the noncancer health effects considered in this study. Recall that the hazard index is computed as the ratio of the exposure dose to the Reference Dose (RfD). The results in TABLE 3-8 are also shown graphically in FIGURES 3-16 and 3-17. Like the previous plots, the verticle axis is on a logarithmic scale. A benchmark hazard index of 1 is also shown on the figures to provide some perspective. Hazard indices greater than 1 indicate that the exposure dose exceeds the reference dose. As explained in Chapter 2, while hazard indices greater than 1 mean that there is an increased probability of adverse effects, it does not suggest certainty that an effect will occur. Likewise, while exposure below the RfD (i.e. H.I.< 1) reduces the chances of adverse effects, it does not guarentee that effects will not occur. In general, the greater hazard index is above 1 , the higher the probability of effects, and the lower hazard index is below 1 , the lower the chances of an effect. Unfortunately, there is not a 1-to-1 relationship between hazard index and probabilty of harm. Consequently, one cannot state that the chances of a noncancer health effect doubles as the hazard index increases from 1 to 2, or from 5 to 10, for instance.

FIGURE 3-16 displays the hazard index for potential systemic toxic effects associated with consuming striped bass from the Delaware Estuary (both the Bay and the spawning ground). These hazard indices reflect the aggregate influence of potential immunological effects from PCBs and DDT/DDD/DDE plus possible liver atrophy due to chlordane. Note from the figure that women of child-bearing age are slightly more suseptible to systemic effects than the average adult receptor. This minor difference merely reflects differences in assumed body weights between the two groups. Note also from the figure that the peak hazard index for both receptor groups is roughly 10 and that it takes somewhere between 2 meals per year and a 1 meal per month for the hazard index to exceed 1.

FIGURE 3-17 shows the hazard indices for possible neurodevelopmental effects in children. Women of child-bearing age are shown in the figure not as primary receptors who risk neurodevelopmental effects but rather as potential vectors for prenatal and postnatal exposure of children. Hazard indices for the child receptor assume that contaminant exposure is via consumption of fish only. If it were assumed that the child is simultaneously being exposed to contamination transferred from the mother and that the child consumes contaminated fish, the hazard indices would be greater than those shown in FIGURE 3-17.


## SYSTEMIC TOXICITY HAZARD PROJECTIONS STRIPED BASS - SPAWNING GROUND AND DELAWARE BAY



■ MEAL/YR ZZ 2 MEALS/YR
$\square 1$ MEAL/MO
1 MEAL/WK
H.I. $=1.0$

ADULT MEAL $=8 \mathrm{oz}$

FIGURE 3-16

## DEVELOPMENTAL TOXICITY HAZARD PROJECTIONS STRIPED BASS - SPAWNING GROUNDS AND DELAWARE BAY

HAZARD
INDEX
100
HAZARD INDICES > 1 INDICATE POTENTIAL HAZARDS

## PROPORTION OF AGGREGATE HAZARD INDICES ATTRIBUTABLE TO PCBs, DDT/DDD/DDE, AND CHLORDANE



SYSTEMIC TOXICITY


NEUROBEHAVIORAL

Although exposure through both routes might be realistic, proper consideration of this scenario would require a more sophisticated pharmacokinetic approach. Such an analysis is beyond the scope of the present study.

With the above limitations in mind, note from FIGURE 3-17 that direct exposure to children through consumption of contaminated fish yields higher hazard indices than indirect maternal transfer. Furthermore, note that it only requires a little over two 4 ounce meals per year for the hazard index for the child receptor to exceed a value of 1 . Finally, note that the peak hazard index for direct childhood exposure is roughly 20 and that the peak hazard index for indirect childhood exposure through maternal transfer is roughly 10 . Both of these values are based on a rather high, yet plausible, consumption rate of 1 meal per week.

With respect to relative contributions of the contaminants to the above-noted haz-rds, PCBs again emerged as the greatest contributor. FCr systemic toxicity, PCBs represented $98 \%$ of the aggregate hazard, while the contribution of PCBs to potential neurodevelopmental pfects was 64.1\%. The contribution of PCBs and the other contaminants to aggregate hazard is shown in FIGURE 3-18.

### 3.3.3 Maximum Nrwber of Meals Associated with a Target Risk and Hazard Level

A natural question that arises in response to the above risk assessment is: What is the maximum number of meals that can be consumed while keeping the incremental cancer risk below a target risk level of 1-in-100,000 and the hazard index below $1 ?$ As explained by Dourson and Clark, the amount of fish that can be consumed while capping risk or hazard at a predefined level is inversely related to the amount of contamination in the fish [Dourson and Clark, 1990]. With this in mind, the equations in Chapter 2 were rearranged by setting risk equal to $10^{-5}$ and hazard index equal to 1 and then solving for meal frequency as a dependent variable. All other variables were unchanged. The results of the calculations are shown in TABLE 3-9.

TABLE 3-9 Humber of Meals* per Year Associated with a 1-in-100,000 Lifetime Cancer Risk and a Hazard Index of 1


$$
\text { *Adult Meal }=8 \text { ounces and Child Meal }=4 \text { ounces }
$$

A number of observations can be made regarding the information in TABLE 3-9. First, for the target risk level and hazard index chosen, the cancer endpoint limits the maximum number of meals that can be consumed of recreational size striped bass from the spawning ground. Adults and children would have to limit their intake to less than a single meal per year ( 3 ounces for adults and 1.5 ounces for children) for lifetime cancer risk to remain below $10^{-5}$. In contrast, adults and children could consume approximately 2 meals per month of the other categories of striped bass without exceeding the $10^{-5}$ level. This is obviously quite a big difference, and it results from the
assumption made in this report that only PCB mixtures with a level of chlorination close to $60 \%$ pose a cancer hazard.

Assuming the above assumption is correct, cancer risk does not control the maximum number of meals that can be consumed for the other categories of striped bass. Potential neurodevelopmental effects are the controlling factor in the case of the child receptor, and potential impairment of the immune system is the controliing factor for adults, and in particular, for women of child-bearing age. The table indicates that children would have to limit their consumption of these other categories of striped bass to no more than three, 4-ounce meals per year to avoid potential neurodevelopmental effects. Similarly, the general adult population would need to restrict its consumption of these other categories of striped bass to no more than six, 8-ounce meals per year to avoid possible effects to the immune system. Women of child-bearing age in particular would need to restrict their intake to no more than five, 8-ounce meals per year to avoid possible effects to the imune system.

### 4.1 SATISFACTION OF STUDY OBJECTIVES

Recall the three primary objectives of this study:

1. Characterize the PCB and chlorinated pesticide content in striped bass from the Delaware Estuary using the best analytical methods available;
2. Determine if there are significant differences in PCB and pesticide content between recreational size striped bass and commercial size striped bass taken from two separate geographic regions of the Estuary; and
3. Assess the human health risk to recreational and subsistence anglers who consume striped bass from the Estuary in support of Delaware's Toxics in Biota Program.

With regard to the first objective, the data collected reflect a level of analysis not previously available for the Delaware Estuary. No agency, with the exception of the National Oceanic and Atmospheric Administration (NOAA), routinely collects PCB homolog or congener data for the Delaware Estuary. Although what constitutes the "best analytical methods" for PCBs is a matter of ongoing debate, the methods used in this study are generally recognized as representing state-of-the-art [Erickson, 1992]. With regard to the second objective, the balance sought between analytical costs and statistical power did not compromise our ability to detect important differences in contaminant characteristics. Finally, the data collected were successfully used within a risk assessment framework to determine potential health effects to recreational and subsistence anglers.

### 4.2 FDA VERSUS RISR-BASED APPROACE

It is worthwhile at this point to discuss important differences between the risk assessment approach presented in this report versus other methods of evaluating fish contaminant data. Comparison of detected concentrations in the edible portion of the fish to the FDA action levels is the most common method used by the states to determine potential harm to fish consumers [Cunningham et al., 1989]. If the concentration in the fish exceed the action level, then the state agency would
typically issue a health advisory warning the public. As noted earlier, this was the approach used by Pennsylvania and New Jersey in issuing the current advisories on the Delaware Estuary, Using this approach for the striped bass, only 1 of the 20 samples exceeded the FDA action level of 2 ppm for PCBs and none of the samples exceeded the action level of 5 ppm for total DDT or 0.3 ppm for chlordane.

However, as pointed out by Reinert and others [Reinert et al., 1991], reliance on the FDA action levels for assessing risks to recreational and subsistence anglers is problematic for several reasons. First, the values were set based upon national fish consumption habits and national fish contamination patterns. The average fish consumption rate for the nation as a whole (which accounts for fish consumers and non-fish consumers combined) is likely to be significantly lower than the consumption rate of the avid sportsfisherman, subsistence angler, or normal seafood lover. For instence, FDA's definition of "average" fish consumption amounts to just 4 ounces of fish once every 40 days [Jacobson et al., 199 1 ]. Furthermore, in considering national fish contanination patterns, the implicit assumption is made that the contamindnt levels in certain fish can be higher than in others, so lony as the average exposure in the diet is below a given level. From a national perspective, this assumption is reasonable. However, from a regional or local perspective, the validity of this assumption starts to come into question if the perion derives all or most of his/her fish from a contaminated waterway. In this situation, the intake of contaminated fish is not offset by "clean" fish from other, lesspolluted, waters.

Another problem with using the FDA action levels to assess risk to recreational and subsistence anglers is the implied hazard of concentrations above the action level and the implied safety of concentrations below the action level. Under this type of approach, a person could consume an unlimited amount of fish with a PCB concentration of say, 1.9 ppm , and not experience any risk. If, however, the PCB concentration in the fish were marginally above the action level, say, 2.1 ppm , the person would be advised not to consume the fish. This notion is counter to the basic toxicological principle that "the dose makes the poison." In other words, a person who consumes large quantities of fish that are only slightly contaminated carry the same risk as a person who occassionally and unknowingly consumes fish which are heavily contaminated. Therefore, risk is determined by the level of contamination in the fish and the amount of the fish consumed.

The final point to mention regarding the FDA action levels is that they are not based soley on public health considerations. Among other factors, the FDA considers the economic impact to commercial fishermen in establishing action and tolerance levels.

Clearly, if the fish under consideration are not tendered in a commercial market, then the consideration of economic impacts to commercial fishermen is not germane. In the case of striped bass from the Delaware Estuary, there is a commercial market, and so economic considerations are a legitimate concern. Any action on the part of the State of Delaware, however, would be restricted to advice given to recreational and subsistence anglers. Ensuring that the commercial catch meets Federal requirements is the responsibilty of the FDA.

Despite the limitations of the FDA action levels, their use has served the states well over the years, particularly considering the absence of a working alternative. Risk assessment has matured to the point where it now represents a more credible and appropriate way of assessing risks to recreational and subsistence anglers. The fact that more and more states are using risk assessment as the basis of their fish contamination programs reflects the broader acceptance of the approach. As with all new ways of looking at a problem, there is a transition phase. Delaware is currently making the transition from the FDA action levels to a risk-based approach.

Although risk assessment is gaining favor, it is not without its problems. Namely, it is more complex and resource intensive than simply comparing detected pollutant levels to an action level. Furthermore, the toxicological data upon which the approach is based are subject to change, thereby giving the impression of great uncertainty. Finally, because it departs from the traditional approach, it is often met with resistance. All the pros and cons considered, Delaware has made a commitment to pursue a risk-based approach to its fish contamination program [DESS and DNREC, 1993].

## 4.3 possible explakations for bige chlorigation levens IN SPANAIMG GROURD FISE

A significant finding in this study was the statistically higher level of chlorination in the striped bass taken from the spawning ground, and in particular, the high level of chlorination in the recreational size fish from the spawning ground. In general, overall level of chlorination in the striped bass is controlled by external factors such as exposure history of the animal and internal factors such as physiological processes. Although both factors are expected to play a role, the results of this study suggest that exposure history is probably more important in determining the high level of chlorination in the striped bass from the spawning ground than physiological factors. Support for this hypothesis is offerred along several lines.

The spawning ground fish as a group (SGREC + SGCOM) had a higher level of chlorinaton than the Bay fish (BAYREC + BAYCOM).

At the same time, the larger, older recreational size fish as a group (SGREC + BAYREC) did not exhibit a higher level of chlorination than the smaller, younger commercial size fish as a group (SGCOM + BAYCOM). While neither of these facts are sufficient in and of themselves to prove that differences in exposure alone account for differences in level of chlorination, or, alternatively, that physiological factors are not responsible for differences in level of chlorination to some degree, taken together, these two findings represent a strong argument in favor of an exposure-driven phenomenon.

Further support for the above hypothesis is that we know that the resident fish in the vicinity of the spawning grounds (e.g. catfish and white perch) are contaminated with highly chlorinated PCBs, while resident fish down in the Bay are generally less contaminated and show lower PCB chlorination levels [DNREC, 1994b]. We might expect then that the level of chlorination in the striped bass would increase as the stripcis move from the Bay to the spawning grounds as their diet shifts frum prey of lesser chlorination to greater chlorination. The Jact that the recreational size stripers from the spawning gri unds had a slightly higher level of chlorination than the commercial size stripers from the same location may simply reflect that the larger recreational size fish are more efficient feeders. Despite the evidence supporting an exposure-driven phenomenon, we cannot dismiss the possibility that the higher level of chlorination in the striped bass from the spewning grounds is due to selective retention of highly chlorinated PCB congeners and/or selective depuration of lesser chlorinated PCB congeners during actual spawning activity.

As to why the resident species exhibit a high level of PCB chlorination, a few possibilities can be offered. First, one or more significant land-based sources of highly chlorinated PCBs are probably located in the area. The PCBs could have been transported into the system by overland flow in the past and may be continuing to do so. This possibility needs to be explored with waste management personnel from Delaware, New Jersey, Pennsylvania, and the EPA. Second, regardless of whether the PCBs are due to past releases, current releases, or both, another possible reason the resident fish exhibit a high level of chlorination in the vicinity of the spawning grounds may have to do with hydrodynamic factors. The spawning grounds is located within a transition zone where freshwater and brackish water mix and dissolved materials flocculate to produce the so-called turbidity maximum. The turbid conditions may act to efficiently trap PCBs delivered to the Estuary. Once trapped, the PCBs weather to a mixture which bears some resemblence to Aroclor 1260.

All of the thoughts in this section are speculation but represent testable hypotheses.


States Issuing Fish and Shellfish


### 4.4 BROADER PERSPECTIVES ON PCB COKTAMIMATIOA

PCB contamination is not confined to striped bass, channel catfish, and white perch from the Delaware Estuary. As shown in FIGURE 4-1, essentially the entire eastern half of the United States has issued fish consumption advisories because of PCBs [EPA, 1993b]. Of the northeastern states, Massachusetts, Rhode Island, Connecticut, New York, and New Jersey all have some type of health advisory or prohibition on the consumption of striped bass due to PCBs. This is primarily due to contamination of migratory \#udson stock. Of the Mid-Atlantic states (DE, MD, PA, VA, and NC), none presently have advisories on striped bass, due to PCBs or otherwise.

Another perspective on the PCB contamination problem can be gained from considering FIGURES 4-2 and 4-3 [EPA, 1993dy. FIGURE 4-2 shows the average PCB content in human adipose tissvo across major census regions of the U.S. This information was ubtained through the National Human Adipose Tissue Survey (NbATS) for fiscal year 1986, which is the most recent year for whica data are available. The survey was designed to be statisticazly representative and involved the collection of 671 individual specimens from autopsied cadavers and surgical patients. Note that the highest PCB levels were found in the northeast and that the concentration was approximately 1003 ppb ( 1 ppm ). Coincidentally, this concentration is equal to the level detected in striped bass from the Delaware Estuary.

FIGURE 4-3 shows an estimate of the level of PCB chlorination by census region as derived from the most recent NBATS. Although the values do not differ greatly across the U.S., all approach 60\%. These final two maps suggest that opportunities should be identified to reduce human exposure to PCBs in the northeast.



## 5. SURGARY AND CONCLUSIONS

Fish contamination is a growing concern in the Delaware Estuary. This study showed that striped bass from the Estuary contain PCBs and chlorinated pesticides. Total PCBs ranged from 0.449 ppm to 2.25 ppm . Toxicity equivalents of AHH-active PCB congeners ranged from 61 pptr to 95.2 pptr. DDT and metabolites ranged 0.084 ppm to 1.07 ppm . Chlordane ranged from 0.00537 ppm to 0.0593 ppm. Dieldrin was detected in 1 sample at 0.0167 ppm .

PCBs, DDT/DDD/DDE, and chiordane have been shown to cause a variety of adverse health effects in laboratory animals when administered at high doses. Observed effects include cancer, immunotoxicity, and neurobehavioral deficits in children. These findings, coupled with suggestive epidemiological evidence, were used to conclude that people who regularly consume striped bass from the Delaware Estuary are at higher risk of illness.

The PCEs in the recreational size striped bass from the spawning ground exhibited a higher level of chlorination than the other size/location categories studied. Eating these fish poses a moderate to high cancer risk. Lifetime cancer risk to adults and children who consume these particular fish is in excess of 1 -in-100,000 (i.e. $10^{-5}$ ) assuming as little as 1 meal per year. At a top end consumption rate of 1 meal per week, risks increase to in excess of l-in-1000 (i.e. $10^{-3}$ ). The higher level of chlorination in the recreational size fish from the spawning ground could be due to localized sources of highly chlorinated PCBs, physical trapping and weathering within the turbidity maximum, and/or selective retention/depuration of specific PCB congeners during spawning activity.

Lifetime cancer risk associated with consuming striped bass from the Delaware Bay or commercial size stripers from the spawning ground is relatively low. A person would have to eat more than 1 meal per week in order for their risk to exceed a $1-i n-100,000$ (i.e. $10^{-3}$ ) level. Although cancer risk is not considered high for these fish, other potential health problems associated with consuming these fish exist. Namely, children who consume these fish are at higher risk of neurobehavioral deficits. In addition, adults are at higher risk of adverse immunological effects.

Although there are known health benefits associated with the consumption of fish, there are also risks. It is the responsibilty of the state environmental and health agencies to
advise the public of the nature and magnitude of those risks so that the public can make informed decisions regarding their fish consumption habits.

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## APPENDIX A

## SAMPLE IDENTIFICATIOR CODES AND RUNBER OF FISE PER SAMPLE



## APREEIDIX B

| vo. | Structure | No. | Strocture | No. | Structure | No. | Stracture |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Monnctiorobiphenyls | S1 Terrehlorobiphenyls |  | Pentechiorctiphenyis |  |  | Hexachiorobiphenyis |
|  |  |  |  | 105 | 2.3.3'4.4' | 161 | 2.3.3'.4.5'.6 |
|  | 3 | 53 | 2.9'5.6 ${ }^{\text {' }}$ | 106 | 2.3.3.4.5 | 162 | 2.3.3'.4'.5.5 |
|  | 4 | 54 | 2.2'.6.6 | 107 | 2.3.3'.4'.5 | 163 | 2.3.3'.4'.5.6 |
|  |  | 55 | 2.1.3.4 | 108 | 2.3.3'4.5' | 164 | 2.3.'4'.5' 6 |
|  | Dichiorobiphenyls | 56 | 2.3.3'.4 | 109 | 2.3.3'4.6 | 165 | 2.3.3'5.5'6 |
| 1 | $2.2 \cdot$ | 57 | 2.3.3'.5 | 110 | 2.3.3'.4'.6 | 166 | 2.3.4.4'3.6 |
| 5 | 2.3 | 58 | 2.3.3'.5' | 111 | 2.3.3'3.5' | 167 | 2.3'.4.4'.5.5' |
| - | $2.3{ }^{\circ}$ | 59 | 2.3.3'6 | 112 | 2.3.3'5.6 | 168 | 2.3'4.4'.5. 6 |
| - | 2.4 | 61 | 2.3.4.4 | 113 | 2.3.3'.5'. 6 | 169 | 3.3'4.4'5.5' |
| ! | $2.4 *$ | 61 | 2.3.4.5 | 114 | 2.3.4.4'. 5 |  |  |
| $\stackrel{ }{*}$ | 2.5 | 62 | 2.3.4.6 | 115 | 2.3.4.4'.6 |  | Heprachlorobiphenyis |
| in | 2.6 | 63 | 2.3.4.3 | 116 | 2.3.4.5.6 | 170 | 2.2'.3.3'4.4'. |
| H | $3.3{ }^{\circ}$ | 64 | 2.3.4'. 6 | 117 | 2.3.4'5.6 | 171 | 2.2'.3.3'4.4'.6 |
| 12 | 3.4 | 65 | 2.3.5. 6 | 118 | 2.3'4.4'3 | 172 | 2.2'.3.3'.4.5.5' |
| 13 | 3.4. | 66 | $2.33^{\prime} .4 .4{ }^{\prime}$ | 119 | 2.3'4.4'. 6 | 173 | 2.2'3.3.4.5.6 |
| 19 | 3.5 | 67 | 2.3'4.5 | 120 | 2.3'4.5.5' | 174 | 2.9'.3.3'4.5.6' |
| 19 | 4.4 | 68 | 2.3',4.5' | 121 | 2.3'4.5'. 6 | 175 | 2.2'.3.3'4.5'.6 |
|  |  | 69 | 2.3'.4.6 | 122 | 2'3.3'4.5 | 176 | 2.2'.3.3'4.6.6 |
|  | Trichlorobiphenyis | 70 | 2.3'4'.5 | 123 | 2'3.4.4'.5 | 177 | 2.2'.3.3'.4'S. 6 |
| 16 | 2.2'3 | 71 | 2.3'.4'.6 | 124 | 2'3.4.5.5' | 178 | 2.9'3.3'5.5' 6 |
| $: 9$ | 2.2.4 | 72 | 2.3'5.5* | 125 | 2'3.4.5.6 | 179 | 2.2'.3.3'5.6.6 ${ }^{\prime}$ |
| : 8 | 2.2'.5 | 73 | 2.3'.5'. 6 | 126 | 3.3'4.4'.5 | 180 | I.2',3.4.4'.5.5' |
| 19 | 2.2'.6 | 74 | 2.4.4'.5 | 127 | 3.3'4.5.5' | 181 | 2.2'3.4.4' 5.6 |
| 20 | 2.3.3' | 75 | 2.4,4'.6 |  |  | 182 | 2.2'.3.4.4'.5.6 ${ }^{\prime}$ |
| 21 | 2.3.4 | 76 | 2.3.4.5 | , | Hexuchiorobiphenyts | 183 | 2.2'3.4.4'.5'. 6 |
| 2 | 2.3.4' | 77 | 3.3'4.4 | 128 | 2.2'3.3'4.4' | 184 | 2.2'3.4.4'.6.6 ${ }^{\circ}$ |
| 23 | 2.3.5 | 78 | 3.3'4.5 | 129 | 2.2',3.3',4.5 | 185 | 2.2'3.4.5.5'.6 |
| 24 | 2.3.6 | 79 | 3.3'4.4" | 130 | 2.2'3.3'4.5' | 186 | 2.2'.3.4.S.6.6 ${ }^{\circ}$ |
| 5 | 2.3 .4 | 80 | 3.3'5.5' | 131 | 2.2'3.3',4.6 | 187 | 2.2', 3.4'S.5.5'6 |
| 5 | 2.3 .5 | 81 | 3.4.4'S | 132 | 2.2'3.3',4.6' | 188 | 2.2',3.4'S.6.6' |
|  | 2.3'.6 |  |  | 133 | 2.2'3.3'5.5' | 189 | 2.3.3'4.4'5.5' |
| $\sim$ | 2.4.4' |  | Pencechlorobiphenyls | 134 | 2.2.3.3'5.6 | 190 | 2.3.3'4.4'S.6 |
| 29 | 2.4 .5 | 82 | 2.2.3.3.4 | 135 | 2.2'3.3'.5.6 ${ }^{\circ}$ | 191 | 2.3.3'.4.4'.3'. 6 |
| 311 | 2.4.6 | 83 | 2.2'3.3'3 | 136 | 2.2'3.3'.6.6' | 192 | 2.3.3'.4.5.5'.6 |
| 31 | 2.4'. 5 | 84 | 2.2'.3.3'.6 | 137 | 2.2'3,4.4'5 | 193 | 2.3.3'.4'S.5'. 6 |
| 32 | 2.4 . 6 | 85 | 2.2.3.4.4 ${ }^{\prime}$ | 138 | 2.2'3.4.4' ${ }^{\prime \prime}$ |  |  |
| 33 | 2.3.4 | 86 | 2.2'.3.4.5 | 139 | 2.2'3,4.4',6 |  | Octactiorobiphenyls |
| 4 | 2.3.5 | 87 | 2.2.3.4.5' | 140 | 2.2'3.4.4'.6' | 194 | 2.2',3.3'4.4'5.5' |
| 35 | 3.3 . 4 | 88 | 2.2'.3.4.6 | 141 | 2.2'3.4.5.5' | 195 | 2.2'3.3'.4.4'5.6 |
| 36 | 3.3'.5 | 89 | 2.2'3.4.6 | 142 | 2.2'3.4.5.6 | 19 | 2.9'.3.3'4.4'5'. 6 |
| 37 | 3.4.4 ${ }^{\prime}$ | 9 | 2.2'3.4'.5 | 143 | 2.2'3.4.5.6 ${ }^{\circ}$ | 197 | 2.2'3.3'4.4.4'.6.6' |
| 38 | 3.4.5 | 91 | 2.2'3.4'. 6 | 144 | 2.2',3,4.5'.6 | 198 | 2.2'3.3'4.5.5'. 6 |
| 39 | 3.4'.5 | 92 | 2.2'.3.5.5' | 145 | 2.2'3,4.6.6' | 199 | 2.2'3.3'4.5.6.6 ${ }^{\circ}$ |
|  |  | 93 | 2.2. 3.5 .6 | 146 | 2.2'3, $4^{\prime}$.5.5' | 200 | 2.2'.3.3'.4.5'.6.6' |
|  | Terrachiorotiphenyls | 94 | 2.2.35.6 | 147 | 2.2'3,4' 5.6 | 201 | 2.2',3.3',4'5.5'. 6 |
| 41 | 2.2'3.3' | 95 | 2.2.3.5. 6 | 148 | 2.2'3.4'5.6' | 202 | 2.2'.3.3'.5.5'.6.6 ${ }^{\prime}$ |
| 41 | 2.2'.3.4 | 96 | 2.2.3.6.6 ${ }^{\prime}$ | 149 | 2.2'3.4'3'.6 | 203 | 2.2'3.4.4' $5.5{ }^{\prime} .6$ |
| 42 | 2.2'3.4 ${ }^{\circ}$ | 97 | 2.9'3'.4.5 | 150 | 2.2'3.4'.6.6' | 204 | 2.2'.3.4.4' S.6.6 ${ }^{\prime}$ |
| 43 | 2.2'3.3 | 98 | 2.2'.3'4.6 | 151 | 2.2'3.3.5'. 6 | 205 | 2,3.3',4.4', 5.5'. 6 |
| 14 | 2.2'3.3 ${ }^{\text {a }}$ | 99 | 2.2'4.4'S | 152 | 2.2.3.3.6.6' |  |  |
| 45 | 2.2'3.6 | 100 | 2.2'.4.4'.6 | 153 | 2.2'4,4'5.5' |  | Nonachlorobiphenyls |
| 46 | 2.2'3.3 ${ }^{\circ}$ | 101 | 2.2.4.5.5 | 154 | 2.2'.4.4'S. 6 | 206 | 2.2'.3.3'.4.4'S.5'.6 |
| 47 | 2.2.4.4 ${ }^{\prime}$ | 102 | 2.2'4.5.6 | 155 | 2.2'.4.4'.6.6' | 207 | 2.2'.3.3'.4.4' $5.6 .6^{\circ}$ |
| 48 | 2.2'.4.5 | 103 | 2.2.4.5'.6 | 156 | 2.3,3'4,4'5 | 200 | 2.2'3.3.3'4.3.5'.6.6 ${ }^{\prime}$ |
| 49 | 2.2'.4.5 ${ }^{\circ}$ | 104 | 2.2.4.6.6 ${ }^{\circ}$ | 157 | 2.3,3',4.4' $5^{\prime}$ |  |  |
| 50 | 2.2'.4.6 |  |  | 158 | 2.3.3'4.4*.6 |  | Decectiorobiphenyl |
| 51 | 2.2'.4.6 ${ }^{\circ}$ |  |  | 159 | 2.3.3'4.5.5' | 209 | 2.2', 3.3',4.4'.5.5 ${ }^{\prime}$.6.6 $6^{\prime}$ |
|  |  |  |  | 160 | 2.3.3',4.5.6 |  |  |

## APPEADIX C

## NON-ORTHO, MONO-ORTHO, AND DI-ORTHO POLYCHLORINATED BIPHENYL CONGENERS

A. NON-ORTHO SUBSTITUTED CONGENERS


3,3',4,4'-TeCB
IUPAC 77


3,3',4,4',5-Pecs IUPAC 126


3,4,4',5-TeC3 IUPAC 81


3, 3',4,4',5,5'-ECB IUPAC 169

TB. MONo-ortho substituted CONGENERS


2,3,31,4,4\%-PeCB IUPAC 106


2, $3^{\prime}, 4,4^{\prime}, 5-\mathrm{PeCB}$ IUPAC 118


2,3,3',4,4',5-ECB Cl
IUPAC 158

$2,3,4,41,5-$ Pecs IUPAC 114

$2^{\prime}, 3,4,4^{\prime}, 5-\mathrm{PeCB}$ IUPAC 123


IUPAC 157


2, 3', 4, 4',5,5'-HC3
IUPAC 167


2,3, $3^{\prime}, 4,4^{\prime}, 5,5^{\prime}-$ ECS
IUPAC 189

## C. DI-ORTHO SUBSTITUTED CONGENERS



$$
2,3,4,4^{\prime}, 5,6-\mathrm{ECB}
$$

IUPAC 186


$$
\begin{aligned}
& 2,3^{\prime}, 4,4^{\prime}, 5^{\prime}, 6-\mathrm{HCB} \\
& \text { IUPAC } 168
\end{aligned}
$$



2,3,3',4,4\%,6-EBCB IUPAC 158


2, 2', 3, $3^{\prime}, 4,4^{\prime}, 5-$ EpCB IUPAC 970


2, 2', 3, 4, 4', 5, 5'- HpC IUPAC 180

$2,3,3^{\prime}, 4,4^{\prime}, 5^{\prime}, 6$-Ерсв
IUPAC 191

$2,3,3^{\prime}, 4,4^{\prime}, 5,5^{\prime}, 6$-octacs
IUPAC 205


2,3,3',4,4',5,6-нрсв IUPAC 190

$2,2^{\prime}, 3,3^{\prime}, 4,4^{\prime}, 5,5^{\prime}$-octacs IUPAC 194

## APPESDIX D

# Analysis of Fish Tissue Samples for Congener Specific PCBs and Pesticides For Assessing Pollutant Bioaccumulation From the Delaware Estuary 

Final Report

For Delaware Department of Natural Resources
And Environmental Control
89 Kings Highway
Dover, DE 19903

MRI Project No. 3123-01

May 13, 1993

## PREFACE

This final report provides the results of the analysis of 20 fish tissue samples for mono-ortho and di-ortho congener specific polychlorinated biphenyls (PCBs) and chlorinated pesticides. Five of the samples were classified as recreational size striped bass from Delaware Bay, five were classified as commercial size striped bass from the Delaware Bay, five were classified as recreational size striped bass from the Delaware River spawning ground, and five were classified as commercial size striped bass from the Delaware River spawning ground. In additional to the analysis of mono-ortho and di-ortho PCB and chlorinated pesticides in all samples, one sample from each of the four categories just noted was also analyzed for non-ortho coplanar PCBs.

The samples were prepared for analysis by Ms. Sherry Winner, Ms. Rose Schimmel, Ms. Kristin Vita, and Mr. Jamie Heiman. The HRGC/MS analyses were performed by Mr. Mike Molloy, and the HRGC/HRMS coplanar PCB analyses were performed by Mr. Robert Conklin and Mr. Mark Horrigan. Ms. Kathy Boggess supervised the sample preparation and analysis activities, reviewed the analytical data, and prepared this report.

MIDWEST RESEARCH INSTITUTE


Kathy E. Bogies


John S. Stanley
Head
Analytical Chemistry Section
Approved:
Dow W. Any
Don D. Gay, Ph.D.
Director
Chemical Sciences Department
May 13, 1993

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## SECTION 1

## INTRODUCTION

Midwest Research Institute (MRI) was contracted by the Delaware Department of Natural Resources and Environmental Control to determine the levels of congener specific mono-ortho and di-ortho PCBs and chlorinated biphenyls in 20 fish tissue samples. Five of the samples were classified as recreational size striped bass from Delaware Bay, five were classified as commercial size striped bass from the Delaware Bay, five were classified as recreational size striped bass from the Delaware River spawning ground, and five were classified as commercial size striped bass fron the Delaware Fiver spawning ground. The coplanar PCBs are considered the most toxic PCEs. Because coplanar PCBs are typically detected at significantly lower concentrations than the more prevalent mono-ortho and di-ortho PCBs, the coplanar PCB analysis required a separate sample preparation and analysis procedure including HRGC/HRMS analysis.

The technical approach and scope of work were presented to Mr. Rick Greene in MRI Proposal No. 0912-041R, dated May 28, 1992. Clarifications of the PCB target analytes were subsequently presented to Mr. Greene in a letter dated July 17, 1992.

The scope of work included gas chromatographylow resolution mass spectrometry of 20 fish samples for 9 chlorinated pesticides and 39 congener specific mono-ortho and di-ortho PCBs, including congeners reported as major constituents in Arocior mixtures and congeners typically detected in humans that consume a high amount of fish. Total PCB concentrations were determined based on the sum of peaks detected for mono through deca PCB homologs.

In addition to the HRGC/LRMS analyses, four samples were analyzed for eight coplanar PCBs using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for parts per trillion ( $\mathrm{pg} / \mathrm{g}$ ) detection limits.

This report describes the methods used to prepare and analyze the fish samples. Section 2 entitled Experimental Approach discusses receipt of the samples by MRI, sample code assignments, analytical standards, sample preparation procedures, HRGC/LRMS analysis, HRGC/HRMS analysis, and data reduction.

Section 3 presents sample results and internal quality control results. Sample results include percent lipid data, congener specific PCBS, pesticides, and total PCBs based on homolog quantitation. Quality control results include instrument calibration data, method blanks, control spikes, duplicate matrix spikes, and the percent recoveries for the carbon-13 internal quantitation standards and surrogate standards.

## SECTION 2

## EXPERIMENTAL

This section describes sample receipt, analytical standards, sample preparation procedures, instrumental analysis, and data reduction.

### 2.1 SAMPLE RECEIPT

The sample collection study design and shipment of samples to MRI were coordinated by Mr. Rick Greene (DNREC). The samples were received at MRI frozen and in good condition on July 31, 1992. The samples designated for coplanar PCB analyses were indicated on the sample jars. The samples were stored at $-20^{\circ} \mathrm{C}$ until sample preparation was initiated.

### 2.2 ANALYTICAL STANDARDS

The analytical standards included native PCB congeners, chlorinated pesticides, and carbon-13 labeled isotopes. Individual stock solutions of each analyte were purchased from Cambridge Isotope Laboratories, Wobum, Massachusetts; Ultra Scientific, Hope, Rhiode Island; and Accustandard, New Haven, Connecticut.

### 2.2.1 Mono-ortho PCBs, Di-ortho PCBs, and Pesticide Standards

Aliquots of the individual stock solutions of native PCBs and pesticides were combined to prepare a mixed stock spiking solution. The components of the mixed spiking solution are shown in Table 1. A mixed surrogate spiking solution (Table 2) was prepared by combining aliquots of the individual ${ }^{13} \mathrm{C}$-PCBs and ${ }^{13} \mathrm{C}$-DDT. The ${ }^{13} \mathrm{C}$-PCBs included congeners from the mono-, tetra-, hexa-, octa-, and deca-substituted homologs. Aliquots of the native spiking solutions, surrogate spiking solutions, and an intemal standard solution containing $d_{12}$-chrysene were combined to prepare instrument calibration standards at the concentrations shown in Table 3.

### 2.2.2 Coplanar PCB Standards

The coplanar PCB standards included native standards for five tetracoplanar PCBs (Congeners 77, 78, 79, 80, and 81), two penta-PCBs (Congeners 126 and 127), and one hexa-PCB (Congener 169). Corresponding ${ }^{13} \mathrm{C}_{12}$-isotopes for each homolog group included ${ }^{13} \mathrm{C}_{12}-3,3$ ',4,4 Tetra-PCB (Congener 77), ${ }^{13} \mathrm{C}_{12}-3,3^{\prime}, 4,4^{\prime} 5$ Penta-PCB (Congener 126), and ${ }^{13} \mathrm{C}_{12}-3,3^{3}, 4,4^{\prime}, 5,5^{\prime}$ Hexa-PCB (Congener 169). Native spiking solutions, surrogate spiking solutions, and instrument calibration solutions were prepared from mixed stock solutions. The coplanar PCB standards are summarized in Tables 4 and 5.

### 2.3 SAMPLE PREPARATION

The analytical procedures used for extraction of the fish samples were evaluated at MRI through previous studies including the analysis of fish tissue for PCDD and PCDF. The procedures used for sample preparation inclúded the extraction techniques for tish tissue presented in EPA Method 8290 (November 1990). The cleanup procedures used for coplanar PCB analysis were modifications of procedures specified in EPA Method 8290 . The fish extracts prepared for mono-ortho PCBs, di-ortho PCBs, and pesticides were put through Gel Permeation Chromatography cleanup described in SW 846 Mothod 3640 (September 1986) and Florisil column cleanup according to procedures given in CLP SOW (August 1991).

### 2.3.1 Mono-ortho PCBs, Di-ortho PCBs, and Pesticides

The 20 fish samples were prepared for PCB and pesticide analysis using Soxhlet extraction followed by GPC cleanup and Florisil column cleanup. Quality control samples prepared with the 20 fish samples included a sodium sulfate method blank ( 20 g ), a control method spike consisting of sodium sulfate ( 20 g ), and duplicate matrix spikes of fish sample RO2SG.

Aliquots of the fish samples, matrix spike, and matrix spike duplicate ( 20 g weighed to the nearest 0.01 g ) were weighed into $250-\mathrm{mL}$ beakers and mixed with sodium sulfate. The fish samples, matrix spikes, sodium sulfate method blank, and sodium sulfate control spike were fortified with ${ }^{13} \mathrm{C}$ surrogate standards shown in Table 2. In addition to the ${ }^{13} \mathrm{C}_{12}$ surrogate standards, the control spike and duplicate matrix spike samples were spiked with 1.0 mL of the native spiking solution shown in Table 1.

The fish samples and quality control samples were placed in Soxtlet extractors and extracted for at least 16 hr with a $50: 50$ mixture of methylene chloride:hexane. The extracts were cooled to ambient temperature, filtered
through a bed of sodium sulfate, and transferred to preweighed $500-\mathrm{mL}$ boiling flasks for concentration of the solvent by rotary evaporation. After the solvent was removed, the weight of the lipid residue remaining in the flask was determined and the percent lipid was calculated.

The lipid residue was diluted in 20 mL methylene chloride, and 5 mL of each sample extract was put through GPC cleanup using an SX-3 Biobeads column and Auto Prep Model 1002 GPC (ABC Laboratories, Columbia, Missouri). The GPC column was calibrated with mixtures of PCB and pesticides in lipid to determine optimum collection times to separate the analytes of interest from the lipid. Based on a solvent flow rate of $5 \mathrm{~mL} / \mathrm{min}$, the GPC parameters were set at 27 min to dump the lipid residue, 30 min to collect the analytes, and 15 min wash between samples.

The collected fraction from the GPC cleanup was concentrated and solvent exchanged to 1.0 mL hexane using a Zymark ${ }^{\circ}$ Turbovap concentrator. The $1.0-\mathrm{mL}$ extract was then put through a Florisil cartridge cleanup according to the procedures specified for PCBs and Pesticides in the CLP Statemert of Work (August 1991). The cleaned extracts were concentrated to a final voluine of 0.5 mL , and $d_{12}$-chrysene internal standard was added at a concentration of $100 \mathrm{pg} / \mu \mathrm{L}$. The extracts were stored in the refrigerator until ready for HRGC/LRMS analysis.

### 2.3.2 Coplanar PCBs

The four samples designated for coplanar PCB analysis included Samples C04SG, R02SG, C01B, and R03B. Quality control samples included a method blank and duplicate matrix spikes using Fish Sample CO4SG. The samples were prepared for analysis using the same procedures discussed in Section 2.2.1 except coplanar PCB spiking solutions were used. Each $20-\mathrm{g}$ sample, the matrix spikes, and method blank were spiked with the ${ }^{13} \mathrm{C}_{12}$ coplanar PCB intemal quantitation standards (Table 4). In addition to the ${ }^{{ }^{13}} \mathrm{C}_{12}$ PCBs, the matrix spike samples were spiked with native coplanar PCBs.

The samples were Soxhlet extracted for 16 hr with methylene chloride: hexane ( $50: 50$ ) and the extracts were solvent exchanged to hexane. The samples were subjected to a sulfuric acid modified silica gel slurry and neutraVacid silica gel chromatography column cleanup described in EPA Method 8290 and MRI SOP CS-152. Subsequent column chromatography cleanup steps included neutral alumina and Cabopak C/Celite.

Following the final cleanup, the coplanar PCB extracts were concentrated under prepurified nitrogen to $100 \mu \mathrm{~L}$, and $5 \mu \mathrm{~L}$ of a recovery standard solution containing ${ }^{13} \mathrm{C}_{12}-1,2,3,4$-TCDD in tridecane was added in addition to $5 \mu \mathrm{~L}$
tridecane. The evaporation was continued until a volume of $10 \mu \mathrm{~L}$ was reached. Sample extracts were transferred to refrigerated storage $\left(4^{\circ} \mathrm{C}\right)$ until HRGC/HRMS analysis was initiated.

### 2.4 HRGCILRMS ANALYSIS-MONO-ORTHO PCBs, DI-ORTHO PCBS, AND PESTICIDES

The PCB and Pesticide analyses were performed using a VG TRIO-1 quadrupole mass spectrometer operated in the full scan mode with the operating parameters shown in Table 6. The instrument was tuned according to manufacturer's specifications, and DFTPP was analyzed at the beginning of each 12-hr day that samples were analyzed to ensure proper mass assignments. A PCB window defining mix, containing the first and last eluting congeners for each homolog group, was analyzed to determine appropriate quantitation windows for total PCB analysis.

Initial calibration of the instrument was performed with the analytical standards shown in Table 3. Continuing calibration included a beginning of the day and end of the day standard to ensure stable instrument periormance. Degradation of DDT was determined with analysis of a daily standard containing only DDT and DFTPP.

### 2.5 HRGC/HRMS ANALYSIS-COPLANAR PCBs

The coplanar PCBs are typically detected at concentrations an order of magnitude below the more prevalent mono- and di-substituted PCBs. Because of these differences in concentrations, it was necessary to develop an analysis technique for coplanar PCBs separate from the ortho-PCB analysis. The analysis of the fish samples for coplanar PCBs was performed using analytical conditions evaluated at MRI through previous studies including the determination of PCDD, PCDF, and coplanar PCBs in human milk and blood.

The coplanar PCB analyses were periormed using a VG70-250S HRMS with mass resolution $>10,000$. Analytical parameters for the HRGC/HRMS determinations are given in Table 7. The calibration curve consisted of a series of six standards ranging in concentration from 4 to $500 \mathrm{pg} / \mu \mathrm{L}$ for the native compounds with constant concentrations of $40 \mathrm{pg} / \mu \mathrm{L}$ for the ${ }^{13} \mathrm{C}_{12}$ compounds.

The day that the fish samples and QC samples were analyzed stanted with the mass calibration of the mass spectrometer. The six-point calibration curve was then analyzed followed by a tridecane blank and the fish samples. The day ended with the analysis of a midpoint standard to ensure stable instrument performance.

### 2.6 CONGENER SPECIFIC PCBs, PESTICIDES, AND TOTAL PCBs DATA REDUCTION

The data from the HRGC/LRMS analyses were reduced using a highspeed computer program that filters noise and calculates the responses of analytes in the appropriate mass windows with ion abundance ratios at $\pm 20 \%$ of the theoretical ratios. The PCB and pesticide quantitation and theoretical ion abundance ratio criteria are specified in EPA Method 680.

Detected peaks must also fall within established relative retention time windows. Relative retention times of analytes to the internal standard were established from the analysis of the calibration standards. The order of elution for congener specific PCBs was determined from previous MRI studies and from the literature.'

For peaks positively identified as PCBs, the computer program calculates an extract concentration, and then the sample weights, extract volumes, and dilution factors are taken into account to arrive at a final sample concentration.

The calculation formulas are shown in the following equations:

$$
\text { relative response factor }=\text { RRF }=\frac{\text { Area }_{\text {md }} \times \text { Conc }_{\mathrm{m}}}{\text { Conc }_{\mathrm{md}} \times \text { Area }_{\mathrm{is}}}
$$

where: $\quad$ area $=$ sum of the area for the primary and secondary masses characteristic of the PCB standard or internal standard, and conc $=$ the concentration ( $\mathrm{pg} / \mu \mathrm{L}$ ) of intemal standard or standard.

$$
\mathrm{pg} / \mathrm{g} \text { Sample }=\left[\frac{\text { Area }_{\text {mampt }} \times \text { Conc }_{\text {is }}}{\text { Area }} \times \text { RRF }\right] \times \frac{\text { final vol }}{w t} \times \text { split factor }
$$

where: $\quad$ final vol $=$ final volume of extract ( $\mu \mathrm{L}$ ), and $\mathbf{w t}=$ is weight of sample (g).

Total homolog PCB results were determined in addition to the congener specific data. The average of the two PCB congeners indicated as Aroclor constituents

[^1]in each homolog group was used to determine homolog concentrations as described by Hong and Bush. ${ }^{2}$

Quantitation windows for the mono- through deca-PCB homologs were established from the analysis of a window defining standard. For peaks that met the homolog specific qualitative ion ratio criteria, responses were calculated relative to the homolog specitic response factor. For each homolog group, the peaks detected above the lowest calibration standard were summed. Total PCBs were calculated by summing the mono through deca homolog concentrations.

Limits of detection for analytes not positively identified were based on the lowest calibration standard.

The concentrations of the surrogate compounds, ${ }^{13} \mathrm{C}$-PCBs and ${ }^{13} \mathrm{C}$-DDT, added to each sample were determined the same as for the native analytes. The amount found was compared to the amount spiked and the percent recovery was calculated. The native concentrations were not adjusted for surrogate recovery.

### 2.7 COPLANAR PCBS DATA REDUCTION

The same computer program used to calculate congener specific ortho PCBs and pesticides was used to calculate the concentrations of coplanar PCBs in tour fish samples. The coplanar PCBs were calculated based on the isotope dilution approach which adjusts the concentration of the native analyte for recovery of the internal quantitation standards (IQS) from the sample matrix.

The instrument was calibrated with the series of calibration standards presented in Table 5, and RRFs were determined for each native compound relative to the corresponding ${ }^{13} \mathrm{C}$-labeled intemal quantitation standard (IQS) (Equation 1) and for each IOS relative to the recovery standard (RS) (Equation 2). The mean RRFs from all standards were then used in subsequent calculations to determine sample amounts for each specific isomer or IQS.

As discussed in the Sample Preparation Section, known amounts of IQS were added to the samples before extraction, and the IOS concentration in the final extract was used to calculate the concentration of the native analytes in the final extract as an isotope dilution calculation technique. This calculation procedure (Equation 3) adjusts for recovery from the sample matrix.
${ }^{2}$ Hong, C. S., and B. Bush, Analytical Letters, 24(6), 1017-1034 (1991).

$$
\begin{equation*}
\text { RRF }=\frac{A_{\text {STD }} \times C_{\text {IS }}}{A_{\text {IS }} \times C_{\text {STD }}} \tag{Eq. 1}
\end{equation*}
$$

where: $\quad A_{\text {stD }}=$ the sum of the area responses for the two characteristic ions of the native standard;
$A_{I S}=$ the sum of the area responses for the two characteristic ions of the corresponding internal quantitation standard;
$\mathrm{C}_{\text {is }}=$ concentration ( $\mathrm{pg} / \mu \mathrm{L}$ ) of the intemal quantitation standard; and
$\mathrm{C}_{\text {sto }}=$ concentration ( $\mathrm{pg} / \mu \mathrm{L}$ ) of the native standard.

$$
\begin{equation*}
R R F_{1 s}=\frac{A_{1 s} \times C_{\text {Rs }}}{A_{R S} \times C_{1 s}} \tag{Eq. 2}
\end{equation*}
$$

where $A_{1 s}$ and $C_{1 s}$ are defined as in Equation 1 and
RRF $_{\text {is }}=$ the average of initial calibration response factors of the internal quantitation standard relative to the intemal recovery standard,
$\mathrm{C}_{\mathrm{Rs}}=$ concentration ( $\mathrm{pg} / \mu \mathrm{L}$ ) of the intemal recovery standard, and
$A_{\text {RS }}=$ the sum of the area responses for the two characteristic ions corresponding to the internal recovery standard.

$$
\begin{equation*}
C_{W T}=\frac{A_{\text {mampe }} \times Q_{\text {is }} \times V_{e}}{A_{\text {IS }} \times R R F \times W t} \tag{Eq. 3}
\end{equation*}
$$

where: $\quad C_{W T}=(\mathrm{pg} / \mathrm{g})$ concentration of the PCB congener,
$A_{\text {mamph }}=$ sum of the area responses for the two characteristic ions of the PCB congener;
$Q_{\text {is }}=$ concentration ( $\mathrm{pg} / \mu \mathrm{L}$ ) of the intemal quantitation standard added to the sample;
$V_{0}=$ final extract volume ( $\mu \mathrm{L}$ );
$A_{\text {IS }}=$ sum of the area responses for the two characteristic ions of the respective intemal quantitation standard;

$$
\begin{aligned}
& \text { RRF }= \text { the average of the initial calibration relative response factors } \\
& \text { for the PCB congener from Equation } 1 \text {; and }
\end{aligned}
$$

$$
\begin{equation*}
\text { Recovery }(\%)=\frac{A_{\text {IS }} \times Q_{\text {RS }}}{A_{\text {RS }} \times R R F_{\text {IS }} \times Q_{\text {IS }}} \times 100 \tag{Eq. 4}
\end{equation*}
$$

where: $\quad A_{\text {Rs }}=$ sum of the area responses for the two characteristic ions of the internal recovery standard;
$\mathrm{Q}_{\mathrm{Rs}}=$ amount of the internal recovery standard added to the final extract; and

RRF $_{\text {Is }}=$ the average of initial calibration response factors of the internal quantitation standard relative to the internal recovery standard.

The recovery standards which are added to the sample at the final concentration step are used to establish the absolute recovery of the carbon-13 intemal standards (Equation 4). The IQS recoveries are used to access overall method periormance and adjust the results for native congeners.

## SECTION 3

## RESULTS

This section provides the results of the ortho substituted congener specific PCBs, pesticides, total PCBs, and coplanar PCBs. Internal quality control results including method blanks, matrix spikes, surrogate recoveries, and instrument calibration data are also presented.

### 3.1 HRGC/LRGC PCBS AND PESTICIDES RESULTS

The results for the 39 congener specific PCBs and 9 pesticides are presented in Table 8. The percent lipid data are also provided in Table 8, but sample results ( $\mathrm{ng} / \mathrm{g}$ ) are based on total tissue weight ( 20 g ) not lipid content. For compounds not detected, the calculated detection limit based on the lowest calibration standard is shown in parentheses.

There were two pairs of congeners that were not separated chromatographically, and the calibration was based on the sum of the coeluting congeners. These pairs include hexa congeners 138 and 158 and hepta congeners 170 and 190. Based on previous studies conducted at MRI and data presented in the literature, concentrations reported as mixtures of 138 and 158 are due primarily to the presence of congener 138.

The congener specific profile is consistent with previous studies performed at MRI showing PCB Congeners 153 and 138 most prevalent with p,p-DDE as a significant pesticide.

Total homolog PCB concentrations are presented in Table 9. The total homologs include other PCB congeners detected in addition to the 39 congener specific PCBs. Figures A-1 to A-14 show the congener specific profiles detected in a typical fish sample (RO2SG). As shown in Figures A-4 and A-9, for tetra PCB and nona PCB, significant response is attributed to congeners other than the 39 target analytes.

### 3.2 COPLANAR PCB RESULTS

The coplanar PCB results are summarized in Table 10. The concentrations ranging from 246 to $500 \mathrm{pg} / \mathrm{g}$ for Tetra PCB Congener 77 and 111 to 168 for Penta PCB Congener 126 are considerably less than the mono-ortho and di-ortho concentrations, but well above the lower level of the calibration curve.

### 3.3 QUALITY CONTROL SAMPLE RESULTS

The quality control samples including a method blank, control spike, and duplicate matrix spikes of sample RO2SG for the 39 PCB congeners and 9 pesticides are summarized in Table 11. Overall, the recoveries are very good (70\% to 130\%). Recoveries for Mono PCB Congener 1 are not reported because a coeluting interference resulted in an unacceptable ion ratio. The ion ratio for dieldrin was unacceptable in the matrix spike samples, and the recovery was not calculated. The control spike to sodium sulfate gave good recovery for dieldrin, indicating a fish matrix effect.

The coplanar PCB method blank results are summarized in Table 10 for comparison to sample results. Uniortunately, the method spike results showed that the tetra and penta PCBs were not spiked at levels high enough above native background levels. The duplicate method spike recoveries for hexa PCB were $73 \%$ and $95 \%$ which indicate acceptable method performance.

### 3.4 SURROGATE RECOVERIES

The results for the six ${ }^{13} \mathrm{C}$ surrogate compounds spiked into the 20 fish samples before extraction are shown in Table 12. In some cases, ${ }^{13} \mathrm{C}_{5}$ mono PCB was not calculated due to a coeluting interference. Overall, the recoveries were very good with mean recoveries ranging from $66.7 \%$ to $116 \%$. The method precision was also very good with relative standard deviation ranging from $9.4 \%$ to 23\%.

## $3.5 \quad{ }^{13} \mathrm{C}_{12}$ INTERNAL QUANTITATION STANDARD RECOVERIES

The percent recoveries for the carbon-13 intemal quantitation standards (IQS) are shown in Table 13. The recovery objective for this analysis was $25 \%$ to $150 \%$. The carbon-13 IQS were added to the samples prior to extraction, and the concentrations of the native compounds were calculated relative to these standards as an isotope dilution technique. The recoveries of the IQS were calculated relative to recovery standards added to the sample extract just before analysis.

The coplanar IQS recoveries were below the recovery objective. Based on the isotope dilution calculation, the native concentrations may not be adversely affected by these low recoveries. Due to the high concentrations of coplanar PCB detected in the samples, the sample extracts may have required dilution to a lower concentration if $100 \%$ IQS recoveries had been achieved. Acceptable accuracy was achieved for the native hexa-PCB Congener 169, even though the IQS recovery was low.

### 3.6 CALIBRATION DATA

The initial and continuing calibration criteria were met for each day that samples were analyzed. The criterion for initial calibration was response factor variability $<20 \%$ RSD, and the criterion for continuing calibration was daily response factors within $\pm 30 \%$ of the mean initial response factor. Five of the 51 analytes were allowed to fail the daily continuing calibration check. Of the 51 analytes, low response factors were observed for DDT, ${ }^{13} \mathrm{C}_{12}$ DDT, deca PCB and ${ }^{13} \mathrm{C}_{12}$ deca PCB.

The initial and continuing calibration data are summarized in Tables 14 through 16.

Table 1. NATIVE PCB CONGENERS AND PESTICIDES SPIKING SOLUTIONS

| Ballschmitar | Chlorination |  | Concentration | Spike level |
| :---: | :---: | :---: | :---: | :---: |
| No. | position |  | Homolog | pg/ul' |

[^2]Table 2. SURROGATE SPIKING SOLUTIONS

|  | Concentration <br> $\mu g / \mathrm{mL}$ | Amount in <br> 0.25 mL <br> spike $\mu \mathrm{g}$ | Spike level <br> pg/g Fish |
| :---: | :---: | :---: | :---: |
| Compound | 1.0 | 0.250 | 12,500 |
| ${ }^{13} \mathrm{C}_{6}(3)^{a}$ | 2.5 | 0.625 | 31,250 |
| ${ }^{13} \mathrm{C}_{12}(77)$ | 4.0 | 1.000 | 50,000 |
| ${ }^{13} \mathrm{C}_{12}(202)$ | 5.0 | 1.250 | 62,500 |
| ${ }^{13} \mathrm{C}_{12}(209)$ | 2.4 | 0.600 | 30,000 |
| ${ }^{13} \mathrm{C}_{12}(138)$ | 2.0 | 0.500 | 25,000 |
| ${ }^{13} \mathrm{C}_{12}$ DDT |  |  |  |

- Ballschmitter number shown in parentheses for congener specific PCB surrogates.

Table 3. PCB CONGENERS AND PESTICIDES CALIBRATION STANDARDS

| PCB Congener | Cone cal 6 pg/uL | Conc cal 5 pg/uL | Conc cal 4 $\mathrm{pg} / \mu \mathrm{L}$ | Cone cal 3 pg/ | Conc cal 2 pg/uL | Conc cal 1 Pg/uL |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 Mono | 400 | 200 | 100 | 50 | 25 | 12.5 |
| 3 Mono | 400 | 200 | 100 | 50 | 25 | 12.5 |
| 4 Di | 400 | 200 | 100 | 50 | 25 | 12.5 |
| 7 Di | 400 | 200 | 100 | 50 | 25 | 12.5 |
| 18 Tri | 400 | 200 | 100 | 50 | 25 | 12.5 |
| 28 Tri | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 52 Tetra | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 44 Totra | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 74 Tetra | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 87 Penta | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 99 Penta | 448 | 224 | 112 | 56 | 28 | 14.0 |
| 101 Penta | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 105 Penta | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 114 Penta | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 118 Penta | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 123 Penta | 665 | 333 | 166 | 83 | 42 | 20.8 |
| 128 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 137 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 138 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 153 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 156 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 157 Hexa | 770 | 385 | 193 | 96 | 48 | 24.1 |
| 158 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 166 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 167 Hexa | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 168 Hexa | 699 | 349 | 175 | 87 | 44 | 21.8 |
| 170 Hepta | 800 | 400 | 200 | 100 | 50 | 25.0 |
| 180 Hepta | 1,200 | 600 | 300 | 150 | 75 | 37.5 |
| 183 Hepta | 1,200 | 600 | 300 | 150 | 75 | 37.5 |
| 185 Hepta | 1,200 | 600 | 300 | 150 | 75 | 37.5 |
| 187 Hepta | 1,200 | 600 | 300 | 150 | 75 | 37.5 |
| 189 Hepta | 1,200 | 600 | 300 | 150 | 75 | 37.5 |
| 190 Hepta | 1,200 | 600 | 300 | 150 | 75 | 37.5 |

Table 3 (Continued)


Table 4. COPLANAR PCB SPIKING SOLUTIONS

| Native Coplanar PCB Spiking Solutions |  |  |
| :---: | :---: | :---: |
| Compound | Concentration $\mathrm{pg} / \mu \mathrm{L}$ | Spike level $\mathrm{pg} / \mathrm{g}$ |
| 77 Tetra | $10^{\circ}$ | 10 |
| 78 Tetra | 10 | 10 |
| 79 Tetra | 10 | 10 |
| 81 Tetra | 10 | 10 |
| 126 Penta | 10 | 10 |
| 127 Penta | 10 | 10 |
| 169 Hexa | 10 | 10 |
| ${ }^{13} \mathrm{C}_{12}$ Coplanar PCB Internal Quantitation |  |  |
| ${ }^{13} \mathrm{C}_{12}-77$ Tetra | $2{ }^{\text {b }}$ | 20 |
| ${ }^{13} \mathrm{C}_{12}-126$ Penta | 2 | 20 |
| ${ }^{13} \mathrm{C}_{12}-169$ Hexa | 2 | 20 |
| : $20 \mu \mathrm{~L}$ spiked to 20 g sample. <br> - $200 \mu \mathrm{~L}$ spiked to 20 g fish. |  |  |

Table 5. HRGC/HRMS COPLANAR PCB CALIBRATION STANDARDS

| Compound | Cal 1 pg/ | Cal 2 pg/ 1 L | Cal 3 pg/ $/ \mathrm{L}$ | Cal 4 pg/ 1 L | Cal 5 pg/ $/ \mathrm{L}$ | Cal 6 pg/ul |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 77 Tetra | 4 | 10 | 40 | 100 | 200 | 500 |
| 78 Tetra | 4 | 10 | 40 | 100 | 200 | 500 |
| 79 Tetra | 4 | 10 | 40 | 100 | 200 | 500 |
| 80 Tetra | 4 | 10 | 40 | 100 | 200 | 500 |
| 81 Tetra | 4 | 10 | 40 | 100 | 200 | 500 |
| 126 Penta | 4 | 10 | 40 | 100 | 200 | 500 |
| 127 Penta | 4 | 10 | 40 | 100 | 200 | 500 |
| 169 Hexa | 4 | 10 | 40 | 100 | 200 | 500 |
| ${ }^{13} \mathrm{C}_{12}-77$ Tetra | 40 | 40 | 40 | 40 | 40 | 40 |
| ${ }^{13} \mathrm{C}_{12}-126$ Penta | 40 | 40 | 40 | 40 | 40 | 40 |
| ${ }^{13} \mathrm{C}_{12}-169$ Hexa | 40 | 40 | 40 | 40 | 40 | 40 |
| ${ }^{13} \mathrm{C}_{12}$-TCDD | 100 | $10 n$ | 100 | 100 | 100 | 100 |

Table 6. OPERATING PARAMETERS FOR HRGCLRMS ANALYSIS

| Mass spectrometer: | VG TRIO-1A |
| :---: | :---: |
| Electron energy | 70 eV |
| Filament current | 4.0 A |
| Source current | $2104 \mu \mathrm{~A}$ |
| Trap current | $103 \mu \mathrm{~A}$ |
| Start mass | $35 \mathrm{~m} / 2$ |
| End mass | $550 \mathrm{~m} / \mathrm{z}$ |
| Gas chromatograph: | Hewlett Packard 5890 |
| Colurnn coating | DE-5 |
| Film thickness | $0.25 \mu \mathrm{~m}$ |
| Column dimensions | $30-\mathrm{m} \times 0.25-\mathrm{mm}$ i.d. |
| Solvent delay | 5 min |
| Injector termp | $280^{\circ}$ |
| Injection size | $2 \mu$ |
| Initial temp | $70^{\circ}$ |
| Initial time | 2 |
| First temperature program | 15\%min to $170^{\circ}$ |
| Second temperature program | 4\%min |
| Final temperature | $300^{\circ}$ |

Table 7. HRGC/HRMS OPERATING CONDITIONS FOR COPLANAR PCB ANALYSIS
Mass Spectrometer VG70 250S
Accelerating voltage: ..... $8,000 \mathrm{~V}$
Trap current: ..... $500 \mu \mathrm{~A}$
Electron energy: ..... 35 eV
Photo multiplier voltage: ..... 320 V
Source temperature: ..... $280^{\circ} \mathrm{C}$
Resolution: $\geq 10,000$ ( $10 \%$ valley definition)
Overall SIM cycle time: ..... 1 sec
Gas Chromatograph
Column coating:
DB 5
Film thickness: $0.25 \mu \mathrm{~m}$
Column dimensions:
He linear velocity: $-25 \mathrm{~cm} / \mathrm{sec}$
$60 \mathrm{~m} \times 0.25 \mathrm{~mm}$ i.d.
He head pressure:
Injection type:
Split flow:
Purge flow:
Injector temperature:
Interface temperature:
Injection size:
$1.75 \mathrm{~kg} / \mathrm{cm}^{2}$ ( 25 psi )
Splitle $3 \mathrm{~s}, 45 \mathrm{sec}$
$30 \mathrm{~mL} / \mathrm{min}$
$6 \mathrm{~mL} / \mathrm{min}$
$290^{\circ} \mathrm{C}$
$290^{\circ} \mathrm{C}$
Initial temperature: ..... $200^{\circ} \mathrm{C}$$2 \mu \mathrm{~L}$
Initial time: ..... 2 min
Temperature program:
$200^{\circ}$ to $270^{\circ} \mathrm{C}$ at $5^{\circ} \mathrm{C} / \mathrm{min}$
Second hold time: 10 min
Second temperature ramp: $270^{\circ}$ to $330^{\circ} \mathrm{C}$ at $5^{\circ} \mathrm{C} / \mathrm{min}$
Final hold time:
己己


|  |  |  | $\square$ |  |  |  |  |  | $\begin{gathered} 00298 \\ \begin{array}{c} 32401 \\ \text { Noun. } \\ 3.09 \end{array} \end{gathered}$ |  | $\begin{aligned} & \text { cove } \\ & \text { splez } \\ & \text { Allap RPT } \end{aligned}$ $400$ | $\begin{aligned} & \text { cove } \\ & 32464 \\ & \text { mone fipy } \\ & 360 \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pcerconemonit |  |  |  |  |  |  |  |  |  |  |  |  |
| 1 Mono |  | No 11.23 cdin | No 11.22 cm | NO 11.23 cdm | NO 11.20 cdm | NO 11.24 cmin | NOO 11.23 cam | NO 11.20 cm | NO (1. 3 am | NO (1.26 call | 001123 cam | No (1. 22 coln |
| 3 Mone |  | N0 11.23 cdm | NOO 11.22 cdy | 0 mol 1.23 cdy | No 11.20 cdy | NO 11.24 cdy | NO 11.25 cdm | N0 11.20 cca | No (1.409 | MO 11.24 cm | WOII 23 cm |  |
| 40 |  | ND (1.64 | N0 (1.3n | 0001.23 cdim | No 11.3 m | NOIS. 24 cm | M0 (1.409 | NOPOOM | NDP过 | NO (1.3n | NO p 294 | NO (0.22 cat |
| 70 |  | No (1.23 call | No 11.22 cdin | NO 1.23 cdt | NO (1.20 cath | NO 11.24 can | NO 11.25 cat | NO (1.28) | No (1.72) | No 1129 cm | Mo (1.309 | N0, 1122 ccoly |
| 16 TM |  | No (4.19) | NOI 11.22 cdin | NO 11.23 cata | NO 11.20 cm$)$ | NO(1.24 cmm | NO (1123 coll | 208 | No (1.51) | 7.15 | NO 11.23 cm | NO (1.22 cdil |
| 80 TH |  | B. 64 | 0 00 | 1.32 | 613 | $00^{0}$ | 12.0 | 7.4 | 12.2 | 131 | -28 | 11.4 |
| es Telva |  | 020 | 807 | 0.28 | -28 | 108 | 10.0 | e. 5 | 17.0 | 130 | 3.17 | 10.4 |
| 62 Tome |  | 11.0 | 11.3 | 122 | 16.1 | 14. | 20.0 | 12.7 | 320 | 230 | 120 | 213 |
| 74 Tomam |  | -18 | 7.30 | $0 \cdot 1$ | 0.97 | 7.52 | 109 | 7.30 | 14.0 | 12.1 | $0 \cdot 0$ | 10.0 |
| 41 Pornt |  | 12.8 | 100 | 001 | 10.3 | 11.0 | 10. | -20 | 30.9 | 103 | 007 | 18.3 |
| ${ }^{4} 9$ Porne |  | 24.7 | 10.0 | 17.4 | 168 | 21.7 | 37.0 | 22. | 47.3 | 200 | 17.2 | 30. |
| 101 Prome |  | 4.2 | 31. | 27.0 | 32.5 | 37.6 | 0.4 | 38.1 | $0{ }^{5}$ | 87. | 30.3 | 82.4 |
| 105 Prome |  | 8.01 | 0.34 | 0.35 | 1.04 |  | 14.3 | 0.08 | 10.0 | 13.7 | 7.1 | 11.1 |
| 114 Pomen |  | NOPRSOCdy | NOP.4som | No pese call | nopesean | NORememm | NOM. 80 cam |  | ND p. 43 cm | No pe.ese cont | Nop. 47 cmam | No p. 2.43 cam |
| 116 Peme |  | 20.4 | 20.7 | 22.1 |  | 243 | 4.1 | 31.6 | ©3.6 | 44.8 | 23.0 | 308 |
| 123 Prome |  | NOPDOe can | N0 prose cm | moprot cat | NO (1.ce adm | No proe can | no presecata | N00 P .00 cam | no p.os caly | Nop.00 caty | No pr.0s caly | NOPORCA |
| 128 5me |  |  | N0 p. 40 cm | ND ¢.esecaly | NO P. 3000 cm | NOP.4ecm | NOPR.80 ${ }^{\text {a }}$ | N0 pr.coem | NO PR, 40 ent |  | Nope.ticaly | wopres edi |
| 137 treme |  | NO penocaly | NOp.asam | M0 Pemem | NO p.3sed | NO R.ese aly | NOP.8004 | M0 p.esam | No Re.43 adm |  | NOp. 47 an | Nop.as ant |
|  |  | 06.7 | 00. | $4{ }^{4}$ | 40. | 63. | 108 | 04.1 | 144 | 020 | 4.1 | 74. |
| SB3 Heme |  | 62.8 | 5.0 | 41.0 | 41.6 | 032 | 020 | 62.0 | 120 | res | 30.1 | 60. |
| 180 then |  | NOP P. 20 cat | 3.2 | 9.07 | 330 | 4.80 | 0.6 | 3.00 | 0.10 | 86 | 324 | N0 p. 43 cal |
| 187 tmmam |  | NOP. 40 adm |  | ND Pr.3804 | NOS 300 ctu | NO P.30 cal | NDP.4.4 ${ }^{\text {a }}$ | 100 p. 31 ad | 2.41 | ND Presemat | NOP. 30 ady | No p.3ncm |
| 160 towe |  | NOP. $0^{\text {coodm }}$ | NOP.4sem |  | ND p.30 and | NO R.as ond | nopreocm |  | N0. P. 43004 | nopene ${ }^{\text {and }}$ | NOp.47 call | Nop.cs can |
| 8197100 |  | 4.30 | 4.30 | 2.64 | 3.80 | 4.71 | 0.05 | 404 | 11.0 | 0.41 | 362 | 0.13 |
| 100 thene |  | 6.0 | 3.41 | 2.10 | 3.04 | 4.35 | 0.0 | 4.13 | 10. | 1.4 | 373 | . 01 |
| 170160 Hopm |  | 13.1 | N0 M.ar ath |  | NOPMen | 7.12 | 11.7 |  | 21.0 | 10.1 | no po.40am | -40 |
| 160 Hople |  | 300 | 13.3 | 14.4 | 14.0 | 10.0 | 31.8 | 14.0 | 00. | 20.0 | 11.3 | 20.3 |
| 100 mopm |  | 10.0 | 4.04 | 4.21 | 4.40 | 0.78 | 10.1 | 4.40 | 10.2 | 0.7 | 4.13 | 1.14 |
| 185 Hmpm |  |  |  | MOpuen | ND p.esent | Nopars aty | N0 proosm | NO p.cooall | Noperam | Nopirsom | ND p.roodm | nop.esom |
| 107 trope |  | 20.8 | ais | 0.30 | -13 | 12.3 | 20.1 | 0.4 | 30. | 17.3 | 0.38 | 14.3 |
| 100 Hepm |  |  | mopescom | NOP.eseath | Mop.se ${ }^{\text {andm }}$ | NO p.ra ${ }^{\text {and }}$ | nob.rs ${ }^{\text {an }}$ | nop.comat | nop.esoan | Mop pincom | Nop.rectim | NOpencm |
| 101 Hapla |  |  | 00 p .08 can | mop.esom | NO 0.60 adm |  | Noprsam | N0 p.cood | nop.esad | NOP.72 ath | NO p .10 cm | MOPDes ent |
| 104000 |  | 4.11 | NO p.ese caly | Mopeceaty | NDPBEO ady |  | 4.00 | MD P.eocan | 7.6 | 378 | NOp.rocall | No pees ent |
| 1200010 |  | Noproan |  | NO poseath | Ki3 3.600 aty | NOp.r2 cat | NOP.ersad | 0008.00004 | NOP3.04 caly | NO p.ir 2 alm | Nop. 70 cos | No p.es ont |
| 2000014 |  | NDPTracaly |  | NO peecaly |  | NO piza ${ }^{\text {a }}$ |  | ND P.000ath |  | NO (3.r2ad | NOPD70 caly | MOpescom |
| 207 Noma |  | NO D.TA cth | No acesem | MO P.eecaly |  | NOpurat | NO p.rsean | MO 0.00 cat | 3.62 |  | Noperoad |  |
| 200 Dice |  | 4.14 |  | NO M. 13 cm | MD (n.en col | NO W. 16 cm |  | NO 0.01 cman | 164 | NOD Niocal | No P. 17 cm | No pose |
| Pamchoo: |  |  |  |  |  |  |  |  |  |  |  |  |
| Craviere (a) |  | 14.0 | 7.00 | 0.37 | 07 | 15.7 | 17.0 | 030 | 31.7 | 20.2 | 0.00 | 100 |
| Camordene (f) |  | NO p. 74.8 cmp | N0 p.ese caly | NO p.emem | NDPAS0 cath | NDP P. 22 cat | 4.00 | NOP.00 0 din | 7.51 | -23 | MO pis 10 catm |  |
| Onodim |  | 10.7 | NO p.ascat | No pe.ss can | NOP $\mathrm{SO}_{30 \mathrm{~cm}}$ | NOPCeman | NOpesocal | NO p. 40 com | NOPR.43 adm | NOP.4e caly | N0 R2.01 | WO 2143 cm |
| 0.p' 000 |  | 130 | 3.22 | 3.10 | -6 | 0.03 | 20.1 | 8.80 | 032 | 335 | ${ }^{6} 9$ | 163 |
| Of, OOE |  | 02 | NOP. 2.43 cal | NOM. 40 cm | 08 | 6.24 | 23.0 | 4.0 | 034 | 290 | 6.41 | 140 |
| p.PP 000 |  | 45.3 | 17.3 | 17.0 | 31.3 | 40.1 | 0.7 | 23.7 | 242 | 110 | 31.0 |  |
| o,p POT |  | M0 pr.s0 call | NO 12.45 cman | MO P .45 cdy | Norse coth | NOPC.40 cill | NO R. 80 cam | NO 12.40 cmm | 4.11 | NOP. 460 cm | NOP.47 call | NOP12.43 ${ }^{\text {cmam }}$ |
| P.P' DOE |  | 150 | 60.4 | 0.1 | 00.3 | 160 | 330 | 60.8 | 652 | 200 | 093 | 161 |
| P.PP DOT |  | 4.17 | 464 | 2.18 | 20 | 3.01 | 14 | 12 | 136 | 3.5 | MOP247 caly | 4.64 |

Table e. CONCENTRATIONS (me/g) OF MONO THROUOH deca PCE homologs

|  | Fiold 10 Extract iD MS Flle | Mothod Blank 32495 MB A08A1.RPT | $\begin{gathered} \text { ROISG } \\ 32480 \\ \text { AOSA7.RPT } \end{gathered}$ | $\begin{gathered} \text { RO23G } \\ 32491 \\ \text { A03A5.RPT } \end{gathered}$ | $\begin{gathered} \text { P03SG } \\ 32486 \\ \text { A0BA10.PPT } \end{gathered}$ | $\begin{gathered} \text { POMSG } \\ 32462 \\ \text { A0BA7.RPT } \end{gathered}$ | $\begin{gathered} \text { R05SS } \\ 32475 \\ \text { A00A3.PPT } \end{gathered}$ | $\begin{gathered} \text { C01sQ } \\ \text { 32474 } \\ \text { A00M2.PPT } \end{gathered}$ | $\begin{gathered} \text { Co2so } \\ 32483 \\ \text { A08A.RPT } \end{gathered}$ | $\begin{gathered} \text { C03sQ } \\ 32469 \\ \text { A0BA13.APT } \end{gathered}$ | $\begin{gathered} \text { CO4SO } \\ 32479 \\ \text { A0BAO.RPT } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PCB Homolog |  |  |  |  |  |  |  |  |  |  |  |
| Mono |  | NO (1.25 cati ${ }^{\text {a }}$ | ND (1.24 cdif | NO (1.24 00\%) | ND (1.25 cdil) | ND (1.24 odi) | ND (1.23 coll) | ND (2.49) | NO (1.20 cdif) | ND (2.47) | 1.63 |
| DI |  | NO (1.25 com | NO (1.24 cill | ND (3.20) | NO (1.83) | NO (1.70) | ND (1.23 cmin) | NO (2.63) | NO (1.20 call) | ND (2.88) | 5.27 |
| TH |  | ND (1.25 cdif) | 8.37 | 6.49 | 4.95 | ND (1.48) | ND (1.23 odif) | 43.4 | ND (2.95) | 16.3 | 7.11 |
| Tetre |  | ND (R.50 odil) | 98.3 | 116 | 60 | 129 | 36.4 | 342 | - 00.9 | 227 | 110 |
| Penta |  | ND p. 50 odil) | 210 | 321 | 171 | 573 | 139 | 568 | 254 | 495 | 230 |
| Hexa |  | ND (2.00 cdia | 200 | 447 | 248 | 925 | 200 | 503 | 274 | 405 | 248 |
| Hopt $\bullet$ |  | NO (2.60 odid | 130 | 168 | 118 | 400 | 99.7 | 177 | 107 | 168 | 85.0 |
| Oota |  | NO 19.76 edid | 20.6 | 25.4 | 33.8 | 124 | 28.2 | 30.7 | 3.91 | 6.70 | 18.0 |
| Nona |  | NO (3.76 odu) | 17.2 | 22.4 | 17.5 | 60.1 | 17.2 | 10.4 | 16.4 | 21.4 | 10.4 |
| Deon |  | NO pe.26 odin | 12.7 | 13.4 | 11.6 | 34.3 | 12.0 | 12.7 | 0.71 | 13.7 | 7.03 |
| Total |  |  | 794 | 1,136 | 657 | 2,253 | 530 | 1,702 | 750 | 1,409 | 731 |

[^3]|  | 管車 |  |  | come |  | come | come | coin |  | coma | come | cen |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\xrightarrow{\text { cosamamo }}$ |  |  |  |  |  |  |  |  |  |  |  |  |
| mom |  | 15 | nornom | 12 com | + | 12 am | 14800 | 10032000 | notum | ${ }^{1012040909}$ | mot30am | amos |
| a |  | motrsam | W01200m | molisam | (120 | no $112 \times 8$ |  | no(4s) | Hopit | mor2am | vo (1, $\mathrm{m}^{\text {a }}$ | 13mm |
| ${ }^{*}$ |  | ${ }^{\circ}$ | -s | ${ }^{130}$ | ". | ${ }^{\circ \infty}$ | 100 | "0 | 13 | ${ }^{20}$ | 1.0 | ${ }^{30}$ |
| ${ }^{100}$ |  | 0.1 | 012 | m. | 12 | 10 | ${ }^{10}$ | $\cdots$ | ${ }^{20}$ | ${ }^{18}$ | 109 | " |
| noter |  | ${ }^{2}$ | " | 180 | ${ }^{10}$ | 210 | ${ }^{\circ}$ | ${ }^{21}$ | ${ }^{41}$ | * | ${ }^{100}$ | ${ }^{20}$ |
|  |  | ${ }^{215}$ | ${ }^{10}$ | 190 | 16 | ${ }^{5}$ | ${ }^{30}$ | 10 | ${ }^{13}$ |  | 10 | ${ }^{23}$ |
| \% |  | 19 | ${ }^{60}$ | $0 \cdot$ | ${ }^{*}$ | 0 | + | $4{ }^{4}$ | " | $0 \cdot$ |  | mo |
| ota |  | ${ }^{213}$ | nope |  | nossoman |  | or | nopamean | *.1 | nopramom |  | \% |
| mom |  | 132 | nopesom |  | 300 | \% | ${ }^{3}$ | nopemom | no | $\pm \infty$ | nosaroam | 0 |
| ome |  | a. 0 | nomaom | no 1.10 ma | mam | nocromom | -1 | no poomas | ${ }^{103}$ |  |  | nomom |
| tax |  | 20 | $\cdots$ | $\stackrel{4}{ }$ |  |  | 1.08 | ${ }^{28}$ | . 1.0 | $\pm$ |  |  |

Table 10. CONCENTRATIONS (pg/g) OF COPLANAR PCBs IN FISH

| Compound | Fietd ID <br> MRI code | Method blank <br> 32468 | C04SG <br> 32467 | RO2SG <br> 32469 | C01B <br> 32470 | R03B <br> 32471 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 77 Tetra | ND(2) | 262 | 246 | 500 | 306 |  |
| 78 Tetra | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ |  |
| 79 Tetra | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ | $\mathrm{ND}(2)$ |  |
| 80 Tetra | $\mathrm{ND}(2)$ | 9.99 | 29.9 | 40.7 | 54.6 |  |
| 81 Tetra | $\mathrm{ND}(2)$ | 4.71 | 6.07 | 10.9 | 8.02 |  |
| 126 Penta | $\mathrm{ND}(2)$ | 111 | 159 | 168 | 146 |  |
| 127 Penta | $\mathrm{ND}(2)$ | 31 | 122 | 126 | 140 |  |
| 169 Hexa |  | $\mathrm{ND}(2)$ | 7.98 | 11.2 | 9.42 | 10.7 |

Table 11. PCB CONGENERS AND PESTICIDES OUALTY CONTROL SAMPLE RESULTS

|  | Fintd ID Extract ID MS Fide | $\begin{gathered} \text { Methodblank } \\ 32495 \mathrm{MB} \\ \text { A06A1.RPT } \\ \text { pg'g } \end{gathered}$ | Metrod spike lovel pg'g | $\begin{aligned} & \text { Control spike } \\ & 32496 \\ & \text { MO6A2.RPT } \\ & \text { \% moovery } \end{aligned}$ | $\begin{aligned} & \text { ROLSGMS } \\ & 32494 \\ & \text { MOGA3.RPT } \\ & \text { \% recovery } \end{aligned}$ | $\begin{aligned} & \text { ROZSG MSD } \\ & 32493 \\ & \text { AOSAA. RPT } \\ & \text { \% neovery } \end{aligned}$ | $\begin{gathered} \text { Mean } \\ \% \\ \text { recovery } \end{gathered}$ | RPD ${ }^{\text {d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| COMPOUND 1 Maso |  | ND (1250 © ${ }_{\text {d }}$ ) | 40000 | NC (a) | NC | NC | NC | NC |
| 3 Mono |  | ND (1250 odl) | 40000 | 79 | 93.1 | 82.1 | 87.6 | 12.5 |
| 4 Di |  | ND (1250 © Cll) | 40000 | 78 | 85.6 | 81.1 | 83.4 | 5.4 |
| 7 Di |  | ND (1250 © اله) | 40000 | 91 | 96.4 | 84.4 | 90.4 | 13.3 |
| 18 Tri |  | ND (1250 dl) | 40000 | 113 | 111.8 | 107.1 | 109.5 | 4.3 |
| 28 Tri |  | ND (2500 edl) | 80000 | 120 | 115.6 | 104.2 | 109.9 | 10.4 |
| 44 Tetra |  | ND (2500 coll) | 80000 | 124 | 108.6 | 105.2 | 106.9 | 3.2 |
| 52 Totra |  | ND (2500 0 (1) | 80000 | 125 | 108.1 | 98.8 | 103.5 | 8.9 |
| 74 Totra |  | ND (2500 هd) | 80000 | 125 | 110.6 | 98.4 | 104.5 | 11.6 |
| 87 Penta |  | ND (2500 coll) | 80000 | 118 | 100.3 | 93.5 | 96.9 | 7.0 |
| 99 Penta |  | ND (\$400 coll) | 43800 | 123 | 102.5 | 88.4 | 95.4 | 14.8 |
| 101 Punta |  | ND (2500 cal) | 80000 | 125 | 104.0 | 88.2 | 96.1 | 16.4 |
| 105 Penta |  | NE (2500 cal) | 80000 | 114 | 98.4 | 90.7 | 94.5 | 8.1 |
| 114 Penta |  | ND (2500 ed) | 80000 | 119 | 106.6 | 93.8 | 100.2 | 12.8 |
| 118 Penta |  | ND (2500 edt) | 80000 | 111 | 100.5 | 115.8 | 108.2 | 14.1 |
| 123 Penta |  | ND (2080 call) | 66500 | $b$ | b | $b$ | $b$ | b |
| 128 Hexa |  | ND (2ss0 ad) | 80000 | 119 | 97.3 | 82.6 | 90.0 | 16.4 |
| 137 Hexa |  | ND (2300 ed) | 80000 | 122 | 111.1 | 98.0 | 104.5 | 12.5 |
| 138/158 Hexa |  | ND (5000 ed) | 160000 | 114 | 83.0 | 74.8 | 78.8 | 10.3 |
| 153 Hexa |  | ND (2500 ed) | 80000 | 122 | 102.3 | 84.1 | 93.2 | 19.6 |
| 156 Hexa |  | ND (2500 cdl) | 80000 | 111 | 89.7 | 79.4 | 84.6 | 12.2 |
| 157 Hexa |  | ND (2410 edl) | 77000 | 116 | 90.3 | 81.0 | 85.7 | 10.8 |
| 166 thexa |  | ND (2500 cal) | 80000 | 125 | 114.1 | 96.6 | 105.3 | 16.6 |
| 167 Hexa |  | $\cdots \mathrm{O}(2500 \mathrm{ccl})$ | 80000 | 117 | 94.1 | 83.2 | 88.7 | 12.2 |
| 168 Hexa |  | ND (2180 cell) | 65860 | 125 | 101.8 | 83.8 | 92.8 | 19.3 |
| 170/150 Hepta |  | ND (6450 call) | 207500 | 108 | 82.4 | 73.5 | 78.0 | 11.3 |
| 180 Hepta |  | ND (3750 cal) | 120000 | 110 | 85.8 | 69.4 | 77.6 | 21.2 |
| 183 Hepta |  | ND (3750 cal) | 120000 | 118 | 95.6 | 79.9 | 87.8 | 17.9 |
| 185 Hepta |  | ND (3750 0d) | 120000 | 114 | 94.0 | 81.5 | 87.8 | 14.3 |
| 187 Hepta |  | ND (2500 col) | 80000 | 120 | 96.6 | 80.8 | 88.7 | 17.8 |
| 189 Нерта |  | ND (3750 cal) | 120000 | 98 | 72.3 | 65.5 | 68.9 | 9.9 |
| 191 Hepta |  | ND (3750 cd) | 120000 | 112 | 87.1 | 63.9 | 75.5 | 30.7 |
| 194 Octa |  | ND (3750 cd) | 120000 | 92 | 85.2 | 57.9 | 61.6 | 11.8 |
| 199 Oeta |  | ND (3750 col) | 120000 | 114 | 92.1 | 78.2 | 85.2 | 16.4 |
| 205 Octa |  | ND (3750 edl) | 120000 | 93 | 67.1 | 59.1 | 83.1 | 12.6 |
| 207 Nona |  | ND (3750 cd) | 120000 | 137 | 101.6 | 85.1 | 93.3 | 17.8 |
| 209 Deca |  | ND (6250 edi) | 200000 | 93 | 62.7 | 53.7 | 58.2 | 15.4 |
| Chiortane (a) |  | ND (3750 cal) | 120000 | 128 | 105.9 | 115.7 | 110.8 | 8.8 |
| Chiordane (9) |  | ND (3750 coll) | 120000 | 131 | 108.4 | 122.0 | 114.2 | 13.6 |
| Dieldrin |  | ND (2500 edr) | 80000 | 117 | NC | NC | NC | NC |
| -0, DDD |  | ND (2500 col) | 80000 | 115 | 90.5 | 114.7 | 108.6 | 23.6 |
| O,P DDE |  | NO ( 2500 cll ) | 80000 | 128 | 107.5 | 103.8 | 105.6 | 3.5 |
| P.P DD |  | ND (2500 cel) | 80000 | 118 | 87.5 | 122.6 | 105.0 | 35.4 |
| O.P DOT |  | ND (2500 ect) | 80000 | 130 | 120.4 | 115.4 | 117.9 | 4.3 |
| P.P' DDE |  | ND (2500 cel) | 80000 | 130 | 107.3 | 90.3 | 98.8 | 17.2 |
| P.P' DDT |  | ND (2500 edf) | 80000 | 125 | 103.4 | 112.7 | 108.1 | 8.6 |

- Congeners 118 and 123 were chromatrographically soparated, but wero innograted as one peak The recovery was based on the sum of both congenors.
- \% Recovery $=$ (lamount found in method spike samplo-mount found in unspiked sample) theoretical amount spiked] $\times 100 \%$.
- RPD $=$ relative pereent difference of duplieate matrix apikes.

Tablo 12．RECOVERIES（\％）OF ${ }^{15} \mathrm{C}$ PCB AND ${ }^{19} \mathrm{C}$ DDT SUAROGATES

|  |  | Spike level（pgg） compound | $\begin{gathered} 12,500 \\ { }^{13} \mathrm{C}_{6}(3) \text { Mono } \end{gathered}$ | $\begin{gathered} 31.250 \\ { }^{33} \mathrm{C}_{12}(77) \\ \hline \end{gathered}$ | $\begin{gathered} 30,000 \\ { }^{13} \mathrm{C}_{12}(138) \end{gathered}$ | $\begin{gathered} 50,000 \\ { }^{13} \mathrm{C}_{12}(202) \end{gathered}$ | $\begin{gathered} 66,500 \\ { }^{13} \mathrm{C}_{12}(209) \end{gathered}$ | $\begin{aligned} & 25,000 \\ & { }^{13} \mathrm{C}_{12} \mathrm{DDT} \\ & \hline \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fieldib | MRIT Code |  |  |  |  |  |  |  |
| Control Spike | 32496 |  | 84.0 | 130.9 | 130.3 | 133.0 | 103.2 | 138.0 |
| RO2SG MS | 32494 |  | 111.4 | 122.7 | 103.8 | 104.6 | 69.1 | 117.8 |
| RO2SG MSD | 32493 |  | NC＊ | 124.5 | 106.1 | 105.7 | 75.7 | 118.0 |
| RO2SG | 32491 |  | NC | 123.8 | 102.1 | 102.8 | 70.1 | 99.5 |
| CO1B | 32485 |  | 104.1 | 109.2 | 92.6 | 90.9 | 61.4 | 84.1 |
| RO1SG | 32480 |  | 108.8 | 112.5 | 89.6 | 91.4 | 71.4 | 84.6 |
| CO4SG | 32479 |  | NC | 110.6 | 92.5 | 92.9 | 70.8 | 90.0 |
| RO1B | 32478 |  | 107.6 | 120.3 | 104.4 | 105.8 | 81.5 | 95.3 |
| Method Blank | 32495 MB |  | 43.9 | 79.0 | 78.7 | 85.2 | 64.0 | 64.8 |
| C03B | 32473 |  | NC | 132.4 | 102.2 | 98.9 | 61.0 | 71.0 |
| C01SG | 32474 |  | NC | 125.0 | 95.8 | 95.1 | 64.6 | 76.9 |
| R05SG | 32475 |  | 104.1 | 110.0 | 88.8 | 90.5 | 66.1 | 65.5 |
| R02B | 32476 |  | 86.5 | 106.0 | 86.0 | 85.6 | 61.8 | 63.2 |
| R04B | 32477 |  | 113.8 | 122.4 | 98.2 | 98.9 | 71.5 | 73.1 |
| C02B | 32481 |  | 105.5 | 115.7 | 90.0 | 90.6 | 66.7 | 70.9 |
| R04SG | 32482 |  | 101.2 | 110.4 | 82.9 | 83.1 | 57.0 | 69.6 |
| C02SG | 32483 |  | 116.8 | 117.5 | 91.8 | 89.9 | 58.7 | 75.5 |
| C05B | 32484 |  | 114.4 | 113.9 | 89.1 | 91.1 | 60.1 | 72.8 |
| R03SG | 32488 |  | 109.2 | 113.0 | 90.3 | 89.5 | 59.9 | 70.2 |
| C05SG | 32487 |  | NC | 116.7 | 94.5 | 90.6 | 61.1 | 71.3 |
| R03B | 32488 |  | NC | 101.9 | 80.4 | 82.3 | 57.5 | 67.3 |
| C03SG | 32489 |  | NC | 122.7 | 96.4 | 96.8 | 63.8 | 80.0 |
| R05B | 32490 |  | 111.2 | 123.5 | 100.0 | 94.2 | 57.6 | 79.6 |
| C04B | 32492 |  | 128.0 | 120.3 | 95.9 | 96.0 | 59.8 | 72.5 |
| Method Blank | 32495 MB Split |  | 63.4 | 108.5 | 94.3 | 95.6 | 74.2 | 70.4 |
| Mean Recovery |  |  | 100.8 | 115.7 | 95.1 | 95.2 | 66.7 | 81.7 |
| RSD |  |  | 20.6 | 9.4 | 10.9 | 10.7 | 14.9 | 23.1 |

－ $\mathrm{NC}=\mathrm{Nof}$ calculated．Qualiative ralio crileria were not mel for the ${ }^{3} \mathrm{C}_{4}$ mono PCB surrogate．

Table 13. RECOVERIES (\%) OF ${ }^{33} \mathrm{C}_{12}$ COPLANAR PCB INTERNAL QUANTITATION STANDARDS

| Field ID | MRI code | ${ }^{13} \mathrm{C}_{12}$ Tetra PCB 77 | ${ }^{13} \mathrm{C}_{12}$ Penta PCB 126 | ${ }^{13} \mathrm{C}_{12}$ Hexa PCB 169 |
| :---: | :---: | :---: | :---: | :---: |
| Method Blank | 32468 | 30.1 | 20.0 | 22.8 |
| CO4SG-MS | 32465 | 8.97 | 4.41 | 9.12 |
| CO4SG-MSdup | 32466 | 26.5 | 11.5 | 17.2 |
| CO4SG | 32467 | 10.6 | 5.89 | 11.2 |
| R02SG | 32469 | 6.85 | 3.36 | 8.3 |
| C01B | 32470 | 11.9 | 6.54 | 12.9 |
| R03B | 32471 | 11.7 | 4.82 | 11.2 |

Table 14. PCE CONGENERS AND PESTICIDES INITAL CALBRATION RESPONSE FACTORS

| Compound | $\begin{gathered} \text { Cal1 } \\ \text { A05AO2.RPT } \\ \text { RF } \end{gathered}$ | Cal 3 <br> A06AO3.RPT | Cal 3 AOSAO4.RPT | Cal 5 M06A05.RTT | $\begin{gathered} \text { Cal } 6 \\ \text { A06A06.RPT } \end{gathered}$ | Mean | ASD |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 Mono | 0.701 | 0.681 | 0.800 | 0.673 | 0.72 | $0.775^{\circ}$ | 7.12 |
| 3 Mono | 0.660 | 0.660 | 0.785 | 0.699 | 0.729 | $0.707^{\text {c }}$ | 7.4 |
| $4{ }^{4} \mathrm{Di}$ | 0.500 | 0.403 | 0.498 | 0.393 | 0.421 | $0.443^{\text {c }}$ | 11.76 |
| 7 Di | 0.758 | 0.710 | 0.798 | 0.672 | 0.703 | $0.728^{\circ}$ | 6.83 |
| 18 Tr | 0.417 | 0.372 | 0.451 | 0.395 | 0.421 | $0.411^{\circ}$ | 7.21 |
| 28 Tri | 0.675 | 0.604 | 0.735 | 0.648 | 0.687 | 0.67 | 7.23 |
| 52 Tetra | 0.451 | 0.382 | 0.464 | 0.416 | 0.431 | $0.429^{\circ}$ | 7.46 |
| 44 Tetra | 0.335 | 0.296 | 0.351 | 0.308 | 0.322 | $0.322^{8}$ | 6.73 |
| 74 Tetra | 0.596 | 0.493 | 0.583 | 0.533 | 0.552 | 0.551 | 7.44 |
| 101 Penta | 0.372 | 0.330 | 0.366 | 0.319 | 0.338 | 0.345 ${ }^{\text {c }}$ | 6.67 |
| 99 Penta | 0.260 | 0.375 | 0.425 | 0.366 | 0.384 | 0.388 | 6.72 |
| 87 Pents | 0.380 | 0.307 | 0.350 | 0.291 | 0.301 | $0.312^{\text {e }}$ | 8.33 |
| 123/118 Penta ${ }^{\text {a }}$ | 0.606 | 0.442 | 0.485 | 0.425 | 0.443 | 0.480 | 13.72 |
| 114 Penta | 0.398 | 0.341 | 0.418 | 0.355 | 0.368 | 0.371 | 9.05 |
| 105 Penta | 0.501 | 0.452 | $0.50 \%$ | 0.438 | 0.457 | 0.471 | 6.58 |
| 153 Hexa | 0.377 | 0.338 | 0.397 | 0.349 | 0.372 | $0.357^{\circ}$ | 6.38 |
| 168 Hexa | 0.427 | 0.362 | 0.405 | 0.404 | 0.489 | 0.417 | 5.89 |
| 137 Hexa | 0.325 | c. 296 | 0.341 | 0.301 | 0.322 | 0.317 | 5.82 |
| 139/158 Hexa | 0.310 | 0.281 | 0.352 | 0.285 | 0.290 | $0.301{ }^{\text {c }}$ | 6.84 |
| 166 Hexa | 0.428 | 0.379 | 0.451 | 0.358 | 0.422 | 0.416 | 6.7 |
| 128 Hexa | 0.469 | 0.412 | 0.482 | 0.424 | 0.451 | 0.448 | 6.59 |
| 167 Hexa | 0.568 | 0.483 | 0.573 | 0.512 | 0.539 | 0.537 | 6.39 |
| 156 Hexa | 0.454 | 0.309 | 0.427 | 0.390 | 0.413 | 0.415 | 6.57 |
| 157 Hexa | 0.627 | 0.558 | 0.644 | 0.573 | 0.603 | 0.595 | 6.38 |
| 187 Hepta | 0.478 | 0.431 | 0.571 | 0.456 | 0.483 | 0.474 | 7.06 |
| 183 Hepta | 0.342 | 0.312 | 0.367 | 0.322 | 0.342 | 0.337 | 6.29 |
| 185 Hepla | 0.278 | 0.292 | 0.300 | 0.247 | 0.264 | 0.272 | 8.24 |
| 180 Hepta | 0.324 | 0.300 | 0.336 | 0.304 | 0.325 | $0.318^{*}$ | 4.79 |
| 191 Hepta | 0.278 | 0.250 | 0.295 | 0.259 | 0.278 | 0.272 | 6.51 |
| 170/190 Hepta | 0.331 | 0.300 | 0.344 | 0.310 | 0.328 | 0.323 | 5.43 |
| 189 Hepta | 0.415 | 0.391 | 0.404 | 0.350 | 0.378 | 0.329 | 5.63 |
| 198 Oeta | 0.372 | 0.325 | 0.374 | 0.320 | 0.342 | 0.347 | 7.34 |
| 190 Octa | 0.291 | 0.258 | 0.318 | 0.254 | 0.285 | $0.27{ }^{*}$ | 9.73 |
| 205 Octa | 0.375 | 0.322 | 0.371 | 0.313 | 0.326 | 0.333 | 7.78 |
| 207 Nona | 0.340 | 0.307 | 0.361 | 0.310 | 0.334 | $0.330^{\circ}$ | 6.78 |
| 209 Dece | 0.251 | 0.229 | 0.276 | 0.236 | 0.255 | $0.240^{\circ}$ | 7.33 |
| Criordiene (a) | 0.206 | 0.190 | 0.233 | 0.205 | 0.218 | 0.212 | 6.37 |
| Chlordane (9) | 0.206 | 0.207 | 0.234 | 0.207. | 0227 | 0.216 | 6.15 |
| Oieldrin | ND | 0.079 | 0.062 | 0.068 | 0.088 | 0.072 | 9.28 |
| $0 . p$ DDD | 0.905 | 0.824 | 0.862 | 0.713 | 0.753 | 0.811 | 9.65 |
| 0.p DDE | 0.786 | 0.593 | 0.671 | 0.590 | 0.623 | 0.620 | 6.08 |
| P.P' DOD | 1.070 | 0.802 | 0.814 | 0.681 | 0.722 | 0.755 | 8.47 |
| Op DDT | 0.411 | 0.360 | 0.430 | 0.408 | 0.474 | 0.417 | 9.88 |
| P.p. DDE | 0.840 | 0.525 | 0.522 | 0.436 | 0.456 | 0.46 | 3.17 |
| P.p' DDT | ND' | 0.358 | 0.391 | 0.447 | 0.518 | 0.424 | 18.21 |
| ${ }^{40} C_{0}(3)$ | 0.814 | 0.755 | 0.813 | 0.674 | 0.704 | 0.737 | 8.28 |
| ${ }^{42} \mathrm{C}_{18}(77)$ | 0.559 | 0.451 | 0.515 | 0.485 | 0.500 | 0.502 | 7.91 |
| ${ }^{40} \mathrm{C}_{12}(138)$ | 0.333 | 0.303 | 0.362 | 0.308 | 0.525 | 0.327 | 6.35 |
| ${ }^{15} C_{12}(202)$ | 0.329 | 0.508 | 0.366 | 0.318 | 0.341 | 0.333 | 6.13 |
| ${ }^{45} \mathrm{C}_{12}(209)$ | 0.241 | 0.224 | 0.257 | 0.225 | 0.242 | 0.238 | 5.07 |
| ${ }^{13} \mathrm{C}_{12}$ DDT | ND | 0.572 | 0.503 | 0.561 | 0.650 | 0.572 | 10.58 |

Even though separatod chromatographicaly, the response factors for Congeners 118 and 123 are basec on the sum of both paaks.

- $N D=$ Qualitative ratio not met
- Total homolog response factors beaed on average of two congeners for aech homolog group.

Table 15. CONTINUTING CALIBRATION RESULTS

| Compound | $\begin{gathered} \text { End day } \\ \text { Cal } 3 \\ \text { A06AQ7.RPT } \end{gathered}$ | $\begin{gathered} \text { Eegin day } \\ \text { Cal } 5 \\ \text { A08AQ2.RPT } \end{gathered}$ | $\begin{gathered} \text { End day } \\ \text { Cal } 5 \\ \text { A08AQ3.APT } \end{gathered}$ | $\begin{gathered} \text { Bogin day } \\ \text { Cal } 5 \\ \text { A11AQ2.RPT } \end{gathered}$ | End day Cal 5 A1IAQ3.RPT |
| :---: | :---: | :---: | :---: | :---: | :---: |
| TMono | 7.05 | 0.968 | 0.974 | 0.921 | 0.965 |
| 3 Mono | 0.989 | 1.000 | 1.010 | 0.954 | 0.971 |
| 4 Di | 0.964 | 0.902 | 0.895 | 0.860 | 0.887 |
| 7 Di | 0.996 | 0.928 | 0.916 | 0.886 | 0.934 |
| 18 Tri | 1.070 | 0.968 | 0.989 | 0.912 | 0.980 |
| 28 Tri | 1.060 | 1.010 | 0.994 | 0.949 | 0.995 |
| 52 Tetra | 1.020 | 0.942 | 0.914 | 0.903 | 0.916 |
| 44 Tetra | 1.030 | 0.979 | 0.917 | 0.906 | 0.938 |
| 74 Tetra | 1.020 | 0.975 | 0.911 | 0.914 | 0.921 |
| 101 Penta | 1.030 | 0.943 | 0.854 | 0.852 | 0.852 |
| 99 Penta | 1.110 | 0.943 | 0.852 | 0.862 | 0.891 |
| 87 Penta | 1.000 | 0.916 | 0.832 | 0.854 | 0.858 |
| 118/123 Penta | 0.908 | 0.870 | 0.777 | 0.793 | 0.810 |
| 114 Penta | 0.962 | 0.907 | 0.844 | 0.845 | 0.872 |
| 105 Penta | 0.921 | 0.891 | 0.814 | 0.832 | 0.845 |
| 153 Hexa | 0.955 | 0.897 | 0.804 | 0.804 | 0.836 |
| 168 Hexa | 0.954 | 0.879 | 0.809 | 0.818 | 0.802 |
| 137 Hexa | 0.950 | 0.888 | 0.809 | 0.812 | 0.830 |
| 138/158Hexa | 0.885 | 0.877 | 0.775 | 0.797 | 0.794 |
| 166 Hexa | 0.979 | 0.874 | 0.815 | 0.816 | 0.840 |
| 128 Hexa | 0.931 | 0.874 | 0.804 | 0.807 | 0.817 |
| 167 Hexa | 0.907 | 0.859 | 0.782 | 0.803 | 0.806 |
| 156 Hexa | 0.946 | 0.859 | 0.829 | 0.818 | 0.812 |
| 157 Hexa | 0.965 | 0.863 | 0.831 | 0.814 | 0.808 |
| 187 Hepta | 0.922 | 0.854 | 0.797 | 0.795 | 0.805 |
| 183 Hepta | 0.920 | 0.856 | 0.789 | 0.788 | 0.789 |
| 185 Hepta | 0.905 | 0.832 | 0.754 | 0.760 | 0.759 |
| 180 Hepta | 0.917 | 0.826 | 0.777 | 0.768 | 0.783 |
| 191 Hepta | 0.860 | 0.840 | 0.709 | 0.793 | 0.794 |
| 170/190 Hepta | 0.921 | 0.822 | 0.792 | 0.762 | 0.771 |
| 189 Hepta | 0.863 | 0.775 | 0.757 | 0.730 | 0.742 |
| 199 Octa | 0.901 | 0.808 | 0.782 | 0.763 | 0.780 |
| 194 Octa | 0.880 | 0.718 | 0.730 | 0.703 | 0.723 |
| 205 Octa | 0.892 | 0.735 | 0.725 | 0.727 | 0.735 |
| 207 Nona | 1.150 | 0.984 | 0.994 | 0.951 | 0.980 |
| 209 Deca | 0.826 | 0.693 | 0.699 | 0.677 | 0.692 |
| Chlordane (a) | 1.030 | 0.946 | 0.867 | 0.877 | 0.881 |
| Chlordane (g) | 1.040 | 0.961 | 0.889 | 0.873 | 0.883 |
| Dieldrin | 1.420 | 1.020 | ND ${ }^{6}$ | 0.913 | 0.916 |
| 0,p DDD | 1.030 | 1.000 | 0.935 | 0.879 | 0.941 |
| O,P DDE | 1.010 | 0.958 | 0.882 | 0.870 | 0.889 |
| P.P' DDD | 1.070 | 1.080 | 1.020 | 0.943 | 1.030 |
| O,P DDT | 0.749 | 0.746 | 0.636 | 0.733 | 0.634 |
| P.P' DDE | 1.030 | 0.983 | 0.884 | 0.874 | 0.901 |
| P, $P^{\prime}$ DDT | 0.681 | 0.678 | 0.517 | 0.697 | 0.559 |
| ${ }^{12} \mathrm{C}_{6}(3)$ | 0.981 | 0.940 | 0.942 | 0.904 | 0.912 |
| ${ }^{13} \mathrm{C}_{12}(77)$ | 0.988 | 0.972 | 0.911 | 0.911 | 0.923 |
| ${ }^{13} \mathrm{C}_{12}(138)$ | 0.983 | 0.867 | 0.760 | 0.810 | 0.820 |
| ${ }^{12} C_{12}(202)$ | 0.946 | 0.828 | 0.790 | 0.779 | 0.795 |
| ${ }^{13} \mathrm{C} \mathrm{C}_{12}(209)$ | 0.835 | 0.691 | 0.696 | 0.672 | 0.691 |
| ${ }^{12} \mathrm{C}_{12}$ DDT | 0.615 | 0.641 | 0.510 | 0.651 | 0.529 |

Table 16. HRGC/HRMS COPLANAR PCB CALIBRATION RESULTS

| Compound | Cal 1 RF | Cal 2 RF | Cal 3 RF | $\begin{gathered} \text { Cal } 4 \\ \text { RF } \end{gathered}$ | $\text { Cal } 5$ RF | Cal 6 RF | Mean RF | RSD | Continuing Cal RF \% of mean |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 77 Telra | 2.91 | 2.75 | 2.86 | 2.92 | 2.85 | 2.85 | 2.86 | 2.1 | 108 |
| 78 Tetra | 3.17 | 2.86 | 3.06 | 3.16 | 3.02 | 3.10 | 3.08 | 3.7 | 110 |
| 79 Tetra | 2.90 | 2.64 | 2.79 | 2.89 | 2.73 | 2.88 | 2.80 | 3.7 | 111 |
| 80 Tetra | 2.86 | 2.49 | 2.64 | 2.77 | 2.57 | 2.74 | 2.68 | 5.1 | 108 |
| 81 Tetra | 2.98 | 2.72 | 2.84 | 2.92 | 2.81 | 2.94 | 2.87 | 3.4 | 110 |
| 126 Penta | 0.664 | 0.611 | 0.666 | 0.662 | 0.661 | 0.692 | 0.659 | 4.0 | 100 |
| 127 Penta | 1.01 | 0.92 | 1.00 | 1.01 | 1.06 | 1.08 | 1.01 | 5.5 | 99.2 |
| 169 Hexa | 1.74 | 1.60 | 1.94 | 1.89 | 1.87 | 1.90 | 1.82 | 7.1 | 101 |
| ${ }^{13} \mathrm{C}_{12}-77$ Telra | 0.465 | 0.474 | 0.531 | 0.492 | 0.512 | 0.519 | 0.499 | 5.3 | 76.0 |
| ${ }^{3} \mathrm{C}_{12}-126$ Penia | 1.23 | 1.24 | 1.32 | 1.26 | 1.19 | 1.21 | 1.242 | 3.7 | 81.1 |
| ${ }^{13} \mathrm{C}_{12}$-169 Hexa | 0.387 | 0.379 | 0.438 | 0.438 | 0.411 | 0.419 | 0.412 | 6.1 | 85.3 |

## APPENDIX

FIGURES A-1 THROUGH A-14 HRGCILRMS ION PLOTS FOR SAMPLE 32491, R02SG


Figure A-1


Figure A-2


Figure A－3
SAMPLE: S,SAM,DIR,32491,2/PCB FISH 2ul inj
COND: $30 M, 0.32 M M, 1.0 U M, 70-178015-30004$ COND. 3B, a.32M,1.bUn,7U-17e日15-3Q日e4 A06A5 Sd/ Tetrachlorabiphengl DATA:A06A5



Figure A-5

Figure A-6
L- $\forall$ ondily



Figure A-8


Flgure A-S


Figure A-10


F
$\dot{8}$
0
高
B

SAMPLE: S,SAM,DIR, 32491,2/PCH FISH 2ul ind
COND: 30M, 0.32MM,1.8UM,70-178015-30004 DATA:A86A5 01/07/93 0814


Figure A-12


Figure A-13


Figure A-14


[^0]:    "Based on the foregoing, a slope factor of 7.7 was applied to all striped bass samples having an overall level of chlorination of approximately $60 \%$. Striped bassisamples with lesser chlorination were not assumed to represent a cancer hazard."

[^1]:    ${ }^{1}$ Erickson, M. D., Analytical Chemistry of PCBs, Lewis Publishers, Inc. (1992).

[^2]:    - 1,000 $\mu \mathrm{L}$ added to 20 g Control Spike and Matrix Spike Fish Samples.
    - Balischmitter No. 199, IUPAC No. 200, all other congeners shown have the same Bellschmiter and IUPAC No.

[^3]:    - ND= Not delected. Value in perentheeest to oalouided detcetton Mrin based on foweot calthretton atandard.

