ABSTRACT

Title of Document: SOURCES OF POLYCHLORINATED BIPHENYLS TO MARYLAND FISH.

Daniel Patrick Liebert, Master of Science, 2006

Directed By: Professor Joel E. Baker, Marine Estuarine Environmental Sciences

Polychlorinated biphenyl congeners were measured in 520 composite fish tissue samples collected from Maryland between 1999 and 2004. Thirty-six species were sampled from 190 sites. PCB concentrations in fish tissues were compared across taxa, regions and to Maryland fish consumption advisory levels. A multivariate analysis of PCB congeners in 126 white perch and 94 channel catfish from diverse locations was used to investigate patterns of PCB transport. The greatest PCB concentrations were measured in channel catfish from the Patapsco (1770 ng/g wet) and Potomac Rivers (1770 ng/g wet), the northern Chesapeake Bay (1000 ng/g wet), the Chesapeake and Delaware Canal (850 ng/g wet), and in carp from Back River (1400 ng/g wet). PCB congener patterns varied spatially and reflected local PCB sources. Congener signatures were used to map the contamination associated with each PCB source region. Apparent congener transport distances correlated positively with hydrophobicity and negatively with volatility.

SOURCES OF POLYCHLORINATED BIPHENYLS TO MARYLAND FISH

By

Daniel P. Liebert

Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Master of Science
2006

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Professor Joel E. Baker, Chair
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Preface

This work is an outgrowth of my involvement in the Maryland Department of the Environment's (MDE) Fish Tissue Monitoring Program (FTM). I was enlisted as a Faculty Research Assistant under Joel Baker at the Chesapeake Biological Laboratory to measure PCBs and pesticides in fish from the Potomac River. This happened as concerns about PCB contamination in fish around the Quantico Marine Base grew and as the FTM program was revitalized after the loss of state laboratory services. Since then, FTM has evolved into an expansive, well-funded and pro-active program addressing human health concerns related to contaminants in fish tissue throughout the state. The role of Chesapeake Biological Laboratory has grown as well, now sometimes analyzing hundreds of fish samples from Maryland waters each year. Here, I summarize the first five years of polychlorinated biphenyl (PCB) data from FTM. This report can not convey to the reader a full appreciation for the original data. There are many aspects of the data and many other contaminants to be investigated, but I try to address just a few points. In the second year of our involvement with FTM I noticed that tissues from the Chesapeake and Delaware (C&D) Canal had a distinctly different pattern of PCB congeners than Potomac River fish and that this different C&D Canal pattern changed gradually over distance from the Delaware state line. It has since been my intention to use the FTM data for the thesis I present here, specifically that PCB congener patterns in fish are derivative of sources local to the fish's site of capture and that PCB congener patterns in fish are spatially consistent enough to be used to trace patterns of PCB transport throughout Maryland waters.

Acknowledgements

If it were not for the hard work of two men, I would not have had any of the data presented here. Charlie Poukish and Chris Luckett of the MDE were responsible for collecting most of the samples in this study. Charlie and Chris were always a pleasure to work with, and I often benefited from Chris' ecological insights. It has also been my pleasure to work with Joe Beaman, who has been the administrator for the Fish Tissue Monitoring program for several years and has organized the annual sampling efforts. I also received help in the wet lab from Eileen Beard, Taylor Woodburn, Jana Siskind, Kristy Richardson, Andy Stephenson, Kristlyn Araujo, among others. And, Dave Secor, Troy Gunderson, Stephen Larsen, and Scott McGuire all helped me by showing me how to sex eels and catfish, and extract otoliths. Chris Rowe was always available to share his thoughts, bounce ideas off, and to share some great musical selections. To many dear friends at the Chesapeake Biological Laboratory I owe thanks for brightening my days there. Finally, I owe a debt of gratitude to my employer of many years and my advisor, Joel Baker, who has allowed me to pursue this thesis project and has supported me financially and academically throughout the process.

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Chapter 1: Overview of the Data and Analytical Objectives

The Maryland Department of the Environment's Fish Tissue Monitoring Program (FTM) samples fish tissue from the Maryland waters on a 5-year cycle to recommend consumption rates of fish caught in the state. The polychlorinated biphenyl (PCB) data presented here are from one such 5-year sample period. The data encompass 35 species sampled from all of the major waterways and regions within the state. Over 500 fish tissue samples were analyzed for 86 PCB chromatographic peaks. Two estuarine species accounted for approximately 40% of these samples; they were channel catfish (94 samples) and white perch (126). This dataset provides powerful means to investigate the accumulation of PCBs in fish and the distribution of PCBs in Maryland waters. In this thesis, total PCB data were analyzed among species, among habitat use types (freshwater, saltwater, estuarine), among sites (geographically), and with regard to ancillary parameters such as lipid content. Patterns of PCB congeners in white perch and channel catfish were used as proxies for environmental patterns to analyze the spatial distribution of PCBs from different sources.

The ultimate objective of this thesis is to use PCB congener patterns in fish to investigate the distribution of PCBs around source locations. To meet this objective, broad-scale geographical trends in total PCB concentrations in fish were first examined to establish the importance of PCB source locations. Concentrations of PCBs may correlate spatially with known sources; however, undocumented disposal sites and non-point sources are also expected to influence PCB spatial trends. Also, since most PCB sources are historical and evident only in residual plumes of contamination, source locations are

best defined as where elevated concentrations occur in sediments, rather than where historical disposal has been documented. PCBs can migrate from their original locations and accumulate in sedimentary sinks where they are then available for bioaccumulation by aquatic biota. Such historical sinks function as current sources of PCBs to fish. While spatial gradients in fish tissue PCB concentrations may be used to discern source locations, the variation in PCB congener composition among PCBs from different sources may be used to discriminate the sources of PCBs to fish throughout the estuary. The analysis of total PCBs and congeneric composition of PCBs was combined to determine the source locations and the regions of influence of each source.

Was this an appropriate application of the Fish Tissue Monitoring data set? Monitoring of sediment and water is generally conducted to assess the potential exposure of aquatic organisms to xenobiotics. Such monitoring is usually conducted to ascertain the spatial distribution of contaminants and hence the spatially differentiated exposure regimes of aquatic species. A limitation of this approach is that environmental contamination, especially of sediments, can be spatially heterogeneous on a small scale. In a Fish and Wildlife Service study of PCBs in Potomac River, concentrations of PCBs at adjacent sites less than 100 meters apart differed up to 16 fold in the Quantico Embayment (Pinkney et al., 1995). An inventory of PCBs in Baltimore Harbor sediments (Ashley and Baker 1999) did not show the same degree of small scale variation seen in Quantico Embayment but did show variation of greater than one order of magnitude within areas comparable to the homeranges of residential fish species like white perch, *Morone americanus*. Therefore, typical coarse-scale sediment sampling may not determine concentrations and spatial distributions of contaminants in aquatic

environments with sufficient accuracy to represent exposure of resident fish to PCBs. Biomonitoring with sentinel species, rather than direct measurement of water or sediment, is a direct measurement of wildlife exposure and avoids problems due to small-scale spatial heterogeneity (Ashley et al., 2000; Steinbacher 2001). An organism accumulates contaminants to which it is exposed throughout its homerange, and its contamination represents a spatially integrated (smoothed) measure of the contamination present in the region occupied by the organism. Spatially smoothed biomonitoring data may be less complex and variable than sediment data. Hence, it is not only appropriate but perhaps preferable to use the Fish Tissue Monitoring data set for the spatial analyses presented here.

There are, however, weaknesses to this approach. Factors aside from source composition affect the congeneric composition of PCBs in the environment and in organisms. These factors can be broken down into the effects of physical properties on geochemical cycling and on bioaccumulation. The 209 PCB congeners have between one and ten chlorines and following this continuum of molecular weight are continua of hydrophobicity, lipophilicity, and volatility. Hydrophobicity and lipophilicity increase with molecular weight, while volatility decreases (Figure 1). In effect, lighter congeners are more prone to aqueous dissolution and subsequent volatilization. Therefore, lighter congeners are removed from estuarine water and sediment more rapidly than heavier congeners. Conversely, heavier congeners' greater hydrophobicity and lower volatility lead to their greater conservation as particle-bound contaminants within estuaries.

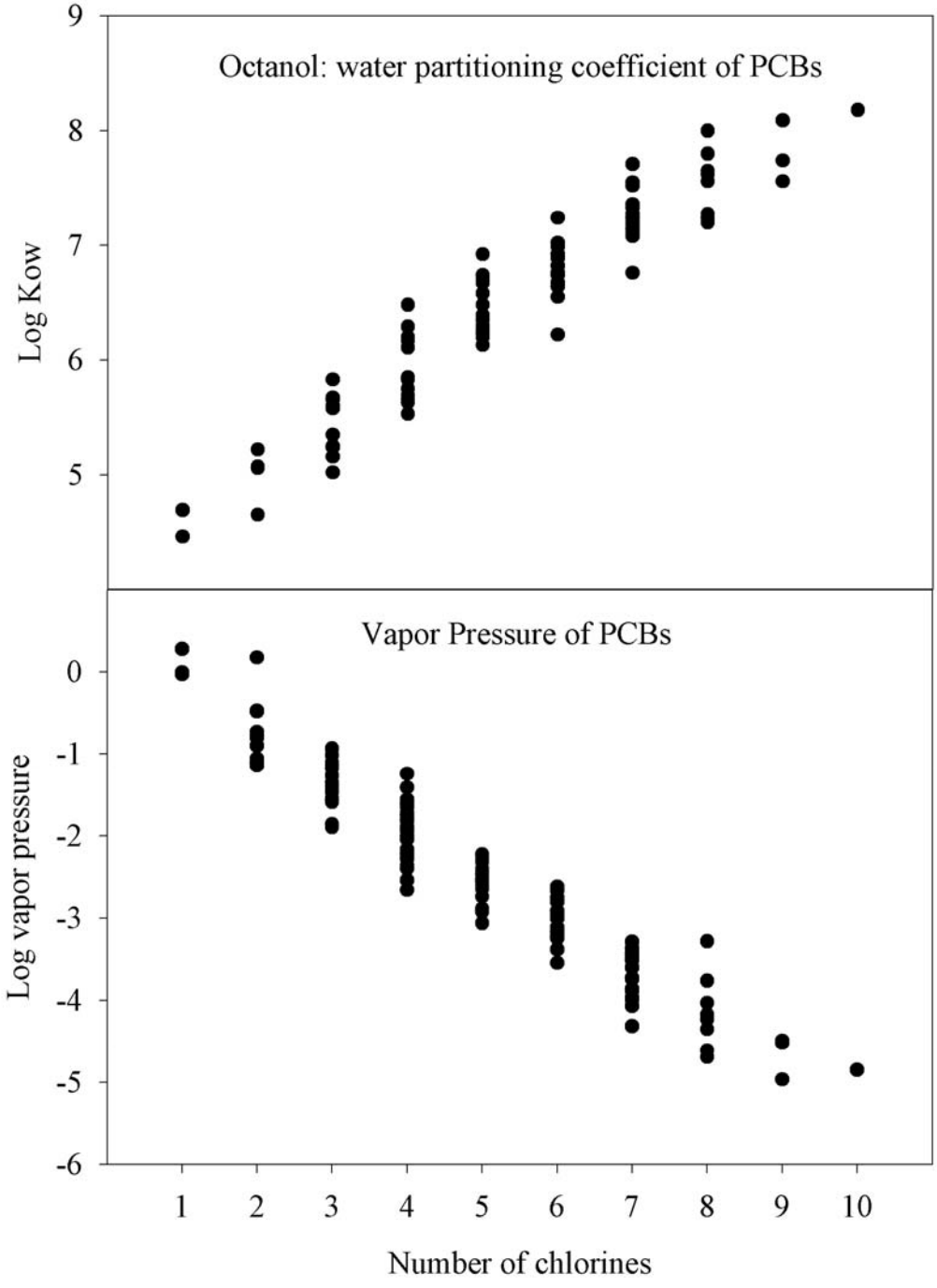

Figure 1. Physical Properties of PCBs measured in this study.

Similar partitioning takes place within the organism. The greater aqueous solubility of lighter congeners makes them more bioavailable in the gut of the fish, but their lower lipophilicity makes them less bioaccumulative. Heavier congeners' lower aqueous solubility and greater lipophilicity makes them less bioavailable but more bioaccumulative. The result is that assimilation efficiency of PCBs is a parabolic function of the number of chlorines, or the octanol-water partition coefficient (Kow), with moderately chlorinated congeners at the apex (Gobas and McCorquodale, 1992).

Realized bioaccumulation of PCB congeners is mitigated by losses after initial assimilation, which are greater for lighter congeners because of their greater solubility in blood and in the aqueous environment. Consequently, selective depuration of lighter PCB congeners may confer a heavier PCB congener pattern to an organism than that found in its environment (as in de Boer et al., 1994). Metabolism of certain PCB congeners has been observed in some fish species (Brown 1992, Stapleton *et al.*, 2001) and is anticipated to affect congener patterns in fish tissue. The analysis of congener patterns presented here focuses on individual species in part to minimize effects of interspecies variability of metabolism. Use of individual species for the spatial analysis was also intended to minimize the variability in PCB congener patterns that results from species' differences in exposure that result from varying trophic position (Harding et al., 1997), movement (e.g. Ashley et al., 2003), and feeding preferences. The many factors affecting transport and bioaccumulation added a layer of complexity to the data used here.

The first goal of this thesis was to summarize data from Maryland Department of the Environment's Fish Tissue Monitoring Program in terms of total PCBs to identify the

relevant areas and species and to describe the spatial distribution of PCBs in Maryland fish. After identifying areas of concern—those with the greatest concentrations which appear to be the sources of PCBs, PCB congener patterns were analyzed. Congener pattern signatures were derived for each PCB source region, and the occurrence and influence of each source signature were evaluated spatially. Delineation of the spatial influence of each source was attempted in this way.

It would be ideal if the signature for one PCB source would decrease with distance from the source uniformly so that as total PCB concentration decreased the concentrations of congeners would also decrease in equal proportion to one another. The signature pattern for a PCB source would be conserved. If this were the case then PCBs from a source could be identified by the source's signature at great distances from the source. If two or more sources were present then one source signature would always be dominant (nearest to its point of origin) up to the point that it was only equally as prevalent as the signature of another source or sources. Beyond that point, the prevalence first source signature would continue to decrease while another source signature would increasingly dominate the observed PCB pattern as that source is approached. If these sources had equal masses available for redistribution and had equal amounts of redistribution between the two sources, then the point at which the two source signatures contributed equally to the observed PCB pattern will be at the midpoint between the two sources.

Since conditions are not likely to be so simple, it will be more realistic to expect the point at which the sources contribute equally to the observed PCB profile will be closer to the lesser source and to the source with the lesser outward transport. It may also

be expected that widely distributed PCBs from a great enough source may eclipse lesser PCB sources, disguising their signature congener patterns and their presence altogether. Since PCB congeners will not be transported equally, even the use of signature patterns as a measure of the influence of sources will be troublesome. For example, if high molecular weight PCBs are the signature of a source, these PCBs will be more tightly bound to sediments than lower molecular weight PCBs and this heavy weight signature might be redistributed less than the lighter PCBs from that source. It is possible the lighter PCBs will be distributed more widely by dissolving in water. Regardless of the scenario, the congener pattern, as a combination of congeners with a wide spectrum of physical properties will not be conserved through this process. The pattern observed in bioaccumulated PCBs in fish tissue exposed to contaminated water and sediment will be further corrupted from the original source signature. The hypothesis of this study was that a spatial analysis of PCB congener patterns in fish tissues can elucidate the distribution patterns of PCBs in Maryland waters. The greater challenge here, rather than analyzing congener patterns to better understand dispersal patterns of PCBs, was to interpret the weathering of PCB congener patterns as PCBs pass through the environment.

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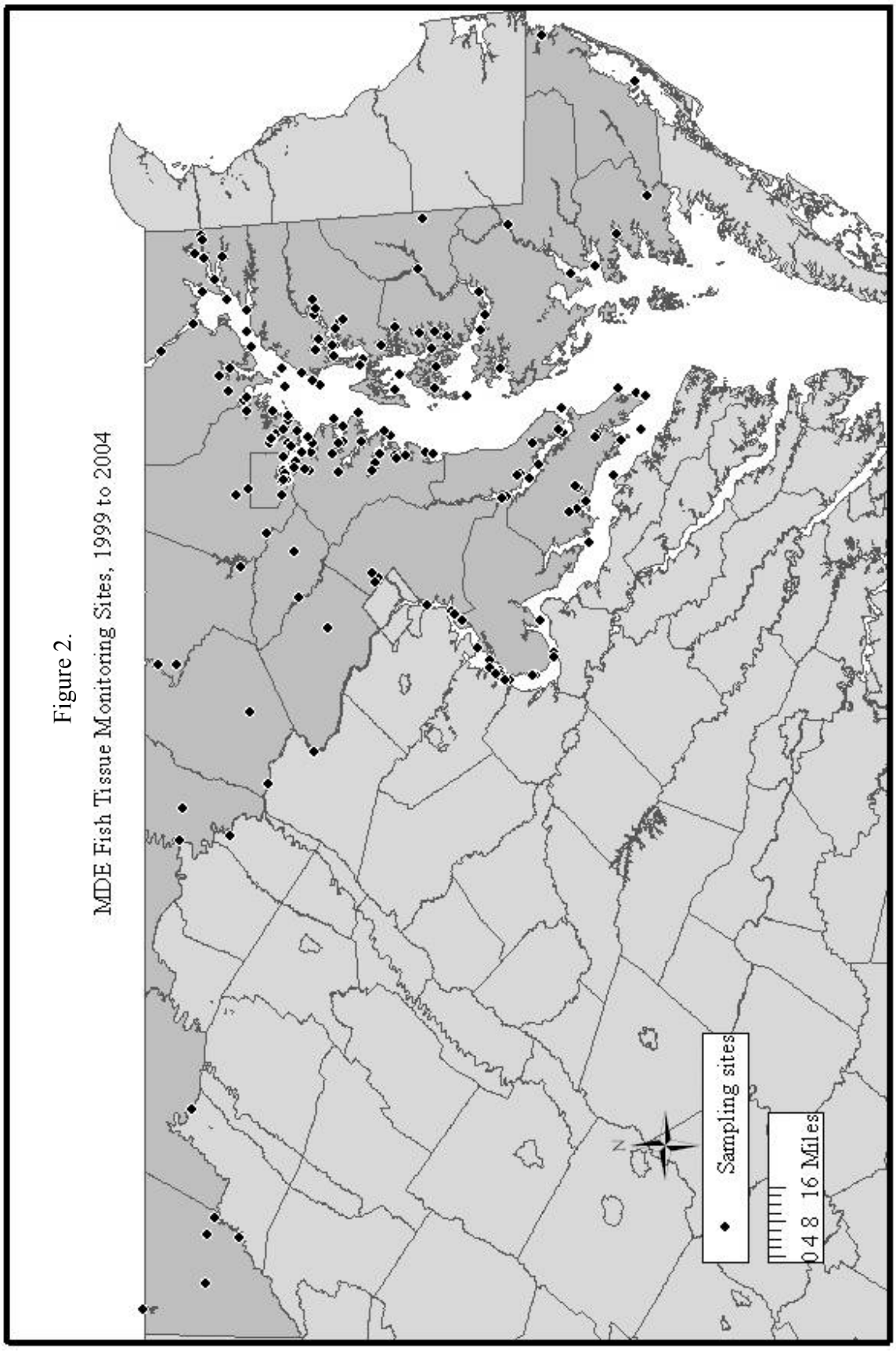
Chapter 2: Methods

Sample Collection

Monitoring efforts targeted bottom-feeding and predator species according to EPA guidance (USEPA, 2000); though, species were collected based on what could be caught at each site. Sufficient numbers of fish were sought to provide at least one five-fish size-segregated composite for each species at each site. Between one and ten samples were taken from each site (Figure2). Fish were collected between February 1999 and November 2003. Collection methods included otter trawl, trot line, hook and line, electroshocker, trap and seine. Maryland Department of the Environment (MDE) was the primary sampling agency. Striped bass were collected in a cooperative effort of the MDE and Maryland Department of Natural Resources (DNR). Supplemental samples of white perch were provided by the Smithsonian Estuarine Research Center (SERC) during 2002 and 2003. Fish sampling was conducted by the MDE primarily in fall but continued throughout the year as required to meet sampling goals. The species, weight and length of each fish were recorded in the field. The fish were individually wrapped, labeled and transported on ice to the Chesapeake Biological Laboratory. The MDE's Fish Tissue Monitoring Program collected 32 composite fish tissue samples for PCB analysis from 18 sites on the Potomac River, Chesapeake and Delaware (C&D) Canal and Elk River in 1999. In 2000, the MDE collected 121 composite samples from 46 sites in the C&D Canal watershed, northern and western Chesapeake Bay tributaries, Back River, and shellfish monitoring stations throughout Maryland tidal waters. One hundred thirty-eight

Figure 2.

MDE Fish Tissue Monitoring Sites, 1999 to 2004



samples were taken from 50 sites in 2001. Year 2001 samples came from the Patapsco River and its tributaries, western Maryland reservoirs streams, and northern Chesapeake Bay tributaries. In 2003, 145 samples were collected from 44 sites located on tributaries and open waters of Chesapeake Bay, reservoirs in eastern Maryland, and the Potomac and Patapsco Rivers. Eighty-four samples were collected from 32 sites during 2003. These samples came from the non-tidal Potomac River and its tributaries, Maryland's coastal bays, and tributaries and open waters of Chesapeake Bay, and the non-tidal Pataspco River. Most samples were collected September and October of each year (Figure 3). The primary exceptions to fall sampling were white perch collected by the Smithsonian Estuarine Research Center in July and August and striped bass collected during the April spawning run.

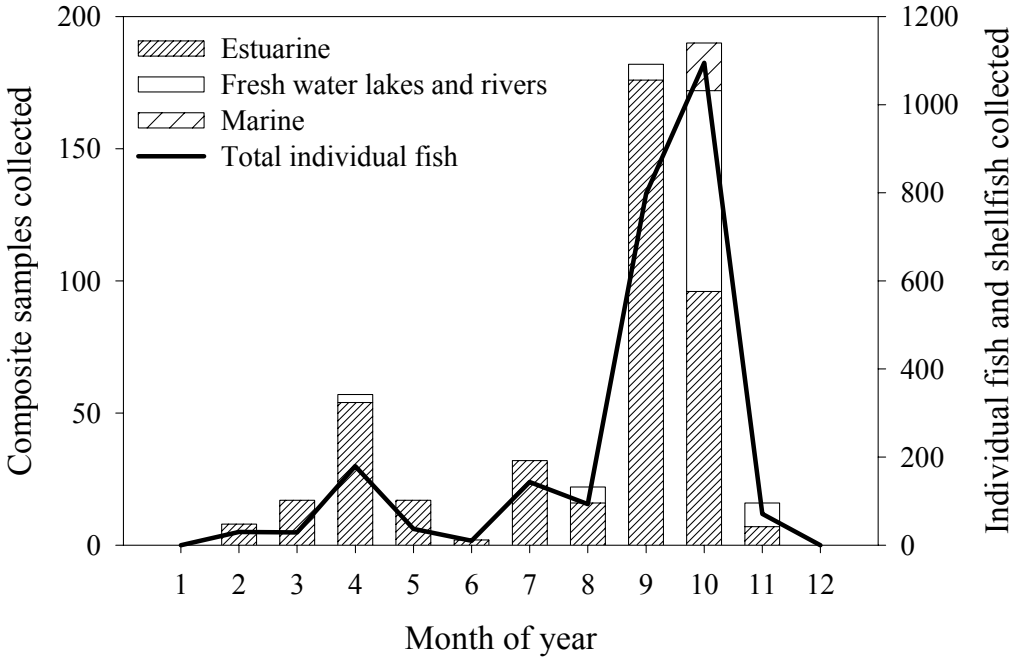


Figure 3. Distribution of sample collection by month of year. Samples were collected between February of 1999 and November of 2003.

Sample preparation

Sample preparation was performed following U.S. EPA recommendations (USEPA, 2000) as closely as possible. Fish were stored at 4°C and processed within 48 hours or were stored at -20°C and processed within 12 months of collection. Fish were filleted at CBL under clean conditions with a stainless steel knife on a glass cutting board wrapped in aluminum foil. All fish except catfish, freshwater game fish, and eels were scaled and filleted with the bellyflap and skin included. The skin and bellyflap were excluded from catfish filets as this is how they are prepared for market sale. Likewise, the skin and bellyflap were excluded from freshwater gamefish following the common practice of recreational fishermen.

One filet from each fish was weighed and diced into 1 cm^2 or smaller pieces. The second filet was removed intact, wrapped in aluminum foil, and archived frozen (-20ºC) for possible future analysis. Smaller fish that did not yield enough tissue for efficient homogenization had both filets homogenized together. For larger fish, individual filets were homogenized and archived in jars with Teflon-lined screw lids instead of archiving the whole second filet. Blue crab muscle and hepatopancreas were removed separately. Oysters were shucked (25 individuals per composite) and all tissues and liquor were collected into a single clean vessel, weighed and homogenized.

When insufficient numbers of fish were caught for compositing, individual fish samples were analyzed. Some individuals were also analyzed to assess the variability of concentrations among individuals. Otherwise, subsamples of the diced or homogenized filet tissue from several individuals from each site and size class were weighed in equal

portions, combined, and homogenized again using either a Black and Decker Handy Chopper (model HC 20) or a Hamilton Beach food processor (model 702 R) to form composite filet tissue samples. The individual fish for each filet tissue composite were chosen based upon the length and weight of each fish of a particular species caught at a site. Size segregation was based on both length and weight; however, length was the overriding factor. The smallest fish in each composite was at least 75% as long as the largest fish in each composite. Blue crab tissues were composited using equal portions of either muscle or hepatopancreas from each individual as with fish tissues. The concentration of a contaminant in a composite tissue sample reflects an arithmetic average of the concentrations found in the composited individuals if equal masses of each individual are composited. The composites, filets, and archivable homogenized tissue from individual filet samples were put in glass jars with Teflon-lined screw lids or wrapped in aluminum foil and stored at –20ºC.

PCB Analysis

Approximately five grams of wet, homogenized tissue from each composite or individual sample were analyzed for PCB congeners using standard methods (Ashley and Baker 1999). Briefly, wet tissue was dried by grinding with anhydrous sodium sulfate and Soxhlet extracted for 24 hours with dichloromethane. The extract was concentrated to approximately 4 ml. A 0.5 ml aliquot was removed for gravimetric lipid analysis in which lipids were measured as dichloromethane-extractible nonvolatiles. Lipids were removed from a 1 to 2 ml aliquot by gel permeation liquid chromatography. This subsample was eluted through two Phenomonex Phenogel 10u 100A (P.N. 006-0642-PO)

columns in series at a rate of 5 ml/min in dichloromethane, and the 19-30 minute time fraction was collected. The resulting elutant was solvent exchanged into hexane, concentrated to 1 ml and fractionated on a Florisil liquid-solid chromatographic column, which isolated PCB congeners and organochlorine pesticides in two successive elutants. Florisil (JT Baker, 60-100 mesh) was activated by baking at 550^{o}C in an open borosilicate container for at least 4 hours then deactivated by adding 2.5% by mass deionized water and shaking vigorously in a sealed container for 15 minutes. Eight grams of deactivated Florisil was poured atop a glass wool plug in a ~1cm diameter solid chromatography column and capped with a ~1 cm layer of anhydrous sodium sulfate. The column was preeluted first with 35 ml of a 50:50 mixture of dichloromethane and petroleum ether then with 35 ml of petroleum ether. After quantitative transfer of the sample to the column, the PCB fraction was eluted with 35 ml petroleum ether, collected, solvent exchanged to hexane and concentrated to approximately 1 ml for analysis.

PCB congeners were identified and quantified by high resolution gas chromatography with electron capture detection on a Hewlett Packard 5890 GC with a 60 meter by 0.32 mm DB-5 column with a 0.25 um film thickness. In this method, which is based on that developed to quantify PCBs in Great Lakes biota by Mullin and co-workers (Mullin 1985), a mixed standard of three Aroclors is used to calibrate the instrument. The electron capture detector was calibrated using two internal standards (PCBs 30 and 204). PCBs were identified by their retention times relative to the two internal standards, using the relative retention times previously published (Mullin et al. 1984). Eighty-six chromatographic peaks were quantified. Some of these peaks contain one PCB congener,

while many are comprised of two or more co-eluting congeners. Total PCBs (119 congeners) are reported as the sum of the concentrations of the 86 PCB congener peaks.

Quality Assurance

Extensive measures were taken to evaluate the quality of the Fish Tissue Monitoring Program PCB data. With each annual batch of samples, a series of matrix blanks, matrix spikes, Standard Reference Materials (SRMs) and replicate samples were analyzed. Also, surrogate PCB congeners were added to each sample prior to extraction. Blanks were analyzed to determine that PCBs measured in samples were native to tissue samples and did not originate in sample processing. Surrogate PCB recoveries were measured to evaluate the overall efficiency of the extraction method. PCBs were quantified in matrix spike samples to evaluate the efficiency of the extraction method with respect to individual PCB congeners. To determine the accuracy of PCB analyses in this study PCBs were measured in SRM samples. Replicate samples were analyzed to determine that PCB measurements in this study were consistent and repeatable.

Blank samples of 60 g sodium sulfate were extracted and analyzed with samples to monitor for contamination that may have originated in the laboratory. Method detection limits were calculated for each PCB congener as the greater of either the mean blank mass for each instrumental run or the instrumental detection limit mass (based on minimum detectable peak area) multiplied by three and divided by the sample mass analyzed. This conservative detection limit calculation was used to strictly avoid over-reporting concentrations. Blank and minimum instrumentally detectable masses are summarized in Figure 4. PCB contamination in blanks was a combination of lighter

PCBs (indicating potential airborne PCB contamination in the laboratory) and of PCBs found in fish samples. Congener-specific detection limits were applied so that the measured mass of a PCB was only reported if it was greater than its method detection limit.

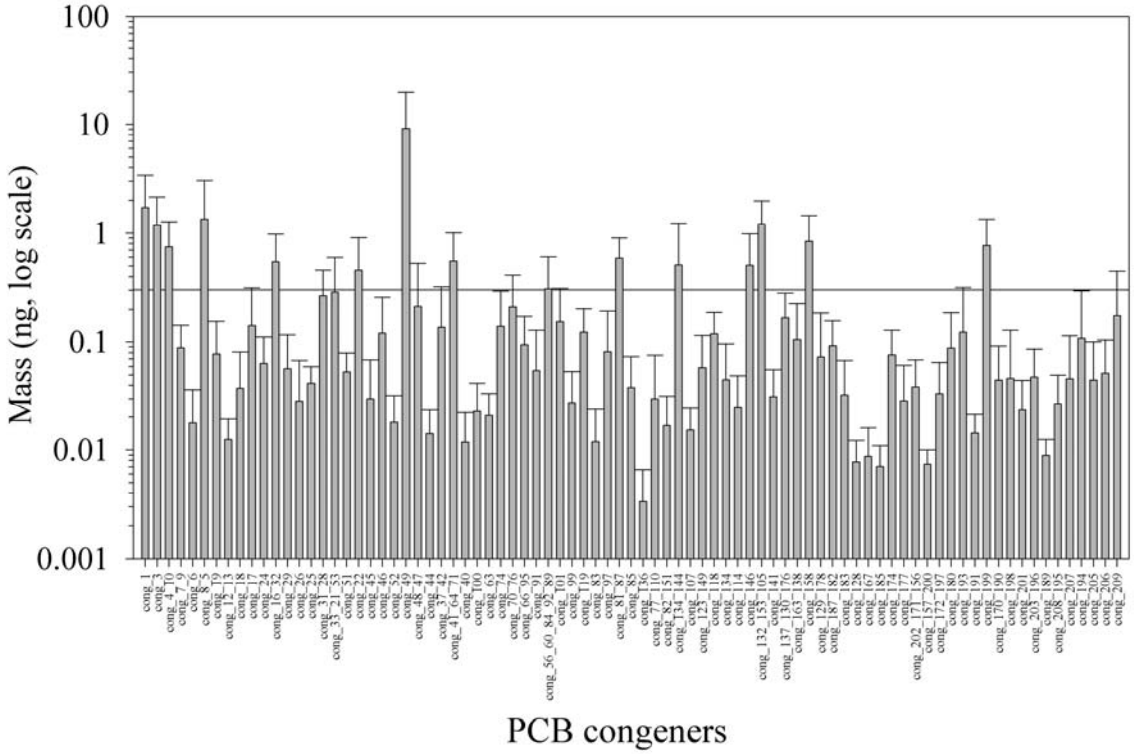


Figure 4. Masses of PCB congeners in blank samples or instrumental detection limit masses for the study. Error bars represent one standard deviation. The horizontal line represents the interannual mean of all congeners (0.301 ng).

To evaluate the recovery and accuracy of quantification of individual PCB congeners, samples fortified with known amounts of PCBs were analyzed. Spike samples consisted of a blank sodium sulfate matrix fortified with the varying amounts of the PCB quantification standard, and one or more of a cocktail of 31 pesticides, toxaphene and polybrominated diphenyl ethers. Results of these analyses showed generally good and consistent recoveries and accurate quantification of PCB congener

peaks. The slope (0.84) of the line fitted to PCBs recovered versus PCBs fortified in spike samples (Figure 5) indicates recoveries of individual congeners reflect losses during processing as indicated by the surrogate recoveries. A few congeners have consistently high recoveries. Congeners 51, 89, and 119 were regularly recovered at greater than 200%. Seven more congeners, 17, 29, 45, 135+144, 137+130+176, 158, and 199, were recovered, on average, at greater than 120%. Eleven congeners were recovered, on average, at less than 80%. Many of these fell just below 80% (congeners 1, 7, 29, 6, 25, 40,191) and only two (congeners 128 and 81+87) were recovered at as low as 50%. Most congeners with recoveries outside of target values (80 to 120%) make up a very small portion of total PCBs in fish tissue samples and have recoveries that may be explained by the large errors associated with integration of very small chromatographic peaks. Other off-target recoveries are explained by coelutant compounds. Congeners 89 and 81+87 coelute with pesticides also present in spike samples. Congener 89 is, as a result, erroneously over-quantified in spike samples. The congener 81+87 peak is resolved, and quantitation consistently errs conservatively for the PCB peak. It should be noted that masses of the coelutant pesticides in tissue samples are usually well below those in spike samples, and the erroneous recoveries suggested for these compounds do not apply to tissue samples in this study. Similarly, over-recovery of congener 199 may result from PBDE congener coelution. (See Appendix 1. for an index of persistent coelutant compounds). This contamination issue was intermittently evident in fish tissue samples and has been dealt with on a sample-by-sample basis. Recoveries of individual PCB congeners were satisfactory when taking into account the each congeners impact on total PCB values in fish tissue samples.

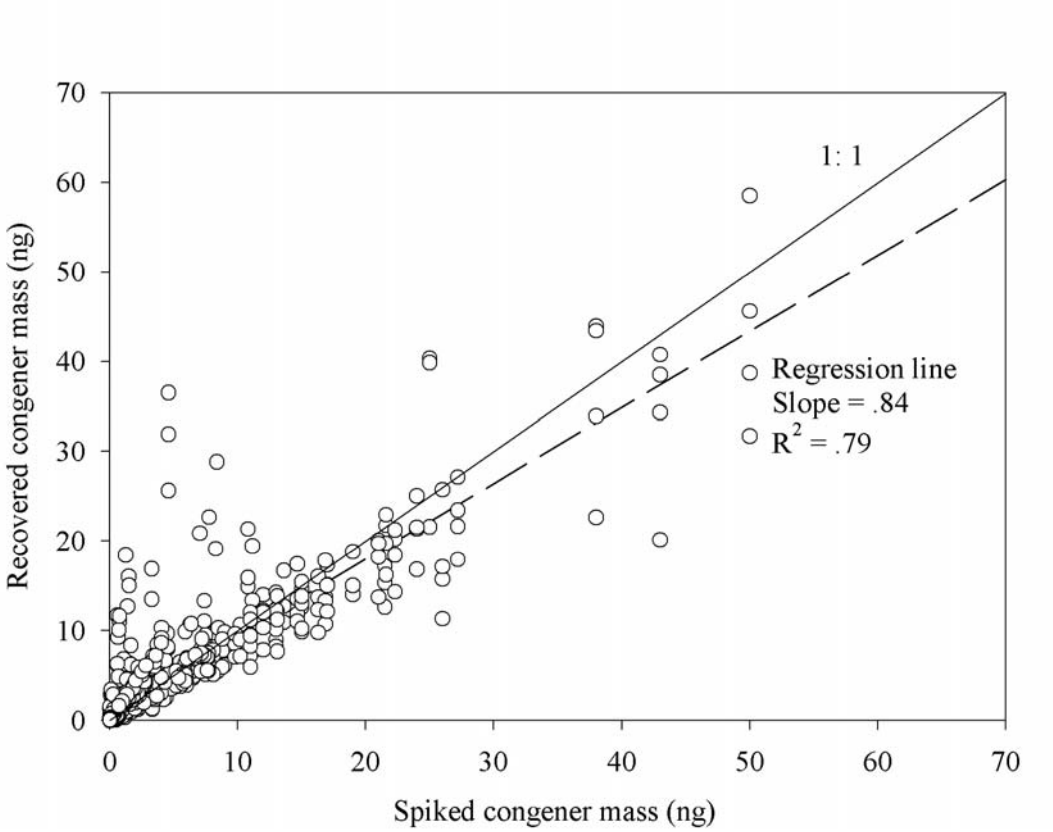


Figure 5. Recovery of PCB congeners in 11 spiked samples.

Three standard reference materials were used in this study. These were National Institute of Standards and Technology SRMs 1974a, Organics in Mussel Tissue, and 1946, Lake Superior Fish Tissue, and National Research Council Canada Certified Reference Material CARP-1. Measured concentrations in these reference materials had strong positive relationships with certified and reference values and were generally conservative measurements of the concentrations in these materials. Figure 6 shows the results from analyses of SRM analyses as percentages of total certified PCBs. The mean absolute biases in total PCB introduced by individual congeners were 1.0% in SRM 1946 and 2.9% in SRM 1974a. The cumulative percent errors in total PCB associated with the individual certified or reference congeners ranged -8.4 to -13.7% in SRM 1946 (n = 6), -

24.7 to -57.4% in SRM 1974a (n = 6), and 4.4 to 7.7% in CARP-1 (n = 3). Cumulative percent errors and scatterplots of individual congener recoveries (Figure 7) demonstrate the generally conservative nature of the PCB measurements presented here.

Measurements of SRM 1974a are biased low relative to certified and reference values; however, the high precision and persistent interannual repeatability of those measurements indicate the reliability of measurements of unknowns in this study. For the Canadian NRC CRM CARP-1, our results appear much more accurate. The maximum bias in total PCB introduced by error in the measurement of any one congener was +4.4% and the mean absolute bias in total PCB was 1.0%. SRM analyses do reveal problems with specific congeners. Congeners 49 and 66+95 had erratic recoveries in SRM 1946 and SRM1974, respectively. The intermittently occurring substantial over recovery of congener 49 and low precision of congener 66+95 measurements indicate the intermittent presence of coeluting interferants in these peaks. In one analysis of 1974a the error in measurement of congener 66+95 gave a 12.7% positive bias in total PCB. In one analysis of SRM 1946 the erroneous over-recovery of congener 49 introduced a 9.4% positive bias in total PCB. It is appropriate to use measurements of congeners 49 and 66+95 with caution.

Replicate analyses showed high consistency and repeatability of PCB measurements. Five duplicate and 12 triplicate analyses of unknowns and SRMs were used to assess the precision of PCB measurements. Most often, relative differences between concentrations in replicate samples were associated with differences in overall extraction efficiency as indicated by surrogate recoveries. In some cases, deviations from a slope of 1 without corresponding differences in surrogate recovery suggested

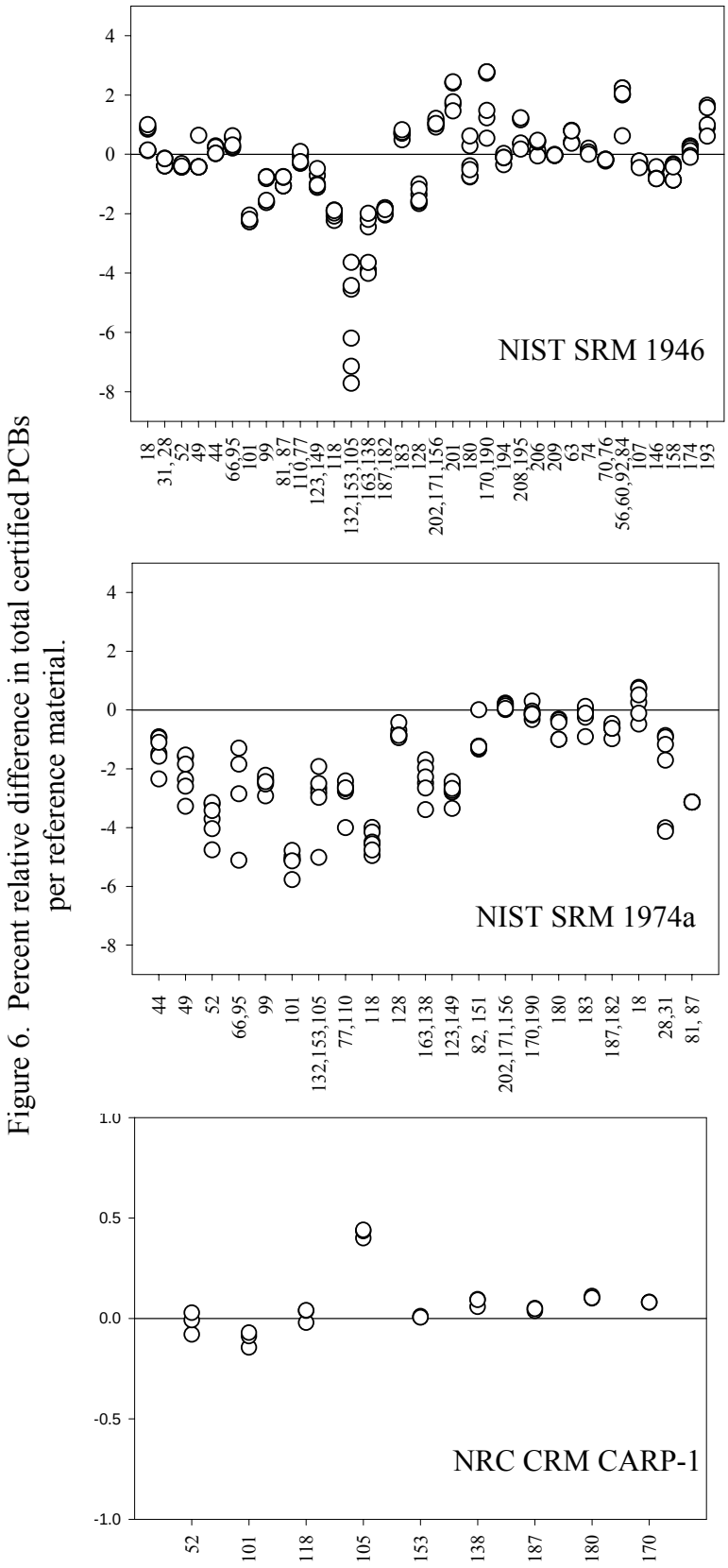


Figure 6. Percent relative difference in total certified PCBs per reference material.

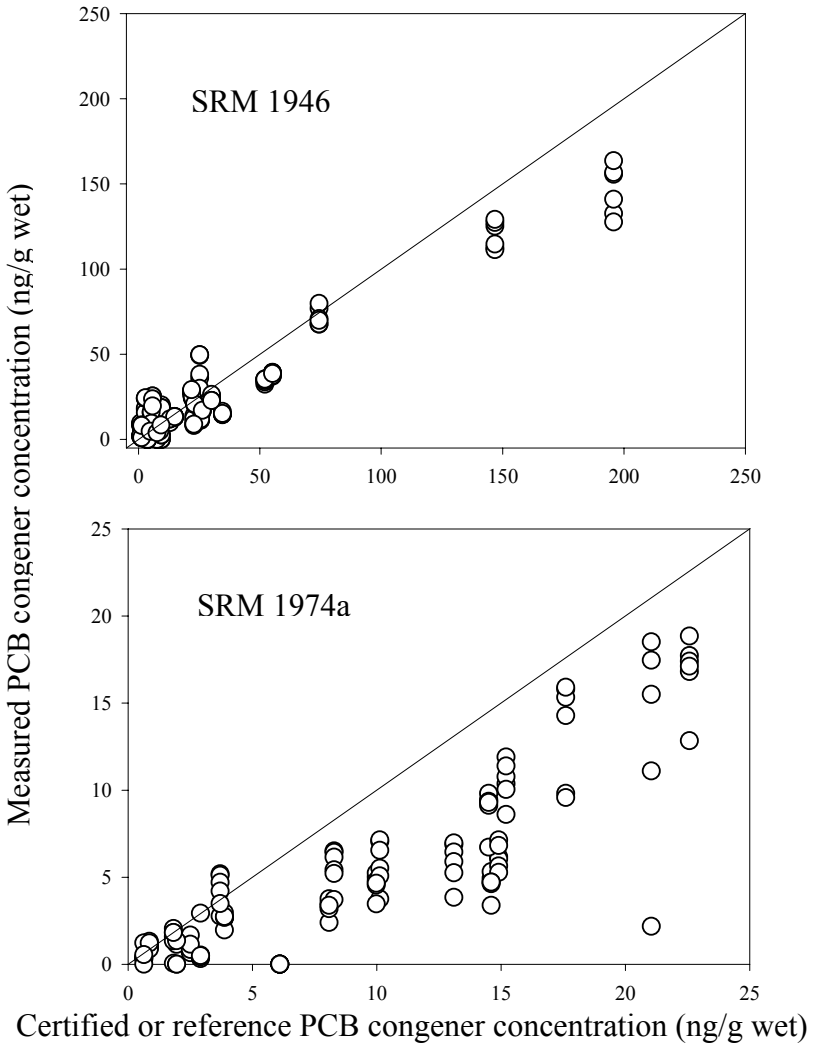


Figure 7. Recovered masses of PCB congeners in NIST reference materials.

incomplete homogenization of tissues. Replicate samples are compared in Figure 8, and regression statistics for these comparisons are in Table 1. These data show a strong 1: 1 relationship between replicate samples and demonstrate reliability and precision. Because one of the ultimate goals of this study was to perform a multivariate analysis that requires precision error estimates for individual data points, relative percent differences from replicate means were calculated for each congener in each sample it was detectable. The mean relative percent differences for each congener in each group of replicates were

then averaged for all groups in which congeners were detected. These data, presented in Table 2, are the mean percentage errors that may be expected for individual congener measurements. The percent errors of individual congener measurements average 11 ± 3.2% and range from 5.8 to 22%. Only congeners 19 and 26 had mean percent errors in excess of 20%. These relatively high errors result from the fact that these congeners are usually present in very low concentrations which make their chromatographic peaks small and magnify the effects of minor differences in integration.

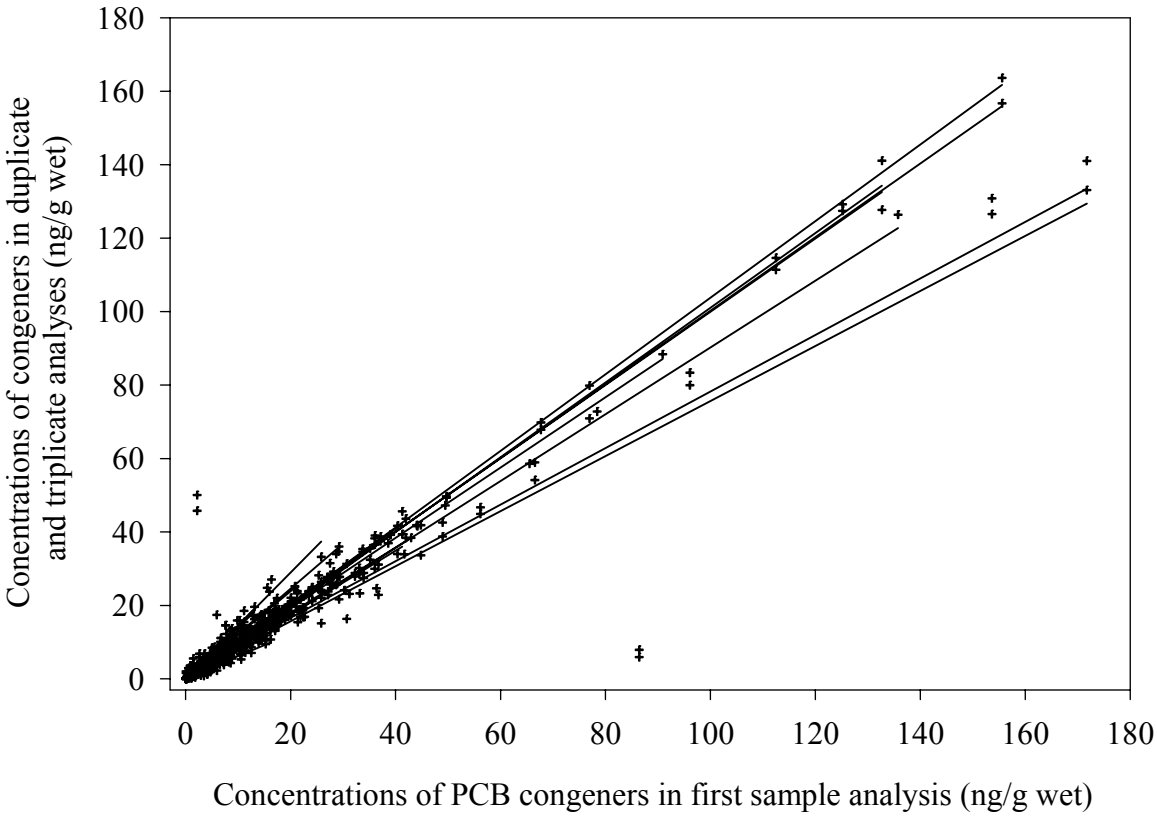
Estimating health risk

The data presented here were collected in an effort to assess human heath risks associated with fish consumption in Maryland. MDE risk-based consumption levels are based on the U.S. Environmental Protection Agency risk assessment guidance (USEPA, 2000). The data are presented in the context of the risk-based consumption levels outlined in Table 3. While the MDE recommends no consumption of fish when concentrations exceed the six-meal-per-year range and unlimited consumption when concentrations are below the eight-meal-per-month range, those consumption levels are expanded here to more explicitly represent the data.

Statistical methods

Relationships between total PCB and lipid content, length, sex, and day of year (i.e., season) were examined for each species within regions and with all regions pooled using Spearman's test for correlation and Hoeffding's test for independence. Results and

Figure 8. Composite plot of duplicate and triplicate analyses of PCBs in fish.



significance levels for Spearman's and Hoeffding's tests agreed in every case and every Spearman test result presented here has a complementary Hoeffding result. Kruskal-Wallis tests were used to identify inter-regional differences in the variables of interest. These tests were performed primarily to identify differences that would warrant normalization of t-PCB by the variable in the case that the variable had a significant effect on t-PCB concentrations. A post-Kruskal-Wallis nonparametric Tukey's Honestly Significant Difference test (HSD) was used for multiple comparisons (Higgins, 2004).

Table 1. Regression statistics for PCB congeners measured in pairs of SRM and unknown tissue matrices.

Sample Matrix	Replicate type[a]	Replicate group[b]	Regression statistics	
			Slope	R^2
Channel catfish	D	1	0.89	1.00
	D	2	0.96	0.99
	D	3	0.91	0.99
	D	4	1.18	0.98
	T	4	1.05	0.98
White perch	D	5	1.03	0.95
	T	5	0.87	0.96
	D	6	0.60	0.90
	T	6	0.75	0.94
SRM 1946	D	7	1.00	1.00
	T	7	1.04	1.00
	D	8[c]	0.90	0.75
	T	8[c]	0.77	0.91
	D	9	1.00	1.00
	T	9	1.02	0.99
SRM 1974a	D	10	1.47	0.98
	T	10	1.40	0.95
	D	11	0.96	0.31
	T	11	0.89	0.32
Striped bass	D	12	1.45	0.98
	T	12	0.97	1.00
Spot	D	13	0.92	0.89
	T	13	0.68	0.88
Oyster tissue	D	14	1.09	0.95
	T	14	0.95	0.98
Largemouth bass	D	15	0.99	0.99
	T	15	1.23	0.99
Redbreast sunfish	D	16	0.88	0.95
Fallfish	D	17	0.84	0.88

[a] Sample type designates duplicate (D) or triplicate (T) samples paired with the first extraction of the respective sample.
[b] Replicate group designates a group number for extractions of the same sample material.
[c] These sample were not used for assessment of SRM results because the homogeneity of this matrix was compromised.

Table 2. Mean relative percent differences from means of duplicate and triplicate analyses of PCBs in fish and shellfish tissues[a].

PCB congeners	N[b]	Mean RPD[c]	PCB congeners	N	Mean RPD
cong_1	7	15.5%	cong_85	11	7.78%
cong_3	2	8.67%	cong_136	16	10.9%
cong_4_10	4	13.6%	cong_110_77	17	6.96%
cong_7_9	7	9.93%	cong_82_151	17	10.4%
cong_6	14	12.6%	cong_135_144	9	6.21%
cong_8_5	9	9.99%	cong_107	16	13.1%
cong_19	8	21.0%	cong_123_149	17	7.05%
cong_12_13	14	12.7%	cong_118	16	8.43%
cong_18	16	9.92%	cong_134	5	14.9%
cong_17	14	9.77%	cong_114	14	13.8%
cong_24	4	12.0%	cong_146	10	7.64%
cong_16_32	12	10.5%	cong_132_153_105	17	5.83%
cong_29	8	11.5%	cong_141	14	12.4%
cong_26	11	21.6%	cong_137_130_176	10	6.35%
cong_25	10	12.0%	cong_163_138	17	8.01%
cong_31_28	10	13.3%	cong_158	7	7.75%
cong_33_21_53	13	11.1%	cong_129_178	16	13.4%
cong_51	11	17.0%	cong_187_182	16	7.02%
cong_22	7	13.5%	cong_183	17	12.7%
cong_45	16	9.36%	cong_128_167	16	11.3%
cong_46	8	16.5%	cong_185	13	9.69%
cong_52	17	7.52%	cong_174	14	7.21%
cong_49	10	12.7%	cong_177	16	9.42%
cong_47_48	14	6.86%	cong_202_171_156	17	9.82%
cong_44	16	10.8%	cong_157_200	16	11.6%
cong_37_42	15	7.49%	cong_172_197	14	10.6%
cong_41_64_71	11	8.42%	cong_180	14	8.06%
cong_40	15	6.84%	cong_193	15	10.7%
cong_100	15	9.29%	cong_191	15	18.7%
cong_63	12	13.4%	cong_199	6	11.7%
cong_74	15	8.53%	cong_170_190	16	10.47%
cong_70_76	14	9.44%	cong_198	12	14.8%
cong_66_95	17	13.6%	cong_201	15	9.62%
cong_91	15	12.9%	cong_203_196	13	9.77%
cong_56_60_92_84_89	16	16.1%	cong_189	14	11.5%
cong_101	17	6.45%	cong_208_195	15	9.42%
cong_99	17	6.73%	cong_207	13	9.96%
cong_119	6	8.51%	cong_194	15	11.7%
cong_83	15	11.4%	cong_205	10	10.1%
cong_97	15	10.3%	cong_206	13	10.7%
cong_81_87	6	10.6%	cong_209	13	9.58%

[a] These data were developed for use in Chapter 4 of this thesis. Some congeners were excluded because of batch-specific non-detection and several congeners were merged into groups in order to create interannually comparable data sets.
[b] Number of replicate groups used in calculation.
[c] Weighted (duplicate, 1/2; triplicate, 1/3) mean relative percent difference from replicate group means.

Table 3. Maryland Department of the Environment recommended fish consumption levels.

Recommended meals	Children	Women	General population
	Fish tissue PCB concentration (ng/g wet)		
16/ month	6	8	10
8/ month	13	17	20
4/ month	26	33	39
3/ month	35	45	52
2/ month	52	67	78
1/ month	104	134	156
6/ year*	208	267	313
4/ year	311	401	469
3/ year	415	534	626
2/ year	623	802	939
1/ year	1246	1603	1877

*The MDE recommends no consumption when tissues exceed the six-meal-per-year concentration range.

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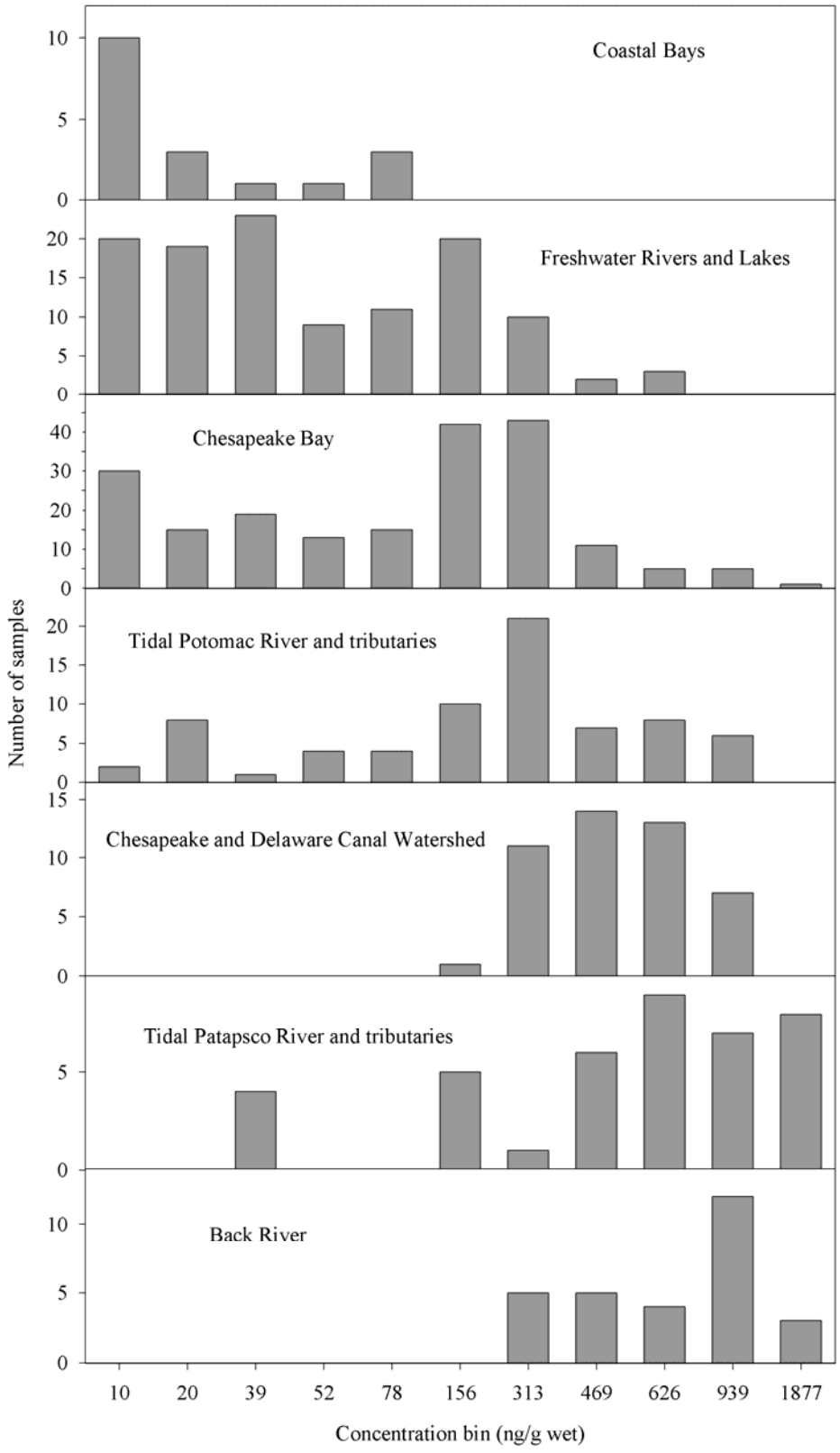
Chapter 3: Total PCBs in Maryland Fish Tissues

Results

Ancillary data for the 520 fish samples presented here include species, the number of fish per composite sample, the average sex of each sample (on a scale of 1 = male to 0 = female), date of capture (and day of year captured), the average length and weight of each sample, site coordinates, and fraction lipid. In many cases, a more extensive list of contaminants was evaluated. PCB data are presented geographically and by species with corresponding lipid values in the context of the MDE's cancer-based health risk advisories.

Most samples with concentrations of PCBs ≥313 ng/g wet (Maryland's "no consumption" threshold) come from a few specific regions: the C&D Canal, northern Chesapeake Bay, Back River, Patapsco River and Potomac River. To summarize the PCB data geographically samples were classified by site into one of seven categories: coastal bays, fresh water rivers and lakes, Chesapeake Bay (which includes open waters and tributaries otherwise unmentioned), tidal Potomac River and tributaries, Chesapeake and Delaware Canal watershed, tidal Patapsco River and tributaries, and Back River. Histograms are used to illustrate the distributions of fish tissue PCB concentrations found among these regions (Figure 9). Concentration classes are MDE's risk-based consumption levels from Table 4. The histograms are presented in order of increasing modes to emphasize the relative differences between regions. Modal PCB concentrations

Figure 9. Histograms of PCB concentrations in fish by region. Bins correspond to consumption levels in Table 3.



are ranked Back River > Patapsco > C&D Canal > Potomac > Chesapeake Bay > rivers and lakes > coastal bays.

To compare concentrations among species, samples were first classified into marine, estuarine, and freshwater habitats (Table 4). Among marine samples, four five-individual composites of blue crab hepatopancreas had a mean concentration in the MDE's two-meal-per-month range (52 to 78 ng/g wet). One four-fish composite of scup had a concentration in the four-meal-per-month range (20 to 39 ng/g wet). The remaining samples of black seabass, summer flounder, black drum, blue crab muscle tissue and quahog clam had average concentrations ≤10 ng/g wet (the upper limit of the 16-meal-per-month range).

Among freshwater samples, only four of the 20 species sampled had mean concentrations <20 ng/g wet; these were yellow bullhead, brown bullhead, walleye, and chain pickerel. Samples of smallmouth bass, rock bass, largemouth bass, bluegill, white perch and redbreasted sunfish had mean concentrations in the four-meal-per-month (20 to 38.9 ng/g wet) range. One four-fish composite of pumpkinseed sunfish and one three-fish composite of fallfish had mean concentrations in the three-meal-per-month concentration range (39 to 52 ng/g wet). White sucker (15 two- to five-fish composites and four individuals), longear sunfish (four five-fish composites) and black crappie (six three- to five-fish composites and an individual) had mean concentrations in the two-meal-per-month concentration range (52 to 78 ng/g wet). Only brown trout (four three- to five-fish composites) and American eel (four two- to five-fish composites) had concentrations in the one-meal per month concentration range (78 to156 ng/g wet).

Channel catfish (eight two- to five-fish composites and two individuals) had the greatest mean concentration, which fell in the six-meal-per-year range (156 to 313 ng/g wet).

Table 4. Total PCBs (ng/g wet mass) and lipid (percent) in edible fish tissues

Estuarine samples from Chesapeake Bay and its tributaries					
Species	N[c]	Mean t-PCB ± 1 std.	Range	Mean lipid ± 1 std.	Range
Channel catfish [a]	84	449 ± 303	22.2 to 1770	3.88 ± 2.13	0.588 to 12.4
White perch [a]	123	251 ± 259	4.32 to 1640	3.15 ± 1.75	0.256 to 7.23
Carp [a]	5	1120 ± 274	717 to 1380	5.13 ± 1.82	2.51 to 8.09
Blue crab hepatopancreas [b]	19	450 ± 410	13.8 to 1320	9.91 ± 3.54	2.67 to 16.6
White catfish	5	547 ± 328	149 to 978	2.80 ± 2.09	0.773 to 6.34
Striped bass	50	259 ± 185	27.4 to 883	3.29 ± 2.17	0.091 to 8.27
American eel [a]	22	382 ± 231	49.7 to 863	10.1 ± 3.43	4.37 to 17.7
Brown bullhead catfish [a]	9	162 ± 129	37.9 to 503	1.33 ± 0.623	0.606 to 2.22
Bluefish	8	95.9 ± 96.2	6.59 to 312	2.81 ± 1.50	0.885 to 5.15
Yellow perch	10	118 ± 67.6	43.6 to 299	0.797 ± 0.071	0.695 to 0.922
Redbreast sunfish [a]	4	128 ± 67.8	64.6 to 242	1.11 ± 0.230	0.716 to 1.27
Largemouth bass [a]	3	142 ± 51.8	104 to 216	1.00 ± 0.472	0.567 to 1.66
Spot [b]	7	67.4 ± 56.6	11.6 to 183	7.76 ± 1.77	5.32 to 11.0
Pumpkinseed sunfish [a]	2	144 ± 27.3	117 to 171	0.528 ± 0.0468	0.482 to 0.575
Atlantic croaker	4	57.4 ± 53.5	11.7 to 147	7.22 ± 1.58	5.87 to 9.92
Blue catfish	1	134 –	– –	2.46 –	– –
White sucker [a]	3	68.7 ± 24.9	34.5 to 93.0	1.08 ± 0.209	0.807 to 1.31
Blue crab muscle [b]	19	12.6 ± 19.3	BDL to 78.1	0.716 ± 0.119	0.535 to 0.974
Oyster	20	9.29 ± 6.79	3.48 to 34.5	1.55 ± 0.285	1.01 to 1.92
Yellow bullhead catfish [a]	1	31.5 –	– –	0.671 –	– –
Weakfish	1	28.1 –	– –	8.10 –	– –
Black crappie [a]	1	27.8 –	– –	1.84 –	– –

Table 4. (cont.) Total PCBs (ng/g wet mass) and lipid (percent) in edible fish tissues

Species	N[c]	Mean t-PCB ± 1 std.	Range	Mean % lipid ± 1 std.	Range
Fresh water samples from Maryland reservoirs and streams					
Channel catfish [a]	10	173 ± 121	52.6 to 483	2.66 ± 1.09	1.35 to 4.13
Brown trout	4	113 ± 166	10.4 to 400	1.43 ± 0.489	0.990 to 2.26
White sucker [a]	19	65.4 ± 94.7	3.38 to 326	1.6 ± 0.936	0.591 to 4.51
Longear sunfish	4	74.5 ± 96.0	14.8 to 241	1.63 ± 0.144	1.46 to 1.83
American eel [a]	4	87.5 ± 62.1	35.2 to 189	9.42 ± 6.44	1.91 to 19.6
Carp [a]	2	143 ± 4.40	138 to 147	2.51 ± 0.408	2.10 to 2.91
Smallmouth Bass	11	37.6 ± 42.1	3.92 to 146	1.33 ± 0.436	0.641 to 2.03
Black crappie [a]	7	61.7 ± 25.4	40.0 to 122	1.45 ± 0.388	0.722 to 1.86
Rock bass	5	25.5 ± 28.9	4.02 to 82.7	1.13 ± 0.302	0.612 to 1.54
Largemouth bass [a]	11	24.4 ± 26.4	0.53 to 80.5	0.597 ± 0.163	0.370 to 1.02
Redhorse sucker	3	43.6 ± 27.0	16.5 to 80.4	2.46 ± 1.40	1.39 to 4.43
Bluegill	4	26.0 ± 12.7	15.9 to 47.7	0.985 ± 0.117	0.827 to 1.16
Pumpkinseed sunfish [a]	1	45.9 –	– –	1.22 –	– –
Fallfish	1	43.7 –	– –	0.405 –	– –
White perch [a]	3	29.7 ± 1.17	28.7 to 31.3	3.67 ± 0.229	3.38 to 3.94
Redbreast. Sunfish [a]	2	25.6 ± 0.759	24.8 to 26.4	1.50 ± 0.156	1.34 to 1.65
Yellow bullhead catfish [a]	3	8.07 ± 4.42	3.13 to 13.9	1.05 ± 0.248	0.787 to 1.38
Walleye	4	6.92 ± 2.21	5.51 to 10.7	0.800 ± 0.170	0.578 to 1.02
Brown bullhead catfish [a]	1	6.68 –	– –	0.564 –	– –
Chain pickerel	1	3.88 –	– –	0.335 –	– –
Marine samples from Maryland coastal bays					
Blue crab hepatopancreas [b]	4	57.4 ± 12.7	40.9 to 76.6	6.56 ± 2.64	4.04 to 11.0
Scup	1	21.6 –	– –	9.63 –	– –
Black sea bass	2	10.0 ± 6.72	3.28 to 16.7	3.43 ± 0.0974	3.33 to 3.52
Summer flounder	3	7.38 ± 5.81	1.84 to 15.4	0.408 ± 0.137	0.245 to 0.580
Spot [b]	1	13.2 –	– –	5.94 –	– –
Black drum	1	4.99 –	– –	3.6 –	– –
Blue crab muscle [b]	4	1.57 ± 1.26	0.518 to 3.72	0.534 ± 0.112	0.392 to 0.683
Quahog clam	2	0.697 ± 0.532	0.165 to 1.23	0.256 ± 0.152	0.104 to 0.408

[a] Species were sampled in both estuarine and fresh water habitats.
[b] Species were sampled in both estuarine and marine habitats.
[c] N = number of samples analyzed or averaged for this table. Most samples are composites of 5 fish. Many are individual fish. Some fish were analyzed individually and then averaged in groups by site and size to form mathematical composites.

Among estuarine samples, only blue crab muscle tissue (19 three- to five-individual composites) and oyster tissue (20 25-individual composites) had mean concentrations below the 20 ng/g wet cut-off for the eight-meal-per-month or unlimited-consumption range. Yellow bullhead catfish, weakfish, and black crappie (one individual each) had mean concentrations in the four-meal-per-month concentration range. Spot

(seven three- to five-fish composites), Atlantic croaker (two composites having five and six fish and two individuals) and white sucker (two four-fish composites and an individual) had mean concentrations in the two-meal-per-month concentration range. Eight individual bluefish, ten composites of four to five yellow perch, four composites of five redbreasted sunfish, three composites of three to four largemouth bass, two composites of four pumpkinseed sunfish, and an individual blue catfish had mean concentrations in the one-meal-per-month range. White perch (123 composites of two to ten fish), striped bass (two individuals and 48 composites of three to six fish) and brown bullhead catfish (two individuals and seven composites of two to five fish) had mean concentrations in the six-meal-per-year range. Mean concentrations of channel catfish, blue crab hepatopancreas, white catfish and American eel fall in the three- to four-meal-per-year range (313 to 626 ng/g wet). The greatest mean t-PCB concentration was found in carp from the estuary. Five composites of five carp had a mean concentration in the one-meal-per-year range of 939 to 1877 ng/g wet.

Figure 10 shows fish tissue PCB concentrations throughout Maryland (detail maps are in Appendix 2). The map shows greatest PCB concentrations in Maryland fish tissues were found in limited regions of the state. Mean concentrations of all species sampled, white perch, and channel catfish in each of the seven geographical regions are in Table 5. The greatest concentrations are observed in the upper reaches of the tidal Patapsco River and its tributary Curtis Creek. Back River has the second most contaminated fish tissues, and fish tissues from the Potomac and C&D Canal watershed also have relatively elevated PCB concentrations.

Figure 10. Total PCBs in Maryland fish and shellfish tissue composites by site. Observations are stacked so that the lowest concentration sample at a location is visible, but only one observation is visible for each consumption category at each site.

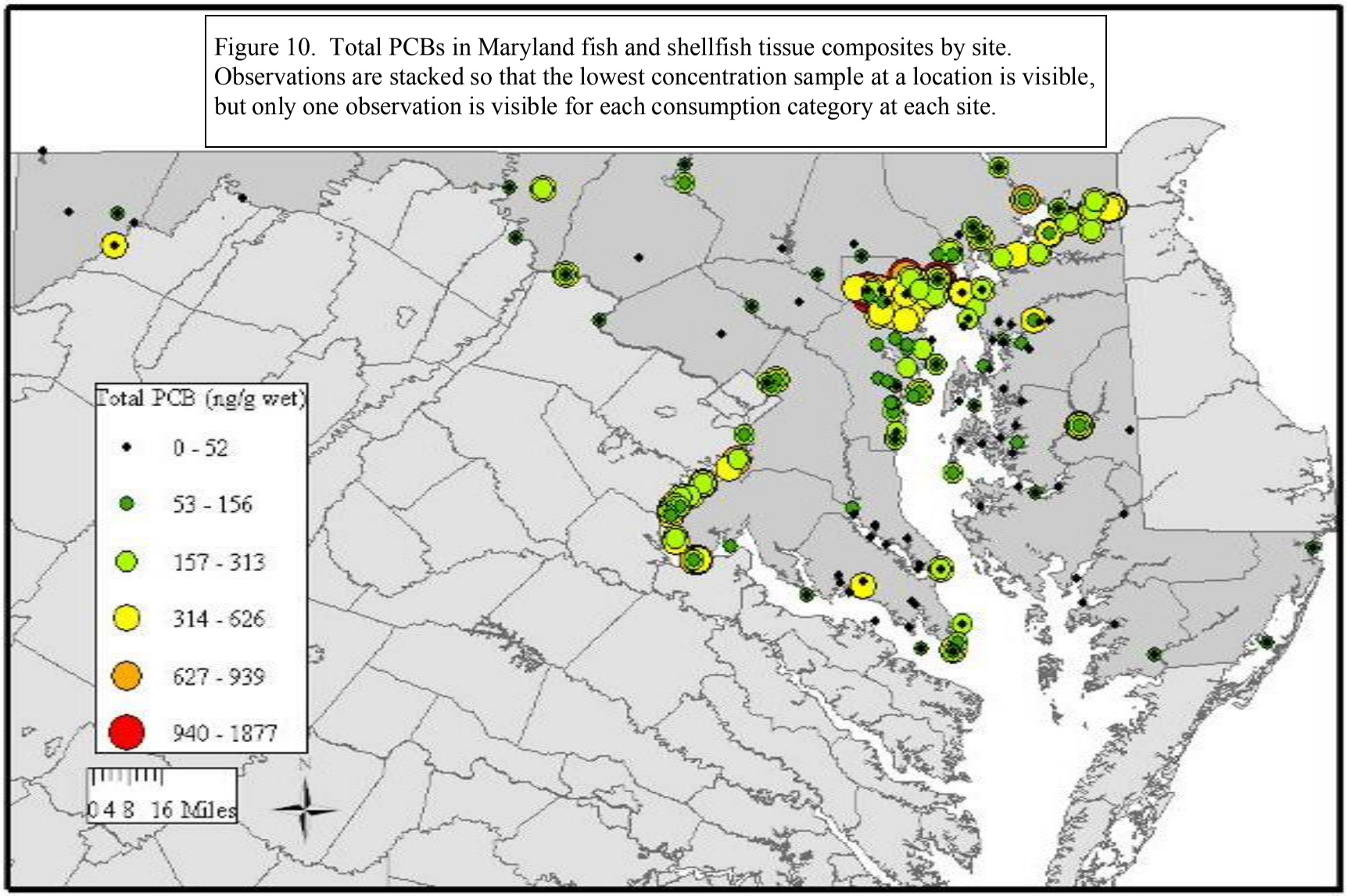


Table 5. PCB concentrations in fish tissues collected in regions of Maryland waters for all species collected and for the two species most sampled. Concentrations are ng/g wet.

Region	All species	White perch	Channel catfish
Coastal Bays	18 ± 23	--	--
	0.17 – 77	--	--
	18	0	0
Freshwater rivers and lakes	77 ± 100	30 ± 1.2	230 ± 160
	0.53 – 500	29 – 31	53 – 500
	117	3	13
Chesapeake Bay	140 ± 170	110 ± 100	220 ± 240
	BDL – 1000	4.3 – 410	22 – 1000
	199	64	20
Tidal Potomac River and tributaries	270 ± 230	79 ± 82	430 ± 230
	0.088 – 920	18 – 320	160 – 920
	71	12	23
Chesapeake and Delaware Canal Watershed	450 ± 190	390 ± 190	480 ± 190
	150 – 850	150 – 760	234 – 850
	46	18	28
Tidal Patapsco River and tributaries	590 ± 440	640 ± 290	1500 ± 250
	24 – 1800	330 – 1600	1300 – 1800
	40	21	2
Back River	640 ± 320	290 ± 67	680 ± 200
	180 – 1400	180 – 390	370 – 920
	29	8	8
Key	mean ± std. dev.		
	min – max		
	N		

Discussion

Literature comparison

PCBs are a ubiquitous pollutant. PCB contamination is second only to mercury in the number of fish consumption advisories it warrants in the United States. Levels of PCBs in Maryland fish are typical of those found in the neighboring states of Virginia and Delaware (Table 6). Comparison of Maryland fish PCB concentrations to those found regionally and in distant locations helps put Maryland t-PCB data in a greater context. PCB levels in Maryland marine fish species, e.g. drum, are lower than in San Francisco Bay estuary, but greater than levels observed in the Southeastern U.S. Throughout the Chesapeake and Delaware Bays migratory striped bass have similar concentrations which are higher than those in San Francisco Bay striped bass and lower than those found in striped bass from the Hudson River. PCB concentrations in semianadromous white perch from the Chesapeake and Delaware bays are highest in the Delaware River in the vicinity of Philadelphia and are lowest in the Virginia portion of the Chesapeake. PCB concentrations in Maryland white perch decrease with distance from the C&D Canal that connects Chesapeake Bay to the Delaware River. PCB concentrations in channel catfish from Chesapeake and Delaware Bays follow the same trend. American eel PCB concentrations are greater in Delaware River than in the Chesapeake or Delaware Bays but are even higher in Raritan Bay on the Atlantic coastline near to the mouth of the Hudson River. Carp PCB concentrations in Maryland's Back River are lower than in the New River below Claytor Lake Dam. Above Claytor Lake Dam, low carp PCB concentrations appear to reflect the moderate

Table 6. Comparison of Maryland edible fish tissue PCBs to regional and other values.

Species		Mean ± std. dev. or	
White perch	Location	Median, range	notes
Morone americanus	Chesapeake Bay, Maryland[a]	87, 400	
	C&D Canal, Maryland[a]	390, 610	
	Delaware River, Philadelphia, PA[b]	690 ±350	
	Delaware River, vicinity of C&D Canal[b]	494 ±160	
	Chesapeake Bay, Virgina[c]	50 ±57	
Channel catfish			
Ictalurus punctatus	Chesapeake Bay, Maryland[a]	140, 990	
	C&D Canal, Maryland[a]	430, 620	
	Delaware River, Philadelphia, PA[b]	810 ±220	
	Delaware River, vicinity of C&D Canal[b]	410 ±150	
Drum spp.			
Weakfish	Maryland, Chesapeake Bay[a]	28, 0	
Atlantic croaker	Maryland, Chesapeake Bay[a]	21, 39	
Red drum	Southeast and Gulf coast, U.S.[d]	12 ±19	
White croaker	San Franciso Bay, California[e]	340 ±140	
Carp			
Cyprinus carpio	Back River, Maryland[a]	1300, 660	
	Claytor Lake, Virginia[c]	120 ±110	
	New River, below Claytor Lake[c]	820 ±1300	
	Turkey, [e]	1, 4.8	Sum of 28 PCBs
American eel			
Anguilla rostrata	Chesapeake Bay, Maryland[a]	150, 350	
	Back River, Maryland[a]	640, 370	
	Delaware Bay, New Jersey[g]	130 ±130	
	Delaware River, New Jersey[g]	900 ±700	Raccoon Creek site
	Raritan Bay, New Jersey[g]	1100 ±590	Atlantic coast
Striped Bass			
Morone saxatilus	Chesapeake and tributaries, Maryland[a]	230, 860	
	San Franciso Bay, California[f]	140 ±75	
	Delaware Bay, New Jersey[g]	680 ±380	
	Raritan Bay, New Jersey[g]	380 ±200	
	James River, Virginia[c]	240, 1500	
	Hudson River, New York[g]	3600 ±700	geomean±pooled s.d.

Sources: a) This study. b) Ashley *et al*., 2004. c) Virginia DEQ, 2006. d) Liebert unpublished data. e) Erdogrul *et al*., 2005. f) Fairey *et al*,. 1997. g) Ashley *et al*., 2003.

industrialization of the watershed, while below the dam greater PCB concentrations surpass those measured in Back River. Carp from the tributary of the Black Sea in Turkey provide a reference for PCBs fish from a remote area with only small atmospheric inputs. Comparisons vary on a site-by-site basis, but Maryland fish have levels of PCB contamination typical of the Mid-Atlantic United States. Maryland fish PCB concentrations greatly exceed what is observed in remote locations like the Turkey site but are comparable to other concentrations in other highly developed regions like San Francisco Bay.

Factors affecting PCB levels in fish

Variables that may affect bioaccumulation of organic contaminants include species, tissue lipid content, fish length, and season of sampling. Length, as a proxy for age, can affect t-PCB concentrations, since PCBs can be sequestered and become increasingly concentrated over the life of a fish. Also, in a very general sense, length can be a proxy for trophic position, for the larger the consumer, the greater its ability to feed higher on the food chain. Length as a proxy for trophic position might reflect effects of biomagnification. Lipid content, of course, has the direct effect of increasing solubility of PCBs in tissues. The primary reason for expecting an effect of sex on PCB concentrations is that PCBs will be shunted to eggs as they develop; spawning females may therefore have lower tissue PCB concentrations (Larsson et. al., 1993). Seasonal fluctuations have been observed in other studies and may result from changing feeding habits or seasonal depuration (Stapleton et al., 2002). To test for regional and overall effects I focused on two species that were present in all regions except Coastal Bays: white perch and channel catfish.

Lipid content, length, sex and day of year

White perch and channel catfish, which had the greatest sample sizes, were used to test for effects of these variables. Data and test results are presented in appendix 3. Spearman correlations indicated significant relationships of pooled channel catfish total PCBs with length and lipid (both with $\rho = 0.31$ and $p < .01$) but no relationship between length and lipid. Scatter plots suggest these are weak relationships. White perch t-PCB had significant relationships with lipid ($\rho = 0.34$, $p < .01$) and day of year (DOY, $\rho = 0.26$, $p < .01$). The correlation of white perch t-PCB with lipid was strongly driven by samples taken from the Patapsco River and its tributaries that had high lipid contents averaging twice that of all other samples (mean ± std. dev., 0.058 ± 0.012 vs. 0.027 ± 0.014). Without the Patapsco samples, the white perch t-PCB-lipid relationship is not significant ($p = .58$). The relationship with DOY is also misleading. This apparent relationship is the result of a combination of factors. First, few samples were taken in Spring and these all had low concentrations. Since most samples were taken in Fall, there was greater variability of concentrations and hence greater detected concentrations in Fall. The apparent relationship with DOY is therefore an artifact of the sampling schedule.

Lipid content was unequal amongst regions for both white perch and channel catfish (Kruskal-Wallis, $p < .01$). Differences were found between lipid contents of regional samples; Potomac channel catfish had greater lipid contents than those from Chesapeake Bay and rivers and lakes (Tukey's HSD, $p < .05$). I examined lipid-content effects for each species in each region and found relationships between channel catfish total PCB and lipid in three regions: Chesapeake Bay ($\rho = 0.74$, $p < .01$), C&D Canal (ρ

0.44, $p < .05$) and rivers and lakes ($\rho = -0.67$, $p < .05$); however, Spearman correlation coefficients indicated no consistent relationship. Scatter plots suggested positive relationships in the case of Chesapeake Bay and C&D Canal channel catfish both with few outliers. Since there were few regional differences in channel catfish lipid content, and relationships between lipid and t-PCB were inconsistent, it does not make sense to lipid normalize the channel catfish t-PCB data.

An intraregional relationship of t-PCB to lipid in white perch was only found in the C&D Canal ($\rho = 0.83$, $p < .01$). In this instance, plotting the data revealed a strong relationship. The strong correlation of PCBs to lipid content in C&D Canal white perch suggests equilibrium partitioning of PCBs between C&D Canal white perch tissues and their habitat. The lack of a relationship in any of the other five regions indicates there is no consistent effect of lipid on t-PCB in white perch.

Kruskal-Wallis tests showed that length differed between regions for white perch ($p < .01$), while this was not the case for channel catfish. Within regions I found a positive linear relationship between length and t-PCB in Potomac channel catfish ($\rho = 0.67$, $p < .01$) and a negative linear relationship between t-PCB and length in Back River white perch ($\rho = -0.72$, $p < .05$). In no other region did I find any correlation or dependence of PCB concentration on length for white perch or channel catfish. Hence, there is no consistent relationship is suggested. There are, however, several factors in this study that hinder our ability to detect such a relationship. Since this study focused on concentrations in edible tissues, collections usually took into account a minimum size cut-off, limiting the smaller fish sampled. Also, a "75% rule" (i.e. the smallest fish in a composite is at least 75% of the length of the largest fish in that composite) was applied

when making size-discriminated composites, so the size variability of collected fish was intentionally limited.

Tests for effects of sex on t-PCB showed no significant effects for pooled or regional sets of catfish and white perch data. If sex does truly have an effect on t-PCB, the ability to detect it in this study was reduced by the compositing scheme which did not separate male and female fish but composited them together and recorded sex as a ratio of the male to female fish in the composite.

Length of Potomac channel catfish and lipid of C&D Canal white perch appear to have strong positive effects on t-PCB, and length appears to have a negative effect on t-PCB in Back River white perch. Lipid has weaker positive effects on t-PCB in C&D Canal and Chesapeake Bay channel catfish. Despite these intraregional correlations, lipid and length do not have a consistent effect on t-PCB in Maryland white perch or channel catfish. Also, day-of-year and sex have no significant effects on t-PCBs in these Maryland fish.

Trends among species

At most sampling locations a limited number of samples were taken and these included relatively few species. Species sampled varied from site to site. In some instances many species were sampled at a single site or within a region. Figure 11 shows concentrations in all samples of species collected in the Back River and Patapsco regions and from two sites—one on Middle River in the northern Chesapeake and one on the Potomac. This figure shows the general trend observed for these species when sampled at a single locale.

Channel catfish were regularly among the most contaminated fish at any site where they were collected. Carp, American eel, white catfish had concentrations that were similar to and sometimes exceeded those of channel catfish. Blue crab hepatopancreas was also regularly among the most contaminated tissue types at locations where it was collected. At the other end of the spectrum, blue crab muscle and white sucker tissues were regularly the least contaminated tissue types at sites where they were collected. Brown bullheads were always less contaminated than other catfish and tended to be among the lesser-contaminated species at sites where they were collected. White perch total PCBs tended to correlate well with and were lower than channel catfish PCB concentrations. In general white perch PCB concentrations were low compared to other species collected at the same sites, but white perch collected from contaminated sites were among the most contaminated samples in this study. One sample of white perch taken from Curtis Creek, on the Patapsco River, had the second greatest concentration of PCBs of all samples in this study and was 27% higher than that of blue crab hepatopancreas collected from the same location.

To investigate what effects interspecies differences in lipid might have on differences in PCB concentration I repeated the interspecies comparison after lipid normalization. When lipid normalized (Figure 12) t-PCB of those species or tissues with high lipid contents—carp, American eel, blue crab hepatopancreas—decrease relatively. And, those species that tend to have lower lipid contents—brown bullhead and white perch increase relatively. In Back River lipid normalized PCB concentrations are roughly equal for all species except American eel which is relatively low. The trend observed in Patapsco samples changes only in that brown bullhead catfish PCB

concentrations are roughly equivalent to blue crab hepatopancreas. The trend among Middle River species changes with brown bullhead and white perch concentrations becoming the second and third greatest behind channel catfish. Lipid normalization changes the rank of every species taken from Maryland Point on the Potomac River with the only exception being white catfish which remains to have the greatest concentration measured at that site. Lipid normalization changes but does not eliminate interspecies differences in Maryland fish tissue PCB concentrations. Lipid therefore does not appear to be the primary variable influencing interspecies differences in t-PCB concentrations. The ability of white perch to accumulate environmental PCBs in a consistent manner that relates to other species present makes them a good monitoring species. Due to their sheer abundance and broad habitat they are a default monitoring species. The importance of their commercial and recreational harvest is another incentive to monitor their concentrations. They appear to be an efficient and representative accumulator and are insensitive to effects of lipid content on accumulation of PCBs.

The species and tissues that appear to be the best accumulators—those consistently having the greatest concentrations—are white catfish, channel catfish, carp, American eel, and blue crab hepatopancreas. These may be the most desirable monitoring species when the greatest potential to accumulate to environmental PCBs is sought. However, effects of lipid on accumulation of PCBs by channel catfish do diminish the ability to detect spatial differences, and the small samples of the rest of these species reflects their occurrence and the efficiency with which they can be collected.

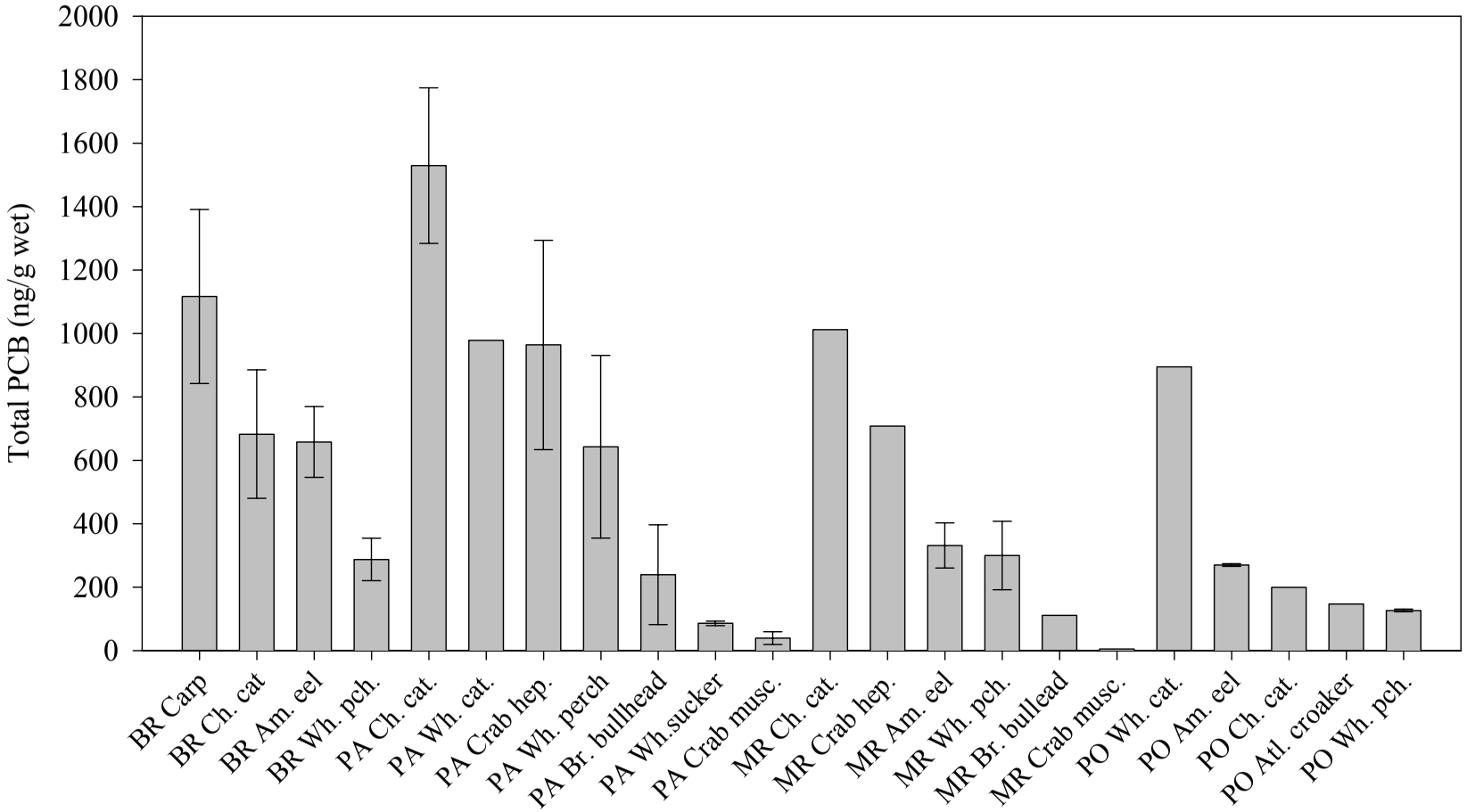


Figure 11. PCB concentration in species collected from Back River (BR), the tidal Patapsco (PA) and tributaties, Middle River (MR) at Bowleys Quarters, and the Potomac (PO) at Maryland Point. Species/tissues are white, channel, and brown bullhead catfish, carp, American eel, white perch, blue crab muscle and hepatopancreas, white sucker, and Atlantic croaker.

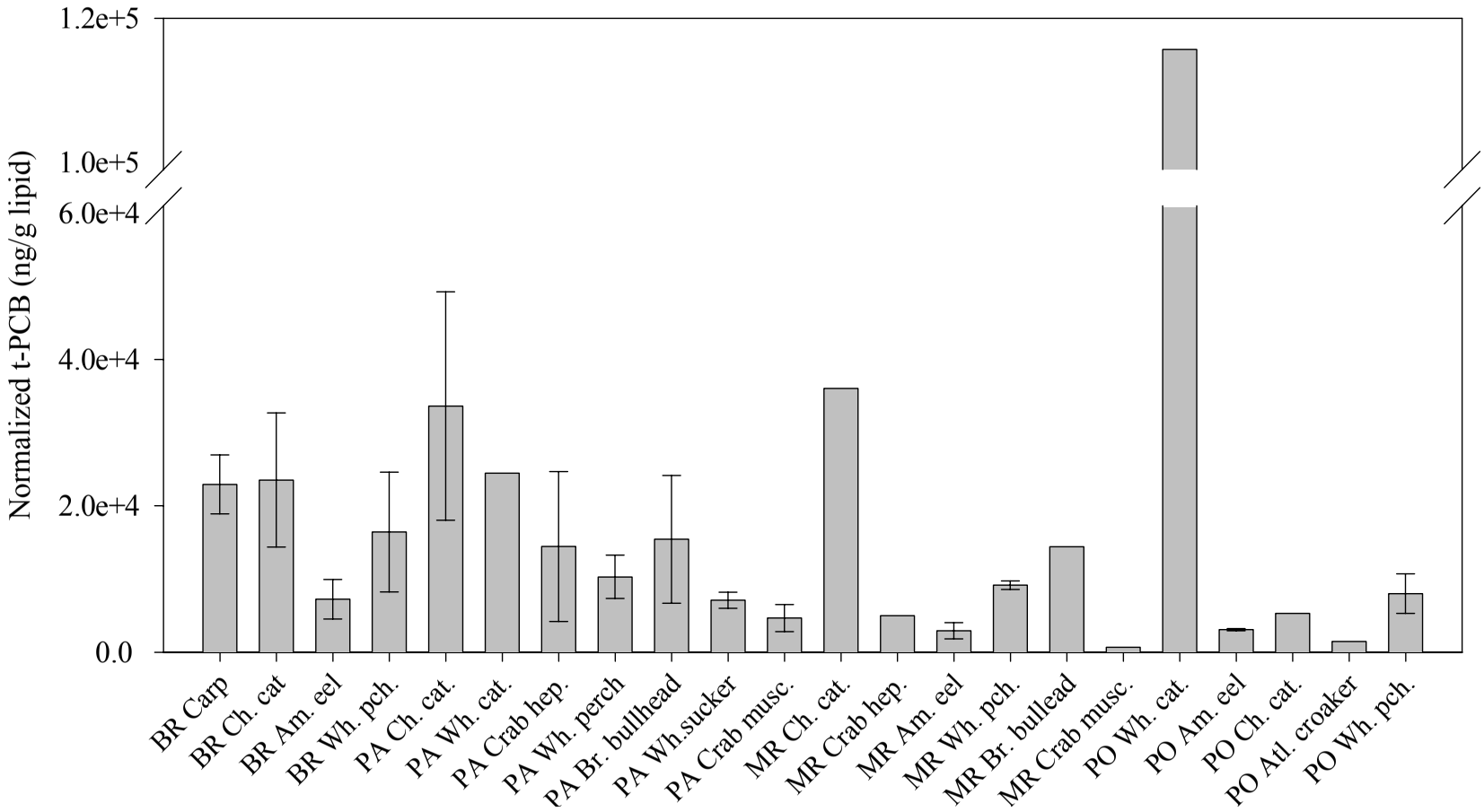


Figure 12. Lipid normalized PCB concentration in species collected from Back River (BR), the tidal Patapsco (PA) and tributaties, Middle River (MR) at Bowleys Quarters, and the Potomac (PO) at Maryland Point. Species/tissues are white, channel, and brown bullhead catfish, carp, American eel, white perch, blue crab muscle and hepatopancreas, white sucker, and Atlantic croaker.

Carp, which is restricted in mobility by salinity, and American eel, which has a small homerange prior to catadramous spawning (Parker, 1995; Morrison and Secor 2003), may be useful monitoring species if collected in sufficient numbers.

Effect of habitat

Fourteen of the 37 species sampled, including blue crab muscle and hepatopancreas separately, were collected in both estuarine and either fresh water or marine habitats. Only in one case (black crappie) was the mean PCB concentration of any of these species sampled in fresh or marine habitats greater than that of the same species sampled in the estuary. Total PCB was unequal among habitats (Kruskal-Wallis, $p < .01$), and estuarine samples had greater PCB than marine and fresh water habitats (Tukey's HSD, $p < .01$). The greatest PCB contamination in Maryland fish is found in estuarine waters. This is not surprising. PCBs accumulate in estuaries, because estuaries are primary sink for human waste and the center of human development and industrial activities. Using a subset of the data presented in this thesis, King et al. (2004) showed that PCB contamination in Chesapeake Bay white perch was strongly correlated to human land use.

Region and Species

Both lipid-normalized and non-normalized PCB concentrations were compared between regions and species. Though effects observed here are inconsistent, lipid does affect bioaccumulation of PCBs. Since lipid varies between species and regions, it should be considered. Taking the data set as a whole, both mean lipid-normalized t-PCB (lip-PCB) and t-PCB were found to vary significantly among species (Kruskal-Wallis, p

< .0001). I repeated the Kruskal-Wallis tests within each of the seven geographical regions (Back River, coastal bays, Chesapeake Bay, C&D Canal, Patapsco, Potomac, rivers and lakes) and again found that mean lip-PCB and t-PCB varied among species within each region with two exceptions (all with $p < .01$ except lip-PCB in Patapsco with $p < .05$). Lip-PCB in coastal bays (eight species) and t-PCB in C&D Canal (two species) did not differ among species; only in these cases did I fail to reject the equality of t-PCB concentrations across species.

The effect of species on PCB concentrations had to be taken into account to compare t-PCB between regions. Sixteen species or tissue types were sampled in two or more regions. Of these species or tissues, five were found to be significantly different among regions where they were collected. These were American eel, blue crab muscle and hepatopancreas, channel catfish, and white perch (Kruskal-Wallis, all with $p < .01$ except blue crab hepatopancreas $p < .05$). Tukey's nonparametric HSD was used to test each combination of sites for each of these species for inequality of lipid normalized t-PCB concentrations. Results provided in Appendix 3.

American eel and blue crab samples were each collected from only four regions and had relatively few samples per region. American eel from Back River had PCB concentrations significantly greater than those from the Potomac, Chesapeake Bay and rivers and lakes regardless of lipid normalization; though, lipid normalization increased the level of significance between Back River and Chesapeake Bay PCB concentrations. No differences were found between American eel PCB concentrations from Chesapeake Bay, Potomac River, and rivers and lakes. Regional differences found in blue crab muscle and hepatopancreas PCB concentrations were identical to each other except that

differences in muscle always had a lower level of significance. Total PCB concentrations in Patapsco blue crab muscle and hepatopancreas were greater than those in coastal bays and Chesapeake Bay. No differences were found between PCB concentrations in blue crab tissues from Chesapeake Bay, Potomac and coastal bays regions. Lipid normalization of blue crab tissue PCB concentrations makes the difference of Patapsco and coastal bays more significant, while making any difference between Patapsco and Chesapeake Bay not significant. Multiple comparisons of lipid normalized and non-normalized regional American eel and blue crab PCB concentrations indicate that Back River American eel are more PCB-contaminated than those from the Potomac, Chesapeake Bay and rivers and lakes and that Patapsco blue crab PCB concentrations are elevated relative to coastal bays. The effect of lipid on these differences varies from case to case.

Channel catfish collected from six regions were the species with the second greatest number of samples. Tukey's HSD detected no differences in t-PCB concentrations between Patapsco, C&D Canal, Back River, and Potomac samples, between Chesapeake Bay and rivers and lakes samples, or between Potomac and rivers and lakes samples. Seven significant differences were detected. Patapsco, C&D Canal, Back River and Potomac channel catfish t-PCB concentrations were significantly greater than those from Chesapeake Bay. And, Patapsco, C&D Canal, and Back River channel catfish t-PCB concentrations were significantly greater than those from rivers and lakes. After lipid normalization, two significant differences remained; C&D Canal and Back River channel catfish had greater PCB concentrations than Chesapeake Bay channel catfish. The reduction in regional differences detected between channel catfish PCB

concentrations by normalization lends support for the weak correlation that suggested there was an effect of lipid on channel catfish PCB concentrations. However, regional differences may simply be confounded by the introduction of the additional variability of lipid content. Since the correlation of PCB to lipid is weak, lipid normalization could have the opposite of the intended effect—over-inflating or over-deflating the outliers and obscuring relevant trends.

White perch were collected in six regions and were the species with the greatest number of samples. Tukey's HSD detected eight significant differences between regional white perch t-PCB concentrations. No difference was detected between t-PCB concentrations in Patapsco, Back River, and C&D Canal white perch, in Potomac, Chesapeake Bay, and rivers and lakes white perch, or in Back River and rivers and lakes white perch. Concentrations of t-PCBs in white perch from the Patapsco and C&D Canal were greater than those from all other regions except Back River. Patapsco, C&D Canal, and Back River white perch had PCB concentrations higher than Potomac and Chesapeake Bay white perch. Lipid normalization had the effect of increasing the level of significance of differences between white perch PCB concentrations in two pairs of regions and brought about a ninth significant difference between Back River and rivers and lakes white perch PCB concentrations.

Regional comparisons of PCB concentrations in white perch and channel catfish follow a general trend. Channel catfish from the Patapsco, C&D Canal, Back River, and Potomac regions are more PCB-contaminated, while those from Chesapeake Bay and rivers and lakes regions are less PCB-contaminated. White perch from the Patapsco, C&D Canal, and Back River are more PCB-contaminated, while those from the Potomac,

Chesapeake Bay, and rivers and lakes regions are less PCB-contaminated. Smaller regional differences among channel catfish PCB concentrations after lipid normalization likely reflect a greater effect of lipid on PCB accumulation in that species compared to white perch. The fact that Patapsco white perch, a majority of which had much greater lipid contents than other white perch samples, still had significantly higher PCB concentrations than Chesapeake Bay, Potomac, and rivers and lakes samples even after lipid normalization suggests that species is relatively insensitive to effects of lipid content on PCB accumulation.

Box and whisker plots for channel catfish and white perch from each of the six regions are shown in Figure 13. The Patapsco River stands out as having both the greatest median and maximum PCB concentrations in both white perch and channel catfish. Chesapeake Bay samples have a broad range of t-PCB concentrations. The high variability of t-PCB concentrations in Chesapeake Bay samples is a result of the diverse areas included in this category, the highly contaminated stretch of the northern Chesapeake between the C&D Canal and Back River and the relatively pristine tributaries of the eastern and western shores of the Chesapeake. Back River and C&D Canal samples have more uniformly high concentrations than the Chesapeake Bay in general. Back River channel catfish have a greater median PCB concentration than C&D Canal channel catfish, while C&D Canal white perch have a greater median PCB concentration than Back River white perch. There is also much lower variability in t-PCB in Back River white perch as compared to those in the C&D Canal. This may reflect the broader region classified as C&D Canal. Fish in the C&D Canal category were from the Canal itself as well as from the Bohemia and Sassafras Rivers that connect

the canal to Chesapeake Bay proper. Back River is a much smaller and more isolated subestuary of the Chesapeake.

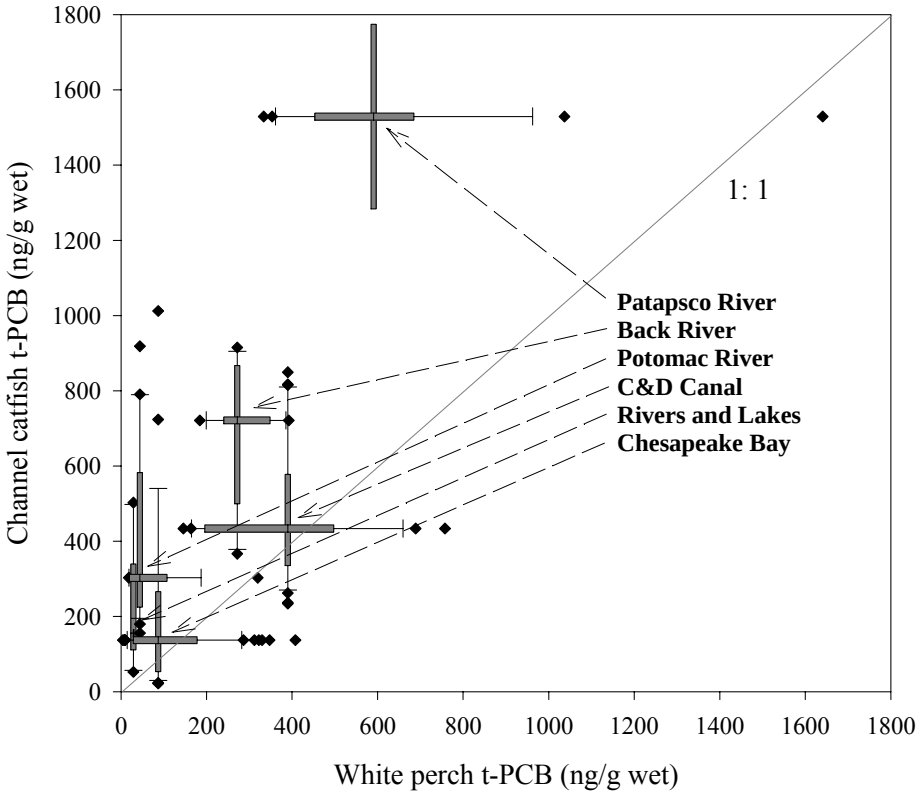


Figure 13. Paired box and whisker plots of total PCBs in white perch and channel catfish from regions of Maryland waters. Box plots intersect at group medians. Boxes are 25 and 75 percentiles. Error bars are 10 and 90 percentiles.

The median Potomac channel catfish t-PCB concentration was approximately twice that of Chesapeake Bay channel catfish, indicating that Potomac River channel catfish are more contaminated in general than those from the Chesapeake Bay. White perch median t-PCB, on the other hand, is greater in Chesapeake Bay than in the Potomac. This reflects the abundance of white perch samples from the contaminated northern Chesapeake and the sampling of white perch from relatively pristine sites on the

lower tidal portion of the Potomac. Rivers and lakes have the lowest median white perch t-PCB concentrations and have median channel catfish t-PCB concentrations only slightly greater than Chesapeake Bay. The ranking of white perch median t-PCB concentrations (Patapsco > C&D Canal > Back River > Chesapeake Bay > Potomac > rivers and lakes) and median channel catfish t-PCB concentrations (Patapsco > Back River > C&D Canal > Potomac > rivers and lakes > Chesapeake Bay) are in agreement with the trend observed in modal t-PCB concentrations of all fish sampled in each region and with the results of multiple comparisons.

While PCB concentrations in Maryland fish vary among species and in some cases with size or lipid content, variation in Maryland fish tissue PCB concentrations is primarily geographical. Maryland fish having the greatest PCB concentrations are found within the Chesapeake Bay estuary. Within the estuary the most highly contaminated fish are found in the Patapsco, C&D Canal, Back River and Potomac regions. The observed trend reflects what is known about PCB contamination in Maryland waters. PCB contamination in the Patapsco and Back Rivers has been well documented (Ashley and Baker 1999) and persistent contamination sources continue to be investigated. The 68th Street Dump, located just upstream of the tidal Back River, and Curtis Bay Coast Guard Yard, on the western shore of Curtis Creek in Baltimore Harbor, are proposed Superfund sites with PCB contamination. The most contaminated fish in the tidal Potomac were collected around Quantico, VA where the U.S. Marine Corps Base Superfund site has been a historical source of PCBs to the Potomac River (Pinkney et al., 1995). Fish tissue PCB contamination in the C&D Canal region likely results from transport of PCBs through the canal from the Delaware Estuary where extensive non-

point PCB sources are evident (Ashley et al., 2003). While high levels of PCBs are found in fish from other parts of the estuary, these hot-spots for PCB contamination in residential fish species are apparently the key source regions for PCBs in Maryland's estuarine waters.

Conclusions

Total PCBs in Maryland fish vary primarily with species and region. Samples from the estuary had the greatest PCB concentrations, and the most contaminated regions were the Patapsco River, C&D Canal, Back River, and Potomac River. Fish from freshwater rivers and lakes and coastal bays had consistently lower PCB concentrations that than those from the estuary. Chesapeake Bay fish PCB concentrations were highly variable and reflected the disparity of environmental concentrations between the more PCB-contaminated northern Chesapeake and less PCB-contaminated eastern and southern Chesapeake.

Channel catfish had the greatest PCB concentrations among estuarine and freshwater species sampled and was the frequently-sampled species with the greatest apparent potential to accumulate environmental PCBs. White perch were perhaps the most useful monitoring species for detecting spatial trends due to broad dispersal throughout the estuary, their availability, and their potential to accumulate environmental PCBs. Blue crab muscle and oyster tissues had the lowest PCB concentrations among estuarine samples and were the only estuarine species or tissues with average concentrations below the MDE's limited-consumption threshold for PCBs.

Fish tissue PCB concentrations are spatially correlated with known PCB sources and contamination of sediments within the Chesapeake estuary. The greatest

concentrations of PCBs in fish tissue were found at sites of historical sediment contamination, and concentrations decreased with distance from contaminated sites. Other sites with elevated fish tissue PCB concentrations can be reasonably suspected to have elevated sediment concentrations. And, all sites with elevated sediment PCBs likely act as sources of PCBs to adjacent contiguous waters. Spatial trends in fish tissue total PCBs suggest fish tissue PCB data might support a multivariate analysis of PCB congener patterns which uses PCB congener patterns in fish to identify source signatures and evaluate the spatial influence of PCB sources in Maryland waters.

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Chapter 4: Multivariate Analysis of FTM Data

Introduction

The goal of this thesis is to identify source signatures for PCBs in Maryland fish and use those signatures to analyze the spatial influence of PCB sources identified in Chapter 3. Multivariable statistical methods were chosen for this analysis. Preliminary investigations of FTM data demonstrated that geographically related groups of samples had very similar PCB congener patterns. Congener profiles from C&D Canal, Back River, Potomac River, and Patapsco River are in Appendix 3. PCB profile plots illustrate the high within-region similarity of congener patterns in channel catfish, white perch and American eel from these regions and that congener patterns are distinctly different among regions. Also, the figures in Appendix 3 illustrate the challenge that this thesis presents: objectively modeling the PCB congener data in a way that simplifies interpretation of these patterns. Principal components analysis (PCA) was first used to identify congeners that accounted for most of the variability in the data so that extraneous data could be eliminated. Also, PCA was used to ordinate congener patterns so that principal component scores could be used to illustrate similarity of congener patterns. Removal of congeners that had low principal component weights from the data greatly reduced the separation of regionally associated clusters in principal components space. This loss of ability to discriminate between regional PCB congener patterns indicated the need to retain all PCB congener data for analysis. PCA also did not result in an ordination that clearly discriminated between all regional congener patterns simultaneously.

I therefore chose a suite of multivariable methods that used the full data set with no loss of information and allowed me to examine the influence of multiple source-specific congener patterns simultaneously. A three-step approach was used in this analysis. First, PCA was used to identify the presence of spatial variability. Second, a non-hierarchical cluster analysis was applied to determine which fish tissue samples had the most similar congener patterns and how those samples grouped spatially. Finally, positive matrix factorization (PMF) was used to derive PCB congener signatures for major sources of PCBs to fish. The contribution of each source signature to total PCB in each sample was mapped to visualize spatial trends in the influence of each source.

PCA is a multivariable ordination technique that is used to reduce data by creating new variables (principal components) that are composites of the original variables such that the variability in the original data is condensed within a minimum number of principal components. Plotting observations' scores for the principal components having the greatest explanatory value allows the researcher to observe the relative dissimilarity of observations with regard to the given set of variables. Evidence of similarity is given by clustering in n-dimensional space (n = the number of principal components), which is impossible to visualize. In our case, distinct groups of observations from different regions are evidence that congener patterns differ spatially and the fish tissue data can therefore be used to evaluate spatial patterns and trends.

Cluster analysis is a family of data reduction procedures that group samples with redundant information. Here, non-hierarchical cluster analysis was used to evaluate in the simplest terms which observations had the most similar congener patterns and inferentially which samples were exposed to the same pattern of PCB congeners.

Matrix factorization (Paatero 1997) is a weighted-least-squares-based analogue to conventional eigen-based factor analysis (FA). Matrix factorization has several advantages that maintain quantitativeness and empirical significance of results. Firstly, it can be applied with non-negativity constraints so that it yields positive solutions that are more realistic in the context of environmental chemistry. It is applied to the original data rather than a covariance or correlation matrix of the original variables as in traditional FA. In combination with non-negativity constraints, use of the original data enables the matrix factorization model to extract a set of factors from the data that are directly interpretable as quantitative source profiles. This is a distinct advantage over conventional FA. Experimental (analytical, sampling, etc.) error is incorporated into the model by down-weighting each element of the observation-by-variable matrix for its associated error term. Conventional FA does not provide a means for down-weighting observations for which there is low confidence and is thus more subject to the effects of outliers.

The greatest advantage of matrix factorization is the immediate utility of results. The matrix factorization model used here was developed to derive source profiles and contributions for aerosol source apportionment (Li *et al.*, 2004, Lee *et al.*, 2004). The application of PMF in this thesis differs substantially from the original application of the model. Fish tissue data, having been processed through the environment by differential partitioning between particles and water, air and water, and prey and predator, is not useful for source apportionment. I use matrix factorization to derive signature components of PCB congener patterns found in fish tissue and to provide contributions of each signature component to total PCBs in samples. If spatially distinct PCB sources

have different PCB congener patterns and the resultant spatial variation in PCB congener patterns in fish tissue is great enough, then the derived PCB signatures should relate to spatially distinct sources of PCBs to fish. The derived signatures cannot be viewed as source profiles but rather as signature components of source profiles. The modeled contributions of each signature likewise are not source contributions but rather are relative measures of the influence of the corresponding signature component. Matrix factorization is the most quantitative and reductive means possible with which to evaluate an unknown underlying structure in multivariable data such as this.

Materials and Methods

The data

PCB congener data described in preceding chapters were used. Due to interannual changes in resolution of chromatographic peaks, some groups of congeners were summed to allow comparisons of the congener data across years. To control for effects like species' differing abilities to metabolize PCBs and differences in accumulated PCB congeners that might result from alternate feeding preferences, two single-species data sets were used in this analysis. White perch and channel catfish data from FTM provided the most spatially expansive single-species data with the greatest number of observations (126 and 94 respectively). Maps of channel catfish and white perch sampling locations are in Appendix 4. Each data set had samples from each of the estuarine and freshwater regions used to identify primary source regions of PCBs to Maryland fish. There are some shortcomings with regard to the spatial coverage of the data. Only two channel catfish were collected from the Patapsco River. This is regrettable since the Patapsco is highly contaminated with PCBs and is a likely source of

PCBs to the rest of the Chesapeake estuary. Sampling of channel catfish was also limited to sites with relatively low salinities, thus leaving data gaps in the open waters of the Chesapeake and its tributaries and in the lower Potomac River. Most white perch from the Potomac were collected from the lower tidal portion of the river, down river of the contaminated region around Quantico, making it less likely that these samples will reflect a local source on the Potomac. There were also strengths of these data. There was expansive sampling of white perch from throughout the open waters on the northern Chesapeake Bay and tributaries of the Chesapeake. Channel catfish were sampled heavily in Back River and northern Chesapeake Bay tributaries, especially the C&D Canal region.

In addition to spatial coverage, there are other advantages to using white perch and channel catfish samples for this analysis. The two data sets provide mutual confirmation. That is to say if I obtain the same result with each data set, then each result stands in support of the other. Also, use of the paired data sets is a way to test the strength of spatial trends. White perch and channel are both resident species of Chesapeake Bay but have differing life histories and feeding habits. So, if I observe the same trends in white perch and channel catfish data, then spatial variability in PCB congener patterns is greater than that introduced by the differing life histories, feeding preferences, and bioaccumulation abilities of white perch and channel catfish.

White perch (*Morone americana*) are semi-anadromous Chesapeake Bay residents that migrate each spring to spawn in upper reaches of the tributaries they inhabit. White perch are an euryhaline species that prefer brackish water. Adult white perch spawn late March and early April in waters ranging from 0 to 4.2 psu—optimally

in salinities less than 1.5 psu (Setzler-Hamilton, 1991). The greatest abundance of adults is found in waters with salinity ranging 5 to 10.7 psu (Mansueti and Scheltema, 1953). Adults migrate to over-winter in deeper, more saline waters in October and November (Mansueti, 1957).

Although white perch can tolerates seawater salinity (Thoits, 1958 as cited by Bowen, 1987) they are generally found in salinities less than 13 to 14 psu (Mansueti, 1957; Bowen, 1987; Mulligan and Chapman, 1989). Salinity is thought to restrict white perch movements between tributaries in the lower Chesapeake Bay to the extent that genetic divergence of the population has occurred. Analysis of mitochondrial DNA has revealed genetically distinct populations of white perch in the York and James, Potomac and Patuxent Rivers (Mulligan and Chapman, 1989). White perch in the northern Chesapeake Bay, unrestricted by salinity, may move freely amongst tributaries and have been found to be a single, genetically homogenous population in Nanticoke, Choptank and Sassafras Rivers and at Hart-Miller Island (Mulligan and Chapman 1989). Kraus and Secor (2004) using otolith microchemistry, found that, in Patuxent River, white perch consistently occupied either fresh or brackish habitats following an ontogenetic divergence of the juvenile population. While white perch display annual semianadromous spawning migrations and show growth-rate-dependent ontogenetic habitat shifts over a salinity gradient, it is unclear if salinity plays a role in daily movements of white perch. Using acoustic tags, McGrath (2005) found movements of white perch in tributaries of the York River to be on the order of only tens of meters and observed that white perch typically resided in two core areas—deeper channels during low tides and shallower creeks and marshes during high tides. In McGrath's study,

sudden changes in salinity were not found to affect movements of white perch. Whether identical behavior may be observed in the less saline northern Chesapeake Bay has not been studied.

Certainly, white perch move among tributaries in the northern Chesapeake Bay, but the scale and frequency of movements is unknown. If the time scale of movements between sources of PCB exposure is less than the time it takes for an individual to accumulate PCBs from the environment and show the local PCB source signature, frequent white perch movement across great distances will diminish observed spatial differences among white perch PCB congener patterns.

Channel catfish are a demersal species. They are occasionally found in waters with salinities of 16 to 19 psu (Scott and Crossman, 1973; Murdy *et al.*, 1997) and are frequently found in waters five psu or greater in Chesapeake Bay (Murdy *et al.*, 1997). In this study channel catfish were not collected from waters exceeding roughly seven psu. Scott and Crossman (1973) review studies of channel catfish behavior in freshwater and estuarine systems. Much like white perch, channel catfish often migrate (generally downstream) to deep water to over-winter and may migrate upstream in spring to spawn (Scott and Crossman, 1973). Pellett *et al*. (1998) confirm this general pattern of behavior in channel catfish of the lower Wisconsin River. Pellett *et al*. (1998) observed that channel catfish would migrate distances of up to approximately 130 km seasonally. Despite traveling great distances, 60% of channel catfish recaptured during the summer were recaptured within 2 km of the previous site of summer capture and individuals often returned to the same summer home range in successive years (Pellett *et al*., 1998). Scott and Crossman (1973) report one study in which marked fish released at the center of a

lake quickly returned to the site of marking. Because this species has strong site fidelity between seasonal migrations, it should be a good species for monitoring localized PCB contamination.

The feeding preferences of white perch and channel catfish are similar. Both are primarily benthivorous. The omnivorous channel catfish is commonly regarded as opportunistic or as a scavenger; this is supported by observations during this study of gut contents ranging from seeds to whole adult fish. An important component of the diet of channel catfish is benthic invertebrates—especially crustaceans and insects (Murdy *et al.*, 1997; Scott and Crossman, 1973). It is also thought that channel catfish, owing to a large mouth and small benthic prey, are likely to ingest sediment directly. While channel catfish maybe less discriminating, their diet is similar to white perch which are primarily benthic predators and are increasingly piscivorous with age (Setzler-Hamilton, 1991). The benthic feeding habits of these two species makes them good sentinels for sediment-bound contaminants like PCBs.

Principal components analysis

Principal components analysis (PCA) is a multivariable statistical technique used primarily for ordination and data reduction. PCA forms composite variables (principal components) from multivariate data and maximizes the amount of information explained by each new composite variable. Multivariable observations are ordinated with respect to the new composite variables, and the dimensionality of the original data is reduced to fewer composite dimensions. PCA is applied to a P by P matrix (P = the number of variables) derived from the original data (usually a covariance or correlation matrix derived from the sample by variable data matrix). PCA is an eigen analysis procedure

which solves the characteristic equation $|R-\lambda I| = 0$, where R is the correlation matrix, λ is the vector of the P eigenvalues that correspond to the P principal components, and I is the identity matrix. Eigenvectors are then computed by solving $|R-\lambda_i I|v_i = 0$ for each ith principal component, where λ_i is the eigenvalue for the ith principal component, and v_i is the eigenvector for the ith principal component. Eigenvectors contain the coefficients (weights) for the variables on each of the principal components. The eigenvector weight for each variable is directly proportional to the correlation of the variable to the corresponding principal component. The eigenvector weights can therefore be interpreted as the importance of the variable on the corresponding principal component. Graphical analysis of the original data uses standardized scores for each sample on each principal component. The standardized score for each sample on each principal component is the product of the vector of standardized eigenvector weights for the principal component and the vector of standardized variable data for each observation. The resultant standardized principal component scores for each sample indicate how many standard deviations from the mean score a sample lies on a principal component. PCA was performed on the correlation matrix of the sample-by-congener data matrices for white perch and channel catfish in SAS with the PRINCOMP procedure (SAS Institute, 1999). Congener concentrations were standardized to the mean concentration of congeners in each sample and scaled to one standard deviation of the corresponding mean to remove the variability of absolute concentrations.

Cluster analysis

The clustering procedure used was the k-nearest neighbor (kNN) clustering method (Wong and Lane, 1983). k-Nearest neighbors cluster analysis was performed

with the SAS procedure MODECLUS (SAS Institute, 1999). MODECLUS is a nonparametric, polythetic, non-hierarchical and agglomerative clustering method. It uses density estimation to form clusters by grouping samples that are in close proximity in n-dimensional hyperspace and separates clusters at minimums in sample cloud density. This method requires no statistical assumptions about the distribution of the data to be met. In MODECLUS, two methods may be used for density estimation. The number of neighbors, k, to be used for density estimation or the radius around each observation in which to estimate density may be designated.

MODECLUS has several advantages. While traditional parametric procedures are biased toward having roughly hyperspherical clusters, clusters with similar numbers of observations or clusters of equal dispersion, density-based clustering has no such biases. In the current application, one advantage of MODECLUS was not realized. This procedure incorporates a probability estimation method for determining the significance of the number of clusters. However, the probability estimation model requires that a constant radius for density estimation be used; hence, there is an implicit requirement of homogeneity of variance among clusters for the technique to be valid. This requirement was not met with the data used in this study. Principal components plots show uneven dispersion of samples in principal components space and suggest that the same is likely true in Euclidean hyperspace. This is especially evident in the PC1:2 plot for perch (Figure 14). Due to inter-cluster heterogeneity of variance, the k-nearest neighbors method was used for density estimation rather than the radius method and the probability estimates were not used.

Results from the MODECLUS procedure were evaluated using a scree plot of the number of clusters versus k neighbors. Appropriate solutions were identified using two criteria. First, the end of the initial precipitous drop in the number of clusters was identified. At the inflection point of the curve a range of k values was sought where the number of clusters was constant. The solutions within this stable range were evaluated for stability of cluster assignment and the optimal solution was chosen based on the criteria of stability of cluster assignments and the meaningfulness of the results. Because saddle tests for significance of the number of clusters could not be used, alternative objective criteria were used to evaluate the solutions. The logarithms of the ratios of density associated with observations within the same cluster and density resulting from observations in adjacent clusters ("log density ratios") were calculated and used to evaluate the separation of clusters in each solution. Log density ratios for alternative solutions were compared and the solution with the best separation of clusters was identified as the one with the greatest log density ratio. A second method was also used to evaluate the separation of clusters. Boundary frequencies, the numbers of samples among the k nearest to within-cluster samples that were assigned to separate clusters, were totaled for each solution and compared. The solution with the minimum boundary frequency was sought as the solution with the best separation of clusters.

Positive matrix factorization

Cluster analysis provides a way of summarizing redundancy in a data set. However, cluster analysis provides no information about the patterns that lead to the clusters. The structure leading to the categorization of samples can be explored by plotting the variables for each cluster and comparing among clusters. A better approach

to discovering the structure underlying the data is factor analysis. The goal of factor analysis is to generate composite variables (factors) that represent the structure within the original data. Traditional factor analysis uses maximum-probability based eigen-analysis like PCA. A more recently applied approach based on weighted least squares is Positive Matrix Factorization (PMF; Paatero, 1994). In matrix notation the PMF model is $X = GF^T + E$, where X is the original observations-by-species data matrix, G is an observation-by-factor-input matrix, F^T is the transpose of a species-by-factor matrix, and E is a matrix of model residuals.

In PMF the factors are ideally interpreted directly as source profiles or source signatures. The matrix G provides an objective estimate of the input (mass or concentration) from each source to each observation. And, the matrix F provides corresponding contributions of each species (PCB congener) in each source as fractions of the total of all sources. The contribution of each congener from a source to an observation's PCB congener pattern can therefore be calculated as the product of the input to that observation from that source and the contribution of each congener to that source from its vector in F. A sample's congener pattern is recreated by summing the contributions of each source in matrix G to each congener in the source's profile in matrix F.

PMF has the advantage of individual data point weighting. For each value in the matrix of sample concentrations there is an associated error estimate, and these error estimates are used to weight each element of X. The model is solved iteratively to minimize the loss function, Q, which is equal to the sum of the squared ratios of model residuals to error estimates for all elements of the data matrix (Lee *et al*., 2004). In the

ideal situation, where model performance and error estimation are perfect, the ratio of modeled to estimated error will equal one for each element and *Q* will equal the number of elements in the data matrix.

The same data were used for PMF as were used for PCA and CA with the addition of the error matrix and substitution of missing (below detection limit) values. The error matrix includes calculated propagation of error values for each element in the original data matrix. The propagation of error calculation took into account sample- and congener-specific method detection limits and precision estimates. Each element in the error matrix was calculated as the square root of the sum of the squared method detection limit and the squared precision error estimate.

Precision error estimates were calculated for each congener from replicate analyses of Standard Reference Material and unknown samples. Relative percent differences (RPDs) from group means were calculated for each replicate analysis of each congener in two to 17 (13 ± 4) replicate (duplicate or triplicate) groups. The RPDs were averaged first for each group and then across groups. This calculation was chosen over averaging the RPDs of each individual sample because triplicate samples generally had lower RPDs than duplicates. Samples used for precision estimation are those in Chapter 1, Table 3.

This precision error calculation differs from the more commonly used pooled standard deviation in that it is based upon residuals as a percent of their corresponding averages rather than on the magnitudes of the residuals. Error estimates generated here using an average of percent differences from means averaged 11 ± 3.2% and ranged 5.8 to 22%. Error estimates calculated as the pooled standard deviation of a congener

divided by its average concentration in all replicates as suggested by Lee et al. (2004) resulted in error estimates of 79 ± 43%. This great error estimate results from the fact that it is calculated as a percent of an average concentration that is small compared to some of the group-specific standard deviations.

Precision estimates calculated from replicate analyses take into account the variability in extraction efficiency, quantitation, tissue homogeneity, and overall analytical technique. Therefore estimating precision error from replicates in the context of this data set is more direct and preferable to a propagation of error that accounts for all potential sources of precision error individually (e.g. uncertainty of mass measurements or variability of surrogate recoveries).

Values below MDLs were eliminated prior to construction of the data set used in this analysis. Because PMF requires all non-zero values in the data matrix, these values had to be replaced. In PMF missing values are commonly dealt with by replacing them with some fraction of their MDL and giving them an error term that is a multiple of the same MDL (Hien et al. 2004**,** Li et al. 2004). Missing values were replaced with a random fraction of the corresponding MDL (Huang et al. 1999) to minimize the introduction of artificial structure in the data matrix. Error terms were simply the MDL multiplied by two (not the propagation of error).

In PMF the number of relevant factors is determined by observing the decrease in residuals with increasing numbers of factors. Ideally, the number of sources is identified on a scree plot where there is a discontinuity in the slope of Q as a function for the number of factors. The residuals will necessarily decrease with each added factor; the user must decide when the added factors are superfluous and choose a solution with the

greatest explanatory ability and the lowest value of *Q* for the optimal number of factors. Since PMF is not designed to deliver a constant solution for a given set of conditions, the PMF model was run seven times for each number of factors to determine that a given solution was global and not local. Larsen et al. (2003) and Frenich et al. (2000) provide more extensive explanations of evaluation of model results.

Results

PCA

Principal components analysis revealed clusters of observations from regions of known local contamination—C&D Canal, Patapsco River, Back River, and Potomac River. Visually, the clusters overlap considerably even when taking into account further (more than 2) principal components (PCs). The plot of PC1 and PC2 for white perch (Figure 14) shows the distinct clusters of samples from the C&D Canal and Patapsco River regions. Potomac River samples also cluster together. Back River samples lie closest to the Patapsco River cluster. Rivers and lakes samples lie amongst Potomac samples. And, Chesapeake Bay samples are not clustered but rather are dispersed amongst samples from all other regions excepting the Patapsco River.

Eigenvectors (Figure 15) show that PC2 represents a transition from less-chlorinated (positive PC2) to more-chlorinated (negative PC2) congener patterns. The corresponding separation of C&D Canal and Patapsco River samples along PC2 reflects dominance of lighter, less-chlorinated congeners in the Patapsco and dominance of heavier, more-chlorinated congeners in white perch samples from the C&D Canal. PCA indicates white perch from Back River have congener patterns similar to those from the Patapsco. The distribution of Chesapeake Bay samples reflects the disparate locations

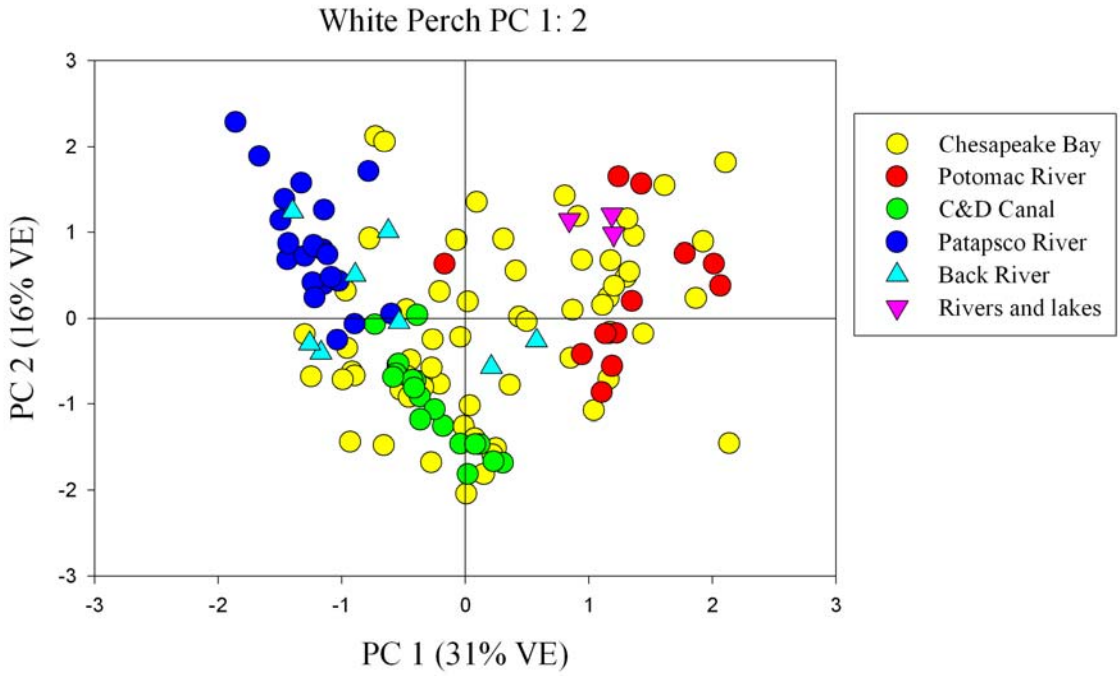


Figure 14. Principal Components plot of PCB congener patterns in white perch.

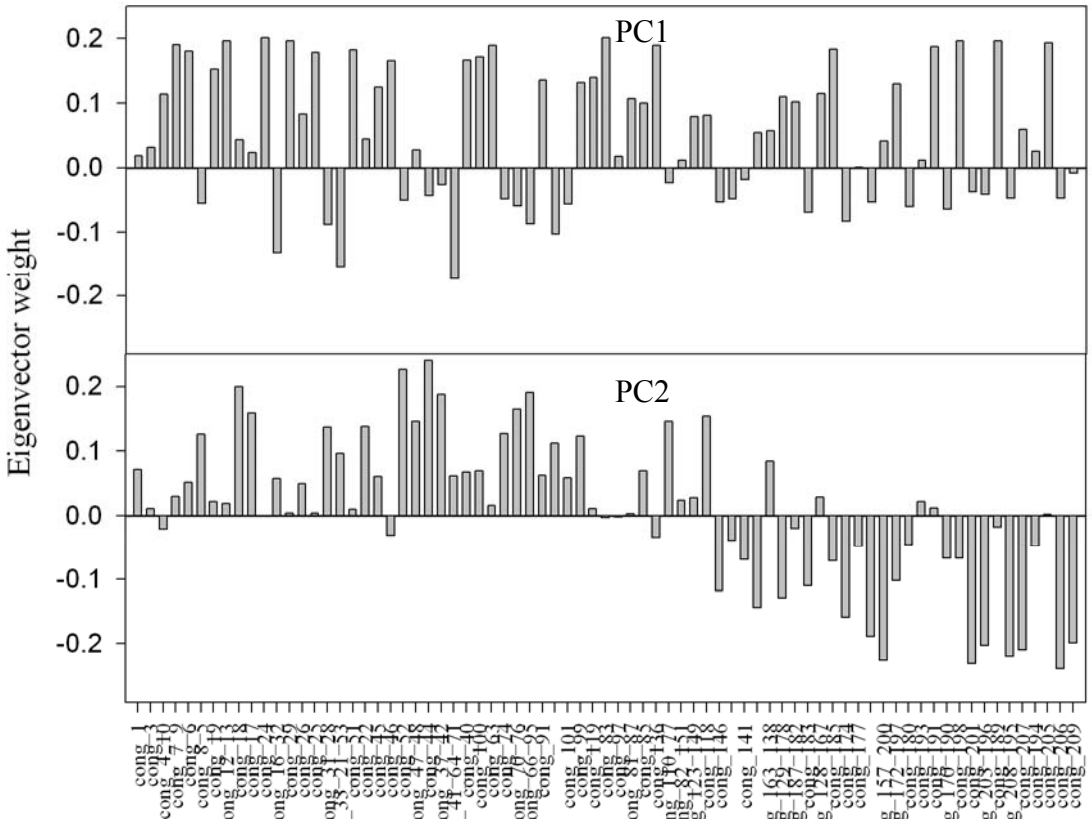


Figure 15. Principal Component weights (eigenvectors) from PCA of white perch PCB congener patterns.

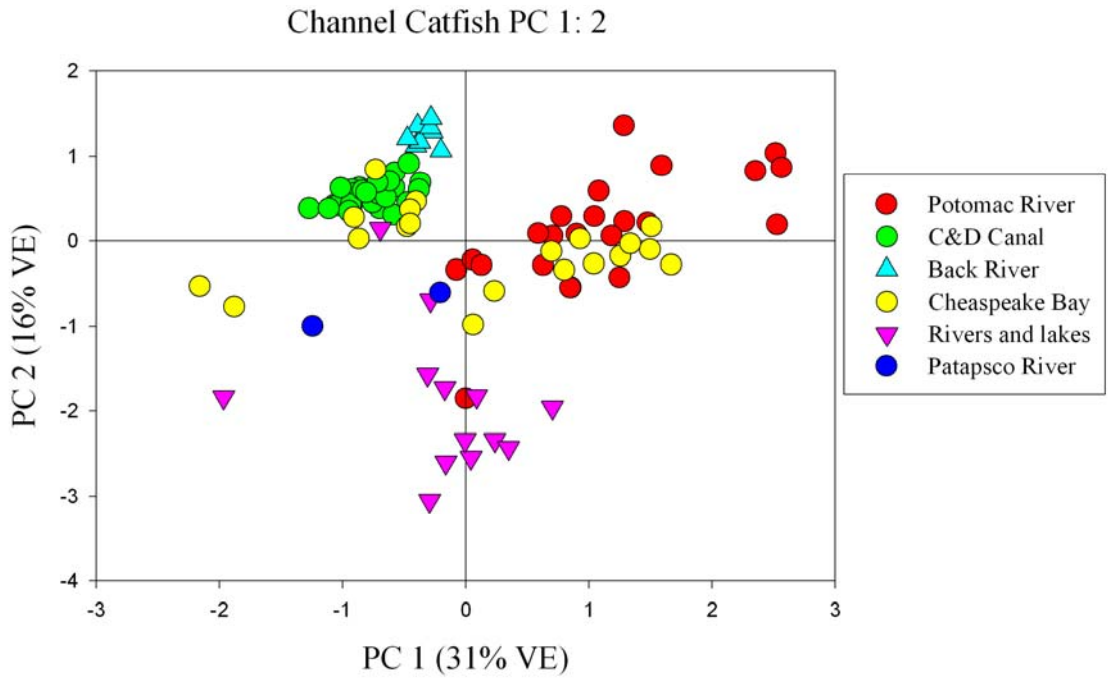


Figure 16. Principal Components plot of PCB congener patterns in channel catfish.

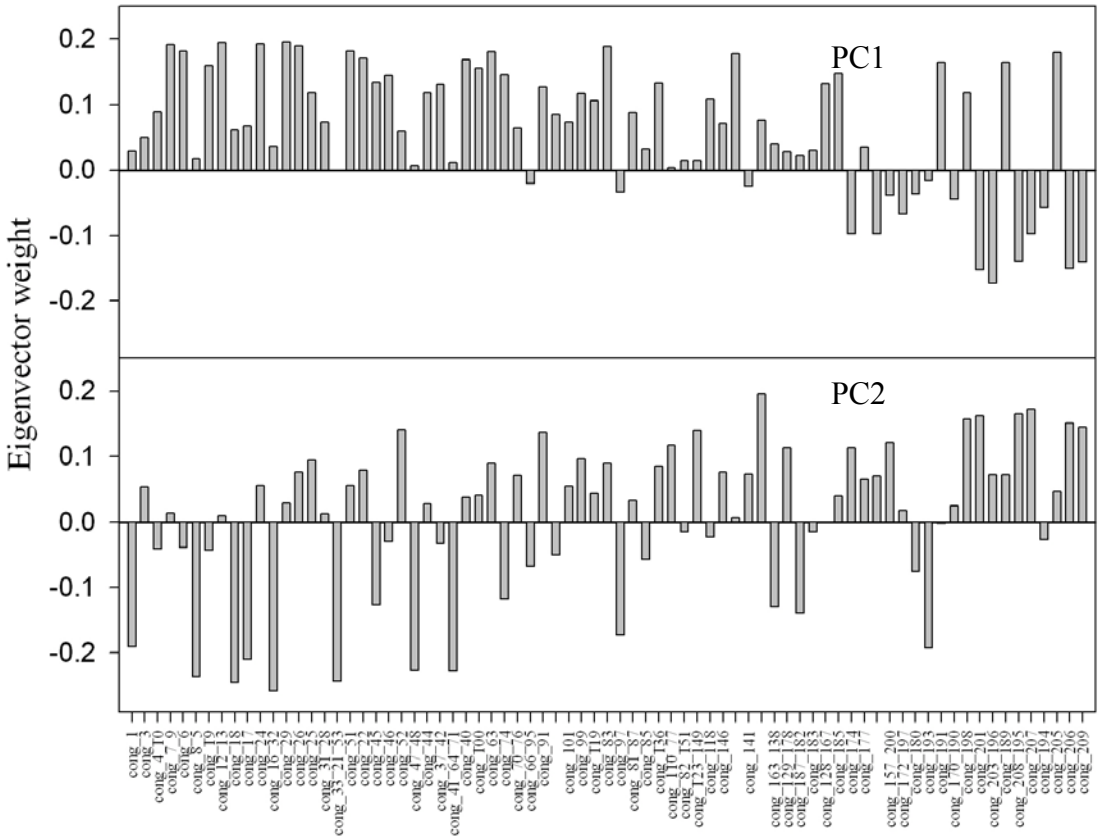


Figure 17. Principal Component weights (eigenvectors) from PCA of channel catfish PCB congener patterns.

where Chesapeake Bay samples were taken. The overlap with regional clusters indicates the congener patterns observed in these fish are similar to the observed patterns in other regions of the estuary.

PCA of channel catfish congener patterns reveals distinct clusters of samples from Back River and C&D Canal, and the tight grouping of samples indicates high consistency of PCB congener patterns among fish from those regions (Figure 16). Most channel catfish from rivers and lakes also appear to have a distinct and consistent congener pattern among them. Eigenvector weights (Figure 17) indicate PC1, like PC2 for PCA of white perch congener patterns, represents a gradient from dominance of more-chlorinated (negative weights) to less-chlorinated (positive weights) congeners. This is reflected by the positioning of Back River and C&D Canal samples on negative PC1 and those from the Potomac River on the positive end of the PC1 axis. PC1 scores for Potomac and some Chesapeake Bay channel catfish indicate those samples also have a relatively high ratio of light-weight to heavy-weight congeners. Rivers and lakes samples appear around the center of PC1, indicating little influence by PC1. However, the samples fall predominantly on negative PC2 indicating a dominant influence of the lighter congeners weighted negative on PC2. The grouping of Chesapeake Bay samples with either Potomac River or C&D Canal clusters likely reflects the proximities with which these samples were taken to those regions.

Cluster analysis

The scree plot for kNN solutions for channel catfish PCB congener patterns (Figure 18) shows the decline in the number of clusters decelerated at k = 5 for channel catfish. Solutions at k = 5, 6, and 7 all had four clusters. There were four sample

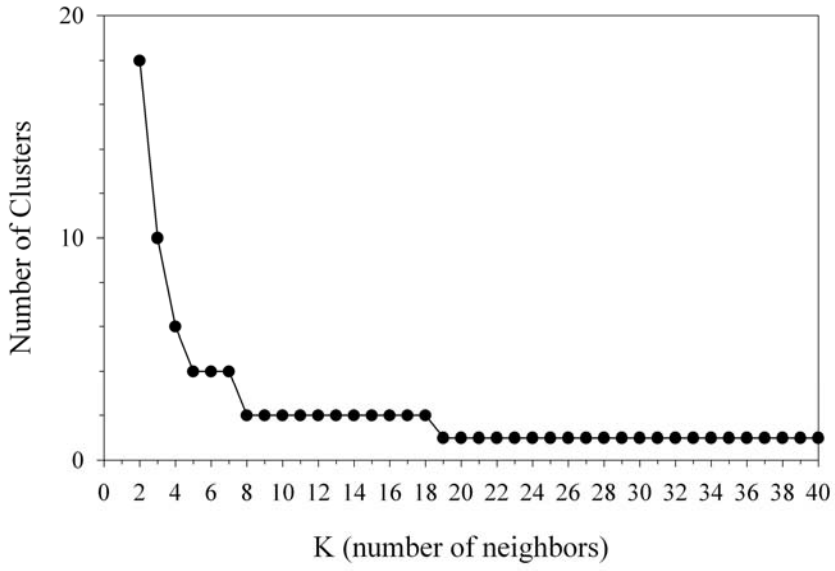


Figure 18. Scree plot of MODECLUS results for channel catfish.

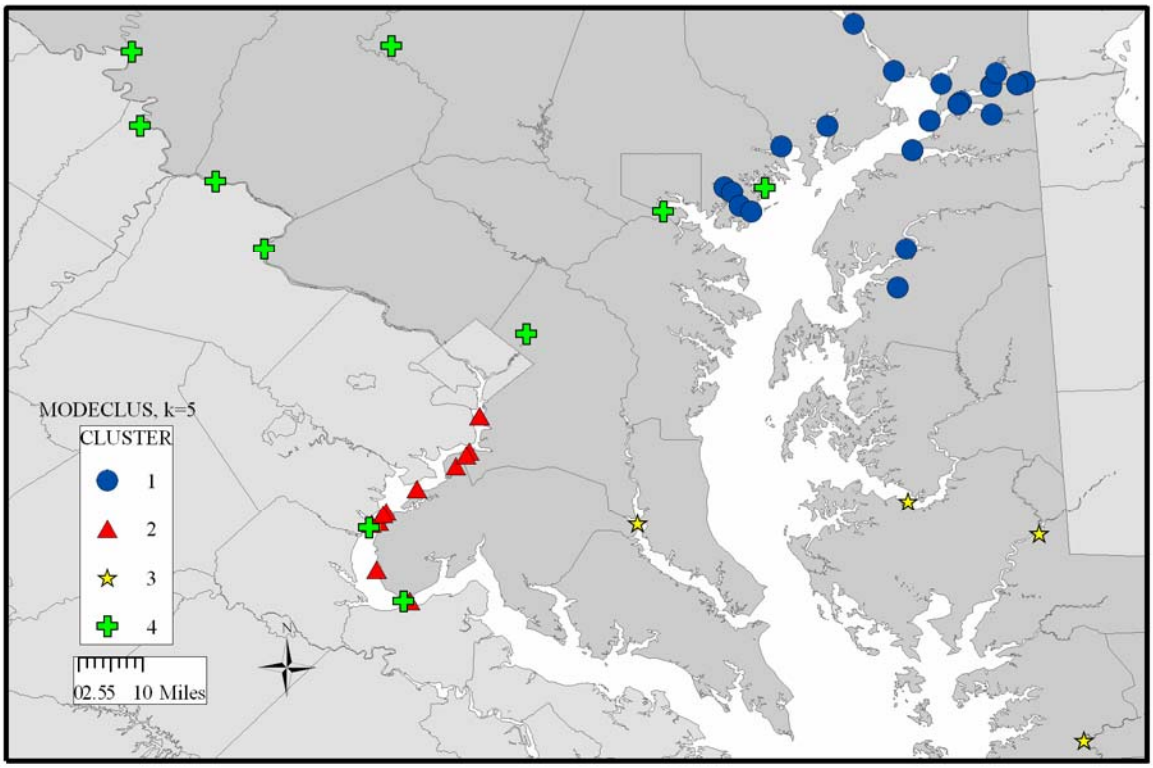


Figure 19. Clusters of PCB congener patterns observed in Maryland channel catfish.

reassignments among the three four-cluster solutions. The first four-cluster solution (k = 5) had the greatest log density ratio of within-cluster to boundary density (49 vs. 36 and 37) and the lowest total boundary frequency (9 vs. 30 and 34), it was chosen as the optimal solution. The four clusters included samples from C&D Canal and Back River; most samples from the upper tidal Potomac; samples from other sites on Chesapeake Bay; and samples from fresh water sites west of the fall line, the Gunpowder River (a Chesapeake Bay site), Patapsco River, and Potomac River. A map of the results is shown in Figure 19.

White perch PCB congener patterns did not provide such clear solutions. The scree plot (Figure 20) shows the clusters: neighbors curve for white perch was both smoother and more erratic than that generated from channel catfish data. This is not an artifact of the analysis but rather reflects the nature of the data. A separate cluster analysis using the SAS K-means procedure, FASTCLUS (SAS Institute, 1999), produced nearly identical results. The solutions in the range k = 5 to 10 were evaluated and all produced very similar results despite varying numbers of clusters. Representative solutions were chosen at k = 5 and 10. The log density ratios were the second and third greatest and the boundary frequencies were the lowest and highest for k = 5 and 10, respectively. The k = 6 solution with seven clusters had a marginally greater log density ratio than the k = 5 solution at the cost of increased boundary frequency and extra complexity. The three clusters identified with k = 10 were from primarily Patapsco River, C&D Canal and the northern Chesapeake Bay, and Chesapeake Bay tributaries and Potomac River (Figure 21). The six-cluster solution for k = 5 (Figure 22) had similar clusters of samples from Patapsco River, the northern Chesapeake Bay, and Potomac

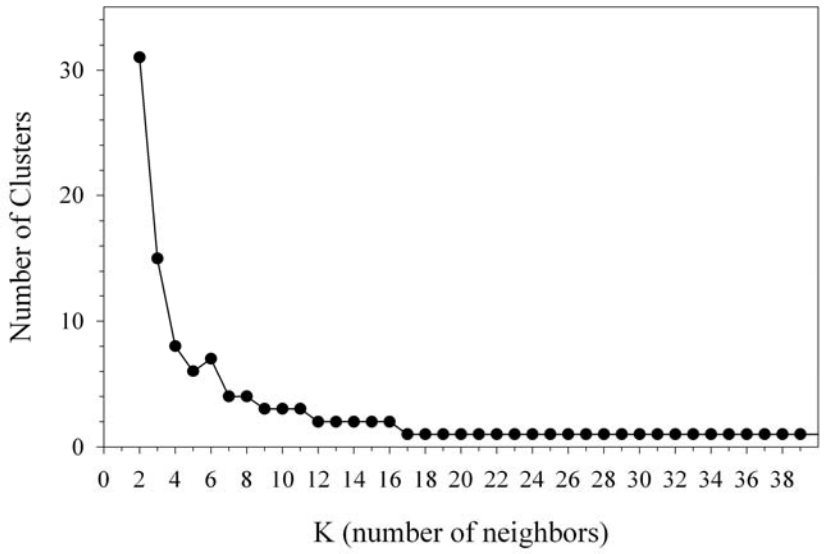


Figure 20. Scree plot of MODECLUS results for white perch.

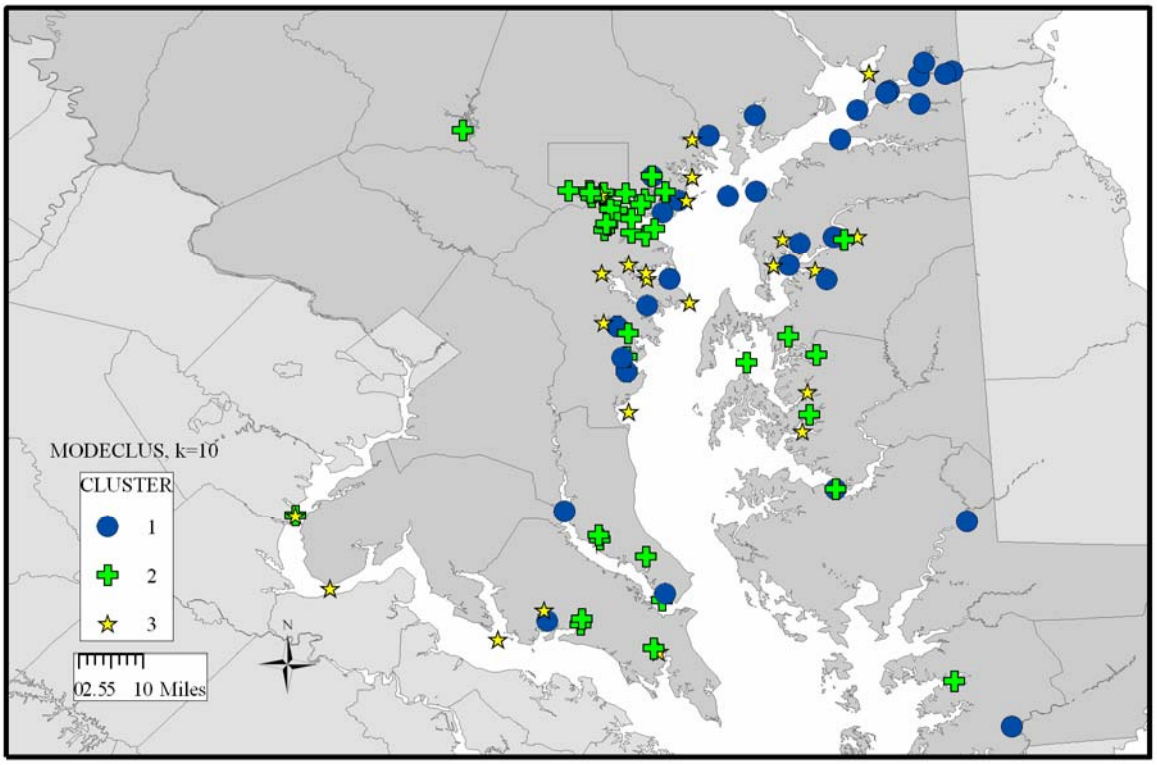


Figure 21. Clusters of PCB congener patterns observed in Maryland white perch, k = 10.

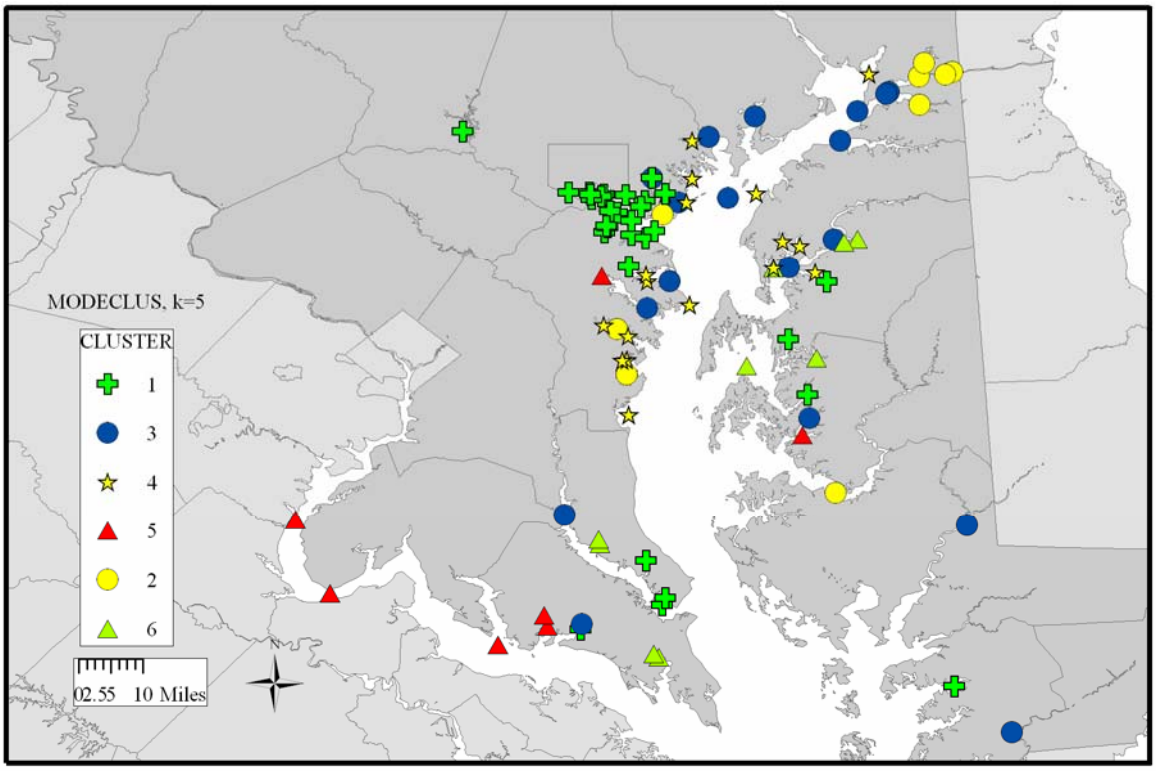


Figure 22. Clusters of PCB congener patterns observed in Maryland white perch, k = 5.

River, but the remaining clusters consisted of samples from more diverse areas. One of the new clusters (Cluster 2) consisted primarily of several samples from the C&D Canal region close to the state line; this was a persistent cluster in many of the solutions not being presented.

Positive Matrix Factorization

The scree plot of *Q* values for channel catfish (Figure 24) shows a change in the slope of the curve at three factors. The seven three-factor solutions were very consistent particularly when compared to adjacent solution sets, and one of the five solutions having the lowest *Q* value was chosen as being the most meaningful for its representation of observed characteristics of the data. Figure 25 shows the factors derived in this solution.

Figures 26, 27 and 28 show the contribution of each factor to modeled t-PCB in channel catfish. Detail maps of PMF results are in Appendix 6. These contributions can be directly interpreted as the proportion of each source signature (factor) composing the total PCB in each sample. Factor 1 is composed primarily of more chlorinated PCB congeners and is most prevalent in samples from the C&D Canal and northern Chesapeake Bay. Factor 1 is also prevalent in the Back River where its contribution to t-PCB decreases with distance upriver. Factor 2 is composed primarily of moderately chlorinated biphenyls, especially the 132+153+105 congener group. Factor 2 makes the greatest contributions to t-PCB in Potomac River samples and is prevalent in samples from upper Back River and lower Chesapeake Bay tributaries. Factor 3 resembles the congener profiles observed in Patapsco fish and has the highest loadings of less-chlorinated congeners of the derived factors for channel catfish PCBs. It is most prevalent in fish from the Patapsco River and those from the western part of Maryland but makes high contributions to some Potomac fish and fish scattered throughout the Chesapeake Bay. As the slope on the scree plot of *Q* values (Figure 29) shows, white perch did not provide such clear results. The three-factor solution was chosen primarily because of the meaningfulness of the solution. The two factor solution failed to reveal qualities of the data that would elucidate spatial differences. The solutions for four or more factors included many redundant factors and factors that appeared extraneous. The three factor solution presented here was one of two having the lowest *Q* value. The signatures and their contributions to t-PCB in white perch samples are shown in Figures 31, 32, and 33. Factor 1 is dominated by less-chlorinated congeners and composes 40 to 50% of t-PCB in white perch samples from the Patapsco River and several samples with lower t-PCB

concentrations throughout the state. Factor 1 contributes very little to t-PCB of C&D Canal and northern Chesapeake Bay white perch. In Back River white perch Factor 1 contributes varying amounts but generally increases in prevalence from the head to the mouth of the river. Factor 2 most reflects congener profiles observed in Potomac River fish but is found in samples from throughout Maryland, reflecting the ubiquitousness of this pattern of PCB congeners. Factor 3 is dominated by higher-chlorinated PCBs and is most prevalent in the northern Chesapeake Bay. The contribution of Factor 3 to t-PCB decreases toward the C&D Canal and southward of Back River. It contributes decreasing proportions of t-PCB with distance up Back River and up Patapsco River and constitutes 40% or more of t-PCB in samples as far south as Herring Bay on the Western Shore of the Chesapeake.

Figures depicting performance of PMF in replicating the data are in Appendix 5. Model performance was generally good, but there were some caveats. PMF slightly underestimates t-PCB concentrations in fish samples (Appendix 5, Figure 1), most likely due to the downweighting of any datum in X that lies outside of four standard deviations of the mean of all values of that variable. This outlier downweighing is intended to prevent excessive influence of true outliers, but in this case downweights extreme values

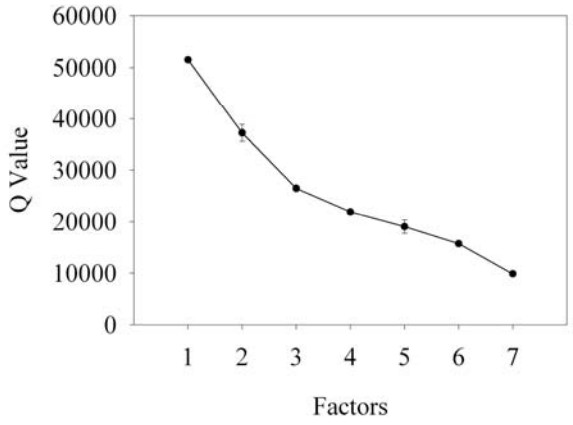
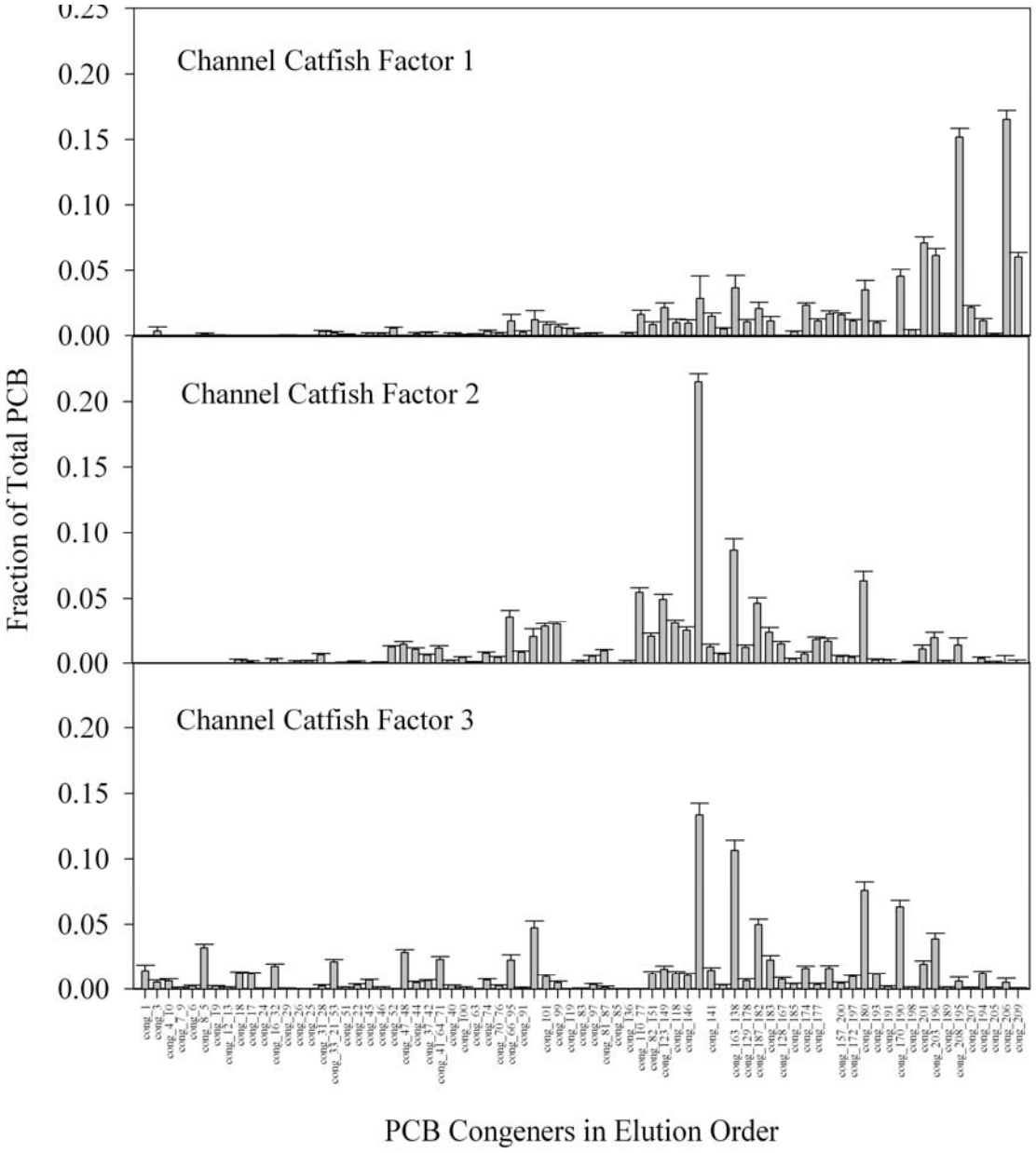


Figure 23. Scree plot of Q values for PMF factorizations of PCB congeners in channel catfish. Error bars are 99% confidence intervals for Q values among seven iterations.

Figure 24. Source signatures derived with PMF from channel catfish PCB congeners.



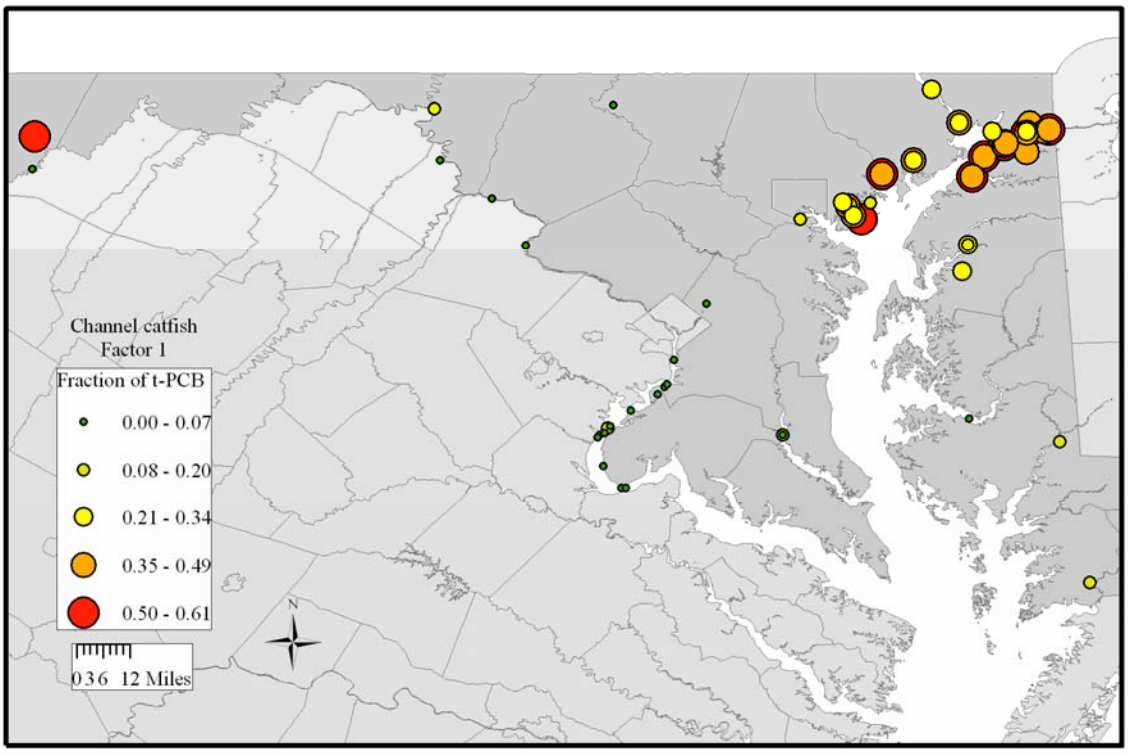


Figure 25. Proportion of Factor 1 constituting t-PCBs in Maryland channel catfish.

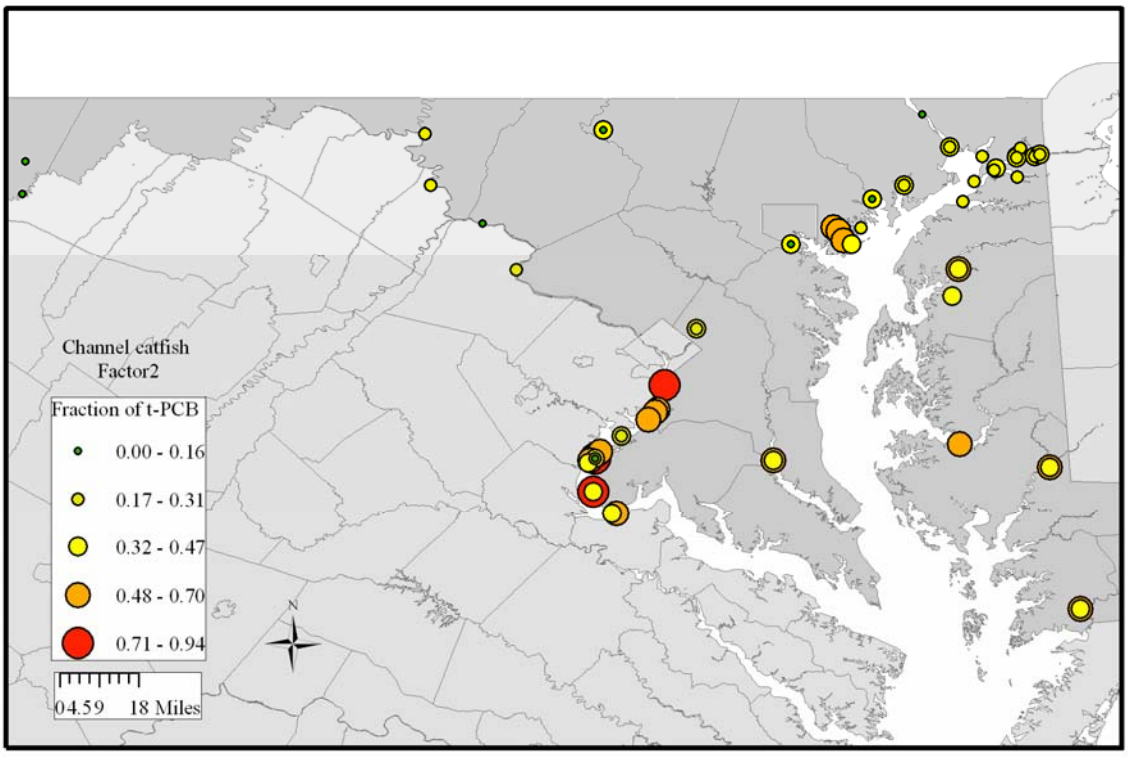


Figure 26. Proportion of Factor 2 constituting t-PCBs in Maryland channel catfish.

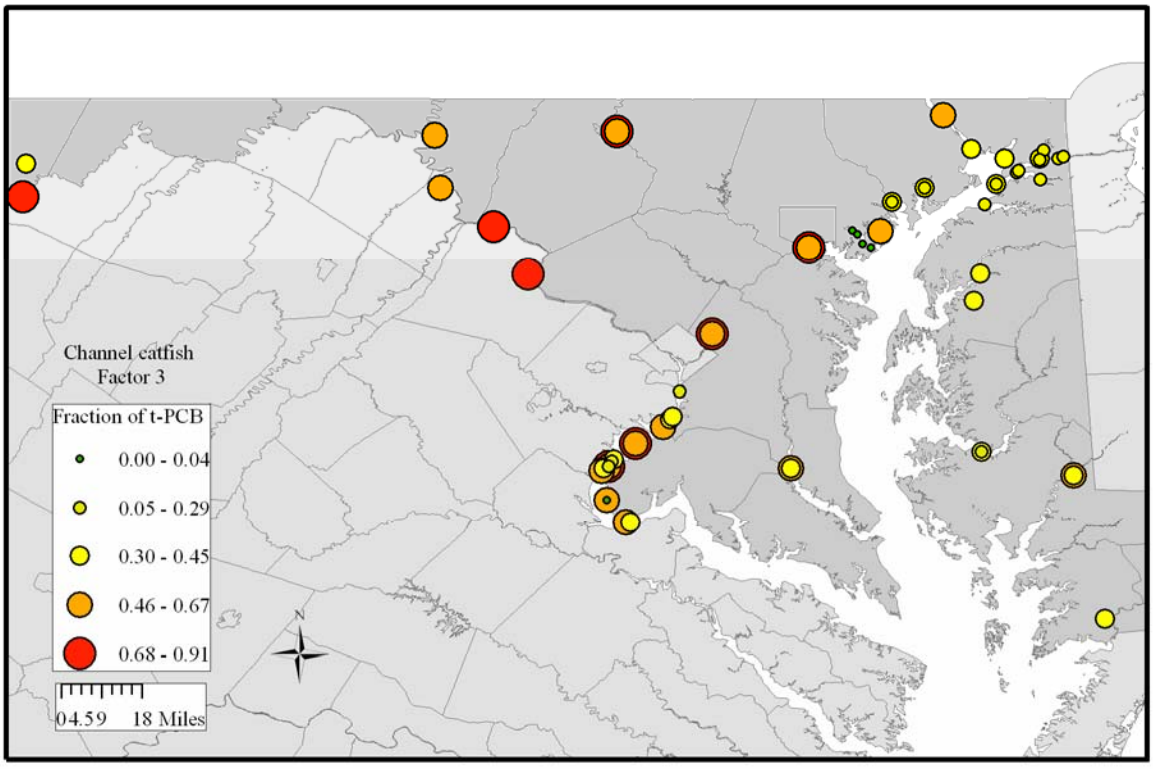


Figure 27. Proportion of Factor 3 constituting t-PCBs in Maryland channel catfish.

resulting in increasingly underestimated model concentrations with increasing measured concentrations (Appendix 5, Figure 2). Our experience with underestimation of measured values by PMF agrees with that of Larsen and Baker (2003). Withstanding this shortcoming, PMF successfully reconstructs the original data as function of the derived factors (representative examples are shown in Appendix 5, Figures 3 and 4). Figures 5 through 8 in Appendix 5 illustrate how the measured congener patterns are reconstructed and how the modeled congener patterns compare to the original data. The data used to generate all PMF figures were all screened for 99% significance using standard deviations provided by the PMF model.

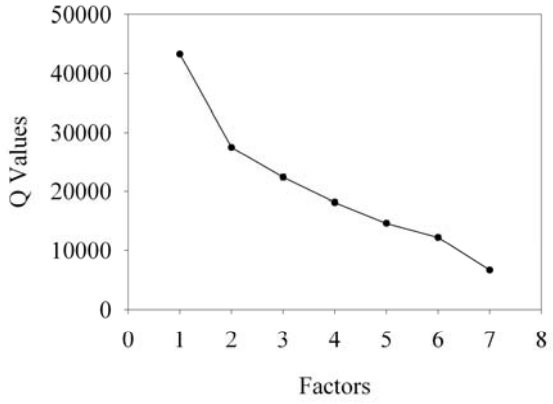
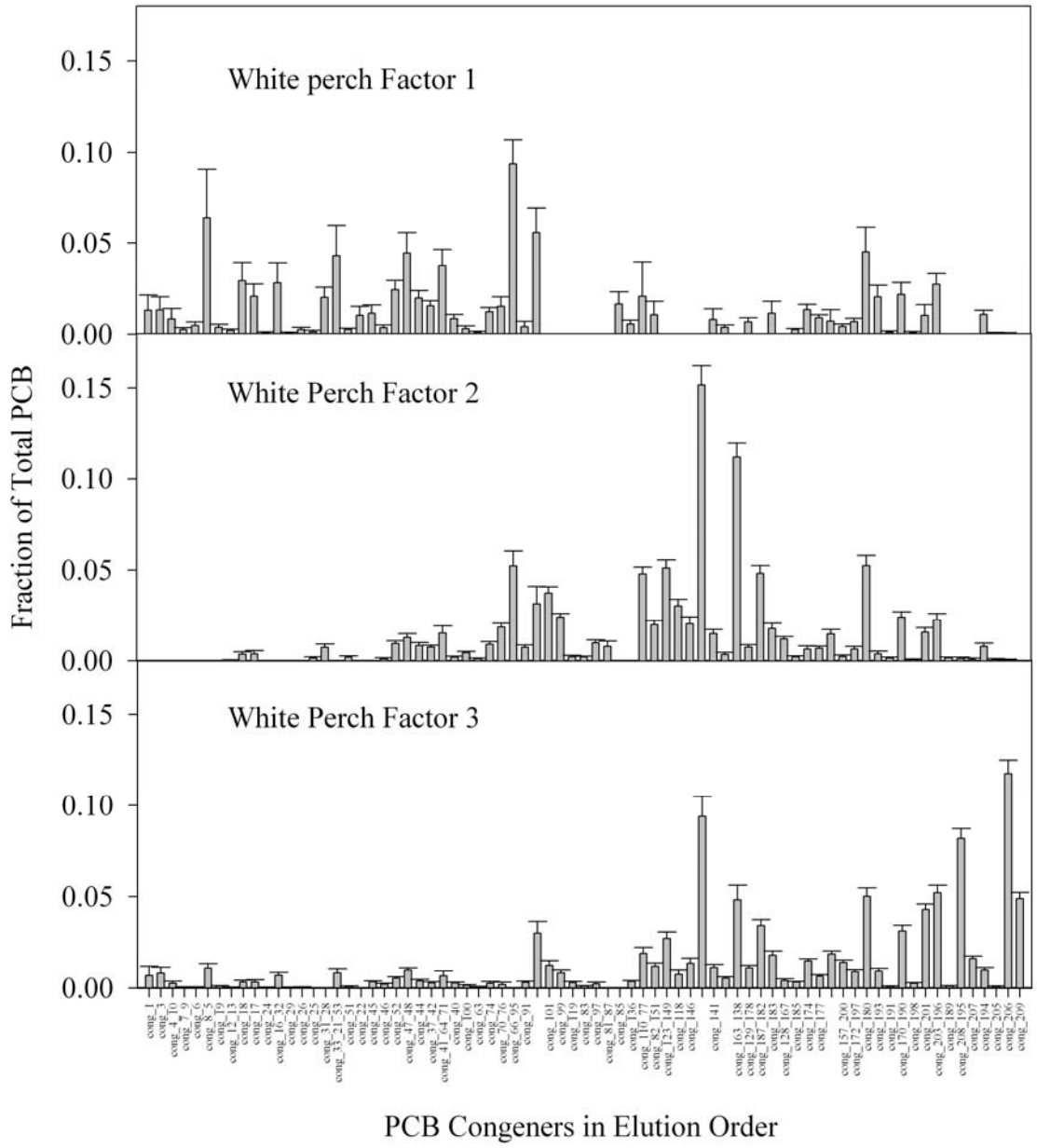


Figure 28. Scree plot of Q values for PMF factorizations of PCB congeners in white perch. Error bars are 99% confidence intervals for Q values among seven iterations.

Figure 29. Source signatures derived with PMF from white perch PCB congeners.



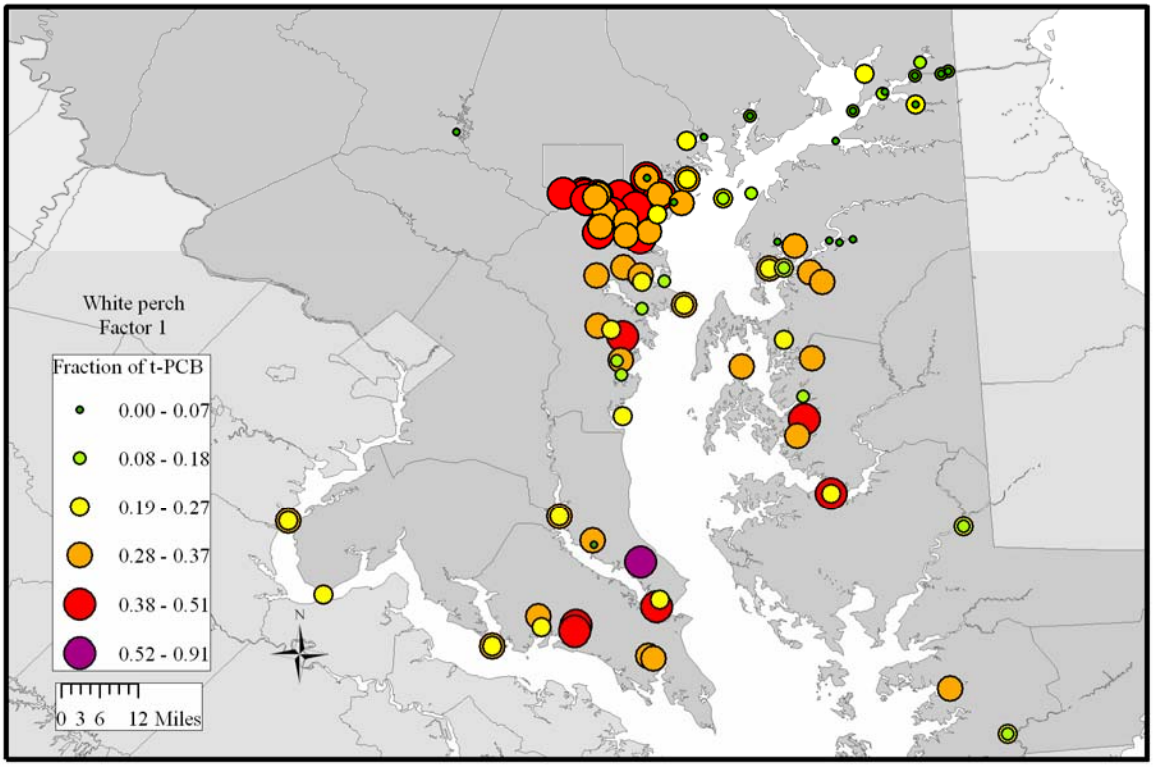


Figure 30. Proportion of Factor 1 constituting t-PCBs in Maryland white perch.

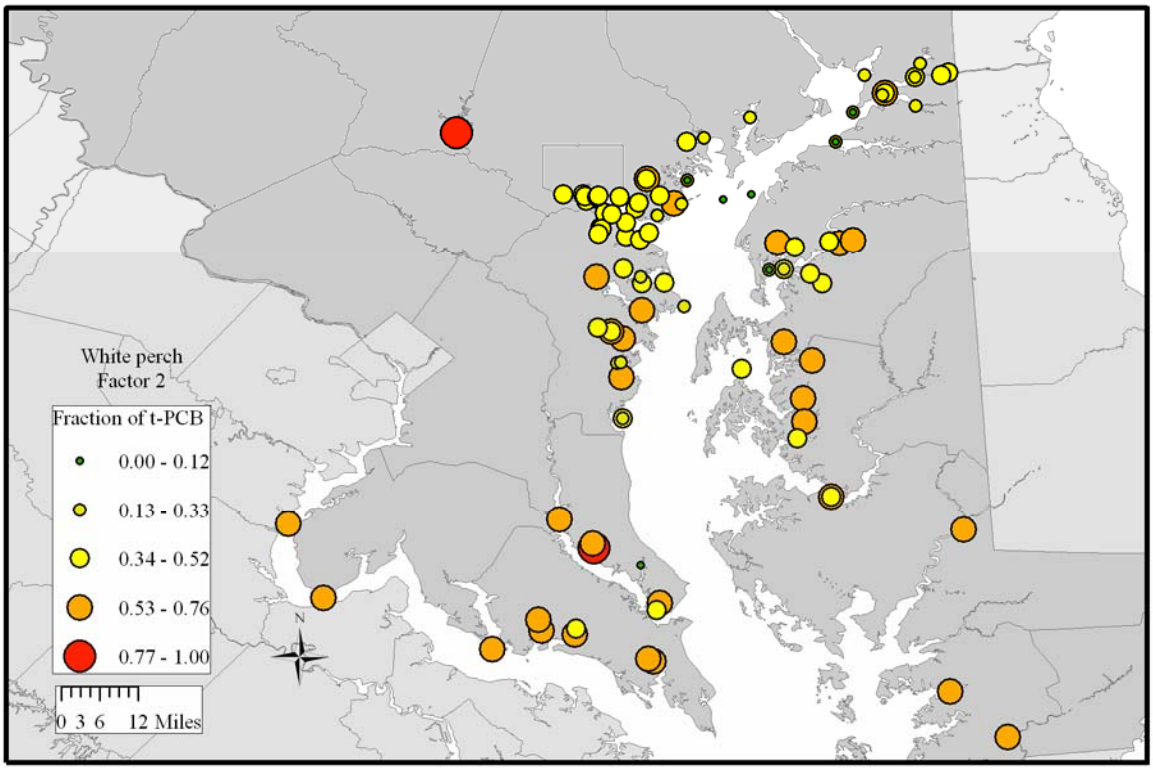


Figure 31. Proportion of Factor 2 constituting t-PCBs in Maryland white perch.

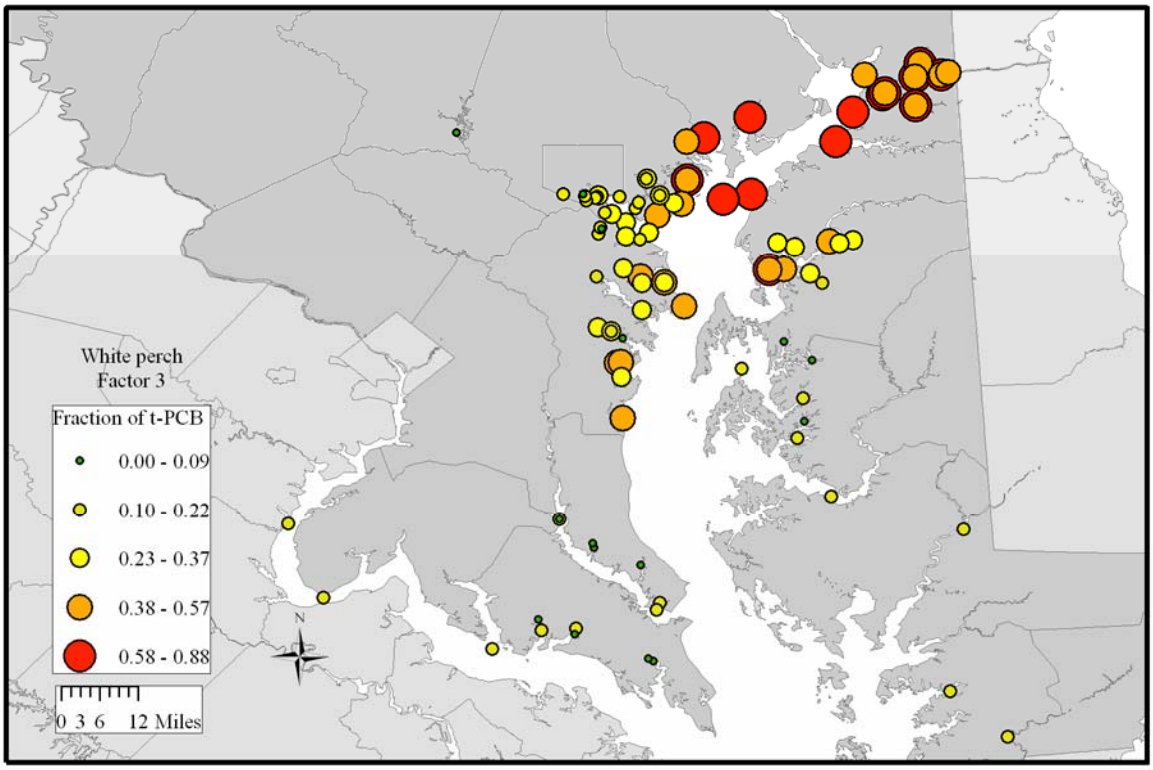


Figure 32. Proportion of Factor 3 constituting t-PCBs in Maryland white perch.

Discussion

Assessment of Results

Combined PCA, cluster analysis, and matrix factorization revealed a predominantly geographical structure of the channel catfish and white perch PCB data matrices. PCA showed that PCB congener patterns of both white perch and channel catfish are similar within regions and different, to varying degrees, among regions. The spatial component of variation of PCB congener patterns in channel catfish was greater, as indicated by the separation of regional clusters in principal components space. The fact that PCA is better able to identify regionally associated clusters of channel catfish samples, as compared to white perch, suggests that congener patterns in channel catfish

better reflect distinct regional congener signatures. This could result from the catfishes' greater accumulation of PCBs and hence greater resemblance to distinct regional congener patterns or from the large geographic gaps between regional catfish samples.

Cluster analysis demonstrated which samples had the most similar congener patterns and reinforced the results of PCA by showing that the clusters of samples collected from each area generally have the most similar congener patterns. The results of kNN cluster analyses were subjective. The changing groupings across results (e.g. white perch solutions for k = 5 and 10) reflect the structure of the data, which is characterized by subtle similarities and differences that are emphasized at different levels of resolution (different k values). Results of cluster analysis were clearer for channel catfish than for white perch, again indicating that channel catfish better reflect regionally distinct congener signatures.

PMF results agree with and elucidate the results of PCA and cluster analysis. PMF illustrates how the relative contributions of certain key groups of PCBs contribute to t-PCB and explains why the groupings of samples formed in PCA and cluster analysis are observed. Where PCA and cluster analysis identified groups of samples with distinct congener patterns, PMF identified factor loadings that were consistent among those groups. PMF was able to model the original sample data using derived congener pattern signatures that can be used to investigate the dispersal of PCBs around source regions.

Regional observations

Potomac River samples did not form a resolved cluster in PCA of either species' congener patterns. This may be due to the fact that the signature component of PCB congener patterns in Potomac River samples (dominance of congeners 132+153+105 and

other moderately chlorinated congeners) is not unique. This component is found in all other regions; however, in those other regions other signature components are also present. The dominance of moderately chlorinated congeners in Potomac channel catfish is suggested by Potomac samples' PC scores which indicate a high presence of light congeners on PC1 and of heavy congeners on PC2. Cluster analysis grouped Potomac River channel catfish showing that they have a consistent congener pattern. Cluster analysis showed that PCB congener patterns in Potomac River white perch are consistent in samples from further up river (k = 5 solution) but that the congener pattern of these samples is similar to that of many other white perch from a broad area of the state. The PCB pattern observed in Potomac River fish is a ubiquitous component of PCB patterns observed in Maryland fish; it is very consistent but not unique. This Potomac River signature is closely replicated by Factor 2 from PMF of the white perch PCB data. Factor 2 is ubiquitous throughout Maryland white perch (Figure 31) and the most notable thing about the geographical distribution of that signature is where it contributes least to total PCB—the Patapsco River and C&D Canal regions where Factors 1 and 3 dominate the PCB profiles. PMF of channel catfish congener patterns also identified a similar congener 132+153+105-dominated PCB signature, which is more specific to Potomac channel catfish than the corresponding signature was to white perch. The sampling of channel catfish was limited to the upper tidal Potomac where the Quantico Marine Base source is located and white perch sampling was both sparse and limited to the lower portion of the river. These weaknesses of sampling cause some difficulty in evaluating spatial trends. Despite the sampling biases and the ubiquitous congener 132+153+105-dominated congener patterns, cluster analyses of the two species combined show that a

characteristic Potomac PCB signature is present in both species and is found in fish from the District of Columbia to the mouth of the Wicomico River. All methods used have distinguished the congener patterns in channel catfish from this section of river from the congener patterns observed upstream of the southern boundary of the District of Columbia. The upper tidal Potomac River is subject to at least one source of PCBs originating south of the District of Columbia and observed PCB congener patterns indicate that PCBs from this source or these sources are found in fish in the river at least as far downriver as the Wicomico River.

Eigenvector weights indicate that PC2 scores for channel catfish from rivers and lakes reflect dominance of less-chlorinated congeners. The grouping of primarily rivers and lakes samples in cluster analysis indicates these fish have a distinct congener pattern. Among channel catfish this signature pattern appears in few other samples. While Patapsco, Anacostia, and some other samples have similarity indicated by cluster analysis and PMF, PCA shows rivers and lakes samples have a unique and strong less-chlorinated PCB signature. This suggests that these fish are subject to a source of less-chlorinated congeners that different from Maryland channel catfish in other regions. It is unlikely that a single source affects fish from such a broad area and the atmosphere may be the primary source of PCBs to these fish. Atmospheric PCBs are typically dominated by more-volatile less-chlorinated PCBs (e.g Brunciak et al. 2001, Rawn et al. 1998).

Channel catfish from both the C&D Canal and Back River regions clustered close together. Resolution in PCA of C&D Canal and Back River channel catfish in two separate clusters of indicates that, while very similar, congener patterns are different between those two regions. PMF results indicate a key difference between C&D Canal

and Back River channel catfish congener patterns is the small proportion of less-chlorinated PCBs in channel catfish from Back River.

Cluster analysis of PCBs in white perch from the C&D Canal and Back River also indicated congener patterns in fish from those regions were similar though not with the consistency seen in channel catfish. The six-cluster solution for white perch indicated that there were distinct differences between congener patterns in groups of white perch from the C&D Canal. White perch from the C&D Canal were split into two clusters, one being composed primarily of fish closer to the state line, and the other being the rest of the C&D Canal cluster from the three-cluster solution. PMF indicated the distinction between the two C&D Canal groups is the relative contributions of moderately chlorinated biphenyls and more-chlorinated biphenyls where the prevalence of moderately chlorinated biphenyls decreases with distance from the state line. A similar observation was made by Ashley et al. (2004). They observed an increase in the fraction of congener 209 along the Delaware River from Philadelphia toward the C&D Canal and a corresponding decrease in t-PCB. The data presented here appear to be a continuation of the same trend. The fraction of the signature pattern observed in C&D Canal fish (dominance of more-chlorinated PCBs including congener 209) increases over a gradient of decreasing concentrations of all PCBs. The trend in t-PCB indicates samples most dominated by this signature are not closest to the source. The trend of increasing fractions of more-chlorinated congeners over a gradient of decreasing t-PCB may indicate that congener 209 and other more-chlorinated PCBs are being transported further within the estuary than lesser chlorinated PCBs. The consistent presence of the more-chlorinated PCB signature in samples from the Chesapeake Bay as far south as Herring

Bay indicated by both PMF and cluster analysis supports the idea that these heavy PCBs are being transported great distances from the C&D Canal while moderately chlorinated PCBs that may originate from the same location(s) are not. The prevalence of this PCB signature in white perch from the Patapsco and Back Rivers decreases with distance up those rivers. This is partially due to the increasing t-PCB and increasing proximity to sources with different PCB signatures. The concentrations from each factor (Appendix 8) rather than the relative contributions indicate that prevalence of Factor 3 PCBs decreases with distance up both the Patapsco and Back River. In the Patapsco it has the greatest prevalence in white perch from Old Road Bay on the northern lip of the river and in white perch from sites along the southern edge of the lower portion, indicating PCBs having this highly chlorinated signature are entering the Patapsco from the Chesapeake Bay.

Cluster analysis assigned Back River white perch to multiple clusters indicating inconsistent congener patterns among those fish. This agrees with the results of PCA where Back River white perch had PC1 and PC2 scores most to Patapsco fish but clearly grouped with them. Cluster analysis and PMF results both indicate a less-chlorinated PCB signature is prevalent toward the head of Back River while moderately and more-chlorinated PCBs compose varying portions of t-PCB in Back River white perch. The most notable difference between congener patterns in Back River white perch and channel catfish is the prevalence of less-chlorinated PCBs in the former. PMF results for channel catfish indicate a decrease in the ratio of more- to moderately chlorinated congeners with distance up river. Since t-PCBs in white perch and channel catfish are relatively constant over the length of the river, the changing congener pattern suggests a

decrease in the influence of the more-chlorinated PCB source with distance upriver (for channel catfish) and a coincident increase in the influence of a source of less-chlorinated PCBs with distance upriver (for white perch). The observed congener patterns in Back River fish indicate they are exposed to multiple sources of PCBs.

The difference between congener patterns observed in white perch and channel catfish from Back River suggests that they do not have the same exposure pathways. It is possible that the observed differences reflect the feeding habits of the two species. Channel catfish may have a stronger benthic linkage that preferentially exposes them to more-chlorinated congeners that are more hydrophobic and more tightly bound to sediments, while white perch may be more pelagic and hence subject to the less-chlorinated, less-hydrophobic PCBs that can be more prevalent higher in the water column. Another possible explanation for the observed differences between the two species' congener patterns is that white perch may move amongst the Back and Patapsco Rivers and hence display the signature PCB patterns of both tributaries. The second explanation seems less likely since white perch displaying the greater prevalence of less-chlorinated PCBs were collected in the upper reaches of the river furthest from the Patapsco.

A less-chlorinated PCB signature was consistently observed in Patapsco River fish. Channel catfish from the Patapsco were grouped in cluster analysis with channel catfish from rivers and lakes which were shown to have a strong less-chlorinated PCB signature by PCA and PMF. PMF and PCA of white perch congener patterns suggested a uniquely strong contribution of less-chlorinated PCBs in the Patapsco, and the grouping of these fish in cluster analysis showed that the less-chlorinated congener signature is

consistently found in white perch from the Patapsco. Although this signature is found in fish from other parts of the state, the low prevalence of this signature in fish collected at sites adjacent to the Patapsco suggests that fish having a less-chlorinated congener signature outside of the Patapsco receive that signature from a different source. As with channel catfish from rivers and lakes this source is likely to be atmospheric. The fact that the spatially disparate samples showing high prevalence of the less-chlorinated PCB signature are ones with low t-PCB concentrations suggests they are not subject to a strong local source and makes the dominance of an atmospheric source in their case likely.

Since Patapsco River fish are among the most contaminated fish found in Maryland, the Patapsco River can be expected to be a source of PCBs to adjacent waters of the Chesapeake Bay. South of the Patapsco in the area around Annapolis I would expect to see a trace of Patapsco PCBs in samples. Samples from that area do not, however, show a marked influence of this less-chlorinated PCB source. In contrast, they do show a greater influence of the more-chlorinated PCB signature. Why is the less-chlorinated congener signature not observed in fish collected in adjacent waters? Less-chlorinated PCBs are both the most soluble and the most volatile PCBs. Because of these physical properties less-chlorinated PCBs will have shorter residence times in the Chesapeake Bay. As there was a greater transport of the more-chlorinated PCBs relative to moderately chlorinated PCBs from the C&D Canal region, here there is little transport of less-chlorinated PCBs from the Patapsco. The apparent differential transport of PCBs may be a reflection of the more rapid removal of less-chlorinated PCBs from the estuary.

The Chesapeake Bay has several PCB-contaminated tributaries. The more-chlorinated signature of PCBs that appears to originate from the C&D Canal is observed

in the Chesapeake Bay from the mouth of the Elk River, which connects the C&D Canal to the Chesapeake Bay, to Herring Bay, south of Annapolis on the Chesapeake's western shore. On the Eastern Shore of the Chesapeake Bay this signature is seen only as far south as the Chester River. PCBs having a distinctive signature of the upper tidal Potomac are not consistently observed downstream of the Wicomico River confluence and, given also the low t-PCB in fish from the lower Potomac and adjacent Chesapeake Bay, the PCBs originating in the upper tidal Potomac do not appear to reach the lower Potomac much less the Chesapeake Bay. The extent of transport of PCBs from the Patapsco into the Chesapeake Bay is unclear. There is a relative elevation of PCB levels in Chesapeake Bay tributaries south of the Patapsco (ie. Magothy, Severn, South, Rhode, and West Rivers, and Herring Bay) and the small contribution of the C&D Canal PCB signature to t-PCBs in these fish implies some other source of PCBs must be present. This other source may be the Patapsco River or there could be other local nonpoint sources. Some of the most contaminated fish in Maryland were collected in Back River. It is one of the most PCB-contaminated tributaries of the Chesapeake Bay. Since Back River fish lack a PCB signature that can be distinguished from Patapsco and C&D Canal PCB signatures, the spatial influence of Back River PCBs in the Chesapeake Bay can not be determined.

In addition, it is possible that there are more sources of PCBs to the Chesapeake Bay than I have identified here. A case in point is Middle River. Middle River was the Chesapeake Bay site where the third most contaminated channel catfish in this study was collected. White perch from this site were no less contaminated than those from the adjacent Back River. White perch from this site had congener patterns that strongly

resembled white perch from C&D Canal and the northern Chesapeake Bay, but channel catfish had a distinctly different profile more like that seen in Patapsco channel catfish with low contributions of more-chlorinated congeners characteristic of PCBs in northern Chesapeake Bay fish. The PCB congener pattern observed in Middle River channel catfish is distinctly different from the congener patterns observed channel catfish from adjacent tributaries (Back River and Gunpowder River). The high t-PCB concentration and distinct congener pattern observed in channel catfish from this site suggest there may be a local source of PCBs.

Congeneric observations

Multivariate analysis was useful for identifying signature components of PCB congener patterns in Maryland fish, but the PCB source signatures identified here were not of equal utility for tracing the spatial influence of PCB sources. While the more-chlorinated PCB signature of C&D Canal fish was observed far to the south, indicating broad distribution of PCBs from a C&D Canal source, the less-chlorinated PCB signature of Patapsco fish was not any more prevalent in waters adjacent to the Patapsco than in samples from more disparate regions of the Chesapeake. The difference in performance of less- and more-chlorinated PCBs as tracers of contamination sources reflects their differing physical properties.

The greater hydrophobicity of more-chlorinated PCBs can be expected to enhance their conservation as particle-bound contaminants, allowing them to be transported downstream greater distances than less-chlorinated PCBs which are more prone to dissociate from particles and volatize, thereby being removed into the atmosphere. As Figure 1 in Chapter 1 shows, there is a difference of 1000 between the octanol-water

partitioning of the least and most chlorinated PCBs, and there is a difference of 10000 in their volatility. Ko and Baker's (1995) measurements of PCBs in the water column of Chesapeake Bay show a trend of binding of PCBs to particulate matter at the base of the water column that increases with increasing PCB chlorination. At the water's surface, an exception to this trend was only seen for di- and trichloribiphenyls. Leister and Baker (1994) have shown the Chesapeake Bay is a net source of PCBs to the atmosphere. In a similar study, Nelson et al. (1998) found that hexa-, hepta-, and octachlorinated biphenyls were being deposited to the Chesapeake Bay throughout most of the year while the annual net efflux of t-PCBs was dominated by less-chlorinated congeners.

Transport of PCB congeners in the Chesapeake Bay and its tributaries varies widely with degree of chlorination. Observations of PCB congener patterns in fish tissue reflect what can be expected given the greater sediment-water-air partitioning paradigm. More-chlorinated PCBs appear to be transported within the water column great distances from sources in the northern Chesapeake Bay, most likely as particle bound contaminants. Less-chlorinated PCBs do not appear to be transported within the water column any great distance from their source(s) because they are volatizing out of the water column. Observations in this study contrast with the observations of Ashley and Baker (1999), who noted a marked increase in the proportion of less-chlorinated PCBs in sediments with distance from the most contaminated upper reaches of the Patapsco River. But, our observations agree with those of Ashley et al. (2003) who noted a relative decrease in the proportions of less-chlorinated PCB congeners with distance from an up-stream source in Hudson River American eels and striped bass. The decrease in the proportion of less-chlorinated PCBs with distance from an upstream source observed in

Hudson River striped bass was attributed to habitat use within the Hudson River (Ashley et al. 2000); decreasing proportions of less-chlorinated biphenyls in that habitat with distance from the source may be attributable to selective removal of less-chlorinated biphenyls from the system. Congeneric differences in transport processes may complicate the use of PCB congener signatures as tracers of PCB sources within the Chesapeake Bay. The observations presented in this study reinforce that in the global sediment-water-air partitioning process, more-chlorinated congeners will be conserved within the local system while less-chlorinated congeners will be transported out of the local system. The failure to observe estuarine transport of less-chlorinated PCBs out of the Patapsco is a product of the greater role atmospheric transport plays for more volatile PCBs. Given the wide dispersal of more-chlorinated PCBs within Chesapeake Bay, the relative immobility of less-chlorinated PCBs indicates that they are being removed from the estuary (especially the Patapsco River) through volatization.

Conclusions

A combined multivariate approach to analysis of PCBs in Maryland fish tissues helps to illustrate the spatial variation in congener patterns that occur. This approach was particularly useful for tracing a highly chlorinated PCB signature throughout the northern Chesapeake. It was less effective for delineating the areas affected by PCBs from the upper tidal Potomac, for which the characteristic signature is less distinct, and the Patapsco River, for which the characteristic signature is composed of more volatile PCBs that may be depleted with distance from the source as the local signature is weathered. I can, nevertheless, draw certain conclusions from PCB congener patterns about transport of PCBs from the most contaminated source areas. PCBs in the upper tidal Potomac

River originate in that section of river, not from upstream, and are not a major source of PCBs to fish downstream of the Wicomico River confluence. PCBs originating from the C&D Canal region appear to be dispersed southward as far as Herring Bay and Chester River on the western and eastern shores of the Chesapeake Bay, respectively. PCBs originating in Patapsco River may contribute to the pool of PCBs in adjacent waters, but can not be traced by a congener signature. The heterogeneity of PCB congener patterns observed in Back River fish suggest multiple sources of PCBs. The heavily chlorinated C&D Canal PCB source contributes decreasing amounts to t-PCBs in channel catfish and white perch with distance up Back River. In Back River less-chlorinated PCBs comprised a greater proportion of t-PCBs in white perch collected up-river. Congener patterns in channel catfish and white perch from Back River were different—the former having a distinct lack of less-chlorinated congeners—indicating the two species have different exposure regimes.

Fish in the tributaries of the northern Chesapeake Bay are highly contaminated with PCBs, and the blending of PCBs from multiple sources having similar congener patterns creates some difficulty in the process of identifying distinct PCB congener signatures for sources. The chief difficulty appears to arise from the roles different transport processes play for different PCBs depending primarily upon their degree of chlorination. It can be inferred from congener patterns observed in fish tissue that the most chlorinated PCBs are conserved within the estuary and transported with sediments, while less chlorinated PCBs are preferentially removed from the estuary by volatization. Observed congener patterns are weathered in this manner, complicating the use of PCB congener patterns as tracers for PCB sources.

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Chapter 5: Conclusions

PCB congeners were measured in 520 fish tissue samples collected from Maryland waters between 1999 and 2004. These samples include 36 species from 190 sites. PCB contamination was found primarily in estuarine fish from the Patapsco, Potomac and Back Rivers, the northern Chesapeake Bay and the C&D Canal. Fish collected from Maryland's coastal bays were among the least contaminated with PCBs, and most species sampled had mean concentrations that did not warrant consumption advisories. Fish collected in freshwater rivers and lakes had lower concentrations, but channel catfish from Jennings Randolph Lake, and the Potomac River below the Shenandoah River confluence and fish from Antietam Creek near Hagerstown had relatively elevated PCB levels. Of 20 species sampled from freshwater sites, four were suitable for unlimited consumption and three had mean concentrations warranting consumption of no more than one meal per month. Of estuarine samples only blue crab muscle and oyster tissue had mean concentrations warranting no consumption advisory. Channel catfish, white catfish, American eel, blue crab hepatopancreas and carp had the greatest PCB mean concentrations of PCBs among estuarine samples, all of which warranted consumption of less than one meal per month. Within estuarine and freshwater habitats, contamination was focused in and around certain tributaries. Within small subsets of the data correlations of PCB concentrations with lipid and length were found, but PCB concentrations varied primarily with species and site of capture. White perch from the Patapsco River, C&D Canal, and Back River had significantly greater PCB

concentrations than those from Potomac River, Chesapeake Bay and rivers and lakes. Channel catfish concentrations followed the same trend with the exception of Potomac River channel catfish being among the more contaminated. The regions with elevated fish tissue PCB concentrations are regions of known contamination and act as sources of PCBs to the Chesapeake Bay.

The congeneric composition of PCBs in fish tissues also varies spatially. Congener profiles of samples collected from the C&D Canal and northern Chesapeake Bay were characterized by especially high fractions of nona- and decachlorobiphenyls. Channel catfish and white perch samples collected from the Patapsco River and channel catfish from rivers and lakes had especially high proportions of less-chlorinated biphenyls. Channel catfish and white perch from the upper tidal Potomac were characterized by uniquely high fractions of PCB congeners 153+132+105 and very small proportions of mono- through tetra- and nona- and decachlorobiphenyls. Channel catfish and white perch collected from Back River had different congener patterns. Channel catfish congener patterns were distinguished by a high proportion of nona- and decachlorobiphenyls and a lack of the least chlorinated congeners, while white perch congener patterns were more variable and had greater proportions of the less-chlorinated congeners found in Patapsco River fish. A multivariate analysis of PCB congener patterns in white perch and channel catfish was useful for investigating the distribution of PCBs from source regions in the Chesapeake Bay. PCBs having a highly chlorinated signature pattern appear to emanate from C&D Canal in the northern Chesapeake Bay and to be dispersed as far south as Herring Bay. PCBs originating in the upper tidal Potomac appear to be confined to the tidal portion of that river between the District of

Columbia and the Wicomico River confluence. Patapsco River PCBs can not be traced by using their unique signature of less-chlorinated congeners, because that signature is rapidly depleted as PCBs undergo weathering and fractionation as they migrate from the source. The complex composition of PCBs in Back River fish suggests multiple sources of PCBs to fish in that river. PCB congener patterns in channel catfish reflected distinct regional signatures to a greater extent than congener patterns in white perch. This difference might stem from a greater association of channel catfish with the benthic habitat and greater exposure to sediment-bound contaminants or from less site fidelity of white perch.

The apparent fractionation of PCBs in the Chesapeake Bay is among the more interesting observations of this study. Highly chlorinated PCBs can be observed to travel great distances within the estuary, presumably as sediment-bound contaminants. A strong prevalence of less-chlorinated PCB congeners was observed close to a Patapsco River source and at sites located far from point source locations. Moderately chlorinated congeners, especially congeners 153+132+105, dominated congener profiles of PCBs in most all samples with the exception of those collected in the northern Chesapeake Bay between the C&D Canal and Back River. These observations reflect the physical properties of PCBs and their behavior in the estuarine environment. The most volatile (least chlorinated) PCBs are removed from the estuary more rapidly than their less volatile (more chlorinated) counterparts, diminishing their proportion of t-PCBs as PCBs are fractionated in the environment. Moderately chlorinated congeners are also removed more rapidly than the most chlorinated PCBs but are redeposited into the estuary after traveling some distance through the atmosphere, enhancing their broad distribution

throughout Maryland waters. The least volatile PCBs with the greatest chlorination have more monotonically decreasing concentrations with distance from their source, suggesting they are to a greater extent conserved within the estuary. The observation of environmental fractionation of PCBs at the biotic level within an estuary underscores the importance of partitioning of these compounds in the environment. It would seem that, barring further inputs of PCBs, the depletion of PCBs in the Chesapeake Bay via atmospheric transport would ultimately selectively eliminate the least chlorinated congeners and leave the pool of these contaminants enriched in more-chlorinated congeners.

Appendices

Appendix 1. PCB coelutant compounds.

Congener(s)	Coelutant
4,10	2,4,5,6-tetrachloro-m-xylene
14	unidentified
49	unidentified
85	pp-DDE
89	op-DDE
97	unidentified PCB congeners
99	cis-Chlordane
107	Endosulfan II
118	PBDE 28
174	PBDE 75
157,200	Methoxychlor
193	PBDE 47
194	PBDE 100
199	unidentified

Appendix 2. Detail maps of total PCBs in Maryland fish.

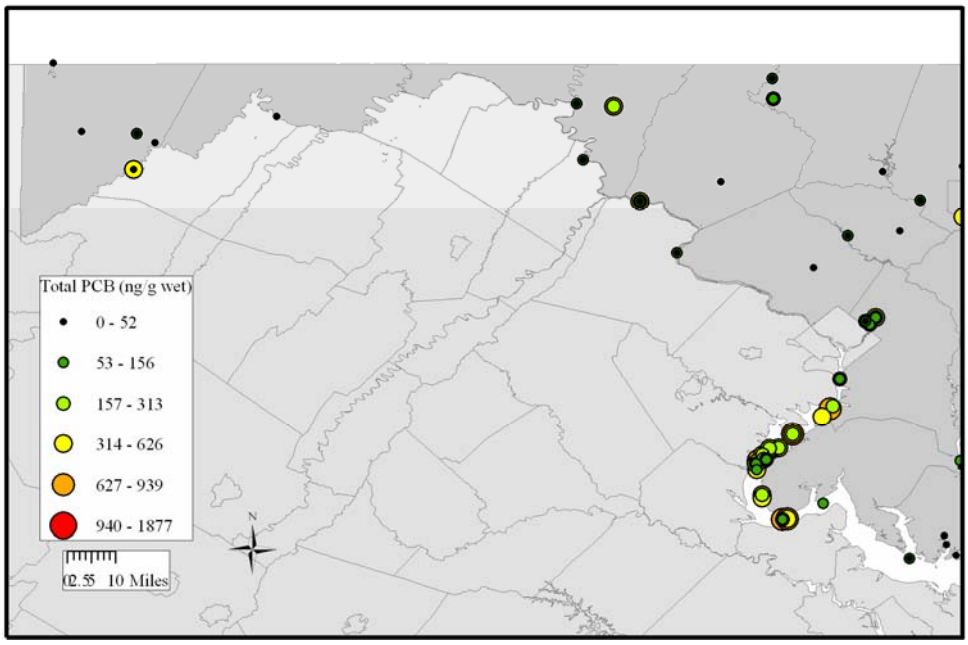


Figure 1. Western Maryland detail map of t-PCB in Maryland fish.

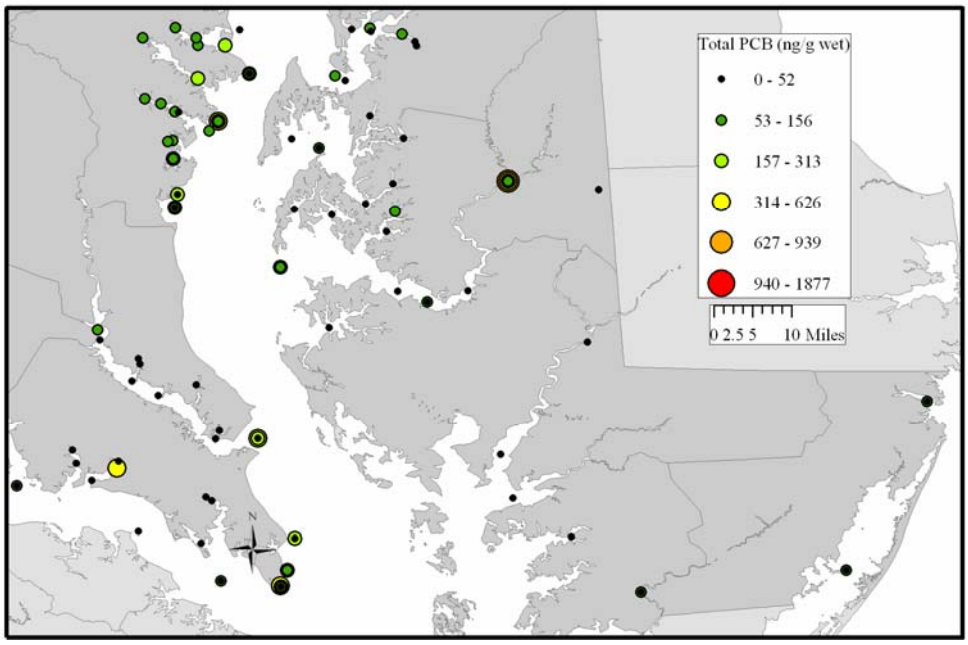


Figure 2. Eastern Maryland detail map of t-PCB in Maryland fish.

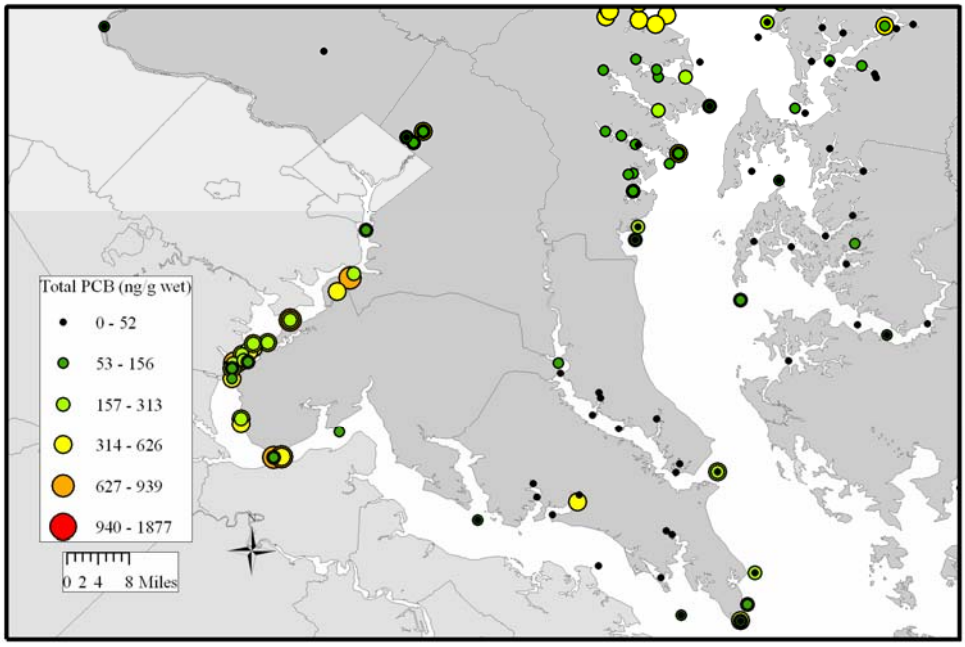


Figure 3. Southern Maryland detail map of t-PCB in Maryland fish.

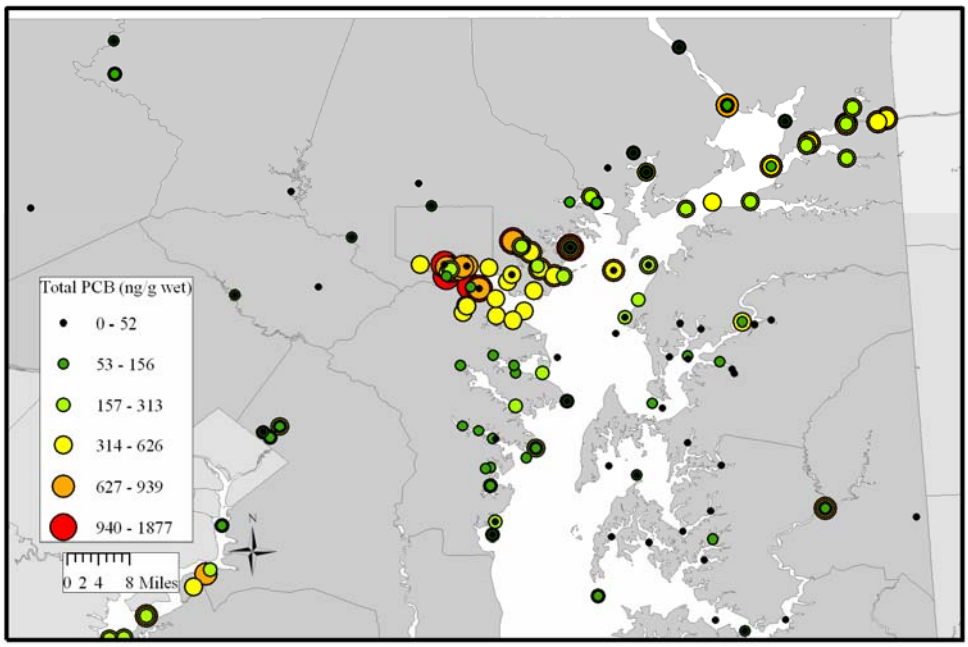
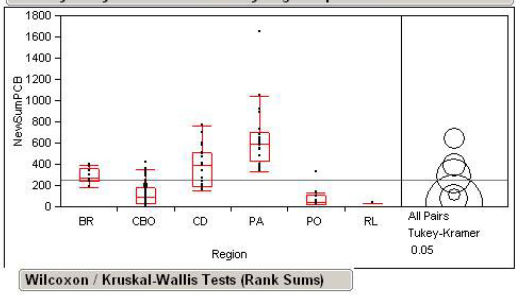


Figure 4. Northern Maryland detail map of t-PCB in Maryland fish.

Appendix 3. Statistical test results for Chapter 3.

Kruskal-Wallis tests and means comparisons for total PCB (SumPCB) in white perch (WP) and channel catfish (CC) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), C&D Canal (CD), Patapsco River (PA), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of NewSumPCB By Region Species=WP



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	675.000	84.375	1.666
CBO	64	2827.00	44.172	-6.034
CD	18	1666.00	92.556	3.643
PA	21	2339.00	111.381	6.579
PO	12	427.000	35.583	-2.780
RL	3	67.000	22.333	-1.968

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
78.8688	5	<.0001*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.89630	0.05

Abs(Dif)-LSD

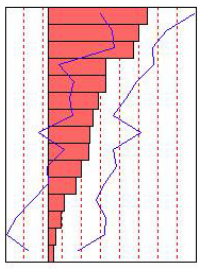
	PA	CD	BR	CBO	PO	RL
PA	-144.02	103.86	161.50	413.36	394.51	325.03
CD	103.86	-155.56	-96.66	152.46	135.71	68.29
BR	161.50	-96.66	-233.34	0.33	-5.01	-58.26
CBO	413.36	152.46	0.33	-82.50	-114.14	-193.33
PO	394.51	135.71	-5.01	-114.14	-190.52	-251.56
RL	325.03	68.29	-58.26	-193.33	-251.56	-381.04

Positive values show pairs of means that are significantly different.

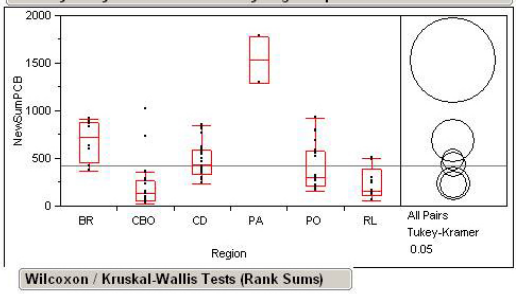
Level		Mean
PA	A	642.74978
CD	B	388.99307
BR	B C	287.35830
CBO	D	112.03000
PO	C D	79.36236
RL	C D	29.68339

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	RL	613.0664	325.029	901.1039
PA	PO	563.3874	394.510	732.2644
PA	CBO	530.7198	413.359	648.0807
CD	RL	359.3097	68.287	650.3321
PA	BR	355.3915	161.500	549.2826
CD	PO	309.6307	135.712	483.5499
CD	CBO	276.9631	152.456	401.4702
BR	RL	257.6749	-58.265	573.6147
PA	CD	253.7567	103.857	403.6562
BR	PO	207.9959	-5.011	421.0025
BR	CBO	175.3283	0.326	350.3311
CD	BR	101.6348	-96.664	299.9331
CBO	RL	82.3466	-193.330	358.0235
PO	RL	49.6790	-251.558	350.9158
CBO	PO	32.6676	-114.137	179.4723



Oneway Analysis of NewSumPCB By Region Species=CC



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	610.000	76.2500	3.110
CBO	20	507.000	25.3500	-4.088
CD	28	1638.00	58.5000	2.542
PA	2	187.000	93.5000	2.397
PO	23	1155.00	50.2174	0.545
RL	13	368.000	28.3077	-2.727

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
38.9742	5	<.0001*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.91347	0.05

Abs(Dif)-LSD

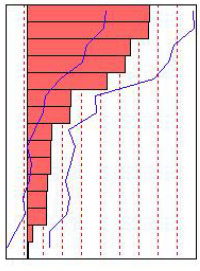
	PA	BR	CD	PO	RL	CBO
PA	-634.55	344.88	582.78	629.82	814.30	834.21
BR	344.88	-317.27	-53.70	-9.38	164.59	192.82
CD	582.78	-53.70	-169.59	-128.18	36.08	71.81
PO	629.82	-9.38	-128.18	-187.12	-21.53	13.18
RL	814.30	164.59	36.08	-21.53	-248.89	-217.53
CBO	834.21	192.82	71.81	13.18	-217.53	-200.66

Positive values show pairs of means that are significantly different.

Level		Mean
PA	A	1528.8052
BR	B	682.2658
CD	B	481.5844
PO	B C	431.1908
RL	C D	232.5355
CBO	D	224.0000

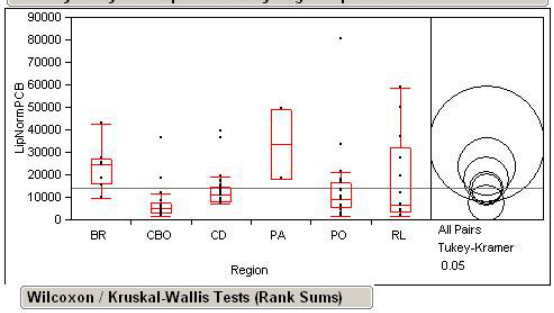
Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	CBO	1304.805	834.211	1775.399
PA	RL	1296.270	814.295	1778.244
PA	PO	1097.614	629.819	1565.410
PA	CD	1047.221	582.779	1511.663
PA	BR	846.539	344.885	1348.194
BR	CBO	458.266	192.815	723.717
BR	RL	449.730	164.590	734.870
CD	CBO	257.584	71.808	443.361
BR	PO	251.075	-9.382	511.533
CD	RL	249.049	36.085	462.013
PO	CBO	207.191	13.183	401.199
BR	CD	200.681	-53.704	455.067
PO	RL	198.655	-21.526	418.837
CD	PO	50.394	-128.176	228.963
RL	CBO	8.536	-217.530	234.602



Kruskal-Wallis tests and means comparisons for lipid normalized total PCB (LipNormPCB, ng/g/fraction lipid) in white perch (WP) and channel catfish (CC) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), C&D Canal (CD), Patapsco River (PA), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of LipNormPCB By Region Species=CC



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	604.000	75.5000	3.028
CBO	20	523.000	26.1500	-3.940
CD	28	1525.00	54.4643	1.608
PA	2	165.000	82.5000	1.821
PO	23	1044.00	45.3913	-0.422
RL	13	604.000	46.4615	-0.142

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
25.9522	5	<.0001*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.91347	0.05

Abs(Dif)-LSD

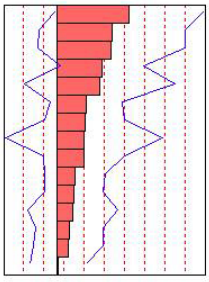
	PA	BR	RL	PO	CD	CBO
PA	-36902	-19074	-12192	-7167	-6724	-765
BR	-19074	-18451	-10845	-5208	-4608	1065
RL	-12192	-10845	-14474	-8604	-7937	-2382
PO	-7167	-5208	-8604	-10882	-10138	-4719
CD	-6724	-4608	-7937	-10138	-9863	-4487
CBO	-765	1065	-2382	-4719	-4487	-11670

Positive values show pairs of means that are significantly different.

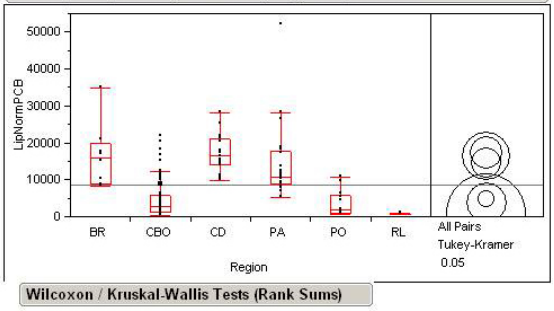
Level		Mean
PA	A B	33627.695
BR	A	23528.010
RL	A B	17790.220
PO	A B	13589.515
CD	A B	13342.286
CBO	B	7025.658

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	CBO	26602.04	-765.5	53969.55
PA	CD	20285.41	-6724.3	47295.16
PA	PO	20038.18	-7166.6	47242.95
BR	CBO	16502.35	1065.0	31939.71
PA	RL	15837.48	-12191.9	43866.81
RL	CBO	10764.56	-2382.4	23911.49
BR	CD	10185.72	-4608.1	24979.57
PA	BR	10099.68	-19074.2	39273.55
BR	PO	9938.50	-5208.5	25085.47
PO	CBO	6563.86	-4718.7	17846.46
CD	CBO	6316.63	-4487.3	17120.53
BR	RL	5737.79	-10844.6	22320.17
RL	CD	4447.93	-7937.0	16832.91
RL	PO	4200.71	-8604.0	17005.41
PO	CD	247.23	-10137.5	10631.98



Oneway Analysis of LipNormPCB By Region Species=WP



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	770.000	96.250	2.616
CBO	64	2954.00	46.156	-5.414
CD	18	1881.00	104.500	5.142
PA	21	1865.00	88.810	3.476
PO	12	493.000	41.083	-2.231
RL	3	38.000	12.667	-2.432

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
63.9852	5	<.0001*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.89630	0.05

Abs(Dif)-LSD

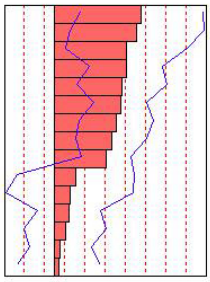
	CD	BR	PA	CBO	PO	RL
CD	-6229	-7137	-3226	7474	6570	4751
BR	-7137	-9343	-5791	4649	4202	2950
PA	-3226	-5791	-5767	4984	3996	2094
CBO	7474	4649	4984	-3303	-4804	-7094
PO	6570	4202	3996	-4804	-7629	-9192
RL	4751	2950	2094	-7094	-9192	-15258

Positive values show pairs of means that are significantly different.

Level		Mean
CD	A	17215.655
BR	A	16412.414
PA	A	14439.772
CBO	B	4756.221
PO	B	3681.575
RL	B	811.660

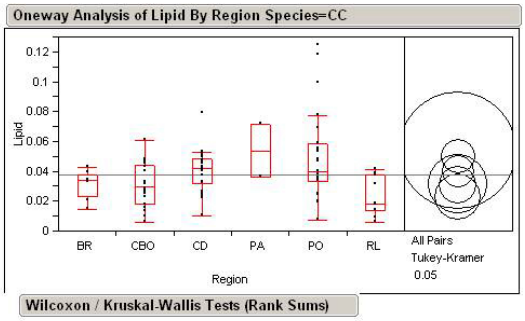
Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
CD	RL	16403.99	4750.84	28057.15
BR	RL	15600.75	2949.85	28251.66
PA	RL	13628.11	2094.48	25161.75
CD	PO	13534.08	6569.99	20498.17
BR	PO	12730.84	4201.60	21260.08
CD	CBO	12459.43	7473.90	17444.97
BR	CBO	11656.19	4648.71	18663.68
PA	PO	10758.20	3996.00	17520.39
PA	CBO	9683.55	4984.17	14382.93
CBO	RL	3944.56	-7094.13	14983.25
PO	RL	2869.91	-9192.25	14932.08
CD	PA	2775.88	-3226.41	8778.18
BR	PA	1972.64	-5791.17	9736.46
CBO	PO	1074.65	-4803.73	6953.02
CD	BR	803.24	-7137.05	8743.53



Kruskal-Wallis tests and means comparisons for fraction lipid (Lipid) in white perch (WP) and channel catfish (CC) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), C&D Canal (CD), Patapsco River (PA), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of Lipid By Region Species=CC



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	321.000	40.1250	-0.793
CBO	20	767.000	38.3500	-1.686
CD	28	1551.00	55.3929	1.823
PA	2	137.000	68.5000	1.087
PO	23	1362.00	59.2174	2.366
RL	13	327.000	25.1538	-3.176

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
19.3307	5	0.0017*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.91347	0.05

Abs(Dif)-LSD

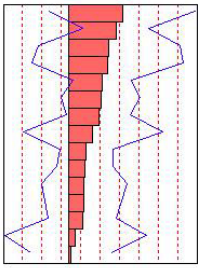
	PA	PO	CD	BR	CBO	RL
PA	-0.05573	-0.03732	-0.02695	-0.02185	-0.01825	-0.01135
PO	-0.03732	-0.01643	-0.00560	-0.00443	0.00228	0.00788
CD	-0.02695	-0.00560	-0.01489	-0.01398	-0.00708	-0.00157
BR	-0.02185	-0.00443	-0.01398	-0.02786	-0.02244	-0.01627
CBO	-0.01825	0.00228	-0.00708	-0.02244	-0.01762	-0.01196
RL	-0.01135	0.00788	-0.00157	-0.01627	-0.01196	-0.02186

Positive values show pairs of means that are significantly different.

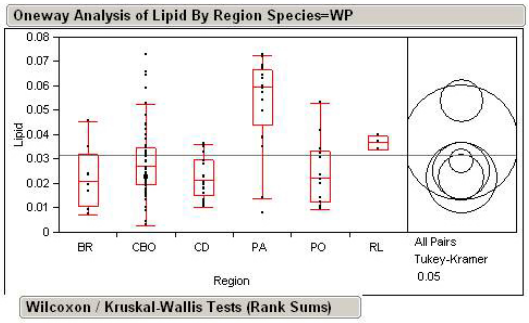
Level		Mean
PA	A B	0.05361897
PO	A	0.04985580
CD	A B	0.03977743
BR	A B	0.03141522
CBO	B	0.03053941
RL	B	0.02264085

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	RL	0.0309781	-0.011352	0.0733079
PO	RL	0.0272149	0.007877	0.0465526
PA	CBO	0.0230796	-0.018251	0.0644099
PA	BR	0.0222038	-0.021855	0.0662620
PO	CBO	0.0193164	0.002277	0.0363553
PO	BR	0.0184406	-0.004434	0.0413155
CD	RL	0.0171366	-0.001567	0.0358403
PA	CD	0.0138415	-0.026949	0.0546316
PO	CD	0.0100784	-0.005605	0.0257614
CD	CBO	0.0092380	-0.007078	0.0255540
BR	RL	0.0087744	-0.016268	0.0338170
CD	BR	0.0083622	-0.013979	0.0307038
CBO	RL	0.0078986	-0.011956	0.0277530
PA	PO	0.0037632	-0.037321	0.0448477
BR	CBO	0.0008758	-0.022438	0.0241893



Oneway Analysis of Lipid By Region Species=WP



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	355.000	44.375	-1.526
CBO	64	3846.00	60.094	-1.061
CD	18	806.000	44.778	-2.346
PA	21	2140.00	101.905	5.276
PO	12	592.000	49.333	-1.409
RL	3	262.000	87.333	1.136

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
33.7937	5	<.0001*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.89630	0.05

Abs(Dif)-LSD

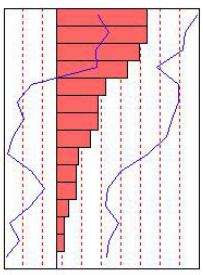
	PA	RL	CBO	PO	CD	BR
PA	-0.01269	-0.00838	0.01416	0.01380	0.01815	0.01435
RL	-0.00838	-0.03357	-0.01679	-0.01486	-0.01128	-0.01341
CBO	0.01416	-0.01679	-0.00727	-0.00875	-0.00411	-0.00849
PO	0.01380	-0.01486	-0.00875	-0.01679	-0.01265	-0.01602
CD	0.01815	-0.01128	-0.00411	-0.01265	-0.01371	-0.01740
BR	0.01435	-0.01341	-0.00849	-0.01602	-0.01740	-0.02056

Positive values show pairs of means that are significantly different.

Level		Mean
PA	A	0.05372139
RL	A B	0.03672059
CBO	B	0.02922216
PO	B	0.02504012
CD	B	0.02236108
BR	B	0.02228846

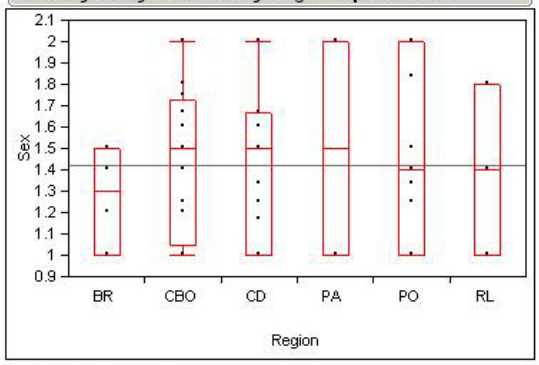
Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	BR	0.0314329	0.014348	0.0485174
PA	CD	0.0313603	0.018152	0.0445685
PA	PO	0.0286813	0.013801	0.0435617
PA	CBO	0.0244992	0.014158	0.0348403
PA	RL	0.0170008	-0.008379	0.0423809
RL	BR	0.0144321	-0.013407	0.0422708
RL	CD	0.0143595	-0.011284	0.0400026
RL	PO	0.0116805	-0.014863	0.0382236
RL	CBO	0.0074984	-0.016793	0.0317894
CBO	BR	0.0069337	-0.008486	0.0223539
CBO	CD	0.0068611	-0.004110	0.0178319
CBO	PO	0.0041820	-0.008753	0.0171176
PO	BR	0.0027517	-0.016017	0.0215205
PO	CD	0.0026790	-0.012646	0.0180037
CD	BR	0.0000726	-0.017400	0.0175455



Kruskal-Wallis tests and means comparisons for sex (1 = female, 2 = male) of white perch (WP) and channel catfish (CC) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), C&D Canal (CD), Patapsco River (PA), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of Sex By Region Species=CC



Missing Rows 21

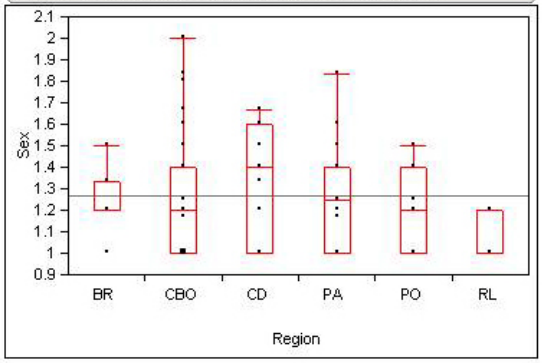
Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	218.500	27.3125	-1.381
CBO	20	778.500	38.9250	0.477
CD	26	965.000	37.1154	0.029
PA	2	80.000	40.0000	0.189
PO	14	552.000	39.4286	0.477
RL	3	107.000	35.6667	-0.099

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
2.1334	5	0.8304

Oneway Analysis of Sex By Region Species=WP



Missing Rows 6

Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

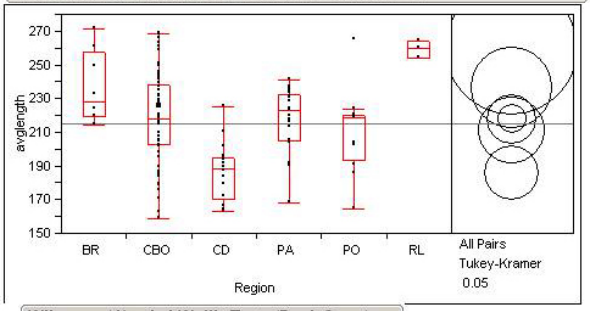
Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	7	404.500	57.7857	-0.213
CBO	63	3826.50	60.7381	0.078
CD	16	1131.50	70.7188	1.293
PA	19	1177.00	61.9474	0.199
PO	12	624.500	52.0417	-0.908
RL	3	96.000	32.0000	-1.468

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
4.4162	5	0.4912

Kruskal-Wallis tests and means comparisons for average length (Avg length) of white perch (WP) and channel catfish (CC) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), C&D Canal (CD), Patapsco River (PA), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of avglength By Region Species=WP



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	722.500	90.313	2.141
CBO	64	4330.00	67.656	1.296
CD	18	447.000	24.833	-4.849
PA	21	1459.00	69.476	0.818
PO	12	689.500	57.458	-0.598
RL	3	353.000	117.667	2.593

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
32.8209	5	<.0001*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.89630	0.05

Abs(Dif)-LSD

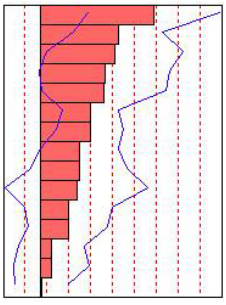
	RL	BR	CBO	PA	PO	CD
RL	-55.941	-23.030	0.823	-0.647	4.183	31.036
BR	-23.030	-34.257	-7.751	-10.179	-6.218	21.294
CBO	0.823	-7.751	-12.112	-16.885	-14.440	14.187
PA	-0.647	-10.179	-16.885	-21.144	-18.025	10.114
PO	4.183	-6.218	-14.440	-18.025	-27.970	-0.181
CD	31.036	21.294	14.187	10.114	-0.181	-22.838

Positive values show pairs of means that are significantly different.

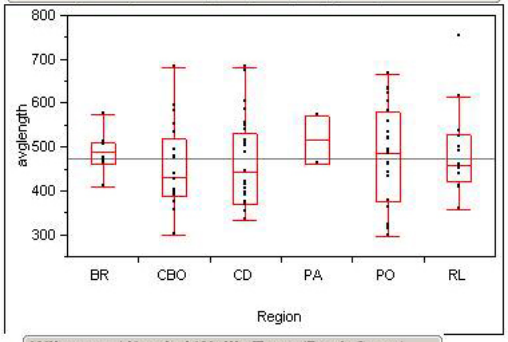
Level		Mean
RL	A	259.33333
BR	A B	235.97917
CBO	B	218.03802
PA	A B	217.69286
PO	B C	210.92500
CD	C	185.57222

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
RL	CD	73.76111	31.0356	116.4867
BR	CD	50.40694	21.2944	79.5195
RL	PO	48.40833	4.1832	92.6335
RL	PA	41.64048	-0.6469	83.9278
RL	CBO	41.29531	0.8227	81.7680
CBO	CD	32.46580	14.1867	50.7449
PA	CD	32.12063	10.1136	54.1277
PO	CD	25.35278	-0.1806	50.8862
BR	PO	25.05417	-6.2177	56.3261
RL	BR	23.35417	-23.0296	69.7379
BR	PA	18.28631	-10.1792	46.7518
BR	CBO	17.94115	-7.7513	43.6336
CBO	PO	7.11302	-14.4397	28.6657
PA	PO	6.76786	-18.0253	31.5610
CBO	PA	0.34516	-16.8848	17.5751



Oneway Analysis of avglength By Region Species=CC



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

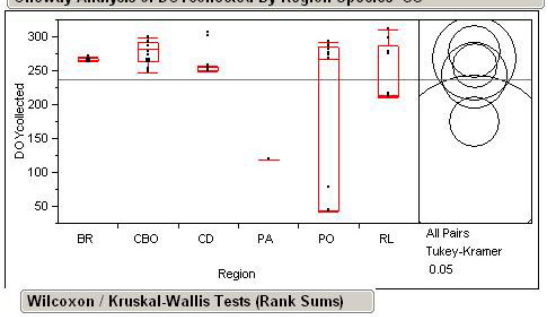
Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	437.000	54.6250	0.766
CBO	20	847.500	42.3750	-0.942
CD	28	1230.50	43.9464	-0.819
PA	2	122.500	61.2500	0.707
PO	23	1164.50	50.6304	0.629
RL	13	663.000	51.0000	0.493

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
2.7520	5	0.7381

Kruskal-Wallis tests and means comparisons for day of year (DOY) collected for white perch (WP) and channel catfish (CC) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), C&D Canal (CD), Patapsco River (PA), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of DOYcollected By Region Species=CC



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	464.000	58.0000	1.133
CBO	20	1323.00	66.1500	3.445
CD	28	1167.00	41.6786	-1.345
PA	2	25.000	12.5000	-1.823
PO	23	941.500	40.9348	-1.325
RL	13	544.500	41.8846	-0.795

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
17.0200	5	0.0045*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.91347	0.05

Abs(Dif)-LSD

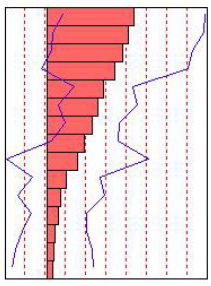
	CBO	BR	CD	RL	PO	PA
CBO	-55.72	-64.01	-30.56	-28.19	49.11	27.53
BR	-64.01	-88.10	-59.32	-54.29	20.96	9.20
CD	-30.56	-59.32	-47.09	-45.57	32.38	8.21
RL	-28.19	-54.29	-45.57	-69.11	7.26	-10.22
PO	49.11	20.96	32.38	7.26	-51.96	-74.68
PA	27.53	9.20	8.21	-10.22	-74.68	-176.20

Positive values show pairs of means that are significantly different.

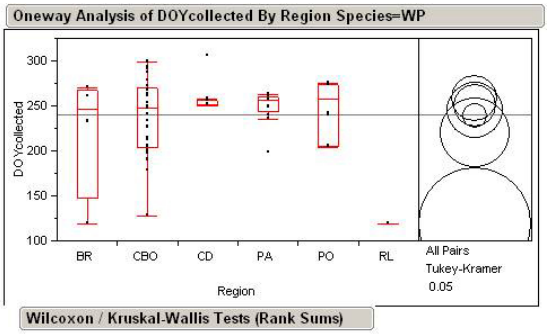
Level		Mean
CBO	A	277.20000
BR	A	267.50000
CD	A	256.17857
RL	A B	242.61538
PO	C	174.21739
PA	B C	119.00000

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
CBO	PA	158.2000	27.5260	288.8740
BR	PA	148.5000	9.2010	287.7990
CD	PA	137.1786	8.2128	266.1444
RL	PA	123.6154	-10.2188	257.4495
CBO	PO	102.9826	49.1106	156.8546
BR	PO	93.2826	20.9590	165.6062
CD	PO	81.9612	32.3762	131.5462
RL	PO	68.3980	7.2582	129.5377
PO	PA	55.2174	-74.6796	185.1144
CBO	RL	34.5846	-28.1892	97.3584
BR	RL	24.8846	-54.2927	104.0620
CBO	CD	21.0214	-30.5649	72.6078
CD	RL	13.5632	-45.5724	72.6988
BR	CD	11.3214	-59.3161	81.9589
CBO	BR	9.7000	-64.0101	83.4101



Oneway Analysis of DOYcollected By Region Species=WP



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	449.000	56.1250	-0.586
CBO	64	3985.00	62.2656	-0.383
CD	18	1313.00	72.9444	1.182
PA	21	1409.00	67.0952	0.491
PO	12	836.000	69.6667	0.611
RL	3	9.000	3.0000	-2.898

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
10.3927	5	0.0648

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.89630	0.05

Abs(Dif)-LSD

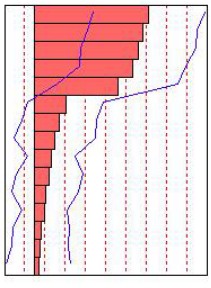
	CD	PA	PO	CBO	BR	RL
CD	-36.191	-26.780	-27.297	-9.040	-7.927	71.625
PA	-26.780	-33.507	-34.219	-15.473	-14.997	64.224
PO	-27.297	-34.219	-44.325	-27.395	-24.516	56.082
CBO	-9.040	-15.473	-27.395	-19.193	-22.434	55.268
BR	-7.927	-14.997	-24.516	-22.434	-54.287	27.620
RL	71.625	64.224	56.082	55.268	27.620	-88.651

Positive values show pairs of means that are significantly different.

Level		Mean
CD	A	258.33333
PA	A	250.23810
PO	A	245.16667
CBO	A	238.40625
BR	A	220.12500
RL	B	119.00000

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
CD	RL	139.3333	71.6253	207.0414
PA	RL	131.2381	64.2245	198.2517
PO	RL	126.1667	56.0821	196.2512
CBO	RL	119.4063	55.2684	183.5441
BR	RL	101.1250	27.6197	174.6303
CD	BR	38.2083	-7.9269	84.3436
PA	BR	30.1131	-14.9968	75.2230
PO	BR	25.0417	-24.5156	74.5989
CD	CBO	19.9271	-9.0402	48.8944
CBO	BR	18.2813	-22.4342	58.9967
CD	PO	13.1667	-27.2967	53.6300
PA	CBO	11.8318	-15.4729	39.1366
CD	PA	8.0952	-26.7798	42.9702
PO	CBO	6.7604	-27.3946	40.9154
PA	PO	5.0714	-34.2188	44.3616



Correlations of measured parameters for pooled white perch (WP) and channel catfish (CC) composite samples. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male).

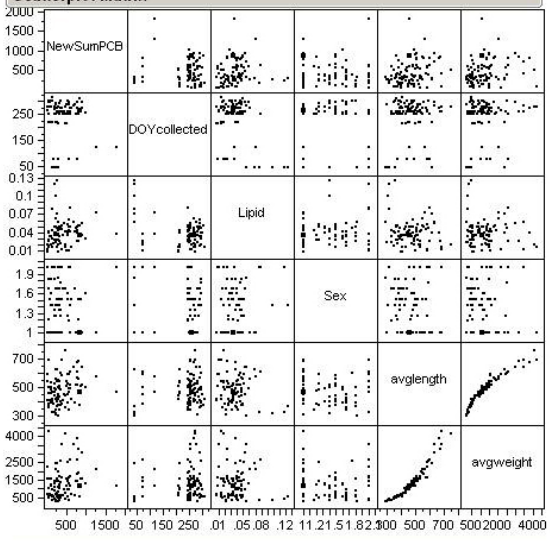
Multivariate Species=CC

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.1275	0.0952	-0.0583	0.2614	0.2008
DOYcollected	-0.1275	1.0000	-0.4755	-0.1210	0.1094	0.0675
Lipid	0.0952	-0.4755	1.0000	0.0658	-0.2062	-0.1520
Sex	-0.0583	-0.1210	0.0658	1.0000	-0.1292	-0.1294
avglength	0.2614	0.1094	-0.2062	-0.1292	1.0000	0.9515
avgweight	0.2008	0.0675	-0.1520	-0.1294	0.9515	1.0000

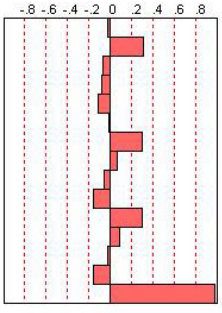
21 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	-0.0221	0.8324
Lipid	NewSumPCB	0.3117	0.0022*
Lipid	DOYcollected	-0.0681	0.5142
Sex	NewSumPCB	-0.0768	0.5182
Sex	DOYcollected	-0.1136	0.3384
Sex	Lipid	-0.0078	0.9481
avglength	NewSumPCB	0.3055	0.0028*
avglength	DOYcollected	0.0687	0.5107
avglength	Lipid	-0.0561	0.5911
avglength	Sex	-0.1582	0.1814
avgweight	NewSumPCB	0.3053	0.0028*
avgweight	DOYcollected	0.0882	0.3980
avgweight	Lipid	-0.0192	0.8542
avgweight	Sex	-0.1615	0.1723
avgweight	avglength	0.9864	<.0001*



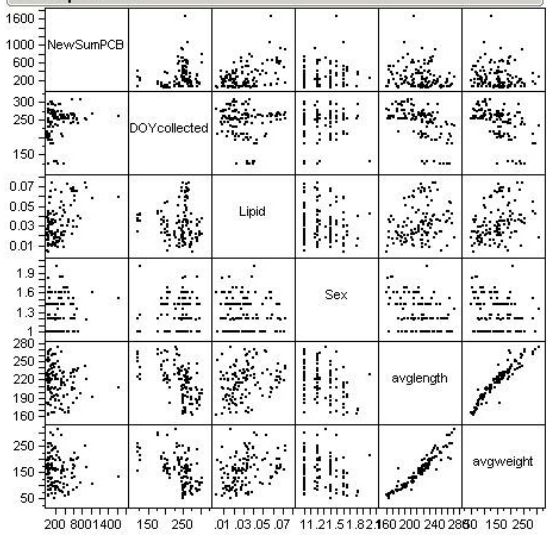
Multivariate Species=WP

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	0.1853	0.4393	0.1574	-0.1575	-0.1283
DOYcollected	0.1853	1.0000	-0.0440	0.0308	-0.5424	-0.5490
Lipid	0.4393	-0.0440	1.0000	-0.0863	0.2840	0.3546
Sex	0.1574	0.0308	-0.0863	1.0000	-0.2945	-0.2447
avglength	-0.1575	-0.5424	0.2840	-0.2945	1.0000	0.9455
avgweight	-0.1283	-0.5490	0.3546	-0.2447	0.9455	1.0000

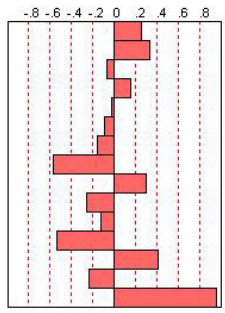
6 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.2602	0.0033*
Lipid	NewSumPCB	0.3372	0.0001*
Lipid	DOYcollected	-0.0692	0.4415
Sex	NewSumPCB	0.1555	0.0898
Sex	DOYcollected	-0.0234	0.7998
Sex	Lipid	-0.0848	0.3573
avglength	NewSumPCB	-0.1515	0.0904
avglength	DOYcollected	-0.5703	<.0001*
avglength	Lipid	0.3062	0.0005*
avglength	Sex	-0.2516	0.0056*
avgweight	NewSumPCB	-0.1268	0.1572
avgweight	DOYcollected	-0.5330	<.0001*
avgweight	Lipid	0.4080	<.0001*
avgweight	Sex	-0.2394	0.0085*
avgweight	avglength	0.9578	<.0001*



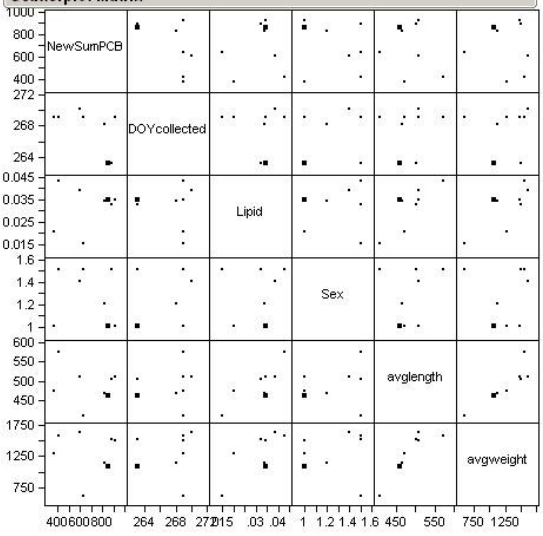
Correlations of measured parameters for Back River white perch (WP) and channel catfish (CC) composite samples. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male).

Multivariate Species=CC, Region=BR

Correlations

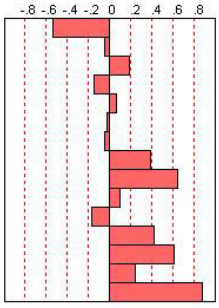
	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.5699	0.1692	-0.2110	-0.2078	-0.0571
DOYcollected	-0.5699	1.0000	-0.0981	0.0741	0.1196	0.0612
Lipid	0.1692	-0.0981	1.0000	0.0833	0.8121	0.7610
Sex	-0.2110	0.0741	0.0833	1.0000	0.1920	0.0289
avglength	-0.2078	0.1196	0.8121	0.1920	1.0000	0.8894
avgweight	-0.0571	0.0612	0.7610	0.0289	0.8894	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	-0.5363	0.1706
Lipid	NewSumPCB	-0.0476	0.9108
Lipid	DOYcollected	0.1916	0.6495
Sex	NewSumPCB	-0.1502	0.7226
Sex	DOYcollected	0.0671	0.8745
Sex	Lipid	-0.0250	0.9531
avglength	NewSumPCB	-0.0476	0.9108
avglength	DOYcollected	0.3959	0.3316
avglength	Lipid	0.6429	0.0856
avglength	Sex	0.1001	0.8135
avgweight	NewSumPCB	-0.1667	0.6932
avgweight	DOYcollected	0.4214	0.2984
avgweight	Lipid	0.6190	0.1017
avgweight	Sex	0.2503	0.5499
avgweight	avglength	0.8810	0.0039*



Warning: sample size of 8 is too small, P value suspect.

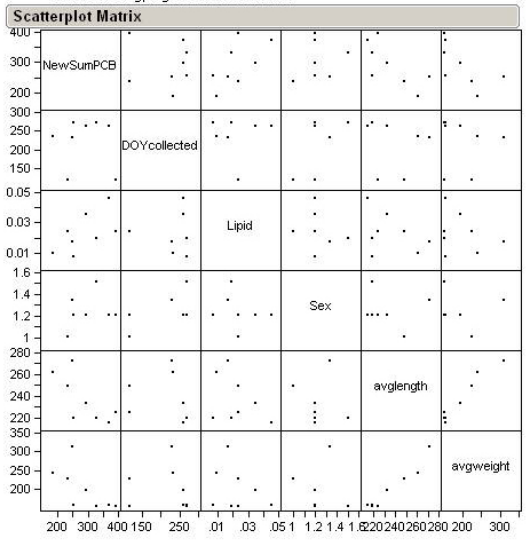
Multivariate Species=WP, Region=BR

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.0665	0.5167	0.2458	-0.6342	-0.6302
DOYcollected	-0.0665	1.0000	0.0476	0.5842	-0.2790	-0.1364
Lipid	0.5167	0.0476	1.0000	-0.2141	-0.2554	-0.1782
Sex	0.2458	0.5842	-0.2141	1.0000	-0.1103	-0.0635
avglength	-0.6342	-0.2790	-0.2554	-0.1103	1.0000	0.9838
avgweight	-0.6302	-0.1364	-0.1782	-0.0635	0.9838	1.0000

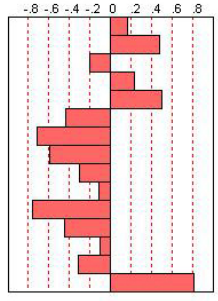
1 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.1697	0.6878
Lipid	NewSumPCB	0.4762	0.2329
Lipid	DOYcollected	-0.2061	0.6244
Sex	NewSumPCB	0.2364	0.6097
Sex	DOYcollected	0.5063	0.2462
Sex	Lipid	-0.4335	0.3313
avglength	NewSumPCB	-0.7186	0.0446*
avglength	DOYcollected	-0.5976	0.1177
avglength	Lipid	-0.2994	0.4713
avglength	Sex	-0.1093	0.8155
avgweight	NewSumPCB	-0.7619	0.0280*
avgweight	DOYcollected	-0.4486	0.2650
avgweight	Lipid	-0.0952	0.8225
avgweight	Sex	-0.3152	0.4910
avgweight	avglength	0.8144	0.0138*



Warning: sample size of 8 is too small, P value suspect.

Correlations of measured parameters for Chesapeake and Delaware Canal white perch (WP) and channel catfish (CC) composite samples. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male).

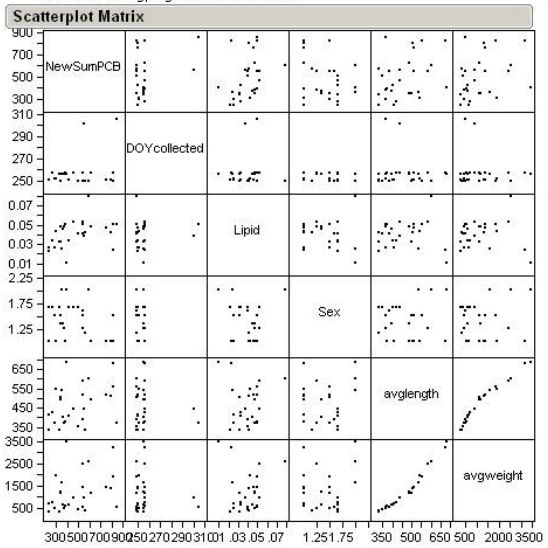
Multivariate Species=CC, Region=CD

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.1515	0.3565	-0.2828	0.4570	0.4246
DOYcollected	-0.1515	1.0000	-0.0366	-0.0436	0.1920	0.2022
Lipid	0.3565	-0.0366	1.0000	-0.1195	0.0431	0.0082
Sex	-0.2828	-0.0436	-0.1195	1.0000	0.0475	0.0906
avglength	0.4570	0.1920	0.0431	0.0475	1.0000	0.9749
avgweight	0.4246	0.2022	0.0082	0.0906	0.9749	1.0000

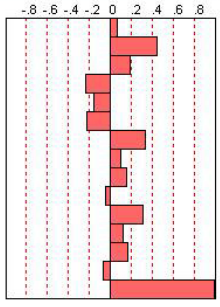
2 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.0656	0.7400
Lipid	NewSumPCB	0.4439	0.0180*
Lipid	DOYcollected	0.1880	0.3380
Sex	NewSumPCB	-0.2295	0.2593
Sex	DOYcollected	-0.1512	0.4610
Sex	Lipid	-0.2229	0.2737
avglength	NewSumPCB	0.3335	0.0829
avglength	DOYcollected	0.0967	0.6245
avglength	Lipid	0.1572	0.4245
avglength	Sex	-0.0462	0.8228
avgweight	NewSumPCB	0.3158	0.1016
avgweight	DOYcollected	0.1235	0.5313
avgweight	Lipid	0.1642	0.4037
avgweight	Sex	-0.0700	0.7340
avgweight	avglength	0.9966	<.0001*



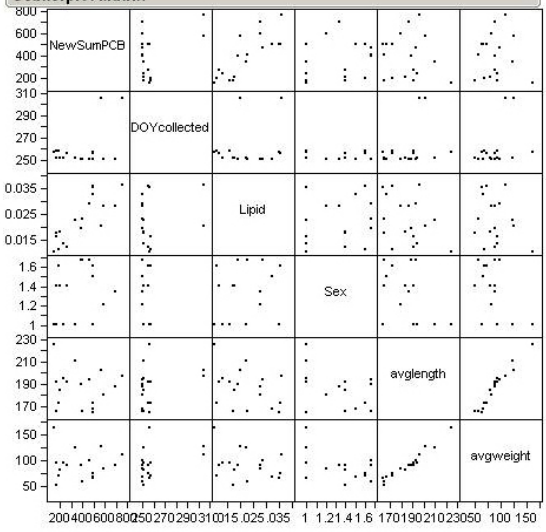
Multivariate Species=WP, Region=CD

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.4419	0.8339	0.2145	-0.3069	-0.2417
DOYcollected	-0.4419	1.0000	-0.2832	-0.3083	0.1032	0.1712
Lipid	0.8339	-0.2832	1.0000	0.1868	-0.4670	-0.3701
Sex	0.2145	-0.3083	0.1868	1.0000	-0.4640	-0.4944
avglength	-0.3069	0.1032	-0.4670	-0.4640	1.0000	0.9751
avgweight	-0.2417	0.1712	-0.3701	-0.4944	0.9751	1.0000

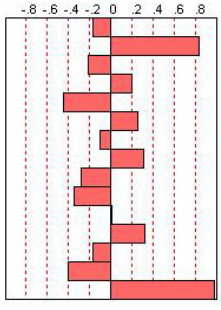
2 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	-0.1695	0.5014
Lipid	NewSumPCB	0.8328	<.0001*
Lipid	DOYcollected	-0.2097	0.4036
Sex	NewSumPCB	0.2014	0.4545
Sex	DOYcollected	-0.4428	0.0859
Sex	Lipid	0.2525	0.3454
avglength	NewSumPCB	-0.1003	0.6922
avglength	DOYcollected	0.3087	0.2126
avglength	Lipid	-0.2739	0.2714
avglength	Sex	-0.3510	0.1826
avgweight	NewSumPCB	0.0155	0.9514
avgweight	DOYcollected	0.3243	0.1893
avgweight	Lipid	-0.1704	0.4991
avgweight	Sex	-0.4046	0.1201
avgweight	avglength	0.9819	<.0001*



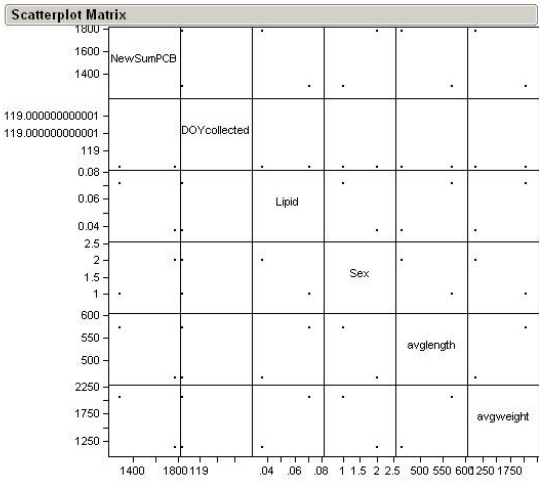
Correlations of measured parameters for Patapsco white perch (WP) and channel catfish (CC) composite samples. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male). Though presented for completeness, insufficient data for channel catfish makes those correlations invalid.

Multivariate Species=CC, Region=PA

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	0.0000	-1.0000	1.0000	-1.0000	-1.0000
DOYcollected	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
Lipid	-1.0000	0.0000	1.0000	-1.0000	1.0000	1.0000
Sex	1.0000	0.0000	-1.0000	1.0000	-1.0000	-1.0000
avglength	-1.0000	0.0000	1.0000	-1.0000	1.0000	1.0000
avgweight	-1.0000	0.0000	1.0000	-1.0000	1.0000	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	.	.
Lipid	NewSumPCB	-1.0000	.
Lipid	DOYcollected	.	.
Sex	NewSumPCB	1.0000	.
Sex	DOYcollected	.	.
Sex	Lipid	-1.0000	.
avglength	NewSumPCB	-1.0000	.
avglength	DOYcollected	.	.
avglength	Lipid	1.0000	.
avglength	Sex	-1.0000	.
avgweight	NewSumPCB	-1.0000	.
avgweight	DOYcollected	.	.
avgweight	Lipid	1.0000	.
avgweight	Sex	-1.0000	.
avgweight	avglength	1.0000	.

Warning: sample size of 2 is too small, P value suspect.

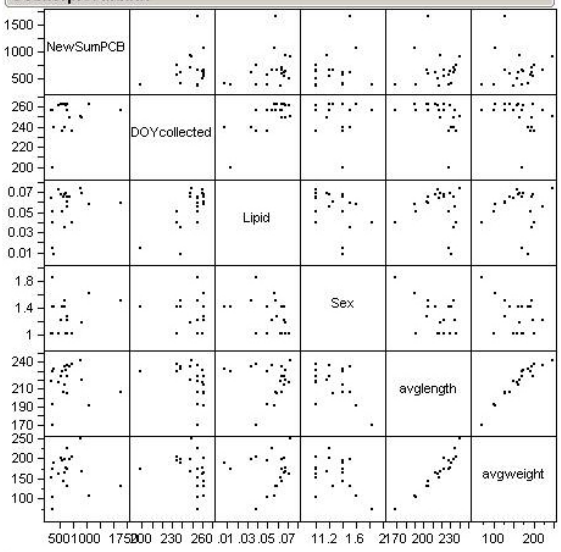
Multivariate Species=WP, Region=PA

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	0.2089	0.2869	0.1930	-0.0859	-0.1041
DOYcollected	0.2089	1.0000	0.7628	-0.1224	-0.4288	-0.3330
Lipid	0.2869	0.7628	1.0000	-0.3820	-0.1671	-0.1121
Sex	0.1930	-0.1224	-0.3820	1.0000	-0.4698	-0.3928
avglength	-0.0859	-0.4288	-0.1671	-0.4698	1.0000	0.9602
avgweight	-0.1041	-0.3330	-0.1121	-0.3928	0.9602	1.0000

2 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.0441	0.8493
Lipid	NewSumPCB	0.3117	0.1690
Lipid	DOYcollected	0.5192	0.0159*
Sex	NewSumPCB	0.0540	0.8262
Sex	DOYcollected	0.0161	0.9480
Sex	Lipid	-0.4644	0.0452*
avglength	NewSumPCB	0.1969	0.3923
avglength	DOYcollected	-0.6003	0.0040*
avglength	Lipid	-0.0318	0.8910
avglength	Sex	-0.2968	0.2172
avgweight	NewSumPCB	0.2247	0.3275
avgweight	DOYcollected	-0.4289	0.0524
avgweight	Lipid	0.0909	0.6951
avgweight	Sex	-0.2511	0.2998
avgweight	avglength	0.9467	<.0001*

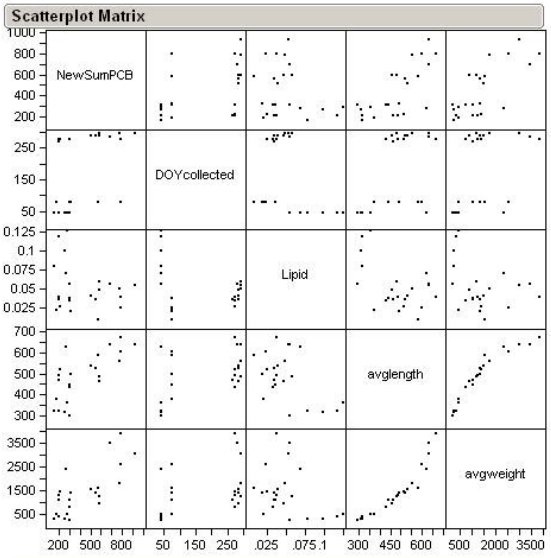
Correlations of measured parameters for Potomac white perch (WP) and channel catfish (CC) composite samples. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male). Insufficient sex data was available for channel catfish.

Multivariate Species=CC, Region=PO

Correlations

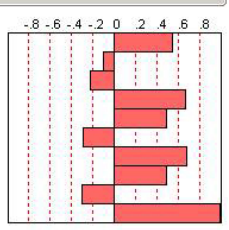
	NewSumPCB	DOYcollected	Lipid	avglength	avgweight
NewSumPCB	1.0000	0.4731	-0.2420	0.7248	0.7481
DOYcollected	0.4731	1.0000	-0.3585	0.5061	0.4242
Lipid	-0.2420	-0.3585	1.0000	-0.4885	-0.3156
avglength	0.7248	0.5061	-0.4885	1.0000	0.9304
avgweight	0.7481	0.4242	-0.3156	0.9304	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.5457	0.0071*
Lipid	NewSumPCB	-0.0998	0.6505
Lipid	DOYcollected	-0.2181	0.3175
avglength	NewSumPCB	0.6719	0.0004*
avglength	DOYcollected	0.4914	0.0172*
avglength	Lipid	-0.2905	0.1787
avgweight	NewSumPCB	0.6769	0.0004*
avgweight	DOYcollected	0.4909	0.0174*
avgweight	Lipid	-0.2964	0.1696
avgweight	avglength	0.9941	<.0001*

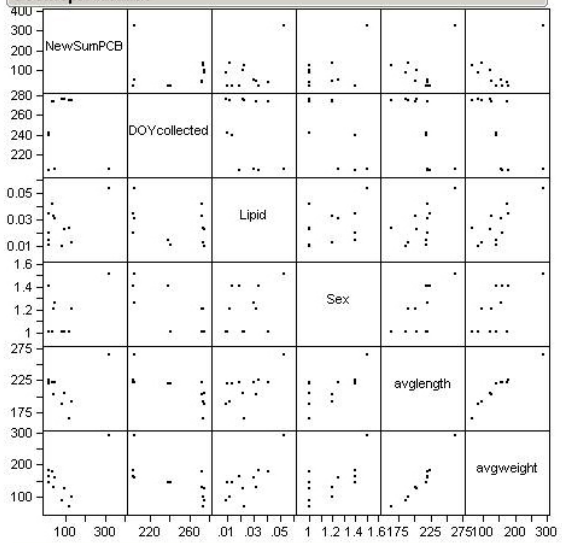


Multivariate Species=WP, Region=PO

Correlations

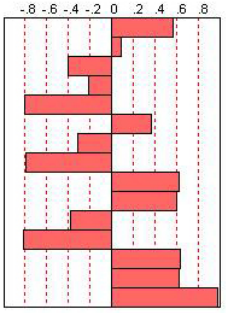
	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.0505	0.4697	0.2283	0.2898	0.4458
DOYcollected	-0.0505	1.0000	-0.3520	-0.7815	-0.7217	-0.6782
Lipid	0.4697	-0.3520	1.0000	0.3852	0.6194	0.7732
Sex	0.2283	-0.7815	0.3852	1.0000	0.6613	0.6436
avglength	0.2898	-0.7217	0.6194	0.6613	1.0000	0.9655
avgweight	0.4458	-0.6782	0.7732	0.6436	0.9655	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.5679	0.0541
Lipid	NewSumPCB	0.0839	0.7954
Lipid	DOYcollected	-0.4021	0.1950
Sex	NewSumPCB	-0.2086	0.5152
Sex	DOYcollected	-0.8013	0.0017*
Sex	Lipid	0.3660	0.2420
avglength	NewSumPCB	-0.3152	0.3182
avglength	DOYcollected	-0.7880	0.0023*
avglength	Lipid	0.6270	0.0291*
avglength	Sex	0.6013	0.0386*
avgweight	NewSumPCB	-0.3846	0.2170
avgweight	DOYcollected	-0.8148	0.0012*
avgweight	Lipid	0.6364	0.0261*
avgweight	Sex	0.6222	0.0307*
avgweight	avglength	0.9807	<.0001*



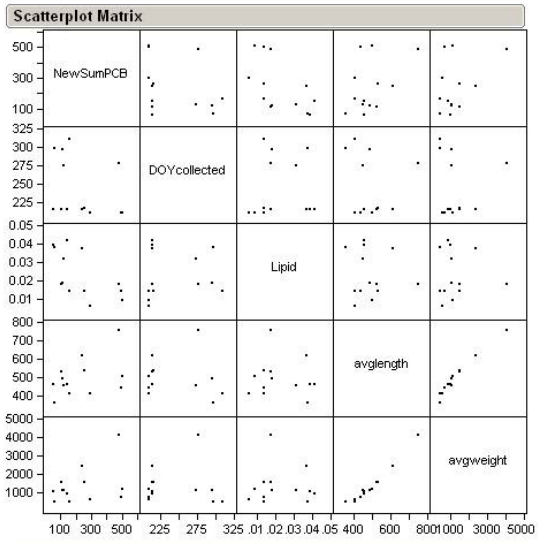
Correlations of measured parameters for white perch (WP) and channel catfish (CC) composite samples from rivers and lakes. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male). Insufficient sex data was available for channel catfish. While presented for completeness, insufficient white perch data was available to make meaningful correlations.

Multivariate Species=CC, Region=RL

Correlations

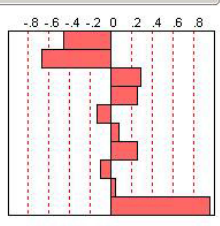
	NewSumPCB	DOYcollected	Lipid	avglength	avgweight
NewSumPCB	1.0000	-0.3127	-0.5878	0.4423	0.4008
DOYcollected	-0.3127	1.0000	0.0596	-0.1042	-0.0032
Lipid	-0.5878	0.0596	1.0000	-0.0663	0.0112
avglength	0.4423	-0.1042	-0.0663	1.0000	0.9790
avgweight	0.4008	-0.0032	0.0112	0.9790	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	-0.4595	0.1142
Lipid	NewSumPCB	-0.6758	0.0112*
Lipid	DOYcollected	0.2942	0.3293
avglength	NewSumPCB	0.2582	0.3943
avglength	DOYcollected	-0.1317	0.6681
avglength	Lipid	0.0824	0.7890
avgweight	NewSumPCB	0.2527	0.4048
avgweight	DOYcollected	-0.1037	0.7361
avgweight	Lipid	0.0440	0.8866
avgweight	avglength	0.9615	<.0001*

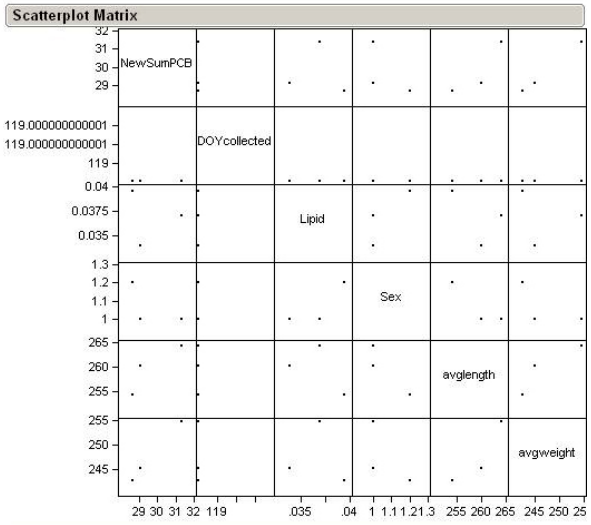


Multivariate Species=WP, Region=RL

Correlations

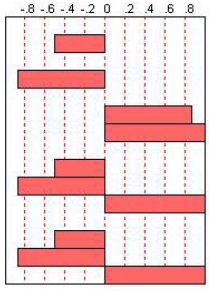
	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	0.0000	-0.0957	-0.6215	0.8816	0.9991
DOYcollected	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
Lipid	-0.0957	0.0000	1.0000	0.8393	-0.5541	-0.1384
Sex	-0.6215	0.0000	0.8393	1.0000	-0.9177	-0.6547
avglength	0.8816	0.0000	-0.5541	-0.9177	1.0000	0.9011
avgweight	0.9991	0.0000	-0.1384	-0.6547	0.9011	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	.	.
Lipid	NewSumPCB	-0.5000	0.6667
Lipid	DOYcollected	.	.
Sex	NewSumPCB	-0.8660	0.3333
Sex	DOYcollected	.	.
Sex	Lipid	0.8660	0.3333
avglength	NewSumPCB	1.0000	0.0000*
avglength	DOYcollected	.	.
avglength	Lipid	-0.5000	0.6667
avglength	Sex	-0.8660	0.3333
avgweight	NewSumPCB	1.0000	0.0000*
avgweight	DOYcollected	.	.
avgweight	Lipid	-0.5000	0.6667
avgweight	Sex	-0.8660	0.3333
avgweight	avglength	1.0000	0.0000*



Warning: sample size of 3 is too small, P value suspect.

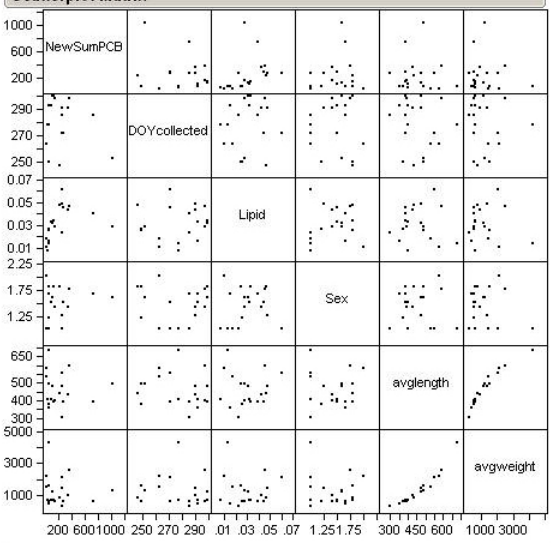
Correlations of measured parameters for Chesapeake Bay white perch (WP) and channel catfish (CC) composite samples. Variables are total PCB (SumPCB, ng/g wet), fraction lipid (Lipid), day of year of capture (DOY), average length (avglength, mm), average weight (avgweight, g) and sex (1 = female, 2 = male).

Multivariate Species=CC, Region=CBO

Correlations

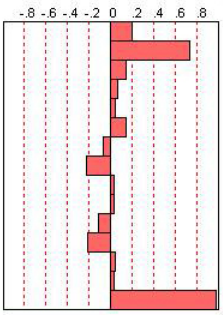
	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	-0.0697	0.3855	0.1683	-0.0450	-0.0961
DOYcollected	-0.0697	1.0000	0.1066	-0.0133	-0.1795	-0.1037
Lipid	0.3855	0.1066	1.0000	0.0963	-0.0070	-0.0671
Sex	0.1683	-0.0133	0.0963	1.0000	-0.0083	-0.1175
avglength	-0.0450	-0.1795	-0.0070	-0.0083	1.0000	0.9543
avgweight	-0.0961	-0.1037	-0.0671	-0.1175	0.9543	1.0000

Scatterplot Matrix



Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.2037	0.3890
Lipid	NewSumPCB	0.7353	0.0002*
Lipid	DOYcollected	0.1464	0.5381
Sex	NewSumPCB	0.0699	0.7696
Sex	DOYcollected	0.0446	0.8519
Sex	Lipid	0.1497	0.5287
avglength	NewSumPCB	-0.0669	0.7792
avglength	DOYcollected	-0.2211	0.3488
avglength	Lipid	0.0323	0.8923
avglength	Sex	0.0338	0.8874
avgweight	NewSumPCB	-0.1069	0.6537
avgweight	DOYcollected	-0.2108	0.3723
avgweight	Lipid	0.0467	0.8450
avgweight	Sex	0.0373	0.8760
avgweight	avglength	0.9793	<.0001*



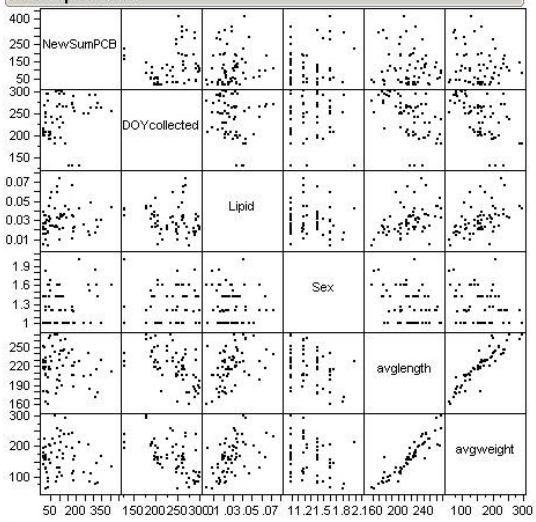
Multivariate Species=WP, Region=CBO

Correlations

	NewSumPCB	DOYcollected	Lipid	Sex	avglength	avgweight
NewSumPCB	1.0000	0.2156	0.0872	0.1724	-0.1203	-0.1311
DOYcollected	0.2156	1.0000	-0.1827	-0.0319	-0.5313	-0.5767
Lipid	0.0872	-0.1827	1.0000	-0.0995	0.4472	0.5139
Sex	0.1724	-0.0319	-0.0995	1.0000	-0.3117	-0.2634
avglength	-0.1203	-0.5313	0.4472	-0.3117	1.0000	0.9134
avgweight	-0.1311	-0.5767	0.5139	-0.2634	0.9134	1.0000

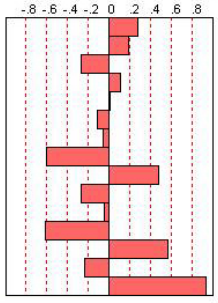
1 rows not used due to missing or excluded values or frequency or weight variables missing, negative or less than one.

Scatterplot Matrix



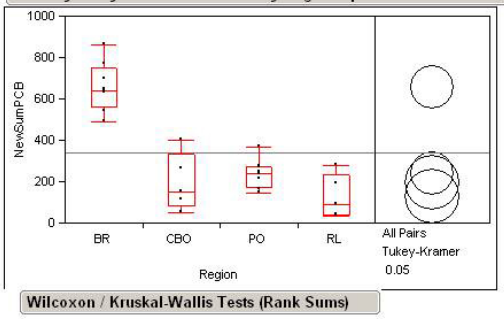
Nonparametric: Spearman's ?

Variable	by Variable	Spearman ?	Prob>|?|
DOYcollected	NewSumPCB	0.2843	0.0228*
Lipid	NewSumPCB	0.1907	0.1312
Lipid	DOYcollected	-0.2664	0.0334*
Sex	NewSumPCB	0.1124	0.3803
Sex	DOYcollected	0.0082	0.9491
Sex	Lipid	-0.1172	0.3603
avglength	NewSumPCB	-0.0542	0.6703
avglength	DOYcollected	-0.5991	<.0001*
avglength	Lipid	0.4832	<.0001*
avglength	Sex	-0.2650	0.0358*
avgweight	NewSumPCB	-0.0435	0.7326
avgweight	DOYcollected	-0.6096	<.0001*
avgweight	Lipid	0.5713	<.0001*
avgweight	Sex	-0.2316	0.0677
avgweight	avglength	0.9385	<.0001*



Kruskal-Wallis tests and means comparisons for total PCB (SumPCB) and lipid-normalized PCB in American eel (AE) composite samples. Regions are Back River (BR), Chesapeake Bay (CBO), Potomac River (PO), and rivers and lakes (RL).

Oneway Analysis of NewSumPCB By Region Species=AE



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	180.000	22.5000	3.972
CBO	5	46.000	9.2000	-1.366
PO	8	93.000	11.6250	-0.806
RL	5	32.000	6.4000	-2.277

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
17.4466	3	0.0006*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.77684	0.05

Abs(Dif)-LSD

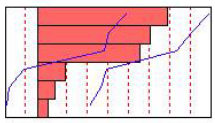
	BR	PO	CBO	RL
BR	-149.32	270.73	292.15	361.80
PO	270.73	-149.32	-127.91	-58.26
CBO	292.15	-127.91	-188.88	-119.23
RL	361.80	-58.26	-119.23	-188.88

Positive values show pairs of means that are significantly different.

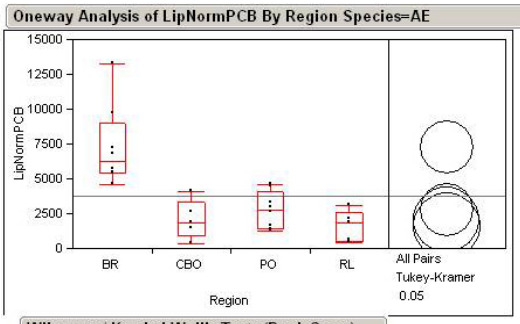
Level		Mean
BR	A	657.54636
PO	B	237.49065
CBO	B	195.14394
RL	B	125.49580

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
BR	RL	532.0506	361.797	702.3039
BR	CBO	462.4024	292.149	632.6558
BR	PO	420.0557	270.734	569.3778
PO	RL	111.9948	-58.258	282.2482
CBO	RL	69.6481	-119.231	258.5273
PO	CBO	42.3467	-127.907	212.6001



Oneway Analysis of LipNormPCB By Region Species=AE



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
BR	8	180.000	22.5000	3.972
CBO	5	42.000	8.4000	-1.627
PO	8	91.000	11.3750	-0.917
RL	5	38.000	7.6000	-1.887

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
16.8927	3	0.0007*

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.77684	0.05

Abs(Dif)-LSD

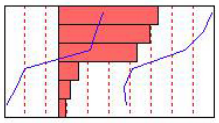
	BR	PO	CBO	RL
BR	-2689.9	1801.5	2119.2	2565.5
PO	1801.5	-2689.9	-2372.1	-1925.9
CBO	2119.2	-2372.1	-3402.4	-2956.2
RL	2565.5	-1925.9	-2956.2	-3402.4

Positive values show pairs of means that are significantly different.

Level		Mean
BR	A	7230.9082
PO	B	2739.5268
CBO	B	2044.7633
RL	B	1598.4874

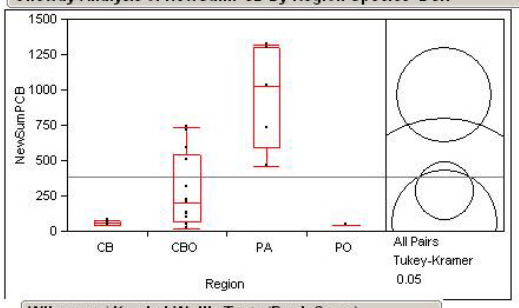
Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
BR	RL	5632.421	2565.51	8699.333
BR	CBO	5186.145	2119.23	8253.057
BR	PO	4491.381	1801.52	7181.242
PO	RL	1141.039	-1925.87	4207.952
PO	CBO	694.764	-2372.15	3761.676
CBO	RL	446.276	-2956.16	3848.710



Kruskal-Wallis tests and means comparisons for total PCB (SumPCB) and lipid-normalized PCB in blue crab hepatopancreas (BCH) composite samples. Regions are coastal bays (CB), Chesapeake Bay (CBO), Patapsco River (PA), and Potomac River (PO).

Oneway Analysis of NewSumPCB By Region Species=BCH



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
CB	4	24.000	6.0000	-1.906
CBO	13	147.000	11.3077	-0.527
PA	5	100.000	20.0000	2.944
PO	1	5.000	5.0000	-0.980

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
11.2876	3	0.0103*

Small sample sizes. Refer to statistical tables for tests, rather than large-sample approximations.

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.81185	0.05

Abs(Dif)-LSD

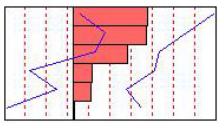
	PA	CBO	CB	PO
PA	-475.2	284.9	402.0	94.9
CBO	284.9	-294.7	-203.9	-542.1
CB	402.0	-203.9	-531.3	-828.2
PO	94.9	-542.1	-828.2	-1062.7

Positive values show pairs of means that are significantly different.

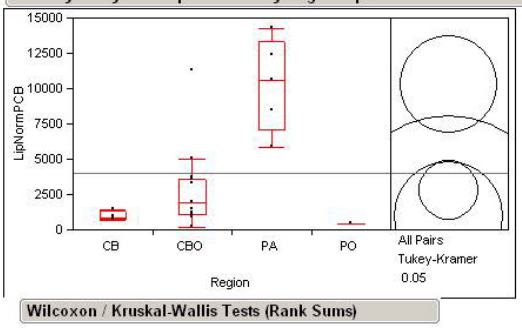
Level		Mean
PA	A	963.46074
CBO	B	283.12540
CB	B	57.38142
PO	B	45.43376

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	PO	918.0270	94.883	1741.171
PA	CB	906.0793	402.009	1410.150
PA	CBO	680.3353	284.910	1075.761
CBO	PO	237.6916	-542.098	1017.481
CBO	CB	225.7440	-203.899	655.387
CB	PO	11.9477	-828.170	852.065



Oneway Analysis of LipNormPCB By Region Species=BCH



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
CB	4	24.000	6.0000	-1.906
CBO	13	148.000	11.3846	-0.465
PA	5	102.000	20.4000	3.093
PO	1	2.000	2.0000	-1.432

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
13.0809	3	0.0045*

Small sample sizes. Refer to statistical tables for tests, rather than large-sample approximations.

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.81185	0.05

Abs(Dif)-LSD

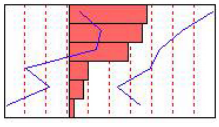
	PA	CBO	CB	PO
PA	-4884	3424	4153	1440
CBO	3424	-3029	-2570	-5602
CB	4153	-2570	-5461	-8067
PO	1440	-5602	-8067	-10921

Positive values show pairs of means that are significantly different.

Level		Mean
PA	A	10287.447
CBO	B	2800.051
CB	B	954.437
PO	B	388.050

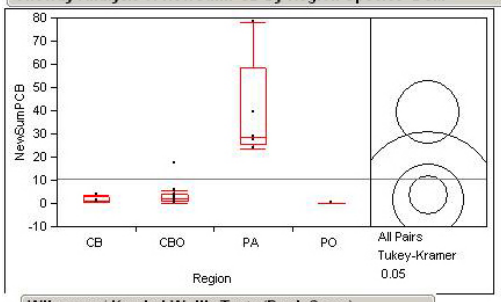
Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	PO	9899.398	1439.99	18358.80
PA	CB	9333.011	4152.70	14513.32
PA	CBO	7487.397	3423.63	11551.16
CBO	PO	2412.001	-5601.85	10425.86
CBO	CB	1845.614	-2569.81	6261.03
CB	PO	566.387	-8067.46	9200.23



Kruskal-Wallis tests and means comparisons for total PCB (SumPCB) and lipid-normalized PCB in blue crab muscle (BCM) composite samples. Regions are coastal bays (CB), Chesapeake Bay (CBO), Patapsco River (PA), and Potomac River (PO).

Oneway Analysis of NewSumPCB By Region Species=BCM



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
CB	4	30.000	7.5000	-1.419
CBO	13	139.000	10.6923	-1.023
PA	5	105.000	21.0000	3.317
PO	1	2.000	2.0000	-1.432

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
13.2224	3	0.0042*

Small sample sizes. Refer to statistical tables for tests, rather than large-sample approximations.

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.81185	0.05

Abs(Dif)-LSD

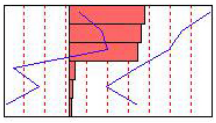
	PA	CBO	CB	PO
PA	-19.437	19.713	17.011	5.439
CBO	19.713	-12.054	-15.830	-28.674
CB	17.011	-15.830	-21.731	-32.882
PO	5.439	-28.674	-32.882	-43.462

Positive values show pairs of means that are significantly different.

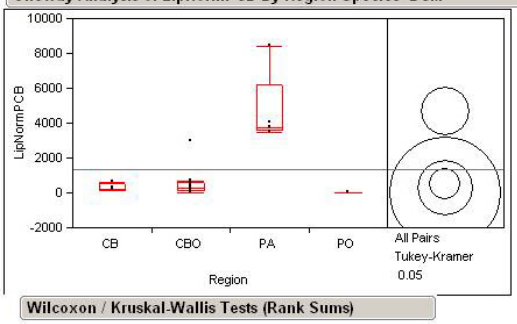
Level		Mean
PA	A	39.192506
CBO	B	3.307040
CB	B	1.565520
PO	B	0.088333

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	PO	39.10417	5.4388	72.76959
PA	CB	37.62699	17.0112	58.24276
PA	CBO	35.88547	19.7131	52.05781
CBO	PO	3.21871	-28.6736	35.11100
CBO	CB	1.74152	-15.8303	19.31332
CB	PO	1.47719	-32.8824	35.83681



Oneway Analysis of LipNormPCB By Region Species=BCM



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
CB	4	34.000	8.5000	-1.095
CBO	13	135.000	10.3846	-1.271
PA	5	105.000	21.0000	3.317
PO	1	2.000	2.0000	-1.432

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
12.7809	3	0.0051*

Small sample sizes. Refer to statistical tables for tests, rather than large-sample approximations.

Means Comparisons

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.81185	0.05

Abs(Dif)-LSD

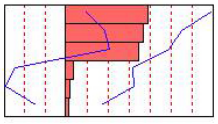
	PA	CBO	CB	PO
PA	-2012.1	2477.6	2247.4	1169.0
CBO	2477.6	-1247.9	-1589.3	-2799.3
CB	2247.4	-1589.3	-2249.6	-3284.5
PO	1169.0	-2799.3	-3284.5	-4499.3

Positive values show pairs of means that are significantly different.

Level		Mean
PA	A	4665.6239
CBO	B	513.8095
CB	B	284.0337
PO	B	11.5119

Levels not connected by same letter are significantly different.

Level	- Level	Difference	Lower CL	Upper CL
PA	PO	4654.112	1168.98	8139.248
PA	CB	4381.590	2247.39	6515.791
PA	CBO	4151.814	2477.61	5826.020
CBO	PO	502.298	-2799.28	3803.875
CB	PO	272.522	-3284.48	3829.524
CBO	CB	229.776	-1589.30	2048.856



Appendix 4. Congener profiles of selected species from selected sites.

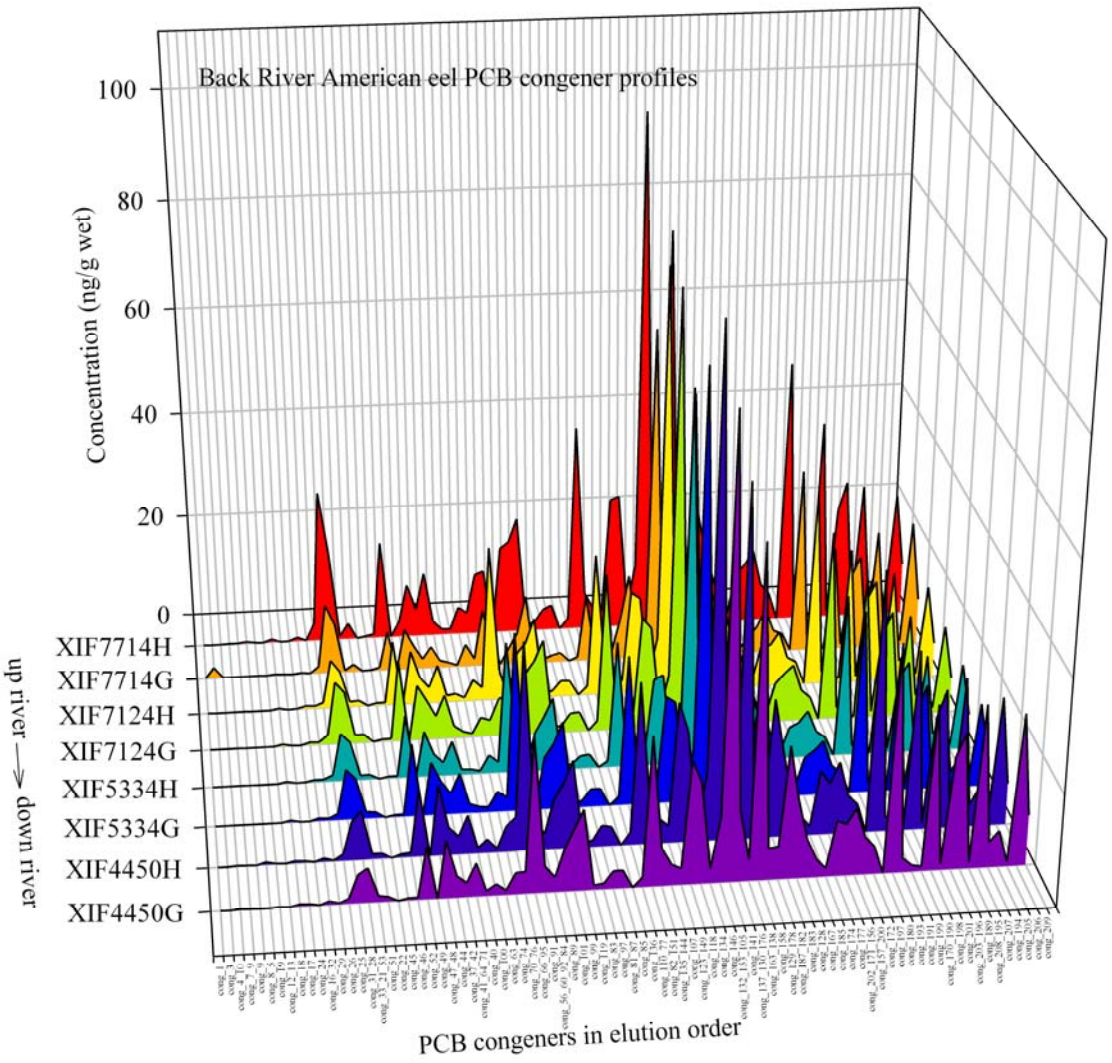


Figure 1. Concentrations of PCB congeners in Back River American eels.

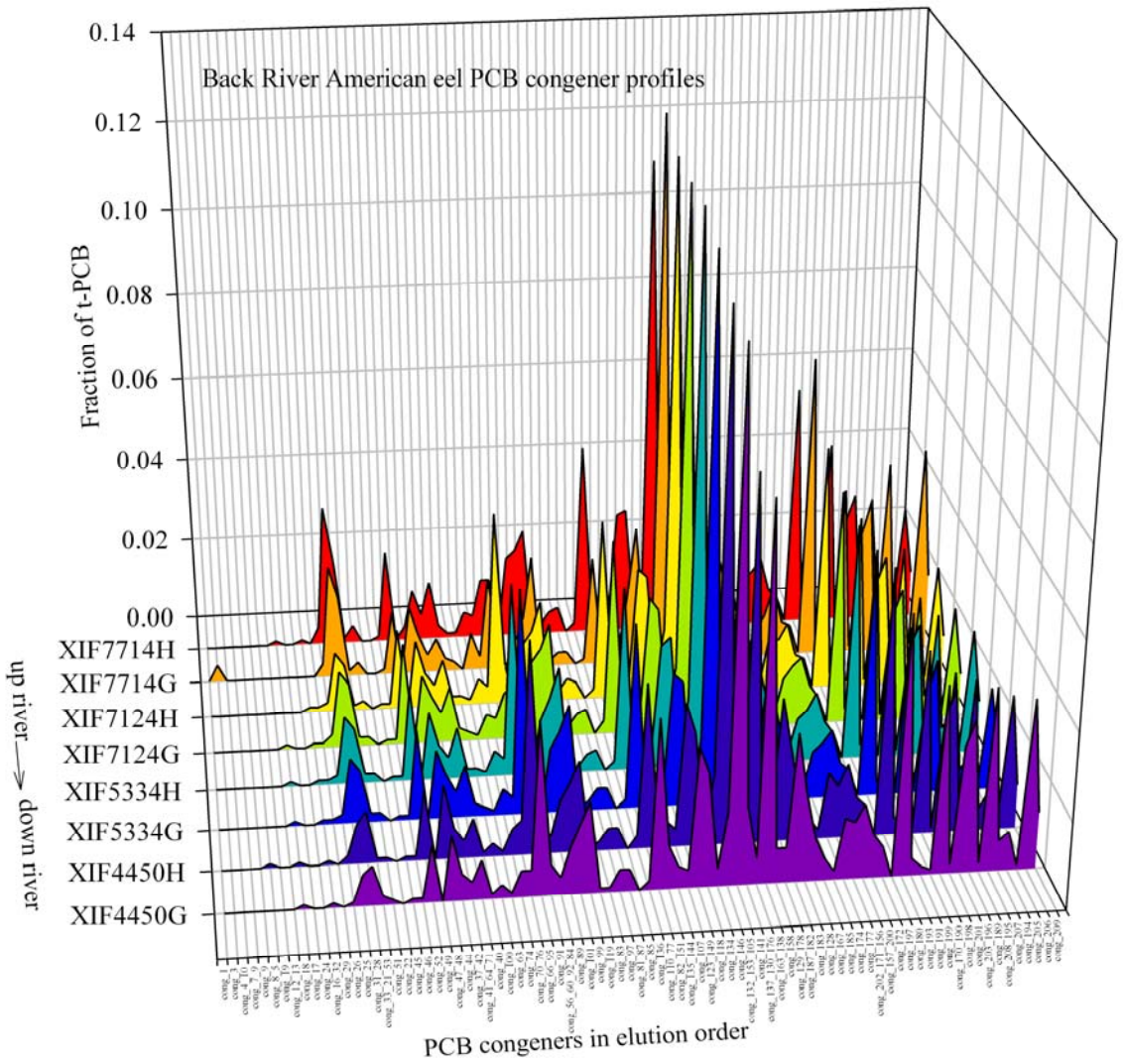


Figure 2. Fractions of PCB congeners in Back River American eels.

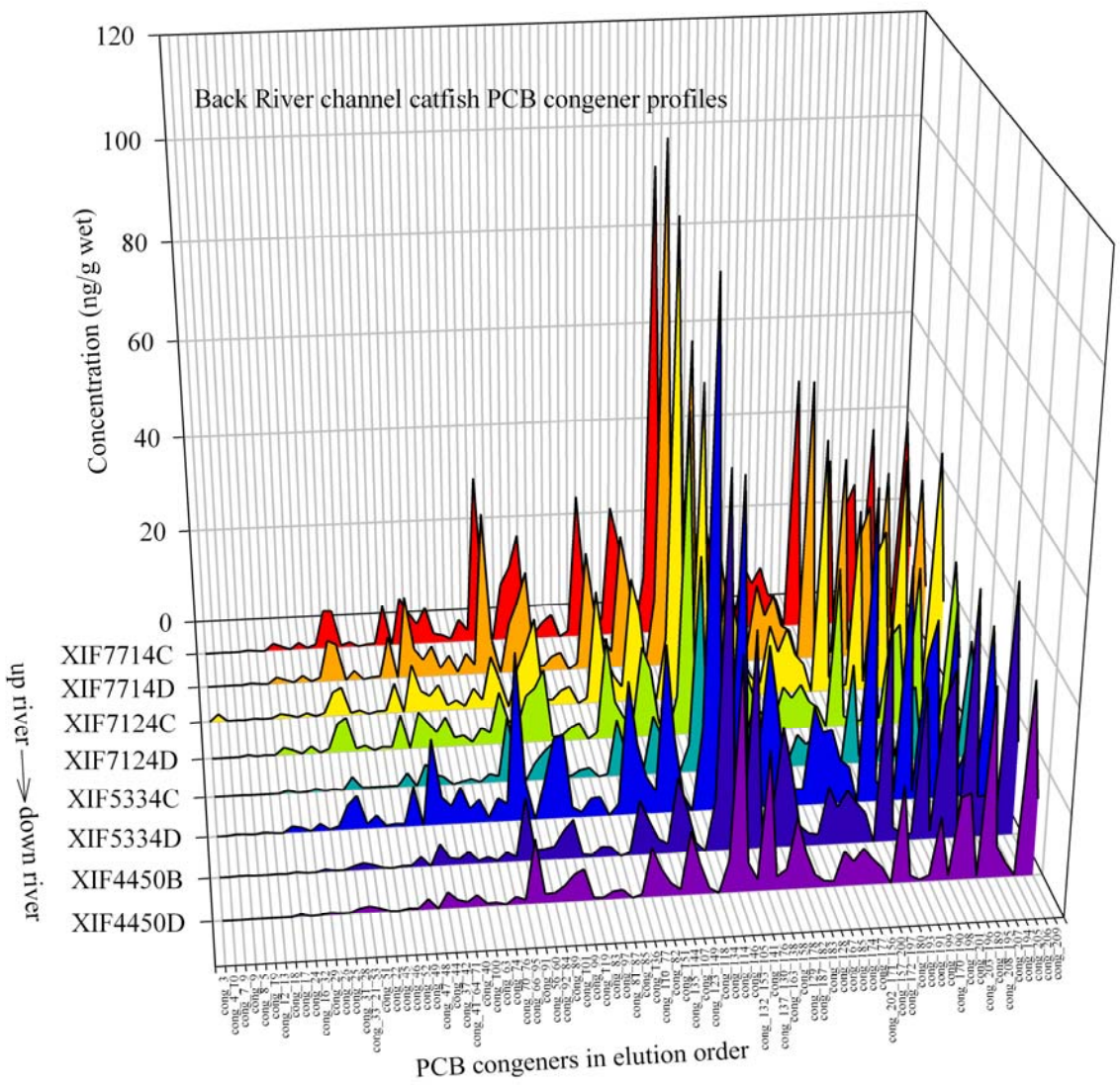


Figure 3. Concentrations of PCB congeners in Back River channel catfish.

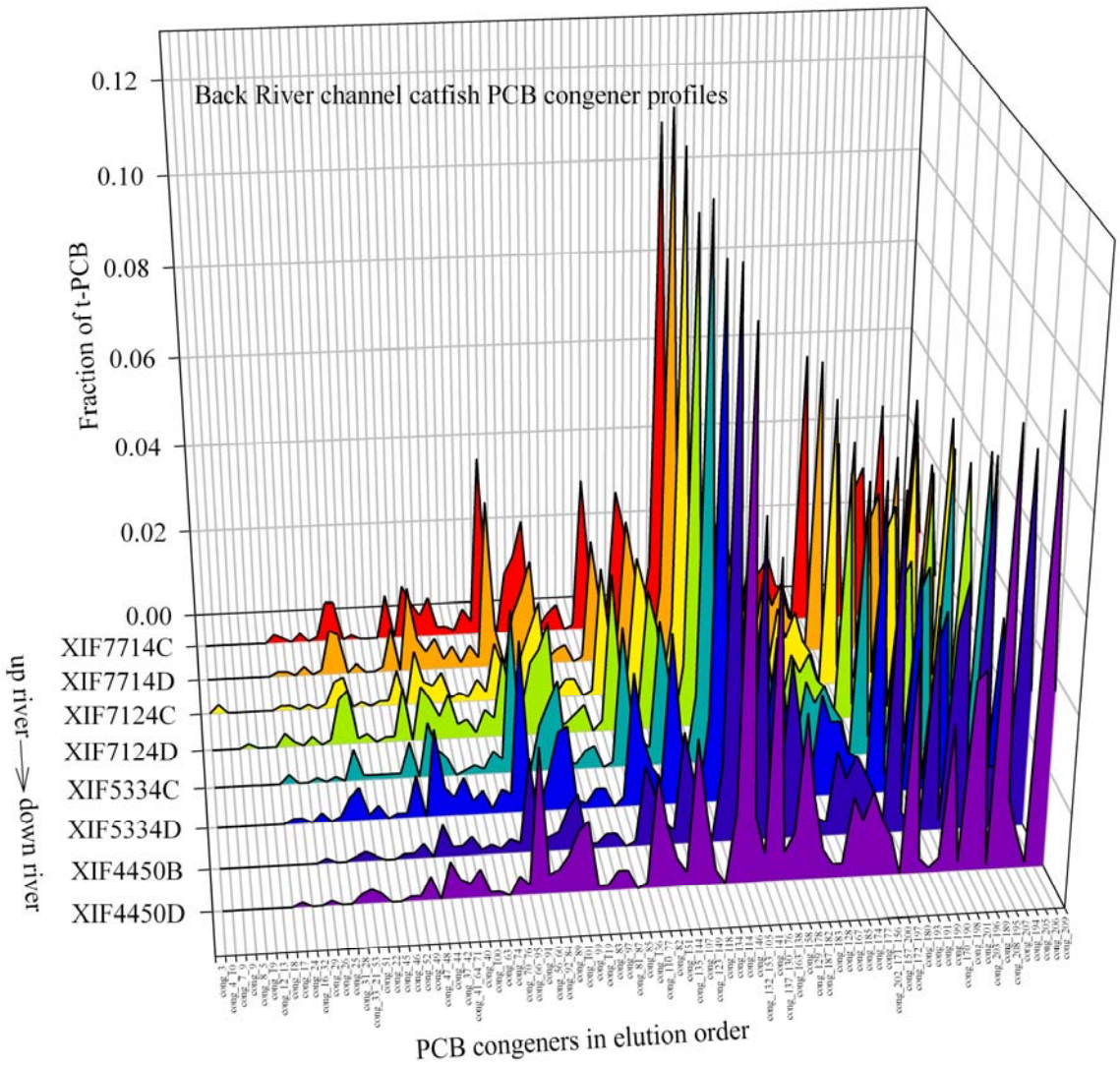


Figure 4. Fractions of PCB congeners in Back River channel catfish.

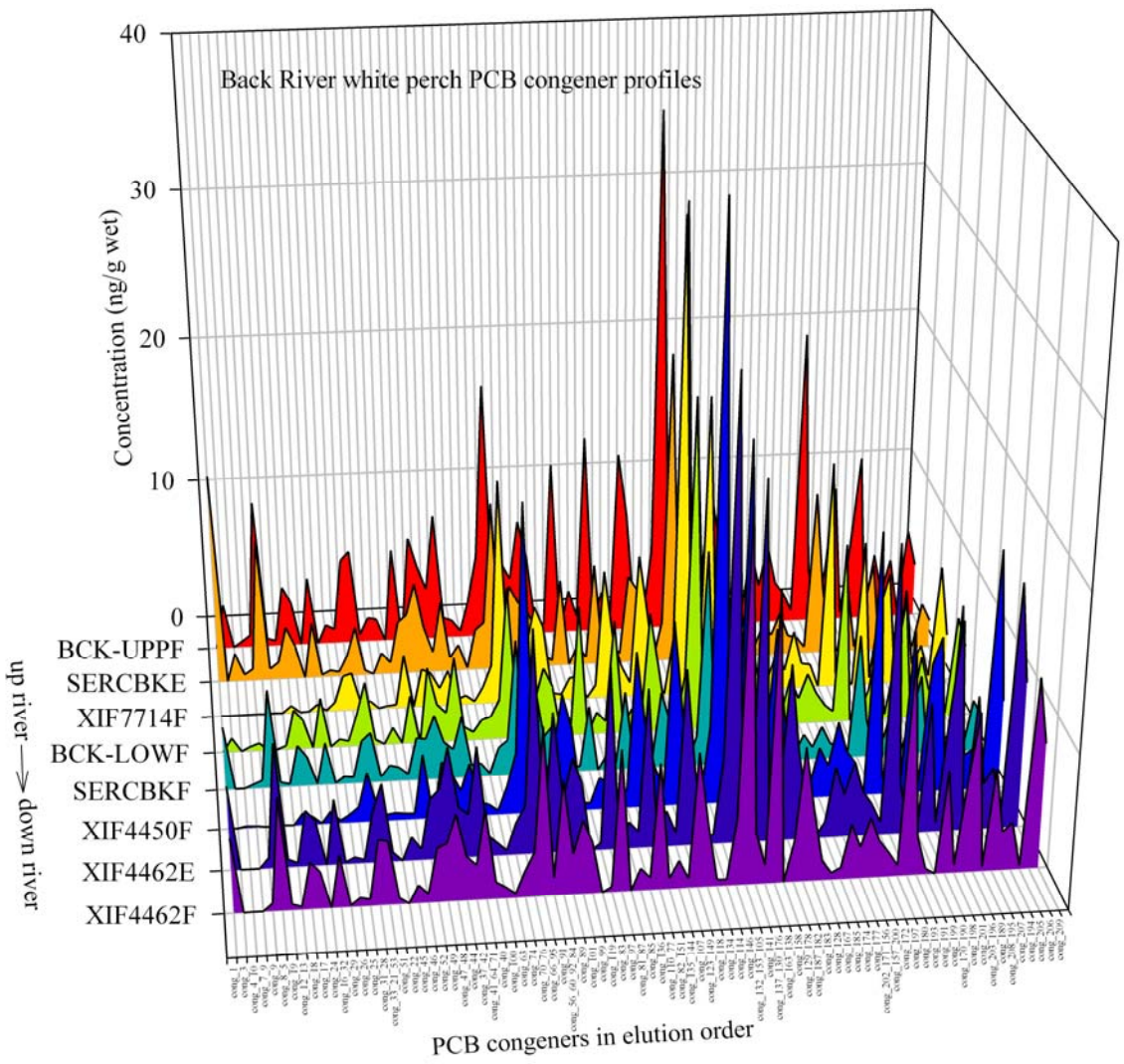


Figure 5. Concentrations of PCB congeners in Back River white perch.

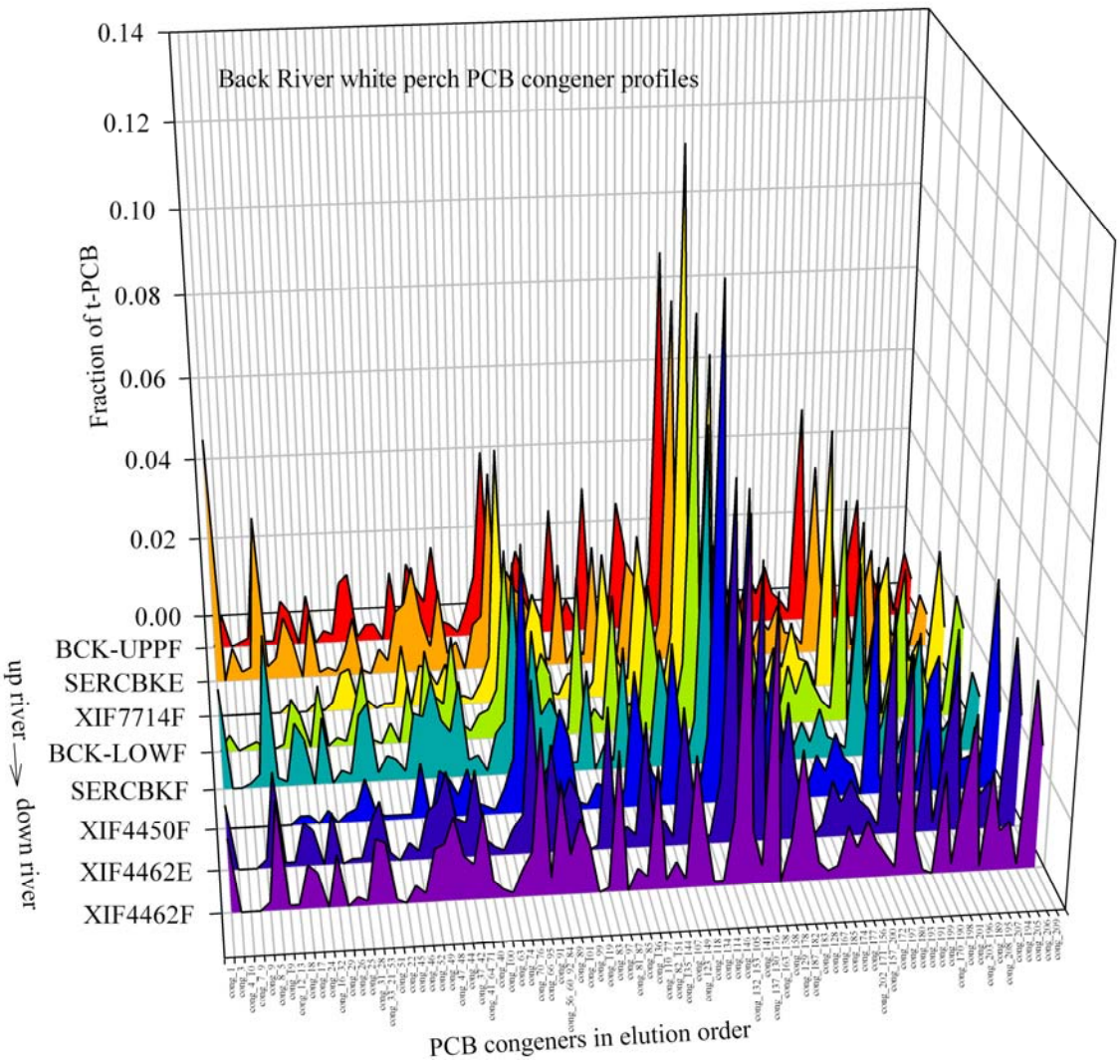


Figure 6. Fractions of PCB congeners in Back River white perch.

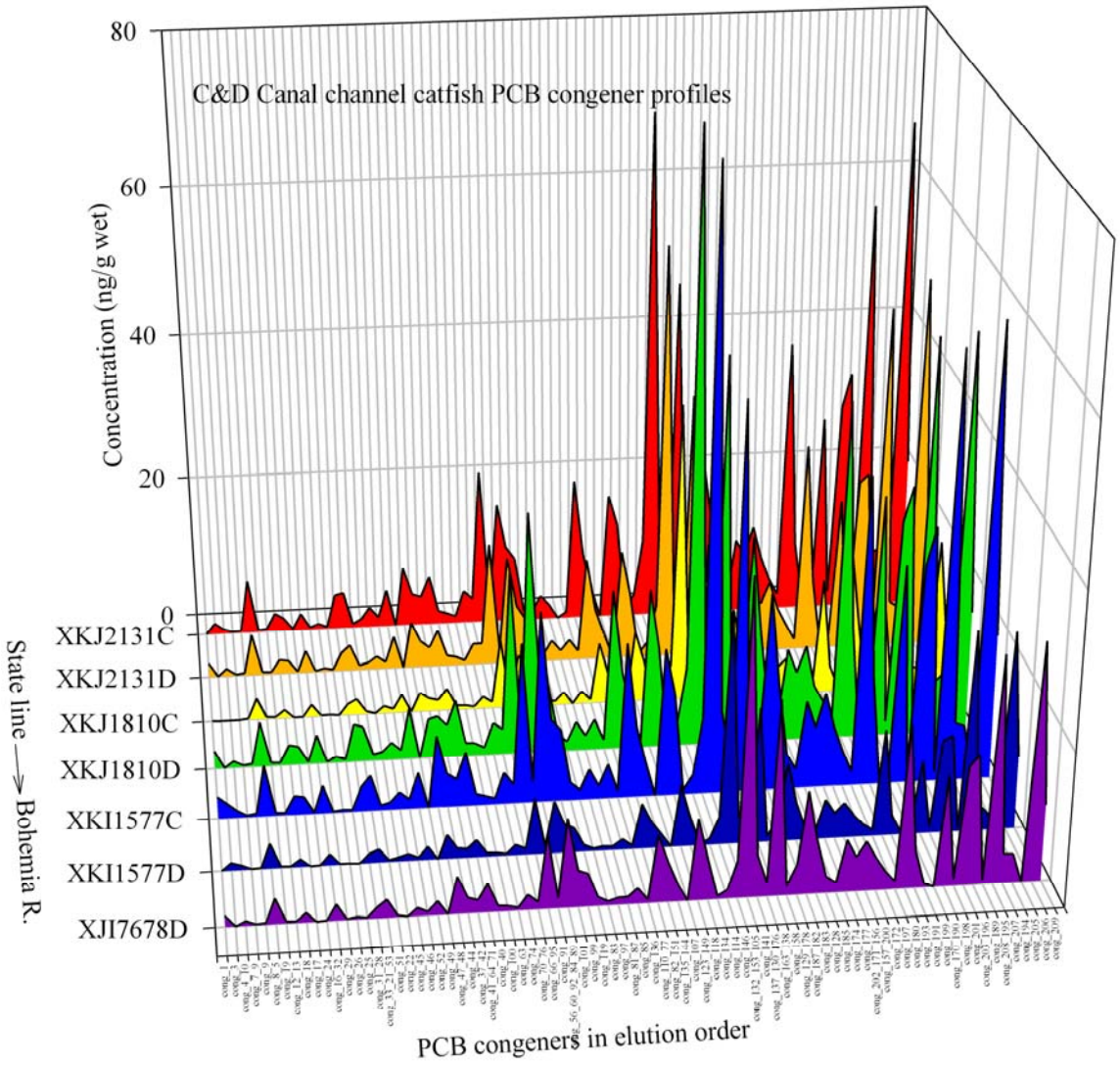


Figure 7. Concentrations of PCB congeners in C&D Canal channel catfish.

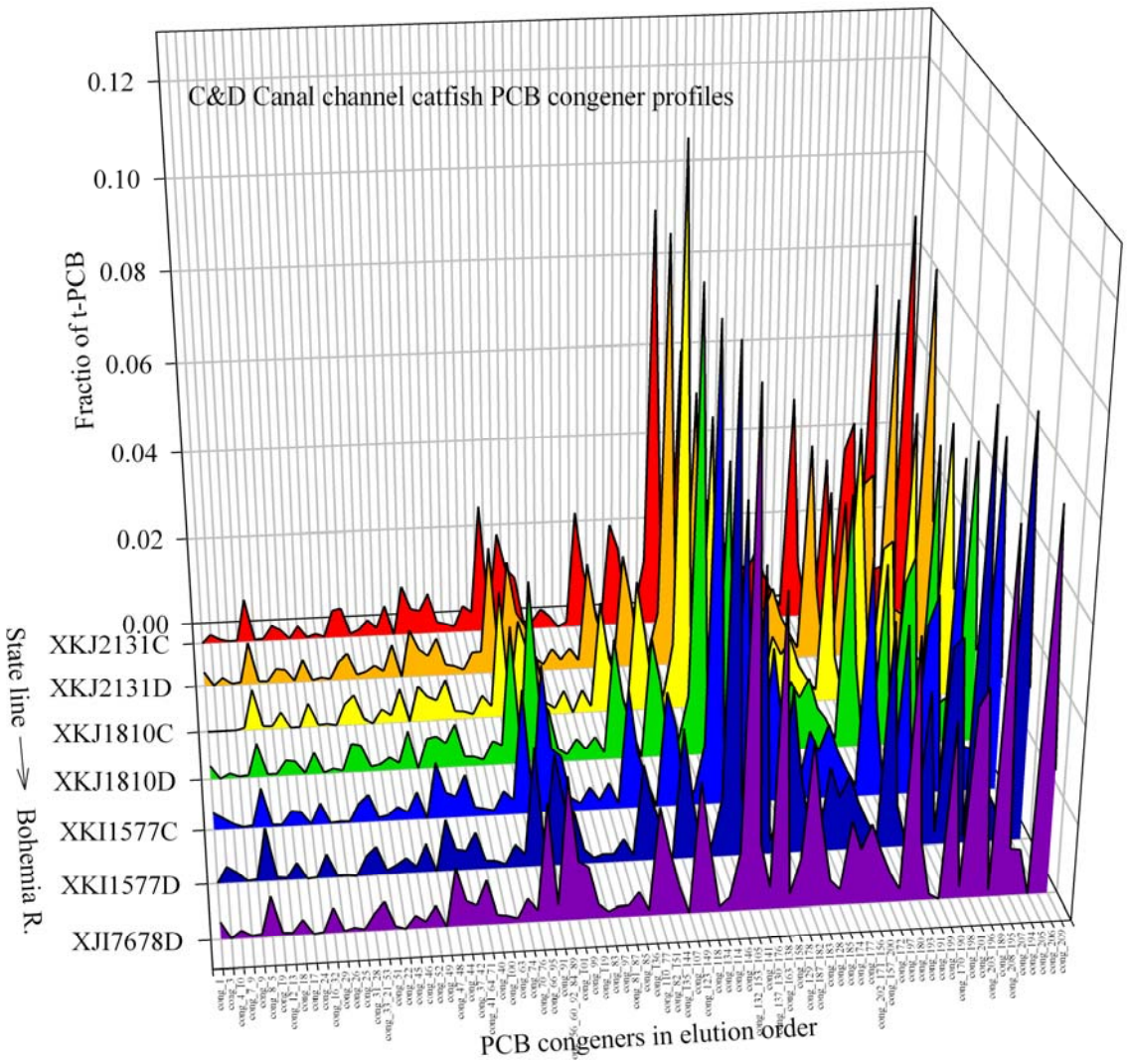


Figure 8. Fractions of PCB congeners in C&D Canal channel catfish.

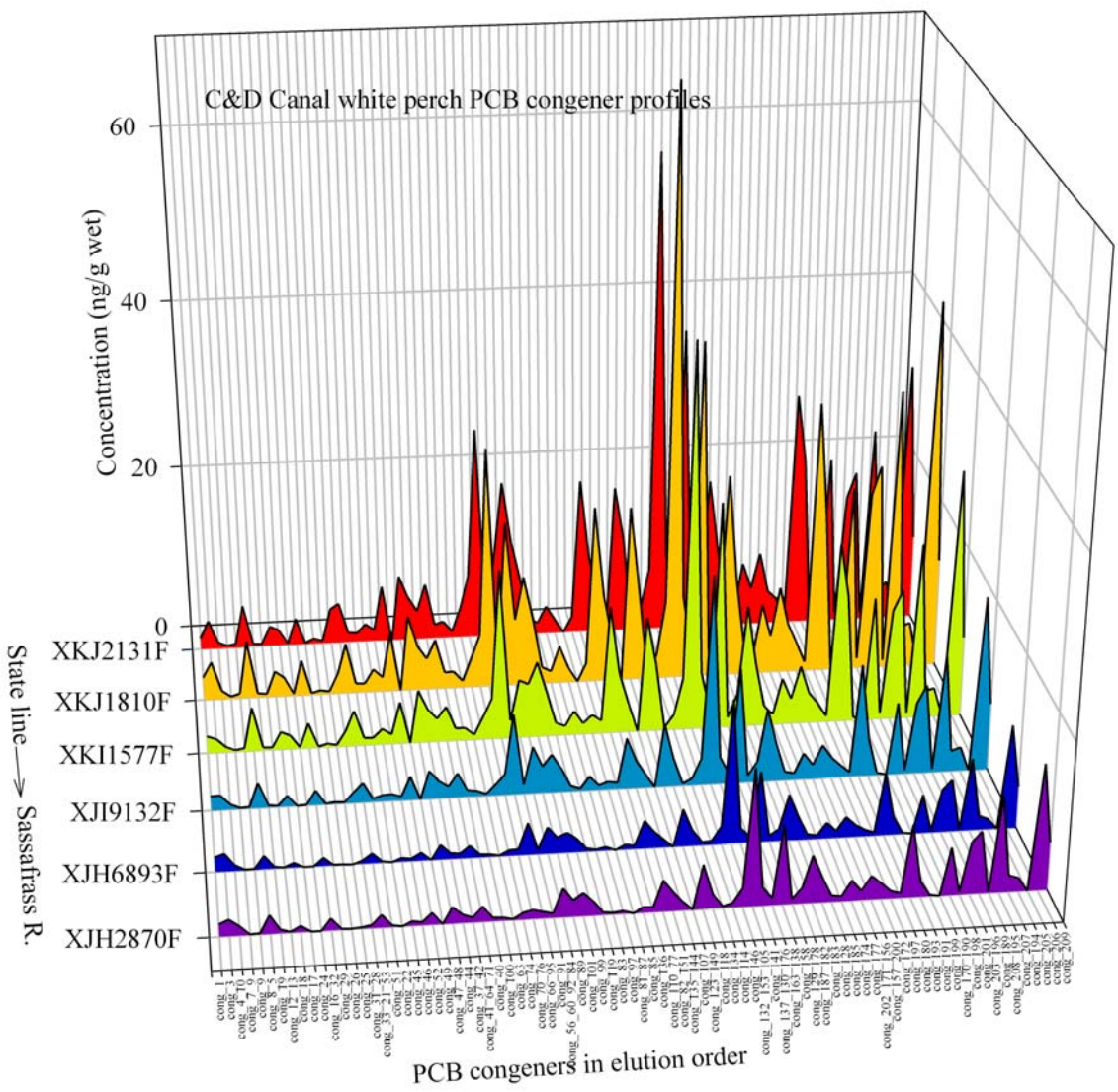


Figure 9. Concentrations of PCB congeners in C&D Canal white perch.

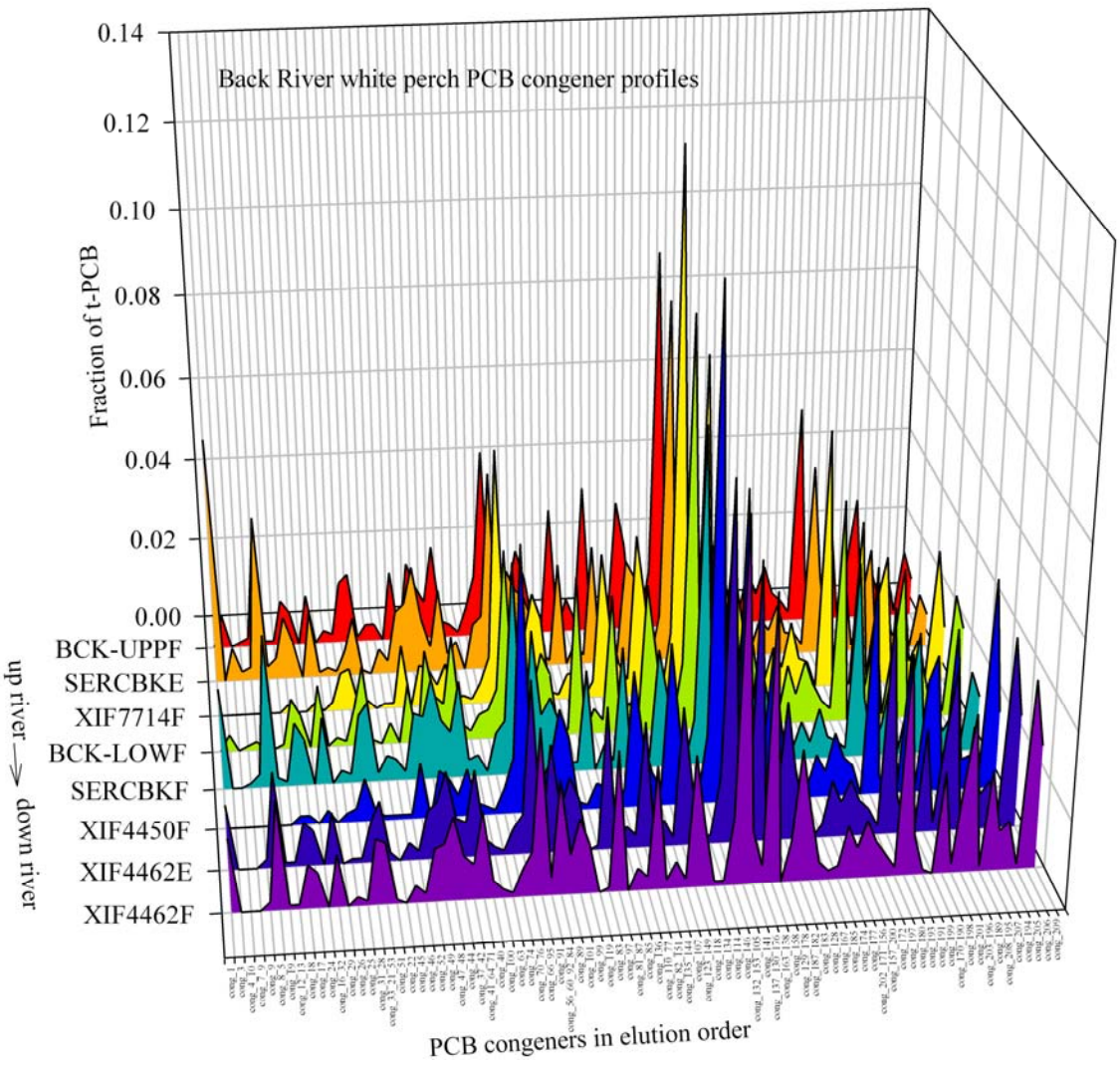


Figure 10. Fractions of PCB congeners in C&D Canal white perch.

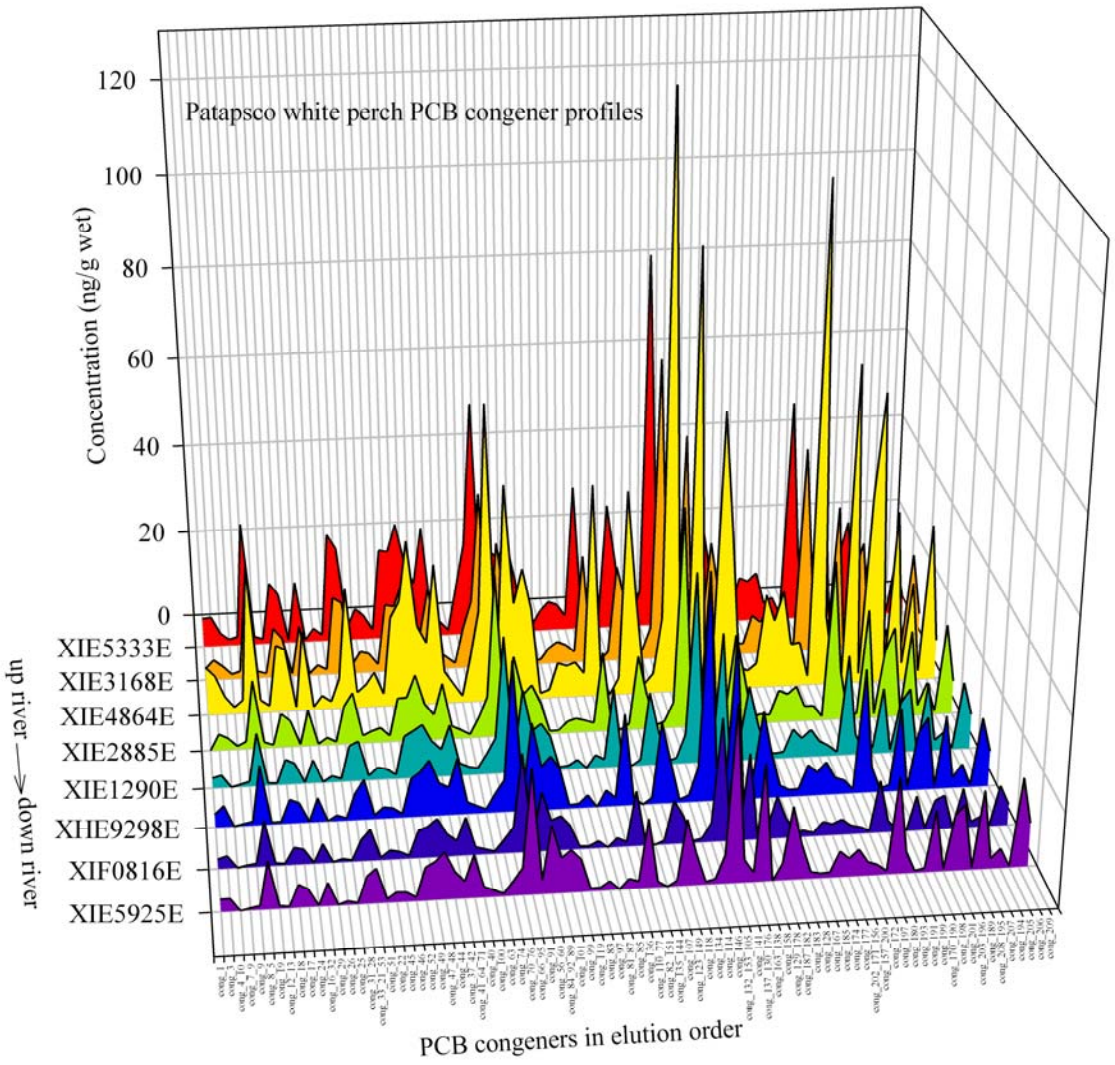


Figure 11. Concentrations of PCB congeners in Patapsco River white perch.

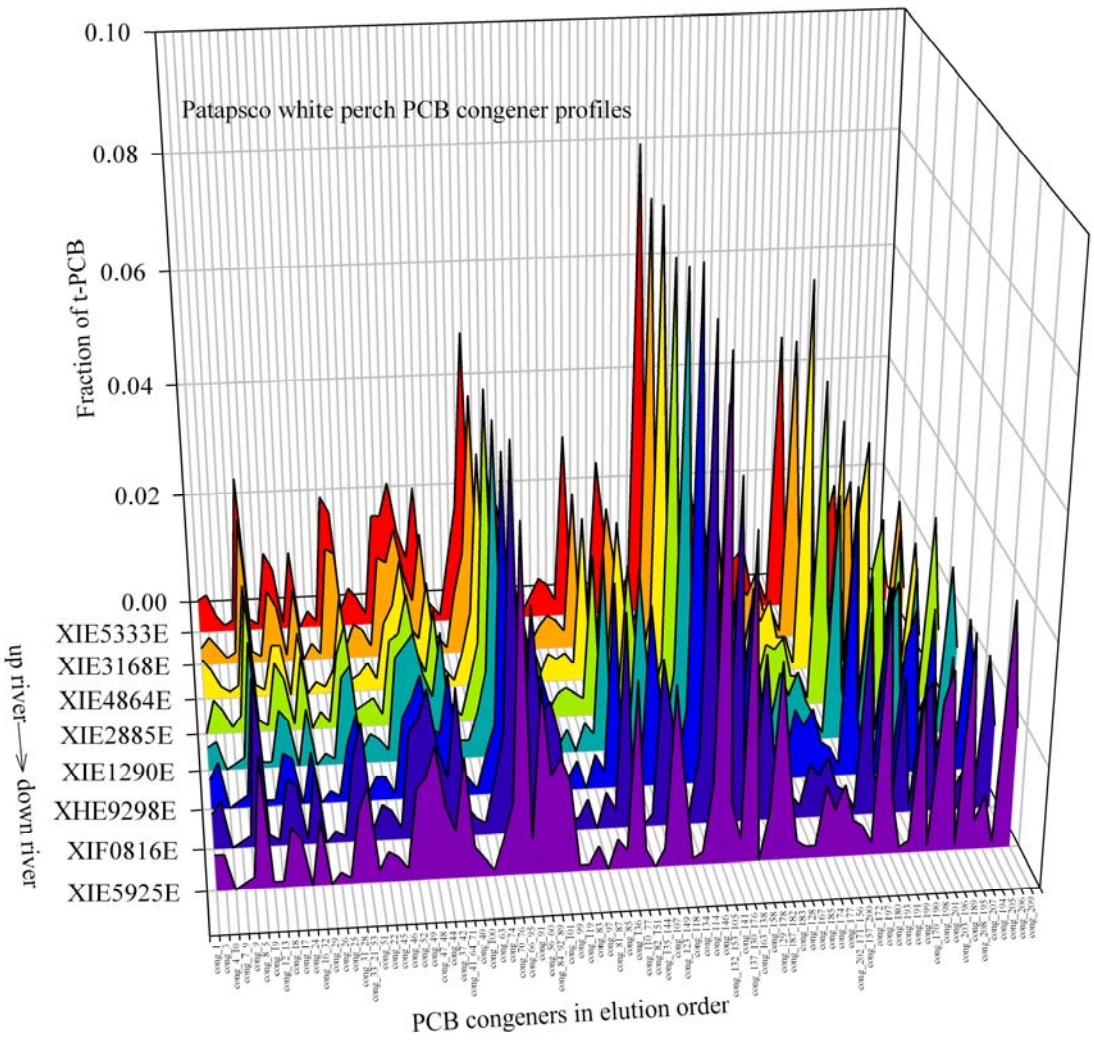


Figure 12. Fractions of PCB congeners in Patapsco River white perch.

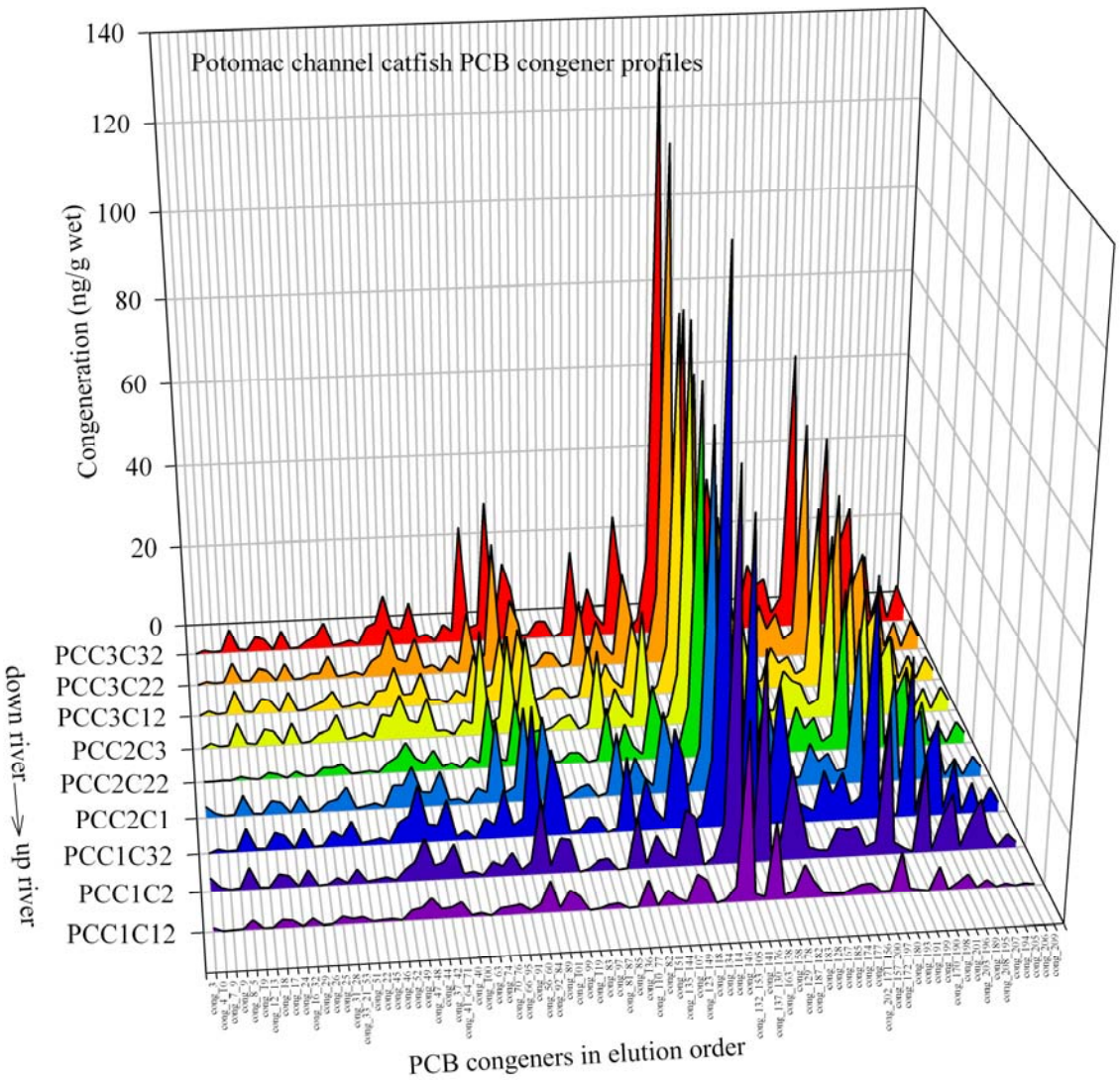


Figure 13. Concentrations of PCB congeners in Potomac River channel catfish.

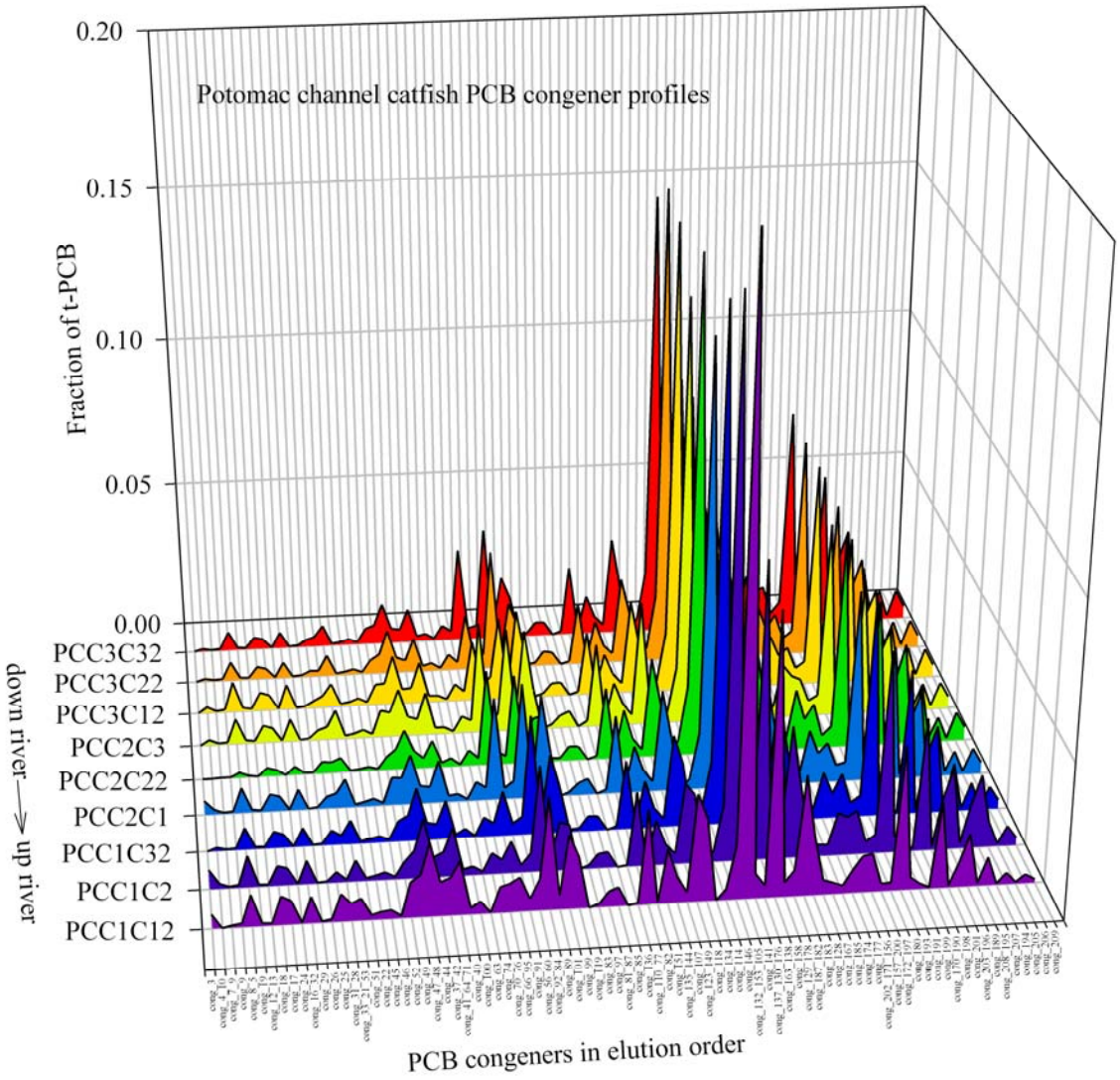


Figure 14. Fractions of PCB congeners in Potomac River channel catfish.

Appendix 5. Maps of regional sampling sites.

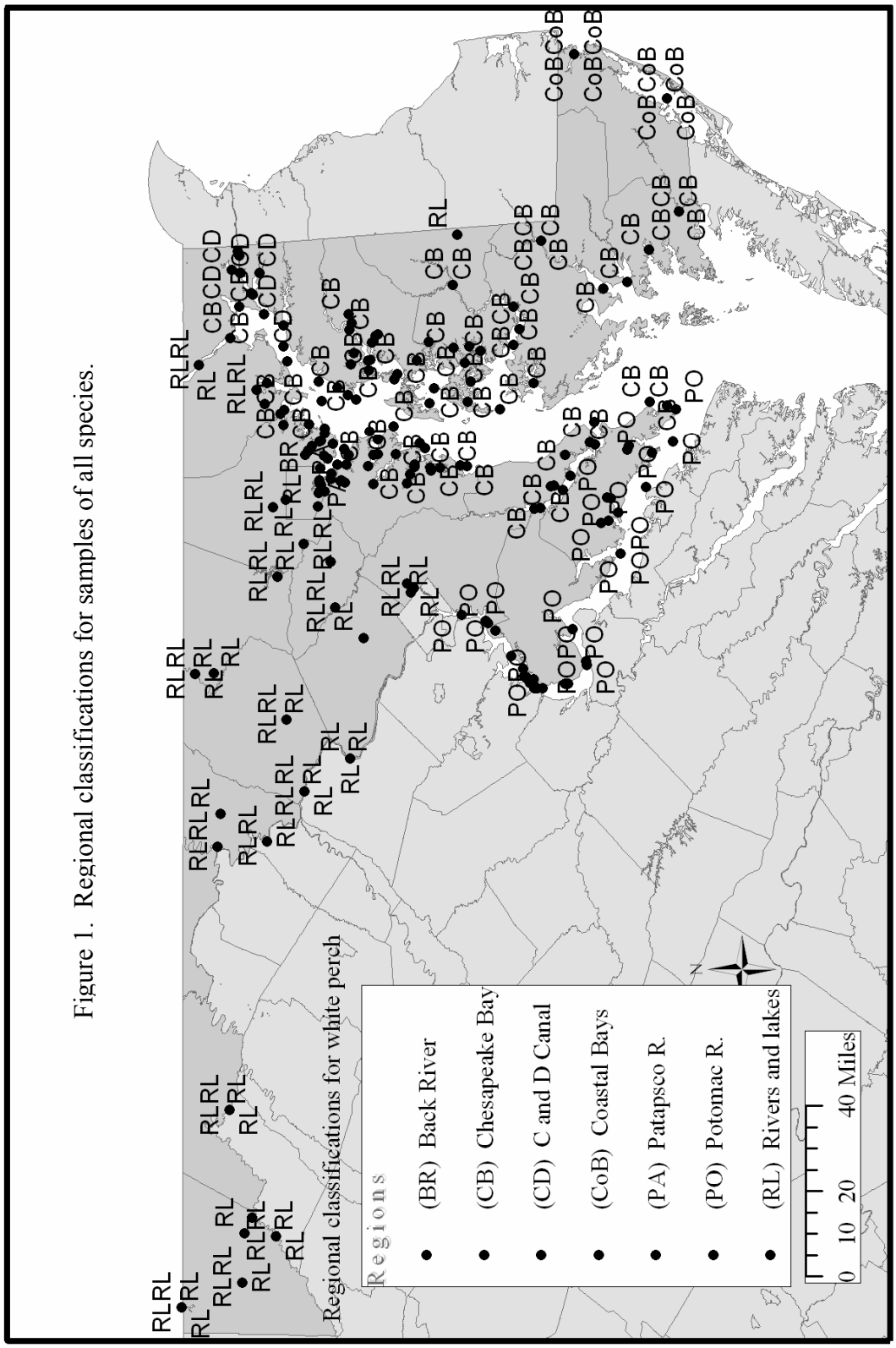
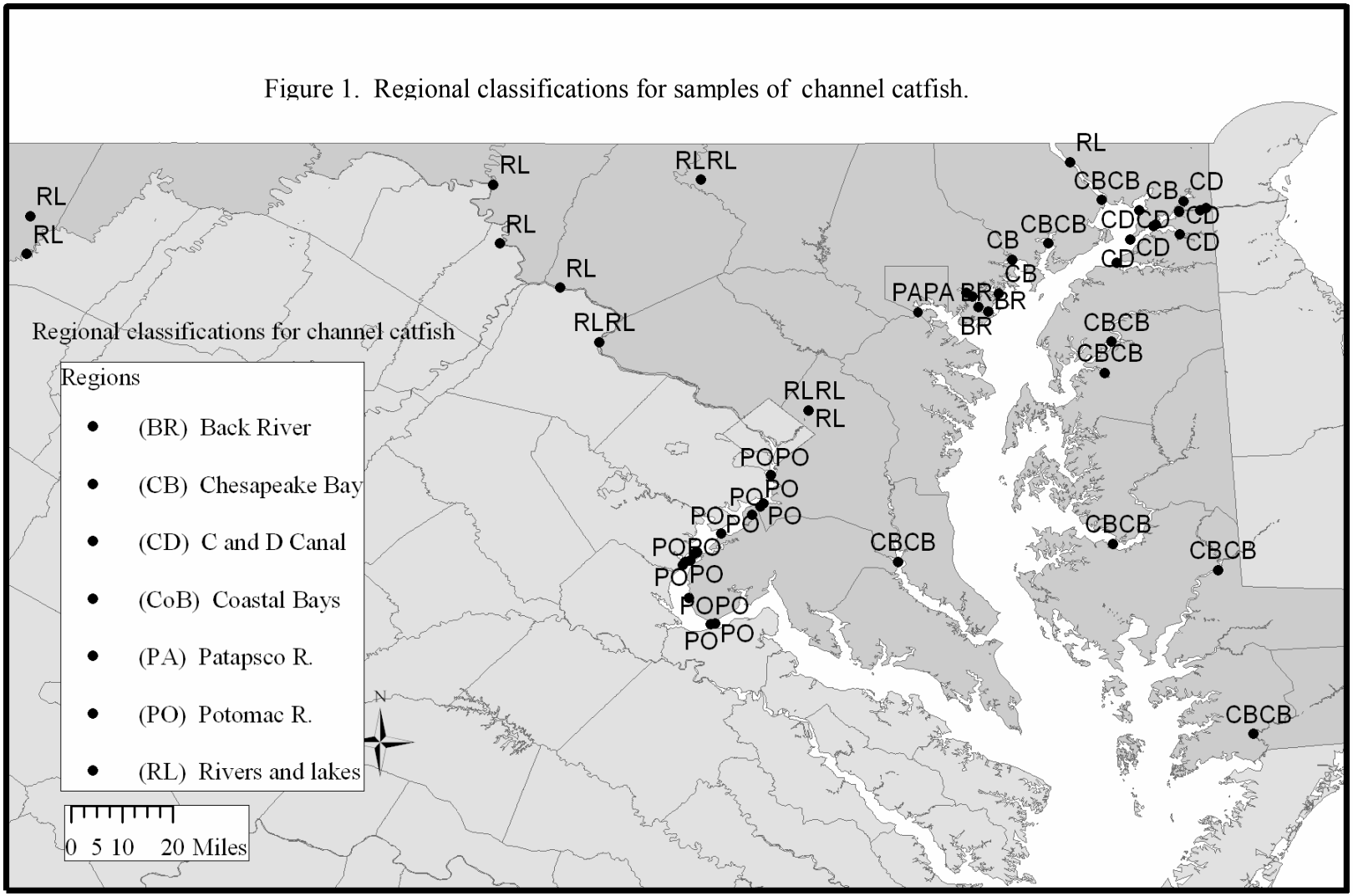


Figure 1. Regional classifications for samples of all species.

Figure 1. Regional classifications for samples of channel catfish.



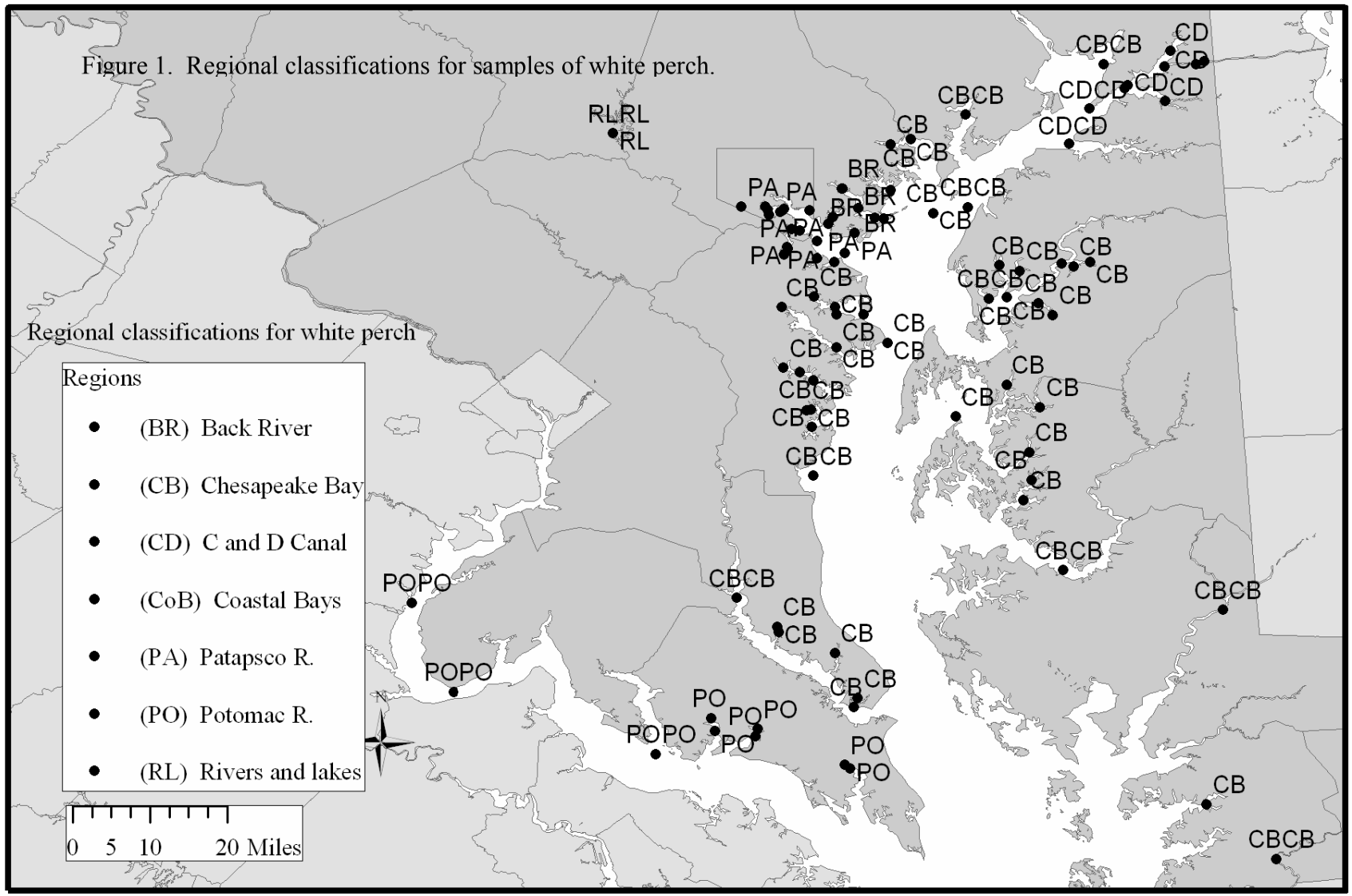


Figure 1. Regional classifications for samples of white perch.
Regional classifications for white perch
Regions
(BR) Back River
(CB) Chesapeake Bay
(CD) C and D Canal
(CoB) Coastal Bays
(PA) Patapsco R.
(PO) Potomac R.
(RL) Rivers and lakes
0 5 10 20 Miles

Appendix 6. Performance plots for PMF models.

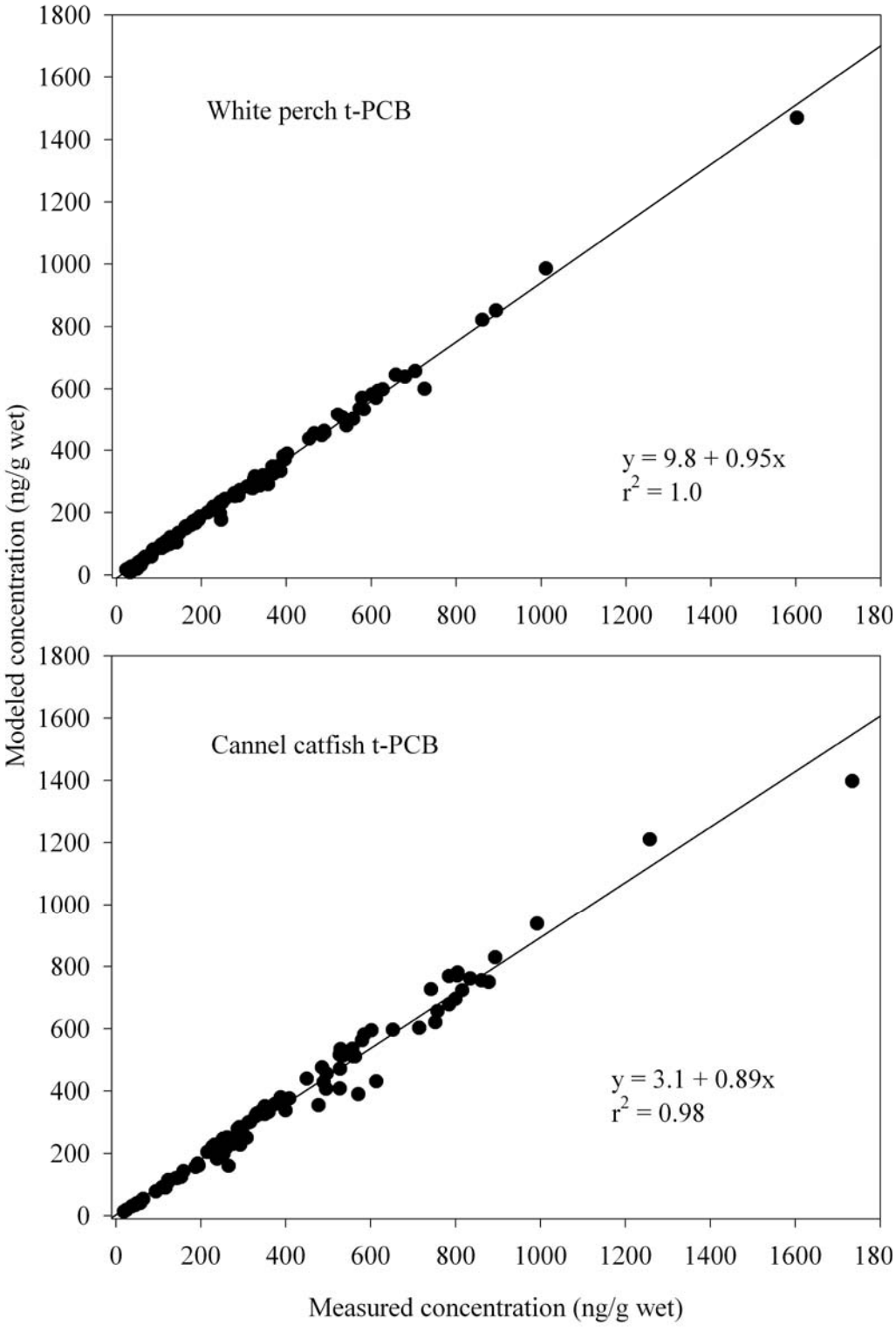


Figure 1. Reproduction of total PCB data by PMF models.

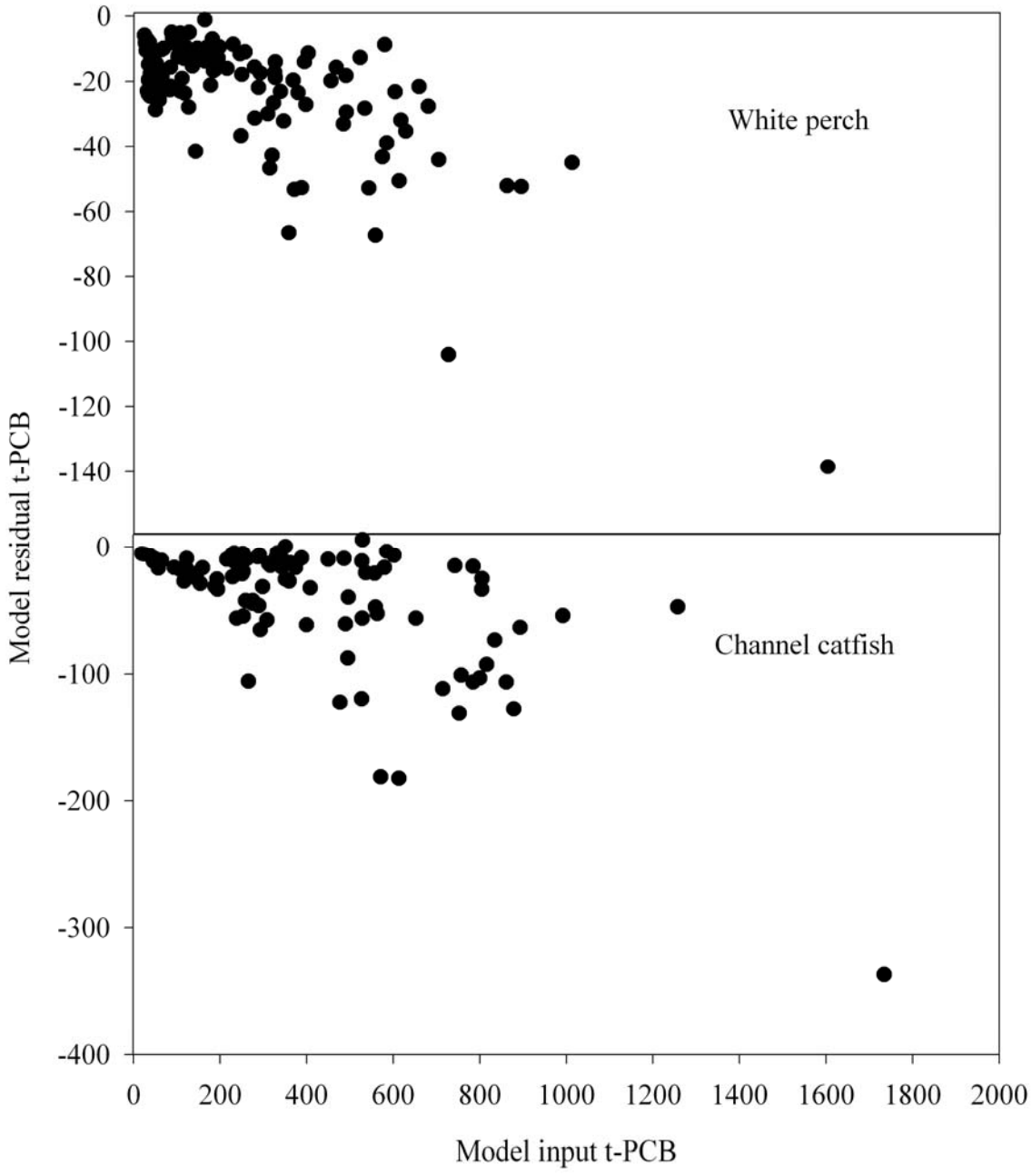


Figure 2. Residuals of t-PCB concentrations produced by PMF.

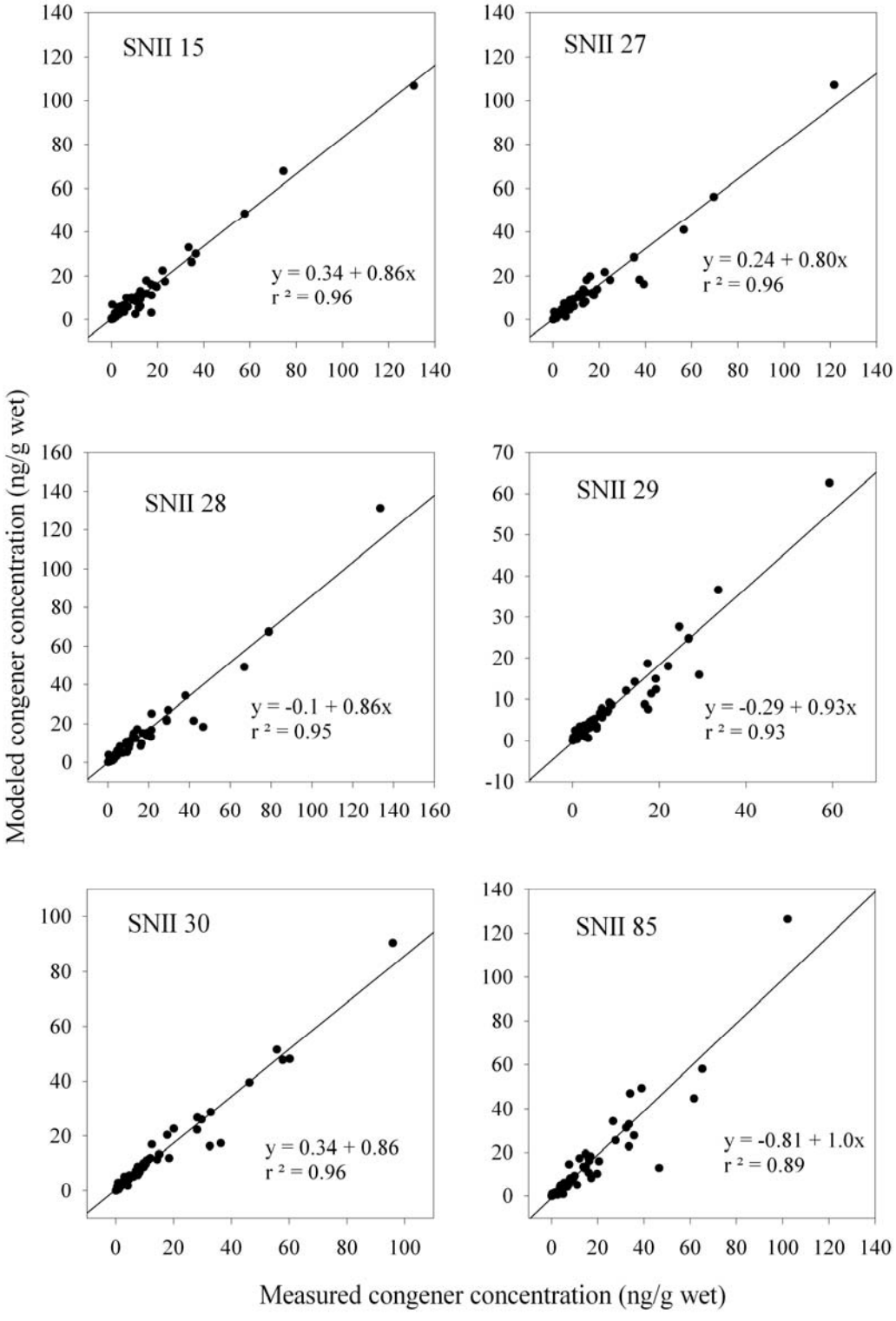


Figure 3. Reproduction of PCB congener concentrations in some channel catfish samples.

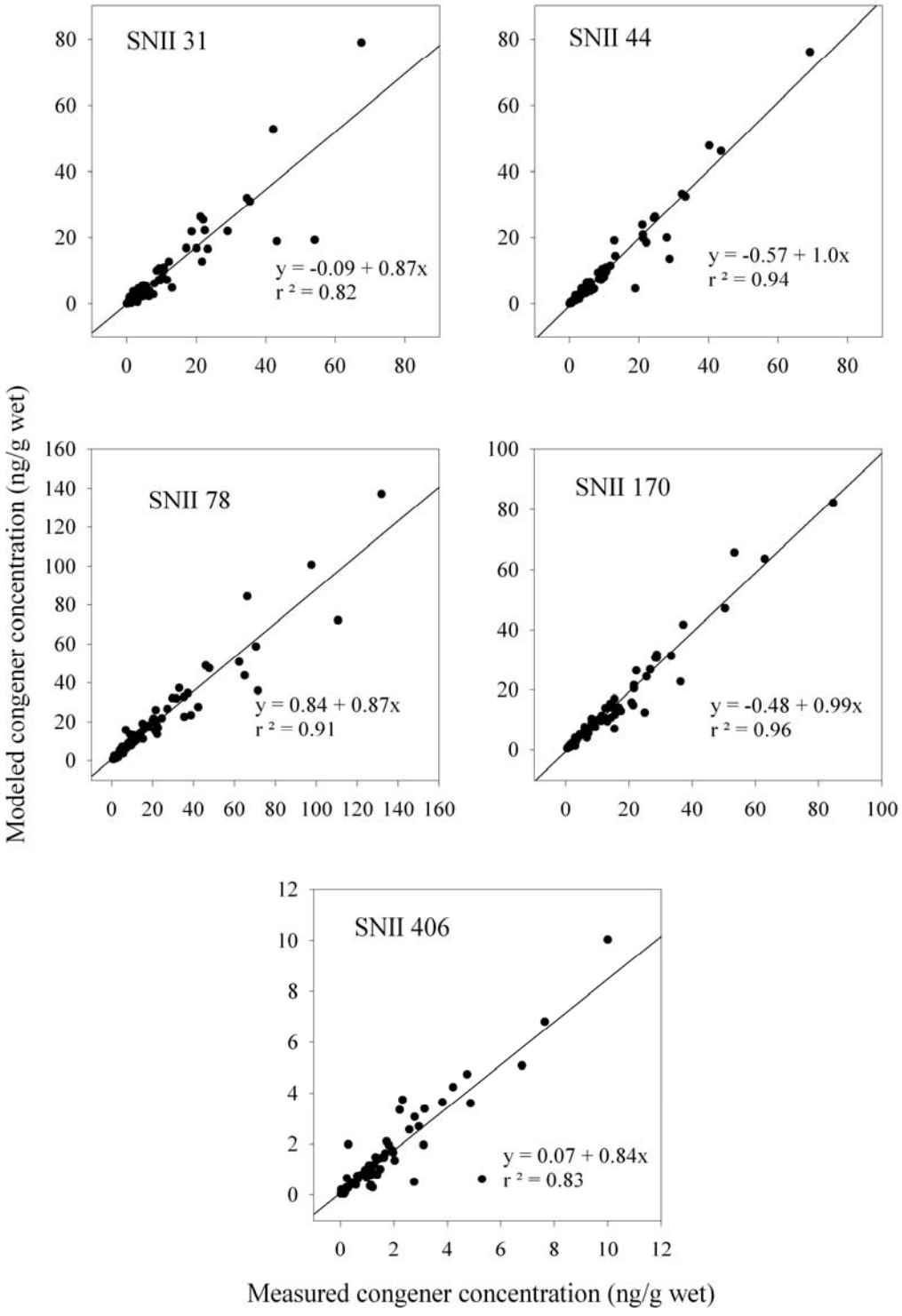


Figure 4. Reproduction of PCB congener concentrations on some white perch samples.

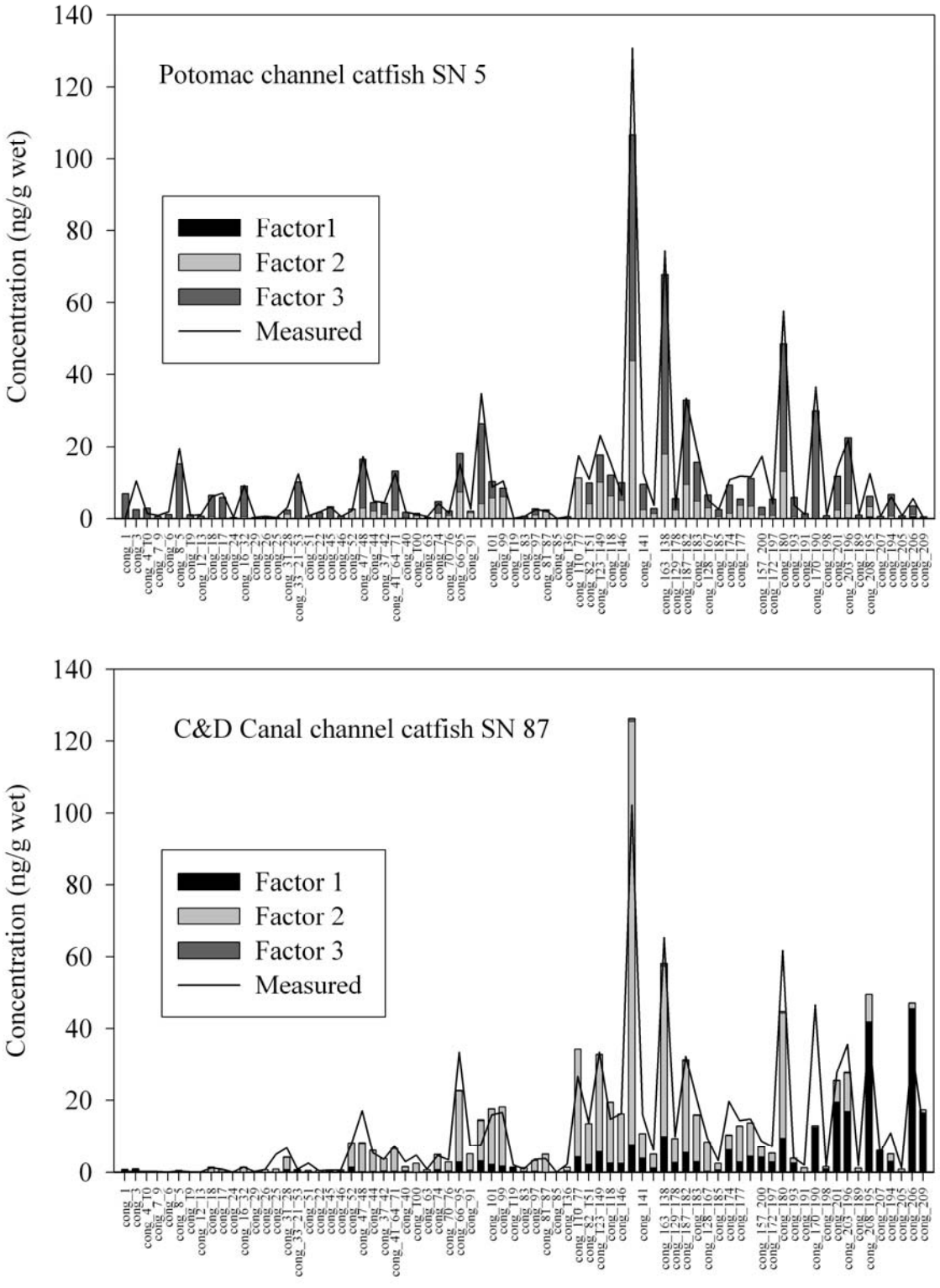


Figure 5. Reproduction of PCB congener profiles in high-concentration samples by PMF.

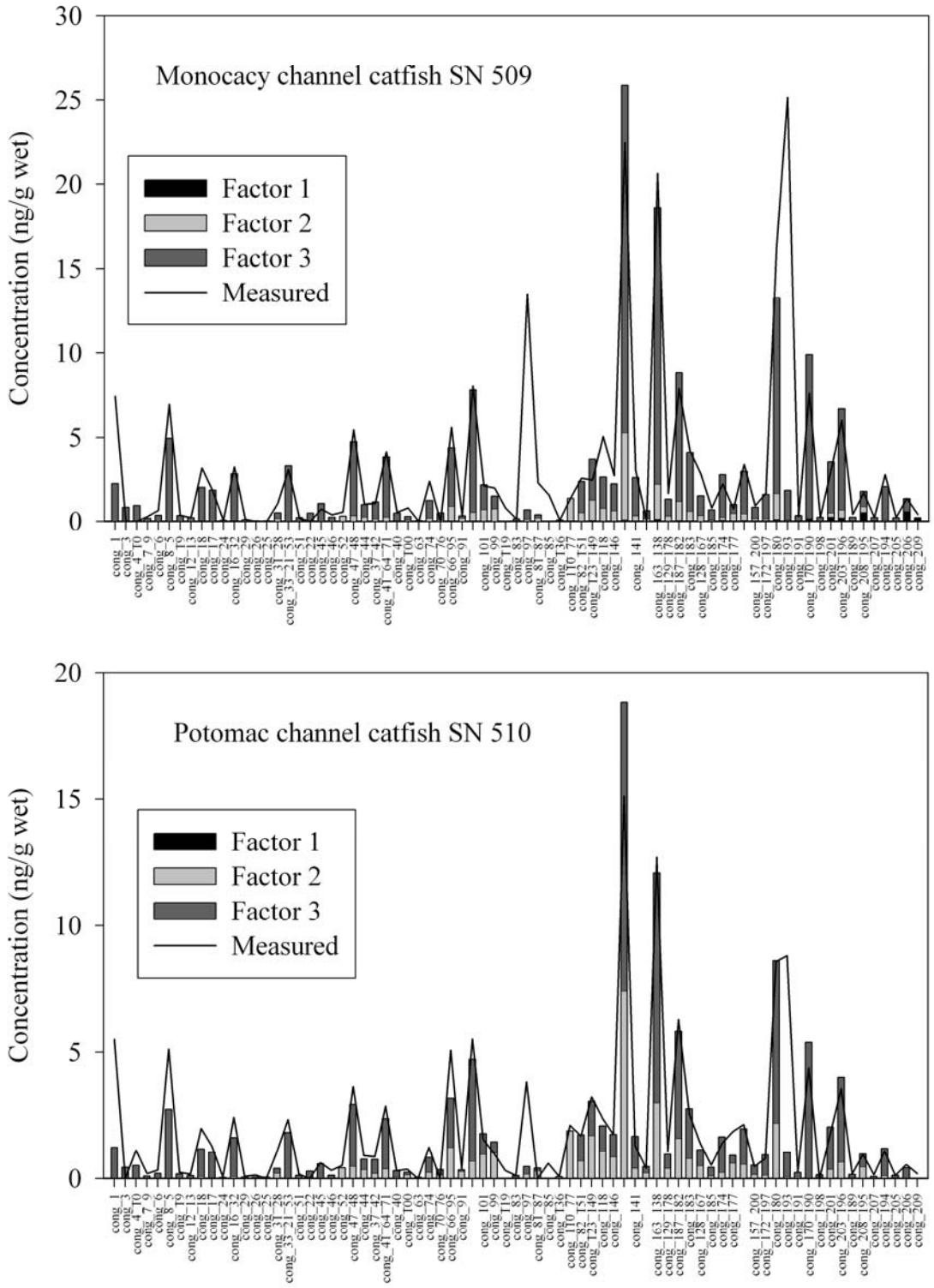


Figure 6. Reproduction of PCB congener profiles in low-concentration channel catfish samples by PMF.

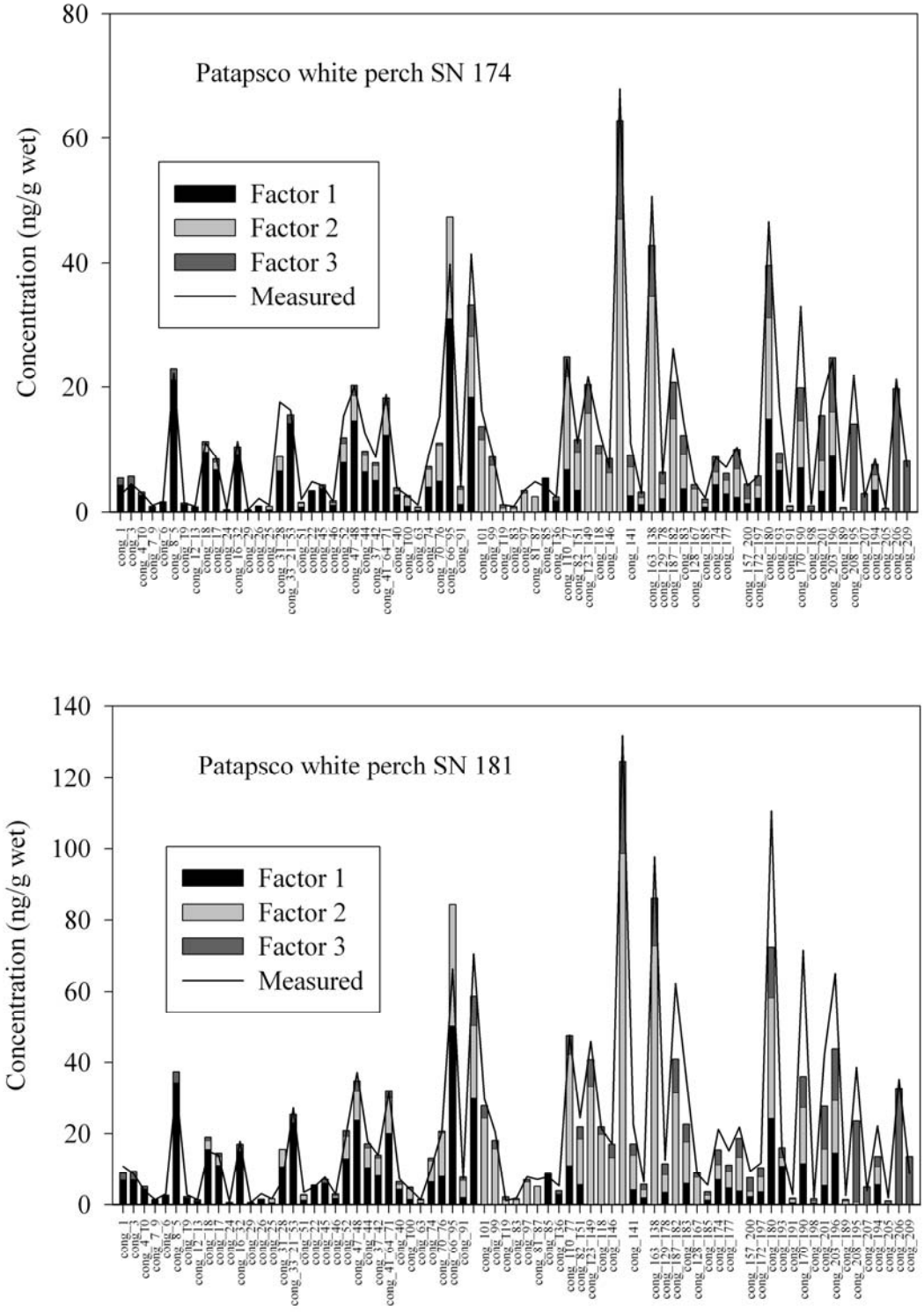


Figure 7. Reproduction of PCB congener profiles in high-concentration white perch samples by PMF.

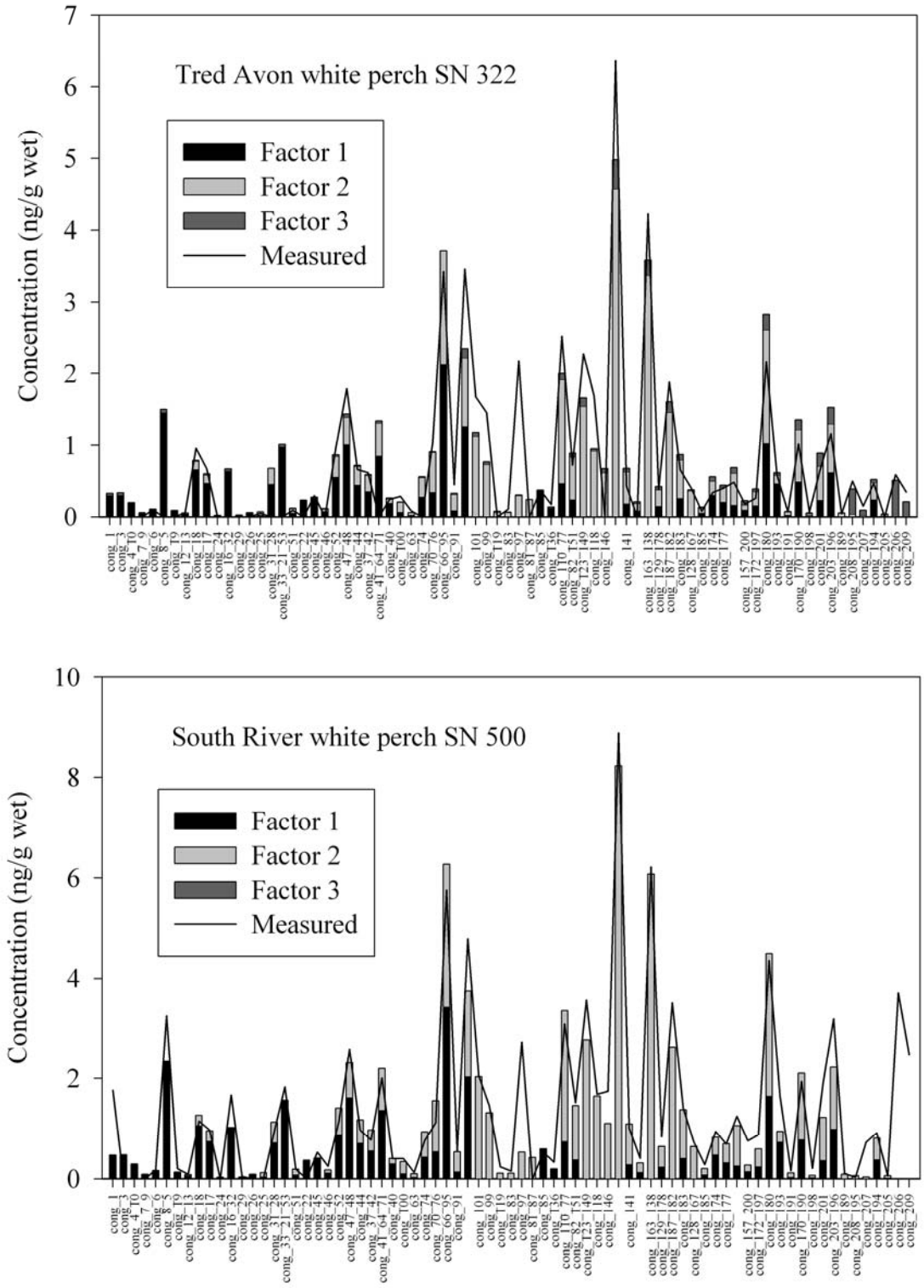


Figure 8. Reproduction of PCB congener profiles in low-concentration white perch samples by PMF.

Appendix 7. Detail maps of PMF results.

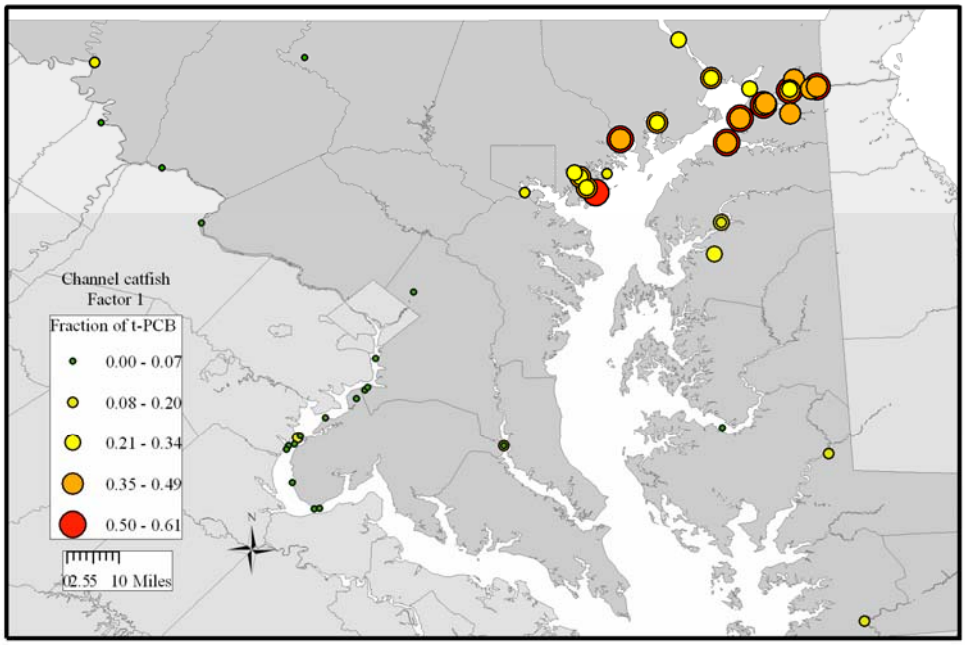


Figure 1. Eastern Maryland detail map of Factor 1 in channel catfish.

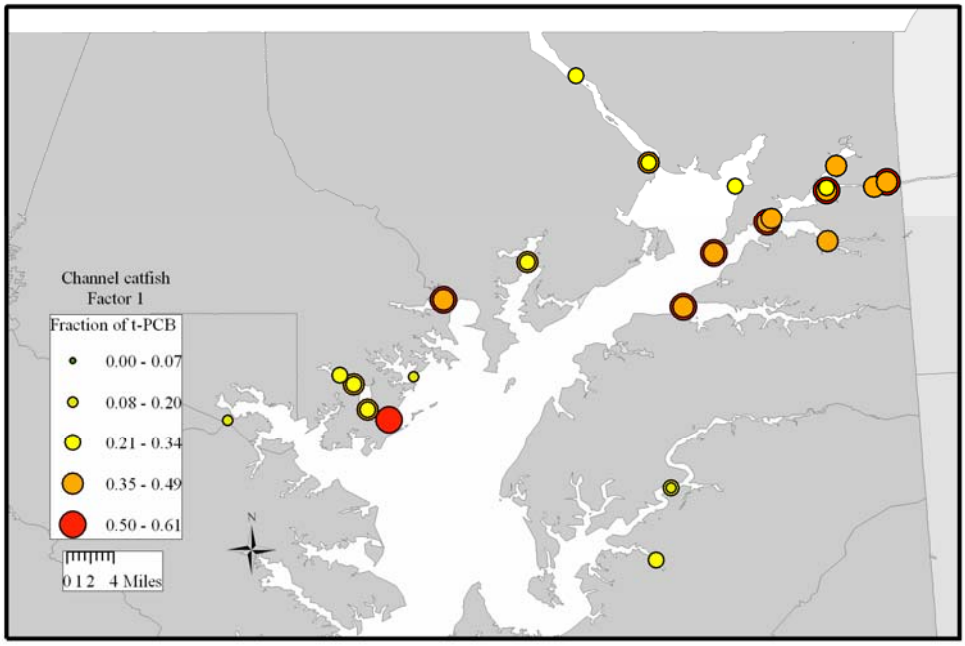


Figure 2. Northern Chesapeake Bay detail map of Factor 1 in channel catfish.

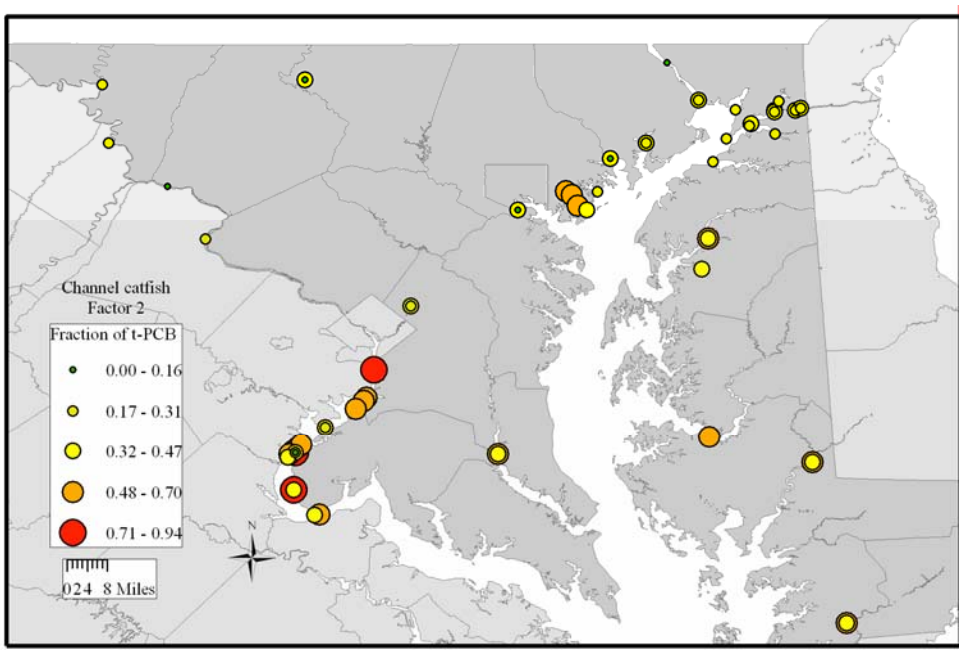


Figure 3. Eastern Maryland detail map of Factor 2 in channel catfish.

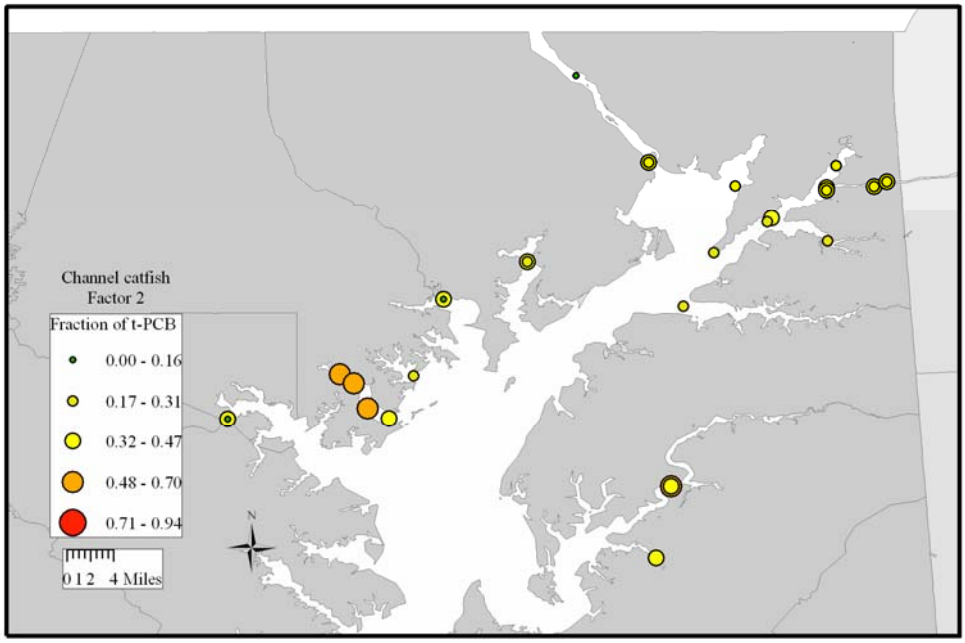


Figure 4. Northern Chesapeake Bay detail map of Factor 2 in channel catfish.

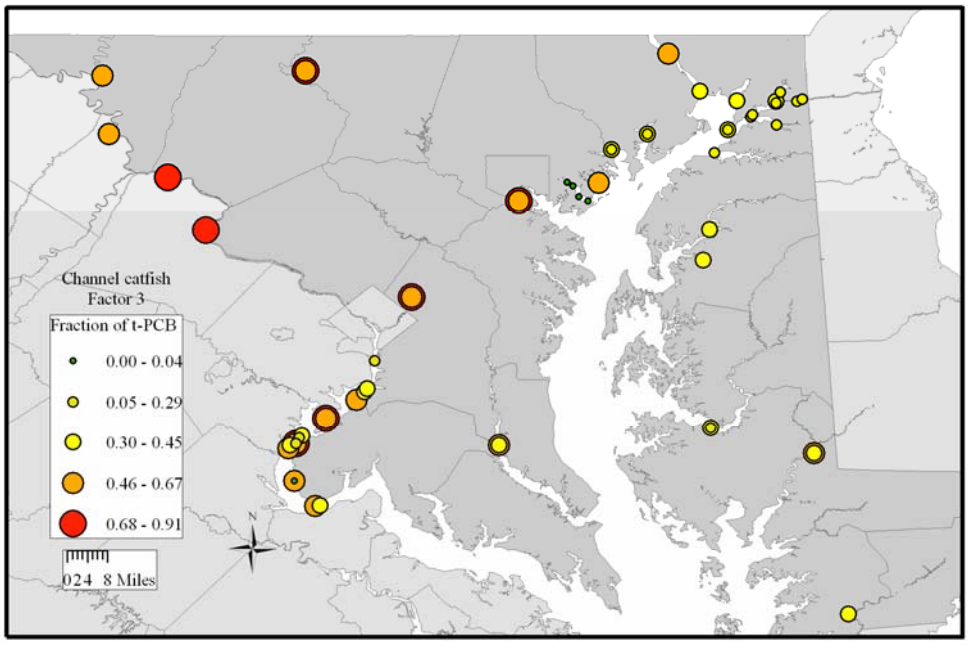


Figure 5. Eastern Maryland detail map of Factor 3 in channel catfish.

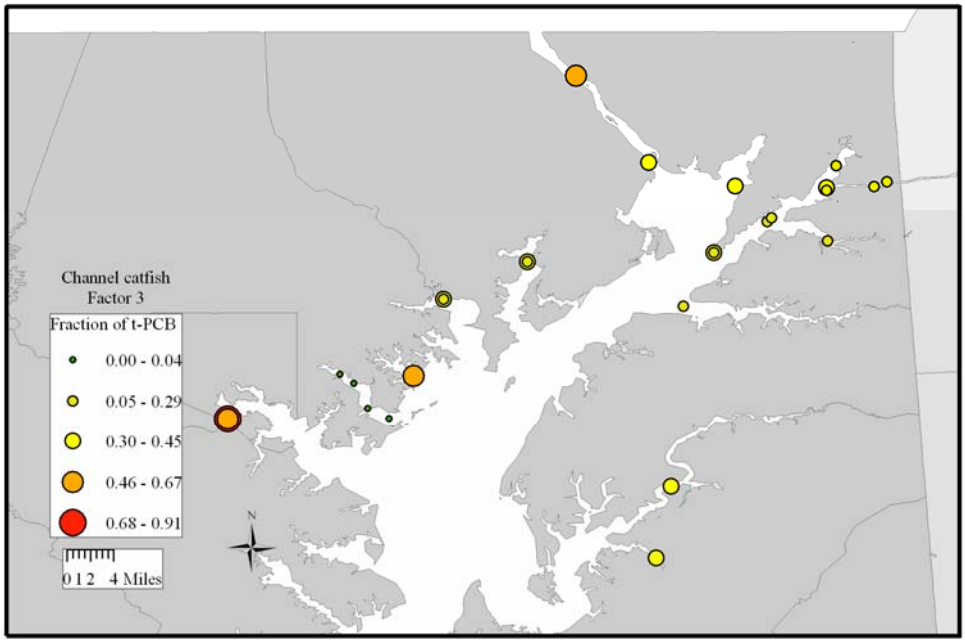


Figure 6. Northern Chesapeake Bay detail map of Factor 3 in channel catfish.

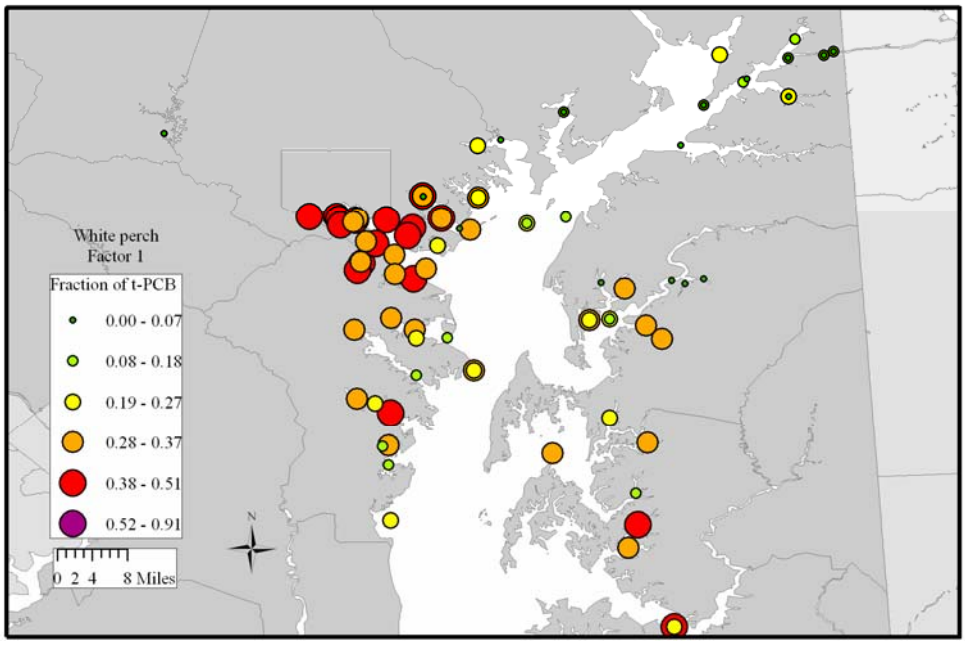


Figure 7. Northern Chesapeake Bay detail map of Factor 1 in white perch.

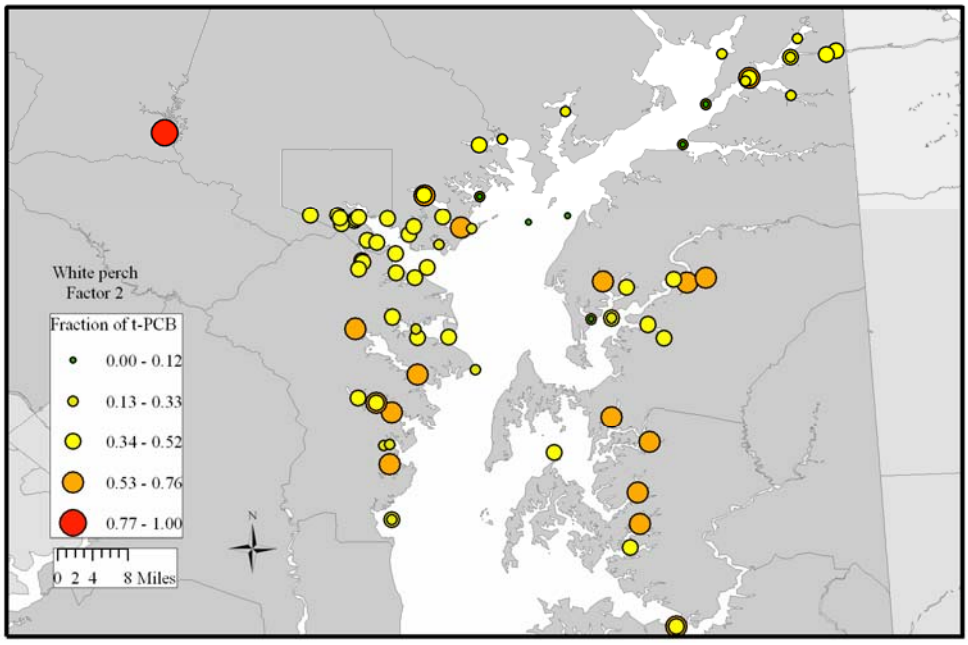


Figure 8. Northern Chesapeake Bay detail map of Factor 2 in white perch.

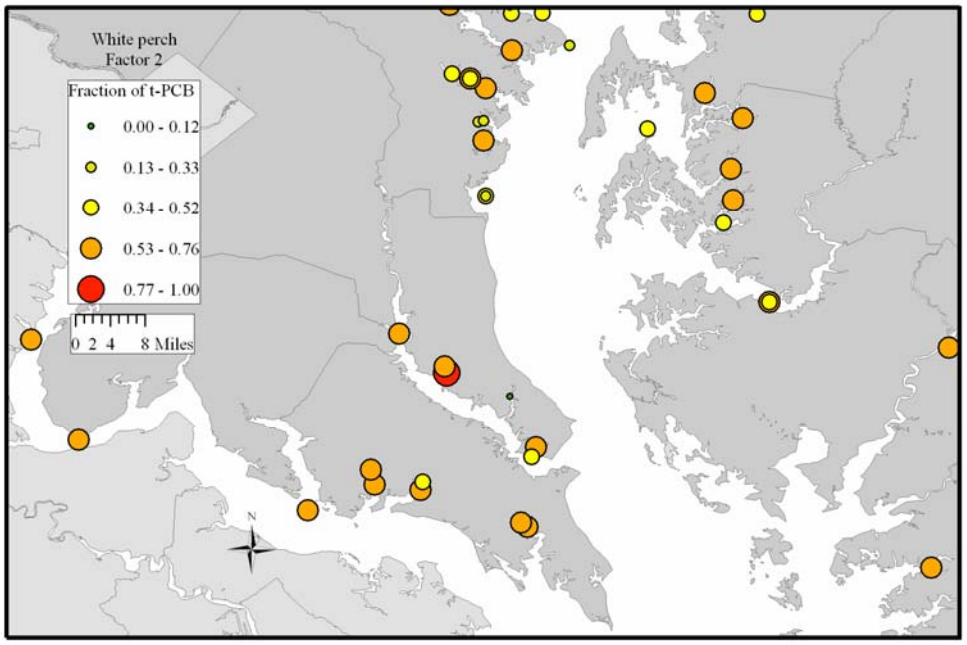


Figure 9. Southern Maryland detail map of Factor 2 in white perch.

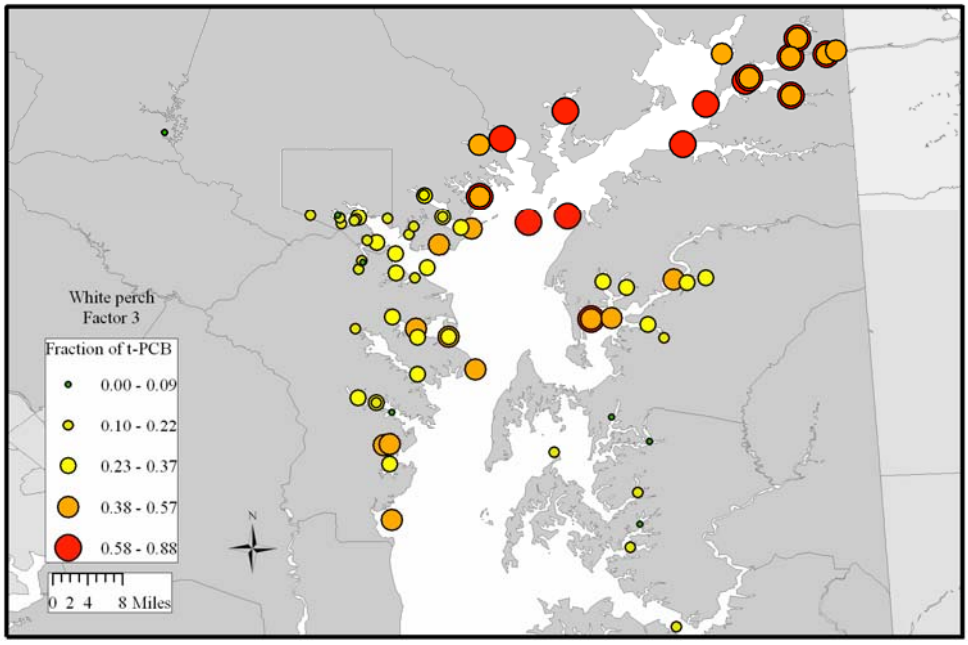


Figure 8. Northern Chesapeake Bay detail map of Factor 3 in white perch.

Appendix 8. Maps of concentrations of PCBs in white perch coming from each factor derived by PMF.

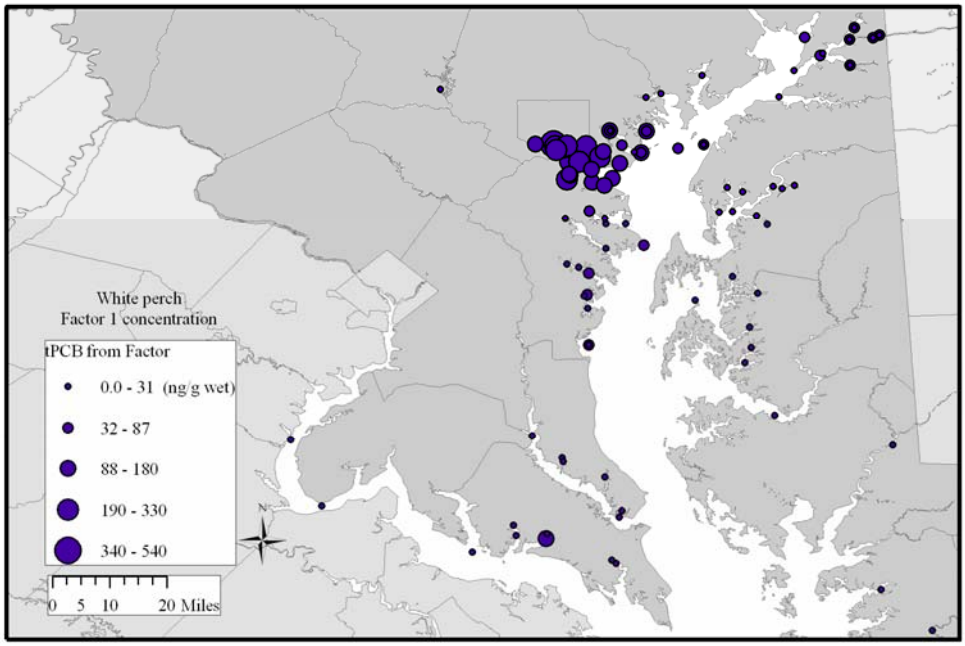


Figure 1. Concentration of Factor 1 PCBs in white perch.

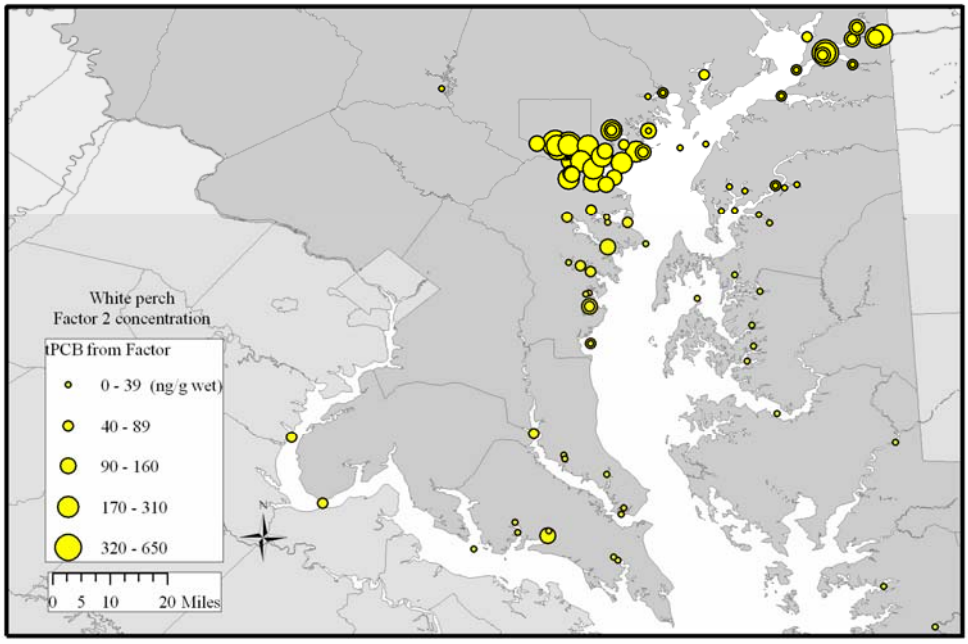


Figure 2. Concentration of Factor 2 PCBs in white perch.

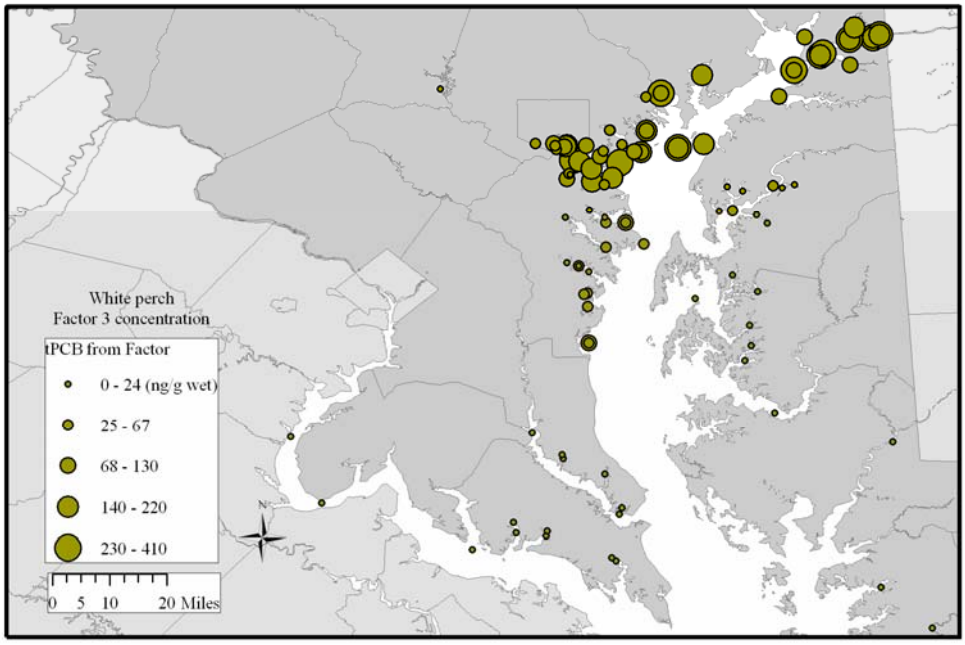


Figure 3. Concentration of Factor 3 PCBs in white perch.

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