ABSTRACT

MORT, SANDRA AMISS. Mass Spectrometric Methods for the Determination of PCB Congeners for Environmental Risk Assessment. (Under the direction of Dr. W. Gregory Cope and Dr. Damian Shea).

Our research provides important advances in the evaluation of alternative, cost effective analytical systems for polychlorinated biphenyl (PCB) risk assessment of environmental matrices. This type of evaluation has previously been limited by a reluctance on the part of regulators, site owners and investigators, to specify U.S. EPA Method 1668, the 209-PCB congener analysis recommended for environmental media, including biota, water, sediments and soils. U.S. EPA Method 1668 specifies a high-resolution gas chromatography / high-resolution mass spectrometry detection system (HRGC/HRMS) that is of limited availability in both federal and state environmental regulatory agency laboratories, as well as in contract environmental laboratories. This leads to a high cost for 209-PCB congener analysis and a reluctance to require it for environmental risk assessment. While additional validation is needed, this research indicates that low resolution tandem mass spectrometry (LRMSMS) gas chromatography systems provide adequate PCB congener resolution and detection sensitivity to provide robust data for environmental risk assessment of weathered (i.e., degraded) PCB contamination. Our results provide additional support for the need for 209-PCB congener-specific analyses to thoroughly assess the environmental risks associated with abiotic weathered PCB sources, or to define food web component specific PCB burdens and predator, and ultimately, human risks.

Based on observations of waterbody, species and trophic guild specific PCB congener profiles in fish collected from four waterbodies of the Yadkin-Pee Dee River system of North

Carolina, alternative human health risk assessment methods suggest that some North Carolina sub-populations ingesting fish from the four Yadkin-Pee Dee waterbodies may not be adequately protected from the potential for increased cancer risks by the N.C. Department of Health and Human Services 2007 fish consumption advisory protocol. Updated population-specific exposure parameters and a more protective threshold cancer risk level indicate elevated risks for frequent consumers of fish from the four waterbodies.

Moreover, we evaluated the suitability of the 2015 updated default U.S. EPA trophic magnification factors (TMFs) to estimate the trophic level concentrations of PCBs. Site-specific fish tissue data and the bioavailable fraction of water column PCB congeners collected with passive sampling devices (PSDs) were used in this analysis. The EPA default TMFs over-predicted the level of biomagnification indicated by the site-specific data, which supported the influence of site-specific ecosystem characteristics upon the default parameters to estimate PCB concentrations at various trophic levels. These findings also demonstrated the viability of using low-density polyethylene (LDPE) passive sampling devices (PSDs) to effectively concentrate the bioavailable PCB congener fraction, indicating a time weighted average concentration that would have not been detected by more traditional static sampling methods. The PSD data also pointed to sources other than bioconcentration from the water column as a significant source of exposure of the fish to PCBs. This finding, along with comparison of congener and homolog profiles of the fish and of native Aroclor mixtures, indicated that unique PCB sources likely exist in the four waterbodies and that historical PCB sources known for Badin Lake, may still be contributing to PCB profiles observed in the Badin Lake fish.

Mass Spectrometric Methods for the Determination of PCB Congeners for Environmental Risk Assessment

by
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DEDICATION

This dissertation is dedicated to my husband, Greg Mort, without whose support and encouragement I could not have completed this effort.

BIOGRAPHY

Sandra Leigh Amiss ("Sandy") was born on the family farm in Wabash County, IN, where she graduated from Manchester High School, North Manchester, IN. The oldest of three sisters, she grew up with a love of the outdoors and all things science. This lead to completing B.S. degrees in Biology-Chemistry and Biology at Manchester College, North Manchester, IN. While attending Manchester College, she married Greg Mort, also a student at Manchester College, and whom she met while both were attending Manchester High School. After a year as a Research Scientist in a cancer research program at Indianan-Purdue University-Fort Wayne (IPFW), she accepted a laboratory position with an environmental consulting company that sparked her interest in environmental science, where she rose to Vice President of Laboratory and Biological Services. During this time, she developed a focused interest in environmental toxicology, risk assessment, and bioremediation. This lead to the pursuit of a M.S. degree in Biology with emphasis in environmental biology and toxicology at Purdue University - IPFW, while continuing her consulting career. After completion of her M.S., she accepted a position with a bioremediation specialty consulting firm in Raleigh, NC, as the Laboratory Manager and Senior Project Scientist. A few years later, an opportunity arose to work in the Aquatic Toxicology Unit (ATU) with the North Carolina Department of Environment and Natural Resources (NC DENR), in Raleigh, NC. She jumped at the chance to take a position with the ATU, which was a national leader in the development and refinement of the U.S. EPA's whole effluent toxicology program. While with the ATU, she was awarded the Division of Water Quality Employee of the Year following her development of a suite of toxicity assays to enhance the assessment of aquatic

ecosystem health. A desire to return to the human-health arena lead to accepting a position with the NC Department of Health and Human Services (DHHS) Division of Public Health (DPH), Raleigh, NC, as the Principal Investigator for an ATSDR/CDC sponsored grant to perform human health risk assessment on federal Superfund sites. At DHHS, she was involved in many high-profile human health issues and was instrumental in enhancing the science of environmental risk assessment and its application to public health issues. It was while at DHHS, she decided to pursue her Ph.D. in Zoology with a minor in Environmental Toxicology at North Carolina State University, while continuing her career at DHHS. During her Ph.D. studies a position as an environmental risk assessor presented itself with the NC DENR Division of Waste Management (DWM). In her current position with the DWM, she works as both a human health and ecological risk assessor, assisting in decisions that directly affect the health of the environment and citizens of North Carolina.

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CHAPTER 1: Introduction

INTRODUCTION

The manufacture and use of polychlorinated biphenyls (PCBs) in the United States (U.S.) was prohibited in 1977, yet PCBs continue to present a legacy human health and ecological hazard. The ingestion of contaminated fish is the primary source of exposure to PCBs for the public.[1] The longevity of the PCB environmental hazard is associated with their unique chemical properties, persistence in the environment, capacity for global transport, ability to accumulate in the aquatic environment, and capacity to biomagnify in both terrestrial and aquatic food webs. Human health and environmental concerns of PCBs are related to their persistence, biomagnification potential, and the toxicity of both the parent compounds and their metabolites. Human population studies commonly identify elevated blood serum and tissue levels of PCBs.[2, 3]

PCBs are a class of 209 structurally-related ("congeners") synthetic chemicals. Each congener consists of a biphenyl backbone with 1 to 10 chlorine atoms attached (Figure 1). The number and position of the chlorine atoms conveys a range of unique physical, chemical, environmental fate, and toxicological properties to the individual congeners. A 12-member sub-set of the 209 congeners (the "dioxin-like" congeners) can take on a planar orientation of the two biphenyl molecules, resulting in a steric binding capacity mimicking dioxin (2,3,7,8-tetrachlorodibenzodioxin, or "TCDD"), acting as aryl hydrocarbon receptor- or AhR-agonists.[4]

PCBs were first manufactured in 1929. The production of PCBs involved catalyst-driven chlorination of biphenyl with anhydrous chlorine, resulting in mixtures of compounds with varied levels and patterns of chlorination.[5] It has been estimated that up to 1 billion

kilograms of PCBs were produced world-wide, and that 1 million kilograms continue to cycle globally in the open environment. Ninety-nine percent of the PCBs used in the United States were PCB mixtures produced by the Monsanto Company, under the trade name "Aroclor". Monsanto was the only U.S. manufacturer of PCBs.[6] Aroclor mixtures were formulated for a desired level of viscosity, heat and flammability resistance. Each Aroclor formulation was a unique range of 50-150 congeners, with some overlap in the congeners making up the different Aroclor formulations. Common Aroclors included Aroclors 1016, 1232, 1242, 1248, 1254, 1260 and 1262.[4] It is estimated that 300 million kilograms of PCBs were sold in the U.S., mostly consisting of the Aroclors 1242, 1254, and 1260.[6] Over their production period, individual Aroclor congener profiles remained relatively consistent, except for Aroclor 1254 that had two primary formulations with major differences.[7]

The primary source of PCBs in the environment resulted from their use as commercial mixtures in industry and the continuing source as byproducts of waste incineration.[8] PCBs were widely used in industrial applications for their insulating properties, as dielectric fluids in capacitors and transformers, as flame retardant coatings, in heat transfer applications, hydraulic systems, electrical switches, circuit breakers, dust control agents, gas turbines and vacuum pumps. They were also used in textiles, surface coatings, elastic sealants and caulking compounds, in fluorescent lighting, and as plasticizers in plastics, adhesives, sealants, carbonless copy paper, in inks and paint. Not all PCBs found in the environment are attributed to Aroclor releases. Non-Aroclor sources include their unintentional production during chlorine bleaching of wood pulp in paper production, and during thermal processes involving organic matter and chlorine, such as in incinerators or cement kilns.[5, 6, 9, 10] Before

1974, PCBs were used in both closed (transformers, capacitors, heat transfer and hydraulic fluids) and open applications (inks, flame retardants, adhesives, carbonless paper, paints, plasticizers, pesticide extenders, commercial waxes). Use was limited to closed system transformers and capacitors from 1974 through 1978. Since 1979, the only permitted uses are as optical liquids and for research and development.[11, 12]

More than 90% of human exposure to PCBs occurs by ingestion, mostly from fatty fish, with lesser contributions from meat and dairy products.[13, 14] Exposure to PCB-contaminated building materials, especially in older buildings, has also been identified as a significant source through direct contact with the contaminated materials, or by inhalation of the more volatile PCB congeners that out-gas from building materials.[15]

The Toxicology of PCBs. Each of the 209 PCB congeners has a unique physicochemical profile related to the number and location of the chlorine atoms attached to the biphenyl backbone. The 12 congeners with a non-*ortho* or mono-*ortho* chlorine substitution pattern are classified as the "dioxin-like" congeners (dl-PCB). Their chlorine substitution pattern permits a planar orientation of the biphenyl rings, which facilitates a distinct toxicological pathway that mimics that of dioxin, or 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD).[16-18] Dioxin and dioxin-like compounds, including the dl-PCBs, bind to the cytosolic aryl hydrocarbon receptor (AhR), functioning as AhR-agonists, and promoting a wide spectrum of toxic effects. The dl-PCB-AhR complex translocates to the nucleus where it complexes with the Arnt transcription factor, enabling the dl-PCB-AhR-Arnt complex to bind to specific DNA sequences, the xenobiotic response element (XRE) present in the promoter regions of certain genes. The binding of the dl-PCB-AhR-Arnt

complex to the XRE modulates the expression of several phase I (CYP) and Phase II enzymes (UDP-glucuronosyltransferase, UGT), and the AhR repressor (AHRR) enzyme which down-regulates the AhR signal.[2, 5, 17, 18] While not acting through the AhR-ligand mechanism, the toxic targets of the remaining non-planar congeners, the "non-dioxin-like-PCBs" (ndl-PCBs) are also mediated through specific nuclear receptor-related mechanisms. Reported mechanisms of ndl-PCB toxicity include activation of the pregnane xenobiotic receptor (PXR) transcription factor, with decreased expression of genes involved in lipid catabolism and loss of energy homeostasis. Constitutive androstane receptor (CAR) agonist activity and peroxisome proliferator-activated receptors (PPARα) antagonist activity have been observed in mammalian cell-line testing of ndl-PCB congeners [2, 5, 17-19] Animal studies report the induction of the hepatic cytochrome P450 phenobarbital receptor (PBR) and hepatic lipid peroxidation.[20, 21]

The spectrum of toxicological effects attributed to PCBs in animal models and epidemiological studies includes carcinogenic, reproductive, neurodevelopmental, immunological, dermatological, and more recently, endocrine system interference. Endocrine systems impacted include two critical to the regulation of brain development and thyroid hormones, the hypothalamic-pituitary-thyroid (HPT) and hypothalamic-pituitary-gonadal (HPG) systems. Impacts to either system during critical developmental windows can have enduring impacts.[13] The negative association of infant and childhood neurophysiological function with developmental exposures are indicated in laboratory studies and epidemiological investigations.[15] Mouse studies indicate that a period of extreme vulnerability to PCB-related developmental defects during the brain growth sprout (BGS), a

period of intense neuronal growth. The rodent BGS occurs during the first 2-4 weeks after birth. The human BGS is from the first trimester through approximately two years of age.[22] More recently, epidemiological studies have associated elevated PCB exposures with non-alcoholic fatty liver disease (NAFLD) and metabolic syndrome. Increasing adipose tissue levels have been associated with Type 2 diabetes, and serum PCBs levels with elevated serum cholesterol and triglycerides.[19]

The range of effects attributed to the dl-PCBs and ndl-PCBs are similar, despite acting through different nuclear receptor pathways. Reported effects include tumor promotion, endocrine disruption, neurotoxicity, impaired cognitive development, immunotoxicity, and hepatotoxicity.[2, 5, 17-19] A recent report proposes a mechanism by which PCB exposure may act in concert with chromosomal aberrations, contributing to the expression of genes implicated in the susceptibility to autism spectrum disorders (ASD). Bioinformatic studies of human brain and experimental models identified a cumulative effect of large chromosome duplications and PCB-95 exposure, combined with a strong genetic predisposition, on genes involved in signal transduction pathways, neuron synapses ion-channel function, cell adhesion, and regulation of transcription. The study identified altered epigenetic hypomethylation patterns and transcriptionally modified genes potentially affecting long-term neuron transcriptional stability.[23]

The U.S. Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC) have classified PCBs as “probable (human) carcinogens”, and IARC has classified congener PCB-126, the most potent of the dl-PCBs, as a group 1 “carcinogenic to humans” compound.[24, 25] Dioxin-like compounds are classified as non-

genotoxic and non-mutagenic tumor promoters in the liver, lung and skin.[26] The mechanisms of dl-PCB carcinogenesis have been linked to the activation of AhR and subsequent toxicity mediated through the induction of chronic inflammation responses, increased formation of reactive oxygen species (ROS) with increased oxidative stress, and immunosuppression.[14]

DNA-adduct formation and oxidative damage are implicated in hepatic carcinogenesis in animal studies, as are the induction of hepatocyte proliferation and activation of the NF-κB transcription factor. The NF-κB transcription factor functions in carcinogenesis by regulating the expression of apoptosis-related genes and cell proliferation.[9, 20, 21] Increased risk of non-Hodgkin's lymphomas, malignant melanoma and breast cancer have been associated with PCB body burden in epidemiological studies.[2, 14, 27]

PCBs are readily absorbed and distributed throughout the body, with the primary deposition to adipose tissue, with lesser levels in the liver, skin and breast milk. Congeners with high degrees of chlorination and a lack of vicinal hydrogen atoms tend to be preferentially bioaccumulated. PCBs can cross the placenta, and human exposure generally begins prenatally, during windows of critical embryonic and fetal development, and enhanced susceptibility to xenobiotics. Neonatal exposures during breast feeding can also provide a significant exposure. Because of the extended half-lives of PCBs, ranging from years to decades for the most persistent congeners, PCBs accumulated in adipose tissue stores can act as a chronic exposure source when re-mobilized by physiological changes, such as pregnancy, fasting, or some diseases.[14, 21, 28, 29]

Characteristics of PCB Releases to the Environment. Octanol-water partition coefficients (K_{ow}) and water solubility values for the 209 congeners span four orders of

magnitude.[30] The range of physicochemical properties making up the 209 possible PCB congeners, the distinctive sub-sets of congeners making up individual Aroclor mixtures, and the impact of these characteristics on congener-specific partitioning and abiotic and biotic transformations once released into the environment, all contribute to the difficulties in identification and quantitation of weathered environmental PCBs, and ultimately estimations of potential human and ecological risks.[6] When released into the environment, a native mixture of PCB congeners is uniquely modified in relation to the original congener mixture composition, the influences of climatic conditions, and the unique properties of the abiotic and biotic environmental matrices with which the mixture interacts.[4] The consequence of these combined influences are situation-specific modifications of the original PCB congener profile, referred to as "weathering". The congener profile continues to be modified as the mixture partitions to each subsequent environmental compartment.[31-33] Ultimately, a heavily weathered PCB may have little similarity to that of the original or native Aroclor profile. Often the modified profile is biased toward the more recalcitrant, higher chlorinated, and generally more toxic congeners.

These profile modifications are not limited to abiotic matrices. The toxicokinetic processes of absorption, distribution, metabolism, and excretion (ADME) alter PCB congener patterns in exposed biota, including fish. As a class, PCBs are highly lipophilic and they are readily absorbed and slowly eliminated, tending to bioaccumulate (a net accumulation from all source environmental sources)[34] in adipose tissue and fatty organs such as the liver. Differences in the rate of congener-specific uptake, metabolism, and excretion contribute to profile differences among biota within a food web. These differences

may be most evident in releases to the aquatic ecosystem, where sediment profiles may vary distinctly from profiles in biota. Within the aquatic environment, profile modifications are related to partitioning between different abiotic media, or uptake from abiotic media to biota. Distinct profiles may be evident in each subsequent trophic level where habitat utilization and food source differences influence both exposure and accumulation. Food web biomagnification (increasing tissue concentrations with trophic level associated with dietary accumulations through predator-prey relationships)[34] leads to higher body burdens of more lipophilic recalcitrant congener profiles in upper trophic level organisms with the accompanying increased risk of toxic impacts to each higher trophic level.[4, 35]

Environmental Monitoring of PCBs. In the U.S., identification and quantitation of PCBs in environmental matrices has historically relied upon the U.S. EPA's Aroclor-pattern matching analytical methods that utilize gas chromatography-electron capture detector (GC/ECD) instrument systems. The Aroclor pattern-matching analytical method relies on comparison of chromatographic profiles of native commercial mixtures of Aroclors to the chromatographic profile of the typically weathered environmental sample profile for source Aroclor identification and concentration estimates reported as the quantity of single or multiple Aroclors most closely resembling the weathered profile. The potential identification and quantitation inaccuracies associated with the Aroclor pattern-matching method for PCB loads in environmental matrices have long been recognized,[30, 36] and suitable analytical alternatives validated by the U.S. EPA have been available since 1998, yet most efforts to quantify PCB loads of environmental matrixes, including those used for human health risk

assessment, continue to rely on the U.S. EPA Method 8082,[37] the "Aroclor" analytical method.

In 1998, the U.S. EPA released Method 1668 that relies on identification and quantitation of individual PCB congeners, eliminating the potential bias associated with analysis of weathered matrices. To achieve the congener separation ability and detection sensitivity, Method 1668 specifies a high-resolution gas chromatograph / high resolution mass spectrometer (HRGC/HRMS) analytical system. Despite the continuing evidence that Aroclor pattern matching cannot provide accurate characterization or risk estimates of PCBs in weathered environmental matrices, the high cost and limited availability of laboratories with the capabilities to run Method 1668 has resulted in a reluctance of regulatory and public health agencies to require it for characterization of PCB releases and health risk estimates.

Passive Sampling Devices and their Application in Environmental Risk Assessment. A critical component of environmental risk assessment is the determination of the bioavailable fraction of chemicals in various environmental matrices.[38] The use of passive sampling devices (PSDs), particularly for sampling in aquatic and sediment pore water matrices, provides a cost-effective means to characterize the bioavailable fraction of lipophilic organic contaminants of concern.[39] The extended deployment of PSDs to reach equilibrium kinetics with the accumulated lipophilic contaminants uptake into the PSD matrix can provide a time-weighted-average (TWA) concentration over the deployment period, which is typically from for several days to several weeks. For environmental exposures, the TWA concentration provides a more ecologically-relevant chronic or sub-chronic exposure characterization than can be estimated with single or multiple grab samples.

PSDs provide additional advantages over traditional grab or composite sampling techniques in aquatic matrices, including surface water, groundwater and sediment pore water, because of their ability to directly sample the bioavailable fraction of organic contaminants. In these matrices, the bioavailable fraction is represented by the freely-dissolved concentration, or the fraction not adsorbed to particulate organic carbon (POC) or dissolved organic carbon (DOC).[40] Other means of separating the bioavailable fraction of lipophilic organics from these matrices, include filtration of water matrices, or centrifuging sediments to separate the porewater, followed by filtration of the porewater to remove the fine particulate phase. These procedures may change the physical or chemical nature of the freely dissolved phase and bias the characterization of the bioavailable fraction. This ultimately will impact the quality of the risk assessment. Risk assessments that underestimate potential risks may lead to unintended adverse health effects to human or ecological receptors. Risk assessments that overestimate potential risks may lead to unnecessary disturbances of the environment and the incurrence of unnecessary remediation costs. Another advantage of PSDs is to effectively concentrate the chemicals in the PSD matrix, increasing the detection sensitivity of the traditional analytical method, without the application of special sample collection, preparation or analytical methods. This can enable detection of the parent chemical or its breakdown products at concentrations that may not have been detected with traditional sampling methods. Better recognition of degradation pathways provides a better assessment of natural or enhanced degradation pathways, and lead to improved risk management decisions. The increased analytical sensitivity afforded by PSD sampling is also facilitated by the relatively

clean matrix that results from PSD solvent extraction, particularly as compared to some surface water and pore water matrices.

Study Objectives. The first objective of this research was to characterize HRGC/HRMS PCB congener profiles for fish collected from the Yadkin-Pee Dee River basin of central North Carolina from 2008 to 2012. These data were initially evaluated for human health-associated ingestion risks following the standard protocol adopted by North Carolina's public health agency. This study evaluated alternative exposure parameters for select North Carolina sub-populations and subsequent risks associated with ingesting these fish. The second objective was to potentially identify more cost-effective and available alternatives to the HRGC/HRMS system required for the current EPA 209-congener analytical method; several low-resolution mass selective detector systems were evaluated for their ability to sufficiently detect and quantify PCB congeners for environmental risk applications. Instrument system comparisons included analysis of fish tissue extracts. The suitability of PSDs to sequester and concentrate trace levels of bioavailable PCB congeners from the water column was also evaluated. The PCB congener data collected with PSDs were used to develop site-specific aquatic trophic level food chain multipliers (FCMs) that were compared to the U.S. EPA 2015 default FCM values developed for non-polar hydrophobic organic compounds with K_{ow} values matching specific PCB congeners.

This research will provide important advances in the evaluation of alternative, cost effective analytical systems for the environmental risk assessment of mixtures of PCB congeners. This research will also demonstrate the viability of cost-effective application of

LDPE PSDs to effectively sequester and concentrate trace levels of bioavailable PCB congeners from water matrices.

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FIGURES

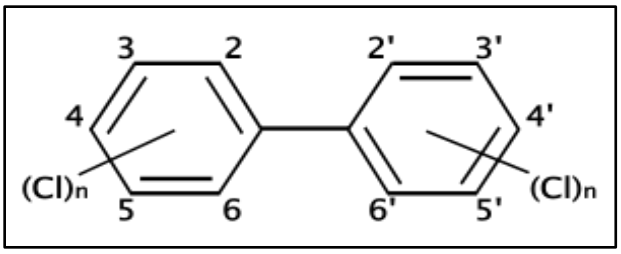

Figure 1. The polychlorinated biphenyl backbone and chlorine attachment sites at 2-6 and 2'-6'. *ortho* attachment sites: 2, 2', 6, 6', *meta* attachment sites: 3,5,3'5', *para* attachment sites: 4,4'

CHAPTER 2: Polychlorinated Biphenyl Profiles in Fish from a Large Atlantic Regulated River and Associated Human Health Ingestion Risks

Polychlorinated Biphenyl Profiles in Fish from a Large Atlantic Regulated River and Associated Human Health Ingestion Risks

ABSTRACT

Forty years after their manufacture and use in the United States was prohibited, polychlorinated biphenyls (PCBs) continue to pose an environmental concern. A major route of exposure to the human population is through the ingestion of PCB-contaminated fish. PCBs are a group of 209 structurally-related congeners, that share common properties of being highly lipophilic and persistent. A common sink for releases of PCBs is the aquatic environment, where they accumulate in sediments, and bioaccumulate and biomagnify in the food web. Accurate determination of environmental risks associated with PCBs requires congener-specific identification and quantitation. To determine the need for fish consumption advisories, congener-specific analysis of fish collected from four reservoirs of the Yadkin-Pee Dee River system in North Carolina were evaluated. Unique PCB concentrations, congener and homolog patterns were identified in the different waterbodies and species of fish collected. Catfish species had the highest mean PCB fillet tissue concentrations (Flathead Catfish, *Pylodictis olivaris* 80,000 ng PCB/kg tissue wet-weight (ng/kg ww); combined catfish species 34,000 ng/kg ww), followed by bass species (White Bass, *Morone chrysops* 25,000 ng/kg ww; Largemouth Bass, *Micropterus salmoides* 18,000 ng/kg ww). Catfish species PCB burdens were likely related to their contact with sediments, ingestion of sediment-associated benthos, and higher tissue percent lipid content (Flathead Catfish 4.85%; combined catfish group 2.61%). Food chain biomagnification explained the PCB-burden of the top predator bass species, as well as the % lipid (0.99%). While the insectivore species

included in the study had a percent tissue lipid similar to the Largemouth Bass, the PCB-burden of their food source appeared to be the major influence on their tissue PCB concentrations (Redear Sunfish, *Lepomis microlophus* 3,900 ng/kg ww PCBs, 0.85% lipid; sunfish group 5,600 ng/kg ww PCBs, 0.83% lipid). These results indicate that regional assumptions of similar PCB burdens among fish and associated ingestion risks may not be appropriate even in hydrologically-connected waterbodies, as differences were observed in the fish populations among the waterbodies and species of the same trophic level. These differences were likely related to waterbody-specific influences of sediment characteristics, species habitat utilization, food web structure, and possibly unique PCB inputs to the four reservoirs. A common assumption that the major portion of PCB risk is associated with the dioxin-like congeners was not supported by the fish tissue data obtained in this study (range of the proportion of dioxin-like risk for all tissue samples, 0.12 – 0.83, mean = 0.31). High levels of human cancer-risk were indicated when fillet tissue was evaluated as total dioxin-like congener TEQ-adjusted risks combined with total non-dioxin-like congener risks. Regional-specific exposed human populations were considered, and a more conservative Acceptable (lifetime excess cancer) Risk Level (ARL) within the U.S. Environmental Protection Agency and Agency for Toxic Substances and Disease Registry recommended threshold risk range was used (at 1.0E-05 ARL: 63% for child; 28% for adult resident; 70% for an immigrant adult, and 77% for subsistence adult; as % of fish fillet samples exceeding the ARL). Our findings support the use of 209-congener analyses for characterization of waterbody specific environmental risk assessment for human health protection.

INTRODUCTION

The Yadkin-Pee Dee River is a large, highly regulated Atlantic Slope drainage; the basin is the second largest in North Carolina, spanning 21 counties and covering approximately 18,600 km^2 (7200 mi^2).[1] The Yadkin-Pee Dee River Basin includes a variety of habitats and drains portions of the Piedmont, Sandhills, and Coastal Plain physiographic regions. The 327 km (203 mi) Yadkin River originates on the eastern slopes of the Blue Ridge Mountains in Watauga County, flows in a northeast direction for approximately 160 kilometers (100 miles), then turns southeast and is joined by the Uwharrie River, forming the Pee Dee River. The 370 km (230 mi) long Pee Dee River continues southeast through North Carolina into South Carolina, where it flows into Winyah Bay at the Atlantic Ocean. There are approximately 9300 total hectares (23,000 acres) of reservoirs impounded by dams in the Yadkin-Pee Dee River Basin system. The basin travels through densely populated areas and includes 93 municipalities and a population of nearly 1.7 million persons.[2] The basin includes seven constructed reservoirs, for which hydroelectric dams were built in the first half of the 20th century to power aluminum smelters and electric utilities. The reservoirs, from upstream to downstream are: W. Kerr Scott, High Rock, Tuckertown, Badin (Narrows), Falls, Tillery and Blewett Falls. Forested land covers half of the Yadkin-Pee Dee watershed and includes the Pee Dee National Wildlife Refuge, the Blue Ridge Parkway and the Uwharrie National Forest.

Fish tissue PCB concentration studies began in the North Carolina portion of the Yadkin-Pee Dee River in 2008 in Badin Lake following a request to the North Carolina (N.C.) Department of Health and Human Services (DHHS) to determine if ingesting fish from the

lake could present a human health hazard. Aroclor PCBs had been detected in Badin Lake sediments collected in 1996, 1997 and 2007. The historical PCB releases were associated with the Badin Works Alcoa aluminum (Alcoa) smelting facility that began operations in 1915 on the southwest shore of Badin Lake in Stanly County, N.C. Prior to this study, PCB congeners were detected in a Flathead Catfish (*Pylodictis olivaris*) that was part of a 2004, four sample study looking at a 19-congener subset. This information prompted a proposal for a broader fish tissue study to better define PCB concentrations in Badin Lake fish and potential health implications for persons regularly consuming fish from the lake. Consequently, in the summer of 2008 a fish tissue sampling and 209-congener PCB analysis plan for Badin Lake was implemented. The results of the Badin Lake fish tissue study led the N.C. DHHS to issue a fish consumptions advisory, and identified the need for the objectives of this study, which were to investigate fish PCB concentrations in three additional waterbodies in the Yadkin-Pee Dee system, High Rock Lake, Falls Reservoir and Lake Tillery and assess their associated human ingestion risks.

METHODS and MATERIALS

Fish Tissue Sampling and Analysis. Fish collected from four of the North Carolina reservoirs of the Yadkin-Pee Dee River were included in this study, High Rock Lake (2011), Badin Lake (2008), Falls Reservoir (2012) and Lake Tillery (2011) (Figure 1).[1]

Fish collections were focused near the end of the fish growing season in the late summer and fall when tissue PCB concentrations were expected to be at the highest level and represent the greatest potential human exposure concentration. Fish collections followed

standard N.C. Department of Environmental Quality (DEQ) protocols for the collection and preparation of freshwater fish for organic contaminant analyses.[3] The DEQ's fish collection and tissue preparation methods reference the U.S. Environmental Protection Agency (EPA) guidance for fish consumption advisory studies.[4] In High Rock Lake, Badin Lake, and Lake Tillery, three separate areas of each lake were selected for fish collections to identify potentially isolated populations that would presumably be reflective of conditions and uptake from that area. Falls Reservoir is a run-of-the-river waterbody and fish were collected throughout its length. Fish of each trophic guild (insectivores, omnivores and piscivores) and feeding habitat (bottom feeders, middle feeders and top predators) were collected per DEQ[3] and DHHS[4, 5] protocols for fish consumption advisory studies to represent all probable human exposure sources and contaminant levels. At each location, boat-mounted electrofishing effort was continued until the desired number of each species (5-15) was collected per the sampling plan. All fish were wrapped in food-grade aluminum foil and immediately placed on ice in a cooler until delivery the next day to DEQ's Water Sciences laboratory (Raleigh, N.C.) for tissue processing. At the laboratory, the fish were stored at -20 ºC until tissue preparation.

Sample Preparation. At the time of processing, the fish were confirmed to species, weighed (to the nearest 1 g) and measured for total length (to the nearest 1 mm). As per N.C. DHHS and N.C. DEQ protocols for risks associated with fish ingestion by humans, homogenized fish fillet samples were prepared for PCB analysis. Fillet tissue samples, rather than whole-body samples, are preferred to represent the most common consumption pattern for the typical N.C. fish consumer. Fillets were cut and homogenized as partially thawed fish

to minimize tissue degradation during processing. Fish fillet tissue for analysis was prepared from individual fillets, or as equal-weight composites of tissue from two to five fish of the same species. Fish combined in a composite were all within ±75% of length to ensure that fish of the same approximate age range were composited.

Tissue samples for analysis were of at least 100 g homogenized in pesticide-grade acetone solvent and organic-free water rinsed glass or stainless-steel grinders. The homogenized tissue samples were wrapped in food-grade aluminum foil and stored at -20 ^{o}C.[3] The tissue preparations were shipped frozen by overnight courier to the analytical laboratories. The Badin Lake fish tissue analyses were completed in the fall of 2008 by SGS Environmental Services, Wilmington, N.C. Analysis of the High Rock Lake, Lake Tillery and Falls Reservoir fish tissue samples were completed in November 2012 by the U.S. EPA Region 4 Science and Ecosystem Support Division (SESD), Analytical Support Branch laboratory located in Athens, GA. All data were directly reported to the N.C. DHHS DPH.

Tissue Analysis. Standard U.S. EPA analytical methods were used for extraction of tissue and for PCB analysis. All prescribed analytical method quality control and performance criteria were met for the PCB analyses. The homogenized tissue samples were extracted with methylene chloride following Method 3540C.[6] All tissue samples were analyzed by EPA Method 1668.[7] This method employs a high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS) system to detect all 209 of the possible PCB congeners. Dependent upon the specific instrument system, approximately 45 to 50 of the 209 PCB congeners are not resolved completely, as all individual congeners by Method 1668 are reported as 2 to 6 co-eluting congeners. The specific reported data points, as a

combination of single congeners and co-eluting congeners differed for the two laboratories, as influenced by the analytical system and conditions. One hundred and sixty-six data points were reported for the Badin Lake tissue samples (43 co-eluting congeners) and 159 data points were reported for the High Rock Lake, Lake Tillery and Falls Reservoir tissue samples (50 co-eluting congeners). The tissue PCB data were reported as ng PCB congener per kg wet weight fillet tissue (ng/kg ww). Fish tissue PCB data for risk analysis are commonly reported as wet weight tissue concentrations to provide relevance for public interpretation of fish consumption advisory recommendations. All method-specific quality control requirements for the tissue extraction and congener analytical methods were implemented and met the method-specified performance criteria. The congener data were utilized as reported from the laboratories for the human health risk assessment. Tissue percent lipids were determined gravimetrically following hexane extraction.[7]

Fish Tissue Data Evaluation for Public Health Ingestion Risk Analysis. Fish tissue PCB congener data analysis and consumption advisory risk calculations for the Yadkin-Pee Dee River were completed with standard spreadsheet software (Microsoft® Excel®). Tissue PCB data evaluation methods for fish consumption advisories followed N.C. DHHS 2007 protocols.[7] Individual tissue analytical sample data were calculated using all detected congeners. The individual tissue sample PCB data were quantified as total PCBs (the sum of all 209 detected congeners), total dioxin-like PCBs (the sum of PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169 and PCB-189) and total non-dioxin-like congeners. Total Toxicity Equivalency Quotient (∑TEQ) adjusted concentrations for the 12 dioxin-like-PCB congeners were calculated for each

sample by multiplying each dioxin-like congener ng/kg ww concentration by the congener-specific Toxicity Equivalency Factor and summing the adjusted values.[8] The congener-specific TEF values adjust the dioxin-like PCB congener concentrations to an 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) equivalent concentration. The TEF relates the individual dioxin-like congeners relative ability to induce the aryl hydrocarbon receptor (AhR) mediated toxicity pathway common to dioxin-like toxicants. 2,3,7,8-TCDD is the most toxic of the identified AhR-inducing toxicants and serves as the indexing chemical for AhR-mediated toxicity (2,3,7,8-TCDD TEF = 1.0)

Preliminary total PCB tissue data evaluations for the fish consumption advisory analysis included three methods of handling the not-detected (ND) congeners, as recommended by the U.S. EPA Region 4 SESD (personal communication, 2008). The three methods included (1) zero concentration contribution for not-detected congeners (ND = 0), (2) contribution at the congener-specific reporting limit (RL) concentration (ND = RL), and (3) at one-half the reporting limit concentration (ND = RL/2). The three ND-data handling methods resulted in identical identification of specific samples with total PCB concentrations exceeding the N.C. DHHS total PCB action level for fish consumption.[5] Subsequent fish tissue PCB data evaluations reported here use the ND = 0 treatment of the individual congener data reported as less-than values. All tissue PCB data are reported as ng PCB/kg wet weight tissue (ng/kg ww) unless otherwise indicated.

The North Carolina DHHS Fish Consumption Advisory Protocol. The N.C. DHHS fish ingestion risk assessment exposure parameters are protective of adult subsistence fishers that rely on fish tissue as their primary protein source (Table 1) and were calculated for a

daily life-long exposure to the specified species. The DHHS daily fillet ingestion rate was 0.170 grams (6 ounces) uncooked wet weight over a 70-year lifetime.[9] This ingestion rate was selected by DHHS and represented the 95th percentile Native American subsistence consumer. As recommended by U.S. EPA[4] (EPA 2000), a 0.5 "loss factor" was applied to the exposure estimates for lipophilic toxicants to adjust for contaminant loss during fish cleaning, fillet trimming, and cooking. The N.C. DHHS total PCB action level (AL) for consumption advisories was 0.050 mg/kg wet-weight tissue (50,000 ng/kg ww).[5] Decisions to issue consumption advisories are species and waterbody specific, and are evaluated as the average contaminant concentration in each species or as the proportion of samples of each species exceeding the total PCB action level. The total PCB action level was developed from the U.S. EPA Integrated Risk Information System (IRIS) cancer potency factor for oral exposures to "high risk and high persistence" PCBs [10] (Slope Factor Oral = 2.0 $(mg/kg\text{-}d)^{-1}$) and was calculated for a maximum 1.0E-04 Acceptable Risk Level (ARL) for lifetime increased cancer risks (1 additional cancer for 10,000 like-exposed persons). This level of increased lifetime cancer risk is the maximum level of cumulative cancer risk recommended by the U.S. EPA and Agency for Toxic Substances and Disease Registry (ATSDR) for environmental risk assessments.[11, 12] The EPA cancer slope factor for oral exposures is an IRIS value representing the upper bound of a linear extrapolation from a 1996 study using female Sprague-Dawley rats exposed to Aroclors 1260, 1254, 1242 and 1016, and male rats exposed to Aroclor 1260 that identified hepatic tumors as the sensitive endpoint.[13]

Fish fillet PCB exposure risks for each waterbody were evaluated as the species mean total PCB concentration, along with consideration of size or age-related toxicant

concentrations. DHHS fish consumption advisories for total PCBs are issued as a recommended maximum number of meals per week or per month calculated to be protective at the 1.0E-04 ARL.

Alternative Population Fish Consumption Advisory Analyses. The N.C. DHHS fish consumption advisory analysis used exposure parameters for a lifetime daily exposure for an adult body weight and ingestion rate throughout the exposure period. Alternative exposure parameters and consumer populations were selected to evaluate potential risks to other N.C.-specific populations associated with eating PCB-contaminated fish from the four Yadkin-Pee Dee waterbodies (Table 1). Additional consumption risk estimates for the alternative vulnerable N.C. receptor populations were calculated for the Yadkin-Pee Dee fish tissue data set using exposure parameters selected from the most recent EPA exposure factors survey (EPA 2011).[14] The alternative receptor scenarios used receptor population-specific updated body weights (BW), ingestion rates (IR), exposure frequencies and exposure durations. The EPA-recommended 0.5 trimming/cooking loss factor for lipophilic contaminants was retained for all calculations. Cancer risks were assessed at the DHHS 1.0E-04 cumulative excess lifetime cancer acceptable risk level (ARL), as well as the more health-protective 1.0E-05 and 1.0E-06 levels. The 1.0E-05 ARL is the level recommended by the EPA in their fish consumption advisory guidance, and the 1.0E-06 level is considered the *de minimis* population cancer risk level.[4]

Alternative receptor populations evaluated included children (“child”), non-subsistence adults (“adult coastal resident”), and a high ingestion rate immigrant population (“adult immigrant”). Total cancer risk estimates for the alternative receptor populations and the

default DHHS adult lifetime-exposure population were calculated as the sum of the TEQ-adjusted total dioxin-like congener risks using the EPA dioxin cancer potency factor (1.30E+05 $(mg/kg\text{-}d)^{-1}$) and the total non-dioxin-like congener risks using the "high persistence PCB" food chain cancer potency factor (2.0 $(mg/kg\text{-}d)^{-1}$). Additionally, tissue PCB concentrations were compared to the current U.S. Food and Drug Administration (FDA) PCB tolerance level for all fish (2.0 ppm ww or 2.0E+06 ng/kg PCBs in the edible portion; "all fish" refers to all freshwater or saltwater finfish and crustaceans).[2]

The scenario of an adult coastal resident 21 years of age and older with an ingestion rate of 62.13 grams per day of uncooked fillet (95^{th} percentile "usual fish consumption rates" total fish ingestion)[14] was selected to represent a high-end recreational consumer. The second alternative receptor scenario represented an adult immigrant population with an ingestion rate of 317.5 grams per day (identified as the 95^{th} percentile Laotian-ethnicity total fish ingestion rate).[14] The adult scenarios used an 80 kg BW as the combined male and female average, a 350-day per year exposure frequency, and a 26-year exposure duration.[10] The EPA identifies 26-years as 90^{th} percentile residential occupancy period for both sexes. The third alternative receptor was a child exposed from 1 to 6-years of age with an ingestion rate of 171 grams per day (the 95^{th} percentile total fish intake) and a 15 kg BW.[10, 14] This age range was chosen for the "child" exposure as it represents the highest exposure dose for all age groups.

Methods for the Statistical and PCB-Profile Characterization of Fish Tissue Data. Statistical analyses were completed using JMP® Pro 12.2 (2015 SAS Institute, Cary N.C.). Analysis of variance (ANOVA) with Levene equal variance verification was used to identify statistically significant differences in PCB concentrations. Welch's test to identify significant

differences was applied to data not meeting equal variance criteria. All significance levels were evaluated at alpha (α) = 0.05. Means differences were identified with the Tukey's Honestly Significant Difference (HSD) test (equal variance) or the Wilcoxon Method (un-equal variance non-parametric data).

Tissue sample characteristics and patterns of PCB distribution related to the waterbody, species, fish weight, fish length, trophic level, trophic guild and trophic status were investigated for the fillet tissue samples collected in the four waterbodies in 2008, 2011 and 2012 in the Yadkin-Pee Dee River. Because of the low numbers of most targeted species in specific waterbodies, data clustering of related species was used to increase the robustness of the statistical and non-statistical comparisons (Table 2). White Crappie (*Pomoxis annularis*) and Black Crappie (*Pomoxis nigromaculatus*) were combined as "crappie", Redear Sunfish (*Lepomis microlophus*) and Redbreast Sunfish (*Lepomis auritus*) were combined as "Sunfish", Yellow Perch (*Perca flavescens*) and White Perch (*Morone americana*) were combined as "Perch", and "Catfish" included all ictalurid species identified as bottom feeding trophic level 3 omnivores, and included Blue Catfish (*Ictalurus furcatus*), Brown Bullhead (*Ameiurus species*), Channel Catfish (*Ictalurus punctatus*), Flat Bullhead (*Ameiurus species*) and White Catfish (*Ameiurus catus*). Flathead Catfish were retained as a separate group for analysis as trophic level 4 top predator piscivores.

Fillet tissue homolog data were summarized as the sum of the combined 1, 2 and 3-chlorinated congeners (∑mono-tri-homologs), the combined 8, 9 and 10-chlorinated congeners (∑octa-deca-homologs), and the remainder as individual homologs (∑tetra, ∑penta, ∑hexa, and ∑hepta). The mean species concentrations by waterbody were evaluated

for homolog profile similarities as the wet-weight, lipid-normalized, and wet-weight-fractions.

RESULTS and DISCUSSION

NC DHHS Fish Consumption Advisories. Badin Lake fish fillet tissue data total PCB concentrations exceeded the N.C. DHHS Action Level (50,000 ng/kg total PCBs wet weight fillet tissue) in 4 tissue samples (2 of 2 Channel Catfish, 1 of 4 White Catfish, and 1 of 9 Largemouth Bass). In February 2009, DHHS issued a fish consumption advisory for catfish and largemouth bass in Badin Lake. In the 2011 and 2012 follow-up sampling, 3 tissue samples each from High Rock Lake, Lake Tillery and Falls Reservoir exceeded the DHHS total PCB action level (Table S1. Supplemental Information). The 2011-2012 PCB action level exceedances consisted of 50% of the catfish species samples (9 exceedances in 18 catfish samples), and all exceedances were in samples with a mean length >450 mm. The average combined catfish fillet total PCB concentrations for samples >450 mm was 55,000 ng/kg ww (standard deviation, SD = 32,000 ng/kg), and 20,000 ng/kg ww (SD = 10,000 ng/kg) for samples ≤450 mm. In May 2013, DHHS issued fish consumption advisories for High Rock Lake, Falls Reservoir, and Lake Tillery for catfish >450 mm in length. The High Rock Lake, Falls Reservoir, and Lake Tillery advisories recommended that women who were pregnant, nursing, or of childbearing age, or children younger than 15 years of age, not eat Largemouth Bass or catfish, and all other populations were recommended to not eat more than one meal per week of these fish.

Alternative Population Fish Ingestion Risks. The *de maximus* 1.0E-04 ARL was exceeded for 23% (30 exceedances/131 samples) of all tissue samples when determining risks associated with an adult daily life-time consumer using the DHHS default exposure parameters and the cancer slope factor risk calculation for dioxin-like and non-dioxin-like PCB concentrations, compared to 8% exceedances (11/131) using the DHHS total PCB action level. Using the more health-protective cancer ARLs, the DHHS exposure parameters and the cancer risk calculation method, 77% (101/131) and 98% (129/131) of the tissue samples exceeded the 1.0E-05 and the 1.0E-06 lifetime cancer risk levels, respectively (Table 3).

The number exceedances at the 1.0E-04 ARL for the alternative exposure scenarios, the adult coastal resident and immigrant consumers, as well as the child consumer, reflect the impact of the reduced exposure periods for these scenarios (Table 3). There were no exceedances at the 1.0E-04 ARL for the adult costal resident consumer, 11% exceedances (15/131) for the adult immigrant, and 6% (8/131) exceedances for the 1-6-year-old child consumer. The number of samples exceeding the more protective, and EPA-recommended 1.0E-05 ARL, increased substantially compared to the 1.0E-04 ARL *de maximus* risk level. Twenty-eight percent of the tissue samples (36/131) exceeded the 1.0E-05 ARL for the adult coastal resident consumer. The higher risk level for the adult immigrant consumer (70%, 92/131) reflects the increased ingestion rate for this group relative to the coastal resident adult. For the child consumer, 63% (83/131) of the tissue samples exceed the 1.0E-05 ARL, reflecting the higher ingestion rate per body weight (dose) for this age group. Seventy eight percent, 98% and 95% of the tissues exceeded the 1.0E-06 ARL *de minimis* risk level,

respectively for the adult coastal resident, adult immigrant and child consumers. Fillet tissues from few species did not exceed the 1.0E-06 ARL in each waterbody and were represented primarily by the Redear Sunfish, crappie, perch and Bluegill (Table S2). None of the fillet tissue samples in this data set exceeded the 2.0 mg/kg-wet weight as total PCBs U.S. FDA PCB Tolerance Level for all fish,[2] indicating that it may not provide adequate protection for typical North Carolina freshwater fish consumers. A non-weighted analysis was done to estimate the maximum number of consumer meals per year allowed to not exceed the cancer ARL levels (Table 3). Ingesting less than one meal per year was required to not exceed the 1.0E-06 ARL for the immigrant adult and the child consumers. Less than four meals per years were indicated for the adult coastal resident to not reach the 1.0E-06 ARL level. To not ingest a meal at the 1.0E-05 ARL-level, <47, <10 and <14 meals were indicated for the adult coastal resident, immigrant adult and the child consumer, respectively. The alternative populations analysis indicates that less-than-life-long daily consumers of fish from these waterbodies may have an elevated cancer risk when more health-protective criteria are considered.

Comparison of Ingestion Risks Between Waterbodies. Comparison of PCB profiles and associated human health risks were evaluated focusing on the Largemouth Bass and combined species groups represented by the catfish, sunfish and crappie. Total cancer risks were higher in Badin Lake for the catfish group, the Largemouth Bass, and the sunfish group, compared to the other waterbodies (Table 2). An increase in the proportion of fish that exceed the cancer risk threshold was evident when moving downstream from High Rock Lake to Badin Lake. For the alternative human receptor population risk estimates, ingesting

fish from Badin Lake presented a higher potential opportunity to be exposed to fish that exceeded the ≥1.0E-05 cancer risk level (Table 4).

The mean proportion of the total cancer risk attributed to the dl-PCBs for all species collected ranged from 0.12 to 0.84, with a combined mean of 0.31 (Table 5). Highly variable proportions of dl-PCB cancer risks were also evident when the selected species were compared between the waterbodies (Figure 2). These data suggest that generating human health risk estimates associated with ingesting fish based solely on the dioxin-like-associated risks may substantially underestimate the potential risks for all congeners. In Badin Lake fish, the proportion of the total cancer risk associated with dl-PCB congeners in the Largemouth Bass, and the catfish and sunfish groups, was greater than in the other waterbodies. In the crappie group, the greatest proportion of dl-PCB cancer risk was observed in the Lake Tillery fish. The relative level of total risk and dioxin-like-specific risk may have been influenced by the lack of crappie collections from Falls Reservoir, and only 2 individuals being collected from Badin Lake. Evaluated as the waterbody mean proportion of total risk attributed to dl-PCBs, Badin Lake fish had the highest proportion for the Largemouth Bass, and the catfish and sunfish groups. Only in the Lake Tillery crappie group was the highest proportion of dl-PCB risk not observed in the Badin Lake fish. The crappie data may reflect the influence of only two samples from Badin Lake, compared to eleven from High Rock Lake and eight from Lake Tillery. The Badin Lake crappie were also smaller (as mean length and mean weight) relative to the crappie from the other two waterbodies. The greater proportion of total PCB and dl-PCB risks associated with Badin Lake fish were likely reflective of the documented historical industrial PCB inputs to this

waterbody, and may indicate a continued source of PCB inputs from contaminated aquatic sediments or adjacent terrestrial soils, or reflect the legacy PCB contamination captured in the aquatic food web of Badin Lake.

Fish Tissue PCB-Profile and Statistical Analysis Comparisons. Tissue PCB concentrations as ∑PCBs, ∑dl-PCBs and ∑dl-PCB-TEQ for the four species groupings (Largemouth Bass, catfish, crappies, and sunfish) were not correlated with tissue percent lipid (R^2 all ≤ 0.25). Percent lipid did not correlate with fish length ($R^2 = 0.31$) or weight ($R^2 = 0.23$). The ∑dl-PCB and ∑ndl-PCB for all combined tissue samples were moderately correlated with fish length ($R^2 = 0.46$, $R^2 = 0.65$, respectively). The lipid-normalized ∑dl-PCB (∑dl-PCB-lipid) were strongly correlated with ∑ndl-PCB-lipid ($R^2 = 0.88$) and ∑PCB-lipid ($R^2 = 0.93$).

Trophic Guild Comparisons. The pattern of mean percent lipid (% lipid) for all tissue samples, combined by trophic guild, was omnivores > piscivores > insectivores. The same relationship held for guild comparisons as ∑PCBs, ∑dl-PCBs and ∑dl-PCB-TEQs, and as the lipid-normalized tissue concentrations ∑PCB-lipid, ∑dl-PCB-lipid and ∑dl-PCB-lipid-TEQs (Table 6).

No statistical differences in trophic guild ∑PCBs and ∑PCB-lipids were detected when compared among the four waterbodies (all $p \geq 0.057$), or in the insectivore and omnivore ∑dl-PCB-lipids by waterbody (all $p \geq 0.55$). Lake Tillery piscivore ∑dl-PCB-lipid were significantly lower compared to the other waterbodies ($p = 0.038$). The Badin Lake omnivore and piscivore ∑dl-PCB-lipid-TEQs were significantly higher than concentrations in the other

waterbodies (all $p \leq 0.019$). There were no differences detected in ∑dl-PCB-lipid-TEQs in the insectivores ($p = 0.44$) (Table 7).

Species Comparisons. The highest mean ∑PCBs, ∑dl-PCBs, ∑PCB-lipids and ∑dl-PCB-lipids for all samples included in the DHHS fish consumption advisory analysis and combined by species were observed in the two Flathead Catfish samples, both samples consisting of a single fish (1 each in High Rock Lake and Lake Tillery). The Flathead Catfish also had the highest mean % lipid of all species or species group. The catfish group (43 total samples), which included all catfish species other than the Flathead Catfish, had the highest mean ∑dl-PCB-TEQs and ∑dl-PCB-lipid-TEQs (Table 8).

Mean species PCB concentrations by waterbody (Table 9) were $\log_{10}$-transformed and compared among the four waterbodies to identify statistically significant differences in the Largemouth Bass, and the catfish, crappie and sunfish groups.

Largemouth Bass in Falls Reservoir had the highest ∑PCB of the four waterbodies (Falls Reservoir (FR) > Badin Lake (BL) > Lake Tillery (LT) > High Rock Lake (HR)). As ∑PCB-lipid, the highest concentrations were in Badin Lake (BL > HR > FR > LT). No differences were detected in Largemouth Bass ∑PCBs, ∑PCB-lipid, or ∑dl-PCB-lipid among the four waterbodies (all $p \geq 0.21$). The Badin Lake Largemouth Bass had significantly greater ∑dl-PCB-lipid-TEQ, compared to the Largemouth Bass in the other three waterbodies ($p = 0.0007$).

In the catfish group, the highest ∑PCB was observed in Falls Reservoir (rank order FR > BL > HR > LT), and the highest ∑PCB-lipid in High Rock Lake (rank was HR > BL > LT > FR). There were no differences detected in the catfish group ∑PCB, ∑PCB-lipid, or ∑dl-

PCB-lipid in any of the four waterbodies (all $p \geq 0.49$). Differences in catfish ∑dl-PCB-lipid-TEQ were identified, with the Badin Lake concentrations statistically higher than each of the other three waterbodies ($p = 0.0003$).

The sunfish group (13 total samples) had significant differences among waterbodies for all PCB evaluations (∑PCB, ∑PCB-lipid, ∑dl-PCB-lipid and ∑dl-PCB-lipid-TEQ). The Badin Lake sunfish had significantly greater ∑dl-PCB-lipid-TEQ compared to sunfish in the other three waterbodies ($p = 0.0007$). The Badin Lake sunfish ∑PCB-lipid ($p = 0.0096$) and ∑dl-PCB-lipid ($p = 0.012$) were significantly greater than those in the Lake Tillery sunfish, and the Lake Tillery ∑dl-PCBs were significantly less than those in the other waterbodies ($p = 0.0099$).

The crappie group (21 total samples) did not differ in the ∑PCB, ∑dl-PCB or ∑dl-PCB-TEQ-lipid concentrations in the three lakes where crappie were collected (High Rock Lake, Badin Lake and Lake Tillery, all $p \geq 0.21$). Crappie ∑PCB-lipid and ∑dl-PCB-lipid concentrations in High Rock Lake were the highest of the three waterbodies and were significantly greater than Lake Tillery concentrations ($p \leq 0.016$). There was not a statistical difference in the crappie ∑PCB-lipid and ∑dl-PCB-lipid for Badin Lake compared to High Rock Lake or Lake Tillery (all $p \geq 0.28$). The crappie ∑PCB concentrations in each waterbody were less than ∑PCB concentrations in the Largemouth Bass, catfish and sunfish. Crappie PCB concentrations less than the sunfish in the other two waterbodies was unexpected. The piscivore crappie would be expected to have a higher potential exposure to PCBs biomagnifying in the food-web, than the anticipated exposure to the insectivore sunfish. The crappie ∑PCB-lipid concentrations in High Rock Lake and Lake Tillery were

higher than the sunfish concentrations in the respective lakes, and in Badin Lake, the crappie ∑PCB-lipid concentration was less than the sunfish concentration.

Species Homolog Profile Characterization. The Largemouth Bass wet-weight, lipid-normalized and weight-fraction PCB homolog profiles were similar among the four waterbodies (Table 9, Figures 3-5). The hexa-homologs dominated, followed by the penta-homologs. Generally, the relative homolog concentrations were: hexa > penta > hepta ≈ tetra > octa-deca > mono-tri. This pattern was consistent in the Largemouth Bass among the three more upstream waterbodies (High Rock Lake, Badin Lake and Lake Tillery). The pattern deviated somewhat in Lake Tillery Largemouth Bass, with similar concentrations of the hexa and penta homologs, and tetra and hepta homologs, followed by the octa-deca and mono-tri homologs (hexa ≈ penta > tetra ≈ hepta > octa-deca > mono-tri).

Statistical analysis of $\log_{10}$-normalized Largemouth Bass homolog data indicated no difference in the tetra, penta, hepta or octa-deca homolog concentrations, compared among the four waterbodies (all $p \geq 0.17$). The Badin Lake Largemouth Bass mono-tri homolog concentrations were significantly greater than the concentrations in High Rock Lake Largemouth Bass ($p = 0.018$). Significantly greater concentrations of the lipid-normalized mono-tri-homologs were present in the High Rock Lake Largemouth Bass compared to those in Lake Tillery ($p = 0.036$), and the Badin Lake concentrations were significantly greater than those in Falls Reservoir ($p = 0.011$) and Lake Tillery ($p = 0.0003$). The Badin Lake hexa-homolog lipid-normalized Largemouth Bass concentrations were also significantly greater than those in Lake Tillery ($p = 0.025$).

The catfish group wet-weight and weight-fraction homolog profiles were similar to those of the Largemouth Bass (Table 9, Figures 3-5). The lipid-normalized homolog profiles were similar to the Largemouth Bass in the three more downstream waterbodies. In High Rock Lake catfish, the lipid-normalized hexa-homolog group dominated, followed by approximately equal concentrations of the hepta and octa-deca-homologs. The mono-penta homologs were present in much reduced proportions.

The only significant difference in catfish wet-weight homolog concentrations were the greater mono-tri-homologs concentrations in Falls Reservoir compared to High Rock Lake ($p = 0.024$). Significant differences in catfish group homolog weight-fraction concentrations among waterbodies were indicated in all but the hexa-homologs ($p = 0.45$). The Badin Lake weight-fraction homolog concentrations were significantly greater than High Rock Lake catfish concentrations for the mono-tri, tetra, hepta and octa-deca groups; and, were significantly greater than Lake Tillery catfish concentrations for the mono-tri, hepta and octa-deca groups (all $p \leq 0.033$). There were no differences in weight-fraction concentrations in Badin Lake and Falls Reservoir, or High Rock Lake and Lake Tillery catfish (all $p \geq 0.058$). Falls Reservoir catfish homolog weight-fraction concentrations were significantly greater than the High Rock Lake catfish for all except the hexa group (all $p \leq 0.023$). The Falls Reservoir catfish mono-tri weight-fraction was significantly increased relative to the Lake Tillery catfish ($p = 0.0093$).

As lipid-normalized data, there were no differences in the penta-deca homologs in the catfish among the four waterbodies (all $p \geq 0.29$). Badin Lake lipid-normalized mono-tri concentrations were significantly greater from those in Falls Reservoir and Lake Tillery

catfish (all $p \leq 0.019$); and, were significantly greater than High Rock Lake concentrations for the tetra group ($p = 0.0076$). Catfish lipid-normalized mono-tri homolog concentrations were significantly increased in Lake Tillery compared to the Falls Reservoir ($p = 0.043$), and Falls Reservoir tetra-homologs were significantly increased compared to High Rock Lake catfish ($p = 0.0098$).

The wet-weight homolog patterns for the sunfish group among the four waterbodies were similar to those of the Largemouth Bass and the catfish group (Table 9, Figures 3-5). The wet-weight concentration pattern of hexa > penta > hepta > tetra > octa-deca > mono-tri was consistent in all waterbodies except Badin Lake, where the pattern was hexa > penta > tetra > hepta > mono-tri > octa-deca. The sunfish lipid-normalized homolog relative concentration patterns were more variable among the four waterbodies than was observed in the Largemouth Bass and catfish. This may be related to trophic level position, feeding regime and habitat utilization influences on PCB exposure and bioaccumulation characteristics. High Rock Lake and Falls Reservoir sunfish had similar lipid-normalized homolog concentration patterns (hexa > penta > hepta > tetra ≈ mono-tri ≈ octa-deca) with a different pattern apparent in the Badin Lake sunfish (hexa > penta > tetra > hepta > mono-tri > octa-deca). Lipid-normalized homolog concentrations in Lake Tillery were lower than those in the other waterbodies, with approximately equal concentrations for all Lake Tillery homolog groups except the tetra group, which was an order-of-magnitude lower than the other homologs.

There were no significant differences in Badin Lake and High Rock Lake sunfish wet-weight homolog concentrations. The Badin Lake sunfish mono-tri homolog wet-weight concentration was significantly greater than Falls Reservoir ($p = 0.0005$) and the Lake Tillery

concentrations ($p = 0.0001$). High Rock sunfish wet-weight mono-tri, penta, and hexa homolog concentrations were statistically increased relative to Lake Tillery sunfish (all p $\leq$0.033). No differences in sunfish weight-fraction homolog concentrations were indicated for the tetra, hexa and hepta homologs (all $p \geq 0.083$). Badin Lake weight-fraction concentrations for the mono-tri homolog group were significantly greater than mono-tri concentrations in the other three waterbodies ($p = 0.0017$). The High Rock Lake and Lake Tillery sunfish octa-deca weight-fractions were both significantly greater than in Badin Lake (all $p \leq 0.012$), and High Rock Lake and Lake Tillery concentrations were significantly increased compared to Falls Reservoir sunfish (all $p \leq 0.021$). The Falls Reservoir sunfish penta-homolog weight-fraction was significantly increased compared to Lake Tillery ($p = 0.043$). As lipid-normalized homolog data, there were no differences in the sunfish concentrations for the mono-tri and octa-deca-homologs (all $p \geq 0.23$). Badin Lake lipid-normalized sunfish concentrations were significantly greater than those in the Lake Tillery sunfish for the tetra-hepta-homologs (all $p \leq 0.041$), and the High Rock Lake lipid-normalized penta-homolog were also significantly increased compared to those in Lake Tillery sunfish ($p = 0.043$).

Wet-weight and lipid-normalized crappie homolog profiles among the three waterbodies were each unique (Table 9, Figures 3-5). In High Rock Lake, the tetra-hexa groups dominated (penta ≈ hexa > tetra > hepta > octa-deca ≈ mono-tri). In Badin Lake, the profile was similar to that observed in the other Badin Lake species (hexa > penta > tetra > hepta > mono-tri ≈ octa-deca). The Lake Tillery crappie wet-weight homolog profile was similar to that of the Lake Tillery catfish. The crappie lipid-normalized homolog profile in High Rock

Lake was dominated by the tetra-hexa and the mono-tri homologs (tetra > penta > hexa > mono-tri > hepta > octa-deca). The lipid-normalized homolog concentrations in the Badin Lake and Lake Tillery crappie were much lower than those of High Rock Lake. In Badin Lake, the mono-tri group concentration was exceeded only by the hexa-homolog (hexa > mono-tri ≈ penta > tetra > hepta > octa-deca). In Lake Tillery crappie, the homolog pattern was similar to the other species (penta > tetra ≈ hexa > mono-tri > hepta ≈ octa-deca), although as mentioned, the concentrations were quite low.

No significant differences in crappie wet-weight homolog concentrations were indicated among the three waterbodies (all $p \geq 0.065$). The crappie ∑PCB-lipid data indicated significantly greater concentrations in High Rock Lake compared to Lake Tillery, for all homolog groups (all $p \leq 0.040$). All other crappie homolog ∑PCB-lipid comparisons were not significant (all $p \geq 0.011$), although the *p*-value for the Badin Lake and Lake Tillery mono-tri group comparison was $p = 0.050$, and the Badin Lake concentration was more than 4 times that of the Lake Tillery crappie.

Comparison of Fish Tissue 209-PCB Profiles to Native Aroclor Profiles. The fish tissue lipid-normalized 209-congener and homolog profiles for the Largemouth Bass and the catfish, sunfish and crappie groups, in the four waterbodies were compared to native Aroclor 209-congener (Figure 6) and homolog profiles (Figure 7) for evidence of tissue PCB-burden attribution. Native Aroclor profiles, as co-eluting congener weight fractions, were prepared for the comparisons to replicate the laboratory-reported co-eluting congeners for the fish tissue profiles. (Native Aroclor congener profiles are presented in Table S3 and Native Aroclor environmental variables in Table S4.)

Largemouth Bass lipid-normalized congener profiles were relatively consistent in High Rock Lake, Badin Lake and Falls Reservoir, and most closely resembled weathered contributions of Aroclors 1254 and 1260 (Figure 8). The Largemouth Bass Lake Tillery profile have a stronger contribution of tetra and penta congeners and may reflect a higher proportional contribution, or a less weathered contribution, attributed to Aroclor 1254. The most prevalent lipid-normalized peaks in the Largemouth Bass tissues for all four waterbodies were the co-eluting PCB-153+168 peak, followed by PCB-129+138+160+163. These combinations of peaks are more prevalent in Aroclor 1260 than in Aroclor 1254. PCB-187 is a significant peak in Aroclor 1260 and is also prevalent in the Largemouth Bass in all four waterbodies. PCB-153 has been noted to preferentially bioaccumulate in fish.[15]

The Largemouth Bass in Badin Lake had a higher proportion of the more hydrophilic lower chlorinated mono-tetra congeners compared to Largemouth Bass in the other three waterbodies (Figure 4). This may indicate a continued source of lower chlorinated PCBs to the Badin Lake aquatic ecosystem relative to inputs to the other three waterbodies. Aroclor PCB analyses of Badin Lake sediments collected in multiple sampling efforts taking place from 2007 through 2011 reported PCB detections identified as Aroclors 1242, 1248, 1254 and 1260.[16]

The catfish group lipid-normalized 209-congener profiles were more similar in the three downstream waterbodies (Figure 9). In High Rock Lake, the most upstream waterbody, a higher proportion of heavier congeners were present (≥6 chlorines) relative to the other waterbodies (Figure 4). The higher proportion of the lower chlorinated congeners in Badin Lake, Falls Reservoir and Lake Tillery may indicate a continuing input source to these

waterbodies. As in the Largemouth Bass, congeners PCB-153+168 and PCB-129+138+160+163 were the most prevalent peaks in the catfish group in three of the four waterbodies. In the Lake Tillery catfish, the 5-chlorine congener PCB-118 was the second most prevalent peak, followed by PCB-129+138+160+163. The 209-congener profile in High Rock Lake most resembled Aroclor 1260, while the other three water body mean lipid-normalized catfish profiles most resembled combined contributions of a weathered Aroclor 1254 and Aroclor 1260. The Aroclor 1254 contribution is supported by the strong PCB-61+70+74+76 signals in the three downstream waterbodies. This co-eluting group is a minor component in Aroclor 1260 (0.09 weight proportion) and comprises 6.7% of native Aroclor 1254.

The lipid-normalized 209-congener profiles in the sunfish compared among the four waterbodies were more variable than were the profiles for the Largemouth Bass and catfish (Figure 10.). The sunfish group 209-congener profile in the Badin Lake fish had a higher proportion of the lesser chlorinated congeners (1-4-chlorine homologs) compared to the sunfish in the other three waterbodies, which had only minimal detections of the 1-4-chlorine congeners (Figure 4). Badin Lake sunfish also had much higher total lipid-normalized PCB concentrations compared to the other waterbodies.

As in the other species, the dominant lipid-normalized peaks in the sunfish in all four waterbodies were PCB-153+168 and PCB-129+138+160+163. The sunfish congener profile for Badin Lake suggests a contribution of Aroclor 1242 as the probable source of the elevated 1-4-chlorine congeners. In addition, the average PCB-11 lipid-normalized concentration in the Badin Lake sunfish was 8.5 ng/g-lipid. The 2-chlorine PCB-11 was not

detected in sunfish in the other waterbodies. Aroclor 1221 is the only native Aroclor reported to include PCB-11 (0.16%). PCB-11 is most commonly associated with pigments, formed as a major unintentional byproduct of their production (Table S3). It has also been documented in consumer products, including papers, inks, cardboard. The global atmospheric distribution of PCB-11 is well documented, with the highest concentrations generally associated with industrialized and urban areas.[16]

The crappie group was collected in three of the four waterbodies (none were collected in Falls Reservoir). Crappie are a trophic level 3 piscivore identified as inhabiting the middle trophic status in the Yadkin-Pee Dee River system. Comparing the congener profile patterns of the crappie to the insectivorous sunfish provided insight into the potential influence of differing food sources (Figure 11). In all three waterbodies, the crappie lipid-normalized PCB concentrations were higher than the sunfish, as would be expected due to food chain biomagnification. It would also be expected that the homolog profile of the crappie would reflect a higher proportion of the more lipophilic and persistent higher homologs (≥6 chlorines), and a lesser proportion of the more hydrophilic and mobile lower-chlorinated homologs, assuming the primary exposure was associated with the food web exposures. Yet, the 7-10 chlorine homologs constituted only 10-15% of the total lipid-normalized PCB-burden in the crappie, and 15-25% in the sunfish among the four waterbodies (Figure 4). This too may indicate an apparent discharge of lower-chlorinated homolog PCBs to these waterbodies that then enter the aquatic food web through exposures to the insectivorous species that serve as prey for piscivores species. The sunfish higher lipid-weight PCB concentrations may be a result of a diet dominated by phytoplankton. Primary producers,

including phytoplankton, because of their large surface area and high organic carbon content, represent a key pathway for hydrophobic organic chemicals to gain access into aquatic food webs,[17, 18] and are able to bioconcentrate hydrophobic organic substances orders of magnitude higher than in the water column dissolved phase. Additionally, preferential algal bioconcentration of the lower chlorinated PCB congeners has been reported for congeners with log K_{ow} values ≤6.5 (the 1-5 chlorine congeners). and suggested that the slower uptake kinetics of the congeners with log K_{ow} values >6.5 was related to their larger molecular size inhibiting their ability to cross the algal membrane.[17] We also suggest that the sunfish may have bioconcentrated a higher proportion of their total PCB burden through direct gill absorption of the more hydrophilic lower chlorinated congeners, as compared to the combined gill absorption to food web-associated uptake in the crappie.

Tissue PCB Attribution. Mean Largemouth Bass lengths were similar among the four waterbodies, while more variability was seen in the mean weight and % lipid measurements. Both the mean weight and % lipid were significantly higher in the Falls Reservoir Largemouth Bass population relative to those of the other 3 waterbodies. Length has been used as an estimator of fish age, while increasing organism weight and % lipid provide an indication the amount of energy available for feeding, as it relates to an inverse relationship of prey availability and capture efficiency.[19, 20] The Largemouth Bass lipid-normalized penta-deca-chlorinated homolog patterns were inversely related to the % lipid values when compared among the four waterbodies, possibly indicating an increased rate of growth dilution of the more recalcitrant and lipophilic congeners, out-pacing their relative bioaccumulation rate in the individual waterbodies.[19, 20] Additionally, an increased

bioaccumulation rate of the tetra-hepta-homologs was indicated in Badin Lake, relative to both the upstream and two downstream waterbody populations, potentially indicating an on-going source of PCB influx to Badin Lake.

On a lipid-normalized basis, there was more dissimilarity in the catfish homolog-patterns among the four waterbodies than was observed for the Largemouth Bass. The mean fish length for the catfish group was also similar among the four waterbodies, with the mean weight of the Falls Reservoir catfish being nearly four times that in the next highest waterbody. The Falls Reservoir catfish also had the highest % lipid values, yet the lipid-normalized tissue concentrations were lower for all homolog groups in the Falls Reservoir catfish, likely an indication of growth dilution. The mean % lipid in the Badin Lake catfish was 67% of the next lowest value. The lipid-normalized hexa-deca homolog concentrations were much higher in the High Rock Lake catfish, the most upstream waterbody included in this study, and the relative concentrations of the hepta-deca homologs were elevated relative to the other three waterbodies. This may indicate a continuing source of exposure of the bottom-feeding catfish to these more lipophilic homologs in High Rock Lake. The more lipophilic hexa-deca homologs (6-10 chlorines) are expected to be less mobile and less susceptible to biotic or abiotic degradation relative to the lesser-chlorinated homologs.[19, 21] The lipid-normalized hexa-deca homolog concentrations in the High Rock Lake catfish were also approximately twice concentrations in the Largemouth Bass in the same waterbody, likely indicating a habitat or food web influence on exposure and uptake leading to the species concentration differences.[15, 20-22] The lipid-normalized homolog concentrations in the Badin Lake catfish were elevated relative to the downstream Falls Reservoir and Lake Tillery

catfish populations, again potentially indicating a continuing source, or elevated residual exposure source, in the Badin Lake sediments relative to the downstream waterbodies. The continuing PCB source in Badin Lake could be associated with releases from PCB-contaminated aquatic sediments, or run-off from adjacent terrestrial soils.

There was less mean length variability among the waterbody sunfish populations than observed in the Largemouth Bass and the catfish. Sunfish mean weight and % lipid values varied over the waterbodies by a factor of 2. Badin Lake sunfish had the lowest % lipid, which was approximately one-half of the Lake Tillery sunfish mean % lipid, which were the highest of the four waterbodies. High Rock Lake sunfish had the lowest mean weight, and the Lake Tillery sunfish had the highest mean weight, at approximately twice the High Rock Lake value. The sunfish homolog patterns and concentrations on a weight-fraction basis were similar among the four waterbodies. Waterbody comparisons for sunfish lipid-normalized homolog patterns revealed that all homologs were elevated in Badin Lake relative to the other waterbodies. There were higher concentrations of the combined mono-tetra homologs in the Badin Lake sunfish compared to the other waterbodies on both a wet-weight and lipid-normalized basis. Sunfish are middle trophic status insectivores[3] and their higher homolog concentrations in Badin Lake likely indicate a continuing source of exposure to the more hydrophilic, lesser chlorinated congeners (≤4-chlorine homologs). The elevated concentrations of the lesser chlorinated congeners in Badin Lake sunfish likely represent a continued elevated local release of these more hydrophilic and more mobile congeners into Badin Lake.[23] The sunfish feeding strategy focused on water column zooplankton prey[24] may

also predispose them to a PCB exposure regime dominated by the more hydrophilic congeners.

Crappie were collected in three of the four waterbodies during this study, with none collected in Falls Reservoir. The Badin Lake crappie were smaller and had a lower mean % lipid than those in High Rock Lake and Lake Tillery. The Lake Tillery crappie had a mean % lipid more than three times the crappie in the other two waterbodies, they were the heaviest, and they had the lowest lipid-normalized homolog concentrations (crappie ∑PCB-lipid: High Rock Lake > Badin Lake > Lake Tillery). The combined mono-tetra homologs made-up 50% of the High Rock Lake crappie ∑PCB-lipid burden, compared to 32-35% in the Badin Lake and Lake Tillery crappie.

The piscivorous crappie and insectivorous sunfish are both trophic level-3 species.[3] The % lipid levels in the High Rock Lake and Badin Lake sunfish populations were approximately twice that of the crappie populations in those lakes. In Lake Tillery, the sunfish mean % lipid was approximately 10% less than that of the crappie population. The differences in feeding regimes for the piscivores and insectivores[24] would be expected to lead to higher piscivores concentrations of ∑PCB-lipid in the same waterbody, and to a higher proportion of the more lipophilic hepta-deca-homologs in the piscivores.[19] Yet, in the High Rock Lake populations, the proportion of sunfish hepta-deca-homologs was more than twice that in the crappie, and the proportion of these homologs in the Lake Tillery sunfish were increased approximately 25% over the proportion in the crappie. In Badin Lake sunfish and crappie populations, the hepta-deca-homolog proportions were similar for both fish. These data may indicate that the High Rock Lake and Lake Tillery crappie were subsisting on a diet

more dependent upon planktonic crustaceans than on smaller fish. It may also indicate that the sunfish were feeding on benthic organisms in contact with PCB-contaminated sediments that serve as a continuing food web source of the more lipophilic, higher-chlorinated congeners. Of the four waterbodies in this study, Badin Lake sunfish had substantially higher ∑PCB-lipid concentrations, which may be a result of the known history of sediment PCB contamination in this waterbody. The lower ∑PCB-lipid burden in Badin Lake crappie relative to the sunfish also suggest a preferential diet of benthic zooplankton for the sunfish and planktonic zooplankton for the crappie.

The top piscivorous predator Largemouth Bass had higher concentrations of lipid-normalized homologs than did the piscivorous crappie. This would be explained by the larger size, longer life-span, higher mean % tissue lipid,[15, 19, 20, 22] and the higher trophic level status of the Largemouth Bass, all leading to increased bioaccumulation and biomagnification of PCBs, and particularly a higher proportion of the more lipophilic congeners (≥6 chlorine homologs).

Implications for the Future of Environmental Risk Assessment. This study found that the lipid-associated dioxin-like-TEQ proportions are greater in Badin Lake Largemouth Bass, catfish and sunfish relative to the other waterbodies studied, and represent an increased cancer exposure risk associated with the human ingestion of Badin Lake fish. This study also indicates the possibility of a continued and unique PCB source pattern to fish in Badin Lake.

By evaluating the relative PCB profiles among selected species or species groups representing different trophic guilds and feeding regimes in the four waterbodies, unique congeners profiles were identified. These PCB profiles represent unique bioaccumulation and

biomagnification patterns, and likely differing exposure patterns, associated with species-related feeding and habitat utilization strategies. Unidentified waterbody-specific habitat features, such as the adsorptive capacity of sediments, may also have influenced localized exposure and bioavailability characteristics.

This research also supports the need to consider all species and trophic structures of potential exposure in both human health and ecological risk assessments for PCBs. It contributes to the endorsement of 209-congener PCB analyses to provide accurate qualitative and quantitative characterization of environmental PCB burdens in abiotic and biotic compartments. The variations in PCB-burden and associated toxicity estimates observed in the food web components investigated in this study have implications for future human health and ecological risk assessments. Risk assessments that may propose to use indicator species, rather than evaluating all trophic levels that may be relevant ingestion sources, or considering all PCB congeners and their associated risks, may lead to unidentified or underestimated risks. This study found that consistently in the different species, trophic guilds and waterbodies within a connected river system, the tissue mass and the proportion of the total cancer risk associated with the 12 dioxin-like congeners did not represent the major portion of the fillet tissue PCB-burden or associated cancer risk estimates. This has important implications for human health risk assessments that focus only on the 12 dioxin-like congeners, or other congeners sub-sets that may not represent the major portion of the total PCB toxicity. With the advent of the USEPA Method 1668 and equivalent analytical methods, there exists a capability to specifically identify and quantify all 209 PCB congeners in a variety of environmental matrices at sensitivity levels adequate for human and ecological

risk assessment. This study supports the application of, and the need for, the full 209-PCB congener analysis to provide appropriate characterization of potential human health and ecological risks associated with PCBs in environmental matrices.

There is more than adequate evidence that the source of PCBs released to the environment, whether that source is a relatively unchanged commercial Aroclor mixtures, or is released as a modified PCB-profile, will undergo continued modification in the environment under the influences of temporal and spatial characteristics that cannot be generalized adequately to provide accurate risk estimates. We recommend that regulatory agencies provide stronger impetus to consider the proper limitations of the “Aroclor method” (USEPA Method 8082), which relies on pattern matching native Aroclor analytical standards for source identification and risk quantitation of weathered PCB profiles in environmental matrices, particularly when the data are to be used for human health and ecological risk assessments. At this juncture of analytical and risk assessment science, USEPA Method 8082 Aroclor-reporting analysis should only be used as a “field screening tool” for rapid-turnaround PCB-burden delineation, with final confirmation of potential environmental risk acquired with 209-congener methods. Even this limited application of the “Aroclor” Method 8082 requires careful consideration and an understanding of how local source and environmental matrix influences may affect correlation of Aroclor and congener-specific patterns.

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TABLES

Table 1. The default N.C. DHHS fish consumption advisory exposure parameters and exposure parameters selected for the alternative receptor population ingestion risk estimates.

Fish consumption risk exposure parameters	DHHS Subsistence Adult, Action Level	DHHS Subsistence Adult, Cancer	EPA 95th% Adult Coastal Resident	EPA 95th% Immigrant Adult	EPA 95th% Child	U.S. FDA Tolerance Level
Body weight, kg	70	70	80	80	15	-----
Lifetime, years	70	70	70	70	70	-----
Ingestion rate, kg/day	0.170	0.170	0.06213	0.3175	0.1719	-----
Loss factor, PCBs [a]	0.5	0.5	0.5	0.5	0.5	-----
Number days per year exposure	365	365	350	350	350	-----
Number years of exposure	70	70	26	26	6	-----
Number of fish meals per day	1	1	1	1	1	-----
N.C. DHHS total PCBs action level (2007), mg/kg ww	0.050	-----	-----	-----	-----	-----
U.S. FDA Tolerance Level, mg/kg ww [b]						2.0
Cancer potency factor, as $(mg/kg\text{-}d)^{-1}$						
Dioxin-like PCBs	-----		1.3E+05			
Non-dioxin-like PCBs	-----		2.0			

[a] Loss factor = proportion of PCB concentration loss attributed to trimming during fillet preparation and cooking

[b] As PCBs in edible portion of all fish

Table 2. PCB-burden and cancer risk summary for selected fish species. (ww = wet weight, dl = dioxin-like)

				ng/kg ww					
Species	Waterbody	No. Samples	% Lipid	Total PCBs	dl-PCBs	dl-PCB-TEQ	Wt. Proportion dl-PCB-TEQ	Total Cancer Risk	Proportion dl-PCB Cancer Risk
Catfish	High Rock Lk	12	3.28	33,375	2,617	0.1478	0.0875	9.8E-05	0.193
	Badin Lk	10	1.57	35,434	2,884	0.7727	0.0822	2.0E-04	0.609
	Falls Res	5	3.94	42,342	3,704	0.1132	0.0898	1.1E-04	0.164
	Lk Tillery	16	2.34	30,444	3,800	0.1918	0.1018	9.5E-05	0.211
Crappie	High Rock Lk	11	0.45	3,752	257.9	0.0084	0.0702	9.8E-06	0.138
	Badin Lk	2	0.38	1,861	103.4	0.0033	0.0560	4.8E-06	0.108
	Lk Tillery	8	1.50	2,761	244.9	0.0690	0.0896	1.7E-05	0.343
Largemouth Bass	High Rock Lk	12	0.78	13,487	962.0	0.0820	0.0741	4.3E-05	0.187
	Badin Lk	9	0.66	19,705	1,253	0.4488	0.0648	1.2E-04	0.633
	Falls Res	4	1.20	26,522	2,233	0.0685	0.0865	7.0E-05	0.159
	Lk Tillery	13	1.34	17,494	1,598	0.3095	0.0800	8.7E-05	0.417
Sunfish	High Rock Lk	3	0.80	6,854	585.7	0.0179	0.0935	1.8E-05	0.169
	Badin Lk	4	0.61	8,960	715.9	0.1577	0.0793	4.5E-05	0.492
	Falls Res	4	0.88	3,664	474.0	0.0145	0.1324	1.0E-05	0.234
	Lk Tillery	2	1.20	1,219	117.3	0.0036	0.0975	3.2E-06	0.178

Table 3. Summary of fish consumption advisory results for the default DHHS method and the alternative receptor analyses. ARL = Acceptable Risk Level (cancer).

Fish consumption risk exposure parameters	DHHS Subsistence Adult, Action Level	DHHS Subsistence Adult, Cancer	EPA 95th% Adult Coastal Resident	EPA 95th% Immigrant Adult	EPA 95th% Child	U.S. FDA Tolerance Level
Cancer Acceptable Risk Level (ARL), Lifetime	Total No. of Exceedances at Each Risk Level (Percent)					No. FDA TL Exceedances
ARL = 1.0E-04	11 (8%)	30 (23%)	0 (0%)	15 (11%)	8 (6%)	
ARL = 1.0E-05		101 (77%)	36 (28%)	92 (70%)	83 (63%)	
ARL = 1.0E-06		129 (98%)	102 (78%)	128 (98%)	124 (95%)	0 (0%)
Number of Meals Allowed to Not Exceed ARL	Total Number of Meals per Year					
ARL = 1.0E-04		<59	>365	<91	<136	
ARL = 1.0E-05		<6	<47	<10	<14	
ARL = 1.0E-06		<1	<4	<1	<1	

Table 4. Yadkin-Pee Dee waterbody summary of the proportion of 1.0E-05 lifetime cancer risk exceedances for alternative fish consumption advisory models using updated exposure parameters selected from *Exposure Factors Handbook: 2011 Edition U.S. EPA.*

Cancer Risk Model	High Rock Lake	Badin Lake	Falls Reservoir	Lake Tillery
		Crappie		
DPH as Cancer Risk	0.364	0.400	-	0.375
Coastal Resident Adult	0.000	0.000	-	0.000
Child Resident	0.000	0.000	-	0.250
Immigrant Adult Resident	0.182	0.000	-	0.250
		Sunfish		
DPH as Cancer Risk	0.667	1.000	0.500	0.714
Coastal Resident Adult	0.000	0.000	0.000	0.143
Child Resident	0.333	0.750	0.000	0.429
Immigrant Adult Resident	0.667	1.000	0.250	0.571
		Catfish		
DPH as Cancer Risk	0.833	1.000	1.000	0.938
Coastal Resident Adult	0.333	0.700	0.600	0.313
Child Resident	0.833	1.000	1.000	0.813
Immigrant Adult Resident	0.833	1.000	1.000	0.875
		Largemouth Bass		
DPH as Cancer Risk	0.917	1.000	1.000	0.923
Coastal Resident Adult	0.167	0.444	0.500	0.462
Child Resident	0.583	0.889	1.000	0.923
Immigrant Adult Resident	0.667	1.000	1.000	0.846

Table 5. The proportion of total cancer risk attributed to the dioxin-like PCB congener burden, as species mean. (dl = dioxin-like)

Species	Scientific Name	No. Samples	Mean dl-Risk
Black Crappie	*Pomoxis nigromaculatus*	16	0.230
Blue Catfish	*Ictalurus furcatus*	4	0.166
Bluegill	*Lepomis macrochirus*	8	0.247
Brown Bullhead	*Ameiurus nebulosus*	3	0.578
Channel Catfish	*Ictalurus punctatus*	23	0.261
Flat Bullhead	*Ameiurus platycephalus*	3	0.377
Flathead Catfish	*Pylodictis olivaris*	2	0.153
Largemouth Bass	*Micropterus salmoides*	38	0.368
Redbreast Sunfish	*Lepomis auritus*	5	0.358
Redear Sunfish	*Lepomis microlophus*	8	0.401
White Bass	*Morone chrysops*	3	0.123
White Catfish	*Ameiurus catus*	10	0.306
White Crappie	*Pomoxis annularis*	5	0.159
White Perch	*Morone americana*	2	0.147
Yellow Perch	*Perca flavescens*	1	0.838
All Samples		131	0.314

Table 6. Mean trophic guild PCB concentrations. (dl = dioxin-like, g = gram, mm = millimeter, ndl = non-dioxin-like, ng = nanogram, TEQ = toxicity equivalence quotient, ww = wet weight)

					ng/kg ww					ng/g-lipid		
Trophic Guild	No. Samples	Length (mm)	Weight (g)	% Lipid	Total PCBs	ndl-PCBs	dl-PCBs	dl-PCB TEQ	Weight Fraction dl-PCBs	Total PCBs	dl-PCBs	dl-PCB TEQ
Insectivore	21	188	138	0.83	4,990	4,512	477	0.0811	0.1023	847	81.2	0.0107
Omnivore	43	409	993	2.61	33,806	30,560	3,246	0.3055	0.0919	2715	238	0.0296
Piscivore	67	327	653	1.04	14,633	13,475	1,158	0.1579	0.0850	1739	132	0.0161

Table 7. Mean trophic guild PCB concentrations summarized by waterbody. (dl = dioxin-like, g = gram, mm = millimeter, ndl = non-dioxin-like, ng = nanogram, TEQ = Toxicity Equivalence Quotient, ww = wet weight)

						ng/kg ww				ng/g-lipid		
Trophic Guild	Waterbody	No. Samples	Length (mm)	Weight (g)	% Lipid	Total PCBs	dl-PCBs	dl-PCB TEQ	Weight Fraction dl-PCBs	Total PCBs	dl-PCBs	dl-PCB TEQ
Insectivore	High Rock Lake	4	166	96.7	0.675	5,243	452	0.0138	0.101	664	61.3	0.00187
	Badin Lake	6	199	159	0.503	6,386	501	0.106	0.0724	1,542	120	0.0195
	Falls Reservoir	4	165	84.7	0.875	3,664	474	0.015	0.132	598	76.9	0.00235
	Lake Tillery	7	205	174	1.19	4,405	472	0.136	0.111	499	61.4	0.0128
Omnivore	High Rock Lake	12	404	751	3.28	33,375	2,617	0.148	0.0875	4,836	341	0.0392
	Badin Lake	10	331	487	1.57	35,434	2,884	0.773	0.0822	2,835	240	0.0615
	Falls Reservoir	5	581	3107	3.94	42,342	3,704	0.113	0.0898	1,023	90.7	0.00277
	Lake Tillery	16	408	831	2.34	30,444	3,800	0.192	0.102	1,578	206	0.0107
Piscivore	High Rock Lake	29	307	501	0.917	11,359	780	0.046	0.0717	1,900	134	0.00564
	Badin Lake	11	336	709	0.607	16,461	1,044	0.368	0.0632	2,334	151	0.0542
	Falls Reservoir	6	434	1503	1.22	36,735	3,455	0.105	0.194	2,476	231	0.00701
	Lake Tillery	21	320	592	1.40	11,882	1,082	0.218	0.0837	994	91.5	0.0133

Table 8. Fish tissue mean PCB concentrations grouped for statistical analyses. (dl = dioxin-like, mm = millimeter, TEQ = Toxicity Equivalence Quotient, ww = wet weight)

									ng/kg ww			
Species	Trophic Status	Trophic Guild	Trophic Level	No. Samples	No. Fish	Length (mm)	Weight (grams)	Lipid (%)	Total PCBs	dl-PCBs	dl-PCB-TEQ	Weight Fraction dl-PCBs
Catfish	Bottom Feeder	Omnivore	3	43	72	409	993	2.61	33,806	3,246	0.3055	0.0919
Crappie	Middle Feeder	Piscivore	3	21	37	262	290	0.846	3,194	238	0.0310	0.0762
Flathead Catfish	Top Predator	Piscivore	4	2	2	583	2,501	4.85	80,242	7,376	0.2231	0.0841
Largemouth Bass	Top Predator	Piscivore	4	38	126	364	828	0.987	17,703	1,382	0.2453	0.0752
Perch	Middle Feeder	Piscivore	3	3	10	202	127	0.500	1,922	173	0.0054	0.2898
Redear	Middle Feeder	Insectivore	3	8	28	217	204	0.850	3,911	409	0.1192	0.1033
Sunfish	Middle Feeder	Insectivore	3	13	54	170	97	0.825	5,653	519	0.0577	0.1017
White Bass	Top Predator	Piscivore	4	3	18	278	277	1.17	24,791	1,590	0.0490	0.0658

Table 8 Continued

Species	Trophic Status	Trophic Guild	Trophic Level	No. Samples	No. Fish	Length (mm)	Weight (grams)	Lipid (%)	ng/g-lipid		
									Total PCBs	dl-PCBs	dl-PCB-TEQ
Catfish	Bottom Feeder	Omnivore	3	43	72	409	993	2.61	2,715	238	0.0296
Crappie	Middle Feeder	Piscivore	3	21	37	262	290	0.846	1,050	73.4	0.00406
Flathead Catfish	Top Predator	Piscivore	4	2	2	583	2,501	4.85	3,302	328	0.00987
Largemouth Bass	Top Predator	Piscivore	4	38	126	364	828	0.987	2,114	161	0.0253
Perch	Middle Feeder	Piscivore	3	3	10	202	127	0.500	462	40.4	0.00126
Redear	Middle Feeder	Insectivore	3	8	28	217	204	0.850	532	59.4	0.0114
Sunfish	Middle Feeder	Insectivore	3	13	54	170	97	0.825	1,041	94.7	0.0102
White Bass	Top Predator	Piscivore	4	3	18	278	277	1.17	2,041	132	0.00406

Table 9. Mean Largemouth Bass, catfish group, sunfish group and crappie group PCB and homolog profile analysis.

Species	Waterbody	No. Samples	Length (mm)	Weight (grams)	% Lipid	ng/kg ww			
						Total PCBs	dl-PCBs	dl-PCB-TEQ	Wt-Fraction dl-PCBs
Largemouth Bass	High Rock Lk	12	354	726	0.78	13,487	962	0.0820	0.0741
	Badin Lk	9	363	827	0.66	19,705	1,253	0.4488	0.0648
	Falls Resvr	4	423	1,351	1.20	26,522	2,233	0.0685	0.0865
	Lk Tillery	13	354	763	1.34	17,494	1,598	0.3095	0.0800
Catfish	High Rock Lk	12	404	751	3.28	33,375	2,617	0.1478	0.0875
	Badin Lk	10	331	487	1.57	35,434	2,884	0.7727	0.0822
	Falls Resvr	5	581	3,107	3.94	42,342	3,704	0.1132	0.0898
	Lk Tillery	16	408	831	2.34	30,444	3,800	0.1918	0.1018
Crappie	High Rock Lk	11	270	293	0.45	3,752	258	0.0084	0.0702
	Badin Lk	2	217	176	0.38	1,861	103	0.0033	0.0560
	Lk Tillery	8	264	313	1.50	2,761	245	0.0690	0.0896
Sunfish	High Rock Lk	3	149	59.6	0.80	6,854	586	0.0179	0.0935
	Badin Lk	4	180	117	0.61	8,960	716	0.1577	0.0793
	Falls Resvr	4	165	84.7	0.88	3,664	474	0.0145	0.1324
	Lk Tillery	2	193	141	1.20	1,219	117	0.0036	0.0975

Table 9 Continued

Species	Waterbody	Homolog Groups (ng/kg ww)					
		Mono-Tri	Tetra	Penta	Hexa	Hepta	Octa-Deca
Largemouth Bass	High Rock Lk	134.1	1,603	3,604	4,654	2,070	1,421
	Badin Lk	478.6	2,309	4,977	7,714	2,761	1,464
	Falls Resvr	374.9	3,245	7,315	10,104	3,633	1,851
	Lk Tillery	291.1	3,452	4,954	4,835	2,823	1,140
Catfish	High Rock Lk	204.7	2,158	6,159	12,203	7,147	5,504
	Badin Lk	932.5	5,018	9,608	14,628	3,816	1,431
	Falls Resvr	1,037	6,455	12,181	15,245	4,865	2,558
	Lk Tillery	566.0	5,903	9,432	8,492	4,133	1,918
Crappie	High Rock Lk	209.2	891.1	1,008.1	1,009.3	389.7	244.3
	Badin Lk	126.9	272.6	472.5	643.8	227.8	117.3
	Lk Tillery	29.99	561.9	871.5	734.5	308.4	255.1
Sunfish	High Rock Lk	63.10	624.1	1,825	2,590	1,106	645.3
	Badin Lk	422.8	1,439	2,509	3,351	900.1	338.4
	Falls Resvr	21.30	404.2	1,151.6	1,377.0	532.5	177.0
	Lk Tillery	3.200	83.40	306.30	447.40	222.00	156.50

Table 9 Continued

		ng/g-lipid			Homolog Group, as ng/g-Lipid					
Species	Waterbody	PCB-Lipid	dl-PCB-Lipid	dl-PCB-Lipid-TEQ	Mono-Tri	Tetra	Penta	Hexa	Hepta	Octa-Deca
Largemouth Bass	High Rock Lk	2,319	169.7	0.008503	79.7	282.5	633.0	791.5	345.7	242.9
	Badin Lk	2,743	177.9	0.066008	82.1	320.9	706.4	1071	379.4	197.1
	Falls Resvr	2,206	188.5	0.005781	33.9	269.6	612.5	842.0	299.6	153.3
	Lk Tillery	1,461	133.3	0.018507	30.1	285.3	403.1	412.1	240.9	95.5
Catfish	High Rock Lk	4,836	341.0	0.039239	35.6	115.5	583.1	1673	1225	1231
	Badin Lk	2,835	239.5	0.061526	51.4	413.4	754.8	1137	312.2	120.0
	Falls Resvr	1,023	90.70	0.002772	12.5	160.4	298.8	361.4	115.2	59.12
	Lk Tillery	1,578	206.1	0.010744	20.1	300.0	498.6	431.6	218.7	102.4
Crappie	High Rock Lk	1,743	117.9	0.004084	211.2	646.8	434.2	310.8	108.0	63.47
	Badin Lk	495	27.78	0.000875	128.8	71.46	125.5	170.0	58.7	30.46
	Lk Tillery	236	23.53	0.004830	28.95	54.26	78.20	58.19	23.36	18.26
Sunfish	High Rock Lk	839	76.06	0.002310	63.87	69.51	221.4	328.1	136.8	77.14
	Badin Lk	2,104	168.5	0.028913	112.3	351.3	585.6	766.4	209.0	78.45
	Falls Resvr	598	76.89	0.002353	58.02	61.57	184.3	232.3	85.87	31.01
	Lk Tillery	106	10.35	0.000321	34.21	8.531	27.14	39.82	16.56	13.22

Table 9 Continued

Species	Waterbody	Wt-Fraction dl-PCBs	Homolog Group, as Wt. Fraction					
			Mono-Tri	Tetra	Penta	Hexa	Hepta	Octa-Deca
Largemouth Bass	High Rock Lk	0.0741	0.0116	0.1285	0.2796	0.3412	0.1436	0.0955
	Badin Lk	0.0648	0.0280	0.1194	0.2581	0.3845	0.1385	0.0716
	Falls Resvr	0.0865	0.0139	0.1246	0.2779	0.3822	0.1333	0.0680
	Lk Tillery	0.0800	0.0114	0.1619	0.2668	0.3015	0.1783	0.0800
Catfish	High Rock Lk	0.0875	0.0114	0.0936	0.2275	0.3474	0.1830	0.1370
	Badin Lk	0.0822	0.0375	0.1481	0.2673	0.3875	0.1131	0.0465
	Falls Resvr	0.0898	0.0288	0.1591	0.2947	0.3503	0.1111	0.0560
	Lk Tillery	0.1018	0.0095	0.1184	0.2476	0.3469	0.1812	0.0965
Crappie	High Rock Lk	0.0702	0.0499	0.2516	0.2858	0.2677	0.0876	0.0575
	Badin Lk	0.0560	0.0783	0.1444	0.2534	0.3434	0.1188	0.0616
	Lk Tillery	0.0896	0.0086	0.2071	0.3155	0.2699	0.1061	0.0928
Sunfish	High Rock Lk	0.0935	0.0068	0.0817	0.2656	0.3961	0.1614	0.0884
	Badin Lk	0.0793	0.0478	0.1611	0.2806	0.3738	0.0994	0.0372
	Falls Resvr	0.1324	0.0078	0.1048	0.3252	0.3820	0.1379	0.0422
	Lk Tillery	0.0975	0.0026	0.0767	0.2552	0.3739	0.1653	0.1263

FIGURES

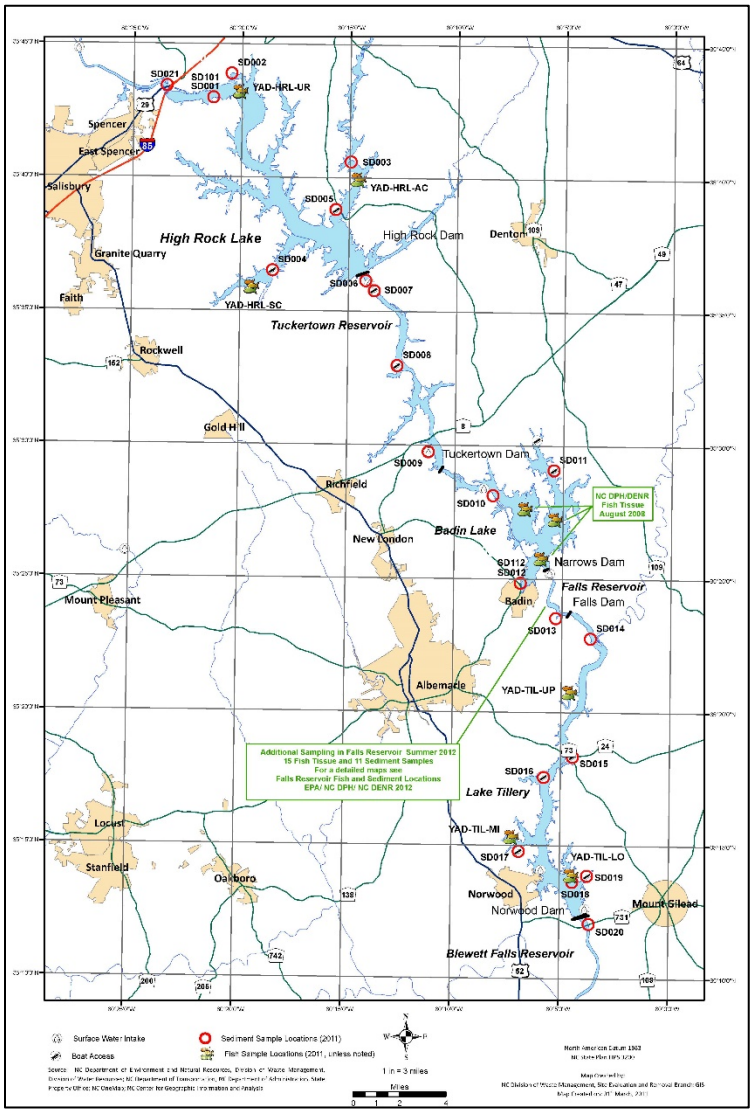


Figure 1. Fish collection locations in the Yadkin-Pee Dee River basin in 2008 (Badin Lake), 2011 (High Rock Lake and Lake Tillery) and in 2012 (Falls Reservoir).

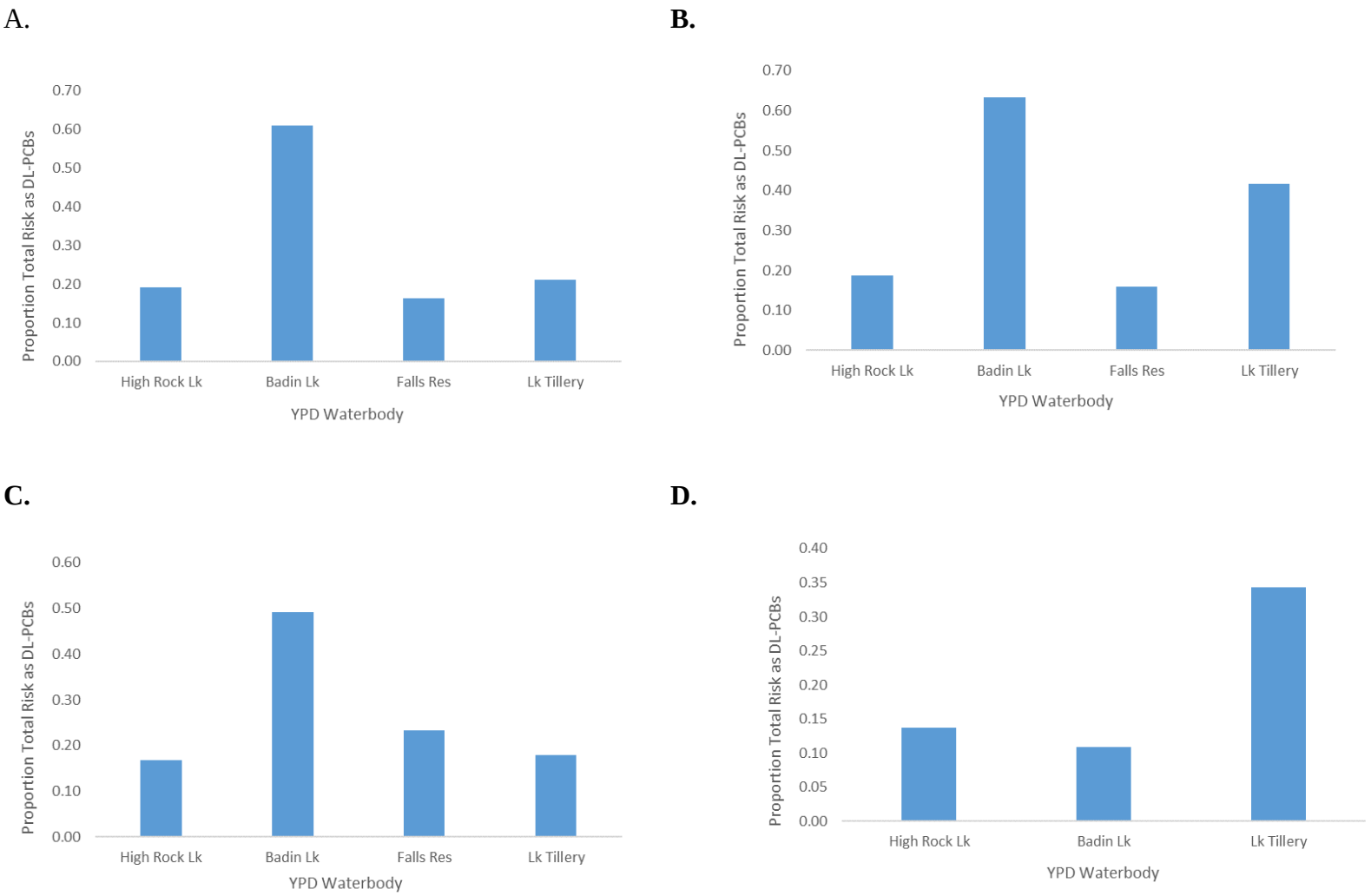
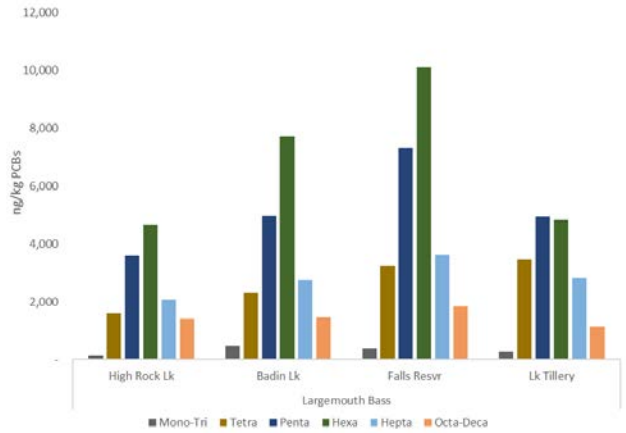


Figure 2. Proportion of cancer risk associated with dioxin-like PCBs, as the species mean in each waterbody. YPD = Yadkin-Pee Dee River system. A = Catfish Group, B = Largemouth Bass, C = Sunfish Group, D = Crappie Group

A.



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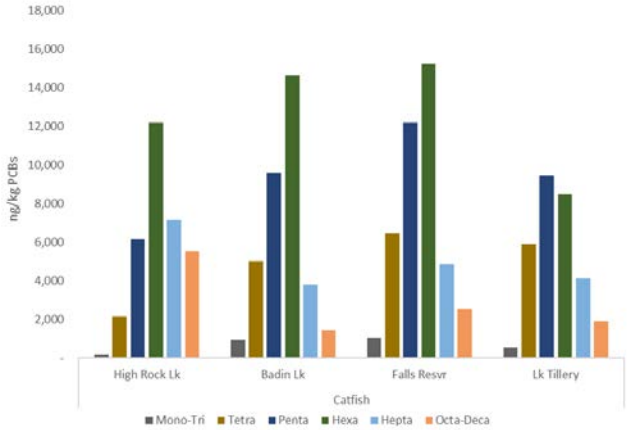

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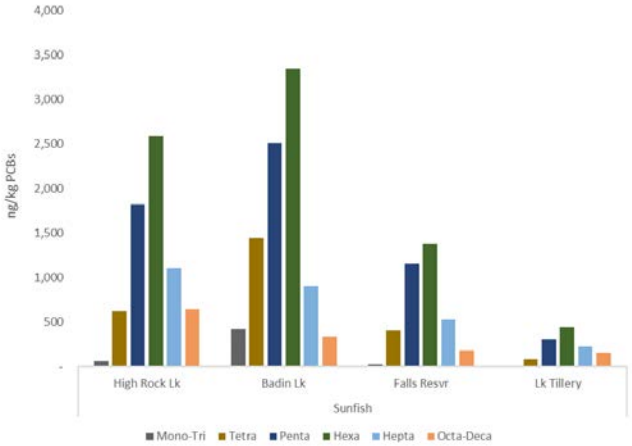


D.

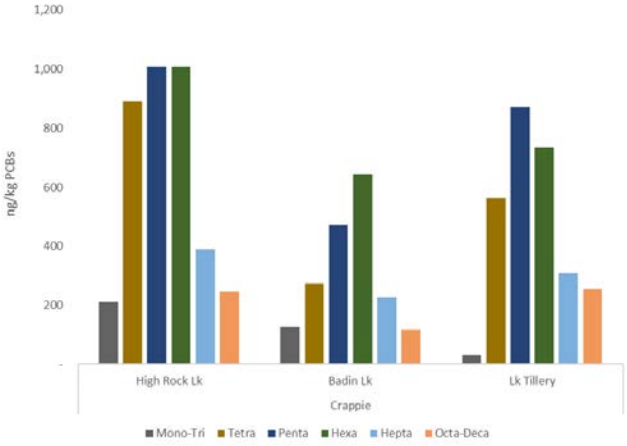
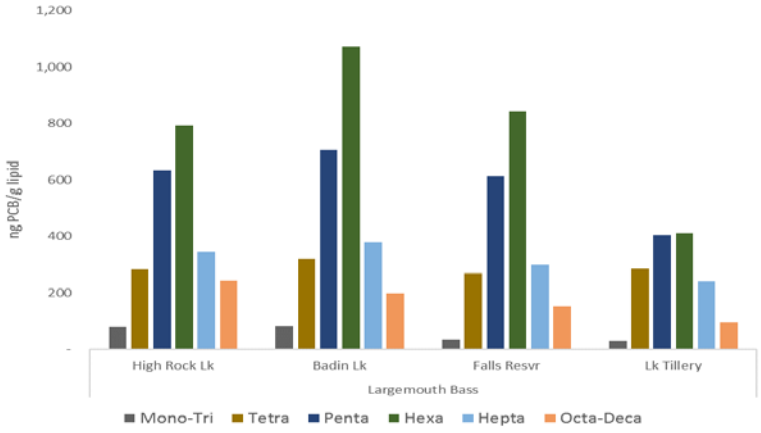


Figure 3. Fish species PCB homolog data, expressed as ng/kg wet weight. A = Largemouth Bass. B = Catfish Group, C = Sunfish Group, D = Crappie Group

A.



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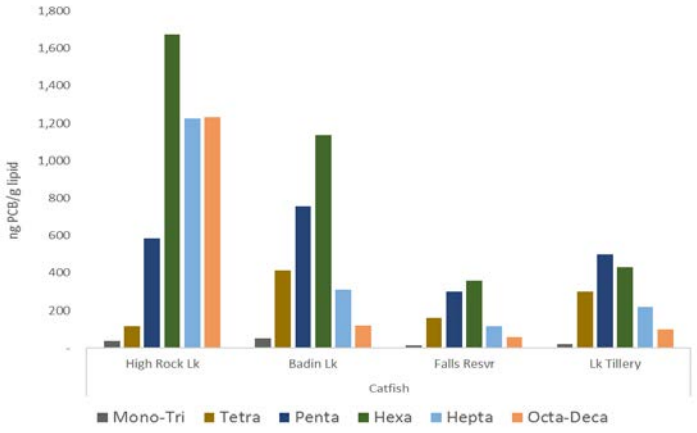

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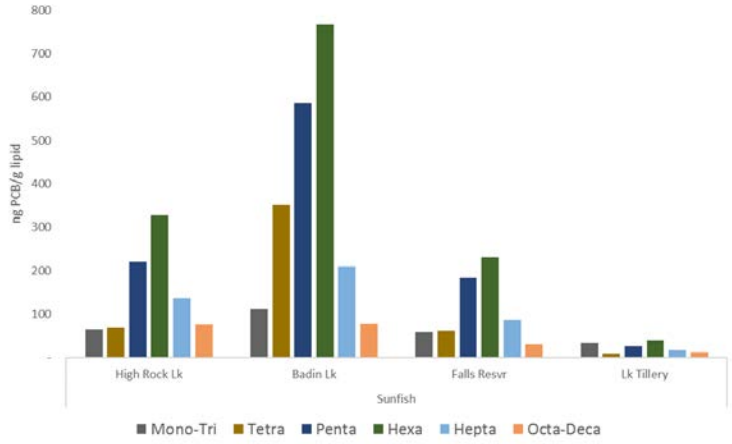

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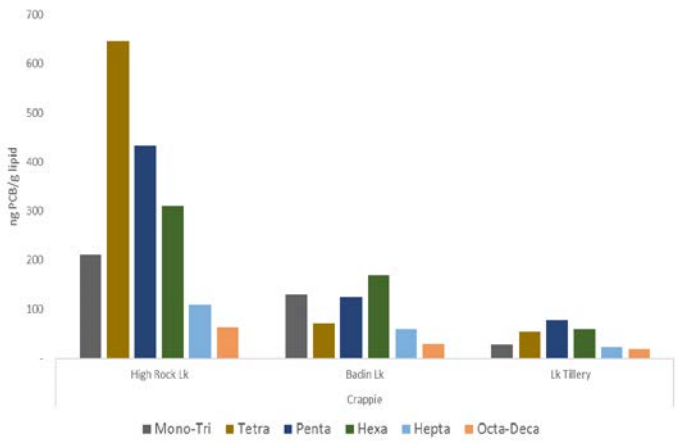
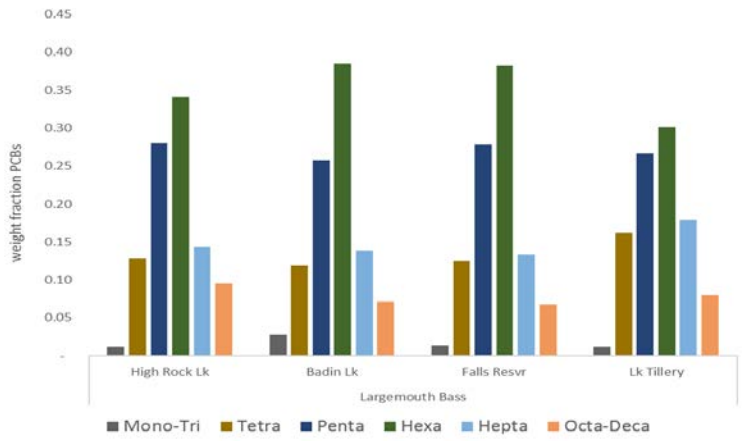


Figure 4. Fish species PCB homolog data, expressed as ng PCB/g-lipid. A = Largemouth Bass. B = Catfish Group, C = Sunfish Group, D = Crappie Group

A.



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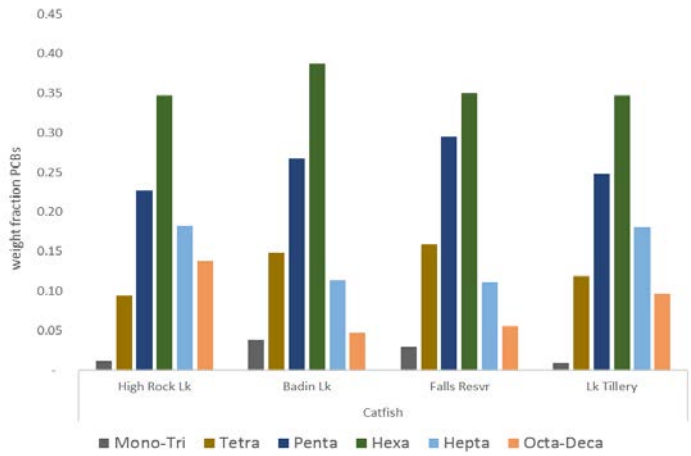

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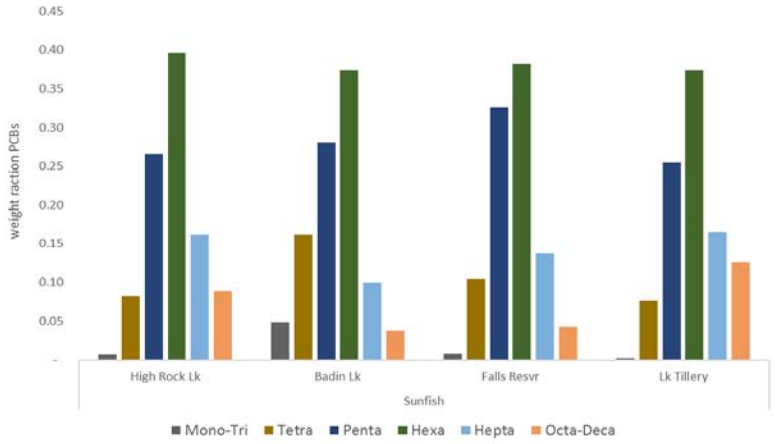

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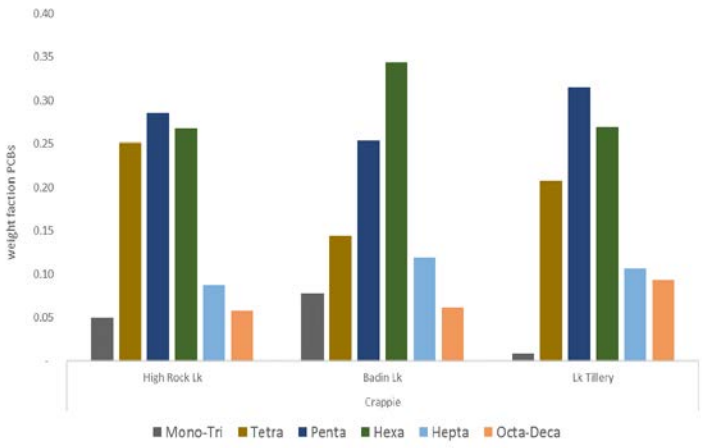


Figure 5. Fish species PCB homolog data as wet-weight fraction. A = Largemouth bass. B = Catfish Group, C = Sunfish Group, D = Crappie

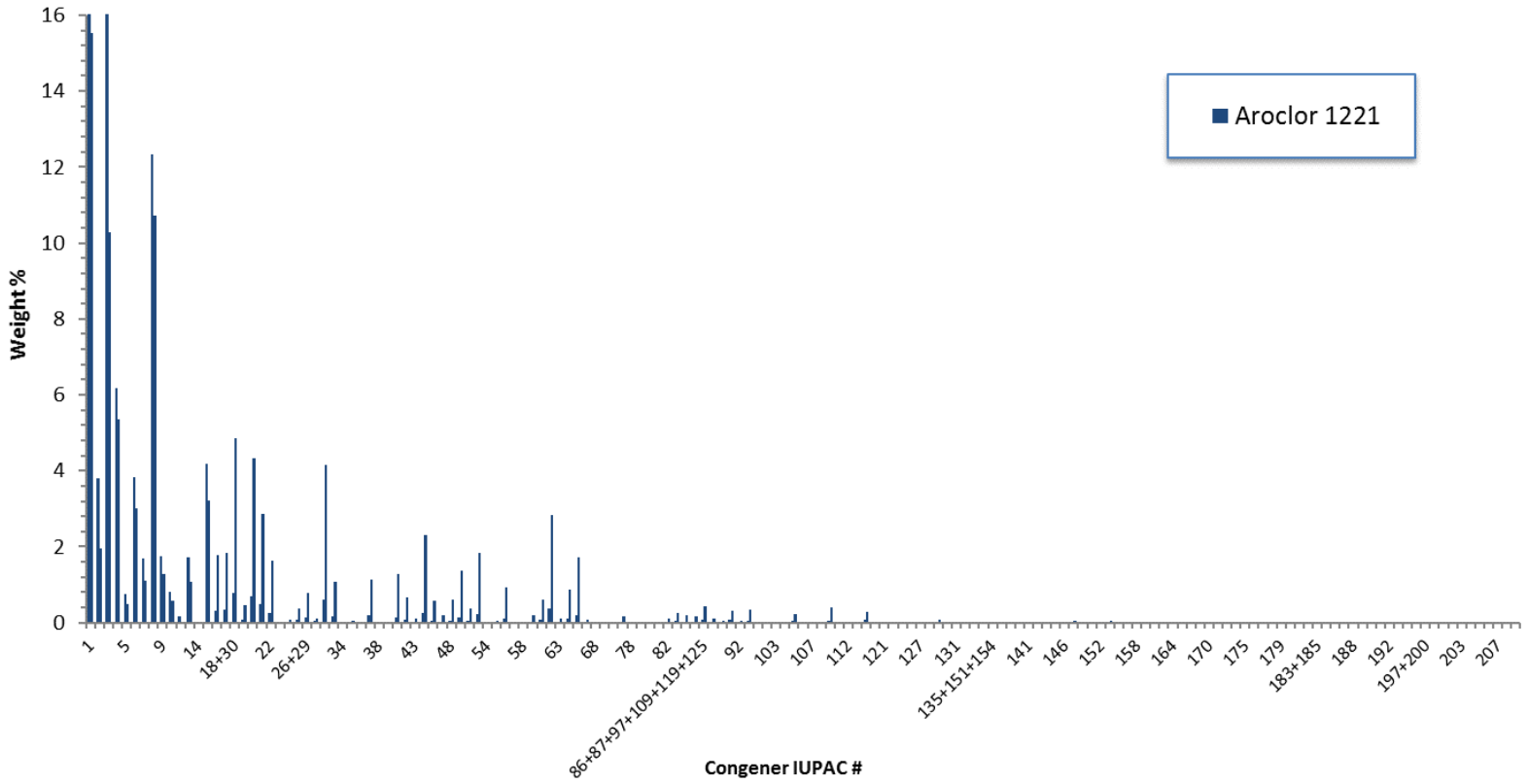
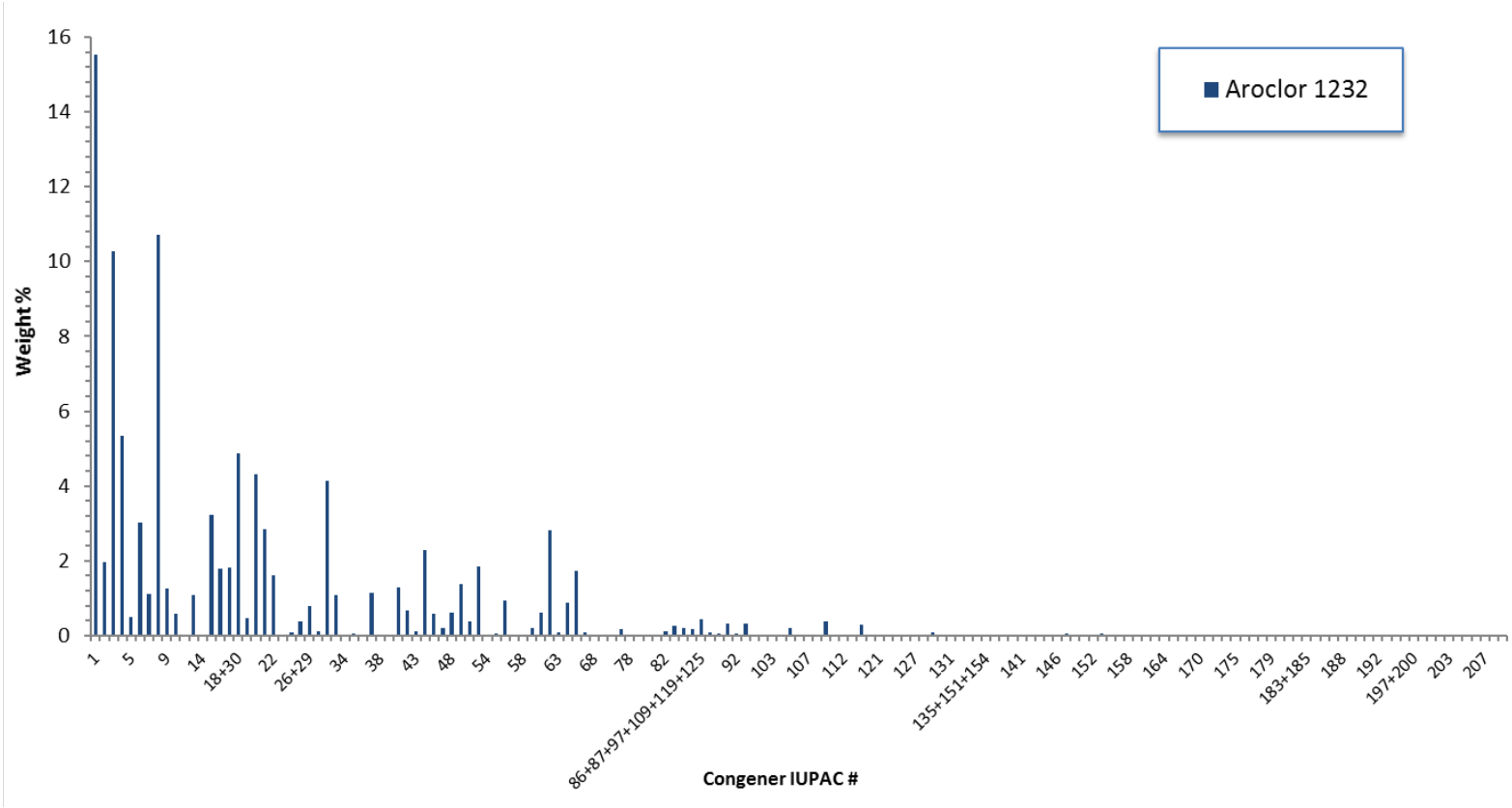


Figure 6. Native Aroclors 209-congener profiles as congener weight percent.



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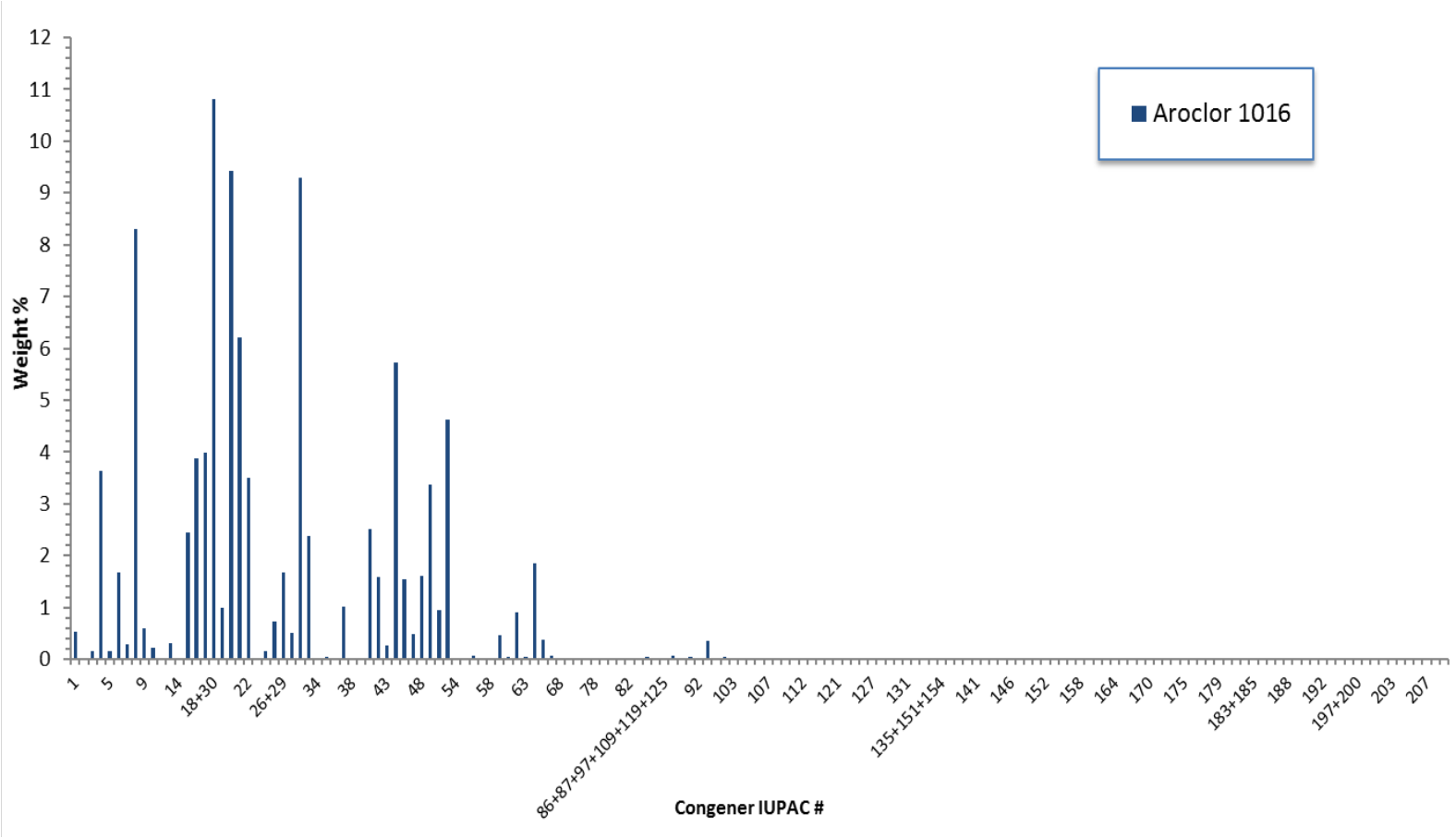

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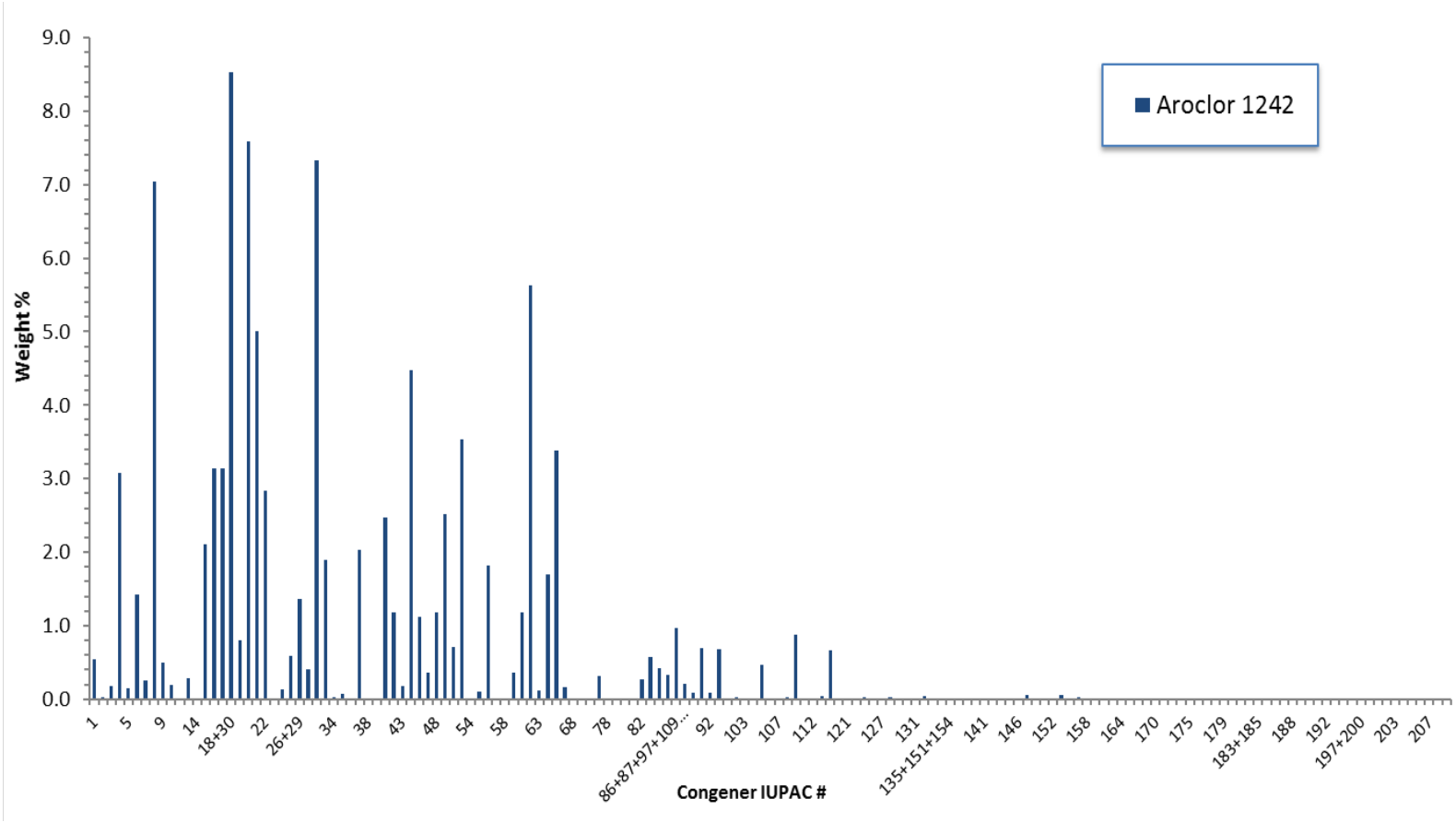

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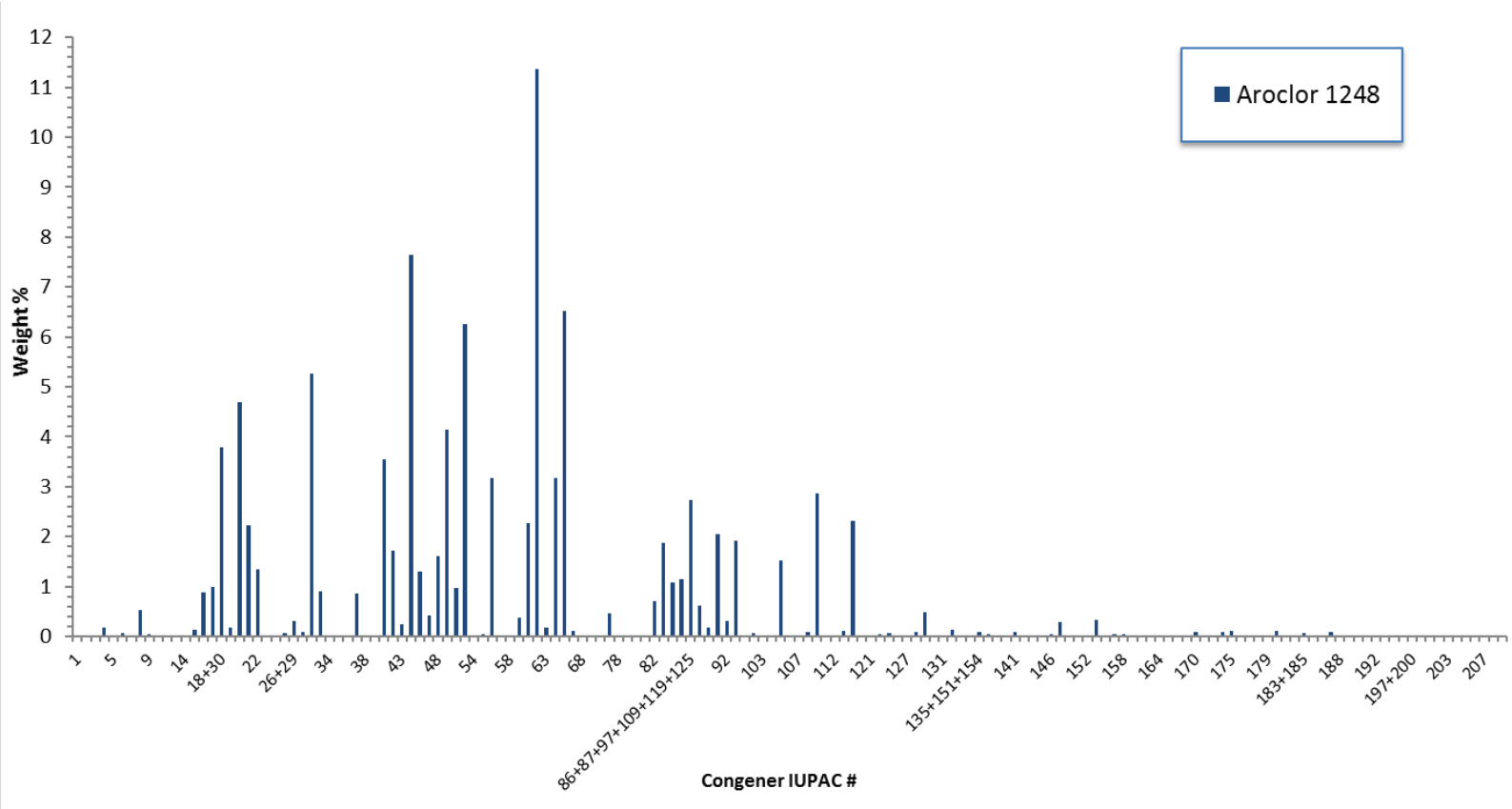

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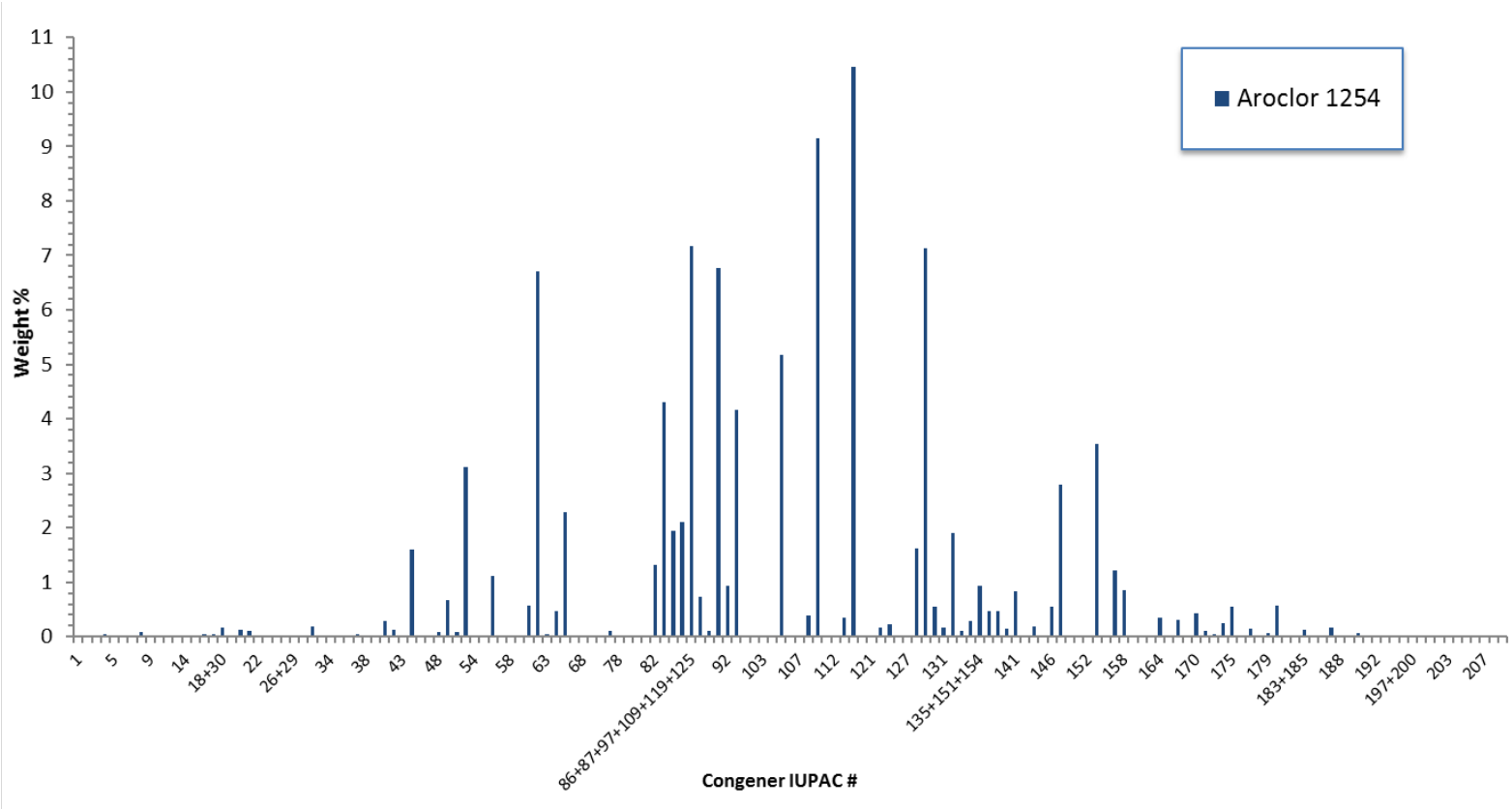

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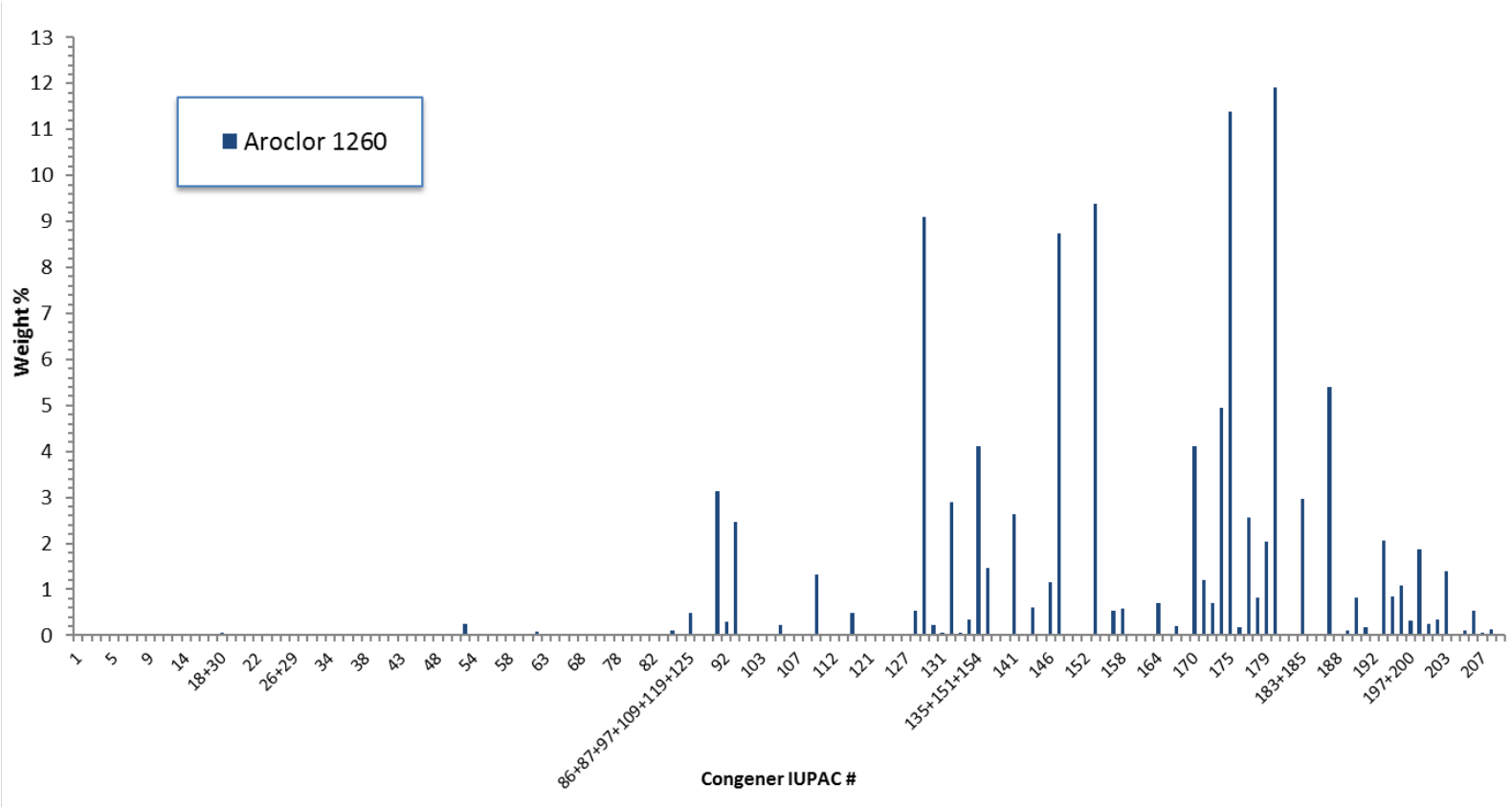

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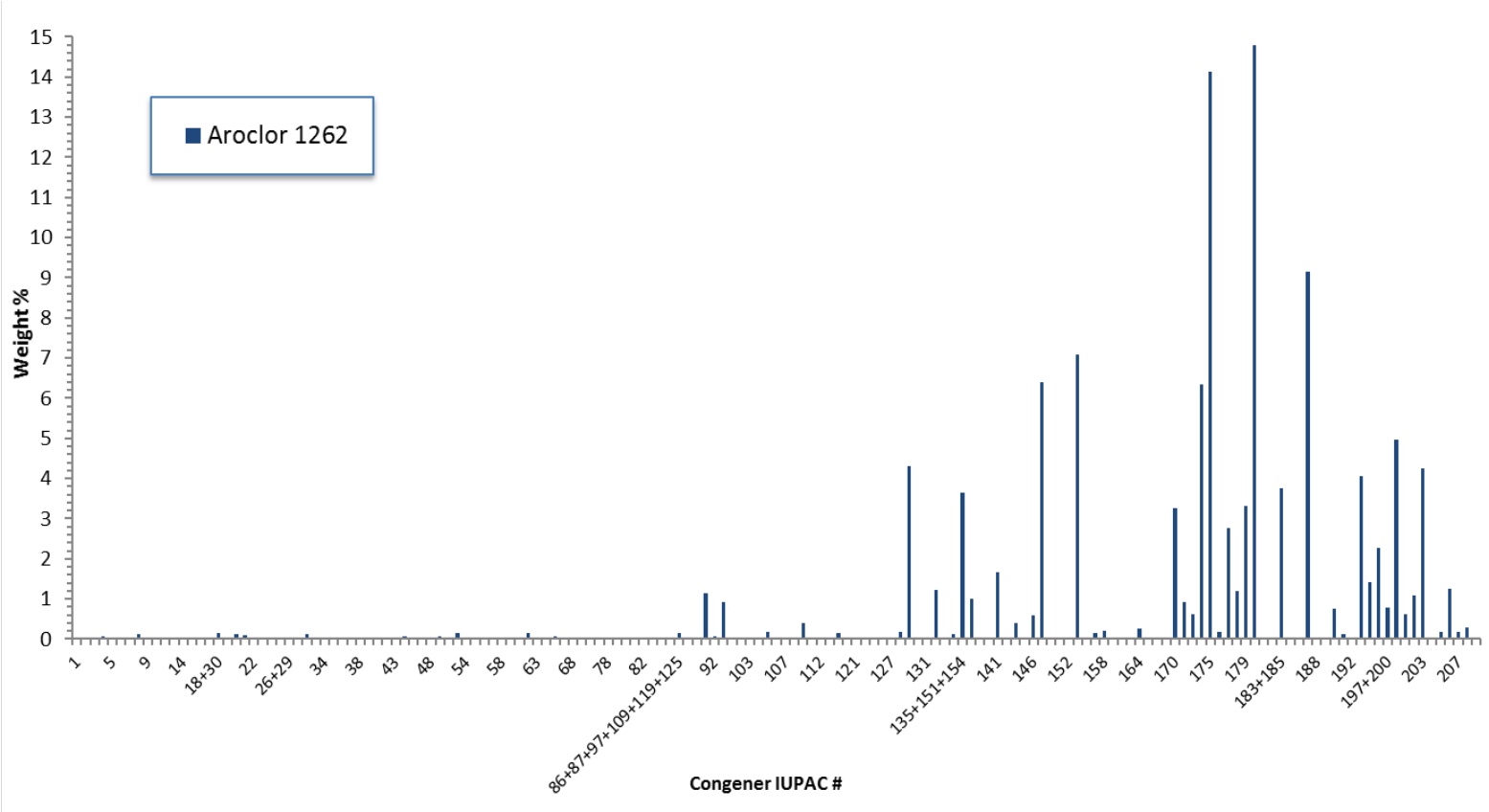

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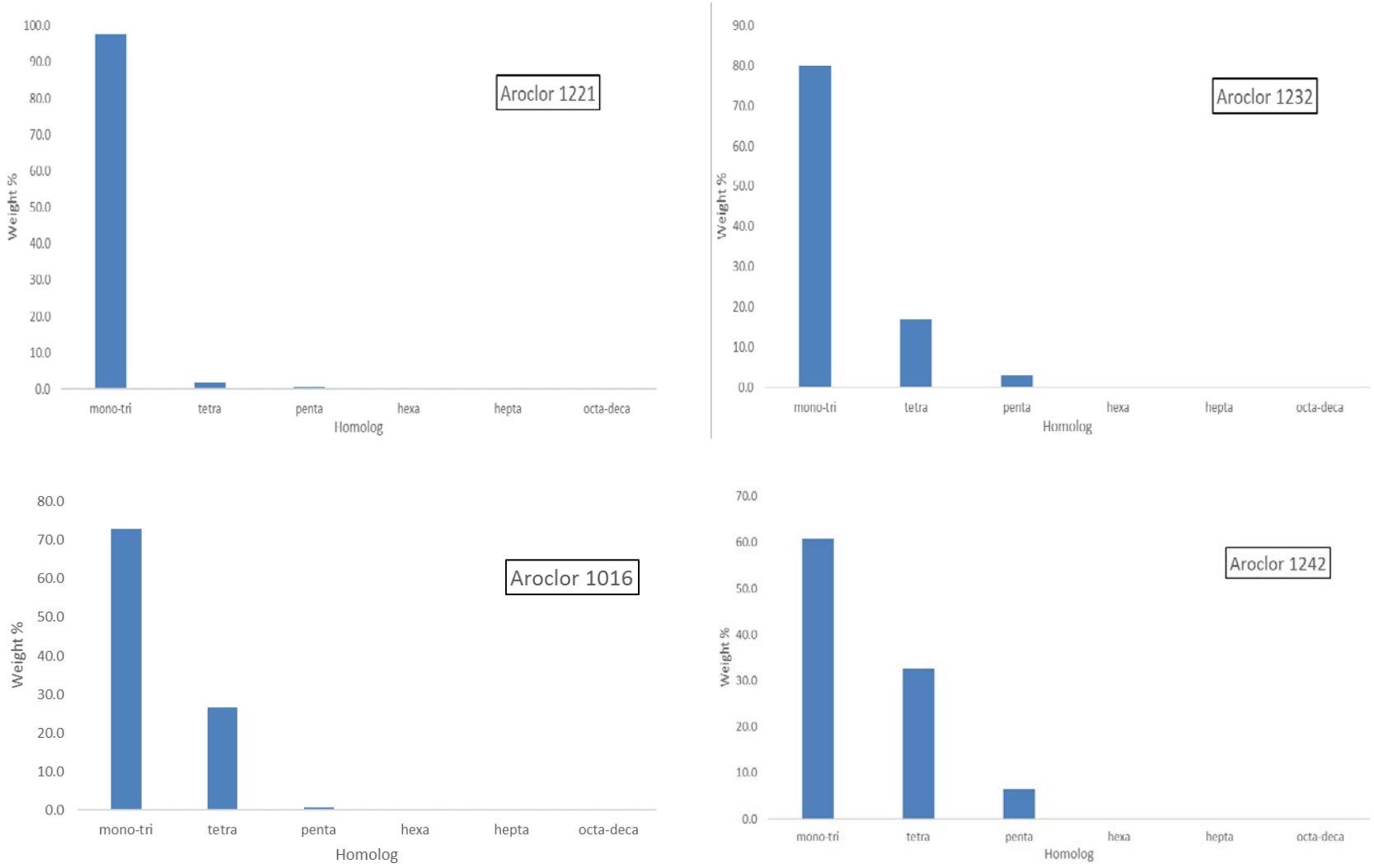
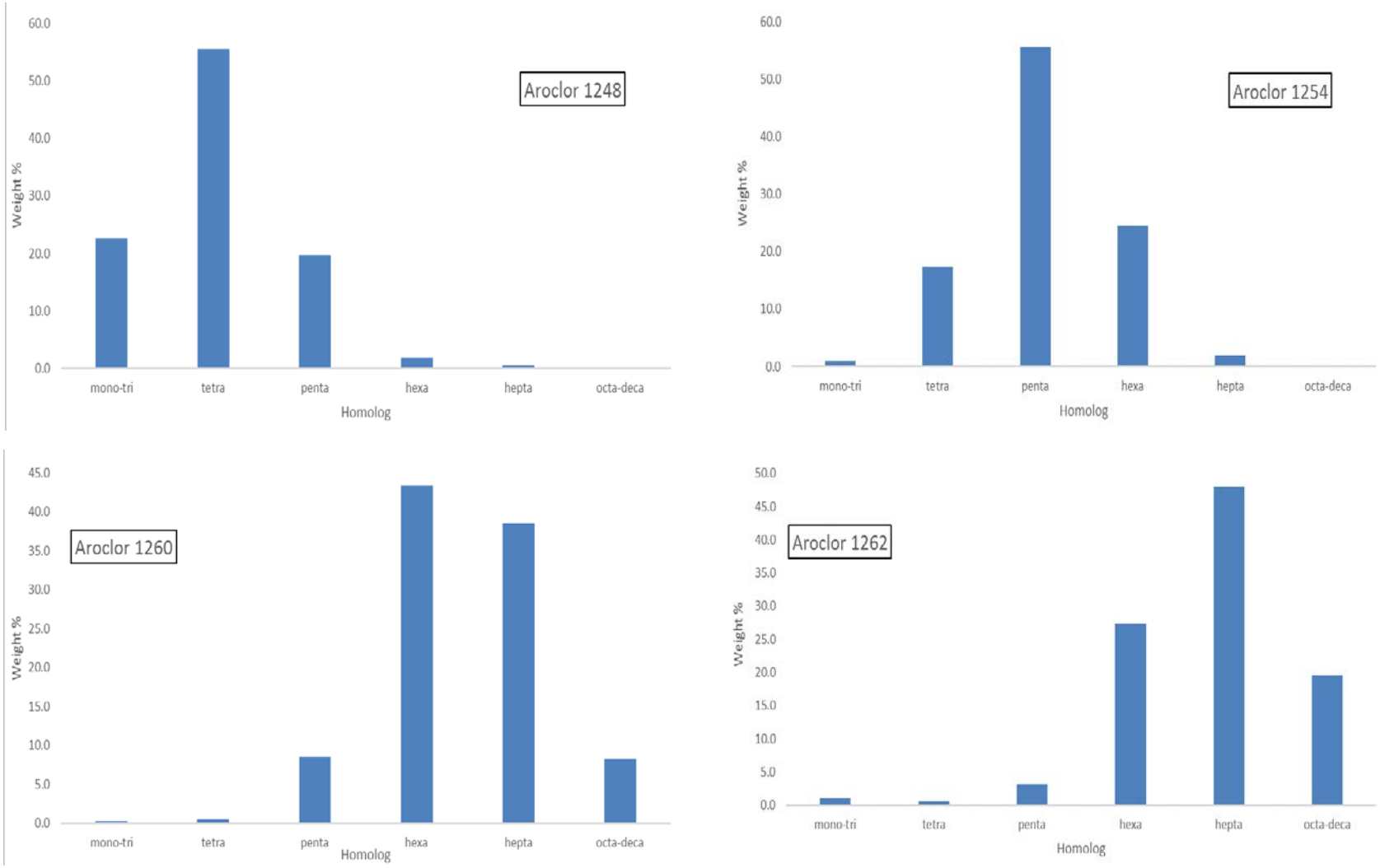


Figure 7. Native Aroclors 209-congener profiles as homolog weight percent.



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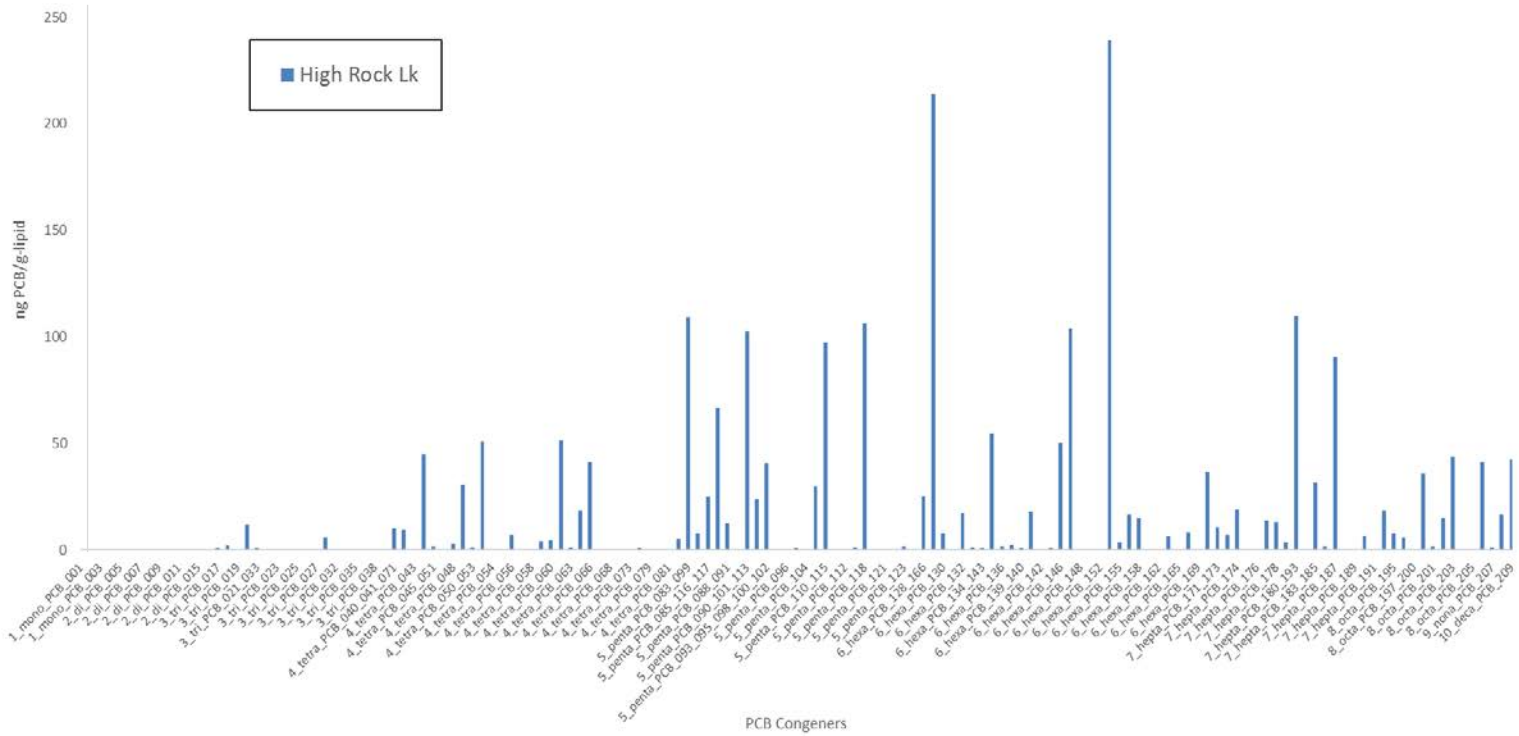
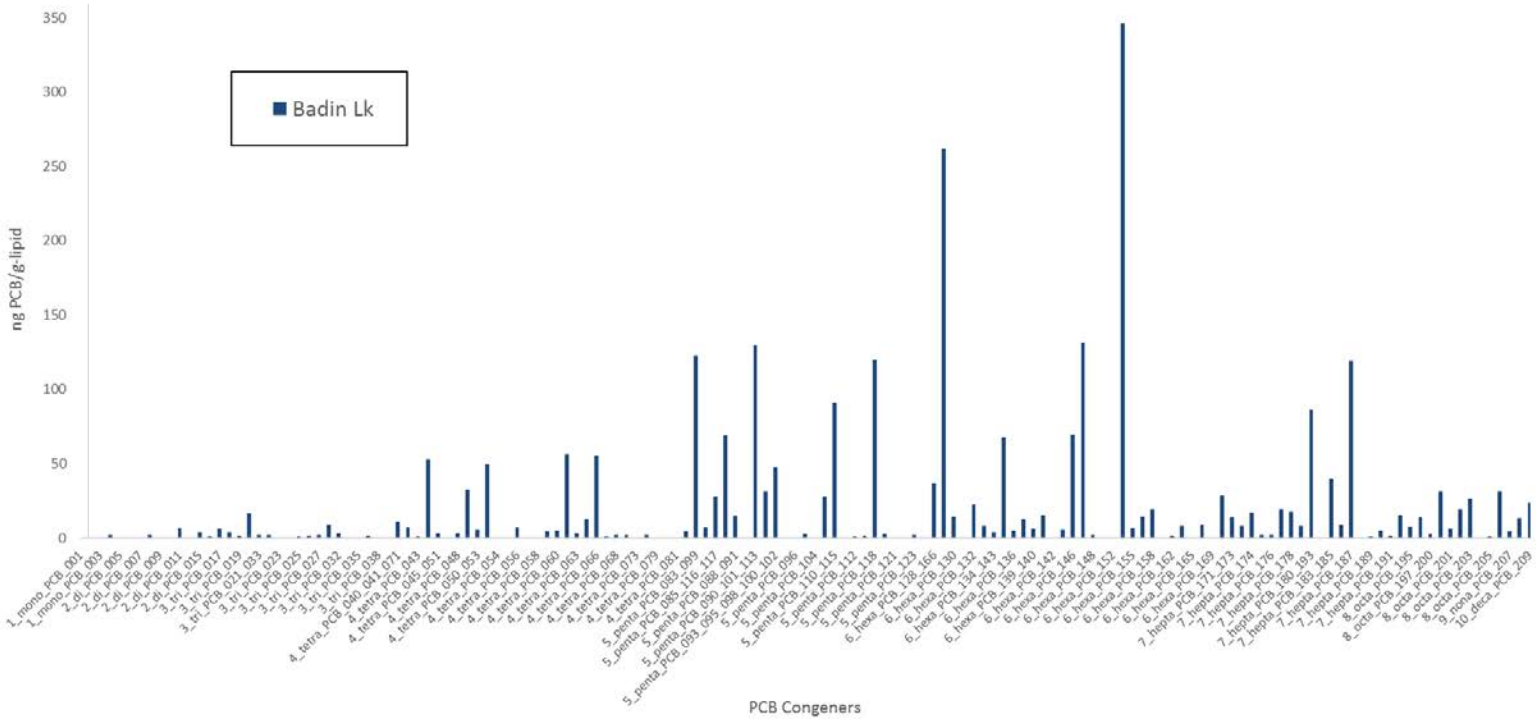


Figure 8. Largemouth Bass lipid-normalized PCB congener profiles (as ng PCB/g-lipid) as the mean by waterbody for High Rock Lake, Badin Lake, Falls Reservoir and Lake Tillery (upstream → downstream).



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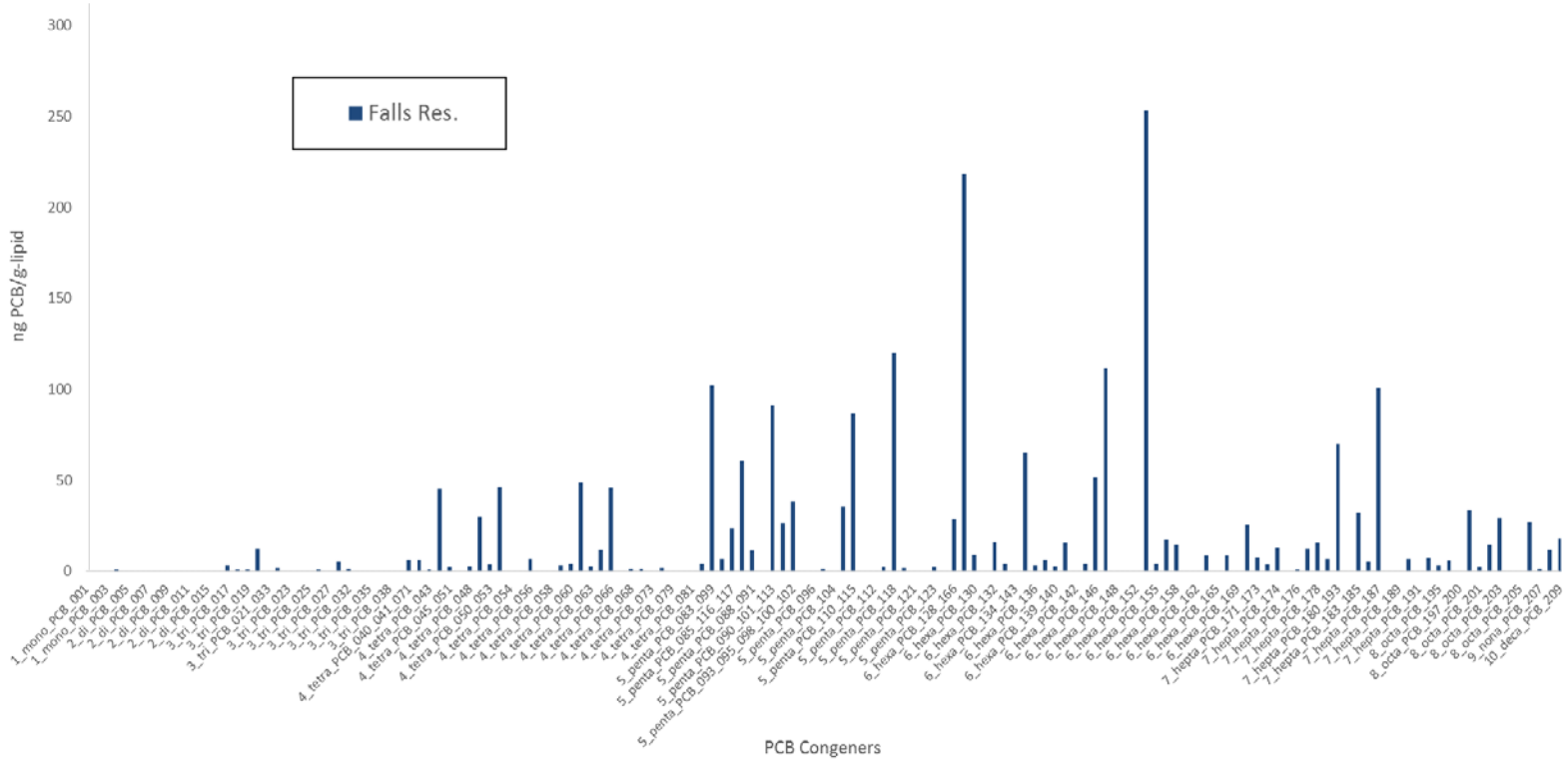

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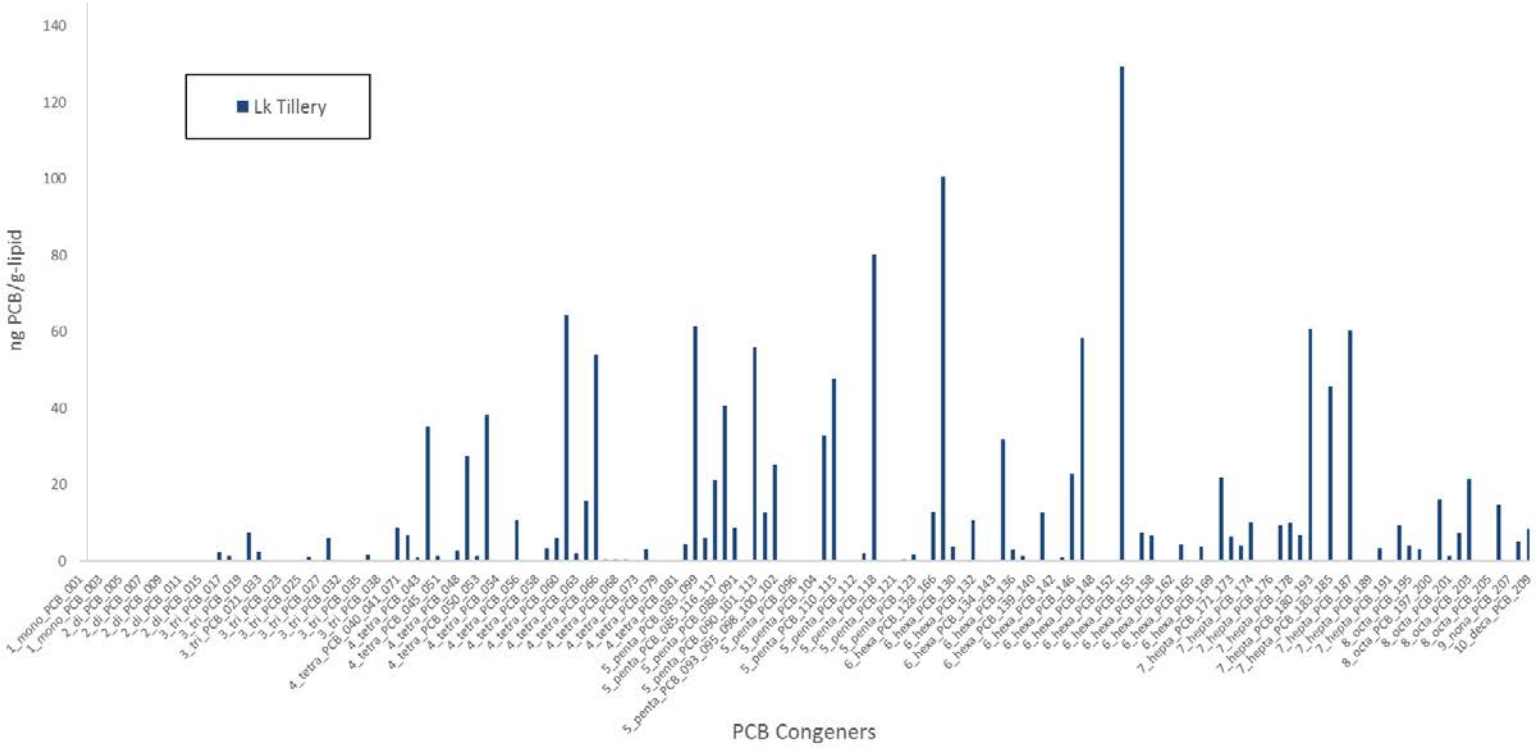

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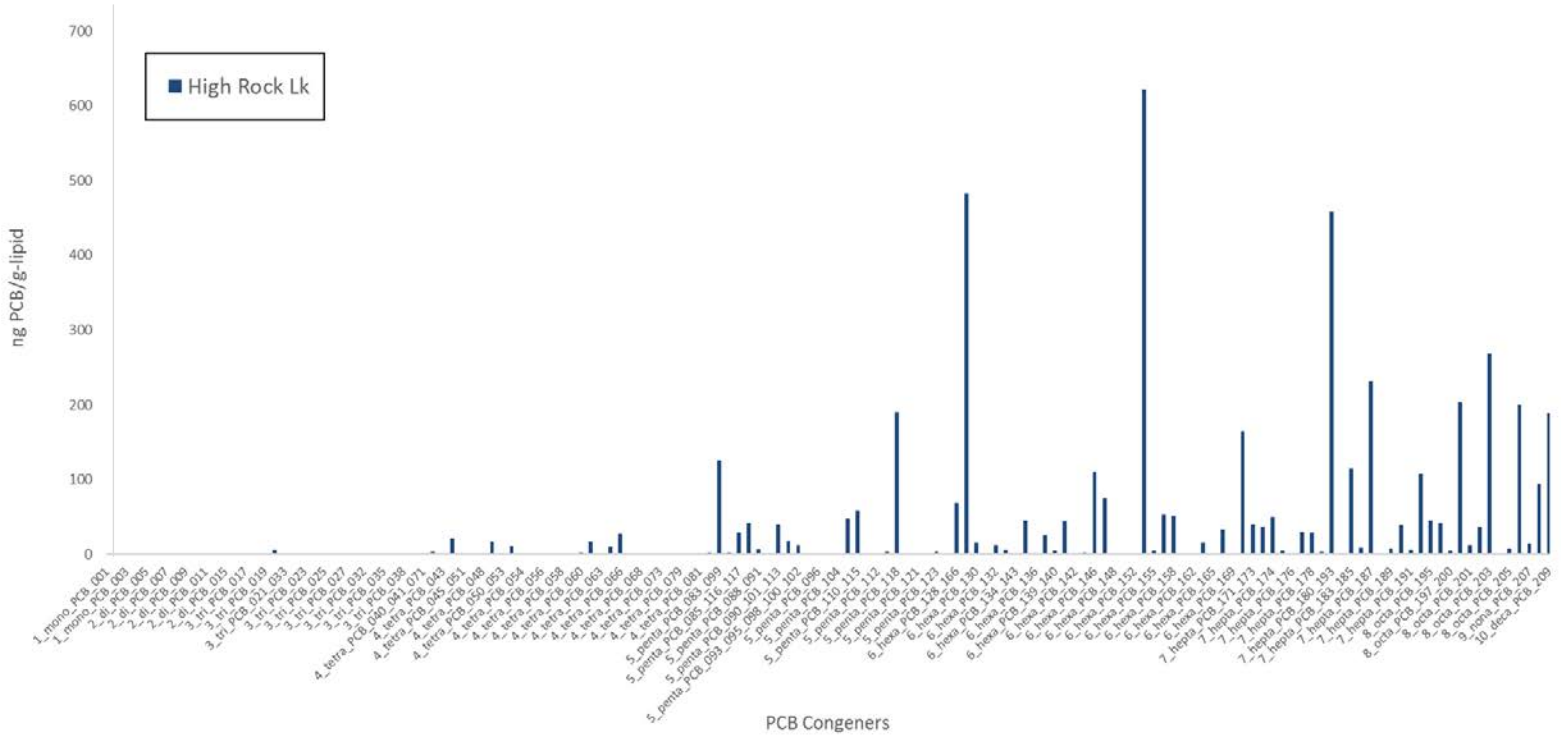
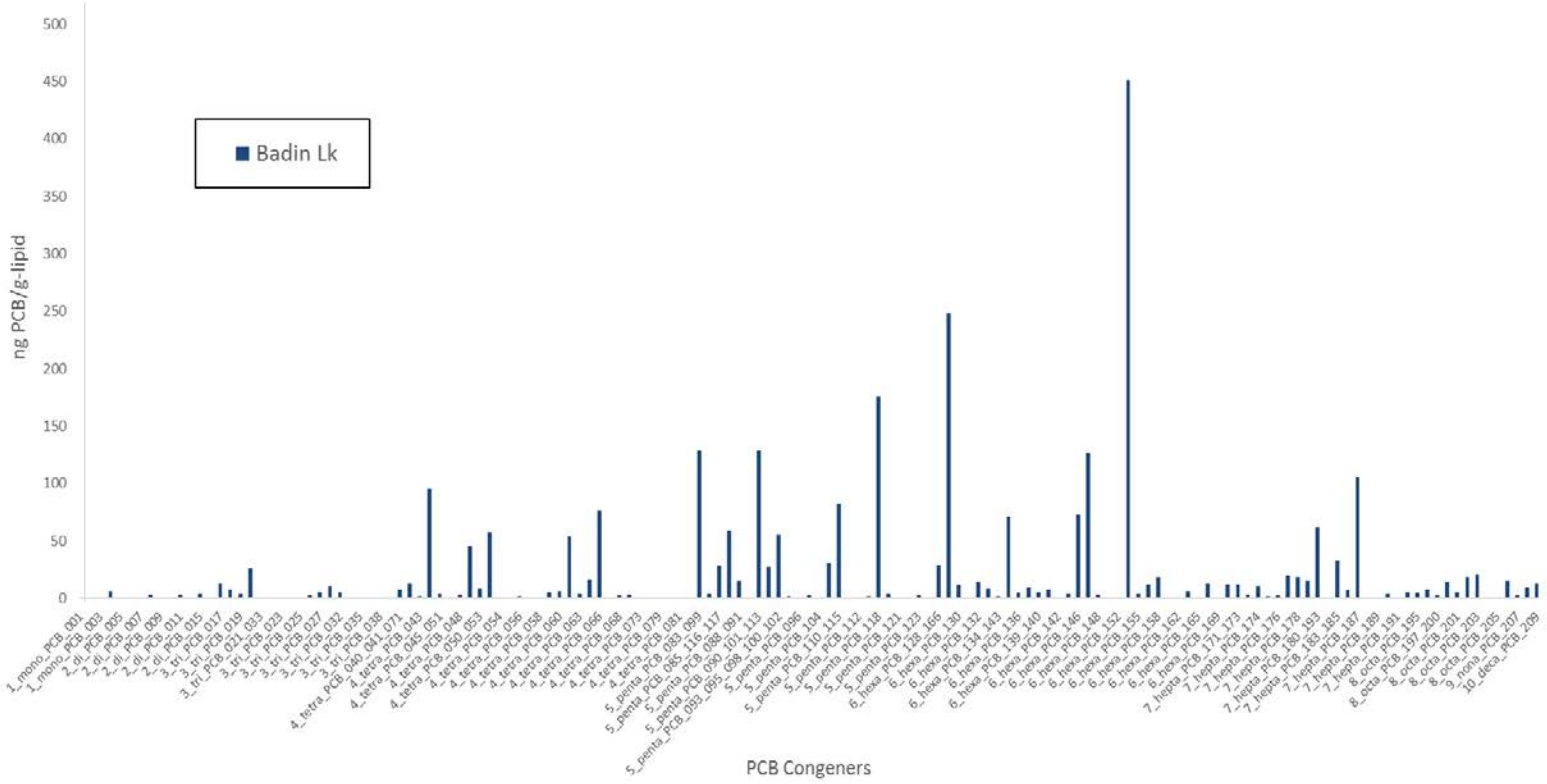


Figure 9. Catfish group lipid-normalized PCB congener profiles (as ng PCB/g-lipid) as the mean by waterbody for High Rock Lake, Badin Lake, Falls Reservoir and Lake Tillery (upstream → downstream).



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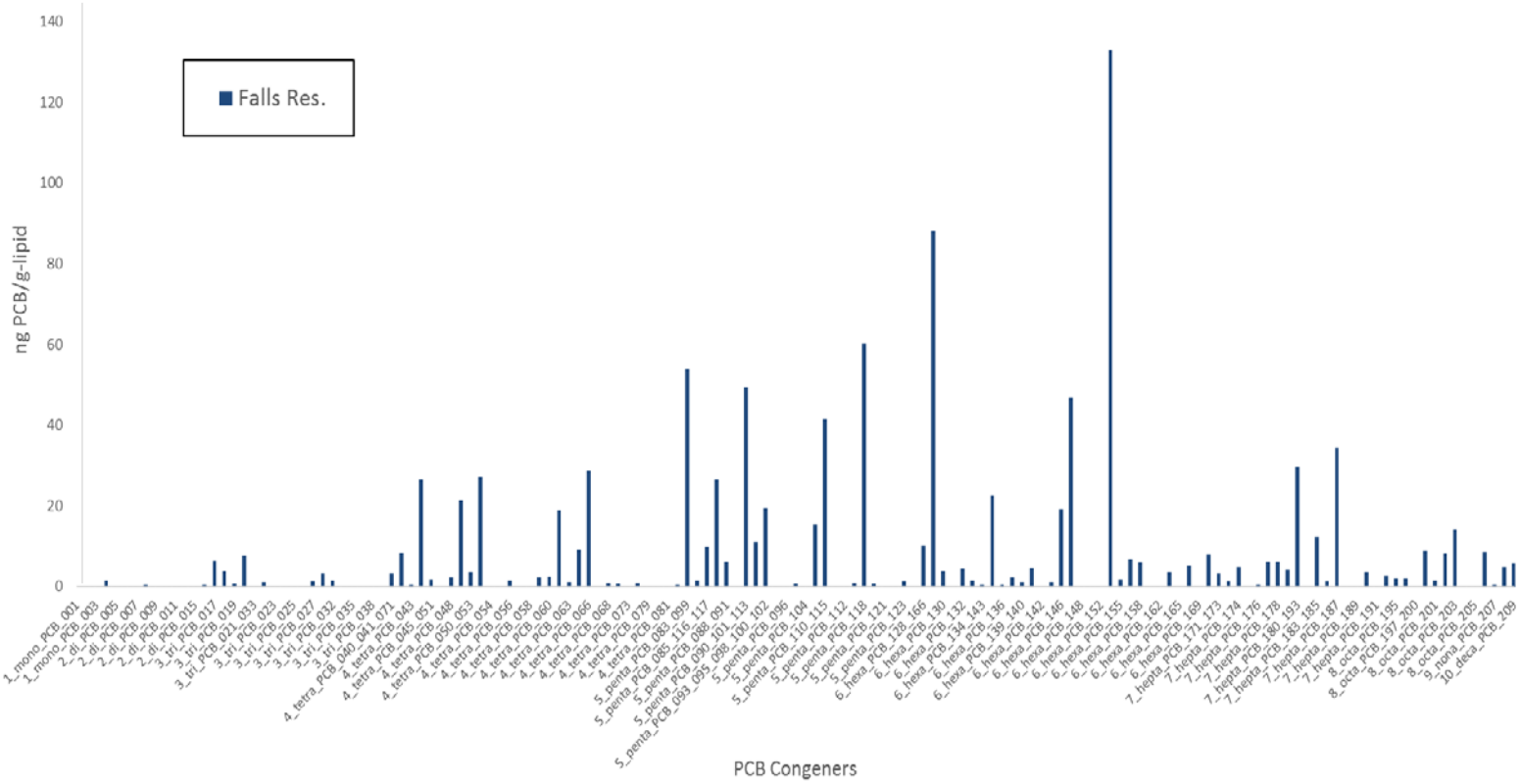

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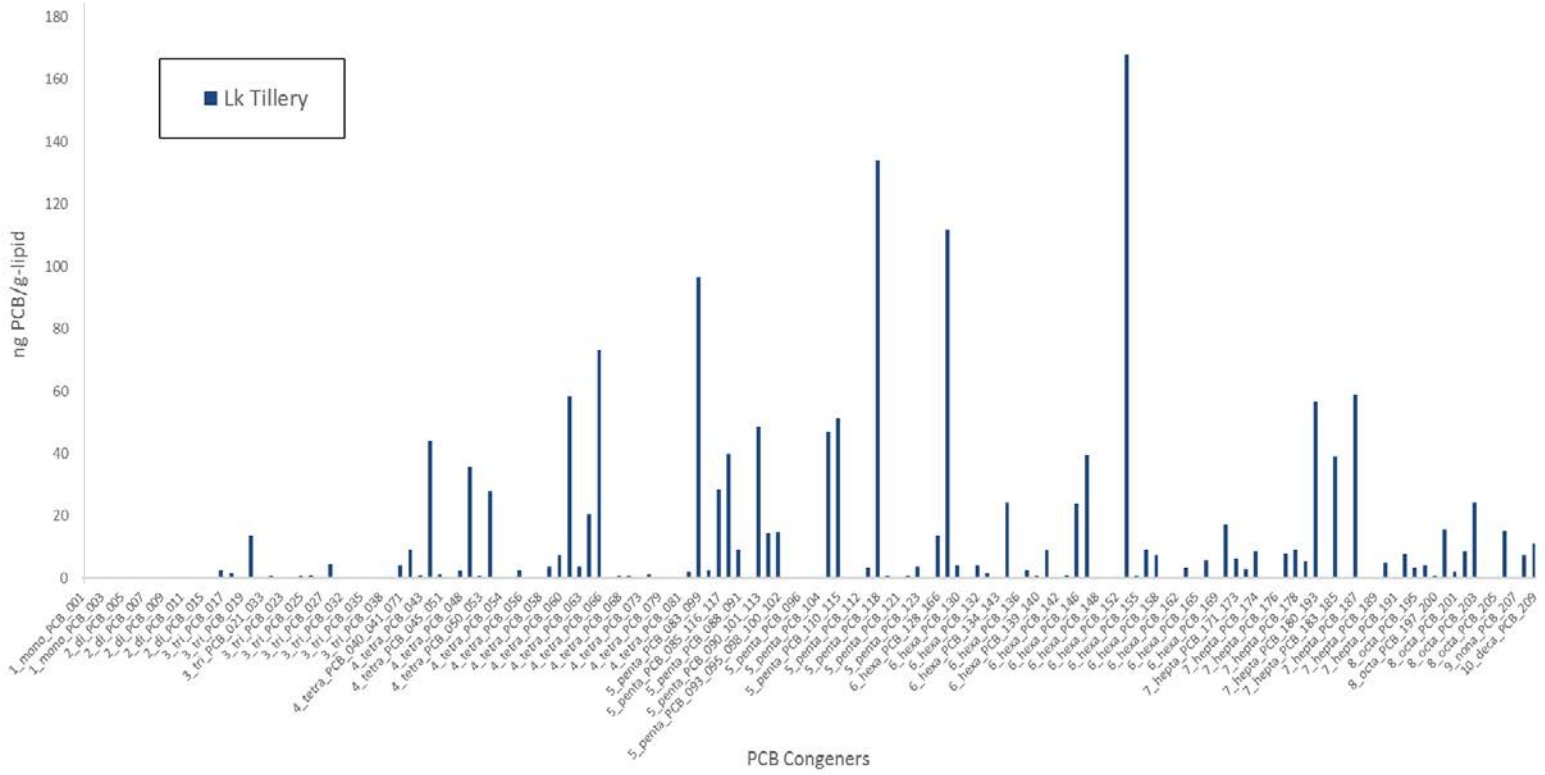

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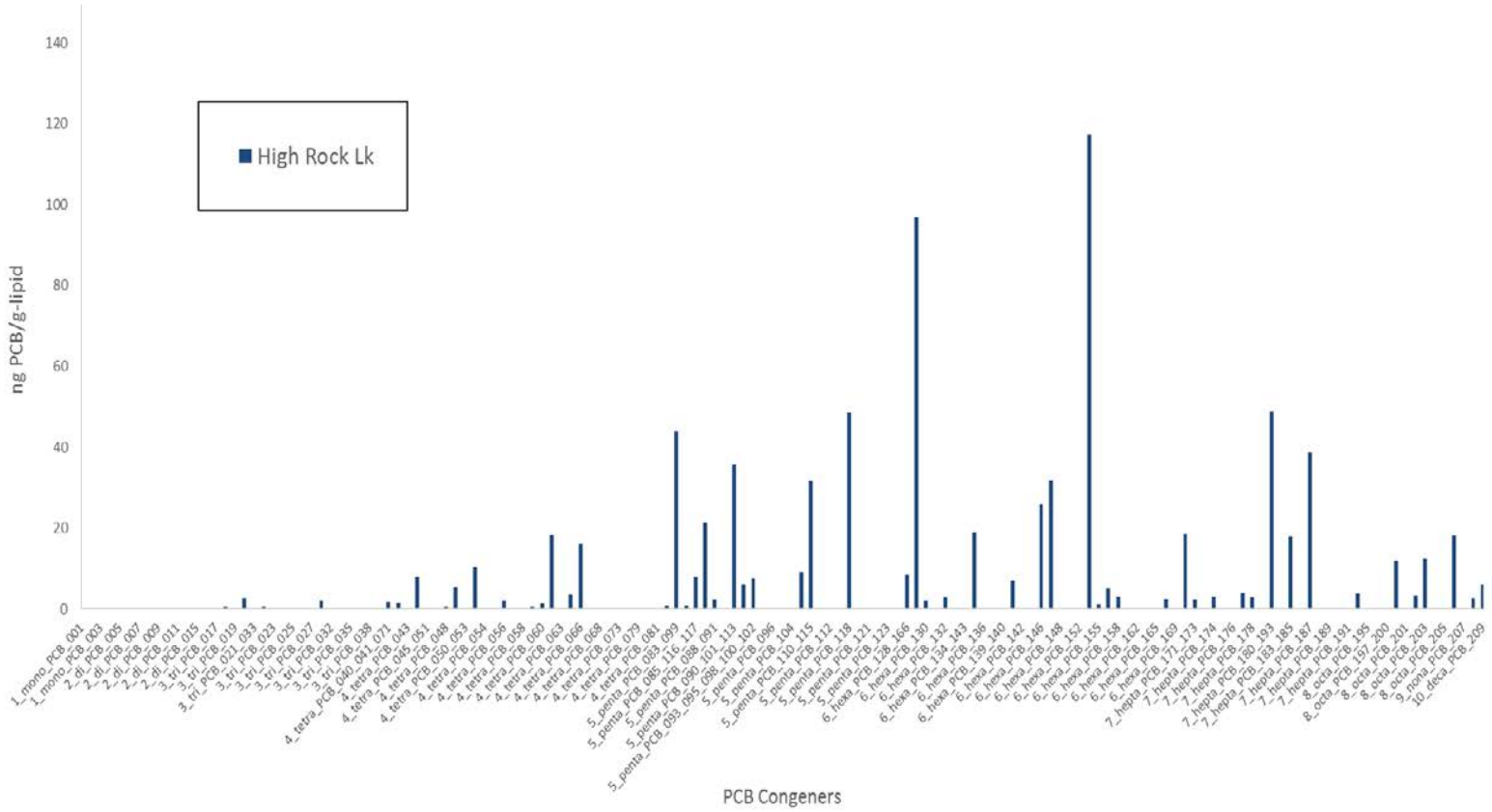
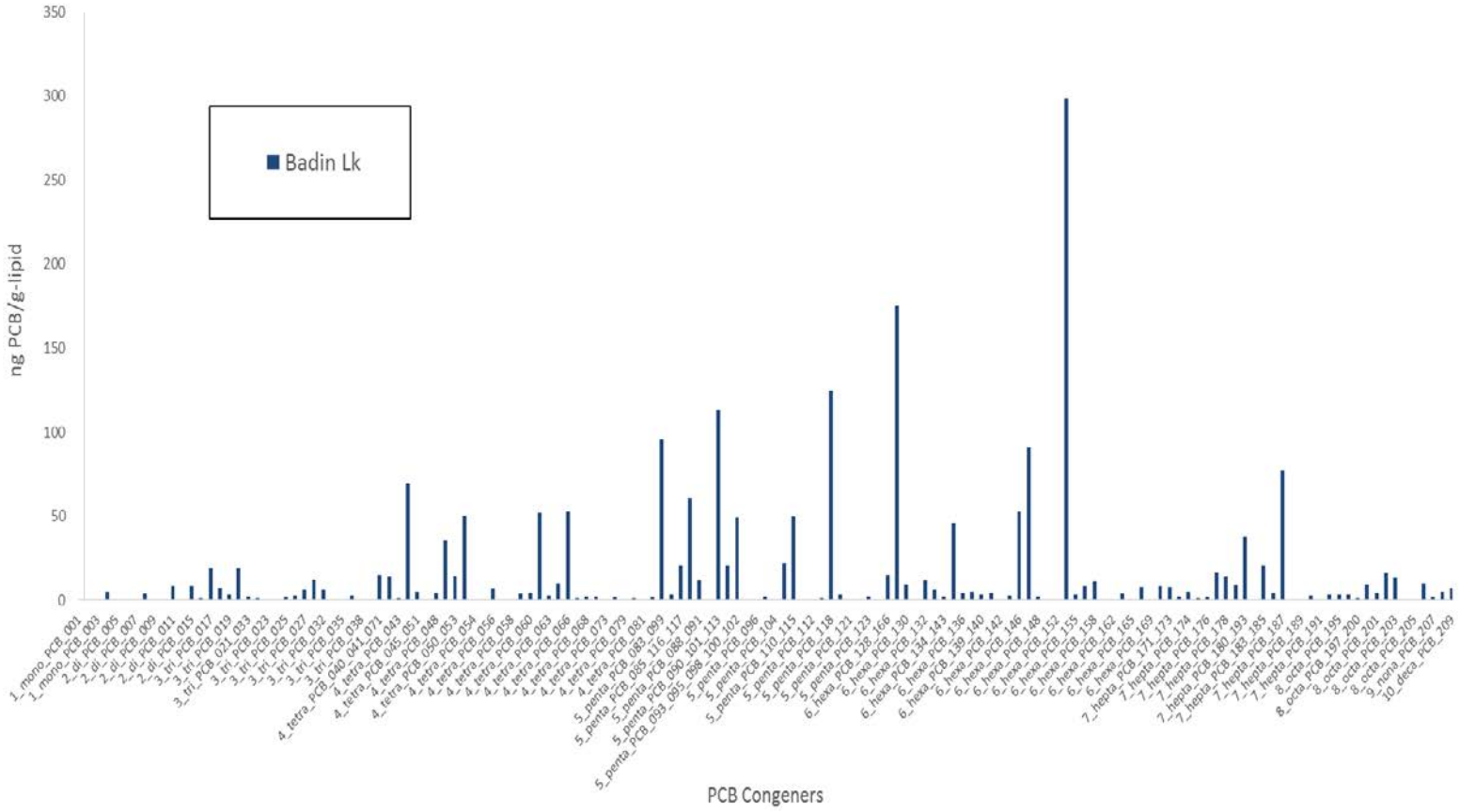


Figure 10. Sunfish group lipid-normalized PCB congener profiles (as ng PCB/g-lipid) as the mean by waterbody for High Rock Lake, Badin Lake, Falls Reservoir and Lake Tillery (upstream → downstream).



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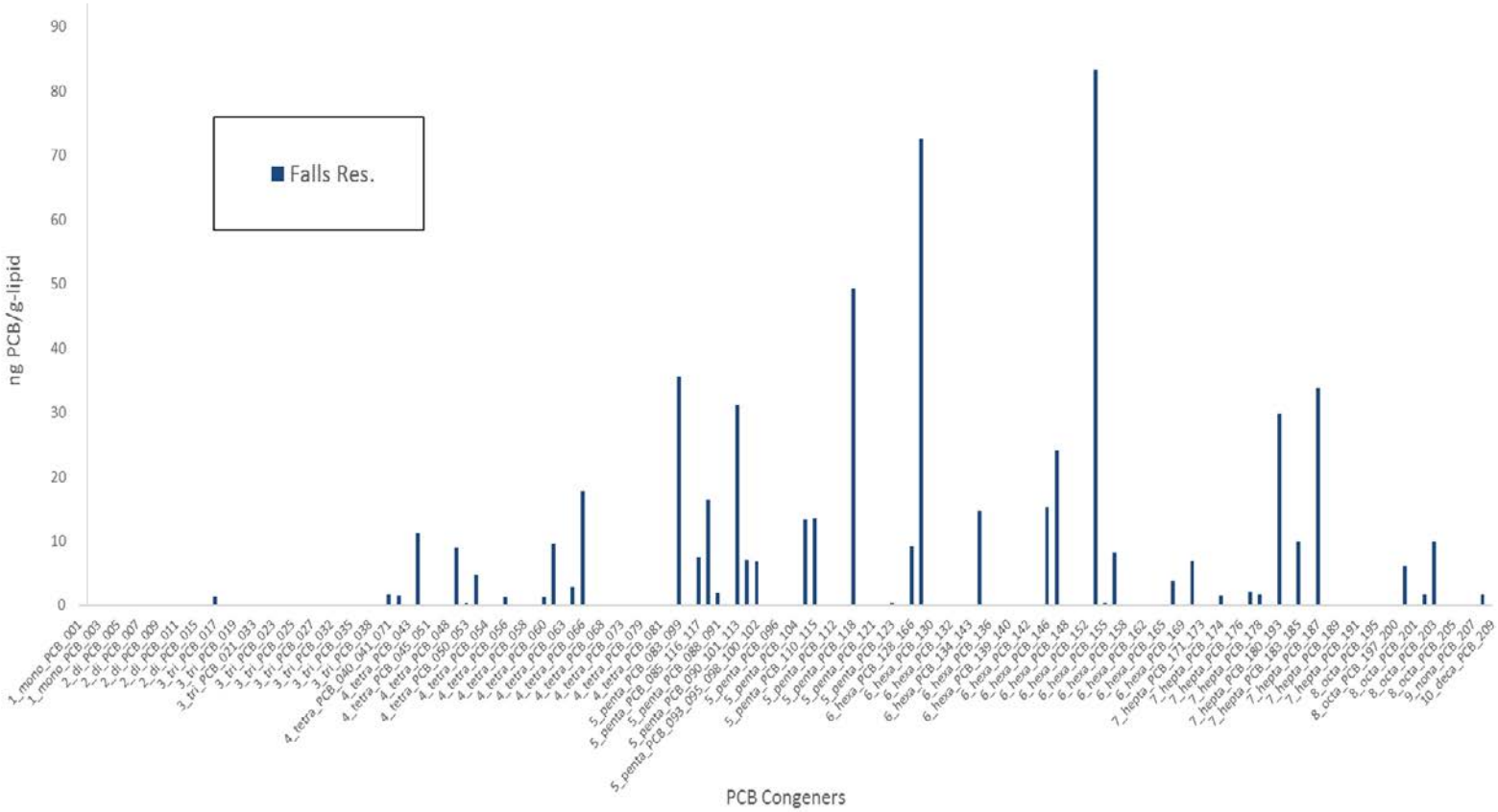

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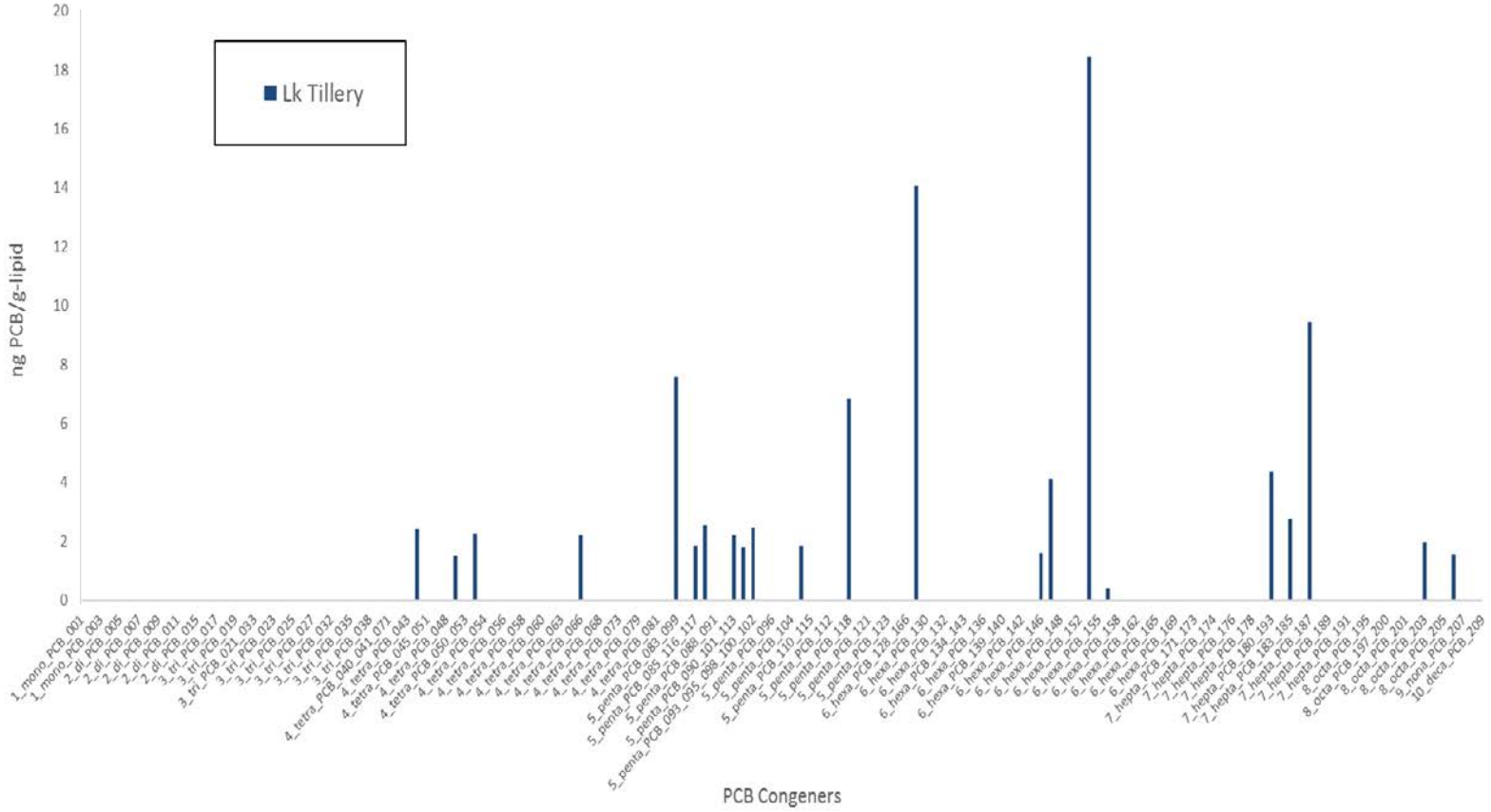

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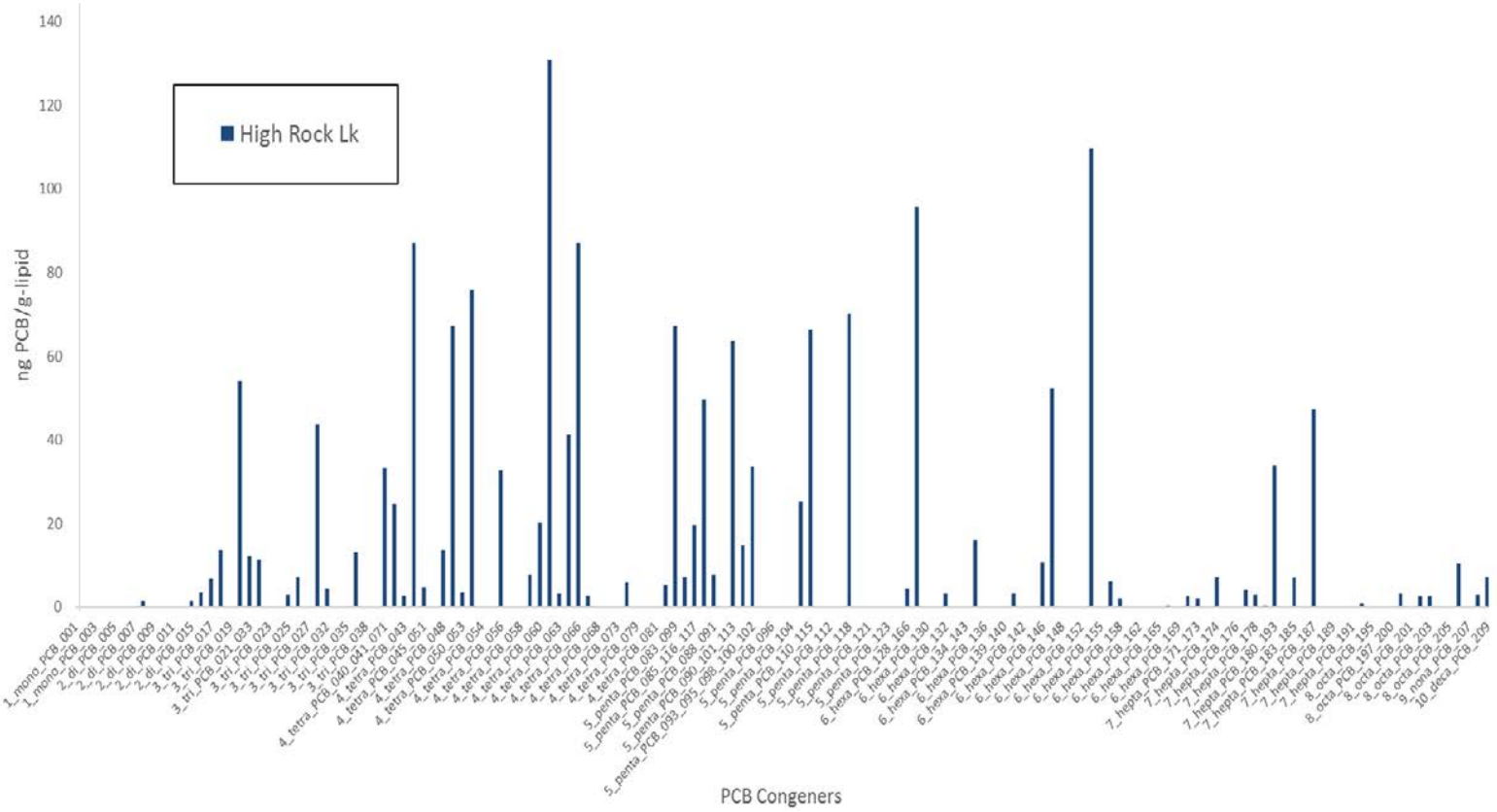

Figure 11. Crappie group lipid-normalized PCB congener profiles (as ng PCB/g-lipid) as the mean by waterbody for High Rock Lake, Badin Lake, Falls Reservoir and Lake Tillery (upstream → downstream). No crappie were collected in Falls Reservoir.

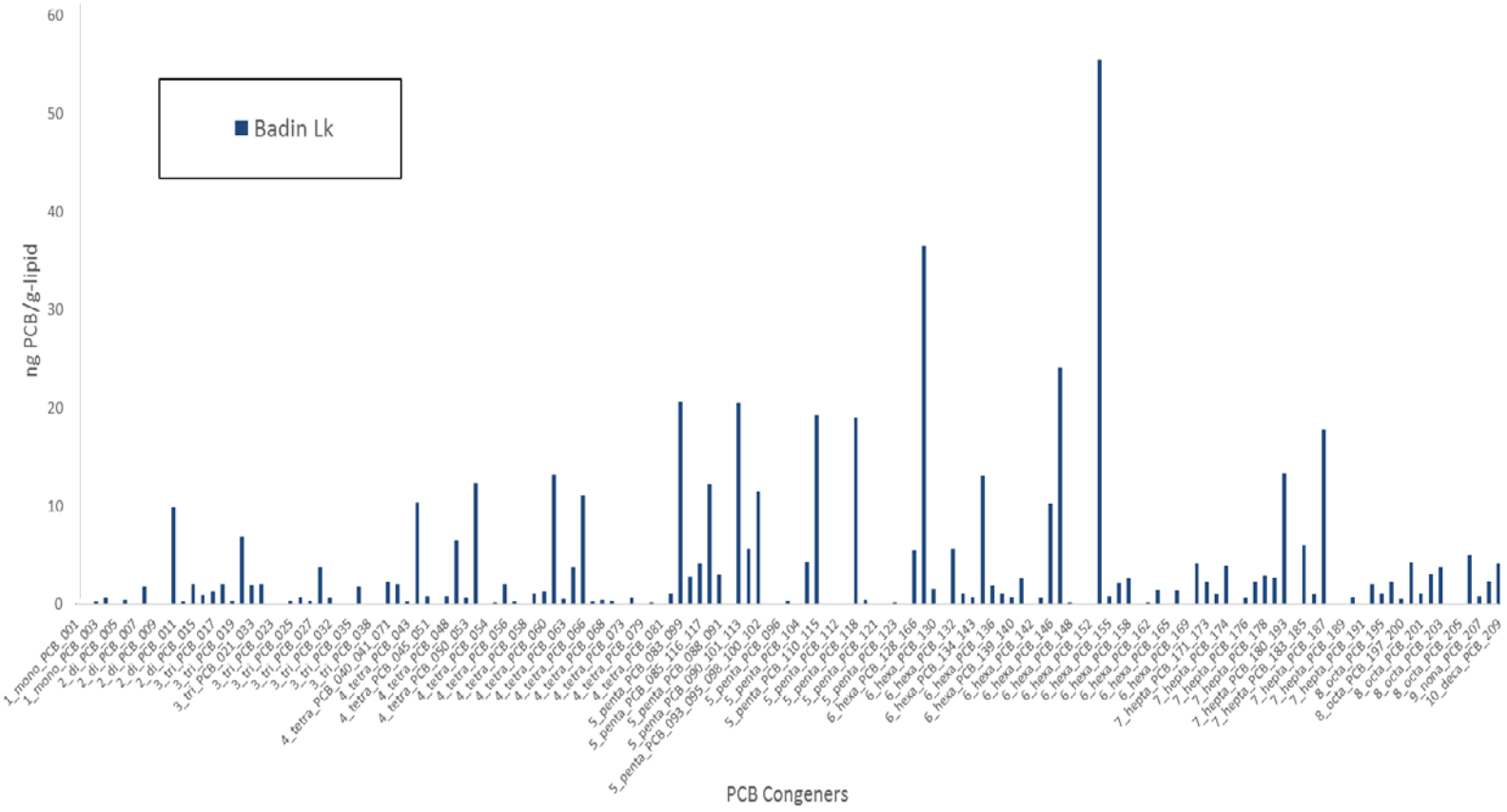

Figure 11 Continued

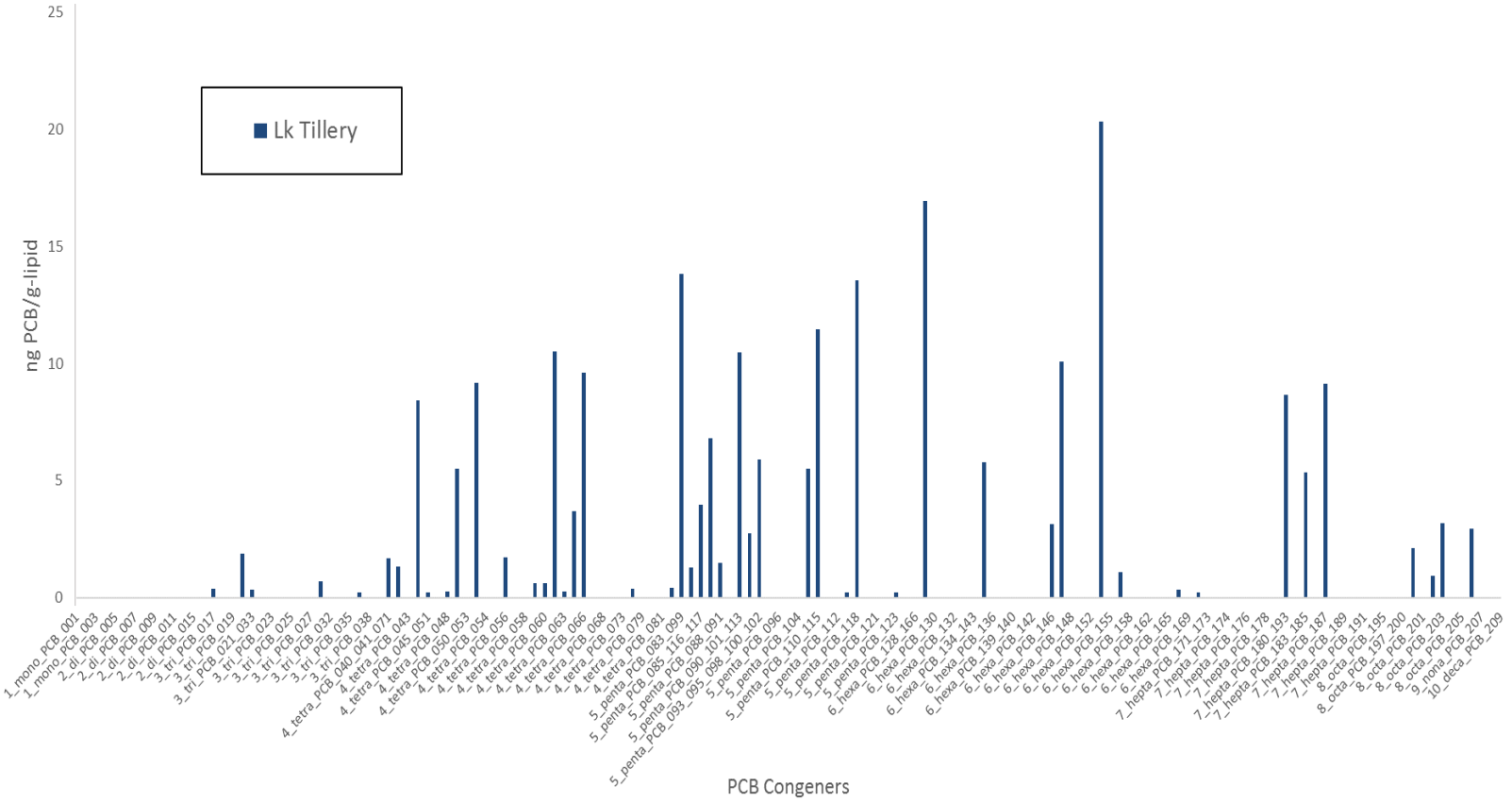

Figure 11 Continued

CHAPTER 3: Assessment of Alternatives to High Resolution Mass Selective Detection for Polychlorinated Biphenyl Congener Analysis in Fish and Passive Sampling Devices

Assessment of Alternatives to High Resolution Mass Selective Detection for Polychlorinated Biphenyl Congener Analysis in Fish and Passive Sampling Devices

ABSTRACT

We compared four mass selective detection systems, combined with gas chromatography separation techniques, for the analysis of fish tissue extracts and extracts prepared from the water column bioavailable fraction sampled with low-density polyethylene (LPDE) passive sampling devices (PSDs). The objective was to evaluate GC/MS instrument systems that could be used as a more cost-effective alternative to the expensive and not-widely available high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS) system specified by the U.S. Environmental Protection Agency's (EPA) Method 1668 for 209-congener PCB analysis of environmental matrices. System comparisons included analysis of fish fillet tissue extracts and water column bioavailable fraction extracts prepared from LDPE PSDs.

Passive sampling devices are a powerful tool for sampling water in a time-integrated manner for environmental risk assessment; they follow first-order kinetics with the surrounding aquatic environment to passively accumulate and concentrate the bioavailable fraction of a chemical, leading to an enhanced detection sensitivity. In the aquatic environment, PSDs provide a means to determine chronic average concentrations of bioavailable trace organic contaminants present in the water column that may not be identified by traditional grab or composite sampling methods. All extracts were analyzed for a sub-set of 21 of the 209-PCB congeners, and included at least one congener from the 2 to 10 PCB homolog groups, and spanned a log K_{ow} range of 5.07 – 8.18. While additional

research is warranted, we determined that the low-resolution tandem mass spectrometry systems (LRMSMS) appear to provide adequate congener separation, resolution, and detection sensitivity to be used with confidence for environmental risk assessments of all 209-PCB congeners. PSD-collected PCB fractions and fish fillet tissue PCB burdens sampled from the Yadkin-Pee Dee River of North Carolina indicated that water column associated PCB congener concentrations were low and not likely a significant source of the fish accumulation of PCBs. Site-specific Food Chain Multipliers (FCMs) were substantially less than the 2015 U.S. EPA national default TMFs, indicating the need for site-specific verification of trophic level PCB burdens. The assumption of default patterns of food web transfer and biomagnification factors may not provide robust estimates of trophic interactions.

INTRODUCTION

Accurate assessment of human or ecological risks associated with exposure to polychlorinated biphenyls (PCBs) requires congener-specific detection and quantitation, often in complex environmental matrices. Practical limitations experienced by risk assessors and risk managers when there are PCB exposure concerns, include a lack of familiarity with the complexity of the fate and transport of PCB mixtures in the environment, a lack of recognition of the need for congener-specific analyses, the relative high cost of the congener-specific analysis, a hesitancy to require its use, and a lack of availability of environmental laboratories with the analytical equipment and staff capable of providing the congener-specific data. To address some of these concerns, this study assessed less costly alternative

analytical instrument systems for their ability to provide PCB-congener-specific detection and quantitation capabilities suitable for use in environmental risk assessment.

When released into the environment, the original PCB mixture composition is uniquely modified under the influences of climatic conditions, and the properties of the individual abiotic and biotic environmental matrices with which the mixture interacts .[1, 2] The congener profile continues to be modified as the mixture partitions to each subsequent compartment. The consequence of these combined influences is the modification of the original PCB congener profile, a process referred to as "weathering".[1-4] The impact of these combined influences on a heavily weathered PCB release is that the resulting congener profile may differ substantially from that of the original release. A heavily weathered PCB release is generally characterized by a congener profile that consists of a higher proportion of the more chlorinated PCB congeners of the original mixture, is more recalcitrant, and often more toxic.[3, 5] These profile modifications are not limited to abiotic matrices. Differences in the rate of congener-specific uptake, limited metabolism and excretion, contribute to profile differences among biota within a food web. These properties are most evident in releases to the aquatic ecosystem, where sediment profiles may vary distinctly from profiles in each subsequent trophic level. In a food web, higher chlorinated congeners tend to persist and preferentially biomagnify in upper trophic level organisms, with the potential for increased toxic effects with trophic level.[4]

Historically, identification and quantitation of PCBs in environmental matrices has relied on the U.S. EPA's Method 8082 that specifies a gas chromatography-electron capture detector (GC/ECD) instrument system.[6] This method relies on native Aroclor commercial

mixtures as calibration standards, serving as the basis of the environmental sample PCB source characterization and quantitation. Sample results are reported as one or more Aroclors, with the Aroclor identification based on 3-5 peaks specified in the native Aroclor commercial mixtures. Relative peak responses are the basis of the sample Aroclor quantitation. The potential for Aroclor identification and PCB quantitation bias associated with the Aroclor pattern-matching in environmental matrices has long been recognized,[1, 2, 4, 7-9] and a suitable validated analytical alternative U.S. EPA method has been available since 1998.[10] Despite this availability, efforts to quantify the PCB burden in environmental matrixes, including those for environmental risk assessment, frequently continue to rely on the "Aroclor" analytical method.

In 1998, the U.S. EPA released Method 1668 that is capable of identification and quantitation of all 209 PCB congeners, eliminating the potential bias of using the Aroclor analysis on weathered environmental samples. To achieve 209 congener separation and detection sensitivity, Method 1668 specifies a high-resolution gas chromatograph / high resolution mass spectrometer (HRGC/HRMS) analytical system.[10] Despite the continuing evidence that Aroclor pattern matching cannot provide accurate characterization or risk estimates of PCBs in weathered environmental matrices,[3, 7, 8] the relative high cost and limited availability of laboratories with the capacity to run Method 1668 has resulted in a reluctance of regulatory and public health agencies to require it for environmental risk assessment.

One approach to the problem of acquiring suitable PCB data for risk assessment is to identify alternative analytical systems that provide suitable PCB-characterization at a reduced

cost. Advances in analytical instrumentation since the release of Method 1668 make this a viable option. This study assessed the ability of three different mass selective detector systems, coupled to gas chromatography, to provide PCB-congener-specific data of adequate detection sensitivity for environmental risk assessment. Instrument system performance was evaluated using PCB congener data collected from extracts of fish tissue and passive sampling device (PSD) water column samples.

The PSD samples used in this study were also used to characterize the bioavailable fraction of individual PCB congeners collected from the same surface waters as the fish. PSDs are a valuable tool for environmental risk assessment because a critical component is the determination of the bioavailable fraction of chemicals in various environmental matrices. The use of passive sampling devices, particularly for sampling in aquatic and sediment pore water matrices, provide a means to characterize the bioavailable fraction of lipophilic organic contaminants of concern. PSDs offer an advantage for the risk assessment of contaminants such as PCBs that have high biomagnification potential, and may be present at environmentally relevant concentrations that are below the detection sensitivity achievable with traditional grab sampling techniques. The PSD-collected water column PCB profiles were used to develop site-specific bioaccumulation factors and food chain multipliers for comparison to the U.S. EPA's national bioaccumulation model.[11, 12]

METHODS AND MATERIALS

PSD Kinetics. Passive sampling devices accumulate contaminants from the water column by first-order one-compartment model exchange kinetics.[13] Linear uptake rate

constants of dissolved chemicals are determined for each PSD material under laboratory-controlled conditions.[14] Uptake rate constants are used in the following equation to determine the freely dissolved concentration of a chemical sampled from the water:

$$C_{W,fd} = C_{PSD} / R_s$$

where $C_{W,fd}$ is the freely-dissolved chemical concentration in water (ng/L), C_{PSD} is the chemical concentration in the PSD (ng), R_s is the first-order uptake rate constant (L/day), and t (days) is the time period of PSD deployment.[13, 14]

PSD Preparation. The PSDs consisted of approximately 100 x 200 mm low-density polyethylene (LDPE) sheets. The PSD sheets were prepared for deployment by solvent rinsing and air drying, after which they were wrapped in combusted aluminum foil (baked at 300 ºC for approximately 18 hours to remove residual organics). The aluminum foil-wrapped PSDs were sealed in zip-type food-grade plastic bags for storage and transport to the deployment locations. Clean nitrile gloves were worn at all times while handling the PSDs.

PSD Deployment. The PSDs for collection of bioavailable PCBs were deployed in the Yadkin-Pee Dee River in North Carolina and South Carolina during June to August 2013. At each of the eight locations, two PSD sheets were placed into a circular mesh protective cage and suspended approximately mid water column depth in flowing reaches of river. The PSD cages were held suspended in the water column with a float affixed to one end and held in place by a brick weighted to the river bottom at the other end. To ensure retention during periods of high flow, the entire PSD cage was secured by rope to stationary objects (i.e., trees) on shore. All deployments were located 2-5 meters from the river bank, in isolated areas away from potential human disturbance. Each deployment was approximately 28 days

to allow significant PCB uptake from the water column. Clean nitrile gloves were worn during deployment and retrieval when handling the PSDs, and care was taken to minimize PSD exposure to the atmosphere. Date, time, temperature, location GPS coordinates and ambient weather conditions were recorded for each location during deployment and retrieval. Photographs were also taken and later used to help identify each deployment location. At the end of the deployment period, PSDs were retrieved from the water and rinsed with ambient surface water to remove any biosolids and other debris. The PSDs were wrapped in clean combusted aluminum foil, placed individually in pre-labelled zip-sealable plastic bags, and held on ice for transport to the laboratory. The PSDs were stored at -20 °C until extraction. PSDs were successfully deployed and retrieved from eight locations in the Yadkin-Pee Dee River during the summer of 2013 (Figure 1).

PSD Extraction and Analysis. Prior to extraction, the PSDs were gently brushed and rinsed with deionized water to remove extraneous particulate material. The PSDs were serially extracted three times over a 24-hour period, with a total of 150 mL pesticide-grade dichloromethane (DCM). The three extracts were combined and concentrated, filtered and stored at -20 °C until analysis. Just prior to analysis, the extracts were taken to a final concentrated volume of 0.5 mL under a stream of nitrogen. The PSD extracts were analyzed for a subset of 21 PCB congeners using an Agilent 6890 gas chromatograph (GC) and Agilent 5973 mass selective detector (MSD) operated in Selected Ion Monitoring (SIM) mode using a modified USEPA Method 1668. The PSD water column data were reported as ng congener per liter surface water (ng/L), at a 0.2 ng/L detection limit for each congener.

Fish Tissue Samples Collected for Fish Consumption Advisory Investigations. Fish were collected in four waterbodies of the North Carolina portion of the Yadkin-Pee Dee River in 2008 (Badin Lake), 2011 (High Rock Lake and Lake Tillery) and 2012 (Falls Reservoir) to evaluate human health risks associated with ingesting fish from these waterbodies. Each of the 131 tissue extracts was analyzed for 209-PCB congeners using the HRGC/HRMS Method 1668. The fish collection, tissue preparation, 209-congener analysis results and human health risk assessment are described in Chapter 2.[15]

Alternative Analytical System Investigations. Fish tissue extracts from the four Yadkin-Pee Dee River waterbodies generated for the fish consumption advisory investigations were also analyzed for a sub-set of 21 PCB congeners using two low-resolution gas chromatography systems. One system was equipped with an Agilent 5975 triple quadrupole (LRMS-A5975) mass selective detector (MSD) and the other, an Agilent A7000B tandem triple quadrupole detector system (LRMSMS-A7000). Additionally, 10 fish tissue extracts were selected for analysis by a second low resolution tandem triple quadrupole instrument system equipped with an Agilent 7010 MSD (LRMSMS-A7010). The Agilent 7010 tandem triple quadrupole MSD system was anticipated to provide an approximate order-of-magnitude increase in detection sensitivity for individual PCB congeners compared to the Agilent 7000B MSD. The mass selective detector sensitivities were *a priori* ranked as: HRMS > LRMSMS-A7010 > LRMSMS-A7000B > LRMS-A5975. Congener quantitation limits for each method were approximately 0.05 pg/L for the HRMS system, 5 pg/L for the LRMSMS-7010 system, 50 pg/L for the LRMSMS and 200 pg/L for the LRMS system. Eight of the 21-congener sub-set included co-eluting peaks in the 209-congener analyses,

resulting in contributions of as many as 33 congeners (Table 1). The potential contribution of the co-eluting congeners was included in the quantitative comparisons. The 21-congeners covered the range of PCB congener physicochemical properties and included at least one congener from each of the 2 to 10-chlorine homolog groups (di-deca-homologs). Log K_{ow}'s range from 5.24 to 8.18 (Table 2).[9]

Statistical Analysis. Statistical analyses of fish tissue and PSD data were accomplished with JMP® Pro 12.2 (2015 SAS Institute, Cary N.C.). Analysis of variance (ANOVA) with the Levene equal variance verification was used to identify statistically significant differences in PCB concentrations. Welch's test to identify significant differences was applied to data not meeting equal variance criteria. All significance levels were evaluated at 0.05 alpha (α). Means differences were identified with the Tukey's Honestly Significant Difference (HSD) test (equal variance) or the Wilcoxon Method (un-equal variance non-parametric data). The JMP® matched pairs analysis (paired *t*-test) was used to test for differences in the PCB measurements generated by the different instrument systems. The Wilcoxon signed rank test for non-parametric data was used to confirm the matched pairs analysis. Because of the low numbers of most targeted species in specific waterbodies, data clustering of related species was used to increase the robustness of the statistical and non-statistical comparisons (Table 2). White Crappie (*Pomoxis annularis*) and Black Crappie (*Pomoxis nigromaculatus*) were combined as "crappie", Redear Sunfish (*Lepomis microlophus*) and Redbreast Sunfish (*Lepomis auritus*) were combined as "Sunfish", Yellow Perch (*Perca flavescens*) and White Perch (*Morone americana*) were combined as "Perch", and "Catfish" included all ictalurid species identified as bottom feeding trophic level 3

omnivores, and included Blue Catfish (*Ictalurus furcatus*), Brown Bullhead (*Ameiurus nebulosus*), Channel Catfish (*Ictalurus punctatus*), Flat Bullhead (*Ameiurus platycephalus*) and White Catfish (*Ameiurus catus*). Largemouth Bass and Flathead Catfish (*Pylodictis olivaris*) each were retained as separate groups for analysis as trophic level 4 top predator piscivores.

RESULTS AND DISCUSSION

Comparison of Low Resolution and High Resolution Instrument Systems with Fish Tissue Extracts. The total 21-congener PCB concentrations (∑PCB-21) generated with the alternate instrument systems correlated well with those of the 209-congener HRMS analyses (∑HRMS-209) (Table S1). As wet-weight tissue comparisons for all combined samples, regression analysis for the LRMSMS-A7000 and LRMS-A5975 system data did not indicate deviations from linearity across the reported concentration range (all $R^2 \geq 0.95$). The R^2 values did not vary significantly when evaluated as the mean for the fish species or species groups analyzed (Largemouth Bass, catfish group, sunfish group or crappie group), by waterbody, or by species grouped by waterbody (all $R^2 \geq 0.92$).

Pair-wise comparisons of the mean ∑PCB-21 wet-weight concentrations for all combined tissue samples generated with the LRMSMS-A7000, LRMS-A5975 and HRMS instrument systems indicated significant differences for all comparisons, and the differences were confirmed with the Wilcoxon Signed Rank test for non-parametric data (all $p \leq 0.0239$) (Table 3). Pair-wise comparisons of the mean ∑PCB-21 as lipid-normalized concentrations

indicated no significant difference in the LRMSMS-A7000 and HRMS data (p = 0.1809), with all other comparisons being significant (p = <0.0001) (Table 4).

Pair-wise comparisons of the ∑PCB-21 wet-weight tissue data from the instrument systems for the fish species or species groups (Largemouth Bass and the catfish, crappie and sunfish groups) indicated significant differences in the LRMSMS-A7000 and HRMS concentrations for the Largemouth Bass and the sunfish group (Table 5). Differences in the LRMS-A5975 and HRMS concentrations were indicated for all but the crappie group. The LRMS-A5975 and LRMSMS-A7000 concentrations also differed for all but the crappie group. Pair-wise comparisons of the ∑PCB-21 lipid-normalized tissue data from the instrument systems for the fish species and groups indicated fewer differences in the LRMSMS-A7000 and HRMS comparisons (Table 6). A difference was detected in the sunfish data and confirmed by the Wilcoxon Signed Rank test. A difference was also indicated in the Largemouth Bass data for the LRMSMS-A7000 and HRMS comparisons in the non-parametric test, but not in the parametric comparison. Differences in the LRMS-A5975 and HRMS data were indicated for the Largemouth Bass and sunfish for the parametric analysis, and additionally for the catfish in the non-parametric comparison. The Largemouth Bass and catfish data differed for the LRMS-A5975 and LRMSMS-A7000 data.

Comparisons with the Agilent A7010 Next-Generation MSD Instrument System. Ten tissue extracts were selected for additional comparison of 21-congener PCB data generated with the LRMSMS-A7010 instrument system. The LRMSMS-A7010 system is a next-generation triple quadrupole mass spectrometer, anticipated to provide approximately

one order-of-magnitude enhanced PCB congener detection sensitivity compared to prior systems.

All 21-PCB congeners were detected in the 10 fish tissue extracts analyzed by the HRMS instrument system (Table 7). A fewer number of congeners were detected by the low-resolution systems, 18/21, 16/21 and 13/21, respectively by the LRMSMS-A7010, LRMSMS-A7000, and LRMS-A5975 systems. The ∑PCB-21 concentrations followed the same trends. The 10-extract mean ∑PCB-21 concentration for the HRMS system was 2494 ng/kg, 2794 ng/kg for the LRMSMS-A7010 system, 3237 ng/kg for the LRMSMS-A7000 system, and 3866 ng/kg for the LRMS-A5975 system, mean increases of 10%, 30% and 55%, respectively, compared to the HRMS concentration. Individual congener concentrations indicated a general pattern of decreasing individual mean congener concentrations with increasing system sensitivity (Figure 2). Pair-wise comparison of the individual congener concentrations generated by the four systems detected differences in the A5975 system data compared to the HRMS system data (Table 8.). No other differences in individual congener concentrations were detected. The differences observed in the LRMS-A5975 and HRMS data did not appear related to chlorination level or to K_{ow}, and was likely an artifact of the reduced congener-detection sensitivity of the LRMS-A5975 system.

The ∑PCB-21 data for the 10 tissue extracts demonstrates the influence of analytical system sensitivity to detect contaminant burden at low PCB concentrations (Figure 3.). At lower PCB contaminant burdens, the more sensitive detector systems produced higher reported total PCB concentrations compared to the lower-resolution systems. At mid-range PCB concentrations, in the range of their sensitivity limits, the lower-resolution systems

produced higher ∑PCB-21 concentrations than the higher-resolution systems. Matched-pairs analysis of the three low-resolution instrument systems ∑PCB-21 wet-weight data to the HRMS system detected a difference only for the LRMSMS-A7010 data (p = 0.0007), but inspection of the statistical parameters indicates a likely Type I error due to the minimal variability in the data sets (standard error = 31 ng/kg-ww) (Table 9). Supporting the similarity of the HRMS and LRMSMS-A7010 is the R^2 = 1.0, and the 95% confidence intervals (-229, -86.4). No other differences were indicated in pairwise comparisons of the other instrument systems for the ∑PCB-21 data. The same pair-wise comparison pattern was observed in the lipid-normalized tissue extracts (Table 10). The only detected difference for the lipid-normalized ∑PCB-21 concentrations were the LRMSMS-A7010 and HRMS comparison (p = 0.0266). As in the wet weight concentrations, the indication of difference was likely due to the limited variability seen in the data set (standard error = 17, 95% CI -82, -6.4) and did not appear to represent a true difference. No differences were detected in the other method comparisons.

Water Column Bioavailable PCB Fractions Collected by LDPE PSDs. Water column bioavailable PCB fractions were sampled from eight locations in the Yadkin-Pee Dee River in 2013 and analyzed for the sub-set of 21-PCB congeners (Table 11). The number of congeners detected in the individual PSD samples ranged from 1 to 10, and the number increased from the upstream to downstream locations (Figure 4). All detections were members of the tri to hexa homologs (3 to 6 chlorines, log K_{ow} 5.24 – 6.92). Location total bioavailable fractions increased from upstream to downstream, ranging from 0.010 to 7.34 ng/L ∑PCB-21.

Regression analysis of the Badin Lake 2013 PSD-collected water column bioavailable fraction congeners were compared to the mean 21-PCB fish tissue wet weight and lipid-normalized for Badin Lake catfish, Largemouth Bass, sunfish and crappie. The fish tissue concentrations were not correlated with the concentrations for the 21-PCB congeners (all R^2 <0.04). This may indicate that bioconcentration was not a significant source of the tissue PCBs.

The bioaccumulation factor (BAF) was calculated for each of the detected PCB congeners in the 2013 Badin Lake PSDs. The BAF (in L/kg-lipid) represents the ratio of concentration of a chemical in the tissue of an aquatic organism to the concentration of the chemical in water, when both the animal and its food source are exposed to the contaminant.[12] The tissue contaminant concentrations are lipid-normalized for comparison across trophic levels and species.

$$BAF = C_B/C_w$$

Where C_B is the lipid-normalized contaminant concentration in biota (ng PCB/kg-lipid), and C_w is the freely dissolved (bioavailable) contaminant concentration in the water column (ng/L). The contaminant freely dissolved fraction in the water column is that not sorbed to particulate organic carbon (POC) or to dissolved organic carbon (DOC). Biomagnification factors (BMF) represent the increase in concentration of a chemical from one trophic level to the next higher trophic level, as the predator consumes the prey organism. The BMF is unitless and is determined as,

$$BMF_{TL,n} = \frac{C_{t(TL,n)}}{C_{t(TL,n-1)}}$$

where $C_{t(TL,\ n)}$ is the tissue concentration of the predator, and $C_{t(TL,\ n-1)}$ is the tissue concentration of the prey, both as lipid-normalized concentrations. The food chain multiplier (FCM) represents the ratio of the biomagnification factors from one trophic level to the next as,

$$FCM = \frac{BMF_{TL,n}}{BMF_{TL,n-1}}$$

The FCMs for individual congeners were calculated for the trophic level 4 Largemouth Bass and the trophic level 3 catfish, crappie and sunfish groups using the Badin Lake 2013 PSD congener data and the 2008 Badin Lake fish tissue data. FCMs were calculated for pelagic species to eliminate potential effects of sediment/water fugacity associated with the bottom-feeding catfish group, as recommended by Mackay et al. (2016).[16] The Badin Lake FCM values were then compared to EPA's national default trophic level FCMs for the detected PCB congener log K_{ow}'s (Figure 5).[10, 12]

The calculated Badin Lake FCMs for the PSD-derived congener data were less than the U.S. EPA model default FCMs. This finding is may be associated with several data issues, including the low bioavailable PCB congener concentrations captured with the PSDs. The PSD data did indicate a bioavailable fraction of PCB congeners in the water column, but these concentrations were quite low. PCB levels in the fish tissue throughout the four waterbodies indicated substantial PCB burdens were widespread across the Yadkin-Pee Dee system, among all trophic guilds, including some insectivorous species. The low PSD-collected PCB concentrations may reflect decreasing water-column-associated PCB inputs to Badin Lake because of contaminated sediment removals in February 2013,[17] well after Badin

Lake fish collections in 2008, and prior to the PSD deployments in 2013. The low water column PCB concentrations may reflect the possibility of decreasing inputs from adjacent terrestrial sources to Badin Lake, or a deployment location that did not capture water column-associated PCBs representative of the fish exposures. A deployment period not adequate for congener equilibration is also possible, but unlikely. The ∑PCB-21 concentrations made-up a substantial proportion of the ∑PCB-209 burden in the Badin Lake Largemouth Bass, crappie and sunfish groups (51%, 47% and 53%, respectively), so this does not seem to provide an explanation of the low PSD concentrations (Table 12). Overall, these data may indicate that there is a substantial exposure source of these congeners for the fish, but it may not be associated with water column exposures. It may be that PCB burdens in Badin Lake fish, and possibly all four waterbodies studied, are incorporated in the food web and sourced primarily from sediments resulting from historical inputs. Other food-web-specific factors may also have contributed to the lower-than-anticipated BMFs, including growth dilution[1, 3] and omnivory, which have both been identified as a factor in lower BMFs in top predators.[16] The relative similarities in the predator and prey percent lipid values may also have contributed to the lower-than anticipated BMFs.[16]

CONCLUSIONS

We found that the current evolution of low-resolution gas chromatography tandem mass spectrometry systems show promise in providing PCB congener separation and detection sensitivity adequate for robust environmental risk assessment investigations. As these systems become more available in commercial and regulatory settings, the utilization of low-

resolution tandem mass selective detector systems should provide cost savings over the current systems specified in the U.S. EPA Method 1668 for 209 PCB-congener analysis. Recognition by the U.S. EPA and other regulatory agencies that low-resolution tandem mass selective detector systems can meet Method 1668 quality performance criteria with slight elevation in detection sensitivity would likely result in broader availability in environmental laboratories with the capability to provide 209-congener PCB analyses at a lower cost. This would result in an increase in the use of the 209-PCB congener analyses for contaminated site investigations, leading to improved characterization, delineation and attribution of environmentally-relevant PCB contamination. An increased emphasis on congener-specific PCB characterization would ultimately lead to more scientifically-sound environmental risk assessments and remediation efforts. I also suggest that 209-congener data gathered with a low-resolution tandem mass spectrometer system is a more tenable solution to providing cost-effective and scientifically valid congener-specific environmental risk assessments than those using a sub-set of the 209 PCB congeners.

Additional research is warranted to validate low-resolution tandem mass spectrometry systems for 209-PCB congener analysis on a variety of complex environmental matrices, ideally with co-analysis of samples with the high-resolution mass spectrometry systems specified by Method 1668.

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TABLES

Table 1. PCB congeners included in the 21-congener sub-set for alternative analytical system investigations, and the co-eluting congeners in the USEPA Method 1668 209-congener HRGC/HRMS analytical method.

NCSU-21 IUPAC No.	Co-Eluting Analytical Congeners	No. Chlorines	NCSU-21 Nomenclature	Co-eluting Congener(s) Nomenclature	Dioxin-Like TEF
8	PCB_8	2	2,4’-Dichlorobiphenyl		
18	PCB_18_30	3	2,2’,5-Trichlorobiphenyl	2,4,6-Trichlorobiphenyl	
28	PCB_20_28	3	2,3,3’-Trichlorobiphenyl	2,4,4’-Trichlorobiphenyl	
44	PCB_44_47_65	4	2,2’,3,5’-Tetrachlorobiphenyl	2,2’,3,4’-Tetrachlorobiphenyl + 2,3,5,6-Tetrachlorobiphenyl	
52	PCB_52	4	2,2’,5,5’-Tetrachlorobiphenyl		
66	PCB_66	4	2,3’,4,4’-Tetrachlorobiphenyl		
77	PCB_77	4	3,3’,4,4’-Tetrachlorobiphenyl		0.0001
101	PCB_90_101_113	5	2,2’,3,4’,5-Pentachlorobiphenyl	2,2’,4,5,5’-Pentachlorobiphenyl + 2,2’,4,5,5’-Pentachlorobiphenyl	
105	PCB_105	5	2,3,3’4,4’-Pentachlorobiphenyl		0.00003
118	PCB_118	5	2,3’,4,4’,5-Pentachlorobiphenyl		0.00003
126	PCB_126	5	3,3’,4,4’,5-Pentachlorobiphenyl		0.1
128	PCB_128_166	6	2,2’,3,3’,4,4’-Hexachlorobiphenyl	2,3,4,4’,5,6-Hexachlorobiphenyl	

Table 1 continued

NCSU-21 IUPAC No.	Co-Eluting Analytical Congeners	No. Chlorines	NCSU-21 Nomenclature	Co-eluting Congener(s) Nomenclature	Dioxin-Like TEF
138	PCB_129_138_160_163	6	2,2',3,3',4,5-Hexachlorobiphenyl	2,2',3,4,4',5'-Hexachlorobiphenyl + 2,3,3',4,5,6-Hexachlorobiphenyl + 2,3,3',4',5,6-Hexachlorobiphenyl	
153	PCB_153_168	6	2,2',4,4',5,5'-Hexachlorobiphenyl	2,3',4,4',5',6-Hexachlorobiphenyl	
170	PCB_170	7	2,2',3,3',4,4',5-Heptachlorobiphenyl		
180	PCB_180_193	7	2,2',3,4,4',5,5'-Heptachlorobiphenyl	2,3,3',4',5,5',6-Heptachlorobiphenyl	
187	PCB_187	7	2,2',3,4,5,5',6-Heptachlorobiphenyl		
195	PCB_195	8	2,2',3,3',4,4',5,6-Octachlorobiphenyl		
201	PCB_201	8	2,2',3,3',4,5',6,6'-Octachlorobiphenyl		
206	PCB_206	9	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl		
209	PCB_209	10	Decachlorobiphenyl		

Table 2. Physicochemical properties and their weight-fraction in native Aroclor commercial mixtures of the 21-congener subset used for alternative analytical method investigations.

NCSU-21 IUPAC No.	MW (g/mol)	VP (atm)	Solubility (µg/L)	Log Kow	H (atm-m3/mol)	Congener Weight Fraction of the Native Aroclor Mixture							
						Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262
8	223.09	195	1510	5.06	3.24E-04	12.34	10.72	8.30	7.05	0.54	0.09	0.04	0.12
18	257.53	892	448	5.24	3.16E-04	0.78	4.86	10.81	8.53	3.79	0.17	0.05	0.15
28	257.53	273	83.3	5.67	2.88E-04	0.69	4.33	9.42	7.58	4.69	0.13	0.03	0.12
44	291.97	145	76.8	5.75	2.29E-04	0.26	2.30	5.73	4.48	7.65	1.60	0.04	0.08
52	291.97	19	33.5	5.84	3.16E-04	0.22	1.85	4.62	3.53	6.26	3.11	0.24	0.14
66	291.97	453	4.52	6.2	2.04E-04	0.21	1.73	0.38	3.39	6.53	2.29	0.02	0.07
77	291.97		0.967	6.36	1.03E-04	0.01	0.17	0.00	0.31	0.47	0.12	0.00	0.00
101	326.41	353	9.41	6.38	2.45E-04	0.07	0.33	0.04	0.69	2.06	6.77	3.13	1.13
105	326.41	698	1.88	6.65	9.93E+14	0.05	0.22	0.00	0.47	1.53	5.18	0.22	0.18
118	326.41	949	1.97	6.74	1.26E-04	0.08	0.29	0.00	0.66	2.32	10.47	0.49	0.16
126	326.41			6.89	8.13E+14	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
128	360.85	354	0.293	6.74	1.05E-04	0.00	0.00	0.00	0.02	0.10	1.62	0.54	0.19

Table 2 Continued

NCSU-21 IUPAC No.	MW (g/mol)	VP (atm)	Solubility (µg/L)	Log Kow	H (atm-m3/mol)	Congener Weight Fraction of the Native Aroclor Mixture							
						Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262
138	360.85	205	1	6.73	1.41E-04	0.00	0.08	0.00	0.01	0.49	7.13	9.10	4.30
153	360.85	654	0.884	6.92	1.66E-04	0.00	0.05	0.00	0.06	0.33	3.53	9.39	7.10
170	395.29	367	0.119	7.27	8.71E+13	0.00	0.00	0.00	0.00	0.08	0.44	4.11	3.26
180	395.29	499	0.225	7.36	1.07E-04	0.00	0.01	0.00	0.00	0.12	0.58	11.92	14.79
187	395.29	59		7.17	2.04E-04	0.00	0.01	0.00	0.00	0.09	0.17	5.40	9.16
195	429.73	979		7.56	1.17E-04	0.00	0.00	0.00	0.00	0.00	0.00	0.84	1.43
201	429.73			7.62	1.32E-04	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.62
206	464.17	102	0.00267	8.09	8.71E+13	0.00	0.00	0.00	0.00	0.00	0.03	0.53	1.26
209	498.61		0.000128	8.18	1.12E-04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Weight-Fraction of NCSU-21 + Co-Eluting Congeners						14.71	26.90	39.28	36.78	37.02	43.39	46.33	44.21

Table 3. Matched pairs comparison of study mean tissue extract concentrations in ng/kg wet-weight for the 21-congener PCB data generated by the three instrument systems. Analysis was verified by Wilcoxon Ranked Sign test for non-parametric data. $\alpha = 0.05$, **bold** value indicates significant difference.

		Tissue Extract Mean ∑PCBs as NCSU-21-Congeners (ng/kg ww)			*Prob* > |*t*|			Correlation		
Samples	No. Samples	HRMS	LRMSMS A7000	LRMS A5975	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS
Yadkin-Pee Dee Fish Tissue Extracts	131	10,335	10,662	12,024	**0.0186**	**<0.0001**	**<0.0001**	0.9937	0.9833	0.9940
Wilcoxon Signed Rank (non-parametric)					**0.0239**	**<0.0001**	**<0.0001**			

Table 4. Matched pairs comparison of study mean lipid-normalized tissue extract concentrations in ng PCB/g-lipid for the 21-congener PCB data generated by the three instrument systems. Analysis was verified by Wilcoxon Ranked Sign test for non-parametric data. $\alpha = 0.05$, **bold** value indicates significant difference.

		Tissue Extract Mean ∑PCBs as NCSU-21-Congeners (ng PCB/g-lipid)			*Prob* > |*t*|			Correlation		
Samples	No. Samples	HRMS	LRMSMS A7000	LRMS A5975	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS
Yadkin-Pee Dee Fish Tissue Extracts	131	1,028	1,068	1,211	0.1809	**0.0016**	**<0.0001**	0.9982	0.9974	0.9987
Wilcoxon Signed Rank (non-parametric)					**0.0308**	**<0.0001**	**<0.0001**			

Table 5. Summary of matched pairs statistical analysis of species mean tissue 21-congener PCB concentrations for the three analytical methods, as ng/kg wet-weight. $t \leq 0.05$ indicates statistically significant difference in reported concentrations by the analytical methods (**bold** values).

				Tissue Extract Mean ∑PCBs as NCSU-21-Congeners (ng/kg ww)			*Prob > |t|*			Correlation		
Species	Trophic Guild	Trophic Status	No. Samples	HRMS	LRMSMS A7000	LRMS A5975	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS
Largemouth Bass	Piscivore	Top Predator	38	8,989	9,350	10,860	**0.0121**	**<0.0001**	**0.0002**	0.9916	0.9663	0.9762
Catfish	Omnivore	Bottom Feeder	43	18,449	18,898	20,823	0.2503	**0.0006**	**<0.0001**	0.9797	0.9805	0.9895
Sunfish	Insectivore	Middle Feeder	13	3,192	3,412	3,952	**0.0215**	**0.0051**	**0.0129**	0.9898	0.9708	0.9795
Crappie	Piscivore	Middle Feeder	21	1,606	1,499	1,633	0.0797	0.8094	0.1034	0.9797	0.9805	0.9895

Table 6. Summary of matched pairs statistical analysis of species mean tissue 21-congener PCB concentrations for the three analytical methods, as ng PCB/g-lipid. $t \leq 0.05$ indicates statistically significant difference in reported concentrations by the analytical methods (**bold** values).

				Tissue Extract Mean ∑PCBs as NCSU-21-Congeners (ng PCB/g-lipid)				*Prob* > |*t*|		Correlation		
Species	Trophic Guild	Trophic Status	No. Samples	HRMS	LRMSMS A7000	LRMS A5975	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS	HRMS vs. LRMSMS	HRMS vs. LRMS	LRMSMS vs. LRMS
Largemouth Bass	Piscivore	Top Predator	38	1,084	1,119	1,306	0.0524	**<0.0001**	**0.0002**	0.9911	0.9809	0.9831
Catfish	Omnivore	Bottom Feeder	43	1,529	1,625	1,801	0.2745	0.1006	**0.0288**	0.9992	0.9989	0.9998
Sunfish	Insectivore	Middle Feeder	13	579	608	712	**0.0175**	**0.0160**	0.0501	0.9972	0.9829	0.9835
Crappie	Piscivore	Middle Feeder	21	498	449	486	0.2622	0.8354	0.2269	0.9604	0.9572	0.9954

Table 7. Mean 21-congener PCB concentrations for 10 fish tissue extracts analyzed by EPA Method 1668 using the HRMS instrument system and analyzed by three low-resolution mass selective detector instrument systems. Data expressed as mean ng/kg wet-weight.

NCSU-21-PCB Congeners	HRMS		LRMSMS_A7010		LRMSMS_A7000B		LRMS_A5975	
	Mean Concentration	No. Detects	Mean Concentration	No. Detects	Mean Concentration	No. Detects	Mean Concentration	No. Detects
PCB_8	11	9	28	1		0		0
PCB_18_30	13	10	31	1		0		0
PCB_20_28	40	10	51	6	78	3	95	3
PCB_44_47_65	114	10	129	8	203	5	260	4
PCB_52	105	10	129	8	129	7	180	4
PCB_66	110	10	145	8	210	5	255	4
PCB_77	6	9	10	6		0		0
PCB_90_101_113	205	10	210	9	232	9	276	9
PCB_105	67	10	88	8	122	6	150	5
PCB_118	237	10	234	10	251	10	319	8
PCB_126	10	7		0		0		0
PCB_128_166	57	10	71	6	86	6	125	3
PCB_129_138_160_163	403	10	407	10	471	9	579	9
PCB_153_168	516	10	569	9	634	9	752	9
PCB_170	64	10	106	5	107	6	230	3
PCB_180_193	166	10	186	9	234	7	321	7
PCB_187	192	10	197	10	240	9	323	7
PCB_195	37	10		0	120	1		0
PCB_201	37	10		0		0		0
PCB_206	52	10	78	6	68	2		0
PCB_209	53	10	79	6	53	2		0
∑PCBs / Ave. No. Detects	2494	9.8	2749	6.0	3237	4.6	3866	3.6
% of HRMS	100%		110%		130%		155%	

Table 8. ANOVA *p*-values for mean 21-congener PCB concentrations (as ng/kg-ww) for 10 fish tissue extracts analyzed by the HRMS instrument system and by three low-resolution mass selective detector instrument systems. *p*-value ≤0.05 indicates statistically significant difference in concentrations (**bold** values).

NCSU-21-PCB Congeners	HRMS vs. LRMSMS_A7010	HRMS vs. LRMSMS_A7000B	LRMSMS_A7010 vs. LRMSMS_A7000B	HRMS vs. LRMS_A5975
	Significance Test *p*-value (α = 0.05)			
PCB_8	0.1374			
PCB_18_30	0.2573			
PCB_20_28	0.3028	0.0519	0.1198	**0.0142**
PCB_44_47_65	0.6567	0.1413	0.3048	**0.0403**
PCB_52	0.3986	0.4620	0.6844	0.1039
PCB_66	0.3069	0.0574	0.2128	**0.0475**
PCB_77	0.0677			
PCB_90_101_113	1.0000	0.5673	0.5955	0.2356
PCB_105	0.1972	0.0507	0.1962	**0.0235**
PCB_118	0.9698	0.8500	0.7336	0.4234
PCB_126				
PCB_128_166	0.1155	0.1147	0.6879	**0.0344**
PCB_129_138_160_163	0.9698	0.5675	0.5401	0.3477
PCB_153_168	0.6534	0.4379	0.7572	0.2364
PCB_170	0.0979	0.2509	0.7832	**0.0341**
PCB_180_193	0.5131	0.2410	0.5251	0.0501
PCB_187	0.8797	0.4869	0.5956	0.2612
PCB_195		0.1356		
PCB_201				
PCB_206	0.2321	0.3337	1.0000	
PCB_209	0.0925	0.5912	0.3115	

Table 9. Matched-pairs statistical analysis of ∑PCB-21 data for 10 tissue extracts generated by the high-resolution and low-resolution instrument systems. PCB data as ng/kg-wet weight (ww). α = 0.05. HRMS = high-resolution mass selective detector (MSD), LRMS = low-resolution MSD, LRMSMS = low-resolution tandem MSD

		Tissue Extract Mean ∑PCBs as NCSU-21-Congeners (ng/kg ww)				*Prob* > |*t*|					
Samples	No. Samples	HRMS	LRMSMS A7010	LRMSMS A7000	LRMS A5975	HRMS vs. LRMSMS -A7010	HRMS vs. LRMSMS -A7000	HRMS vs. LRMS	LRMSMS -A7010 vs. LRMSMS -A7000	LRMSMS -A7010 vs. LRMS	LRMSMS -A7000 vs. LRMS
Yadkin-Pee Dee Fish Tissue Extracts	10	2,490	2,332	2,379	2,641	**0.0007**	0.2693	0.5081	0.6380	0.1781	0.1588
Wilcoxon Signed Rank (non-parametric)						**0.0039**	0.3223	0.6250	0.9219	0.5566	0.1934

Correlations					
HRMS vs. LRMSMS - A7010	HRMS vs. LRMSMS - A7000	HRMS vs. LRMS	LRMSMS - A7010 vs. LRMSMS - A7000	LRMSMS - A7010 vs. LRMS	LRMSMS - A7000 vs. LRMS
0.9979	0.9908	0.9825	0.9871	0.9816	0.9807

Table 10. Matched-pairs statistical analysis of ∑PCB-21 data for 10 tissue extracts generated by the high-resolution and low-resolution instrument systems. PCB data as ng PCB/g-lipid. α = 0.05. HRMS = high-resolution mass selective detector (MSD), LRMS = low-resolution MSD, LRMSMS = low-resolution tandem MSD

		Tissue Extract Mean ∑PCBs as NCSU-21-Congeners (ng PCB/g-lipid)				*Prob* > |*t*|					
Samples	No. Samples	HRMS	LRMSMS A7010	LRMSMS A7000	LRMS A5975	HRMS vs. LRMSMS -A7010	HRMS vs. LRMSMS -A7000	HRMS vs. LRMS	LRMSMS -A7010 vs. LRMSMS -A7000	LRMSMS -A7010 vs. LRMS	LRMSMS -A7000 vs. LRMS
Yadkin-Pee Dee Fish Tissue Extracts	10	565	521	537	599	**0.0266**	0.3577	0.6160	0.5895	0.2219	0.3250
Wilcoxon Signed Rank (non-parametric)						**0.0039**	0.3223	0.8457	0.7695	0.5566	0.5566

Correlations					
HRMS vs. LRMSMS -A7010	HRMS vs. LRMSMS -A7000	HRMS vs. LRMS	LRMSMS -A7010 vs. LRMSMS -A7000	LRMSMS -A7010 vs. LRMS	LRMSMS -A7000 vs. LRMS
0.9941	0.9894	0.9832	0.9877	0.9941	0.9739

Table 11. Passive Sampling Device PCB congener data sampled in 2013 from the Yadkin-Pee Dee River System, as ng/L. Locations arranged left to right from upstream to downstream.

IUPAC Congener No.	Kerr Scott Res.	Donaha	Tangle - wood	Badin Lake	Red Hill	Blewett Lake	Blewett Tailrace @ Hwy 74	Diggs Tract
8								
18							0.060	0.240
28			0.203		0.150	0.280	0.220	0.420
44				0.110	0.300	0.250	0.410	0.960
52		0.290	0.180	0.110	0.500	0.330	0.780	1.450
66				0.080	0.380	0.310	0.390	0.550
77								
101				0.050	0.480	0.750	0.610	1.020
105				0.060	0.160	0.050	0.180	0.270
118						0.190	0.140	0.660
126								
128								
138	0.010	0.060	0.074	0.180	0.510	0.600	0.450	0.970
153		0.050		0.100	0.390	0.810	0.520	0.800
170								
180								
187								
195								
201								
206								
209								
total, ng/L	0.010	0.400	0.457	0.690	2.870	3.570	3.760	7.340

Table 12. Summary of fish tissue data for Yadkin-Pee Dee fish tissue study, as species mean by waterbody. Data as ng/kg-wet weight for 209 congener and 21-congener analyses reported for the high-resolution and low-resolution instrument systems. HRMS = high-resolution mass spectrometry, LRMS = low-resolution mass spectrometry

Waterbody	Species	No. Samples	Length, mm	Wt, g	% Lipid	Total PCBs	dl-PCBs	dl-PCB-TEQ	21-PCBs by HRMS	21-PCBs by LRMS-A5975	21-PCBs by LRMSMS-A7000B
High Rock Lk	Catfish	12	404	751	3.28	33,375	2,617	0.148	18,913	23,814	21,052
	Crappie	11	270	293	0.45	3,752	258	0.00842	1,859	2,067	1,795
	Flathead Catfish	1	515	1,637	7.80	46,270	3,032	0.0940	22,430	27,300	25,440
	Largemouth Bass	12	354	726	0.78	13,487	962	0.0820	6,950	9,614	7,467
	Perch	2	171	65	0.45	2,830	221	0.00686	1,659	1,665	1,600
	Redear	1	219	208	0.30	412	51	0.00163	274	160	240
	Sunfish	3	149	60	0.80	6,854	586	0.0179	3,939	5,230	4,397
	White Bass	3	278	277	1.17	24,791	1,590	0.0490	11,792	17,780	12,977

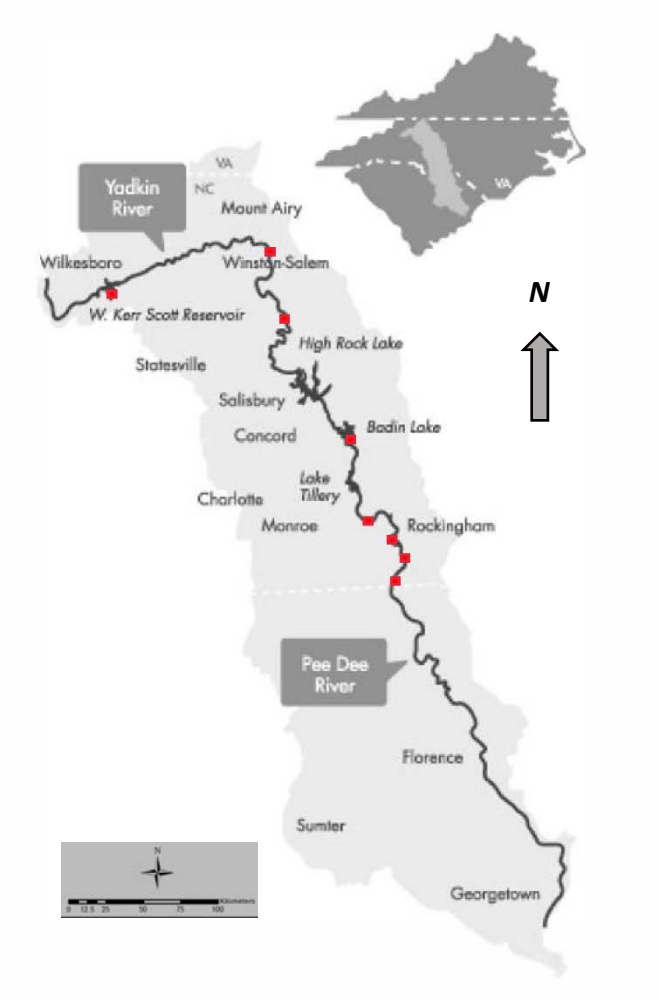
Table 12 Continued

Waterbody	Species	No. Samples	Length, mm	Wt, g	% Lipid	Total PCBs	dl-PCBs	dl-PCB-TEQ	21-PCBs by HRMS	21-PCBs by LRMS-A5975	21-PCBs by LRMSMS-A7000B
Badin Lk	Brown Bullhead	3	274	291	1.07	19,534	1,522	0.356	9,932	12,385	9,932
	Catfish	6	375	631	1.96	48,665	3,984	1.09	26,764	28,289	26,764
	Crappie	2	217	176	0.38	1,861	103	0.00325	879	497	879
	Flat Bullhead	1	242	204	0.71	3,745	372	0.148	2,154	2,535	2,154
	Largemouth Bass	9	363	827	0.66	19,705	1,253	0.449	10,070	11,872	10,070
	Redear	2	237	243	0.30	1,238	73	0.00227	630	490	630
	Sunfish	4	180	117	0.61	8,960	716	0.158	4,723	5,694	4,723

Table 12 Continued

Waterbody	Species	No. Samples	No. Fish	Length, mm	Wt, g	% Lipid	Total PCBs	dl-PCBs	dl-PCB-TEQ	21-PCBs by HRMS	21-PCBs by LRMS-A5975	21-PCBs by LRMSMS-A7000B
Falls Resv	Catfish	5	10	581	3,107	3.94	42,342	3,704	0.113	22,373	27,390	23,521
	Flathead Catfish	1	1	650	3,365	1.90	114,215	11,719	0.352	65,298	79,620	68,240
	Largemouth Bass	4	16	423	1,351	1.20	26,522	2,233	0.0685	13,692	17,050	15,003
	Perch	1	1	264	250	0.60	106	76	0.00243	67	100	155
	Sunfish	4	19	165	85	0.88	3,664	474	0.0145	2,285	2,845	2,676
Lk Tillery	Catfish	16	29	408	831	2.34	30,444	3,800	0.192	16,370	16,452	15,615
	Crappie	8	12	264	313	1.50	2,761	245	0.0690	1,440	1,321	1,246
	Largemouth Bass	13	48	354	763	1.34	17,494	1,598	0.309	8,674	9,404	8,852
	Redear	5	21	210	187	1.18	5,680	614	0.190	3,167	3,308	3,101
	Sunfish	2	5	193	141	1.20	1,219	117	0.00361	823	765	785

FIGURES



PSD Deployment Locations, 2013 (upstream to downstream)	GPS Coordinates	
W Kerr Scott Reservoir, NC	36.12846	81.23321
Donaha, NC	36.21583	80.43367
Tanglewood, NC	36.01492	80.41708
Badin Lake, NC	35.42477	80.09847
Red Hill, NC	35.08527	80.00161
Blewett Lake, NC	34.99747	79.89754
Blewett Tailrace @ Hwy 74, NC	34.94227	79.86812
Diggs Tract, NC	34.86773	79.88104

Figure 1. Location of passive sampling devices (PSDs) deployed in the Yadkin-Pee Dee River Basin in 2013.

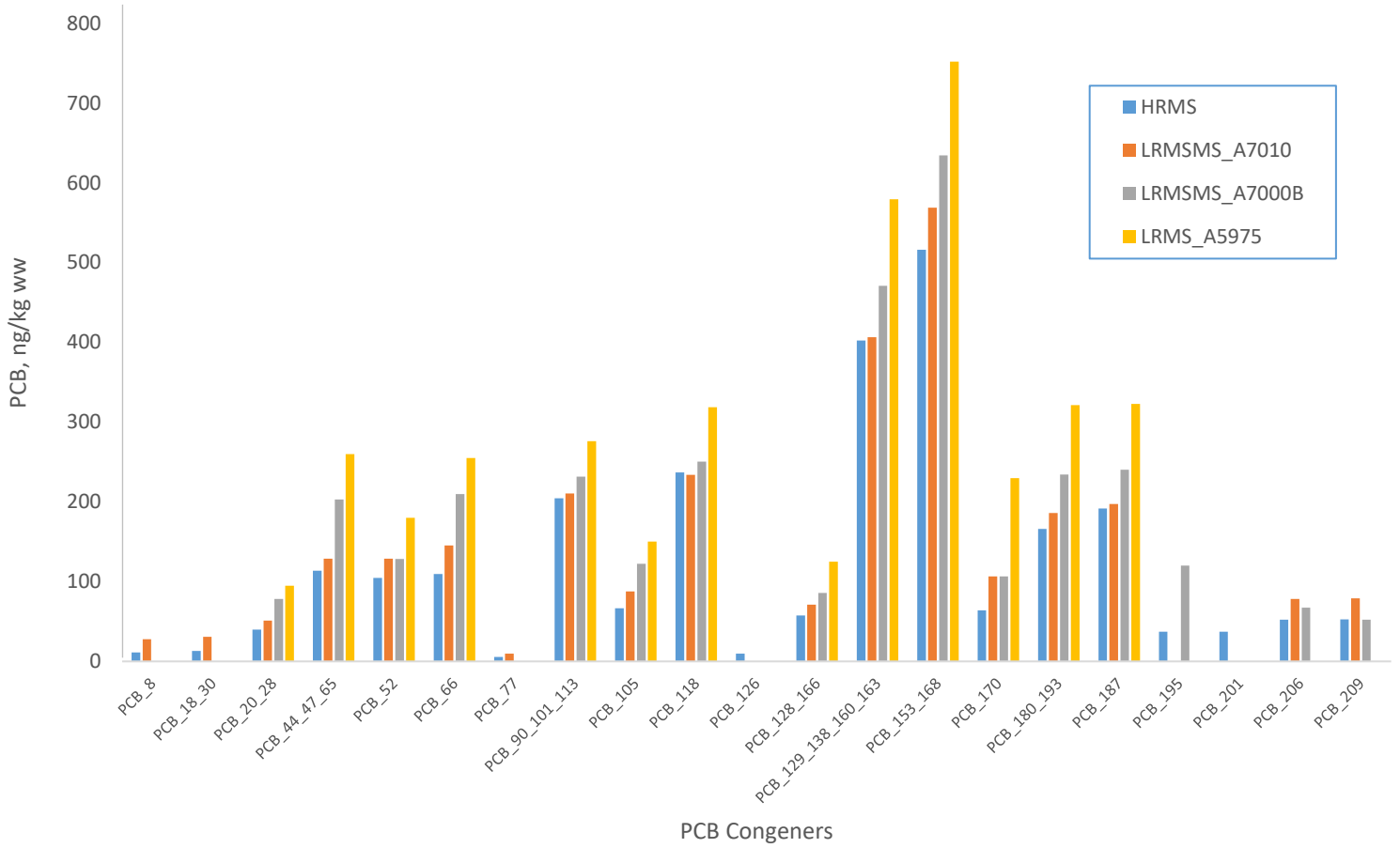


Figure 2. Individual reported 21-PCB congener concentrations for 10 fish tissue extracts analyzed by the HRMS instrument system and by three alternative low-resolution mass selective detector instrument systems.

A.

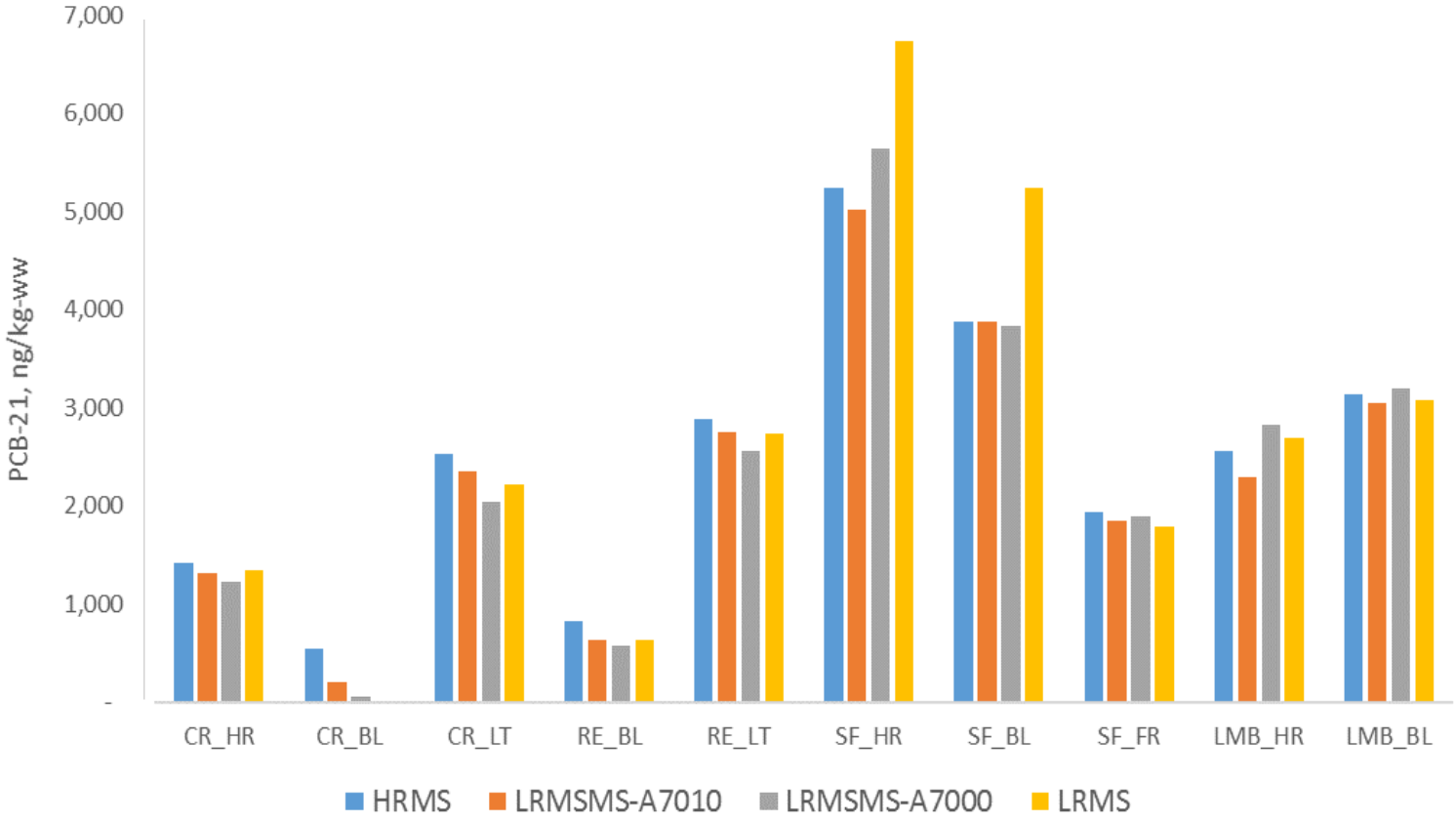


Figure 3. Mean ∑PCB-21 congener concentrations for 10 fish tissue extracts analyzed by four instrument systems. Data as (A) ng/kg wet-weight, and (B) ng PCB/kg-lipid. CR = crappie, RE = redear, SF = sunfish, LMB = largemouth bass, HR = High Rock Lake, BL = Badin Lake, FR = Falls Reservoir, LT = Lake Tillery

B.

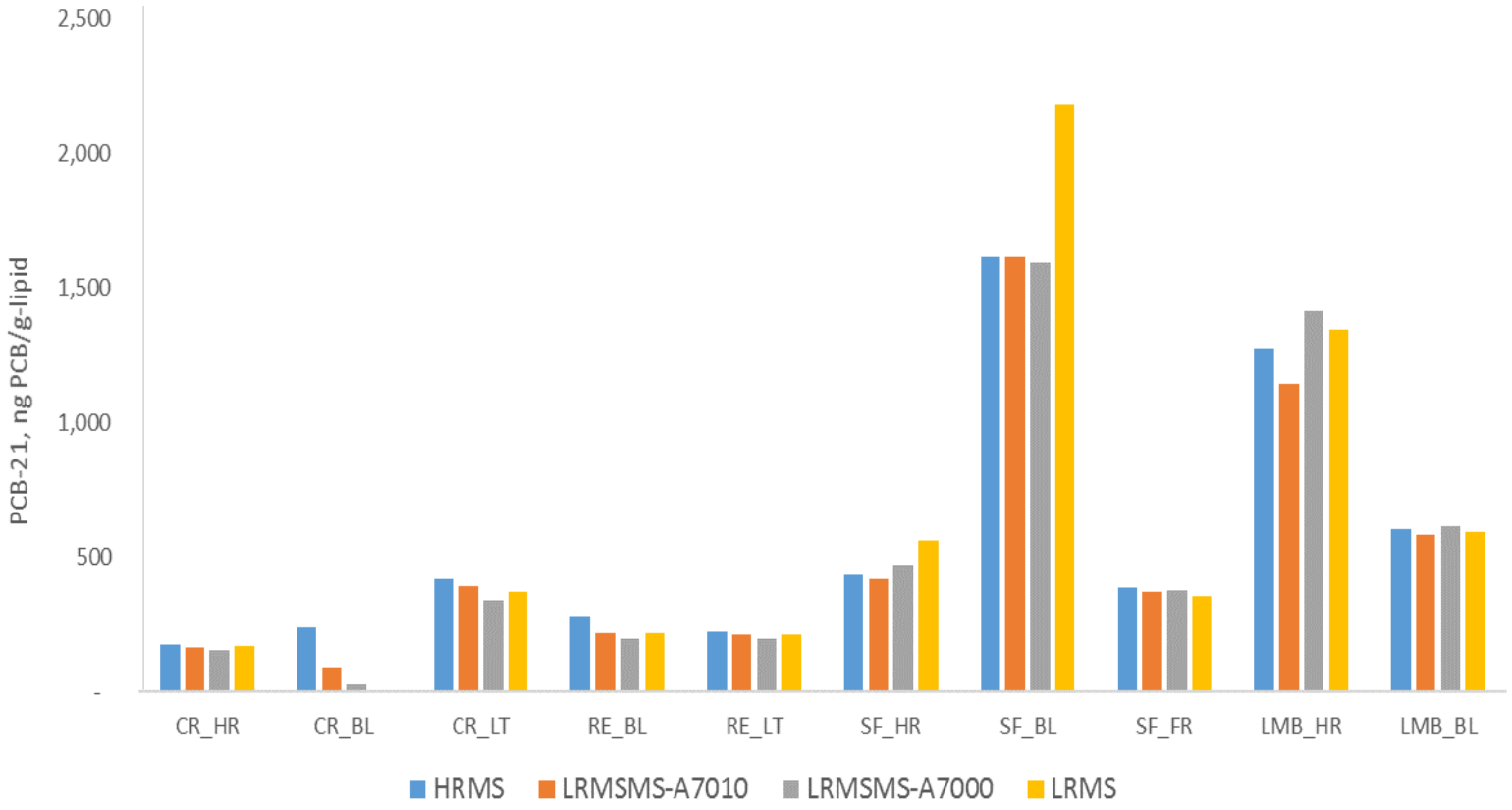


Figure 3 Continued

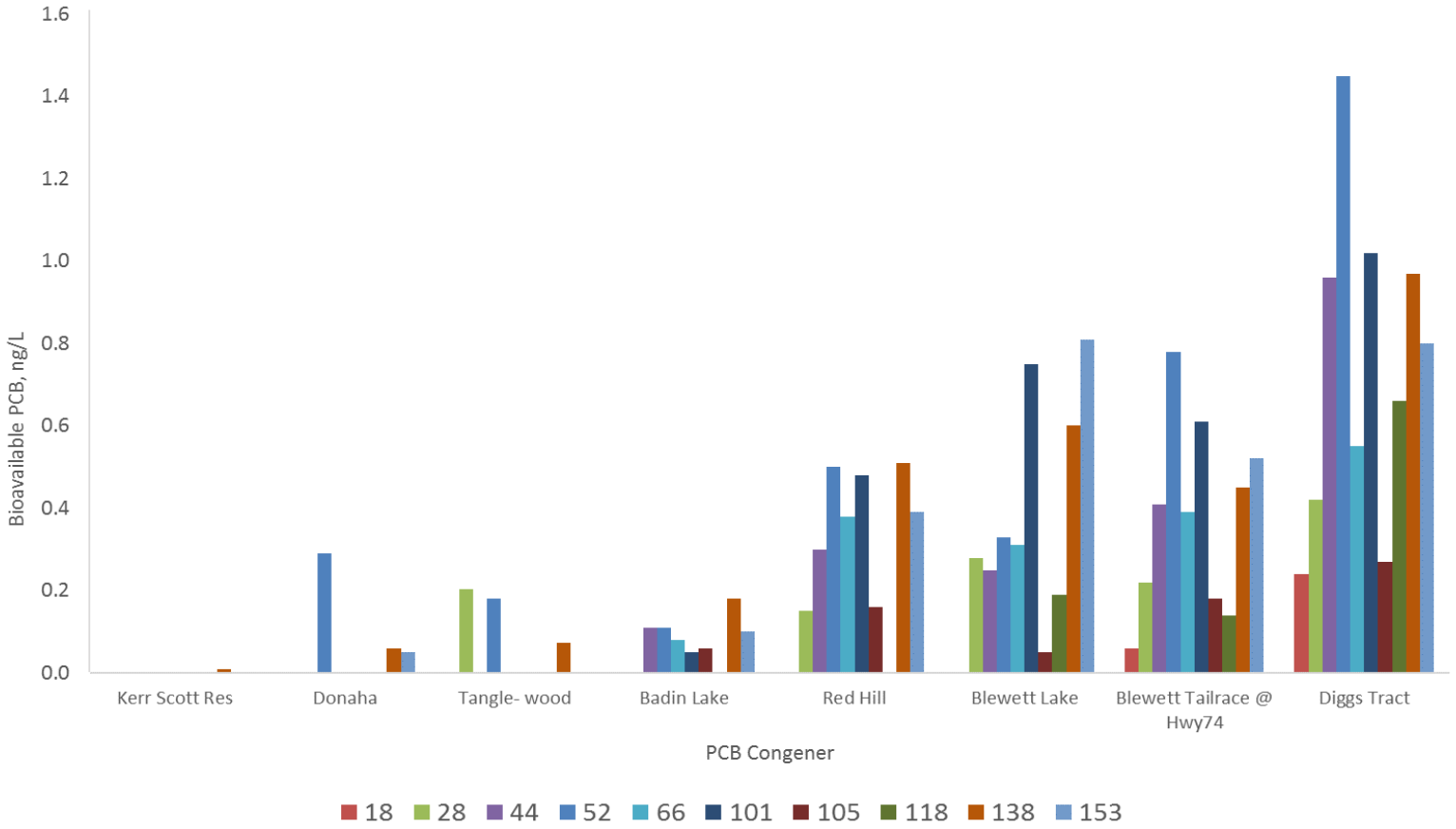


Figure 4. 2013 PSD deployment 21-PCB bioavailable concentration, as ng congener/L. Locations arranged left to right from upstream to downstream.

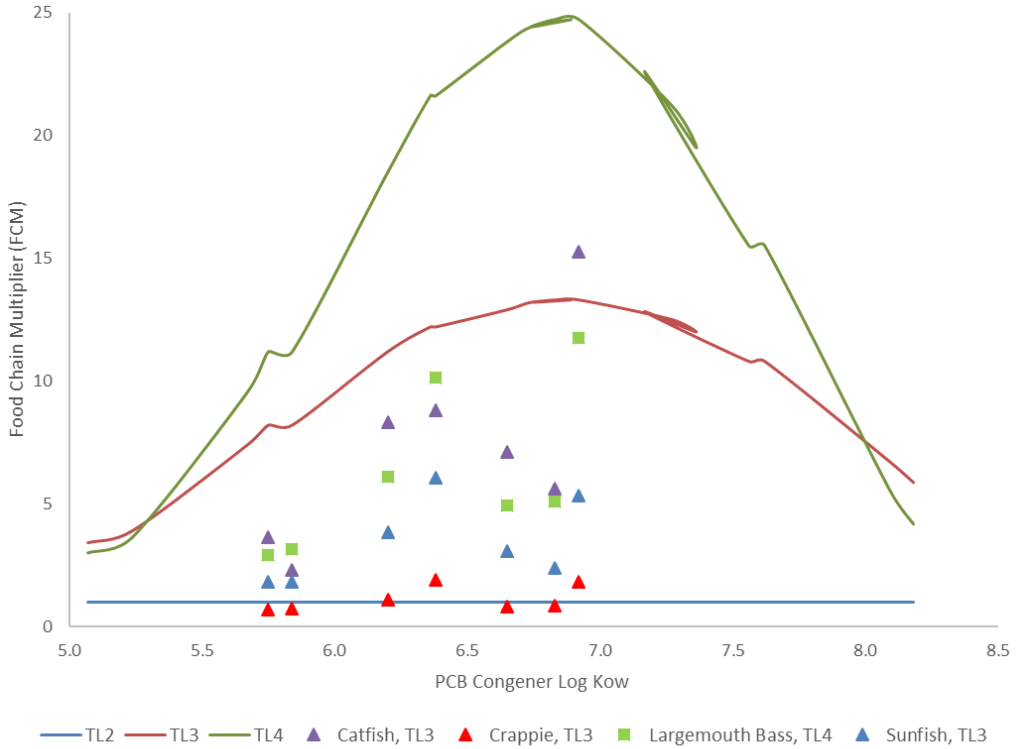


Figure 5. Food chain multiplier (FCM) for Badin Lake PSD and fish tissue data (hollow circles) compared to EPA default values (solid circles and line).

APPENDIX A: Supplemental Information for Chapter 2

Table S1. N.C. DHHS fish consumption advisory data as species mean total PCB concentrations by waterbody, as ng/kg wet-weight. AL = N.C. DHHS Action Level for Total PCBs, 50,000 ng/kg wet-weight

	High Rock Lake, 2011					Badin Lake, 2008					Falls Reservoir, 2012					Lake Tillery, 2011				
Trophic Status / Species	No. fish	No. samples	No. > AL	PCB range	PCB average	No. fish	No. samples	No. > AL	PCB range	PCB average	No. fish	No. samples	No. > AL	PCB range	PCB average	No. fish	No. samples	No. > AL	PCB range	PCB average
Bottom feeders																				
Blue Catfish	1	1	1	78,648	78,648						6	3	2	19,676 - 77,895	50,104					
Brown Bullhead Catfish						7	3		7,618 - 32,224	19,523										
Channel Catfish	12	10	2	4,529 - 88,328	33,839	3	2	2	50,469 - 117,055	83,762	4	2	0	26,001 - 40,966	33,483	11	9	3	8,660 - 128,068	44,267
Flat Bullhead Catfish						1	1		3,726	3,726						2	2	0	3,542 - 5,629	4,586
Flathead Catfish	1	1	0	47,220	47,220						4	1	1	114873	114,873					
White catfish	1	1	0	3,501	3,501	8	4	1	11,888 - 53,233	31,097						16	5	0	10,138 - 25,878	19,802
Middle feeders																				
Black Crappie	13	6	0	2,291 - 9,677	5,630	5	2		1,150 - 2,529	1,839						12	8	0	2,640 - 6,025	4,416
Bluegill Sunfish	18	3	0	5,160 - 11,241	9,166	3	1		6928	6,928	12	2	0	4,200 - 5,607	4,904	5	2	0	2,751 - 3,202	2,976
Redbreast Sunfish						9	3		7,639 - 10,115	9,620	7	2	0	3,705 - 7,902	5,804					
Redear Sunfish	2	1	0	2,349	2,349	5	2		861 - 1,565	1,213						21	5	0	5,723 - 10,182	7,239
White Crappie	7	5	0	2,666 - 7,049	5,489															
White Perch	9	2	0	4,567 - 4,639	4,603															
Yellow Perch					4,603						1	1	0	2,262	2,262					
Top predators																				
Largemouth Bass	41	12	0	3,937 - 27,640	14,793	21	9	1	4,472 - 52,562	19,691	16	4	0	13,462 - 36,835	27,468	48	13	0	5,155 - 39,422	18,975
White Bass	18	3	0	12,659 - 34,387	25,901															

Table S2. Proportion of lifetime cancer risk exceedances for the alternative fish consumption advisory models using updated exposure parameters. ARL = acceptable (cancer) risk level

Waterbody	Species	No. Samples	DHHS Cancer Risk	Coastal Resident Adult	Child Resident	Immigrant Adult Resident	DHHS Cancer Risk	Coastal Resident Adult	Child Resident	Immigrant Adult Resident
			Proportion of tissue samples @ ≥1.0E-06 ARL				Proportion of tissue samples @ ≥1.0E-05 ARL			
High Rock Lake	Black Crappie	6	0.83	0.50	0.83	0.83	0.33	0.00	0.00	0.33
	Blue Catfish	1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Bluegill	3	1.00	0.67	1.00	1.00	0.67	0.00	0.33	0.67
	Channel Catfish	10	1.00	0.90	1.00	1.00	0.90	0.30	0.90	0.90
	Flathead Catfish	1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Largemouth Bass	12	1.00	0.92	1.00	1.00	0.92	0.17	0.58	0.67
	Redear	1	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	White Bass	3	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00
	White Catfish	1	1.00	0.00	1.00	1.00	0.00	0.00	0.00	0.00
	White Crappie	5	1.00	0.40	0.80	1.00	0.40	0.00	0.00	0.00
	White Perch	2	1.00	0.00	1.00	1.00	0.00	0.00	0.00	0.00
Badin Lake	Black Crappie	2	1.00	0.00	1.00	1.00	0.00	0.00	0.00	0.00
	Bluegill	1	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00
	Brown Bullhead	3	1.00	1.00	1.00	1.00	1.00	0.67	1.00	1.00
	Channel Catfish	2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Flat Bullhead	1	1.00	1.00	1.00	1.00	1.00	0.00	1.00	1.00
	Largemouth Bass	9	1.00	1.00	1.00	1.00	1.00	0.44	0.89	1.00
	Redbreast Sunfish	3	1.00	1.00	1.00	1.00	1.00	0.00	0.67	1.00
	Redear	2	1.00	0.00	0.50	1.00	0.00	0.00	0.00	0.00
	White Catfish	4	1.00	1.00	1.00	1.00	1.00	0.75	1.00	1.00

Table S2 Continued

Waterbody	Species	No. Samples	DHHS Cancer Risk	Coastal Resident Adult	Child Resident	Immigrant Adult Resident	DHHS Cancer Risk	Coastal Resident Adult	Child Resident	Immigrant Adult Resident
			Proportion of tissue samples @ ≥1.0E-06 ARL				Proportion of tissue samples @ ≥1.0E-05 ARL			
Falls Reservoir	Blue Catfish	3	1.00	1.00	1.00	1.00	1.00	0.67	1.00	1.00
	Bluegill	2	1.00	0.50	1.00	1.00	0.50	0.00	0.00	0.00
	Channel Catfish	2	1.00	1.00	1.00	1.00	1.00	0.50	1.00	1.00
	Flathead Catfish	1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Largemouth Bass	4	1.00	1.00	1.00	1.00	1.00	0.50	1.00	1.00
	Redbreast Sunfish	2	1.00	0.50	1.00	1.00	0.50	0.00	0.00	0.50
	Yellow Perch	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lake Tillery	Black Crappie	8	1.00	0.38	0.88	1.00	0.38	0.00	0.25	0.25
	Bluegill	2	1.00	0.00	0.50	1.00	0.00	0.00	0.00	0.00
	Channel Catfish	9	1.00	1.00	1.00	1.00	1.00	0.56	1.00	1.00
	Flat Bullhead	2	1.00	0.50	1.00	1.00	0.50	0.00	0.00	0.00
	Largemouth Bass	13	1.00	0.92	1.00	1.00	0.92	0.46	0.92	0.85
	Redear	5	1.00	1.00	1.00	1.00	1.00	0.20	0.60	0.80
	White Catfish	5	1.00	1.00	1.00	1.00	1.00	0.00	0.80	1.00

Table S3. Native Aroclor profiles as congener weight-fraction and pigment-associated congeners. Dioxin-like congeners IUPAC no.: 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189.

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
1	2-Monochlorobiphenyl	35.8	15.53	0.53	0.54	0.04	0.02	0.02	0.03	2,3	2		2,3
2	3-Monochlorobiphenyl	3.81	1.96	0.03	0.03					2,3	2	3	2,3
3	4-Monochlorobiphenyl	20.44	10.28	0.16	0.18	0.01			0.01	2,3	2		2,3
4	2,2'-Dichlorobiphenyl	6.19	5.35	3.64	3.08	0.18	0.04	0.02	0.06	2,3	2	3	2,3
5	2,3-Dichlorobiphenyl	0.74	0.50	0.16	0.14					2,3	2	3	2,3
6	2,3'-Dichlorobiphenyl	3.82	3.01	1.67	1.43	0.07	0.01	0.01	0.03	2,3	2	3	2,3
7	2,4-Dichlorobiphenyl	1.70	1.11	0.30	0.26	0.02				2,3			2,3
8	2,4'-Dichlorobiphenyl	12.34	10.72	8.30	7.05	0.54	0.09	0.04	0.12	2,3	2	3	2,3
9	2,5-Dichlorobiphenyl	1.74	1.27	0.59	0.50	0.04			0.00	2,3	2		2,3
10	2,6-Dichlorobiphenyl	0.80	0.59	0.23	0.20					2			2
11	3,3'-Dichlorobiphenyl	0.16								1,2,3	2,3		2,3
12	3,4-Dichlorobiphenyl	0.59	0.35	0.07	0.06					2,3	2,3		2,3
13	3,4'-Dichlorobiphenyl	1.12	0.73	0.25	0.21	0.02				2,3	2,3		2,3
14	3,5-Dichlorobiphenyl		0.01										
15	4,4'-Dichlorobiphenyl	4.18	3.22	2.45	2.11	0.14	0.02	0.01	0.03	2,3	2,3		2,3

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
16	2,2',3-Trichlorobiphenyl	0.31	1.79	3.88	3.14	0.88	0.06	0.01	0.05	2,3			2,3
17	2,2',4-Trichlorobiphenyl	0.34	1.83	3.98	3.13	0.99	0.05	0.01	0.05	2,3	2,3		
18	2,2',5-Trichlorobiphenyl	0.78	4.86	10.81	8.53	3.79	0.17	0.05	0.15	2,3	2,3		2
19	2,2',6-Trichlorobiphenyl	0.08	0.47	1.00	0.79	0.18		0.00	0.02				
20	2,3,3'-Trichlorobiphenyl	0.07	0.42	0.89	0.72	0.11				2,3	2		2,3
21	2,3,4-Trichlorobiphenyl	NM	NM	NM	NM								
22	2,3,4'-Trichlorobiphenyl	0.26	1.62	3.51	2.84	1.36	0.03	0.01	0.05	2	2		
23	2,3,5-Trichlorobiphenyl			0.02	0.01					2	2		
24	2,3,6-Trichlorobiphenyl	0.02	0.08	0.17	0.13					2	2		
25	2,3',4-Trichlorobiphenyl	0.09	0.37	0.72	0.59	0.08				2	2		
26	2,3',5-Trichlorobiphenyl	0.13	0.75	1.58	1.28	0.32	0.02		0.02	2	2		2
27	2,3',6-Trichlorobiphenyl	0.05	0.12	0.51	0.41	0.10							
28	2,4,4'-Trichlorobiphenyl	0.62	3.91	8.54	6.86	4.58	0.13	0.03	0.12	1,2	2		
29	2,4,5-Trichlorobiphenyl	0.01	0.05	0.10	0.08	0.00				2	2		
30	2,4,6-Trichlorobiphenyl			0.00						2	2		
31	2,4',5-Trichlorobiphenyl	0.60	4.14	9.29	7.34	5.27	0.20	0.04	0.12	2	2		2
32	2,4',6-Trichlorobiphenyl	0.17	1.08	2.37	1.90	0.91	0.03	0.01	0.04				

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
33	2',3,4-Trichlorobiphenyl	0.48	2.86	6.20	5.01	2.22	0.11	0.03	0.10	2,3	2		2,3
34	2',3,5-Trichlorobiphenyl		0.01	0.03	0.02								
35	3,3',4-Trichlorobiphenyl		0.06	0.06	0.08					2,3	2,3		
36	3,3',5-Trichlorobiphenyl												
37	3,4,4'-Trichlorobiphenyl	0.19	1.14	1.02	2.03	0.87	0.04		0.03	2	2		
38	3,4,5-Trichlorobiphenyl												
39	3,4',5-Trichlorobiphenyl												
40	2,2',3,3'-Tetrachlorobiphenyl	0.04	0.38	0.58	0.76	1.03	0.14			2,3			2,3
41	2,2',3,4-Tetrachlorobiphenyl	0.03	0.36	0.76	0.68	0.76	0.02						
42	2,2',3,4'-Tetrachlorobiphenyl	0.09	0.68	1.59	1.18	1.73	0.12		0.02				
43	2,2',3,5-Tetrachlorobiphenyl		0.11	0.27	0.18	0.25							
44	2,2',3,5'-Tetrachlorobiphenyl	0.21	1.81	4.48	3.55	5.70	1.49	0.04	0.08				
45	2,2',3,6-Tetrachlorobiphenyl	0.04	0.46	1.23	0.89	1.00	0.04			2	2		
46	2,2',3,6'-Tetrachlorobiphenyl	0.02	0.19	0.49	0.36	0.43							
47	2,2',3,4'-Tetrachlorobiphenyl	0.05	0.49	1.25	0.93	1.95	0.11		0.01				
48	2,2',4,5-Tetrachlorobiphenyl	0.06	0.62	1.60	1.18	1.60	0.09		0.01	2	2		
49	2,2',4,5'-Tetrachlorobiphenyl	0.15	1.37	3.38	2.52	4.15	0.68	0.01	0.06	2	2		

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
50	2,2',4,6-Tetrachlorobiphenyl			0.01									
51	2,2',4,6'-Tetrachlorobiphenyl		0.13	0.32	0.23	0.31							
52	2,2',5,5'-Tetrachlorobiphenyl	0.22	1.85	4.62	3.53	6.26	3.11	0.24	0.14	1,2,3	2,3		
53	2,2',5,6'-Tetrachlorobiphenyl	0.04	0.37	0.95	0.71	0.97	0.08						
54	2,2',6,6'-Tetrachlorobiphenyl			0.02									
55	2,3,3',4'-Tetrachlorobiphenyl		0.05		0.10	0.06							
56	2,3,3',4'-Tetrachlorobiphenyl	0.12	0.93	0.07	1.82	3.18	1.13	0.01	0.03	2,3	2		2,3
57	2,3,3',5-Tetrachlorobiphenyl		0.01	0.01	0.02	0.02							
58	2,3,3',5'-Tetrachlorobiphenyl												
59	2,3,3',6-Tetrachlorobiphenyl	0.01	0.18	0.40	0.32	0.30	0.01		0.00	2	2		
60	2,3,4,4'-Tetrachlorobiphenyl	0.07	0.61	0.04	1.18	2.26	0.57	0.04	0.02				
61	2,3,4,5-Tetrachlorobiphenyl												
62	2,3,4,6-Tetrachlorobiphenyl												
63	2,3,4',5-Tetrachlorobiphenyl		0.10	0.06	0.12	0.18	0.05			2	2		
64	2,3,4',6-Tetrachlorobiphenyl	0.10	0.87	1.86	1.70	3.17	0.48	0.01	0.03	2	2		
65	2,3,5,6-Tetrachlorobiphenyl												
66	2,3',4,4'-Tetrachlorobiphenyl	0.21	1.73	0.38	3.39	6.53	2.29	0.02	0.07				

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
67	2,3',4,5-Tetrachlorobiphenyl		0.09	0.06	0.16	0.12	0.00			2	2		
68	2,3',4,5'-Tetrachlorobiphenyl												
69	2,3',4,6-Tetrachlorobiphenyl			0.00									
70	2,3',4',5-Tetrachlorobiphenyl	0.24	1.90	0.58	3.73	7.34	5.16	0.04	0.10	2	2		
71	2,3',4',6-Tetrachlorobiphenyl	0.06	0.54	1.17	1.03	1.77	0.13		0.01				
72	2,3',5,5'-Tetrachlorobiphenyl				0.01	0.02							
73	2,3',5',6-Tetrachlorobiphenyl												
74	2,4,4',5-Tetrachlorobiphenyl	0.12	0.92	0.33	1.81	3.91	1.52	0.05	0.05	2	2		
75	2,4,4',6-Tetrachlorobiphenyl		0.02	0.06	0.04	0.08							
76	2',3,4',5-Tetrachlorobiphenyl				0.08	0.13	0.03						
77	3,3',4,4'-Tetrachlorobiphenyl	0.01	0.17		0.31	0.47	0.12			1,2,3	2,3		2,3
78	3,3',4,5-Tetrachlorobiphenyl												
79	3,3',4,5'-Tetrachlorobiphenyl												
80	3,3',5,5'-Tetrachlorobiphenyl												
81	3,4,4',5-Tetrachlorobiphenyl				0.01	0.02							
82	2,2',3,3',4-Pentachlorobiphenyl		0.12		0.26	0.72	1.32						
83	2,2',3,3',5-Pentachlorobiphenyl		0.05		0.11	0.23	0.52			2	2		

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
84	2,2',3,3',6-Pentachlorobiphenyl	0.02	0.19	0.05	0.41	1.09	1.95	0.11	0.04	2	2		
85	2,2',3,4,4'-Pentachlorobiphenyl	0.03	0.17	0.00	0.31	1.06	1.89	0.01	0.02				
86	2,2',3,4,5-Pentachlorobiphenyl		0.01		0.04	0.10	0.08			2	2		
87	2,2',3,4,5'-Pentachlorobiphenyl	0.04	0.22		0.46	1.28	3.70	0.41	0.11				
88	2,2',3,4,6-Pentachlorobiphenyl				0.00	0.02							
89	2,2',3,4,6'-Pentachlorobiphenyl		0.05		0.09	0.19	0.10						
90	2,2',3,4',5-Pentachlorobiphenyl					NM	NM			2	2		
91	2,2',3,4',6-Pentachlorobiphenyl		0.10	0.06	0.21	0.60	0.73		0.01	2	2		
92	2,2',3,5,5'-Pentachlorobiphenyl	0.02	0.05		0.09	0.32	0.93	0.30	0.08	2	2		
93	2,2',3,5,6-Pentachlorobiphenyl					0.04				2,3	2	3	
94	2,2',3,5,6'-Pentachlorobiphenyl					0.03	0.01						
95	2,2',3,5',6-Pentachlorobiphenyl	0.05	0.30	0.31	0.61	1.70	4.05	2.46	0.93	2,3	2	3	
96	2,2',3,6,6'-Pentachlorobiphenyl		0.01	0.04	0.03	0.07	0.03						
97	2,2',3',4,5-Pentachlorobiphenyl	0.03	0.18	0.02	0.38	1.10	2.70	0.09	0.05	2	2		
98	2,2',3',4,6-Pentachlorobiphenyl									2,3	2	3	
99	2,2',4,4',5-Pentachlorobiphenyl	0.04	0.21	0.01	0.46	1.64	3.78	0.04	0.05	2	2		
100	2,2',4,4',6-Pentachlorobiphenyl												

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
101	2,2',4,5,5'-Pentachlorobiphenyl	0.07	0.33	0.04	0.69	2.06	6.76	3.13	1.13	2,3	2,3	3	
102	2,2',4,5,6'-Pentachlorobiphenyl		0.03	0.04	0.07	0.18	0.12			2	2		
103	2,2',4,5,6'-Pentachlorobiphenyl					0.01	0.03						
104	2,2',4,6,6'-Pentachlorobiphenyl												
105	2,3,3'4,4'-Pentachlorobiphenyl	0.05	0.22		0.47	1.53	5.18	0.22	0.18				
106	2,3,3',4,5-Pentachlorobiphenyl												
107	2,3,3',4',5-Pentachlorobiphenyl												
108	2,3,3',4,5'-Pentachlorobiphenyl												
109	2,3,3',4,6-Pentachlorobiphenyl		0.03		0.06	0.16	0.58			2	2		
110	*2,3,3',4',6-Pentachlorobiphenyl*	0.05	0.38		0.83	2.76	8.86	1.33	0.39	2	2		
111	*2,3,3',5,5'-Pentachlorobiphenyl*												
112	*2,3,3',5,6-Pentachlorobiphenyl*												
113	*2,3,3',5',6-Pentachlorobiphenyl*						0.01						
114	2,3,4,4',5-Pentachlorobiphenyl		0.02		0.04	0.12	0.34						
115	2,3,4,4',6-Pentachlorobiphenyl		0.01		0.04	0.11	0.29						
116	2,3,4,5,6-Pentachlorobiphenyl												
117	2,3,4',5,6-Pentachlorobiphenyl		0.01		0.03	0.10	0.21						

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
118	2,3',4,4',5-Pentachlorobiphenyl	0.08	0.29		0.66	2.32	10.47	0.49	0.16	2	2		
119	2,3',4,4',6-Pentachlorobiphenyl					0.06	0.10						
120	2,3',4,5,5'-Pentachlorobiphenyl									2	2		
121	2,3',4,5,6-Pentachlorobiphenyl												
122	2',3,3',4,5-Pentachlorobiphenyl				0.01	0.06	0.18						
123	2',3,4,4',5-Pentachlorobiphenyl				0.03	0.08	0.24						
124	2',3,4,5,5'-Pentachlorobiphenyl				0.03	0.09	0.38						
125	2',3,4,5,6'-Pentachlorobiphenyl				0.02	0.04	0.03						
126	3,3',4,4',5-Pentachlorobiphenyl						0.01						
127	3,3',4,5,5'-Pentachlorobiphenyl												
128	2,2',3,3',4,4'-Hexachlorobiphenyl				0.02	0.10	1.57	0.54	0.19				
129	2,2',3,3',4,5-Hexachlorobiphenyl					0.02	0.39	0.14	0.04				
130	2,2',3,3',4,5'-Hexachlorobiphenyl					0.03	0.55	0.22	0.05				
131	2,2',3,3',4,6-Hexachlorobiphenyl						0.17	0.07					
132	2,2',3,3',4,6'-Hexachlorobiphenyl		0.02		0.04	0.15	1.90	2.90	1.21				
133	2,2',3,3',5,5'-Hexachlorobiphenyl						0.11	0.07	0.04				
134	2,2',3,3',5,6-Hexachlorobiphenyl					0.01	0.29	0.34	0.13				

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
135	2,2',3,3',5,6'-Hexachlorobiphenyl					0.04	0.45	1.08	0.66	2	2		
136	2,2',3,3',6,6'-Hexachlorobiphenyl					0.06	0.47	1.46	1.01	2	2		
137	2,2',3,4,4',5-Hexachlorobiphenyl					0.03	0.47	0.02	0.01				
138	2,2',3,4,4',5'-Hexachlorobiphenyl		0.06			0.40	5.88	6.54	2.74				
139	2,2',3,4,4',6-Hexachlorobiphenyl						0.15						
140	2,2',3,4,4',6'-Hexachlorobiphenyl												
141	2,2',3,4,5,5'-Hexachlorobiphenyl					0.08	0.84	2.62	1.66				
142	2,2',3,4,5,6-Hexachlorobiphenyl												
143	2,2',3,4,5,6'-Hexachlorobiphenyl												
144	2,2',3,4,5',6-Hexachlorobiphenyl					0.01	0.18	0.61	0.41				
145	2,2',3,4,6,6'-Hexachlorobiphenyl												
146	2,2',3,4',5,5'-Hexachlorobiphenyl					0.05	0.56	1.15	0.59	2	2		
147	2,2',3,4',5,6-Hexachlorobiphenyl						0.06						
148	2,2',3,4',5,6'-Hexachlorobiphenyl												
149	2,2',3,4',5',6-Hexachlorobiphenyl		0.05		0.06	0.29	2.74	8.75	6.40	2	2		
150	2,2',3,4',6,6'-Hexachlorobiphenyl												
151	2,2',3,5,5',6-Hexachlorobiphenyl		0.01			0.06	0.46	3.04	2.98				

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
152	2,2',3,5,6,6'-Hexachlorobiphenyl												
153	2,2',4,4',5,5'-Hexachlorobiphenyl		0.05		0.06	0.33	3.53	9.39	7.10	2,3	2,3		
154	2,2',4,4',5',6-Hexachlorobiphenyl						0.03						
155	2,2',4,4',6,6'-Hexachlorobiphenyl												
156	2,3,3',4,4',5-Hexachlorobiphenyl				0.02	0.05	0.98	0.52	0.16				
157	2,3,3',4,4',5'-Hexachlorobiphenyl						0.25	0.02					
158	2,3,3',4,4',6-Hexachlorobiphenyl				0.02	0.04	0.86	0.58	0.20				
159	2,3,3',4,5,5'-Hexachlorobiphenyl												
160	2,3,3',4,5,6-Hexachlorobiphenyl												
161	2,3,3',4,5',6-Hexachlorobiphenyl												
162	2,3,3',4',5,5'-Hexachlorobiphenyl												
163	2,3,3',4',5,6-Hexachlorobiphenyl		0.02		0.01	0.07	0.87	2.43	1.53				
164	2,3,3',4',5',6-Hexachlorobiphenyl				0.00	0.03	0.36	0.69	0.27				
165	2,3,3',5,5',6-Hexachlorobiphenyl												
166	2,3,4,4',5,6-Hexachlorobiphenyl						0.05						
167	2,3,4,4',5,5'-Hexachlorobiphenyl					0.00	0.31	0.19	0.04				
168	2,3',4,4',5',6-Hexachlorobiphenyl												

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
169	3,3',4,4',5,5'-Hexachlorobiphenyl												
170	2,2',3,3',4,4',5-Heptachlorobiphenyl					0.08	0.44	4.11	3.26				
171	2,2',3,3',4,4',6-Heptachlorobiphenyl						0.11	1.11	0.88				
172	2,2',3,3',4,5,5'-Heptachlorobiphenyl						0.05	0.70	0.63	2	2		
173	2,2',3,3',4,5,6-Heptachlorobiphenyl							0.10	0.04				
174	2,2',3,3',4,5,6'-Heptachlorobiphenyl					0.08	0.24	4.96	6.33	2	2		
175	2,2',3,3',4,5',6-Heptachlorobiphenyl							0.18	0.18				
176	2,2',3,3',4,6,6'-Heptachlorobiphenyl						0.02	0.59	0.70	2	2		
177	2,2',3,3',4',5,6-Heptachlorobiphenyl					0.03	0.14	2.57	2.78				
178	2,2',3,3',5,5',6-Heptachlorobiphenyl						0.03	0.83	1.21	2	2		
179	2,2',3,3',5,6,6'-Heptachlorobiphenyl					0.02	0.06	2.03	3.33	2	2		
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl		0.01		0.00	0.12	0.55	11.38	14.13	2	2		
181	2,2',3,4,4',5,6-Heptachlorobiphenyl							0.00					
182	2,2',3,4,4',5,6'-Heptachlorobiphenyl												
183	2,2',3,4,4',5',6-Heptachlorobiphenyl					0.06	0.14	2.41	2.88	2	2		
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl												
185	2,2',3,4,5,5',6-Heptachlorobiphenyl							0.55	0.87				

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
186	2,2',3,4,5,6,6'-Heptachlorobiphenyl												
187	2,2',3,4,5,5',6-Heptachlorobiphenyl		0.01			0.09	0.17	5.40	9.16	2	2		
188	2,2',3,4',5,6,6'-Heptachlorobiphenyl												
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl						0.01	0.10	0.04				
190	2,3,3',4,4',5,6-Heptachlorobiphenyl						0.06	0.82	0.76				
191	2,3,3',4,4',5',6-Heptachlorobiphenyl							0.17	0.13				
192	2,3,3',4,5,5',6-Heptachlorobiphenyl												
193	2,3,3',4',5,5',6-Heptachlorobiphenyl						0.03	0.53	0.66				
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl						0.01	2.07	4.06	2,3	2	3	
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl							0.84	1.43				
196	2,2',3,3',4,4',5,6'-Octachlorobiphenyl							1.09	2.27	3		3	
197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl							0.07	0.14				
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl							0.10	0.23	3		3	
199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl						0.01	1.78	4.74	2,3	2	3	
200	2,2',3,3',4,5,6,6'-Octachlorobiphenyl							0.25	0.65				
201	2,2',3,3',4,5',6,6'-Octachlorobiphenyl							0.24	0.62				
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl							0.33	1.08	3		3	

IUPAC No.	Congener	Native Aroclor Make-up as Congener Weight Fraction [4]								PCB Congeners Reported in Pigments (by Reference Number)			
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Pigments, Combined	Azo Pigments	Phthalocyanine Pigments	Polycyclic Pigments
203	2,2',3,4,4',5,5',6-Octachlorobiphenyl						0.02	1.40	4.24	2,3	2	3	
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl												
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl							0.10	0.17	3		3	
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl						0.03	0.53	1.26	1,2,3		2,3	
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl							0.05	0.18	1,2,3		2,3	
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl						0.01	0.13	0.28	1,2,3		2,3	
209	Decachlorobiphenyl							NM	NM	1,2,3		2,3	
∑ndl-Congeners, as weight-fraction		0.1400	0.6800	0.0000	1.537	4.570	17.89	1.543	0.5650				
∑dl-Congeners, as weight-fraction		4.900E-06	3.195E-05	0.000E+00	6.960E-05	1.737E-04	1.559E-03	3.532E-04	1.209E-04				

Table S4. Environmental variables for 209 PCB congeners and dioxin-like-congener Toxicity Equivalence Factors (TEF).

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
1	2-Monochlorobiphenyl	mono		5697	188.7		4.46	2.95E-04
2	3-Monochlorobiphenyl	mono		4738	188.7		4.69	2.88E-04
3	4-Monochlorobiphenyl	mono		768	188.7		4.69	2.75E-04
4	2,2'-Dichlorobiphenyl	di		1283	223.1	418	4.65	3.31E-04
5	2,3-Dichlorobiphenyl	di		1344	223.1		4.97	2.40E-04
6	2,3'-Dichlorobiphenyl	di		N/A	223.1	163	5.06	3.27E-04
7	2,4-Dichlorobiphenyl	di		1067	223.1		5.07	3.80E-04
8	2,4'-Dichlorobiphenyl	di		643	223.1	145	5.07	3.02E-04
9	2,5-Dichlorobiphenyl	di		1508	223.1	195	5.06	3.24E-04
10	2,6-Dichlorobiphenyl	di		2561	223.1		4.84	4.27E-04
11	3,3'-Dichlorobiphenyl	di		705	223.1		5.28	2.88E-04
12	3,4-Dichlorobiphenyl	di		396	223.1		5.22	2.34E-04
13	3,4'-Dichlorobiphenyl	di			223.1		5.29	2.51E-04
14	3,5-Dichlorobiphenyl	di		643	223.1		5.28	4.17E-04
15	4,4'-Dichlorobiphenyl	di		23	223.1		5.30	2.24E-04
16	2,2',3-Trichlorobiphenyl	tri		589	257.5	681	5.16	2.51E-04
17	2,2',4-Trichlorobiphenyl	tri			257.5	79	5.25	3.72E-04
18	2,2',5-Trichlorobiphenyl	tri		447	257.5	892	5.24	3.16E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
19	2,2',6-Trichlorobiphenyl	tri			257.5	165	5.02	4.37E-04
20	2,3,3'-Trichlorobiphenyl	tri			257.5		5.57	2.19E-04
21	2,3,4-Trichlorobiphenyl	tri		47	257.5		5.51	2.29E-04
22	2,3,4'-Trichlorobiphenyl	tri		69	257.5	236	5.58	1.91E-04
23	2,3,5-Trichlorobiphenyl	tri		224	257.5		5.57	3.16E-04
24	2,3,6-Trichlorobiphenyl	tri			257.5		5.35	3.09E-04
25	2,3',4-Trichlorobiphenyl	tri			257.5	309	5.67	3.16E-04
26	2,3',5-Trichlorobiphenyl	tri		257	257.5	348	5.66	2.95E-04
27	2,3',6-Trichlorobiphenyl	tri			257.5	644	5.44	3.98E-04
28	2,4,4'-Trichlorobiphenyl	tri		83	257.5	273	5.67	2.88E-04
29	2,4,5-Trichlorobiphenyl	tri			257.5		5.60	2.95E-04
30	2,4,6-Trichlorobiphenyl	tri		204	257.5		5.44	5.75E-04
31	2,4',5-Trichlorobiphenyl	tri		95	257.5	309	5.67	2.74E-04
32	2,4',6-Trichlorobiphenyl	tri			257.5		5.44	3.89E-04
33	2',3,4-Trichlorobiphenyl	tri		151	257.5	24	5.60	2.40E-04
34	2',3,5-Trichlorobiphenyl	tri			257.5		5.66	4.17E-04
35	3,3',4-Trichlorobiphenyl	tri			257.5		5.82	1.78E-04
36	3,3',5-Trichlorobiphenyl	tri			257.5		5.88	3.39E-04
37	3,4,4'-Trichlorobiphenyl	tri		28	257.5	83	5.83	1.52E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
38	3,4,5-Trichlorobiphenyl	tri			257.5		5.76	2.34E-04
39	3,4',5-Trichlorobiphenyl	tri		30	257.5		5.89	3.02E-04
40	2,2',3,3'-Tetrachlorobiphenyl	tetra		12	292.0	111	5.66	1.82E-04
41	2,2',3,4-Tetrachlorobiphenyl	tetra			292.0		5.69	2.44E-04
42	2,2',3,4'-Tetrachlorobiphenyl	tetra		33	292.0	129	5.76	2.51E-04
43	2,2',3,5-Tetrachlorobiphenyl	tetra			292.0		5.75	3.31E-04
44	2,2',3,5'-Tetrachlorobiphenyl	tetra		76	292.0	145	5.75	2.29E-04
45	2,2',3,6-Tetrachlorobiphenyl	tetra			292.0	393	5.53	3.55E-04
46	2,2',3,6'-Tetrachlorobiphenyl	tetra		27	292.0	268	5.53	3.39E-04
47	2,2',3,4'-Tetrachlorobiphenyl	tetra		49	292.0	149	5.85	3.72E-04
48	2,2',4,5-Tetrachlorobiphenyl	tetra			292.0	165	5.78	3.02E-04
49	2,2',4,5'-Tetrachlorobiphenyl	tetra		41	292.0	168	5.85	3.55E-04
50	2,2',4,6-Tetrachlorobiphenyl	tetra			292.0		5.63	6.03E-04
51	2,2',4,6'-Tetrachlorobiphenyl	tetra			292.0		5.63	5.13E-04
52	2,2',5,5'-Tetrachlorobiphenyl	tetra		33	292.0	19	5.84	3.16E-04
53	2,2',5,6'-Tetrachlorobiphenyl	tetra		47	292.0		5.62	4.27E-04
54	2,2',6,6'-Tetrachlorobiphenyl	tetra		14	292.0		5.21	5.75E-04
55	2,3,3',4'-Tetrachlorobiphenyl	tetra			292.0		6.11	1.82E-04
56	2,3,3',4'-Tetrachlorobiphenyl	tetra		11	292.0		6.11	1.51E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
57	2,3,3',5-Tetrachlorobiphenyl	tetra			292.0		6.17	2.69E-04
58	2,3,3',5'-Tetrachlorobiphenyl	tetra		5.	292.0		6.17	2.51E-04
59	2,3,3',6-Tetrachlorobiphenyl	tetra			292.0		5.95	3.02E-04
60	2,3,4,4'-Tetrachlorobiphenyl	tetra		2.	292.0	421	6.11	1.51E-04
61	2,3,4,5-Tetrachlorobiphenyl	tetra		18.	292.0		6.04	2.40E-04
62	2,3,4,6-Tetrachlorobiphenyl	tetra			292.0		5.89	3.72E-04
63	2,3,4',5-Tetrachlorobiphenyl	tetra		7	292.0		6.17	2.40E-04
64	2,3,4',6-Tetrachlorobiphenyl	tetra			292.0	136	5.95	2.69E-04
65	2,3,5,6-Tetrachlorobiphenyl	tetra		43	292.0		5.86	3.39E-04
66	2,3',4,4'-Tetrachlorobiphenyl	tetra		4	292.0	453	6.20	2.04E-04
67	2,3',4,5-Tetrachlorobiphenyl	tetra			292.0		6.20	2.34E-04
68	2,3',4,5'-Tetrachlorobiphenyl	tetra			292.0		6.26	3.80E-04
69	2,3',4,6-Tetrachlorobiphenyl	tetra			292.0		6.04	5.01E-04
70	2,3',4',5-Tetrachlorobiphenyl	tetra		11	292.0	512	6.20	2.04E-04
71	2,3',4',6-Tetrachlorobiphenyl	tetra			292.0		5.98	3.16E-04
72	2,3',5,5'-Tetrachlorobiphenyl	tetra		11	292.0		6.26	3.63E-04
73	2,3',5',6-Tetrachlorobiphenyl	tetra			292.0		6.04	5.25E-04
74	2,4,4',5-Tetrachlorobiphenyl	tetra		4	292.0	572	6.20	2.14E-04
75	2,4,4',6-Tetrachlorobiphenyl	tetra			292.0		6.05	4.68E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
76	2',3,4',5-Tetrachlorobiphenyl	tetra			292.0		6.13	2.39E-04
77	3,3',4,4'-Tetrachlorobiphenyl	tetra	0.0001	1	292.0		6.36	1.03E-04
78	3,3',4,5-Tetrachlorobiphenyl	tetra			292.0		6.35	1.63E-04
79	3,3',4,5'-Tetrachlorobiphenyl	tetra		3	292.0		6.42	1.95E-04
80	3,3',5,5'-Tetrachlorobiphenyl	tetra			292.0		6.48	3.75E-04
81	3,4,4',5-Tetrachlorobiphenyl	tetra	0.0003		292.0		6.36	1.43E-04
82	2,2',3,3',4-Pentachlorobiphenyl	penta		2	326.4	198	6.20	1.45E-04
83	2,2',3,3',5-Pentachlorobiphenyl	penta			326.4	295	6.26	2.14E-04
84	2,2',3,3',6-Pentachlorobiphenyl	penta			326.4	64	6.04	2.51E-04
85	2,2',3,4,4'-Pentachlorobiphenyl	penta			326.4	23	6.30	1.91E-04
86	2,2',3,4,5-Pentachlorobiphenyl	penta			326.4		6.23	2.40E-04
87	2,2',3,4,5'-Pentachlorobiphenyl	penta		3	326.4	259	6.29	1.84E-04
88	2,2',3,4,6-Pentachlorobiphenyl	penta			326.4		6.07	3.80E-04
89	2,2',3,4,6'-Pentachlorobiphenyl	penta			326.4		6.07	2.95E-04
90	2,2',3,4',5-Pentachlorobiphenyl	penta			326.4		6.36	2.95E-04
91	2,2',3,4',6-Pentachlorobiphenyl	penta			326.4	742	6.13	3.47E-04
92	2,2',3,5,5'-Pentachlorobiphenyl	penta			326.4		6.35	2.60E-04
93	2,2',3,5,6-Pentachlorobiphenyl	penta			326.4		6.04	3.39E-04
94	2,2',3,5,6'-Pentachlorobiphenyl	penta			326.4		6.13	3.89E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
95	2,2',3,5',6-Pentachlorobiphenyl	penta		10	326.4	838	6.13	3.00E-04
96	2,2',3,6,6'-Pentachlorobiphenyl	penta			326.4		5.71	4.07E-04
97	2,2',3',4,5-Pentachlorobiphenyl	penta		8	326.4	269	6.29	1.78E-04
98	2,2',3',4,6-Pentachlorobiphenyl	penta			326.4		6.13	3.89E-04
99	2,2',4,4',5-Pentachlorobiphenyl	penta			326.4	312	6.39	2.51E-04
100	2,2',4,4',6-Pentachlorobiphenyl	penta			326.4		6.23	0.00E+00
101	2,2',4,5,5'-Pentachlorobiphenyl	penta		9	326.4	353	6.38	2.45E-04
102	2,2',4,5,6'-Pentachlorobiphenyl	penta			326.4		6.16	3.72E-04
103	2,2',4,5,6'-Pentachlorobiphenyl	penta			326.4		6.22	5.01E-04
104	2,2',4,6,6'-Pentachlorobiphenyl	penta			326.4		5.81	7.41E-04
105	2,3,3'4,4'-Pentachlorobiphenyl	penta	0.00003	1	326.4	698	6.65	9.93E+14
106	2,3,3',4,5-Pentachlorobiphenyl	penta			326.4		6.64	1.66E-04
107	2,3,3',4',5-Pentachlorobiphenyl	penta			326.4		6.71	1.58E-04
108	2,3,3',4,5'-Pentachlorobiphenyl	penta			326.4		6.71	1.78E-04
109	2,3,3',4,6-Pentachlorobiphenyl	penta			326.4	622	6.48	2.82E-04
110	*2,3,3',4',6-Pentachlorobiphenyl*	penta			326.4	*225*	6.48	*1.96E-04*
111	*2,3,3',5,5'-Pentachlorobiphenyl*	penta			326.4		6.76	*2.69E-04*
112	*2,3,3',5,6-Pentachlorobiphenyl*	penta			326.4		6.45	*2.69E-04*
113	*2,3,3',5',6-Pentachlorobiphenyl*	penta			326.4		6.54	*3.24E-04*

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
114	2,3,4,4',5-Pentachlorobiphenyl	penta	0.00003	2	326.4		6.65	1.43E-04
115	2,3,4,4',6-Pentachlorobiphenyl	penta			326.4		6.49	2.45E-04
116	2,3,4,5,6-Pentachlorobiphenyl	penta		4	326.4		6.33	2.95E-04
117	2,3,4',5,6-Pentachlorobiphenyl	penta			326.4		6.46	2.40E-04
118	2,3',4,4',5-Pentachlorobiphenyl	penta	0.00003	1	326.4	949	6.74	1.26E-04
119	2,3',4,4',6-Pentachlorobiphenyl	penta			326.4		6.58	3.09E-04
120	2,3',4,5,5'-Pentachlorobiphenyl	penta			326.4		6.79	2.45E-04
121	2,3',4,5,6-Pentachlorobiphenyl	penta			326.4		6.64	5.62E-04
122	2',3,3',4,5-Pentachlorobiphenyl	penta			326.4		6.64	1.26E-04
123	2',3,4,4',5-Pentachlorobiphenyl	penta	0.00003		326.4		6.74	1.74E-04
124	2',3,4,5,5'-Pentachlorobiphenyl	penta			326.4		6.73	1.70E-04
125	2',3,4,5,6'-Pentachlorobiphenyl	penta			326.4		6.51	2.88E-04
126	3,3',4,4',5-Pentachlorobiphenyl	penta	0.1		326.4		6.89	8.13E+14
127	3,3',4,5,5'-Pentachlorobiphenyl	penta			326.4		6.95	1.55E-04
128	2,2',3,3',4,4'-Hexachlorobiphenyl	hexa		0.3	360.9	354	6.74	1.05E-04
129	2,2',3,3',4,5-Hexachlorobiphenyl	hexa		N/A	360.9	205	6.73	1.41E-04
130	2,2',3,3',4,5'-Hexachlorobiphenyl	hexa		N/A	360.9	528	6.80	1.51E-04
131	2,2',3,3',4,6-Hexachlorobiphenyl	hexa			360.9		6.58	2.40E-04
132	2,2',3,3',4,6'-Hexachlorobiphenyl	hexa			360.9	114	6.58	2.04E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
133	2,2',3,3',5,5'-Hexachlorobiphenyl	hexa		0.4	360.9		6.86	2.04E-04
134	2,2',3,3',5,6-Hexachlorobiphenyl	hexa			360.9	243	6.55	2.29E-04
135	2,2',3,3',5,6'-Hexachlorobiphenyl	hexa			360.9	171	6.64	2.69E-04
136	2,2',3,3',6,6'-Hexachlorobiphenyl	hexa		3	360.9	369	6.22	3.24E-04
137	2,2',3,4,4',5-Hexachlorobiphenyl	hexa		1	360.9	238	6.83	1.86E-04
138	2,2',3,4,4',5'-Hexachlorobiphenyl	hexa		1	360.9	481	6.83	1.29E-04
139	2,2',3,4,4',6-Hexachlorobiphenyl	hexa			360.9		6.67	3.31E-04
140	2,2',3,4,4',6'-Hexachlorobiphenyl	hexa		3	360.9		6.67	3.09E-04
141	2,2',3,4,5,5'-Hexachlorobiphenyl	hexa			360.9	269	6.82	1.74E-04
142	2,2',3,4,5,6-Hexachlorobiphenyl	hexa		1	360.9		6.51	3.16E-04
143	2,2',3,4,5,6'-Hexachlorobiphenyl	hexa			360.9		6.60	2.95E-04
144	2,2',3,4,5',6-Hexachlorobiphenyl	hexa			360.9	34	6.67	2.95E-04
145	2,2',3,4,6,6'-Hexachlorobiphenyl	hexa			360.9		6.25	4.68E-04
146	2,2',3,4',5,5'-Hexachlorobiphenyl	hexa			360.9	718	6.89	1.86E-04
147	2,2',3,4',5,6-Hexachlorobiphenyl	hexa			360.9		6.64	3.16E-04
148	2,2',3,4',5,6'-Hexachlorobiphenyl	hexa			360.9		6.73	4.27E-04
149	2,2',3,4',5',6-Hexachlorobiphenyl	hexa			360.9	155	6.67	2.34E-04
150	2,2',3,4',6,6'-Hexachlorobiphenyl	hexa			360.9		6.32	5.01E-04
151	2,2',3,5,5',6-Hexachlorobiphenyl	hexa		2	360.9	318	6.64	2.82E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
152	2,2',3,5,6,6'-Hexachlorobiphenyl	hexa			360.9		6.22	4.27E-04
153	2,2',4,4',5,5'-Hexachlorobiphenyl	hexa		0	360.9	654	6.92	1.66E-04
154	2,2',4,4',5',6-Hexachlorobiphenyl	hexa			360.9		6.76	3.80E-04
155	2,2',4,4',6,6'-Hexachlorobiphenyl	hexa		2	360.9		6.41	8.32E-04
156	2,3,3',4,4',5-Hexachlorobiphenyl	hexa	0.00003		360.9	724	7.18	8.91E+14
157	2,3,3',4,4',5'-Hexachlorobiphenyl	hexa	0.00003		360.9		7.18	8.51E+14
158	2,3,3',4,4',6-Hexachlorobiphenyl	hexa			360.9	914	7.02	1.66E-04
159	2,3,3',4,5,5'-Hexachlorobiphenyl	hexa			360.9		7.24	1.55E-04
160	2,3,3',4,5,6-Hexachlorobiphenyl	hexa		1	360.9		6.93	2.14E-04
161	2,3,3',4,5',6-Hexachlorobiphenyl	hexa			360.9		7.08	2.82E-04
162	2,3,3',4',5,5'-Hexachlorobiphenyl	hexa			360.9		7.24	1.32E-04
163	2,3,3',4',5,6-Hexachlorobiphenyl	hexa			360.9		6.99	1.66E-04
164	2,3,3',4',5',6-Hexachlorobiphenyl	hexa			360.9		7.02	1.78E-04
165	2,3,3',5,5',6-Hexachlorobiphenyl	hexa			360.9		7.05	2.75E-04
166	2,3,4,4',5,6-Hexachlorobiphenyl	hexa		0.2	360.9		6.93	1.82E-04
167	2,3,4,4',5,5'-Hexachlorobiphenyl	hexa	0.00003		360.9	186	7.27	1.10E-04
168	2,3',4,4',5',6-Hexachlorobiphenyl	hexa		0.9	360.9		7.11	2.75E-04
169	3,3',4,4',5,5'-Hexachlorobiphenyl	hexa	0.03	0.04	360.9		7.42	6.46E+14
170	2,2',3,3',4,4',5-Heptachlorobiphenyl	hepta		0.1	395.3	367	7.27	8.71E+13

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
171	2,2',3,3',4,4',6-Heptachlorobiphenyl	hepta			395.3	463	7.11	1.74E-04
172	2,2',3,3',4,5,5'-Heptachlorobiphenyl	hepta			395.3	548	7.33	1.20E-04
173	2,2',3,3',4,5,6-Heptachlorobiphenyl	hepta			395.3		7.02	1.82E-04
174	2,2',3,3',4,5,6'-Heptachlorobiphenyl	hepta		0.3	395.3	119	7.11	1.70E-04
175	2,2',3,3',4,5',6-Heptachlorobiphenyl	hepta			395.3		7.17	2.24E-04
176	2,2',3,3',4,6,6'-Heptachlorobiphenyl	hepta			395.3		6.76	2.95E-04
177	2,2',3,3',4',5,6-Heptachlorobiphenyl	hepta			395.3	434	7.08	1.62E-04
178	2,2',3,3',5,5',6-Heptachlorobiphenyl	hepta			395.3	648	7.14	2.14E-04
179	2,2',3,3',5,6,6'-Heptachlorobiphenyl	hepta			395.3	14	6.73	2.75E-04
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	hepta		0.2	395.3	499	7.36	1.07E-04
181	2,2',3,4,4',5,6-Heptachlorobiphenyl	hepta			395.3		7.11	2.29E-04
182	2,2',3,4,4',5,6'-Heptachlorobiphenyl	hepta			395.3		7.20	2.57E-04
183	2,2',3,4,4',5',6-Heptachlorobiphenyl	hepta			395.3	63	7.20	2.00E-04
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl	hepta			395.3		6.85	4.57E-04
185	2,2',3,4,5,5',6-Heptachlorobiphenyl	hepta		0.2	395.3	718	7.11	2.14E-04
186	2,2',3,4,5,6,6'-Heptachlorobiphenyl	hepta			395.3		6.69	3.72E-04
187	2,2',3,4,5,5',6-Heptachlorobiphenyl	hepta			395.3	59	7.17	2.04E-04
188	2,2',3,4',5,6,6'-Heptachlorobiphenyl	hepta			395.3		6.82	4.47E-04
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	hepta	0.003	0.04	395.3		7.71	6.61E+14

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
190	2,3,3',4,4',5,6-Heptachlorobiphenyl	hepta		0.2	395.3	193	7.46	1.12E-04
191	2,3,3',4,4',5',6-Heptachlorobiphenyl	hepta			395.3		7.55	1.32E-04
192	2,3,3',4,5,5',6-Heptachlorobiphenyl	hepta			395.3		7.52	1.91E-04
193	2,3,3',4',5,5',6-Heptachlorobiphenyl	hepta			395.3		7.52	1.35E-04
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	octa		0.02	429.7	381	7.80	6.76E+14
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	octa			429.7	979	7.56	1.17E-04
196	2,2',3,3',4,4',5,6'-Octachlorobiphenyl	octa			429.7		7.65	1.17E-04
197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl	octa		0.1	429.7		7.30	2.51E-04
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl	octa			429.7		7.62	1.55E-04
199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	octa			429.7	316	7.20	2.29E-04
200	2,2',3,3',4,5,6,6'-Octachlorobiphenyl	octa			429.7		7.27	2.40E-04
201	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	octa			429.7		7.62	1.32E-04
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	octa		0.04	429.7		7.24	2.24E-04
203	2,2',3,4,4',5,5',6-Octachlorobiphenyl	octa			429.7	133	7.65	1.41E-04
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl	octa			429.7		7.30	3.47E-04
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl	octa			429.7		8.00	8.71E+13
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	nona		0.003	464.2	102	8.09	8.71E+13
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	nona			464.2		7.74	1.70E-04
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	nona			464.2		7.71	1.66E-04

IUPAC No.	Congener	Homolog	Dioxin-Like TEF, Human [5]	Solubility (µg/L) [6]	MW (g/mol) [6]	VP (atm) [6]	Log K_{ow} [6]	HLC (atm-m^3/mol) [6]
209	Decachlorobiphenyl	deca		0.000	498.6		8.18	1.12E-04

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Table S5. Native Aroclor weight percent by homolog and average environmental variable values. MW = molecular weight, HCL = Henry's Law Constant, na = not available.

Homolog	No. Chlorines	Native Aroclor Homolog Make-up, as Total Weight Percent								Average MW	Average Solubility, µg/L	Average Log K_{ow}	Average Vapor Pressure (atm)	Average HCL, atm-m^3/mol
		Aroclor 1221	Aroclor 1232	Aroclor 1016	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262					
mono	1	60.05	27.8	0.710	0.750	0.045	0.020	0.023	0.035	188.7	4000	4.61	na	2.86E-04
di	2	33.38	26.8	17.6	15.0	1.000	0.160	0.080	0.220	223.1	1600	5.09	230.3	3.12E-04
tri	3	4.20	25.5	54.6	44.9	21.6	0.810	0.190	0.730	257.5	650	5.55	336.9	3.06E-04
tetra	4	1.89	16.9	26.5	32.5	55.6	17.3	0.463	0.600	292.0	260	5.98	260.1	3.04E-04
penta	5	0.480	2.95	0.560	6.44	19.8	55.5	8.59	3.13	326.4	99.0	6.40	417.6	3.93E+13
hexa	6	0.000	0.200	0.000	0.218	1.81	24.4	43.4	27.4	361.7	38.0	6.81	370.6	5.76E+13
hepta	7	0.000	0.015	0.000	0.000	0.475	2.030	38.5	47.9	395.3	14.0	7.17	343.8	3.12E+13
octa	8	0.000	0.000	0.000	0.000	0.000	0.040	8.27	19.6	429.7	5.50	7.52	452.3	6.36E+13
nona	9	0.000	0.000	0.000	0.000	0.000	0.040	0.700	1.71	464.2	2.00	7.85	102.0	2.90E+13
deca	10	0.000	0.000	0.000	0.000	0.000	0.000	na	na	498.6	0.760	8.18	na	1.12E-04

References, Table S5:

1. Frame, G. M.; Cochran, J. W.; Bøwadt, S. S., Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resol. Chromatog.* **1996,** *19*, (12), 657-668.

2. Wischkaemper, H. K.; Beliveau, A. F.; Henderson, R. W., US EPA Region 4 Technical Services Section Issue Paper for Polychlorinated Biphenyl Characterization at Region 4 Superfund and RCRA Sites, 2013.

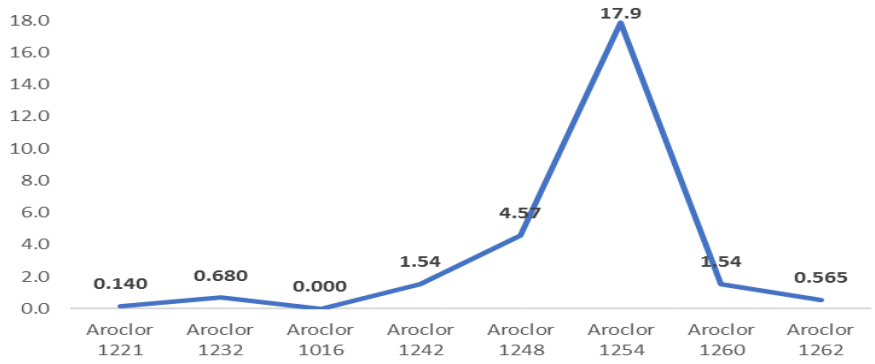

Figure S1. Dioxin-like congener weight fractions in native Aroclor mixtures.

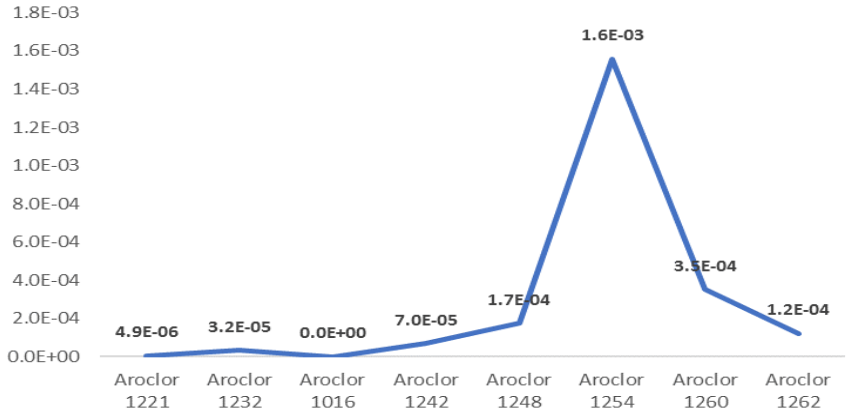

Figure S2. TEQ-adjusted dioxin-like congener weight fractions in native Aroclor mixtures.

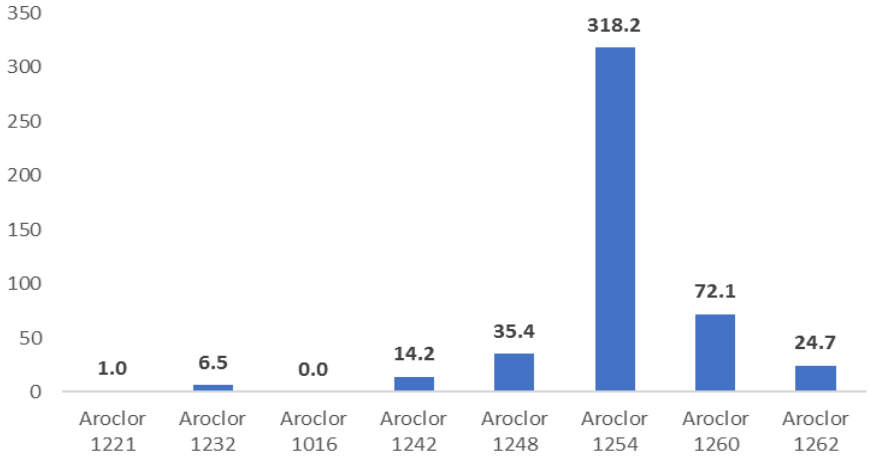

Figure S3. Relative TEQ-adjusted dioxin-like congener concentrations in native Aroclor mixtures.

APPENDIX B: Supplemental Information for Chapter 3

Table S1. Individual sample information and NCSU-21-PCB congener results for the 10 fish tissue extracts analyzed by the high resolution and the low-resolution instrument systems.

									NCSU-21-PCBs			
Extract No.	Waterbody	Species	Trophic Status	Trophic Guild	Trophic Level	Length (mm)	Weight (grams)	% Lipid	∑PCBs HRMS	∑PCBs LRMSMS A7000	∑PCBs LRMSMS A7010	∑PCBs LRMS A5975
1	High Rock Lake	Bluegill	Middle	Insectivore	3	142	52	1.2	5,001	5,019	5,630	6,730
2		Black Crappie	Middle	Piscivore	3	230	178	0.80	1,231	1,307	1,220	1,340
3		Largemouth bass	Top predator	Piscivore	4	275	256	0.20	2,429	2,291	2,825	2,690
4	Badin Lake	Redbreast sunfish	Middle	Insectivore	3	179	102	0.24	3,874	3,878	3,874	5,230
5		Redear	Middle	Insectivore	3	238	239	0.29	818	634	818	630
6		Black Crappie	Middle	Piscivore	3	194	120	0.23	547	203	547	0
7		Largemouth Bass	Top predator	Piscivore	4	294	361	0.52	3,146	3,038	3,146	3,072
8	Falls Reservoir	Bluegill	Middle	Insectivore	3	158	67.5	0.50	1,554	1,851	1,890	1,780
9	Lake Tillery	Redear	Middle	Insectivore	3	239	283	1.3	2,646	2,752	2,560	2,730
10		Black Crappie	Middle	Piscivore	3	247	211	0.60	2,290	2,349	2,030	2,210

Table S1 Continued

HRGC / HRMS Instrument System Data (ng/kg wet-weight)																					
	NCSU-21-PCB Congener																				
Extract No.	8	18	28	44	52	66	77	101	105	118	126	128	138	153	170	180	187	195	201	206	209
1	18	18	45	130	160	160	5.6	340	140	480	18	130	960	1100	200	490	380	91	91	150	130
2	10	10	19	44	52	35	2.3	90	34	110	10	50	230	250	51	120	92	50	50	48	54
3	10	11	37	120	110	110	5.4	250	67	240	10	54	430	450	81	180	150	50	50	67	67
4	21.8	35.2	87.6	290	203	199		419	78.2	445		66.9	565	993	24.1	122	252	10.5	13.4	27.6	20.9
5	5.96	4.67	22.7	25.7	36.4	39.1	1.59	80.3	14.6	63.7		19.9	148	185	14.9	38.9	72.6	4.05	4.04	17.6	17.9
6	5.8	6.48	19.4	24.4	29.3	23.3	1.58	47.2	10.9	45.2		13.3	84.3	134	8.42	28.5	40.5	2.48	2.8	10.6	8.58
7	13.5	16	66	222	140	162	7.25	300	70.7	307	1.3	78	508	671	50.5	153	240	13.7	12.1	65.5	48.5
8	10	10	24	51	55	56	3.1	130	53	190	10	53	350	370	50	140	170	50	50	69	39
9	10	10	10	41	62	42	4.2	190	39	120	10	59	500	740	110	270	430	50	50	29	100
10	10	10	68	190	200	270	19	200	160	370	10	50	250	270	50	120	92	50	50	40	41

Table S1 Continued

LRMSMS-A7010 Instrument System Data (ng/kg wet-weight)																					
	NCSU-21-PCB Congener																				
Extract No.	8	18	28	44	52	66	77	101	105	118	126	128	138	153	170	180	187	195	201	206	209
1			31	110	180	190	8	300	160	440		110	1040	1020	230	440	430			180	150
2			28	31	60	44	4	72	39	102			260	230	60	140	107			60	70
3			47	105	100	130	7	220	79	270		60	410	490	68	165	140				
4	28	31	80	270	210	230		405	87	470		62	520	1080		130	275				
5								72		55			170	200		49	88				
6										63			95				45				
7			60	190	170	145	9	280	80	270		65	470	700	74	165	230			60	70
8				67	80	84		145	66	215		70	360	320		170	155			74	45
9				48	45	50	6	170	47	135		61	470	780	100	310	405			40	85
10			61	210	185	290	25	230	145	320			270	300		105	98			55	55

Table S1 Continued

LRMSMS-A7000 Instrument System Data (ng/kg wet-weight)																					
	NCSU-21-PCB Congener																				
Extract No.	8	18	28	44	52	66	77	101	105	118	126	128	138	153	170	180	187	195	201	206	209
1				190	140	210		320	170	540		170	1100	1250	260	590	570	120			
2								130		130			340	280	50	180	110				
3				90	160	140		290	180	350		65	390	750	70	150	190				
4			77	360	140	260		370	65	370		80	510	1200		95	300				
5								94		77			160	140			92				
6										58											
7			78	205	160	180		320	89	330		61	450	720	70	135	250			85	55
8					50			160	70	150		50	490	360	50	190	220			50	50
9					80			230		110		90	570	690	140	300	350				
10			80	170	170	260		170	160	390			230	320			80				

Table S1 Continued

LRMS-A5975 Instrument System Data (ng/kg wet-weight)																					
	NCSU-21-PCB Congener																				
Extract No.	8	18	28	44	52	66	77	101	105	118	126	128	138	153	170	180	187	195	201	206	209
1				170	120	270		390	210	760		180	1400	1300	410	800	720				
2								110		150			300	510		270					
3								340	200	300			560	880	140	270					
4			90	400	230	410		520	100	420		90	880	1600		150	340				
5								115					205	170			140				
6																					
7			95	230	190	120		260	112	250		105	420	780		140	370				
8								200		240			450	310		240	340				
9								300		150			660	810	140	380	290				
10			100	240	180	220		250	130	280			340	410			60				