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Polychlorinated biphenyls (PCBs) and hydroxylated PCBs in serum from U.S. children and their mothers and in sediment from a Lake Michigan waterway

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POLYCHLORINATED BIPHENYLS (PCBS) AND HYDROXYLATED PCBS IN

SERUM FROM U.S. CHILDREN AND THEIR MOTHERS AND IN SEDIMENT

FROM A LAKE MICHIGAN WATERWAY

by

Rachel Frances Marek

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CERTIFICATE OF APPROVAL

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PH.D. THESIS

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I have had the good fortune of seeing science in action from a young age thanks to my mom. Since then I have had many other wonderful informal and formal science mentors – my grandfathers, Dr. Ann Russell, Dr. Keith Woo, Dr. Michelle Graham, my high school chemistry teacher, my college chemistry professors, and others – and now my thesis advisor, Dr. Keri Hornbuckle. I am grateful to Keri for recruiting me to her research group, for her advice and support, and for encouraging my personal and professional development. I am also thankful for the feedback from my dissertation committee that has helped me improve the quality of my research.

This dissertation is a product of collaboration with many people as part of the Iowa Superfund Research Program led by Professor Larry Robertson. Participating in the ISRP has made me a better researcher and colleague. The design, development, and maintenance of the human cohorts and the collection of blood samples were conducted by Professor Peter Thorne and his staff as part of ISRP Project 6, the AESOP Study (Airborne Exposure to Semi-volatile Organic Pollutants). The design and implementation of the surficial sediment sampling were conducted by Professor Keri Hornbuckle as part of ISRP Project 4. The initial development of instrument and wet-chemistry methods and instrument maintenance was conducted by Professor Keri Hornbuckle and her research team including post-doctoral researcher Dr. A. Karin Norström, lab director Collin Just, and lab manager Jon Durst as part of the ISRP Analytical Core. Advice regarding statistical methods was provided by Professor Kai Wang of the ISRP Administrative Core.

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ABSTRACT

In this dissertation I compare concentrations of polychlorinated biphenyls (PCBs) and hydroxylated PCBs (OH-PCB) in serum of children and their mothers from urban and rural U.S. communities, determine the variability of these concentrations from year to year, and report the detection of OH-PCBs in sediment from a Lake Michigan waterway and original commercial Aroclors. I developed extraction and analytical methods for the analysis of PCBs and OH-PCBs in 377 human serum samples and 20 sediment samples. I also developed a quality assurance protocol and analyzed more than 300 quality control samples for the purpose of generating an accurate, reproducible, representative, and precise data set.

I found that concentrations of PCBs were much higher in mothers than their children, and concentrations of OH-PCBs were slightly higher in mothers than their children. Children were enriched in lower molecular weight PCBs indicating the importance of environmental exposure to their blood concentrations. I also determined that concentrations were similar between the urban and rural residents. These concentrations were similar to concentrations reported in the U.S. general population and other populations without high dietary PCB intake. In East Chicago and Columbus Junction participants, concentrations of OH-PCBs demonstrated a strong positive relationship with PCBs. Variability in PCB and OH-PCB concentration from the first year to the second in most participants exceeded the estimated analytical variability. Observed variability could be due to exposure differences, physiological changes such as metabolism and weight, or a combination.

I also discovered the presence of OH-PCBs in the sediment from the Indiana Harbor and Ship Canal (IHSC), a Lake Michigan Waterway. In a first-approach, evidence from analysis of the correlations between OH-PCBs and PCBs in the same sediment is consistent with limited biotic activity. I also report OH-PCBs as contaminants in original

commercial Aroclors, and OH-PCB profile similarities between the Aroclors and sediment suggest that Aroclors are the major source of OH-PCB contamination in IHSC. This is a significant finding because OH-PCB contamination of sediment exists anywhere that PCB contamination from Aroclors is present.

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INTRODUCTION

Polychlorinated Biphenyls and their Metabolites and

Breakdown Products

Polychlorinated biphenyls (PCBs) are anthropogenic chemicals that were widely

used in a variety of industrial applications around the world, including in capacitors and

transformers, heat transfer fluid, hydraulic fluid, lubricating oil, paint, ink, carbonless

copy paper, adhesives, sealants, and plastics.[1] The structure of a PCB consists of one to

ten chlorines positioned around a biphenyl, and there are 209 different compounds,

referred to as congeners, depending on the number and position of the chlorines (Figure

1). In the United States different mixtures of PCBs were sold by the chemical company

Monsanto under the trade name Aroclor until their production ended in 1977.
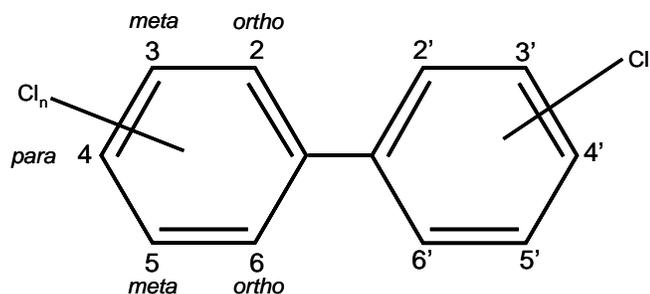
Figure 1 PCB structure, where one to ten chlorines are positioned around a biphenyl.
There are 209 different PCBs.

PCBs were widely used because of their effective chemical properties such as

stability, low flammability, and insulation. For those same reasons PCBs persist in the

environment. Most PCBs in the environment are a result of Aroclor use;[2] however, a

recent study discovered the presence of PCBs in paint pigments as a possible explanation

for their continued release into the environment.[3] PCBs bioconcentrate, biomagnify, and

bioaccumulate, and they have been widely reported in humans and other non-laboratory animals. PCB accumulation in humans is a function of multiple exposures including direct transfer through the placenta from mother to fetus, diet beginning with the mother's milk, dermal, and inhalation. Humans metabolize PCBs to monohydroxylated PCBs (OH-PCBs) via cytochrome P450 enzymes, either through direct insertion of the OH or an intermediate epoxide formation that can lead to a 1,2 shift of the OH and adjacent chlorine (also called the NIH shift).[4] There are 837 possible mono OH-PCBs, although only a small sub-set of those have been reported in humans and animals.[4, 5] A large body of literature implicates PCBs and OH-PCBs in causing numerous negative health effects such as endocrine disruption, neurotoxicity, and developmental disorders, and an International Agency for Research on Cancer (IARC) Working Group recently classified the entire group of PCBs as a Group 1carcinogen (carcinogenic to humans) as it became clear that their carcinogenicity could not be solely attributed to the dioxin-like PCBs.[6]

Microbial degradation of PCBs has been studied as a potential bioremediation strategy. Microbes degrade PCBs anaerobically through dechlorination and aerobically through the upper biphenyl pathway (Figure 2). The aerobic degradation process involves a dioxygenase that leads to the formation of dihydroxylated PCB intermediates. However, there is no known pathway for the microbial formation of mono OH-PCBs.
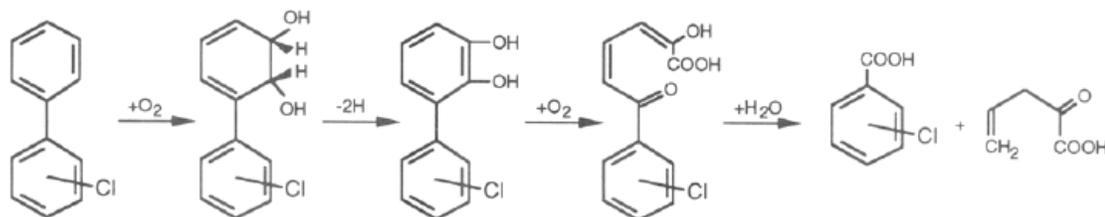
Figure 2 Aerobic microbial degradation pathway of PCBs occurs via a dioxygenase to form a dihydroxylated intermediate metabolite.[7]

<p style="text-align:center">Study Areas and Research Cohorts</p>

East Chicago, Indiana is a highly industrialized community (pop. 32,400) on the southwestern shore of Lake Michigan (Figure 3). Major industries in the area include a steel manufacturer (Mittal Steel USA) and a gas refinery (BP Products North America). Bisecting East Chicago and flowing into Lake Michigan is the Indiana Harbor and Ship Canal (IHSC) which is used by the area's industries. IHSC is designated as an Area of Concern by the International Joint Commission[8] due to extensive contamination with heavy metals, polycyclic aromatic hydrocarbons, and PCBs, and IHSC is a major source of PCBs to Lake Michigan.[9] IHSC flows near junior and senior high schools, and PCBs are of particular concern to this community due to a navigational dredging project that began in 2012 and will continue for 30 years.

Figure 3 East Chicago, Indiana is bisected by the Indiana Harbor and Ship Canal (IHSC), which is contaminated with high levels of PCBs. A navigational dredging project will place contaminated sediment in the confined disposal facility (CDF).

In contrast, the Columbus Community School District in Iowa is situated in a rural agricultural setting and includes residents of the small towns of Columbus City (pop. 381), Columbus Junction (pop. 1900), Conesville (pop. 428), Cotter (pop. 47), and Fredonia (pop. 241). These towns have no known current or historical industrial PCB sources.

Residents of both East Chicago and the Columbus Junction area have lower median household incomes and are mostly Hispanic or African-American. Most students receive free or discounted school lunch.

<u>Hypotheses and Objectives</u>

I addressed the following research hypotheses:

1. Mothers and children living in a community with a known source of airborne PCBs have higher concentrations and different distributions of PCBs in their blood than mothers and children living in a community with no such source.

2. Mothers have higher concentrations of PCBs in their blood than their adolescent children.

3. The concentration of OH-PCBs in the blood of mothers and children shows similar trends as the PCBs: mothers and children in the urbal community have higher concentrations and different distributions than mothers and children living in the rural community, and mothers have higher concentrations than their children.

4. Sum OH-PCB concentration has a linear correlation with sum PCB concentration.

5. Year to year variability of PCBs and OH-PCBs in mothers and children from the urban and rural cohorts is small.

6. The Indiana Harbor and Ship Canal sediment and Monsanto Aroclors are contaminated with OH-PCBs.

To address the study hypotheses, I accomplished the following objectives:

1. Develop a method for measuring PCB and OH-PCB congeners in human blood serum. This method must be highly selective and sensitive. This method must also be effective for small sample sizes (about 4 mL serum) and reliable for irreplaceable samples. For these reasons, this method must also include rigorous quality control.

2. Measure PCBs and OH-PCBs in a representative, reproducible, and comparable manner in 377 human blood serum samples collected from mothers and children in two communities.

3. Report quantitative and statistically significant differences between the major groups of individuals in this study: urban compared to rural residents; mothers compared to their children; boys compared to girls; and this study's cohorts compared to the U.S. general population and others around the world.

4. Investigate PCB metabolism through analysis of parent and metabolite congener data.

5. Quantify the variability in year to year concentrations of PCBs and OH-PCBs in mothers and children from East Chicago and Columbus Junction.

6. Develop a sensitive and selective method, including rigorous quality control, for measuring OH-PCBs in highly anthropomorphically-impacted sediment.

7. Determine levels of OH-PCBs in IHSC sediment and original commercial Aroclors.

Thesis Overview

Chapter 1 addresses hypotheses 1 through 4 and objectives 1 through 4 with respect to method development and measurement of PCBs and OH-PCBs in mothers and children from East Chicago and Columbus Junction. Chapter 1 was published in *Environmental Science & Technology* (Marek, R.F.; Thorne, P.S.; Wang, K.; DeWall, J.; Hornbuckle, K.C., PCBs and OH-PCBs in serum from children and mothers in urban and

rural U.S. communities. *Environ Sci Technol* **2013**, 47, 3353-3361|
dx.doi.org/10.1021/es304455k) and is included in this thesis with permission from the
editor of *Environmental Science & Technology*. Supplemental material for Chapter 1 is in
Appendix A.

Chapter 2 addresses hypothesis 5 and objective 5 with respect to the year to year
variability in PCB and OH-PCB concentrations in mothers and children from East
Chicago and Columbus Junction. Chapter 2 will be submitted as a manuscript.
Supplemental material for Chapter 2 is in Appendix B.

Chapter 3 addresses hypothesis 6 and objectives 6 through 7 with respect to OH-
PCBs in the Indiana Harbor and Ship Canal. Chapter 3 was published in *Environmental
Science & Technology* (Marek, R.F.; Martinez, A.; Hornbuckle K.C.; Discovery of
Hydroxylated Polychlorinated Biphenyls (OH-PCBs) in sediment from a Lake Michigan
waterway and original commercial Aroclors. *Environ Sci Technol* **2013**, 47, 8204-8210|
dx.doi.org/ 10.1021/es402323c) and is included in this thesis with permission from the
editor of *Environmental Science & Technology*. Supplemental material for Chapter 3 is in
Appendix C.

In addition to the above first-author papers, using methods developed to analyze
human serum for PCBs and OH-PCBs I also generated data and figures, and wrote and
edited a portion of a journal article about the toxicology of PCB 11 and its metabolites in
humans. This paper was accepted for publication in *Toxicological Sciences* (Zhu, Y.;
Mapuskar, K.A.; Marek, R.F.; Xu, W.; Lehmler, H.J.; Robertson, L.W.; Hornbuckle,
K.C.; Spitz, D.R.; Aykin-Burns, N.; A new player in environmentally induced oxidative
stress: Polychlorinated biphenyl congener, 3,3'-dichlorobiphenyl (PCB11). *Toxicol Sci*|
dx.doi.org/10.1093/toxsci/kft186). A summary of the methods and results I generated for
this paper is in Appendix D.

CHAPTER 1
PCBS AND OH-PCBS IN SERUM FROM CHILDREN AND THEIR
MOTHERS IN URBAN AND RURAL U.S. COMMUNITIES[1]

Abstract

East Chicago, Indiana is a heavily-industrialized community bisected by the Indiana Harbor and Ship Canal, which volatilizes ~7.5 kg/yr polychlorinated biphenyls (PCBs). In contrast, the rural Columbus Junction, Iowa area has no known current or past PCB industrial sources. Blood from children and their mothers from these communities were collected April 2008-January 2009 (n=177). Sera were analyzed for all 209 PCBs and 4 hydroxylated PCBs (OH-PCBs). Sum PCBs ranged from non-detect to 658 ng/g lw (median = 33.5 ng/g lw). Sum OH-PCBs ranged from non-detect to 1.2 ng/g fw (median = 0.07 ng/g fw). These concentrations are similar to those reported in other populations without high dietary PCB intake. Differences between the two communities were subtle. PCBs were detected in more East Chicago mothers and children than Columbus Junction mothers and children, and children from East Chicago were enriched in lower-molecular weight PCBs. East Chicago and Columbus Junction residents had similar levels of total and individual PCBs and OH-PCBs in their blood. Concentrations of parent PCBs correlated with concentrations of OH-PCBs. This is the first temporally and methodologically consistent study to evaluate all 209 PCBs and major metabolites in two generations of people living in urban and rural areas of the United States.

Introduction

Polychlorinated biphenyls (PCBs) are anthropogenic persistent organic pollutants historically used in a variety of applications including capacitors, transformers, lubricants, plastics, adhesives, and carbonless copy paper.[1] Despite discontinued

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production in the United States in 1977, PCBs persist in the environment and in humans. A major metabolic pathway for PCBs in humans is hydroxylation via the Cytochrome P450 enzyme system, with direct insertion of the OH group or an intermediate epoxide formation followed by a 1,2-hydride shift (NIH shift).[4] A large body of literature indicates that PCBs and their metabolites cause negative health effects including carcinogenicity[10] and endocrine disruption.[11] Children's exposure to PCBs is particularly concerning because PCBs cause neurotoxicity and developmental disorders.[12-14]

PCB accumulation in humans is a function of an array of exposures including diet, dermal, inhalation, and direct transfer in breast milk from mothers to infants. Because PCBs are anthropogenic, it is commonly assumed that living in a community with PCB contamination will result in higher PCB body burdens. The overall research question we address here is 'how does environment affect PCB body burden?'

Previous studies offer strong evidence that differing environments yield different PCB body burdens. DeCaprio *et al*. observed serum PCB profiles in some participants that were similar to the air profile above a nearby PCB-contaminated water body.[15] Choi *et al*. found that babies born after dredging of the contaminated New Bedford Harbor had significantly lower PCB body burdens than babies born before and during the dredging.[16] Costopoulou *et al*. discovered PCB concentrations were different in people living in urban compared to rural Greece.[17] McGraw and Waller found evidence for airborne exposure to PCBs in a cohort of pregnant African-American women living in Chicago.[18] Dirtu *et al*. found differences in levels of OH-PCBs, but not PCBs, in residents of two differently-contaminated European cities.[19]

Although several studies demonstrate the possibility of contributions to body burden from sources other than diet, few studies have been conducted on a large scale that compare two communities in a temporally and methodologically consistent manner. Few studies compare PCB accumulation in humans as a function of local industrialization or control for known predictors of PCBs in humans such as age, sex, and demographics.

Our study uniquely includes the following three aspects: 1) we sampled blood in residents of two communities in the United States with similar demographics, one industrial and one rural; 2) our cohort includes adolescent children and their mothers; and 3) we analyzed for all 209 PCBs and major metabolites (OH-PCBs). We hypothesized that the concentrations and distribution of PCBs and OH-PCBs in blood would differ between the two communities and age groups. We further hypothesized that mothers would have higher concentrations than their children and that PCB concentration would correlate with OH-PCB concentration.

Study subjects from Indiana live in the urban community of East Chicago. It is a highly industrialized community of 32,400 people bisected by the Indiana Harbor and Ship Canal (IHSC) on the southern shore of Lake Michigan. Major industries in the area include a steel manufacturer (Mittal Steel USA, Inc.) and a gas refinery (BP Products North America, Inc.). The International Joint Commission designated IHSC as an Area of Concern due to extensive contamination with heavy metals, polycyclic aromatic hydrocarbons, and PCBs.[8] PCBs are particularly interesting to this community because of plans for a navigational dredge of IHSC. IHSC flows within 0.5 km of the junior and senior high schools and is a known source of airborne PCBs. Martinez *et al.* found that ~7.5 kg/yr PCBs volatilize from IHSC,[9] and sediment core profiles show that dredging may increase this release by exposing highly contaminated deep sediments.[20] It is unknown whether there are other sources of airborne PCBs in the community.

In contrast, the Columbus Community School District in Iowa is a rural community of 3000 people with no known current or historical PCB sources. The town of Columbus Junction was incorporated in 1893 and was historically a small railroad and steel community situated in a rural and agricultural setting. Residents of both East Chicago and the Columbus Junction area have lower median household incomes and are mostly Hispanic or African-American. Most students receive free or discounted school lunch.

In this paper we compare the levels of PCBs and OH-PCBs between residents in the two locations, compare mother and child body burdens, and investigate the metabolic relationship between PCBs and OH-PCBs in participants.

Experimental

Sample Collection

Serum samples were collected from junior high school-aged students and their mothers who were enrolled in the Airborne Exposures to Semi-volatile Organic Pollutants (AESOP) Study, a community-based participatory exposure assessment cohort study, between April 2008 and January 2009. In the first year of the study, serum was available for analysis from 41 mothers and their 44 children participating in East Chicago, and from 44 mothers and their 48 children in the Columbus Junction area. More than one child was enrolled from 6 participating families.

Blood and questionnaire data were collected from enrolled AESOP subjects who gave informed consent and assent under an established Institutional Review Board protocol. A standard veinapuncture procedure was used. Blood was drawn into empty glass Vacutainer tubes and allowed to clot for 30 minutes. The blood was centrifuged to fully separate the serum from cells. Serum was transferred from the Vacutainer tubes into glass vials with Teflon caps and kept frozen at -20 ^{o}C until extraction. Two serum samples were removed from the sample set after being accidentally stored in plastic vials instead of glass vials. Cholesterol and triglyceride concentrations were measured by the University of Iowa Diagnostic Laboratories, Iowa City, IA, USA.

Analytical

Extraction. The extraction, separation, derivatization, and cleanup methods employed are a modification of Hovander et al.[21] Briefly, serum (4 g) was spiked with 5 ng of each surrogate standard PCB 14 (3,5-dichlorobiphenyl, AccuStandard, New Haven,

CT, USA), deuterated-PCB 65 (2,3,5,6-tetrachlorobiphenyl-d5, Cambridge Isotope Laboratories, Inc., Andover, MA, USA), PCB 166 (2,3,4,4',5,6-hexachlorobiphenyl, AccuStandard) and 4'OH-PCB 159 (4-hydroxy-2',3,3',4',5,5'-hexachlorobiphenyl, AccuStandard), denatured with hydrochloric acid (HCl) and 2-propanol, and extracted with 1:1 hexane:methyl tert-butyl ether (MTBE). The extract was washed with 1% potassium chloride (KCl) and separated into PCB and OH-PCB fractions by liquid-liquid partitioning with potassium hydroxide (KOH) and hexane. The OH-PCBs were re-protonated with HCl (2 M) and extracted using 9:1 hexane:MTBE. OH-PCBs were derivatized to the methoxylated form (MeO-PCBs) using diazomethane. Lipids and interferences were removed from each fraction, first by mixing with concentrated sulfuric acid and then by passing the extract through a sulfuric acid-activated silica gel column. PCBs were eluted from the silica column with hexane, and MeO-PCBs were eluted with dichloromethane (DCM). All solvents were pesticide residue analysis quality and the reagent water for aqueous solutions was Optima quality (ThermoFisher Scientific).

Analysis and Quantification. The sample extracts containing PCBs were spiked with 5 ng each of internal standard PCB 204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl, AccuStandard) and deuterated-PCB 30 (2,4,6-trichlorinatedbiphenyl-d5, Cambridge Isotope Laboratories, Inc.) immediately prior to analysis. The PCB instrumental method applied is a modification of US EPA Method 1668.[22] A gas chromatograph with tandem mass spectrometer (GC-MS/MS, Agilent 6890N Quattro Micro™ GC, Waters Micromass MS Technologies) in multiple reaction monitoring mode was employed to analyze samples for all 209 PCBs as 160 individual or co-eluting congener peaks. Concentrations are reported for 202 PCBs after standards and congeners that co-elute with the standards were removed from the data set. Additional details are in Appendix A.

The sample extracts containing MeO-PCBs were spiked with 5 ng internal standard PCB 209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl, AccuStandard)

immediately prior to analysis using gas chromatography with electron capture detection (GC-ECD, Agilent 6890N).

There are 837 possible monohydroxylated–PCBs,[23] and while commercial standards are available for all 209 PCBs, they are not available for most monohydroxylated-PCBs. The extracts were analyzed for four OH-PCBs as MeO-PCBs: 4-MeO PCB 107 (2,3,3',4',5-pentachloro-4-methoxybiphenyl), 3-MeO PCB 138 (2,2',3,4,4',5-hexachloro-3-methoxybiphenyl), 4-MeO PCB 146 (2,2',3,4',5,5'-hexachloro-4-methoxybiphenyl), and 4-MeO PCB 187 (2,2',3,4',5,5',6-heptachloro-4-methoxybiphenyl). These congeners were selected because they are commonly reported hydroxylated metabolites in humans.[24] MeO-PCB standards were purchased from Wellington Laboratories (Guelph, ON, Canada).

Congener mass calculation was performed by applying a relative response factor obtained from the calibration curve for each congener. Surrogate standards were used to adjust final concentrations to percent recovery on a per sample basis, where recovery of surrogate standard PCB 14 was used for mono to tri chlorinated biphenyls, d-PCB 65 was used for tetra to penta chlorinated biphenyls, PCB 166 was used for hexa to deca chlorinated biphenyls, and OH-PCB 159 was used for all OH-PCBs. PCB concentration is reported as per lipid weight (lw, Table A6) and fresh weight (fw, Table A7), where total lipids were determined from measured cholesterol and triglyceride values using an empirical equation from Bernert *et al.*[25] OH-PCB concentrations are reported as per fresh weight (Table A6).

Quality Control. In this study, a full suite of QC was assessed using surrogate standards, field and instrument blanks, method blanks, and replicates of laboratory reference material (LRM) and Standard Reference Material (SRM) from National Institute of Standards and Technology (NIST SRM 1589a: PCBs, Pesticides, PBDEs, and Dioxins/Furans in Human Serum).

A field blank study was undertaken to determine any PCB mass inadvertently contributed to the blood samples. Field staff used phlebotomy tubing and needle sets to puncture combusted glass vial reservoirs filled with 4% KCl (the same matrix used for method blanks) and dispensed the solution into blood collection tubes. Mimicking serum transfer, field staff pipetted the field blank solution from the tubes into glass vials equipped with Teflon-lined caps and returned them to the laboratory as is done for samples. After undergoing the same extraction and analysis methods as samples, it was determined that there was no significant mass contribution to serum samples from the field.

Instrument blanks consisting of vials of hexane were analyzed before and after the calibration standard and at the beginning and end of each sample batch. PCBs and OH-PCBs detected in instrument blanks were always below the limit of quantification (LOQ).The LRM consisted of homogenized archived human serum purchased from a Chicago blood bank and was analyzed for three target PCBs with every batch of samples to evaluate reproducibility. Analysis of congeners PCB 138, PCB 153, and PCB 180 in the LRM resulted in an average relative standard deviation of 16%. Replicates of NIST SRM 1589a were analyzed to evaluate accuracy and resulted in an average difference of 9% between our laboratory measurements and NIST certified and reference values. Detailed QC results are included in Appendix A.

Statistical Analysis

Limit of Quantification. Sum PCBs and OH-PCBs in the method blanks ranged from 0.47 ng to 3.5 ng per sample (2.3 ng per sample average) in the 6 batches used to determine the PCB LOQ and 0.030 to 0.14 ng per sample (0.092 ng per sample average) in the 9 batches used to determine the OH-PCB LOQ. Most PCB and all OH-PCB congeners were detected in the method blank as consistently low background noise, and the congener-specific LOQ was determined as the 95% confidence interval (mean +

2*SD) of the normally-distributed method blank data. Most of these congener LOQs were below 0.05 ng per sample (~0.01 ng/g fw) but ranged as high as 0.13 ng per sample (~0.03 ng/g fw) for PCBs 110+115 and 0.16 ng per sample (~0.04 ng/g fw) for 4-OH-PCB 107. Congener-specific LOQs are shown in Table A2 and Table A3.

Variable levels of 10 PCB congeners as 5 chromatographic peaks (11, 52, 61+70+74+76, 90+101+113, and 95) were detected in the method blanks above background noise. The average relative standard deviation was much greater between batches (59-123%) than within (4-22%). For these congeners, masses detected in the blanks were subtracted from measured values in the samples. Then a separate 95% confidence interval (mean + 2*SD) was applied where mean was the value measured in the blank, and standard deviation was determined for each of the 5 congener groups from the separate analysis of multiple blanks in one batch. The separate blank analysis confirmed that although there was high batch-to-batch variation for these congeners in the blanks, within a batch each sample was affected similarly by contamination. Sample values for these congeners are reported as detect/non-detect only to reflect the increased likelihood of reporting false detections with blank subtraction.[26] These congeners were not included in ΣPCB determination and reporting. Techniques for handling data below the LOQ were explored, including imputation of LOQ/2 and LOQ/√2. Data were found to be significantly affected by these substitutions in a misleading way; therefore data below the LOQ were given a most conservative value of 0 for calculation of summary statistics and presentation of the data.

Statistical Tests. The concentration was first dichotomized at the threshold of the congener-specific LOQ (Table A2 and Table A3). Then the non-parametric Fisher's exact test, Wilcoxon Signed Ranks test, and Wilcoxon Rank Sum test ($\alpha = 0.05$) were applied to data from Columbus Junction and East Chicago separately. Mantel-Haenszel tests ($\alpha = 0.05$) were employed for a combined analysis of these two cohorts. A parametric Tobit regression analysis was also employed. Instead of imputing the unknown values below

LOQ, this method models the probability a value is below LOQ under the normality assumption. Since each subset of data appears to be skewed to the right, log transformation was applied to the data. This method was employed to determine statistically significant differences between concentrations of the 5 congeners detected in at least 30% of samples (83, 118, 129+137+138+163+164, 153+168, 180+193).[27]

Results

Ninety-two PCB congeners as 62 unique chromatographic peaks and all 4 OH-PCB congeners were detected in the samples (Figure 4, Table A6 and Table A7) including commonly-detected congeners: 118, 138+129+137+163+164, 153+168, and 180+193 and dioxin-like congeners: 105, 118, 126, 156+157, 167, and 169. We also report the detection of PCB congeners 11 and 83, which to our knowledge have not been previously reported in human blood. PCBs 156+157, 187, 11, 113+90+101, and 95 were detected more frequently in East Chicago children than in Columbus Junction children, and PCBs 11 and 95 were detected more frequently in East Chicago mothers than Columbus Junction mothers ($p<0.05$). Considering all congeners together the total frequency of detections was statistically significantly higher in East Chicago than Columbus Junction in both mothers and children ($p<0.05$ and $p<0.01$, respectively).

East Chicago and Columbus Junction residents had similar concentrations of total PCBs (Table A6 and Table A7, $p = 0.6$ and $p = 0.3$ for mothers and children, respectively) and OH-PCBs (Table A6, $p = 0.3$ and $p = 0.8$ for mothers and children, respectively). PCB concentrations in the overall sample set ranged from below detection to 210 ng/g lw with an outlier at 625 ng/g lw (a Columbus Junction mother). OH-PCB concentrations in the overall sample set ranged from below detection to 0.3 ng/g fw with an outlier at 1.2 ng/g fw (the same Columbus Junction mother). East Chicago and Columbus Junction residents also have similar levels of individual congeners in their serum (Table A6 and Table A7).
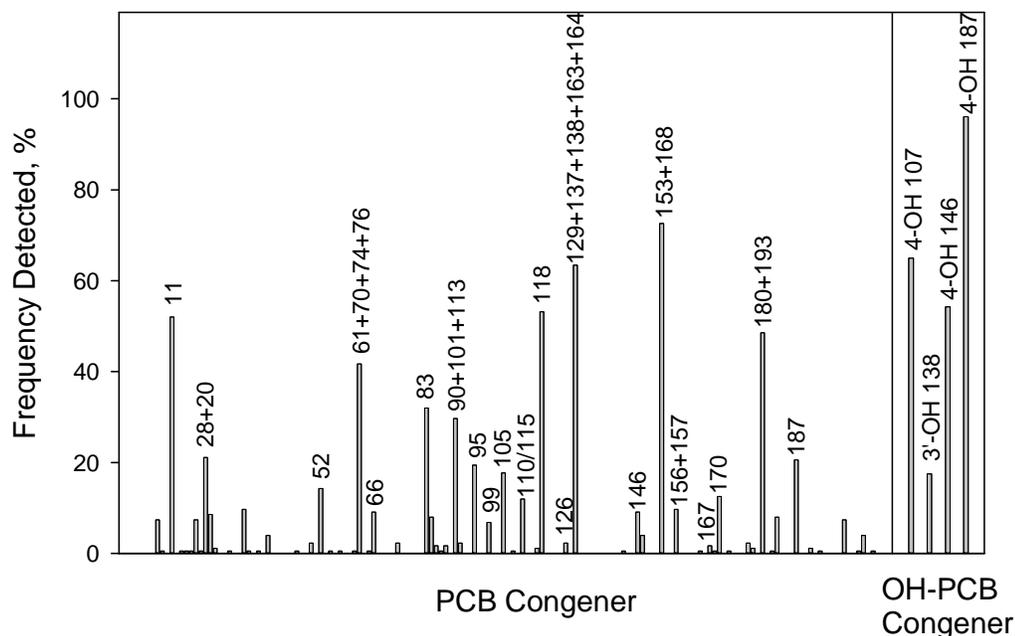
Figure 4 Detection frequency of each PCB and OH-PCB congener in our sample set of East Chicago and Columbus Junction residents (n=175). See Table A6and Table A7 for congener-specific data.

Mothers had higher levels of ΣPCBs (p<0.01) and ΣOH-PCBs (p<0.01) than their children, with the difference more pronounced for PCBs than OH-PCBs. The proportion of low- molecular weight PCBs was calculated for each individual as sum PCBs from homolog groups 1 through 5 divided by the sum of all PCBs. Interestingly, East Chicago children had a higher proportion of less chlorinated PCBs compared to their mothers (Figure 5, $p < 0.0001$) than Columbus Junction children and their mothers ($p = 0.013$).

Concentrations of OH-PCBs and their parent PCBs in each individual were compared to investigate whether a metabolic relationship exists. Grouping all participants together, sum OH-PCBs had a strong positive c with the sum of their parent PCBs (Figure 6). Investigating specific congeners (Figure 7), 4-OH-PCB 146 correlated with parent PCB 146 more strongly than parent PCBs 138 and 153, and 4-OH-PCB 187 correlated with parent PCB 187 more strongly than parent PCB 183, indicating possible

preference for direct insertion. No such correlation was determined for 3'-OH-PCB 138.

A correlation could not be tested for 4-OH-PCB 107 because PCB 107 was only detected

in one participant.
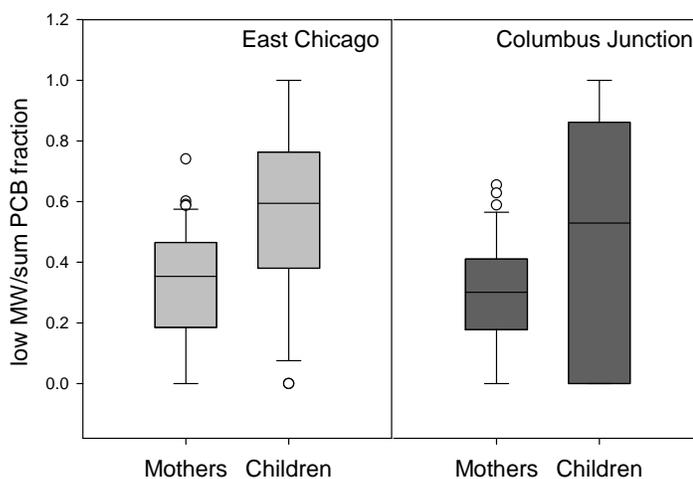
Figure 5 Fraction of low-molecular weight PCBs, defined as mono- to penta-chlorinated biphenyls divided by total PCBs in mothers and children from East Chicago (left) and Columbus Junction (right). Data are plotted as box plots with the median indicated by the bold horizontal line, the two middle quartiles shown as polyhedrons above and below the median and the 95th percentiles shown as the horizontal lines connected by the dashed line. Outlier points are indicated by open circles.
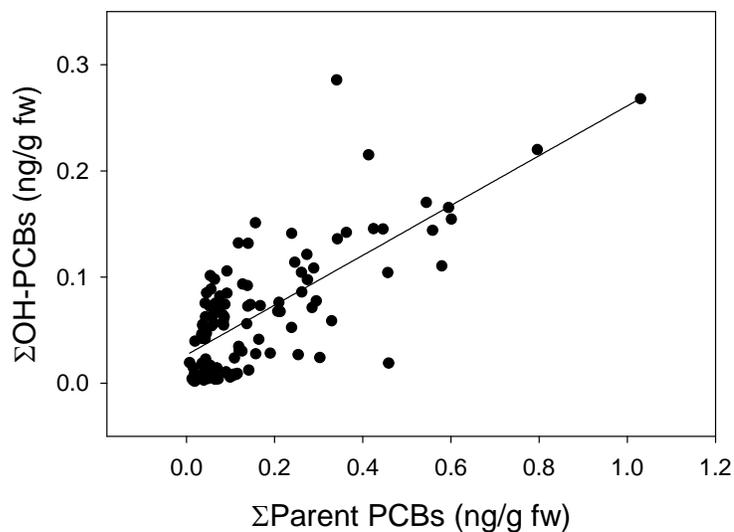
Figure 6 Fresh weight concentrations of sum OH-PCBs and sum of their precursor PCBs display a linear trend ($R^2 = 0.53$, $p < 0.0001$). Each data point represents one participant. One leverage point, a mother with much higher concentrations than the other participants, was excluded. Participants with values <LOQ were excluded.
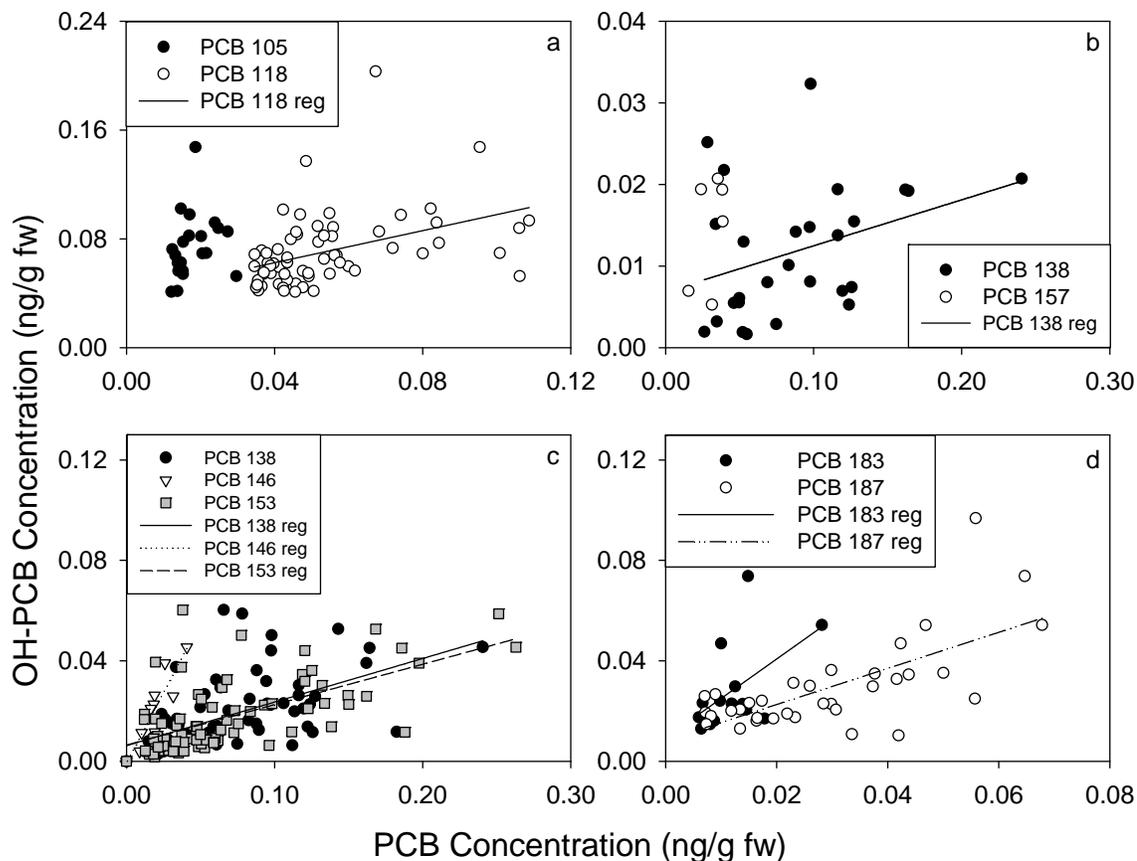
Figure 7 Best fitting linear regressions between specific PCB parents and their OH-PCB metabolites in mothers and children: (a) 4-OH-PCB 107 with PCB 105 ($R^2 = 0.059$) and PCB 118 ($R^2 = 0.17$, $p = 0.0006$); (b) 3'-OH-PCB 138 with PCB 138 ($R^2 = 0.13$), and PCB 157 ($R^2 = 0.23$); (c) 4-OH-PCB 146 with PCB 138 ($R^2 = 0.31$, $p < 0.0001$), PCB 146 ($R^2 = 0.81$, $p = 0.0004$), and PCB 153 ($R^2 = 0.40$, $p < 0.0001$); (d) 4-OH-PCB 187 with PCB 183 ($R^2 = 0.27$, $p = 0.057$) and PCB 187 ($R^2 = 0.47$, $p < 0.0001$). One leverage point, a mother with much higher concentrations than the other participants, was removed from all 4 graphs. An outlier, a mother with a very high concentration of 4-OH-PCB 146 compared to the other metabolites was also removed from graph (c). Participants with values <LOQ were excluded; it was therefore not possible to determine correlations between PCB 107 and PCB 130 and their respective metabolites.

Discussion

In this study we measured serum samples for all 209 PCBs and their 4 major metabolites. Congener-specific analysis is necessary for elucidating the role of

environment on levels of PCBs in the blood as well as understanding the role of metabolism.

Sum PCB and sum OH-PCB levels measured in this study are similar to those found in populations not targeted for high dietary PCB consumption (Figure A2, Figure A3, and Figure A4). PCB levels measured in this study are similar to levels detected in serum from the U.S. general population[28] and teachers in PCB-containing schools[29] but are lower than in samples from Hudson River communities collected 2000-2002[30] and samples collected 1994-1999 from African-American women in Chicago.[18] PCB levels measured here are also similar to Polish[31] and Japanese[32] mothers and women from Russia living in the vicinity of a chemical plant[33] but are somewhat lower than levels measured in Belgium and Romania.[19] PCB levels measured in this study are much lower than levels detected in populations consuming seafood[34, 35] or food grown near a former PCB-producing plant in Eastern Slovakia.[36] This result is likely because our participants eat very little seafood and food grown near PCB-contaminated IHSC.

OH-PCB levels measured in this study are similar to those detected in California mothers sampled before the PCB ban,[37] Belgium and Romanian adults,[19] Slovakian women living near a former PCB-producing plant,[38] and Japanese breast cancer patients[39] but are much lower than levels detected in populations consuming high amounts of seafood.[34, 40, 41] It is interesting that the California and Slovakian cohorts had somewhat higher levels of PCBs but similar levels of OH-PCBs to this study's participants. This result is probably because OH-PCBs can be excreted more readily than PCBs, and seafood was not a major part of the diets of this study's participants.

The PCB 28, 105, and 153 concentrations reported in this study are compared to other studies (Figure 8). These three congeners were chosen for comparison because they are more commonly reported and they represent a range of low- to high-molecular weight congeners. PCB 28 is a lighter, more volatile congener, 105 is a dioxin-like congener, and PCB 153 is commonly associated with dietary PCB intake. For all three congeners, serum

concentrations measured in subjects from East Chicago and Columbus Junction fall within the same range as the U.S. general population.[28] Compared with older men and women living near the PCB-contaminated Hudson River,[30] East Chicago and Columbus Junction subjects' blood contained similar levels of PCB 28 and 105 but lower levels of PCB 153. Participants from East Chicago and Columbus Junction had similar blood levels of PCB 28, lower levels of PCB 105, and much lower levels of PCB 153 compared to men and women in the Russian arctic consuming high amounts of marine mammals.[40] These congener-specific comparisons support the idea that PCB 153 in serum is an indicator of dietary PCB intake. Similar levels of PCBs 28 and 105 across the different cohort studies may reflect similar exposure to those PCBs, faster metabolism than higher-chlorinated PCBs, or a combination.

Concentrations of individual OH-PCBs measured in this study were comparable with concentrations measured in other studies (Figure 9) including those from California mothers pre-PCB ban,[37] Canadian Inuit,[41] pregnant women near a former PCB-producing plant in Eastern Slovakia,[38] Japanese breast cancer patients,[39] and adults in Belgium and Romania.[19] Pregnant women in the Faroe Islands with high blubber consumption had much higher levels of OH-PCBs in their blood than participants in this study.[34] Differences among individual OH-PCB levels in the various cohorts are most obvious in 4-OH-PCB 187, the highest-chlorinated OH-PCB measured in this study, and least obvious in 3'-OH-PCB 138. This result may reflect different PCB exposures, different OH-PCB excretion rates, or a combination.

It is commonly believed that lifetime body burdens reflect the accumulation due to dietary exposure, yet the focus in the United States has recently shifted to include environmental exposures, particularly those arising from indoor air. Despite the expectation of a large environmental exposure difference, East Chicago and Columbus Junction participants in our study had only subtle differences in their PCB and were enriched in lower-molecular weight PCBs, but concentrations measured were similar
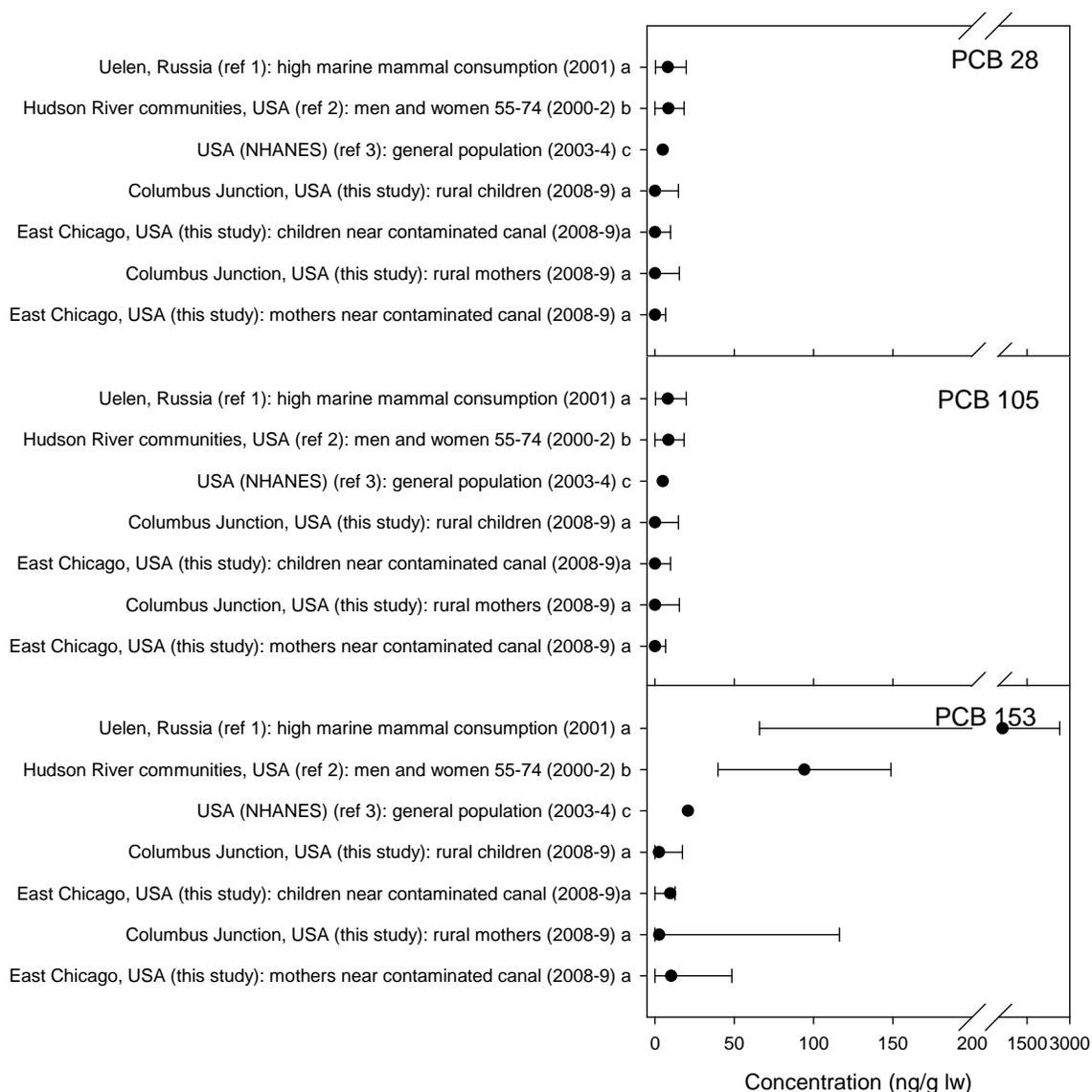
Figure 8 Comparison of PCBs 28, PCB 105, and PCB 153 levels in units of nanogram per gram lipid weight in populations around the world, including this study. Population demographics and sample collection years are indicated in the figure. The published reports did not all use consistent measures of central tendency or range. These differences are indicated a-c, where a = min, median, max; b = mean & standard deviation; c = median. (ref 1),[40] (ref 2),[30] (ref 3).[28] These references were chosen for comparison because they provided lipid weight concentration data for all three congeners and represented a variety of target populations.
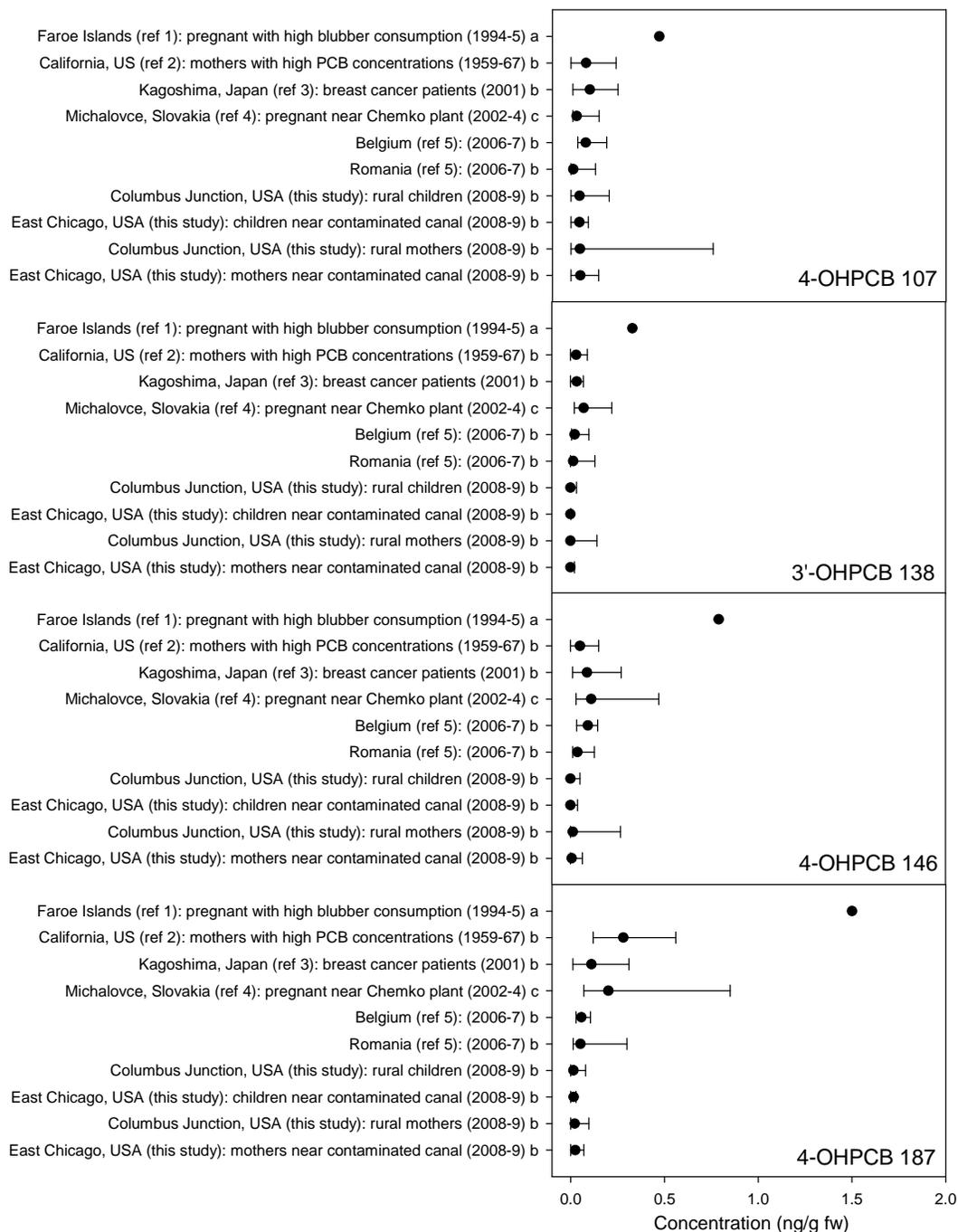
Figure 9 Comparison of OH-PCB levels in units of nanogram per gram fresh weight in populations around the world, including this study. Population demographics and sample collection years are indicated in the figure. The published reports did not all use consistent measures of central tendency or range. These differences are indicated a-c, where a = median; b = min, median, max; c = 5%, median, 95%. (ref 1),[34] (ref 2),[37] (ref 3),[39] (ref 4),[38] (ref 5).[19] These references were chosen for comparison because they provided data for all four congeners and represented a variety of target populations.

between the two locations. Our findings of similar levels of PCBs in East Chicago and Columbus Junction residents are consistent with recently published studies from Fitzgerald *et al*. that measured PCBs in the serum from older residents living near General Electric facilities along the Hudson River. These residents had serum concentrations similar to residents living upstream of the contamination even though the ambient air concentrations varied significantly by proximity to PCB-contaminated areas.[42] Their findings suggest that indoor air had a larger influence than ambient air on PCB serum concentrations. Further investigation found significant associations between PCB blood levels and indoor air levels, where duration of exposure was an important factor.[30] Also highlighting the significance of PCBs in indoor air to PCB body burden, a pilot study from Herrick *et al*. of 18 teachers in PCB-containing schools found higher blood PCB concentrations than referent populations.[29] Further research to clarify the role of inhalation exposure, particularly inhalation of indoor air, in our participants' PCB blood levels is underway.

Our detection of PCB 11 in more than 50% of participants is important when considering environment as a source of PCB exposure. A volatile low-molecular weight PCB present in only a very small amount in one Aroclor,[43] PCB 11 was recently determined to be an inadvertent byproduct of paint production and was measured in a wide variety of organic paint pigments from multiple manufacturers[3] and in air.[44] PCB 11 is neurotoxic.[45]

In contrast to PCB 11, PCB 83 was a minor component of Aroclors 1232, 1242, 1248, and 1254 and was not measured in paint pigment but was frequently detected in our participants. It is neither dioxin-like, nor considered a neurotoxin. PCB 118, another abundant congener in our participants, is a mono-ortho substituted dioxin-like congener that is both an AhR agonist[46] and neurotoxic.[45] Other abundant PCBs 28, 52, 95, 101, 138, 51, 180, and 187 have neurotoxic effects.[45]

Many studies have found correlation between age and PCBs in the blood,[28, 39, 47] yet few studies have made observations about age and types of congeners. DeCaprio *et al.* found that the presence of patterns of low-persistence congeners was most apparent in younger individuals and was negatively correlated with age. Further, the pattern observed in serum that was most similar to a recently-measured air profile was more common in younger individuals.[15] We discovered that East Chicago children are enriched in lower-molecular weight PCBs compared to their mothers. It is likely that children have not yet accumulated the upper-molecular weight PCBs, commonly associated with dietary PCB intake, that were measured in higher concentrations in their mothers. This evidence highlights the importance of environmental exposure to children's blood PCB levels.

We found a strong c between levels of metabolites and their possible parent PCBs in the East Chicago and Columbus Junction participants ($R^2 = 0.53$, $p < 0.0001$). A correlation was also shown by Dirtu *et al.* in samples from adults living in Belgium and Romania,[19] Nomiyama *et al.* in samples from Japanese breast cancer patients,[39] and Park *et al.* in samples from pregnant women from eastern Slovakia.[38] Examining specific metabolites, our results indicate preference for direct insertion in the formation of 4-OH-PCB 146 and 4-OH-PCB 187 with no preference for the formation of 3'-OH-PCB 138. Nomiyama *et al.*[39] found preference for direct insertion in the formation of 4-OH-PCB 187 and for NIH shift in the formation of 4-OH-PCB 107, 3'-OH-PCB 138, and 4-OH-PCB 146. In contrast, Dirtu *et al.*[19] found no clear preference for one mechanism over the other, whereas Park *et al.*[38] found preference for the NIH shift in formation of the metabolite 4-OH-PCB 146. The mixed findings from the small number of published studies measuring both OH-PCBs and their parent compounds points to the need for further investigation of PCB metabolism in humans.

CHAPTER 2
VARIABILITY IN PCB AND OH-PCB SERUM LEVELS IN
CHILDREN AND THEIR MOTHERS IN URBAN AND RURAL U.S.
COMMUNITIES

Abstract

Environmental exposures to PCBs, dietary intake, and physiological changes are complex factors influencing human PCB body burden that are not fully understood. Quantifying year to year variability of PCBs and their metabolites in humans is important to better understand the impact of these factors. Blood from children and their mothers from urban and rural U.S. communities were collected April 2009-March 2010 (n=200), and sera were analyzed for all 209 PCBs and 12 hydroxylated PCBs (OH-PCBs). Sum PCBs ranged from below detection to 676 ng/g lw (median = 45 ng/g lw). Sum OH-PCBs ranged from 0.1 to 0.75 ng/g fw (median = 0.09 ng/g fw). A sub-set of these participants (n = 155) also had blood PCB and OH-PCB concentration analyzed during the previous calendar year, and variability in serum concentrations were determined to be surprisingly high in many participants. Variability in ΣPCBs ranged from -100% to 2140%, and 82% of participants had variability more significant than estimated analytical variability. Individual congeners with the highest variability included PCBs 20+28, 66, 83+99, 105, 118, 129+137+138+163+164, 153+168, 180+193, and 187. Variability in ΣOH–PCBs ranged from -800 to 3600%, and 4-OH-PCB 107 had the highest variability of individual congeners. Variability between urban and rural cohorts was similar. More children had significant ΣPCB variability than their mothers. This is the first study to report variability of all 209 PCBs and 4 major metabolites in two generations of people.

Introduction

Polychlorinated biphenyls (PCBs) are a class of 209 anthropogenic, chlorinated organic compounds that were manufactured and widely used around the world in a variety of industries and products like electrical capacitors, transformers, and building materials.[1] Production of commercial mixtures of PCBs ended in the United States in

1977, but PCBs are still measured in humans[5, 28] due to their persistent and bioaccumulative properties. Nost et al. found that the relative contribution of PCBs to total POPs (including PCBs, hexachlorocyclohexanes hexachlorobenzene, chlordanes, Mirex, and DDT and its metabolites) in human serum has increased,[48] indicating the continuing importance of studying PCBs in people. Humans metabolize PCBs to hydroxylated PCBs (OH-PCBs) via cytochrome P450 enzymes, and OH-PCBs have also been measured in people.[5, 37] An International Agency for Research on Cancer Working Group recently classified PCBs as human carcinogens, and both PCBs and OH-PCBs also target the endocrine system.[6, 11] In some instances OH-PCBs were shown to be more toxic than their precursor PCB.[49-52] PCBs are neurotoxic and have been implicated in developmental problems,[12, 13, 53-55] so detection of PCBs in children is of particular concern.

Several cross-sectional population studies have shown that PCBs in serum, especially the middle and higher chlorinated congeners, demonstrate strong positive correlations with age.[17, 28, 56-58] Yet others show no correlation,[59] and using the CoZMoMAN model Quinn and Wania found that cross-sectional concentration-age relationships are not the same as concentration-age relationships of individuals over time.[59] A major finding of this study was that PCB bioaccumulation does not actually monotonically increase with age and that the previously observed correlations with age were likely due to a combination of the amount of time elapsed after peak emissions and human metabolic and environmental degradation rates.

There are few recent studies of PCBs with repeat sampling of the same participants over time using congener-specific analysis, and no studies have evaluated all 209 PCBs and OH-PCBs over time. These few studies found an overall decrease in selected PCBs over periods ranging from four to 28 years, though trends for individual congeners and participants varied.[33, 48, 60-62] In most cases, a major source of exposure (i.e.

a nearby chemical plant or fish consumption) was identified as having been removed or decreased between the first and last sampling date.

PCB metabolism in the body is congener-specific depending on the number and position of chlorines[4] and therefore congener-specific analysis for all 209 PCBs is desirable for determining the variability of PCBs in people over time. In this study we quantified blood concentrations of two groups of target analytes, 209 PCBs and 12 OH-PCBs, in two generations from urban and rural locations.

Residents of our urban cohort live in East Chicago, Indiana. East Chicago was incorporated in 1893 as a railroad and steel community and is still heavily industrialized. East Chicago is bisected by the Indiana Harbor and Ship Canal (IHSC), an artificial waterway created to serve the manufacturing industries. A large steel mill (ArcelorMittal USA) and oil refinery (BP North America) are adjacent to IHSC. IHSC also flows near junior and senior high schools. IHSC is a source of about 7.5 kg/yr of PCBs to the air.[9] The U.S. Army Corps of Engineers is supervising a navigational dredge of IHSC from 2012 to 2042 and dredging may expose heavily contaminated deeper sediment that could increase the release of PCBs to the air.[20]

Residents of our rural cohort live in the Columbus Community School District, a collection of small Iowa towns and rural dwellers including Columbus Junction, Columbus City, Conesville, Cotter, and Fredonia with the schools located in Columbus Junction. Columbus Junction was incorporated in 1874 as a railroad and steel town but in contrast to East Chicago, Columbus Junction is now predominantly an agricultural setting. The Columbus Community School District has no known current or historical industrial sources of PCBs.

Dietary habits, environmental exposures, and physiological changes like body composition and metabolism are thought to remain fairly consistent in a shorter period of time, and therefore it is commonly assumed that PCB concentration in an individual does not change much in a short period of time. We hypothesized that little variability from

year to year would be observed in our participants. To address this hypothesis, in this paper we characterize the second annual data set of PCBs and OH-PCBs from residents of the two communities and compare them with the first data set in order to quantify the variability from one year to the next. We are the first to quantify variability for all 209 PCBs and the commonly reported OH-PCBs in the same people.

Methods and Materials

Sample Collection, Extraction, and Instrument Analysis

Serum samples and survey data were collected from junior high school-aged students and their mothers who were enrolled in the Airborne Exposures to Semi-volatile Organic Pollutants (AESOP) Study in their homes between April 2009 and March 2010. In this second year of the study, serum was analyzed from 50 East Chicago mothers and their 50 enrolled children and from 46 Columbus Junction area mothers and their 54 enrolled children. Of those 200 participants, 155 had also provided blood for the year 1 data set. More than one child was enrolled from nine families. All AESOP subjects gave informed consent and assent according to an established Institutional Review Board protocol. Additional sample collection details are described elsewhere.[5]

Extraction, separation, and cleanup methods employed are described in detail elsewhere.[5] Briefly, sera were weighed (~4 g) and spiked with 5 ng ^{13}C-labeled surrogate standard and 4'-OH-PCB 159 (Table B1). The OH-PCB extract was derivatized to the methoxylated form (MeO-PCBs) using diazomethane. Immediately prior to instrument analysis, PCB extracts were spiked with 2 ng ^{13}C-labeled internal standards and OH-PCB extracts were spiked with 5 ng PCB 209 (Table B1). Nine samples were removed from the PCB and OH-PCB data sets for having less than 4 g serum available for extraction, and 33 samples were removed from the OH-PCB data set following extraction errors.

GC-MS/MS (Agilent 7000 and Agilent 6890N with Waters Micromass MS) in multiple reaction monitoring mode was used for identification and quantification of 209

PCB congeners as 159 chromatographic peaks. GC-ECD was used for identification and quantification of 12 OH-PCB congeners as MeO-PCBs. Instrument operating parameters are in Appendix B. Instrument blanks of hexane were analyzed with each instrument run before and after the calibration and after the samples to clean the system.

Calibration standards were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) and AccuStandard, Inc. (New Haven, CT, USA). The OH-PCB congeners were chosen based on the known metabolic pathways for the most common PCB congeners detected in the year 1 serum samples and the OH-PCBs that were commercially available (as MeO-PCBs). Congener mass was calculated by applying a relative response factor obtained from the calibration for each congener.

A common congener list was used when comparing the two data sets. Therefore, PCBs 11, 52, 61+70+74+76, 90+101+113, and 95 and 14, 44+47+65, 128+166, and 204 were removed from the year 2 data set for the year to year comparison because they were not part of the year 1 data set, the former group because of high variability in the method blanks as discussed elsewhere,[5] and the latter because they were used as surrogate or internal standards or co-eluted with those standards. Median change in PCB concentration was 8 ng/g lw (28%) considering all congeners and 6 ng/g lw (14%) using the common congener list.

<center>Statistics</center>

The concentration was first dichotomized at the threshold of the congener-specific LOQ (Table B3 and Table B4). Distribution of sum and individual congener concentrations were skewed to the right, and data was not normalized following logarithmic transformation. Therefore non-parametric Wilcoxon Rank Sum test and Wilcoxon Signed Ranks test were used to compare sum and individual congener concentrations and paired mother-children sum concentrations, respectively.

Analysis was carried out in R 2.13.1[63] and Minitab 16 (7.14.0.739). In all statistical tests, the level of significance was $\alpha = 0.05$.

Quality Control

Data were evaluated for representativeness, precision, reproducibility, and accuracy using a suite of quality control measures including method blanks, surrogate standards, and replicates of Standard Reference Material from the National Institutes of Standards and Technology (NIST SRM 1957: Organic Contaminants in Non-Fortified Human Serum).

Method blanks consisting of 4 mL KCl were extracted, analyzed, and quantified with each batch of samples. Most congeners were detected in the method blanks at low levels below 0.05 ng representing background noise (mean 0.012 ± 0.028 ng and mean $0.016 \pm .042$ ng for PCBs and OH-PCBs, respectively). A limit of quantification (LOQ) for each congener was determined as the 95% confidence interval (average mass in the method blanks plus two times the standard deviation). The ΣPCBs in five batches were higher than in the blank mass in the other 20 batches ($p = 0.0001$); consequently a separate LOQ was determined for those batches. PCB LOQ ranged from 0.0021 ng for PCB 24 to 0.68 ng for PCB 52 (mean 0.035 ± 0.067 ng). OH-PCB LOQ ranged from 0.0039 ng for 3'-OH-PCB 118 to 0.066 ng for 4'-OH-PCB 107 (mean 0.025 ± 0.021 ng). Congener mass below the LOQ was given a conservative value of 0 after it was previously determined that other common imputations such as LOQ/2 and LOQ/$\sqrt{2}$ significantly affected the data in a misleading manner.[5]

Surrogate standards (Table B1) were used to evaluate extraction efficiency, and sample mass was corrected according to surrogate recoveries. Recovery of the 11 surrogate standards ranged from 9 to 213% (mean $85 \pm 26\%$) (Table B5). Recovery of ^{13}C-PCB 194 on the Agilent GC-MS/MS was consistently poor compared to the

unlabeled standard, and therefore the hepta 13C-labeled SS was used to correct the mass of octa-PCBs.

Analysis of PCBs in the SRM using the same extraction and quantification as the samples (Figure B1) resulted in a mean difference of 6 ±17% between the NIST certified or reference values and our measured values for 22 congeners. Although their identity and concentration are not certified by NIST, we also report values for OH-PCBs detected in the SRM (Table B6).

Results and Discussion

PCBs and OH-PCBs in year 2 participants

202 PCB congeners as 152 unique chromatographic peaks and all 11 OH-PCBs were detected in the samples (Table B7, Table B8, Table B9).
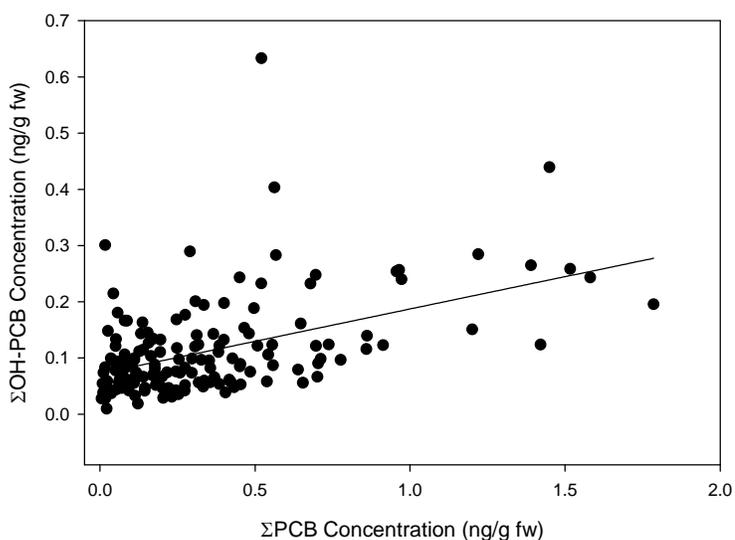
Figure 10 ΣPCBs correlate with ΣOH-PCBs ($R = 0.48$, $p < 0.0001$). Each point represents one participant. One leverage point with ΣPCBs and ΣOH-PCBs much higher than the other samples was removed. Concentrations are given in units of nanograms per gram fresh weight so PCB and OH-PCB concentration could be compared.

ΣPCB concentrations ranged from below detection to 676 ng/g lw (median 45 ng/g lw). ΣOH-PCB concentrations ranged from 0.01 to 0.75 ng/g fw (median 0.09 ng/g fw). After removing one leverage point with ΣPCB and ΣOH-PCBs much higher than the other samples, there was a significant positive correlations between ΣPCBs and ΣOH-PCBs (Figure 10, $R = 0.48$, $p < 0.0001$).

Concentrations of the 31 PCBs and 9 OH-PCBs that were detected in at least 20% of participants are shown in Figure 11 and Figure 12, respectively. Concentrations of sum (mothers $p = 0.08$, children $p = 0.43$) and individual PCBs ($p = 0.015$ to 0.099) were similar between East Chicago and Columbus Junction participants, except for PCB 11 (East Chicago children > Columbus Junction children, $p = 0.025$), PCB 178 (Columbus Junction children > East Chicago children, $p = 0.040$), and PCBs 61+70+74+76, 180+193, 194, and 203 (Columbus Junction mothers > East Chicago mothers, $p = 0.0072$ to 0.46) (Table B7, Table B8, and Figure 11). Concentrations of sum (mothers $p = 0.91$, children $p = 0.16$) and individual OH-PCBs ($p = 0.29$ to 0.094) were similar between East Chicago and Columbus Junction participants, except for 3'-OH-PCB 118 (East Chicago children > Columbus Junction children, $p = 0.087$) and 4'-OH-PCB 187 (East Chicago mothers > Columbus Junction mothers, $p < 0.0001$; East Chicago children > Columbus Junction children, $p < 0.0001$) (Table B9 and Figure 12. Our finding of similar concentrations between the urban and rural locations is consistent with the results from the first year of sample analysis.[5]

Children had lower levels of OH-PCBs in their blood than their mothers ($p < 0.0001$) and much lower levels of PCBs ($p < 0.0001$). East Chicago and Columbus Junction children had median ΣPCBs of 46% (7-272%) and 30% (2-110%), respectively of their mothers. In contrast, East Chicago and Columbus Junction children had median ΣOH−PCBs of 79% (15-321%) and 67% (5-237%), respectively of their mothers. This observation could be due to children's faster metabolism[4] or our focus on OH-PCBs of middle and higher molecular weights.
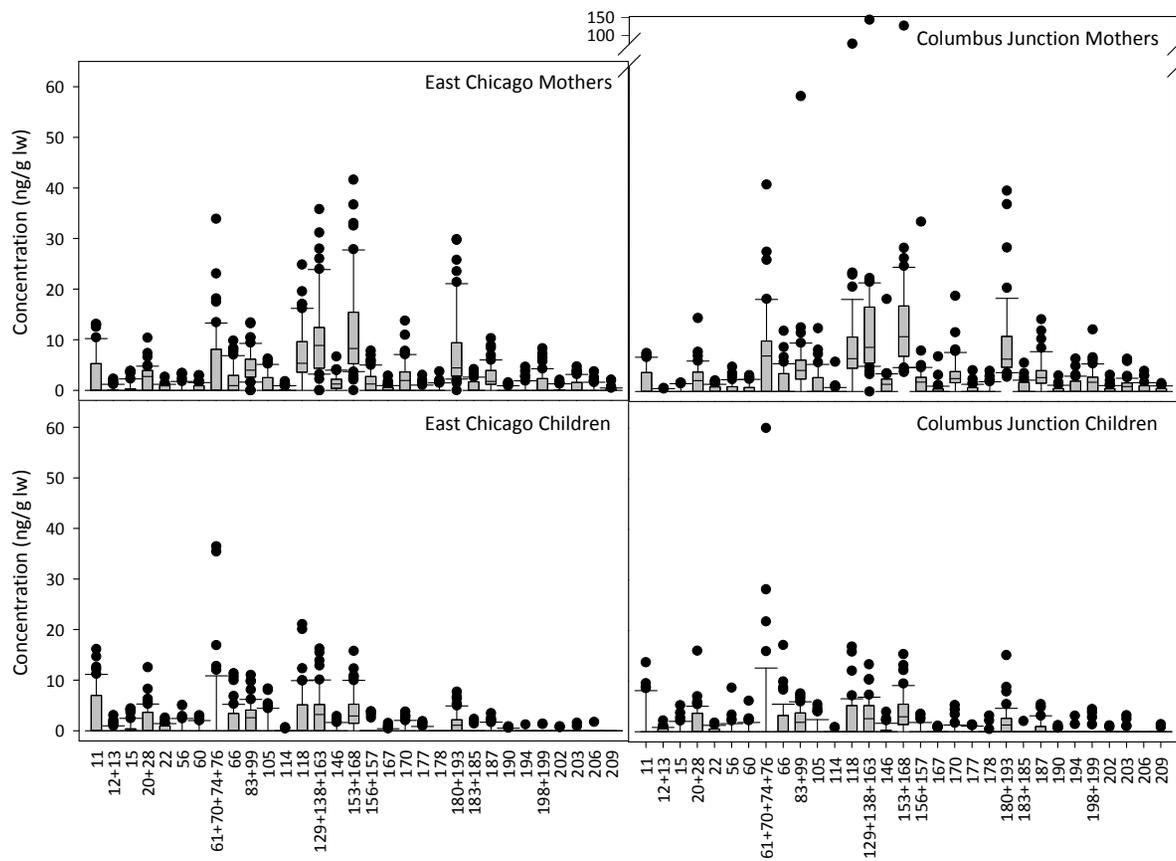
Figure 11 PCB concentrations in are similar between East Chicago and Columbus Junction mothers and East Chicago and Columbus Junction children. The 31 congeners detected in at least 20% of a subgroup are shown. Concentrations are given in units of nanograms per gram lipid weight because PCBs are lipophilic.
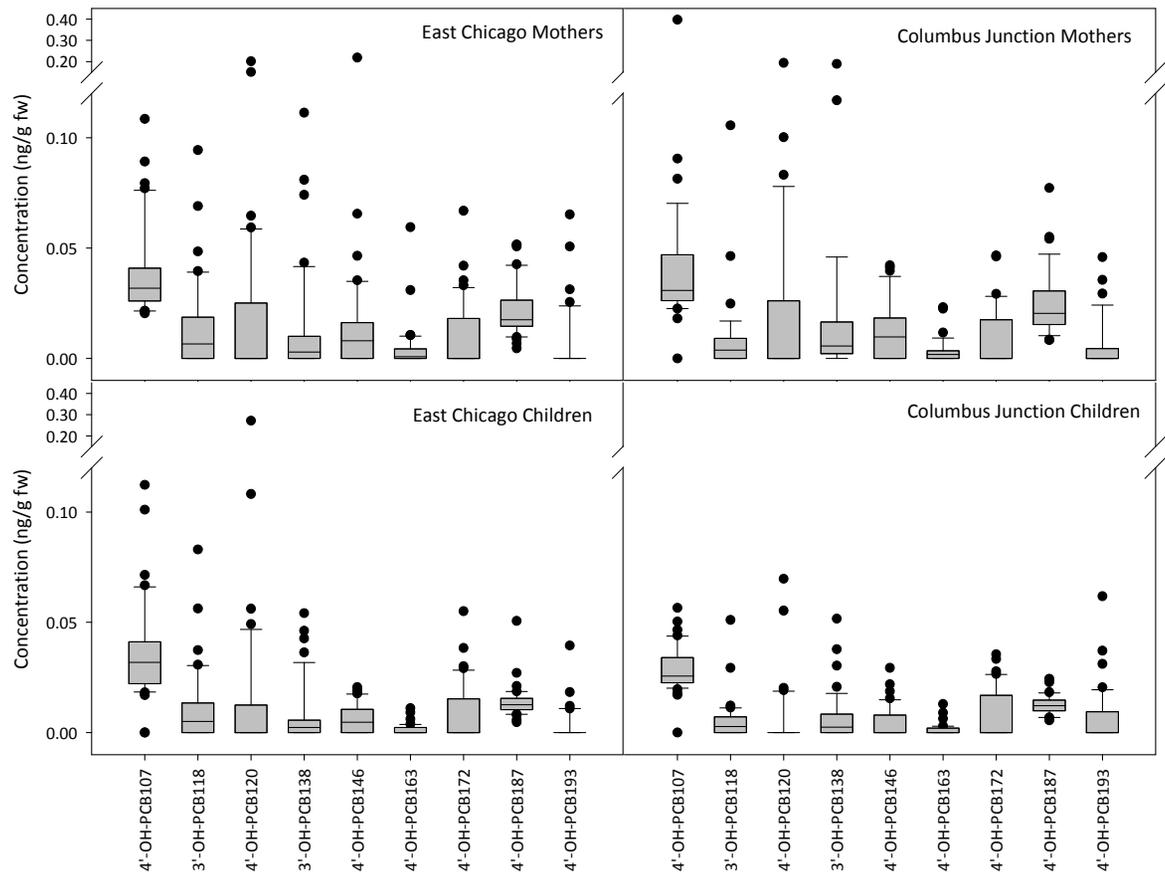
Figure 12 OH-PCB concentrations are similar in East Chicago and Columbus Junction mothers and children. The 9 congeners detected in at least 20% of a subgroup are shown. Concentrations are given in units of nanogram per gram fresh weight because OH-PCBs are hydrophilic.

Children are enriched in low molecular weight PCBs (homologs 1 to 5) compared to their mothers. An average of 64% and 59% of ΣPCBs are from low molecular weight PCBs in East Chicago and Columbus Junction children, respectively, compared with an average of 42% and 40% in East Chicago and Columbus Junction mothers, respectively. Unlike their mothers, we presume the children have not yet accumulated the higher molecular weight PCBs associated with dietary intake. Therefore low molecular weight PCB exposure in children is important to their blood PCB levels.

Comparison between year 1 and year 2

The median change in ΣPCBs from year 1 to year 2 was 6 ng/g lw but ranged from -115 to 164 ng/g lw indicating high variability in some participants (Figure 13). After removing seven participants with ΣPCBs < LOQ in year 1, this change represented a median of 14% of the participants' year 1 ΣPCBs and ranged from -100% to 2140%. Of all participants, 27% lost or gained more than 40 ng/g lw ΣPCBs (the median ΣPCBs in year 2). Analytical variability of measurements between year 1 and year 2 can be approximated by the 22% difference in ΣPCBs in the NIST SRM 1957 extracted and analyzed in year 1 and again extracted and analyzed in year 2. Of the 148 AESOP participants with ΣPCBs > LOQ in both year 1 and year 2, the vast majority (82%) had a change more significant than ±22%. More children (86%) had significant change than mothers (77%). There is no correlation of percent change between mothers and their children ($R^2 = 0.061$, $p = 0.05$).

While the median variability for most PCBs was zero, large variability was found in several congeners (Figure 14). PCBs with the largest range of variability in concentration are shown in Table 1 along with the percent of mothers and children whose variability was greater than the estimated analytical variability. These congeners include higher molecular weight PCBs commonly reported in people (118, 138, 153, 180, and 187) that have been associated with dietary intake. It is possible that the large variability
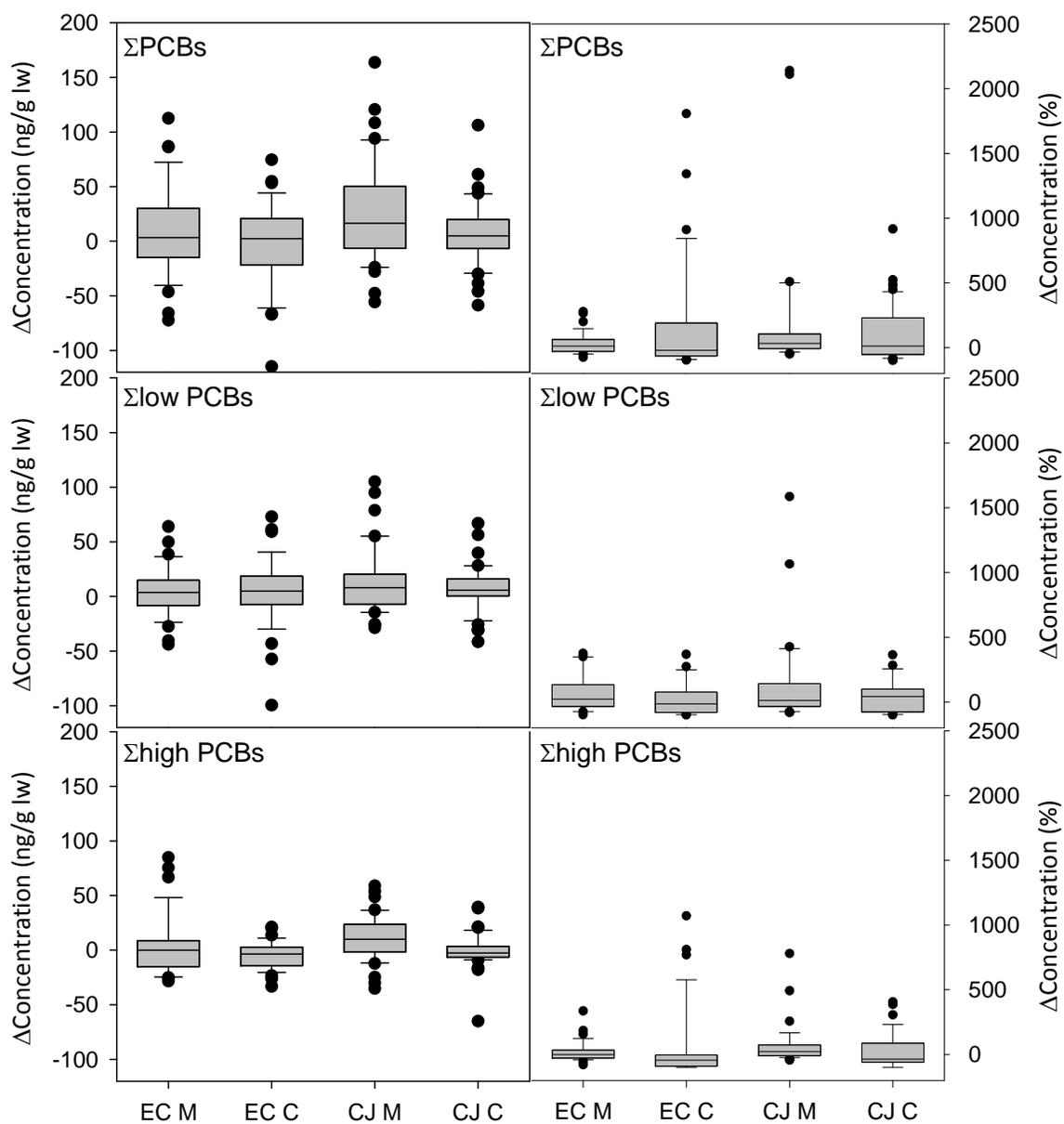
Figure 13 Change in concentration of total, low, and high PCBs, where low PCBs are the sum of homologues 1 to 5 and high PCBs are the sum of homologues 6 to 10. A positive number indicates an individual whose concentration increased from year 1 to year 2.
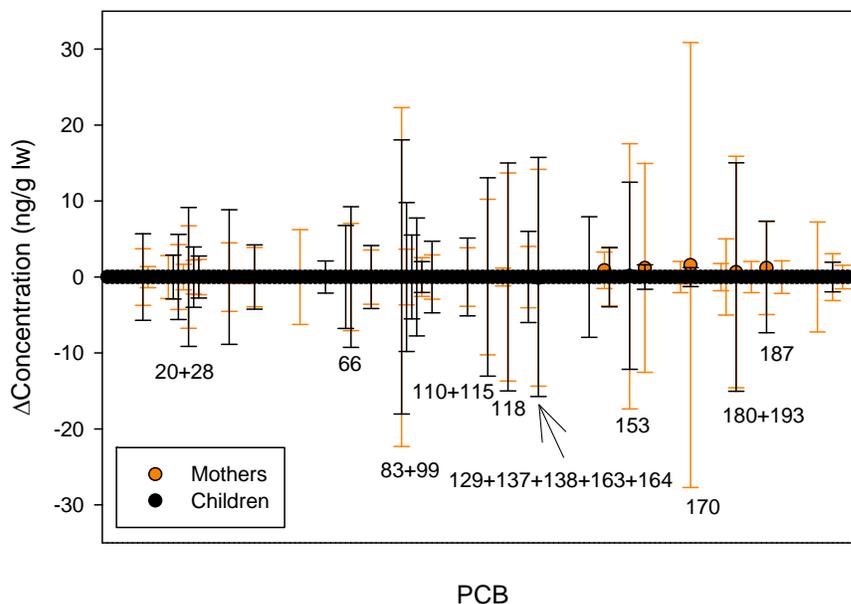
Figure 14 Change from year 1 to year 2 of each PCB congener in mothers and children. A positive value indicates concentration increased. Error bars represent the ranges of change in concentration.

Table 1 Sum and individual PCBs with largest change from year 1 to year 2.

PCB	Change in concentration (min to max)	% change (min to max)	Estimated % change due to analytical variability	% M, C change > analytical variability
20+28	-7 to 7	-257 to 315	87	10,3
66	-9 to 17	-337 to 109	136	1,1
83+99	-22 to 12	-471 to 394	-2	85,64
105	-5 to 8	-119 to 322	58	10,1
118	-15 to 21	-483 to 804	8	72,28
129+137+138+163+164	-16 to 26	-771 to 495	-14	44,21
153+168	-17 to 25	-534 to 478	-8	50,29
180+193	-15 to 15	-275 to 280	4	72,31
187	-7 to 10	-248 to 168	1	81,25
ΣPCBs	-115 to 164	-100 to 2140	22	77,86

Note: Concentration is in units of nanograms per gram lipid weight. The estimated % change due to analytical variability was determined from extraction and analysis of NIST SRM 1957 in both year 1 and year 2.

associated with these congeners reflects day-to-day variability from a large dietary intake of PCBs prior to sapmling, although daily or monthly short-term variability is unexplored in the peer-reviewed literature. For all but one of these high variability congeners, more mothers had significant variability in concentration than children, and mothers gained more high molecular weight PCBs than their children. These differences between mothers and children could be a reflection of exposure or metabolism differences, or a combination. No difference in PCB concentration changes between boys and girls were observed.

A similar median variability but smaller range compared to the AESOP participants was observed in two published studies measuring changes in PCB levels across three and nine years. In two different cohorts of Californian pregnant women sampled in 2008-2009 and 2011-2012, the geometric mean of sum of 5 tetra- to hepta-chlorinated congeners decreased 25% (range -68 to 7%), while PCB 180 declined 71% (range -141 to -22%) between the earlier and later cohorts.[64] A pilot study of 8 women who gave serum samples in 2000 and 2009 found that concentration of sum of 36 PCBs decreased by an average of 19% (range -48% to 54%) during those 9 years.[33] The women lived near a chlorinated chemical plant that ended operations in 2003, between the two sampling time points.

A greater decrease of serum PCBs was observed in participants sampled across larger time periods of 15, 25, and 28 years. A study of 179 participants in Michigan Fisheater Cohort collected 1980 to 1995 measured a 50% decline of sum of 25 tetra- to octa-chlorinated PCBs that occurred in conjunction with an 83% decrease in mean fish consumption.[61] A median decline of 67% (sum of 8 penta- to hepta-chlorinated PCBs) was found in a cohort of 123 women in the United States who were pregnant at the time of first sample collection in 1978 and then were sampled again in 2003-2004.[60] In another study of fisheaters, Norwegian men sampled between 1979 and 2007, concentrations of 5

penta- and 9 hexa-chlorinated PCBs declined while 6 ≥hepta-chlorinated PCBs initially increased and then decreased.[48] Across all 20 congeners, the median decrease was 68%.

The change in ΣOH-PCBs from year 1 to year 2 was an order of magnitude less variable. The median change was 0.004 ng/g fw but ranged from -0.5 to 0.4 ng/g fw, again indicating high variability in some participants (Figure 15). After removing one participant with ΣOH-PCBs < LOQ in year 1, this change represented a median of 4% of the participants' year 1 ΣOH-PCBs and ranged from -800 to 3600%. Of all participants, only 6% lost or gained more than 0.09 ng/g fw OH-PCBs (the median ΣOH-PCBs in year 2). The median change was non-zero for 3 of 4 OH-PCBs in mothers and only 1 of 4 OH-PCBs in children. Of the four OH-PCBs, year to year variability was largest for 4-OH-PCB 107 for both mothers and children (Figure 16). No difference in OH-PCB concentration changes between boys and girls were observed.

The only other study quantifying variability in OH-PCB concentrations, though in different people from year to year, supports our finding that OH-PCB concentrations are less variable. Sum of the three measured congeners were not different between the two cohorts across three years,[64] although most of the California pregnant women had concentrations of the three OH-PCBs measured below the detection limit which makes their results harder to interpret.

A quartile analysis of the PCB and OH-PCB year to year variability within each participant sub-group was also performed. Most participants' concentrations remained in the same quartile rank from year 1 to year 2, or changed only by one quartile. A small number (8%) of East Chicago mothers' concentrations increased or decreased more than one quartile compared with 32% of East Chicago children. Concentrations in Columbus Junction mothers and children were more similar year to year, with 24% and 26%, respectively increasing or decreasing by more than one quartile.
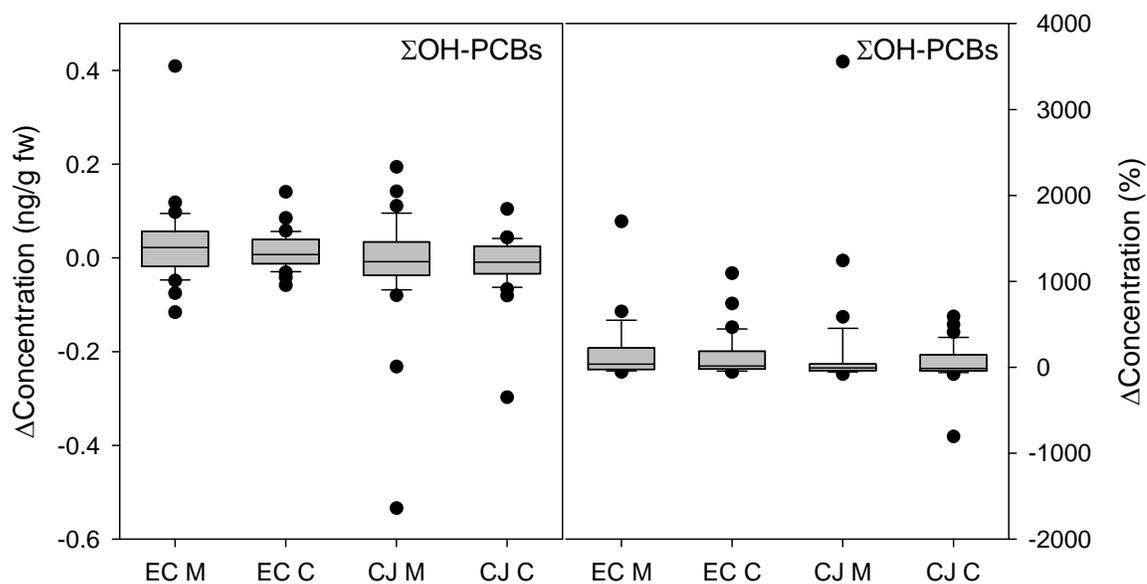
Figure 15 Change in concentration of 4 OH-PCBs. A positive number indicates an individual whose concentration increased from year 1 to year 2.
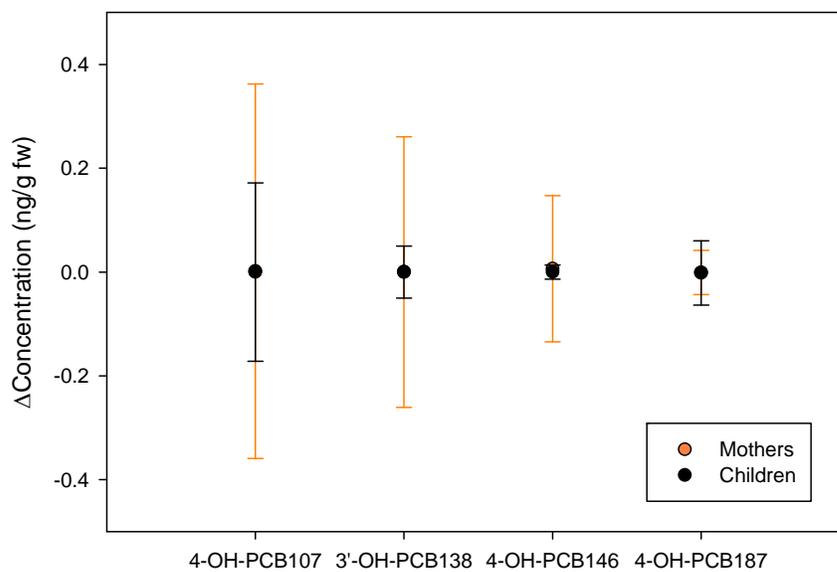
Figure 16 Change from year 1 to year 2 of each OH-PCB congener in mothers and children. A positive value indicates concentration increased. Error bars represent the ranges of change in concentration.

Previous studies of several higher-exposed populations found that PCB concentrations generally decrease over several years after exposure is reduced. However, because dietary habits, environmental exposures, and physiological changes like body composition and metabolism are thought to remain fairly consistent in a shorter period of time, it is commonly thought that PCB concentration does not change much from year to year. In this paper we examined variability in the same population from one year to the next, and we are the first to quantify variability for all 209 PCBs and the commonly reported OH-PCBs in the same people. Although many participants had similar levels of PCBs and OH-PCBs in their blood from one year to the next, a subset of participants had surprisingly different levels, and most participants (82%) had variability in blood concentrations beyond changes due to analytical method differences. Some PCBs and OH-PCBs had much greater variability than other congeners. This variability could be due to exposure differences, physiological changes such as metabolism and weight, or a combination, and further research to clarify the cause of the observed variability is ongoing. In addition, quantifying the variability in PCB and OH-PCB blood concentrations before the navigational dredging of IHSC will help determine the significance of any dredging exposure effect on blood concentration during and after the dredging.

CHAPTER 3
DISCOVERY OF HYDROXYLATED POLYCHLORINATED
BIPHENYLS (OH-PCBS) IN SEDIMENT FROM A LAKE MICHIGAN
WATERWAY AND ORIGINAL COMMERCIAL AROCLORS[2]

Abstract

Hydroxylated polychlorinated biphenyls (OH-PCBs) were measured in surficial sediment from Indiana Harbor and Ship Canal (IHSC), East Chicago, IN and five original Monsanto Aroclors. These compounds were measured using gas chromatography with tandem mass spectrometry (GC-MS/MS) and certified standards that allowed us to identify 65 individual or co-eluting congeners. Concentrations in the sediment ranged from 0.20 to 26 ng/g dry weight. Profiles of most samples were similar and were dominated by mono- to penta-chlorinated OH-PCBs. Interestingly, most of the samples strongly resembled the OH-PCB profiles of Aroclors 1221, 1242, 1248 and 1254, yet 25% of OH-PCBs measured in the sediment were not detected in Aroclors. A strong positive correlation was found between ΣOH-PCB and ΣPCB ($p < 0.0001$) and also between many individual OH-PCB:PCB pairs ($p < 0.05$). Analysis of OH-PCB:PCB pairs suggest PCB degradation is unlikely as a source of OH-PCBs in IHSC sediment. We are the first to report levels of OH-PCBs in sediment and Aroclors, and our discovery is significant because it is likely that OH-PCB contamination exists in sediment anywhere that PCB contamination from Aroclors is present.

Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants that were used in industrial applications around the world. In the United States mixtures of PCBs were sold as Aroclors until production stopped in the 1970s.[1] It is well-known that PCBs are metabolized to the hydroxylated form (OH-PCBs) by humans and other mammals via

cytochrome P450 (CYP450)-mediated oxidation.[4] Although the octanol-water partition coefficient (K_{ow}) of OH-PCBs is theoretically slightly lower than their parent PCBs,[65] OH-PCBs are still likely to bioaccumulate due to their relative hydrophobicity and also because of their binding affinity with the transport protein transthyretin (TTR) thought to be due to the structural similarity of some OH-PCBs with the hormone thyroxine.[4] PCB sulfates, which are metabolites of OH-PCBs, also have binding affinity to TTR.[66] OH-PCBs can affect brain development and function[67-69] and the endocrine system.[70-75] Certain OH-PCBs such as 4-OH-PCB 52 and 5-OH-PCB 66, have been shown to be more toxic than their parent PCBs in cell toxicity assays and LD_{50} studies in mice, respectively.[49, 50]

While levels of OH-PCBs have been reported in humans and non-laboratory animals,[4, 5, 39, 41, 76-80] OH-PCBs were first reported in abiotic matrices by Ueno et al. in surface water, rainwater, and snow samples collected 2002-2004 from Ontario, Canada.[23] To our knowledge, there have been no further publications of levels of OH-PCBs in soil or sediment matrices from natural systems.

Microbes degrade PCBs anaerobically through dechlorination and aerobically through the upper biphenyl pathway, and microbial degradation of PCBs in sediment has been well-studied as a bioremediation strategy.[81-83] One intermediary metabolite of the upper biphenyl pathway is dihydroxylated-PCB. A further metabolite of the upper biphenyl pathway is chlorinated benzoic acid, which has been measured in Hudson River sediment.[7] While microbes have CYP450 enzymes implicated in animals' PCB metabolism to monohydroxylated-PCBs, there is no published research showing microbes are capable of metabolizing PCBs to monohydroxylated-PCBs, and neither monohydroxylated- nor dihydroxylated-PCBs have been directly identified in sediment samples.

In addition to the possibility of microbial transformation as a source, OH-PCBs are potentially present as contaminants in the original Aroclors. Although banned from

production, PCBs produced as Aroclors remain in use throughout the world. Contaminants such as chlorinated naphthalenes, dibenzofurans, and chlorinated dibenzofurans have already been reported in Aroclors. [84-87]

In North America, the urban areas of the Great Lakes region in particular are known to be contaminated with elevated PCB levels. The Indiana Harbor and Ship Canal (IHSC) branches off the southwestern edge of Lake Michigan in East Chicago, IN and has been designated an Area of Concern by the International Joint Commission.[8] In a previously-published study we measured concentrations of PCBs in surficial sediment from IHSC that ranged from 53 to 35,000 ng/g dry weight (dw).[88] PCB congener profiles in these sediments closely resemble Aroclor 1248,[88] and IHSC is a major source of PCBs to Lake Michigan and to the air.[9]

The aims of this study were to develop an OH-PCB analytical method and determine OH-PCBs in the PCB-contaminated IHSC surficial sediment and in original Aroclors. In this paper we describe our extraction and GC-MS/MS analytical methods for 65 OH-PCBs and report congener-specific results from analysis of 20 sediment samples and 5 Aroclors. This is the first published report of OH-PCB concentrations in sediment and relative levels in Aroclors. We compare the OH-PCB sediment results to PCBs already reported in the same samples. Given their toxic properties and unknown environmental abundance, our study's identification and quantification of OH-PCBs in sediment is a first approach toward understanding the fate of OH-PCBs in the environment.

Methods and Materials

Sample Collection and Extraction

Surficial sediment samples were collected in 2006 from IHSC in East Chicago, Indiana (Figure 1). The sampling campaign is described elsewhere.[88] In preparation for analysis, 20 sediment samples were weighed (~ 3 g), mixed with a known amount of

combusted diatomaceous earth, and spiked with 100 ng surrogate standard 4'-OH-PCB 159 (4'-hydroxy-2,3,3',4,5,5'-hexachlorobiphenyl, AccuStandard, New Haven, CT, USA). Samples were extracted using pressurized solvent extraction according to Martinez et al.[88] Original Monsanto Aroclors 1016, 1221, 1242, and 1254 in their original containers were obtained from Dr. Larry Robertson at The University of Iowa. Aroclor 1248 was purchased from AccuStandard. A known amount of Aroclor (6 to 23 mg) was dissolved in 4 mL hexane and spiked with 5 ng of the same surrogate standard as used for the sediment samples.

In both sediment samples and Aroclors, the OH-PCB fraction was separated from the PCB fraction by liquid-liquid partitioning, derivatized, and cleaned as described in detail in Marek et al.[5] Briefly, the ASE extracts containing PCBs and OH-PCBs were mixed with a solution of potassium hydroxide in ethanol to deprotonate the OH-PCBs and move them to the aqueous layer. After the PCB fraction was extracted with hexane, OH-PCBs were re-protonated using hydrochloric acid (2M) and extracted from the aqueous layer with 9:1 hexane:MTBE. OH-PCBs were derivatized to their methoxylated form (MeO-PCBs) using diazomethane. Maintenance of yellow sample color after 3 hours indicated presence of excess diazomethane and was interpreted as an indication of complete derivatization. Interferences were removed by mixing the OH-PCB extracts with sulfuric acid (H_2SO_4) and then by passing the sample through H_2SO_4 silica gel columns. Immediately prior to analysis on the instrument, sediment samples were spiked with 30 ng and Aroclors were spiked with 25 ng internal standard PCB 209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl, AccuStandard). All solvents were pesticide residue analysis quality (ThermoFisher Scientific).

<div align="center">Instrument Analysis</div>

A GC with tandem MS (Agilent 7000) was employed for identification and quantification. The GC program operated as follows: The GC was equipped with a

Supelco SPB-Octyl capillary column (5% phenyl methyl siloxane, 30 m x 250 μm ID, 0.25 μm film thickness) with helium as the carrier gas flowing at 0.8 mL/min and nitrogen/argon as the collision gas. The GC operated in solvent vent injection mode at the following injection conditions: initial temperature 45 °C, initial time 0.06 min, ramp 600 °C/min to inlet temperature 325 °C at 4.4 psi. The GC oven temperature program was 45 °C for 2.56 min, 45 to 75 °C at 100 °C/min and hold at 75 °C for 5 min, 75 to 150 °C at 15 °C/min and hold at 150 °C for 1 min, 150 to 280 at 2.5 °C/min and final hold 5 min (total run time 70.86 min). The triple quadrupole MS Electron Ionization source was set to 260 °C.

Samples were quantified for 65 OH-PCBs as 59 individual or co-eluting MeO-PCB chromatographic peaks. Although there are 837 theoretically-possible OH-PCBs,[89] these 65 (Table C1) were the commercially available standards at the time of analysis. Calibration standards were purchased from Wellington Laboratories (Guelph, ON, Canada) and AccuStandard. Sixty-three of the targeted OH-PCBs were mono-hydroxylated and two were di-hydroxylated. The 65 standards ranged from mono- to nona-chlorinated and were assigned an abbreviation (Table C2) by using the BZ PCB number and then assigning the position of the OH group according to that PCB's primed or unprimed ring.[4, 90] Full congener names with their corresponding abbreviations are listed in Appendix C.

The MS/MS method was optimized for each standard. Elution time of each standard was determined in Select Ion Mode (SIM). The dominant product ion was then determined using product scan experiments. Congeners within the same homologue displayed different product ions, usually depending on the position of the methoxy group. In general, congeners with an ortho-substituted MeO group lost a Cl or a Cl plus a CH_3 group, and congeners with a meta- or para-substituted MeO group lost the MeO group plus another C. In some cases the 2nd-most predominant ion was used in order to reduce the overall total number of mass scans required in the final Multiple Reaction Monitoring

(MRM) method. The final MS/MS method was confirmed in MRM mode using the precursor and product ions for each standard (Table C1).

Congener identity in IHSC sediment samples were confirmed using GC-HRMS equipped with a DB5 column by Canada Centre for Inland Waters, Environment Canada (Burlington, ON). Congeners were identified with GC-HRMS when chromatographic peaks in the samples matched the retention times and isotopic ratios of primary and secondary ions of the pure, analytical standards.

Congener mass was calculated by applying a relative response factor calculated from each calibration standard and the internal standard recovery in each sample. Surrogate standard recoveries were used to evaluate extraction efficiency, but sample mass was not corrected according to surrogate recovery.

Statistics

Distribution of the ΣOH-PCB sample concentrations were skewed to the right, and concentration data was approximately normalized following logarithm transformation. Statistical analysis comparing sample groups was performed on the transformed data.

Concentration of sum and individual OH-PCBs was modeled by simple linear regression with sum and individual PCBs as the explanatory variable. The overall linear correlation between ΣOH-PCBs and ΣPCBs was assessed by an F-test using $\alpha = 0.05$. Analysis was carried out in R 2.13.1[63] (ΣOH-PCBs) and MATLAB R2012a (7.14.0.739)(individual OH-PCBs).

The Welch two sample t-test was employed for determining significant differences of ΣOH-PCBs in harbor, channel, and branches of IHSC and the ratios of ΣOH-PCBs/ΣPCBs. Analysis was carried out in R 2.13.1.[63]

Principal component analysis (PCA) was performed on the congener profiles of the samples and Aroclors using MATLAB R2012a (7.14.0.739).

Cosine theta (cosθ) was calculated for each combination of sediment and Aroclor pairs for the purpose of comparing OH-PCB profiles,[91] where cosθ = 0 describes two completely different profiles and cosθ = 1 describes two identical profiles. Prior to cosine theta analysis, each congener was normalized to the sum of all congeners in that sample.

Quality Control

A full suite of Quality Control samples were assessed using surrogate standards, instrument blanks, method blanks, and replicates of Standard Reference Material (SRM) from National Institute of Standards and Technology (NIST SRM 1944: New York, New Jersey Waterway sediment).

OH-PCB surrogate standard recoveries ranged from 61 to 144% (106 ± 27%) in sediment samples and from 95 to 160% (119 ± 29%) in Aroclor samples. Instrument blanks consisting of hexane were analyzed with each instrument run. OH-PCBs detected in instrument blanks were always below the limit of quantification (LOQ). LOQ was calculated for each congener as the average plus 2 times the standard deviation in the method blanks (Table C3), and congener mass below LOQ was given a value of zero. Method blanks consisting of combusted diatomaceous earth were extracted and analyzed along with the samples. Six OH-PCB congeners were removed from the sediment sample data set because they contributed the majority of contamination in the OH-PCB method blanks (70-89% of the total mass). Prior to their removal these six OH-PCB congeners represented 17-55% (29 ± 10%) of the total identified OH-PCB mass in the sediment samples. OH-PCBs are not certified in the NIST sediment SRM; however, analysis of PCBs in the SRM using the same extraction and quantification procedure resulted in 15 ± 15 % average difference between measured and certified values.[88]

Results and Discussion

Concentration of OH-PCBs in surficial sediment

ΣOH-PCB$_{58}$ in the 20 samples ranged from 0.20 to 26 ng/g dw with a mean of 8.5 $\pm$ 5.9 ng/g dw not including two outliers. Individual congener concentrations ranged from below LOQ to 10.24 ng/g dw (Table C4). The spatial extent of measured ΣOH-PCB$_{58}$ in IHSC is shown in Figure 17. There is a general trend of increasing OH-PCBs from the harbor to the branches of the canal. Concentrations of ΣOH-PCB$_{58}$ were higher in the main channel ($p = 0.089$) and branches ($p = 0.036$) than in the harbor.
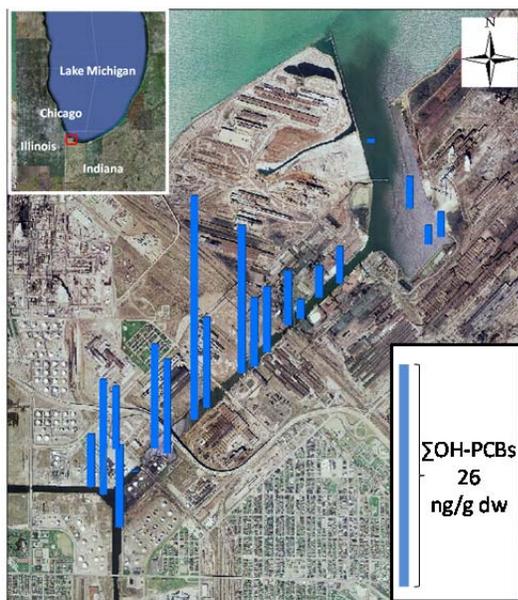
Figure 17. Spatial distribution of ΣOH-PCBs in IHSC. ΣOH-PCB$_{58}$ in the 20 samples ranged from 0.20 to 26 ng/g dw.

Of the 58 mono- and di-hydroxylated PCBs analyzed, 40 mono-hydroxylated PCBs were detected in the sediment samples. Neither di-hydroxylated PCB was detected. Several peaks in the chromatograms were unidentifiable due to lack of availability of standards. The most prominent identifiable congeners measured were 3'-OH-PCB 65, 6-

OH-PCB 2, and 4'-OH-PCB 18 which comprised an average of 46%, 16%, and 9%, respectively, of the sum concentrations in the 20 samples. Though mono- to nona-chlorinated congeners were detected in the samples, the most prominent congeners had five or fewer chlorines (Figure 18).
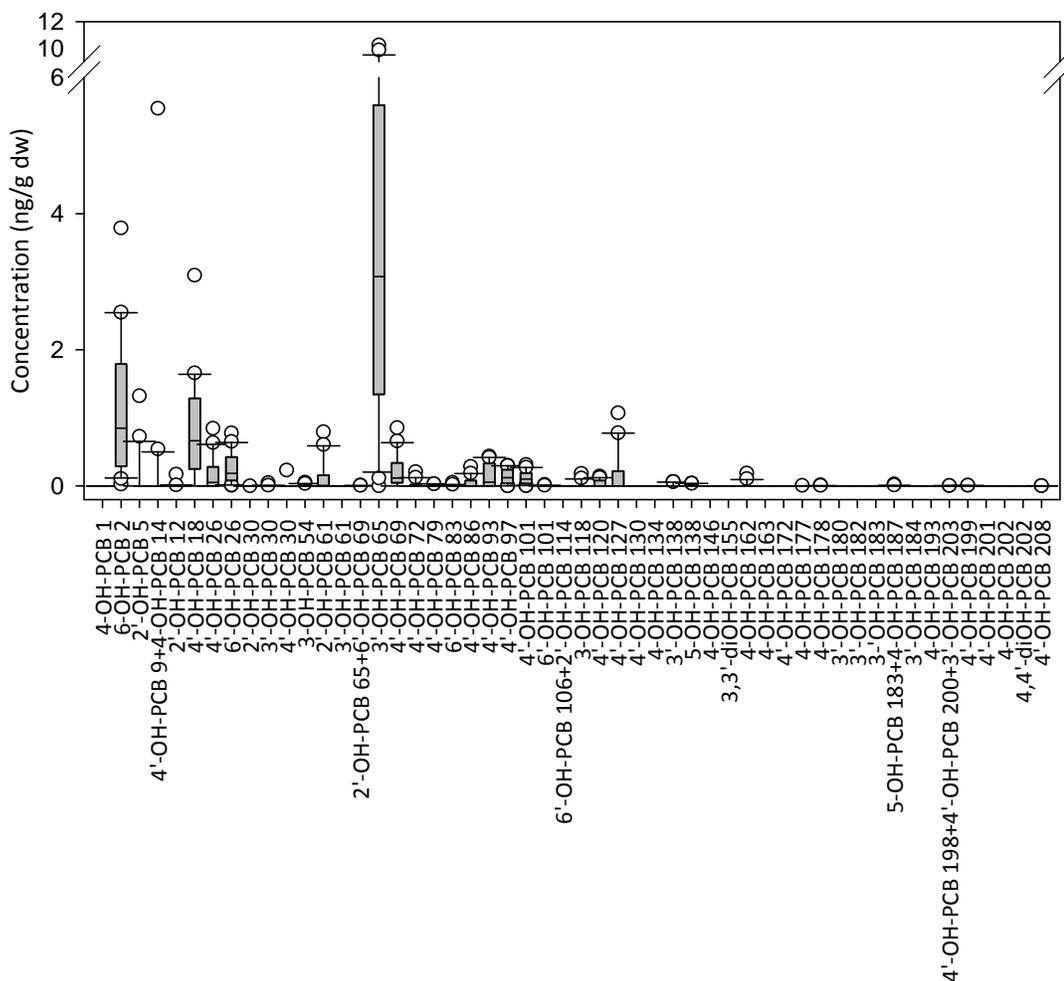
Figure 18 Distribution of concentration of OH-PCBs in sediment samples (n = 20). Congeners are listed from low to high PCB number and are grouped according to homologue. Data are plotted as box plots with the median indicated by the bold horizontal line, the two middle quartiles are shown as polyhedrons above and below the median and the 95th percentiles are shown as the horizontal lines connected by a solid vertical line. Outlier points are indicated by open circles. Congener mass below LOQ was given a value of zero. The most prominent congener, 3'-OH-PCB 65, is also the most prominent congener in Aroclors 1221, 1242, 1248, and 1254. Data are in Table C4.

ΣOH-PCB concentrations show a weak positive correlation with total organic carbon (TOC) in the sediment ($R^2 = 0.20$, p = 0.048, Figure C1). Concentrations of OH-PCBs were normalized to TOC and ranged from 5.0 to 440 ng/g TOC dw (160 ± 110 ng/g TOC dw). These TOC-normalized concentrations are much higher than concentrations (0.23 and 0.99 ng/g TOC) reported by Ueno et al. in particulates from two surface water samples.[23]

Evaluation of the variability in the OH-PCB congener profiles is limited by the lack of availability of all OH-PCB standards, yet comparisons among samples are still illuminating. PCA shows that most samples are similar (Figure 19). Indeed, the OH-PCB congener profiles of 18 of the 20 samples are very similar (cosθ = 0.9 ± 0.07). One sample in the harbor and one sample in the main channel have very different profiles (cosθ = 0.3 ± 0.2). Those two samples also have OH-PCB concentrations much lower than the rest of the samples. The difference in profiles and concentration is due to the low number of congeners detected in these samples and because the few congeners detected in those samples were at lower concentration than in the other samples.

Comparison of OH-PCBs with PCBs in Surficial Sediment

There was a significant increase in ΣOH-PCB concentration with increasing ΣPCB concentration ($R^2 = 0.61$, $p < 0.0001$, Figure 20). Individual congeners were also investigated to determine whether there was evidence of PCB degradation to OH-PCBs in the sediment. Every combination of OH-PCB and PCB was analyzed to determine whether the association was significant and whether it was a positive or negative correlation.

There are 8268 theoretically-possible pairs from 52 OH-PCB and 159 PCB congeners or co-eluting congeners. However, each pair was only evaluated if both congeners in the pair were measured in at least 3 samples, and 2764 pairs met these criteria. The Pearson's Correlation Coefficient and p-value were determined for each
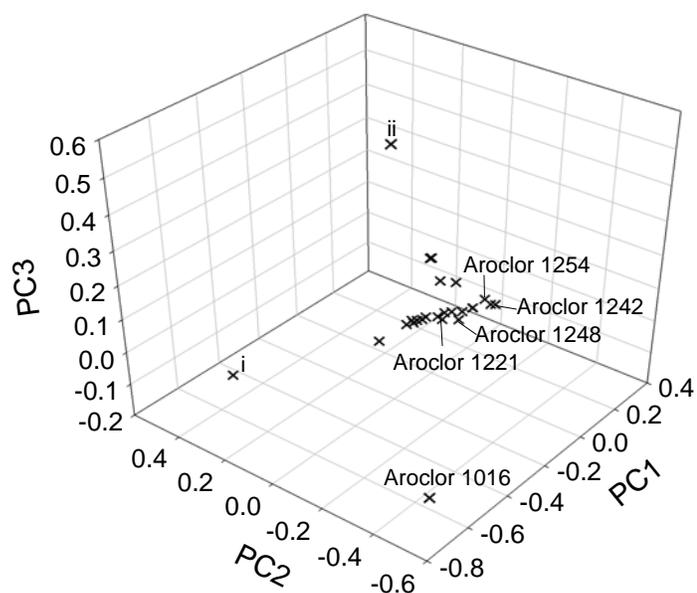
Figure 19 Principal Component Analysis of congener profiles of sediment (n = 20) and Aroclors (n = 5). The first 3 principal components explained 84% of the variance (PC1 43%, PC2 21%, PC3 20%). Samples i and ii are different from the average sediment profile and have lower concentrations of OH-PCBs than the other samples.
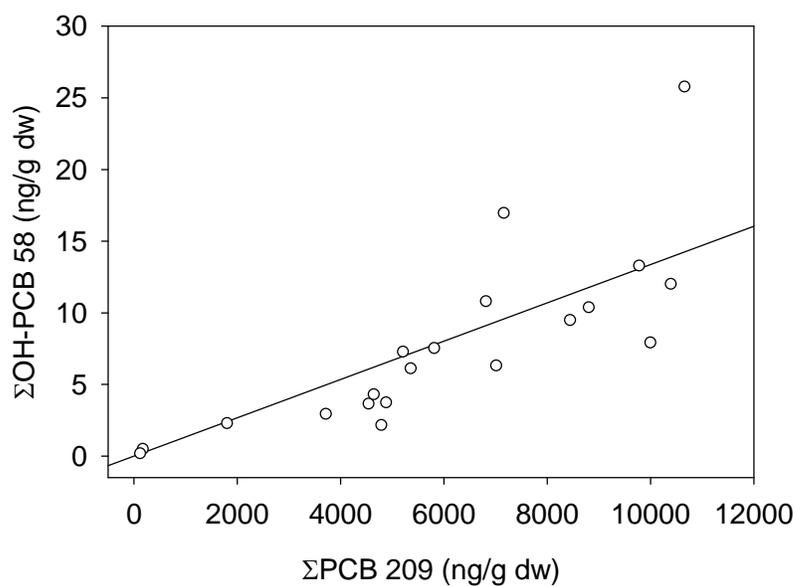
Figure 20 Comparison of ΣPCB_{209} with $\Sigma OH\text{-}PCB_{58}$ with regression. Each open circle represents one sample. The line represents the regression ($R^2 = 0.61$, $p < 0.0001$).

congener pair (Figure C2), and 713 (26%) had significant associations ($p < 0.05$). Of those significant pairs, almost all correlations (705 pairs) were positive. Of the pairs with a statistically-significant association, 99 could theoretically be a degradation pair and 614 could not. We identified a degradation pair as an OH-PCB with equal or fewer chlorines as the PCB and chlorines in the same positions around the biphenyl as the PCB. By this definition we assume degradation could include dechlorination but not chlorination or rearrangement of the chlorines.

There are 120 statistically significant pairs involving OH-PCBs detected in sediment but not Aroclors, and of those pairs only four could theoretically be a degradation pair. Thus it is unlikely that the presence of OH-PCBs in the sediment is solely due to PCB degradation *in-situ*. Figure C3 shows the correlations and structures of four example pairs.

The ratio of ΣOH-PCBs to ΣPCBs was calculated for each sample in order to investigate whether the source of OH-PCBs was the same from sample to sample. Ratios ranged an order of magnitude from 4.5×10^{-4} to 2.9×10^{-3}, but there is no clear trend from harbor to branches of IHSC (Figure 21). Higher ratios were detected in one sample from the harbor and two samples from the main channel ($p < 0.0001$). The ratios in IHSC samples are mostly lower than those determined by Ueno et al. from snow, rain, surface water, and particulate organic carbon samples (Figure 21).[23] This difference could be from Ueno et al.'s inclusion of unidentified OH-PCBs for determining their ratios or from differences in the source of OH-PCB contamination.

<div align="center">Aroclor Analysis and Discussion of Potential Sources</div>

There are several possible sources of OH-PCBs in the sediment, including their presence in the original Aroclors. We analyzed five original Monsanto Aroclors (1016, 1221, 1242, 1248, and 1254) and detected OH-PCBs in every Aroclor (Table C5).
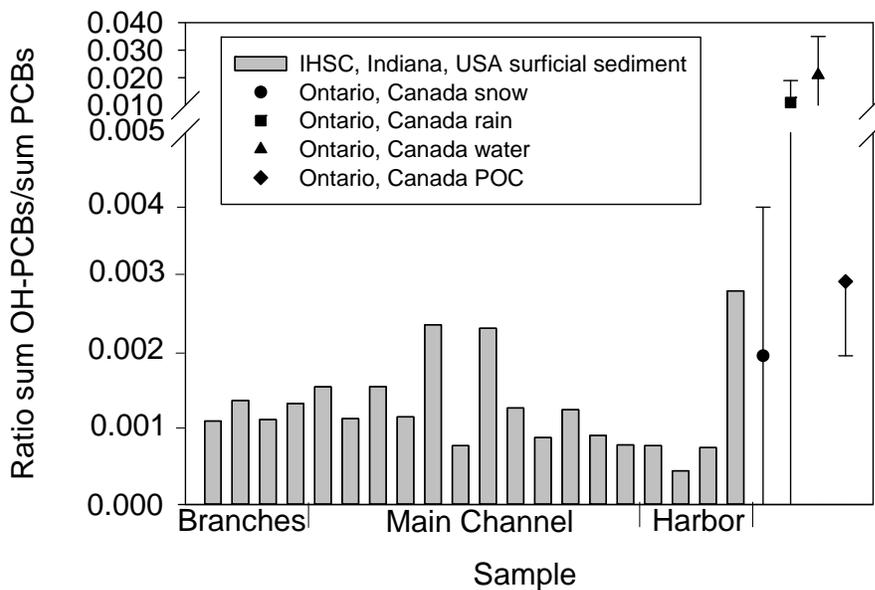
Figure 21 Ratio of Ratio of ΣOH-PCBs/ΣPCBs in sediment from IHSC and snow, rain, surface water, and particulate organic carbon (POC) from Ontario, Canada.[23] Sediment samples are ordered from the branches to the harbor of IHSC.

The most prominent OH-PCB congener identified in sediment, 3'-OH-PCB 65, is also the most prominent congener in Aroclors 1221, 1242, 1248, and 1254. In total, 75% of detected congeners in sediment were also detected in at least one Aroclor. PCA shows most Aroclors are similar to each other and to the samples (Figure 19). The congener profiles (Figure 22, Table C5) of Aroclors 1221, 1242, 1248, and 1254 were similar to the samples ($\cos\theta = 0.8 \pm 0.2$) and each other ($\cos\theta = 0.9 \pm 0.07$), while the congener profile of Aroclor 1016 was dissimilar to the samples ($\cos\theta = 0.1 \pm 0.03$) and the other Aroclors ($\cos\theta = 0.1 \pm 0.0$). The difference in congener profiles between Aroclor 1016 and the other Aroclors could be explained based on the process that Monsanto used to produce Aroclor 1016. Aroclor 1016 was distilled from Aroclor 1242 in order to remove higher chlorinated PCBs.[1] This process presumably also removed some OH-PCBs. OH-PCBs could form through degradation of PCBs in the sediment; however, we did not

detect di-hydroxylated PCBs and there is no known pathway for the microbial formation of mono-hydroxylated PCBs.

Figure 22 Congener profiles of OH-PCBs in original commercial Aroclors. Aroclor 1221 and Aroclor 1248 profiles represent the average and error bars represent the standard deviation of three replicates. Asterisks indicate congeners not included in the sediment data set. The profile of Aroclor 1016 is different from the samples and other Aroclors. Aroclor data are in Table C5.

Effluent from sewage treatment plants (STPs) could also contain OH-PCBs from human excretion of OH-PCBs in feces or as disinfection by-products from the reaction of PCBs with hydroxyl radicals used in treating the effluent immediately prior to discharge. In the only published study of OH-PCBs in abiotic matrices, Ueno et al. concluded that STPs are a likely source of OH-PCBs into the aquatic environment after measuring the highest concentrations in water samples collected within 0.5-2 km of STPs.[23] An East Chicago STP with a permit to treat municipal, industrial, commercial, and agricultural waste discharges its effluent into the East Branch of the Grand Calumet River, 5.5 km upstream of IHSC. We note that the OH-PCBs we detected in IHSC sediment are not the same OH-PCBs commonly detected in Americans' human blood serum.[5, 37] OH-PCBs could also be industrial byproducts or formed in the atmosphere or in natural water through reaction of PCBs and OH radicals.[92-96] Because a quarter of identified detected OH-PCBs could not be accounted for by Aroclor contamination, these additional sources require further investigation.

In this paper we reported levels of OH-PCBs in sediment and relative levels in Aroclors for the first time. These measurements suggest that the presence of OH-PCBs in sediment is at least partly due to OH-PCB contamination of the original Aroclors. Our discovery of OH-PCBs in Aroclors is significant because it is likely that OH-PCB contamination exists in sediment anywhere that PCB contamination from Aroclors is present.

SUMMARY AND FUTURE RESEARCH

Summary

I have analyzed and evaluated PCBs and OH-PCBs in human serum from East Chicago, Indiana and the Columbus Junction, Iowa area and sediment from the Indiana Harbor and Ship Canal in East Chicago. My research included wet chemistry and analytical method development, and extraction and analysis of almost 400 human serum samples, 20 sediment samples, and 5 Monsanto Aroclors. I utilized gas chromatography with tandem mass spectrometry in multiple reaction monitoring mode as a highly selective and sensitive tool for identifying and quantifying these PCBs and OH-PCBs in complex matrices. My research also included development of a quality assurance protocol with analysis of more than 300 quality control samples. A significant amount of time was spent understanding the quality control data and using it in a way to generate a large accurate, reproducible, representative, and precise data set.

Serum concentrations between East Chicago and Columbus Junction participants were similar. PCB concentrations in mothers ranged from below detection to 658 ng/g lw in year 1 and 8 to 676 ng/g lw in year 2, and were generally much higher than concentrations in their children which ranged from below detection to 138 ng/g lw in year 1 and below detection to 216 ng/g lw in year 2. OH-PCB concentrations in mothers ranged from below detection to 1.2 ng/g fw in year 1 and 0.03 to 0.75 ng/g fw in year 2, which were slightly higher than concentrations in their children which ranged from 0.007 to 0.4 ng/g fw in year 1 and 0.01 to 0.2 ng/g fw in year 2. These concentrations are similar to the concentrations reported in the U.S. general population and other populations that do not have high levels of dietary PCB exposure.

Although the toxicology data is incomplete with respect to many of the congeners detected, several neurotoxic PCBs were measured in the participants. The detection of PCB 11 in many participants is significant because it could represent current, ongoing

exposure to a volatile PCB that is a by-product of current paint production. Children were enriched in lower molecular weight PCBs compared to their mothers indicating the importance of environmental exposure to their PCB blood concentrations. Concentrations of OH-PCBs demonstrated a strong positive linear correlation with PCBs, while analysis of individual precursor PCBs and their metabolites suggest that human metabolism is complex. PCB variability from the first sample collection year to the second was greater than the estimated analytical variability in 82% of participants.

OH-PCB concentrations in sediment ranged from 0.20 to 26 ng/g dw and were higher in the main channel and branches than in the harbor, and congener profiles were very similar between most samples. OH-PCB concentration strongly correlates with PCB concentration in the same samples, and analysis of the OH-PCB and PCB data from the same sediment samples suggests that microbial degradation is not a major source of OH-PCBs to the sediment. My co-authors and I were also the first to report the detection of OH-PCBs in original Monsanto Aroclors, and congener profiles of four of 5 Aroclors were very similar to the sediment. This research finding is significant because it suggests that OH-PCB contamination of sediment exists anywhere that PCB contamination from Aroclors is present. Therefore, OH-PCBs could be a significant environmental contaminant.

<div align="center">Future Research</div>

I have provided a solid framework for understanding the potential impact of IHSC dredging and airborne exposure to PCBs on East Chicago residents. My methods and data are supporting the analysis of additional blood samples collected before the dredging, and I expect my methods and data will support the future analysis of blood samples collected after the dredging, toxicology experiments, analysis of human exposure data, and model development to better understand the impact of human exposure to airborne PCBs.

My research also showed that IHSC is contaminated with OH-PCBs, and that one major source of those toxic pollutants is the original commercial Aroclors. However, we do not know whether this is the only source, or whether microbial degradation of PCBs and/or formation of OH-PCBs through reaction of PCBs with hydroxy radicals could also contribute to their presence in the environment. My methods are supporting the analysis of air samples, both gas and particulate phases, for OH-PCBs. I expect my methods and data will support future analysis of IHSC core sediment and a used light capacitor to give greater insight into sources of OH-PCBs in the sediment. I also expect my methods to support future analysis and publication of NIST sediment SRM data to provide a benchmark for future internal and external quality control. Finally, partitioning coefficient experiments will allow the determination of sediment porewater concentrations and the bioavailability of OH-PCBs.

APPENDIX A
SUPPLEMENTAL INFORMATION TO CHAPTER 1

Methods

PCBs

The GC was equipped with a Supelco SPB-Octyl capillary column (30 m x 0.25 mm ID, 0.25 μm film thickness) with helium as the carrier gas and argon as the collision gas. The GC operated at the following conditions: injector temperature 270 °C, interface temperature 230 °C, initial temperature 75 °C, initial time 2 min. The GC temperature program used was 75 to 150 °C at 15 °C min^{-1}, 150 to 290 °C at 2.5 °C min^{-1}, and final hold 1 min. The MS-MS operated with the precursor-product transitions in Table A1.

The PCB Limit of Quantification (LOQ) is shown in Table A2.

Table A1 Precursor and product masses employed in Multiple Reaction Monitoring mode on the tandem MS-MS.

Homolog	Precursor Mass	Product Mass
Mono	188.00	152.00
Di	222.00	152.10
Tri	255.96	186.00
d-Tri	260.96	191.00
Tetra	291.92	222.00
d-Tetra	296.92	227.00
Penta	325.88	255.90
Hexa	359.84	289.90
Hepta	393.80	323.90
Octa	427.76	357.80
Nona	461.72	391.80
Deca	497.68	427.70

Table A2 Limit of Quantification (LOQ) for each PCB congener, in units of nanograms per sample.

PCB Congener	LOQ (ng/sample)	PCB Congener	LOQ (ng/sample)
1	0.0366	59+62+75	0.0121
2	0.0175	60	0.0361
3	0.0203	63	0.0452
4	0.0293	64	0.0376
5	0.008	66	0.1022
6	0.0097	67	0.0078
7	0.005	68	0.0231
8	0.048	72	0.0346
9	0.0097	73	0.0173
10	0.0102	77	0.08
12+13	0.0113	78	0.0428
15	0.0477	79	0.0108
16	0.0198	80	0.0051
17	0.0326	81	0.0317
18+30	0.0515	82	0.0282
19	0.0269	83	0.0145
20+28	0.1013	84	0.0254
21+33	0.035	85+116+117	0.0877
22	0.0439	86+87+97+109+119+125	0.094
23	0.0314	89	0.0234
24	0.012	88+91	0.037
25	0.0089	92	0.0532
26+29	0.0227	93+100	0.0133
27	0.0105	94	0.0113
31	0.0748	96	0.0124
32	0.0079	99	0.08
34	0.0078	98+102	0.0393
35	0.0132	103	0.0223
36	0.0091	104	0.0104
37	0.0658	105	0.049
38	0.0061	106	0.0198
39	0.0079	107	0.0191
40+41+71	0.0681	108+124	0.0252
42	0.0386	110+115	0.129
43	0.048	111	0.0115
45+51	0.0466	112	0.0091
46	0.0256	114	0.0189
48	0.0289	118	0.1378
49+69	0.0898	120	0.0094
50+53	0.0204	121	0.0131
54	0.028	122	0.0229
55	0.0275	123	0.0365
56	0.0718	126	0.0571
57	0.0343	127	0.0139
58	0.0235	130	0.0196

Table A2, continued

PCB Congener	LOQ (ng/sample)	PCB Congener	LOQ (ng/sample)
131	0.0321	175	0.0322
132	0.0293	176	0.0118
133	0.025	177	0.0262
134+143	0.0382	178	0.0473
135+151	0.0179	179	0.015
136	0.0251	180+193	0.0114
139+140	0.0322	181	0.0169
141	0.0133	182	0.0241
142	0.0074	183	0.0179
144	0.0192	184	0.015
145	0.0171	185	0.0422
146	0.0171	186	0.0114
147+149	0.0742	187	0.0192
148	0.0335	188	0.0397
150	0.0118	189	0.0367
152	0.008	190	0.0355
153+168	0.0316	191	0.0172
154	0.0243	192	0.0208
155	0.0137	194	0.0359
156+157	0.0099	195	0.0453
158	0.0317	196	0.0733
159	0.0237	197	0.0307
160	0.0091	198+199	0.0634
161	0.0158	200	0.0188
162	0.0109	201	0.0163
129+137+138+163+164	0.0565	202	0.0209
167	0.0328	203	0.0209
169	0.0176	205	0.063
170	0.0793	206	0.106
171+173	0.0354	207	0.0391
172	0.0316	208	0.0329
174	0.0378	209	0.0629

OH-PCBs

The GC was equipped with a HP DB-5 capillary column (5% phenyl methyl siloxane, 30 m x 0.25 mm ID, 0.25 μm film thickness) with helium as the carrier gas flowing at 1.3 mL/min and Argon/Methane (95%/5%) as the collision gas. The GC operated at the following conditions: injector temperature 250 °C at 20.52 psi, initial temperature 150 °C, initial time 2 min. The GC temperature program used was 150 to

200 °C at 30 °C min^{-1}, 200 to 230 °C at 1 °C min^{-1}, 230 to 300 °C at 10 °C min^{-1}and

final hold 15 min. Detector temperature was set to 360 °C.

The OH-PCB Limit of Quantification (LOQ) is shown in Table A3.

OH-PCBs are commonly present at lower levels than PCBs in human serum, and

the ECD was chosen for its lower detection limits. However, because the ECD is less

selective than MS/MS, OH-PCB results were confirmed on a DB-1 column using a sub-

set of samples. After accounting for LOQ differences, 95% of the peak assignments

matched between the two columns.

Table A3 Limit of Quantification (LOQ) for each OH-PCB congener, in units of
nanograms per sample.

OH-PCB Congener	LOQ (ng/sample)
4-OH-PCB107	0.16
3'-OH-PCB138	0.0018
4-OH-PCB146	0.0066
4-OH-PCB187	0.0065

Quality Control

Surrogate Standard Recoveries

Samples were spiked with surrogate standards prior to extraction. Recoveries of

those surrogates are shown in Table A4. Sample masses were corrected based on

surrogate recoveries.

Table A4 Average, median, and range of PCB and OH-PCB surrogate standard percent
recoveries.

Surrogate	Average (Standard Deviation)	Median	Range
PCB 14	75% (17)	78%	46%-114%
d-PCB 65	82% (15)	82%	53%-130%
PCB 166	91% (15)	92%	54%-125%
4-OH-PCB159	68% (12)	68%	40%-110%

Laboratory Reference Material

One aliquot of LRM (~4 g), homogenized human serum purchased from a

Chicago blood bank, was analyzed in every batch to ensure internal consistency. Results

are shown in Table A5.

Table A5 Average, median, and range of the three PCB congeners monitored in
Laboratory Reference Material (LRM) in units of nanograms per gram fresh
weight and relative standard deviation in units of percent.

Congener	Average (Standard Deviation)	Median	Range	Relative Standard Deviation
PCB 138	0.089 (0.026)	0.079	0.051-0.152	15
PCB 153	0.125 (0.016)	0.126	0.092-0.155	13
PCB 180	0.102 (0.031)	0.105	0.069-0.148	15

Note: One aliquot of homogenized LRM was analyzed with each batch of samples.

Standard Reference Material

SRM was purchased from NIST and analyzed in replicates. The results are shown

in Figure 20 and represent good agreement between NIST certified or reference values

and our own measured values.
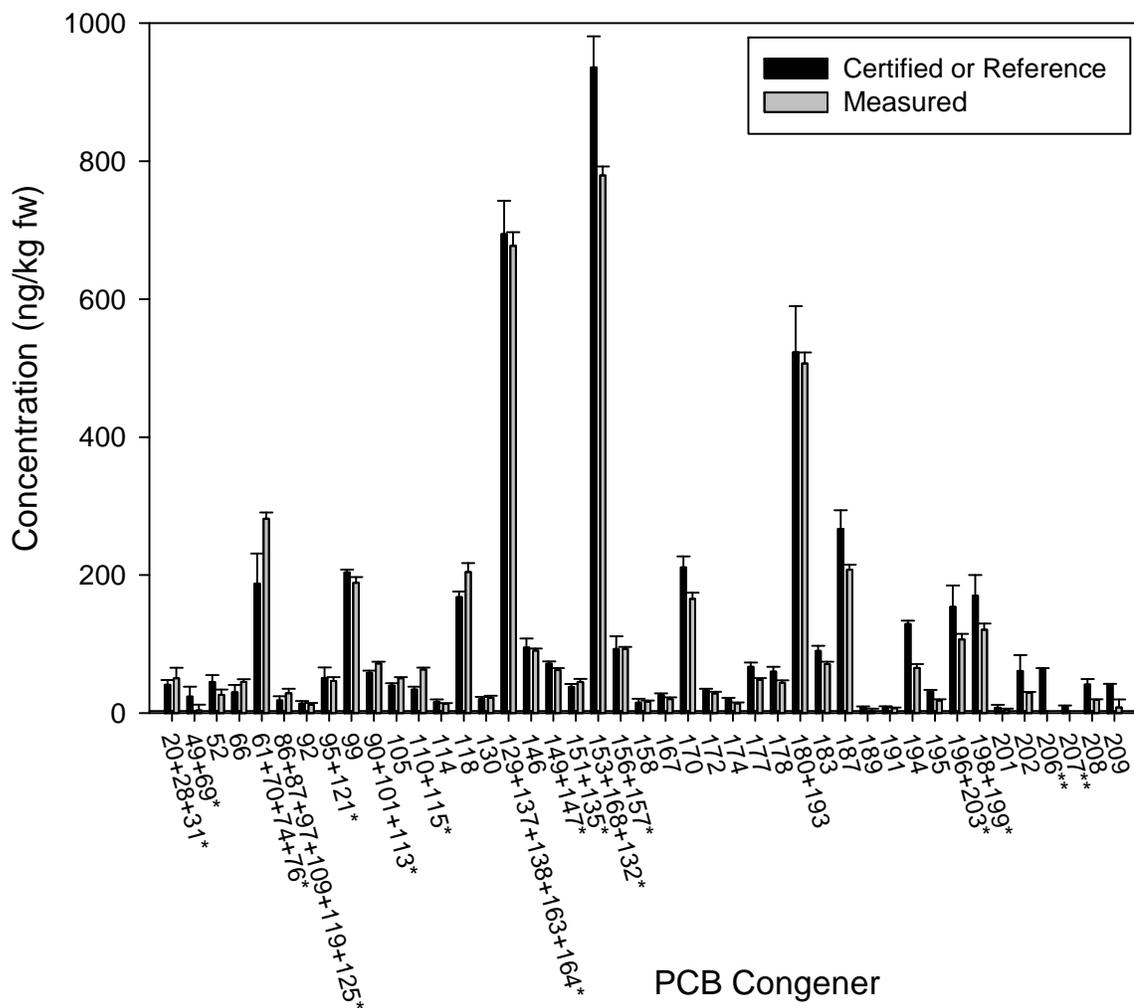
Figure A1 NIST SRM 1589a quantification results. The grey bars represent the measured values obtained using our analytical method. Uncertainty on the measured concentrations is 2 times the standard deviation of five replicates. The black bars are the certified and reference values provided by the National Institute of Standards and Technology. Uncertainty on the NIST certified and reference concentrations is an expanded uncertainty about the mean calculated by NIST. The single asterisks represent congeners which eluted differently between methods. The double asterisks represent congeners measured below detection limits

Results

Table A6 and Table A7 contain supplementary data.

Table A6 Frequency of detection (Det), median (Med) and range (5th-95th percentile) of PCBs (nanograms per gram lipid weight) and OH-PCBs (nanograms per gram fresh weight) detected in mothers and children from East Chicago and Columbus Junction.

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n=41) | | | | Children (n=44) | | | | Mothers (n=43) | | | | Children (n=47) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
8	10	<LOQ	<LOQ	2.44	5	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	11	<LOQ	<LOQ	2.42
9	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
15	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
16	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
17	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
18+30	10	<LOQ	<LOQ	2.27	9	<LOQ	<LOQ	3.30	5	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	1.97
19	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
20+28	29	<LOQ	<LOQ	5.39	16	<LOQ	<LOQ	7.79	28	<LOQ	<LOQ	6.12	13	<LOQ	<LOQ	5.88
21+33	5	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ	3.02	12	<LOQ	<LOQ	1.53	4	<LOQ	<LOQ	<LOQ
22	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
25	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
31	10	<LOQ	<LOQ	3.64	9	<LOQ	<LOQ	4.97	7	<LOQ	<LOQ	2.99	13	<LOQ	<LOQ	4.52
32	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
35	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
37	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	1.80	6	<LOQ	<LOQ	2.44
45+51	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
49+69	7	<LOQ	<LOQ	2.39	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
55	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
57	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
60	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
64	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
66	20	<LOQ	<LOQ	5.36	7	<LOQ	<LOQ	4.55	9	<LOQ	<LOQ	4.49	2	<LOQ	<LOQ	<LOQ
77	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
83	44	<LOQ	<LOQ	14.85	30	<LOQ	<LOQ	11.77	40	<LOQ	<LOQ	13.34	17	<LOQ	<LOQ	8.85
84	7	<LOQ	<LOQ	2.92	7	<LOQ	<LOQ	3.02	7	<LOQ	<LOQ	2.26	11	<LOQ	<LOQ	3.07

Table A6, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n=41) | | | | Children (n=44) | | | | Mothers (n=43) | | | | Children (n=47) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
85+ 116+ 117	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	3.75	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
86+87+97+ 109+ 119+125	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
88+91	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
92	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
99	15	<LOQ	<LOQ	4.29	5	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	3.89	2	<LOQ	<LOQ	<LOQ
105	22	<LOQ	<LOQ	3.52	18	<LOQ	<LOQ	4.51	26	<LOQ	<LOQ	3.47	6	<LOQ	<LOQ	1.87
107	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
110+ 115	12	<LOQ	<LOQ	6.92	16	<LOQ	<LOQ	9.49	9	<LOQ	<LOQ	6.01	11	<LOQ	<LOQ	7.34
114	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
118	76	8.23	<LOQ	14.47	43	<LOQ	<LOQ	13.45	60	7.77	<LOQ	18.52	36	<LOQ	<LOQ	10.66
126	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ		<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
129+ 137+ 138+ 163+ 164	5	0.22	<LOQ	26.46	52	3.14	<LOQ	11.86	84	9.52	<LOQ	27.45	36	<LOQ	<LOQ	12.51
142	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
146	24	<LOQ	<LOQ	3.51	2	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	1.85	0	<LOQ	<LOQ	<LOQ
147+ 149	5	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	2.65	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
153+ 168	95	10.28	2.28	35.67	57	2.71	<LOQ	9.95	88	9.68	<LOQ	33.29	53	2.57	<LOQ	11.76
156+ 157	20	<LOQ	<LOQ	6.52	9	<LOQ	<LOQ	1.57	12	<LOQ	<LOQ	6.16	0	<LOQ	<LOQ	<LOQ
162	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
167	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
169	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
170	27	<LOQ	<LOQ	10.41	2	<LOQ	<LOQ	<LOQ	21	<LOQ	<LOQ	14.52	2	<LOQ	<LOQ	<LOQ
172	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
177	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
178	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
180+ 193	71	5.10	<LOQ	24.38	30	<LOQ	<LOQ	5.62	74	5.55	<LOQ	29.51	23	<LOQ	<LOQ	10.07
182	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
183	20	<LOQ	<LOQ	1.93	0	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ	1.44	0	<LOQ	<LOQ	<LOQ
187	39	<LOQ	<LOQ	9.08	11	<LOQ	<LOQ	2.50	35	<LOQ	<LOQ	9.37	0	<LOQ	<LOQ	<LOQ
190	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ

Table A6, continued

| | | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | |
| | | Mothers (n=41) | | | | Children (n=44) | | | | Mothers (n=43) | | | | Children (n=47) | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
192	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
198+ 199	17	<LOQ	<LOQ	6.10	0	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ	6.90	0	<LOQ	<LOQ	<LOQ
202	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
203	12	<LOQ	<LOQ	2.64	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
206	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
Σ PCB$_{209}$		50.37	12.41	171.75		23.45	<LOQ	82.73		49.85	2.53	137.52		13.56	1.42	53.01
4-OH-PCB 107	61	0.050	<LOQ	0.098	61	0.044	<LOQ	0.082	72	0.047	<LOQ	0.093	64	0.046	<LOQ	0.097
3'-OH-PCB 138	54	0.006	<LOQ	0.059	36	<LOQ	<LOQ	0.021	77	0.012	<LOQ	0.045	49	<LOQ	<LOQ	0.025
4-OH-PCB 146	15	<LOQ	<LOQ	0.017	2	<LOQ	<LOQ	<LOQ	47	<LOQ	<LOQ	0.022	6	<LOQ	<LOQ	0.003
4-OH-PCB 187	98	0.024	0.011	0.047	95	0.016	0.006	0.023	95	0.021	0.004	0.072	96	0.014	0.007	0.030
ΣOH-PCB$_4$		0.072	0.015	0.192		0.060	0.012	0.110		0.089	0.011	0.220		0.060	0.011	0.157

Note: Detections are reported as percent of the subgroup. Table excludes PCBs 11, 52, 61+70+74+76, 90+101+113, and 95 as described in the Statistical Analysis section. Other PCBs not listed were not detected in any samples.

Table A7 Frequency of detection (Det), median (Med) and range (5th-95th percentile) of the PCBs (nanograms per gram fresh weight) detected in mothers and children from East Chicago and Columbus Junction.

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n=41) | | | | Children (n=44) | | | | Mothers (n=43) | | | | Children (n=47) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
8	10	<LOQ	<LOQ	0.01	5	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	11	<LOQ	<LOQ	0.01
9	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
15	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
16	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
17	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
18+30	10	<LOQ	<LOQ	0.02	9	<LOQ	<LOQ	0.02	5	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.01
19	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
20+28	29	<LOQ	<LOQ	0.04	16	<LOQ	<LOQ	0.03	28	<LOQ	<LOQ	0.04	13	<LOQ	<LOQ	0.03
21+33	5	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ	0.01	12	<LOQ	<LOQ	0.01	4	<LOQ	<LOQ	<LOQ
22	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
25	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
31	10	<LOQ	<LOQ	0.02	9	<LOQ	<LOQ	0.02	7	<LOQ	<LOQ	0.02	13	<LOQ	<LOQ	0.02
32	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
35	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
37	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.01	6	<LOQ	<LOQ	0.01
45+51	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
49+69	7	<LOQ	<LOQ	0.02	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
55	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
57	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
60	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
64	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
66	20	<LOQ	<LOQ	0.03	7	<LOQ	<LOQ	0.02	9	<LOQ	<LOQ	0.03	2	<LOQ	<LOQ	<LOQ
77	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
83	44	<LOQ	<LOQ	0.08	30	<LOQ	<LOQ	0.06	40	<LOQ	<LOQ	0.07	17	<LOQ	<LOQ	0.04
84	7	<LOQ	<LOQ	0.02	7	<LOQ	<LOQ	0.02	7	<LOQ	<LOQ	0.01	11	<LOQ	<LOQ	0.02
85+116+117	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.02	0	<LOQ	<LOQ	<LOQ	0	<LO	<LOQ	<LOQ
86+87+97+109+119+ 125	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
88+91	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ

Table A7, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n=41) | | | | Children (n=44) | | | | Mothers (n=43) | | | | Children (n=47) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
92	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
99	15	<LOQ	<LOQ	0.02	5	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.02	2	<LOQ	<LOQ	<LOQ
105	22	<LOQ	<LOQ	0.02	18	<LOQ	<LOQ	0.02	26	<LOQ	<LOQ	0.03	6	<LOQ	<LOQ	0.01
107	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
110+115	12	<LOQ	<LOQ	0.04	16	<LOQ	<LOQ	0.05	9	<LOQ	<LOQ	0.04	11	<LOQ	<LOQ	0.04
114	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
118	76	0.05	<LOQ	0.08	43	<LOQ	<LOQ	0.06	60	0.04	<LOQ	0.11	36	<LOQ	<LOQ	0.05
126	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
129+137+ 138+163+164	85	0.06	<LOQ	0.13	52	0.01	<LOQ	0.06	84	0.05	<LOQ	0.16	36	<LOQ	<LOQ	0.05
142	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
146	24	<LOQ	<LOQ	0.02	2	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	0.02	0	<LOQ	<LOQ	<LOQ
147+149	5	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.02	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
153+168	95	0.06	0.01	0.19	57	0.01	<LOQ	0.05	88	0.05	<LOQ	0.18	53	0.01	<LOQ	0.05
156+157	20	<LOQ	<LOQ	0.04	9	<LOQ	<LOQ	0.01	12	<LOQ	<LOQ	0.04	0	<LOQ	<LOQ	<LOQ

Note: Detections are reported as percent of the subgroup. Table excludes PCBs 11, 52, 61+70+74+76, 90+101+113, and 95 as described in the statistical analysis section. Other PCBs not listed were not detected in any samples.

Discussion

Figure A2, Figure A3, and Figure A4 contain information supplementary to the
discussion.
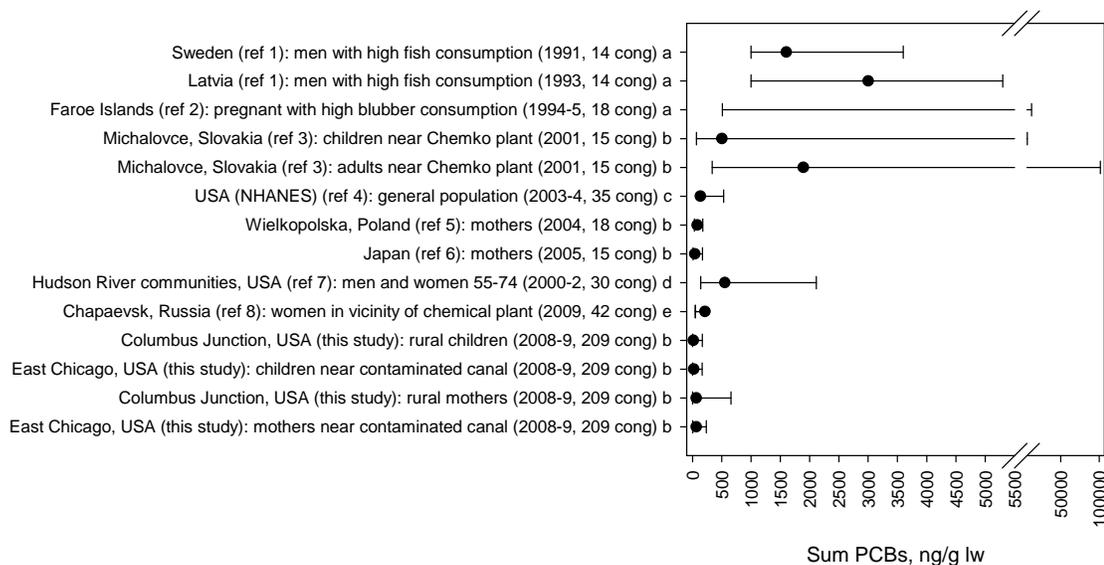
Figure A2 Comparison of sum PCB levels in units of nanogram per gram lipid weight in
populations around the world, including this study. Population demographics,
sample collection years, and number of congeners analyzed are indicated in
the figure. The published reports did not all use consistent measures of central
tendency or range. These differences are noted as a-e, where a = 10%, median,
90%; b = min, median, max; c = geometric mean, 95%; d = min, mean, max; e
= mean, standard deviation. (ref 1)[35], (ref 2)[34], (ref 3)[36], (ref 4)[28], (ref 5)[31], (ref
6)[32], (ref 7)[30], (ref 8)[33]
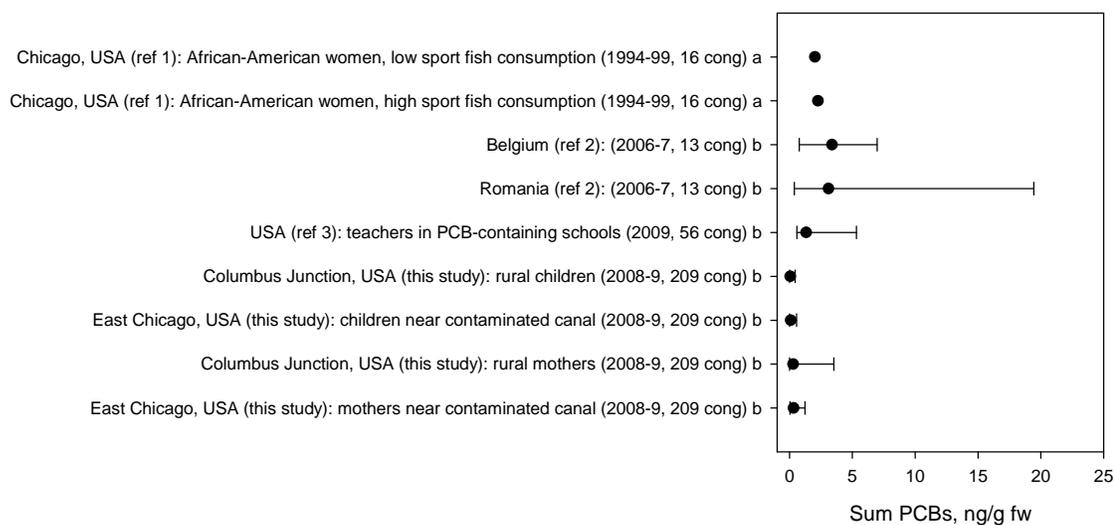
Figure A3 Comparison of sum PCB levels in units of nanogram per gram fresh weight in populations around the world, including this study. Population demographics, sample collection years, and number of congeners analyzed are indicated in the figure. The published reports did not all use consistent measures of central tendency or range. These differences are noted as a-b, where a = geometric mean; b = min, median, max. (ref 1)[18], (ref 2)[19], (ref 3)[29]
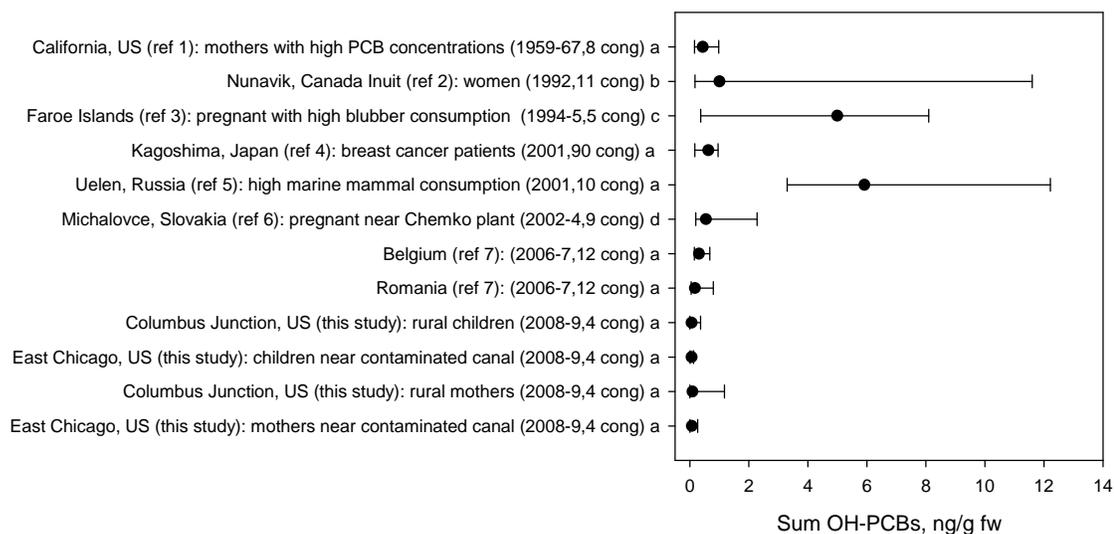
Figure A4 Comparison of sum OH-PCB levels in units of nanogram per gram fresh weight in populations around the world, including this study. Population demographics, sample collection years, and number of congeners analyzed are indicated in the figure. The published reports did not all use consistent measures of central tendency or range. These differences are indicated a-d, where a = min, median, max; b = min, geometric mean, max; c = 10%, median, 90%; d = 5%, median, 90%. (ref 1)[37], (ref 2)[41], (ref 3)[34], (ref 4)[39], (ref 5)[40], (ref 6)[38], (ref 7)[19]

APPENDIX B
SUPPLEMENTAL INFORMATION TO CHAPTER 2

Methods and Materials

Table B1 Surrogate and internal standards purchased from Cambridge Isotope
Laboratories, Inc., Andover, MA, USA (CIL) and AccuStandard, Inc., New
Haven, CT, USA (AccuStd).

Congener	Abbreviation	Source
Surrogate Standards		
4-monochlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 3	CIL
4,4'-dichlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 15	CIL
2,4,4'-trichlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 28	CIL
2,2',5,5'-tetrachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 52	CIL
2,3',4,4',5-pentachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 118	CIL
2,2',4,4',5,5'-hexachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 153	CIL
2,2',3,4,4',5,5'-heptachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 180	CIL
2,2',3,3',4,4',5,5'-octachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 194	CIL
2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 208	CIL
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 209	CIL
4'-hydroxy-2,3,3',4,5,5'-hexachlorobiphenyl	4'-OH-PCB 159	AccuStd
Internal Standards (PCBs)		
2,3',4',5-tetrachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 70	CIL
2,3,3',5,5'-pentachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 111	CIL
2,2',3,4,4',5'-hexachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 138	CIL
2,2',3,3',4,4',5-heptachlorobiphenyl ($^{13}C_{12}$)	^{13}C-PCB 170	CIL
Internal Standard (OH-PCB)		
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	PCB 209	AccuStd

PCBs

The Agilent 6890N GC was equipped with a Supelco SPB-Octyl capillary column
(30 m x 0.25 mm ID, 0.25 μm film thickness) with helium as the carrier gas and argon as
the collision gas. The GC operated at the following conditions: injector temperature 270
°C, interface temperature 230 °C, initial temperature 75 °C, initial time 2 min. The GC

temperature program used was 75 to 150 °C at 15 °C min^{-1}, 150 to 290 °C at 2.5 °C min^{-1}, and final hold 1 min.

The Agilent 7000 was equipped with a Supelco SPB-Octyl capillary column (5% phenyl methyl siloxane, 30 m x 250 μm ID, 0.25 μm film thickness) with helium as the carrier gas flowing at 0.8 mL/min and nitrogen/argon as the collision gas. The GC operated in solvent vent injection mode at the following injection conditions: initial temperature 45 °C, initial time 0.06 min, ramp 600 °C min^{-1} to inlet temperature 325 °C at 4.4 psi. The GC oven temperature program was 45 °C for 2.56 min, 45 to 75 °C at 100 °C min^{-1}, 75 to 150 °C at 15 °C/min, 150 to 280 at 2.5 °C/min and final hold 5 min (total run time 70.86 min). The triple quadrupole MS Electron Ionization source was set to 260 °C. The MS-MS operated with the precursor-product transitions in Table B2. The PCB limit of quantification (LOQ) is shown in Table B3.

Table B2 Precursor and product masses employed in Multiple Reaction Monitoring mode on the tandem MS-MS.

Homolog	Precursor Mass	Product Mass
mono	188.00	152.00
di	222.00	152.10
tri	255.96	186.00
tetra	291.92	222.00
penta	325.88	255.90
hexa	359.84	289.90
hepta	393.80	323.90
octa	427.76	357.80
nona	461.72	391.80
deca	497.68	427.70
^{13}C-mono	200.00	164.00
^{13}C-di	234.00	164.00
^{13}C-tri	268.0	198.00
^{13}C-tetra	304.00	234.00
^{13}C-penta	338.00	268.00
^{13}C-hexa	372.00	302.00
^{13}C-hepta	406.00	336.00
^{13}C-octa	440.00	370.00
^{13}C-nona	474.00	404.00
^{13}C-deca	410.70	438.90

Table B3 Limit of Quantification (LOQ) for each PCB congener, in units of nanograms per sample.

PCB	LOQ		PCB	LOQ	
1	0.0073	0.0077	107+123	0.0160	0.0160
2	0.0100	0.0071	108+124	0.0310	0.0170
3	0.0160	0.0260	110+115	0.2700	0.0650
4	0.0600	0.0120	111	0.0054	0.0110
5	0.0078	0.0054	112	0.0170	0.0140
6	0.0190	0.0075	114	0.0100	0.0097
7	0.0110	0.0200	118	0.2500	0.0710
8	0.0820	0.0310	120	0.0100	0.0093
9	0.0043	0.0061	121	0.0058	0.0080
10	0.0057	0.0043	122	0.0170	0.0110
11	0.3500	0.1200	126	0.0093	0.0180
12+13	0.0210	0.0093	127	0.0280	0.0290
14	0.0270	0.0280	128+166	0.0140	0.0150
15	0.0600	0.0310	129+138+163	0.0680	0.0370
16	0.0320	0.0130	130	0.0150	0.0200
17	0.0440	0.0087	131	0.0380	0.0150
18+30	0.0820	0.0200	132	0.0340	0.0280
19	0.0092	0.0052	133	0.0360	0.0180
20+28	0.1500	0.0660	134+143	0.0340	0.0160
21+33	0.0870	0.0620	135+151	0.0420	0.0210
22	0.0580	0.0180	136	0.0300	0.0130
23	0.0140	0.0048	137+164	0.0350	0.0190
24	0.0021	0.0064	139+140	0.0160	0.0098
25	0.0120	0.0160	141	0.0310	0.0170
26+29	0.0150	0.0140	142	0.0240	0.0250
27	0.0042	0.0041	144	0.0130	0.0110
31	0.1000	0.0500	145	0.0160	0.0059
32	0.0270	0.0091	146	0.0200	0.0110
34	0.0088	0.0055	147+149	0.0690	0.0280
35	0.0160	0.0079	148	0.0170	0.0120
36	0.0096	0.0082	150	0.0077	0.0076
37	0.1100	0.0230	152	0.0110	0.0075
38	0.0028	0.0052	153+168	0.0530	0.0260
39	0.0062	0.0090	154	0.0200	0.0110
40+41+71	0.0440	0.0230	155	0.0082	0.0048
42+59+62+75	0.0270	0.0280	156+157	0.0250	0.0350
43+73	0.0140	0.0360	158	0.0088	0.0120
44+47+65	0.2400	0.0600	159	0.0130	0.0120
45+51	0.0330	0.0200	160	0.0063	0.0230
46	0.0240	0.0200	161	0.0057	0.0110
48	0.0200	0.0190	162	0.0098	0.0120
49+69	0.1200	0.0320	165	0.0160	0.0110
50+53	0.0260	0.0140	167	0.0350	0.0110
52	0.6800	0.1400	169	0.0052	0.0250
54	0.0140	0.0092	170	0.0420	0.0190
55	0.0610	0.0160	171+173	0.0100	0.0130
56	0.0400	0.0190	172	0.0180	0.0170
57	0.0150	0.0074	174	0.0280	0.0210

Table B3, continued

PCB	LOQ		PCB	LOQ	
58	0.0140	0.0130	175	0.0270	0.0160
60	0.0260	0.0210	176	0.0200	0.0110
61+70+74+76	0.5300	0.1900	177	0.0180	0.0200
63	0.0330	0.0160	178	0.0075	0.0210
64	0.0600	0.0240	179	0.0110	0.0150
66	0.1300	0.0520	180+193	0.0089	0.0200
67	0.0170	0.0062	181	0.0086	0.0150
68	0.0098	0.0130	182	0.0094	0.0120
72	0.0079	0.0110	183+185	0.0320	0.0300
77	0.1500	0.0280	184	0.0130	0.0150
78	0.0160	0.0210	186	0.0120	0.0160
79	0.0100	0.0150	187	0.0100	0.0190
80	0.0093	0.0087	188	0.0090	0.0120
81	0.0093	0.0270	189	0.0310	0.0150
82	0.0490	0.0110	190	0.0150	0.0110
83+99	0.1100	0.0430	191	0.0160	0.0160
84	0.1400	0.0280	192	0.0180	0.0170
85+116+117	0.0590	0.0250	194	0.0120	0.0280
86+87+97+109+119+125	0.1900	0.0740	195	0.0290	0.0200
88+91	0.0580	0.0210	196	0.0210	0.0270
89	0.0078	0.0097	197+200	0.0250	0.0170
90+101+113	0.3000	0.0780	198+199	0.0320	0.0270
92	0.0580	0.0200	201	0.0150	0.0220
93+100	0.0160	0.0120	202	0.0230	0.0130
94	0.0110	0.0140	203	0.0250	0.0200
95	0.4400	0.0690	204	0.0066	0.0150
96	0.0110	0.0067	205	0.0230	0.0220
98+102	0.0170	0.0110	206	0.0140	0.0240
103	0.0160	0.0100	207	0.0140	0.0220
104	0.0120	0.0068	208	0.0190	0.0180
105	0.0790	0.0450	209	0.0057	0.0053
106	0.0078	0.0180			

Note: Two LOQ are given for each congener because of high variability of a few congeners in five of the 20 sample batches as discussed in the Quality Control section of Chapter 3.

OH-PCBs

The GC was equipped with a HP DB-5 capillary column (5% phenyl methyl siloxane, 30 m x 0.25 mm ID, 0.25 µm film thickness) with helium as the carrier gas flowing at 1.3 mL/min and Argon/Methane (95%/5%) as the collision gas. The GC operated at the following conditions: injector temperature 250 °C at 20.52 psi, initial temperature 150 °C, initial time 2 min. The GC temperature program used was 150 to 200 °C at 30 °C min^{-1}, 200 to 230 °C at 1 °C min^{-1}, 230 to 300 °C at 10 °C min^{-1}and

final hold 15 min. Detector temperature was set to 360 °C. The OH-PCB Limit of

Quantification (LOQ) is shown in Table B4**.**

Table B4 Limit of quantification (LOQ) for each OH-PCB congener (as MeO-PCB) in
units of nanogram per sample.

Congener	Abbreviation	LOQ (ng/sample)
4-methoxy-2,3,3',4',5-pentachlorobiphenyl	4'-MeO-PCB107	0.066
3-methoxy-2,3',4,4',5-pentachlorobiphenyl	3'- MeO -PCB118	0.0039
4'-methoxy-2,3',4,5,5'-pentachlorobiphenyl	4'- MeO -PCB120	0.044
4'-methoxy-2,2',3,3',4,5'-hexachlorobiphenyl	4'- MeO -PCB130	0.017
3'-methoxy-2,2',3,4,4',5'-hexachlorobiphenyl	3'- MeO -PCB138	0.0044
4-methoxy-2,2',3,4',5,5'-hexachlorobiphenyl	4'- MeO -PCB146	0.018
4-methoxy-2,3,3',4',5,6-hexachlorobiphenyl	4'- MeO -PCB163	0.0061
4'-methoxy-2,2',3,3',4,5,5'-heptachlorobiphenyl	4'- MeO -PCB172	0.050
3'-methoxy-2,2',3,4,4',5,5'-heptachlorobiphenyl	3'- MeO -PCB180	0.018
4-methoxy-2,2',3,4',5,5',6-heptachlorobiphenyl	4'- MeO -PCB187	0.014
4-methoxy-2,3,3',4',5,5',6-heptachlorobiphenyl	4'- MeO -PCB193	0.028

Quality Control

Table B5 Sample surrogate standard recoveries. Average, standard deviation, median, and range are given in units of percent.

Surrogate Standard	Homolog applied to	Average (Standard Deviation)	Median	Range
^{13}C-PCB 3	PCB mono	58 (21)	56	22-113
^{13}C-PCB 15	PCB di	83 (22)	82	39-139
^{13}C-PCB 28	PCB tri	89 (15)	87	54-140
^{13}C-PCB 52	PCB tetra	89 (16)	88	49-127
^{13}C-PCB 118	PCB penta	93 (12)	92	65-123
^{13}C-PCB 153	PCB hexa	95 (14)	93	53-157
^{13}C-PCB 180	PCB hepta&octa	90 (15)	90	45-132
^{13}C-PCB 194	(none)	82 (30)	79	9-185
^{13}C-PCB 208	PCB nona	92 (26)	87	39-167
^{13}C-PCB 209	PCB deca	80 (45)	66	27-213
4'-OH-PCB 159	all OH-PCB	70 (11)	70	40-113

Note: The surrogate standard recovery was used to adjust each sample mass. Recoveries of ^{13}C-PCB 194 were not used to adjust sample mass because of large variability in recoveries between instruments.
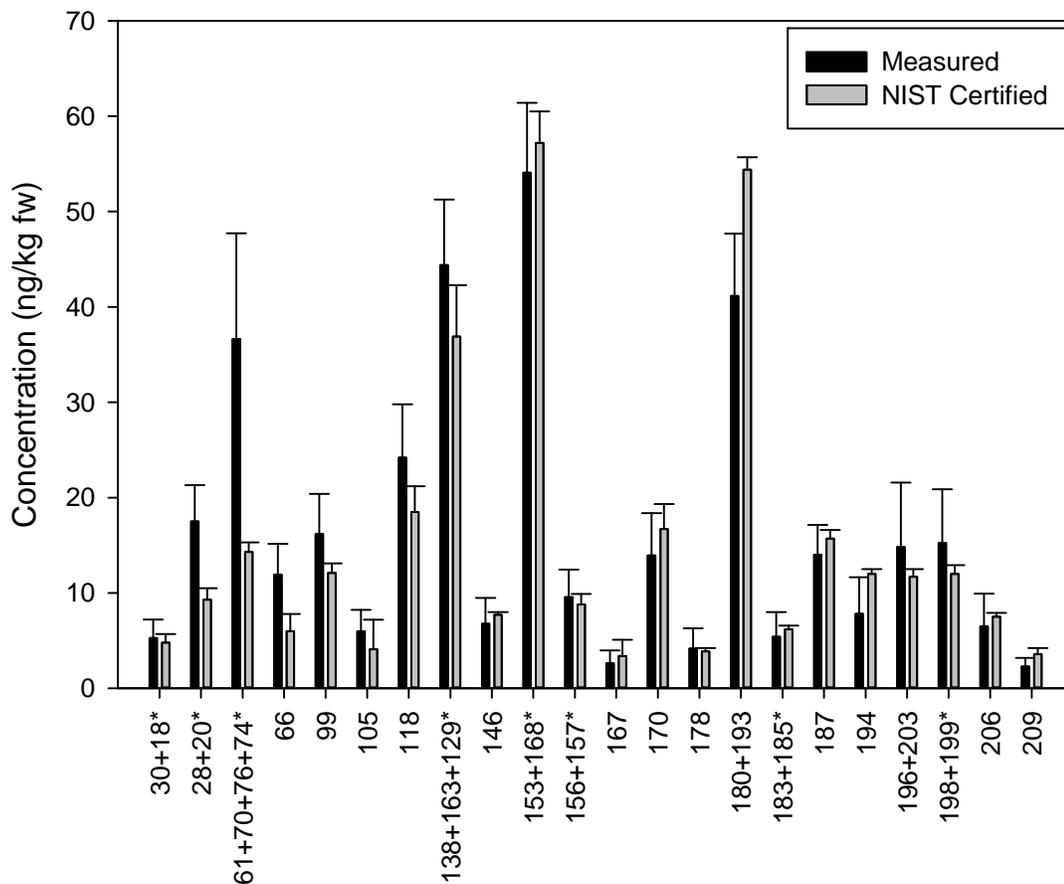
Figure B1 Results of NIST SRM 1957 quantification. Gray bars represent average values measured using our analytical method, and error bars represent the standard deviation (n=20). Black bars represent values certified by NIST. Error bars on the NIST values represent an expanded uncertainty about the mean as calculated by NIST. Asterisks represent congeners that eluted differently between methods.

Table B6 Average, standard deviation, median, and range of the four OH-PCBs measured in 20 aliquots of NIST SRM 1957 in units of nanograms per gram fresh weight.

OH-PCB	Average (Standard Deviation)	Median	Range
4'-OH-PCB 107	0.034 (0.0044)	0.033	0.029-0.46
3'-OH-PCB 138	0.011 (0.0092)	0.0056	0.0017-0.031
4'-OH-PCB 146	0.012 (0.0048)	0.012	0.0056-0.022
4'-OH-PCB 187	0.023 (0.0064)	0.022	0.018-0.048

Note: One aliquot of homogenized SRM was analyzed with every batch of samples.

<u>Results</u>

Table B7, Table B8, and Table B9 contain supplementary data.

Table B7 Frequency of detection (Det), median (Med) and range (5th-95th percentile) of PCBs (nanograms per gram lipid weight) detected in mothers and children from East Chicago and Columbus Junction.

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n =49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
1	10	<LOQ	<LOQ	0.44	14	<LOQ	<LOQ	0.61	5	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.51
2	18	<LOQ	<LOQ	1.57	18	<LOQ	<LOQ	1.28	9	<LOQ	<LOQ	0.35	8	<LOQ	<LOQ	0.37
3	12	<LOQ	<LOQ	4.21	20	<LOQ	<LOQ	2.18	2	<LOQ	<LOQ	<LOQ	10	<LOQ	<LOQ	1.09
4	10	<LOQ	<LOQ	0.9	6	<LOQ	<LOQ	0.37	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
5	12	<LOQ	<LOQ	0.33	10	<LOQ	<LOQ	0.84	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
6	16	<LOQ	<LOQ	0.64	12	<LOQ	<LOQ	1.16	12	<LOQ	<LOQ	0.42	8	<LOQ	<LOQ	0.44
7	6	<LOQ	<LOQ	0.46	6	<LOQ	<LOQ	0.71	7	<LOQ	<LOQ	0.84	6	<LOQ	<LOQ	0.99
8	20	<LOQ	<LOQ	2.59	14	<LOQ	<LOQ	2.98	14	<LOQ	<LOQ	1.95	12	<LOQ	<LOQ	2.24
9	8	<LOQ	<LOQ	0.39	12	<LOQ	<LOQ	0.42	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
10	10	<LOQ	<LOQ	0.43	8	<LOQ	<LOQ	0.3	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
11	30	<LOQ	<LOQ	12.78	34	<LOQ	<LOQ	12.42	26	<LOQ	<LOQ	6.97	16	<LOQ	<LOQ	8.78
12+13	24	<LOQ	<LOQ	1.39	22	<LOQ	<LOQ	1.55	14	<LOQ	<LOQ	0.64	35	<LOQ	<LOQ	1
14	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
15	24	<LOQ	<LOQ	3.56	24	<LOQ	<LOQ	3.88	19	<LOQ	<LOQ	1.69	16	<LOQ	<LOQ	2.55
16	10	<LOQ	<LOQ	0.73	4	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.67	4	<LOQ	<LOQ	<LOQ
17	10	<LOQ	<LOQ	0.44	8	<LOQ	<LOQ	0.71	9	<LOQ	<LOQ	1.17	12	<LOQ	<LOQ	0.78
18+30	6	<LOQ	<LOQ	0.46	6	<LOQ	<LOQ	0.98	7	<LOQ	<LOQ	2.72	6	<LOQ	<LOQ	0.53
19	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
20+28	54	2.76	<LOQ	5.86	38	<LOQ	<LOQ	6.1	51	2.18	<LOQ	7.03	33	<LOQ	<LOQ	5.7
21+33	14	<LOQ	<LOQ	3.52	4	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ	3.14	0	<LOQ	<LOQ	<LOQ
22	36	<LOQ	<LOQ	1.24	28	<LOQ	<LOQ	1.53	33	<LOQ	<LOQ	1.64	24	<LOQ	<LOQ	1.5
23	10	<LOQ	<LOQ	0.28	8	<LOQ	<LOQ	0.45	2	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	0.48
24	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
25	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
26+29	8	<LOQ	<LOQ	0.55	8	<LOQ	<LOQ	1.08	7	<LOQ	<LOQ	0.62	10	<LOQ	<LOQ	0.86

Table B7, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n =49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
27	6	<LOQ	<LOQ	0.16	6	<LOQ	<LOQ	0.12	5	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.23
31	16	<LOQ	<LOQ	2.78	14	<LOQ	<LOQ	3.56	12	<LOQ	<LOQ	3.92	4	<LOQ	<LOQ	<LOQ
32	4	<LOQ	<LOQ	<LOQ	10	<LOQ	<LOQ	0.62	7	<LOQ	<LOQ	0.55	10	<LOQ	<LOQ	0.51
34	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
35	8	<LOQ	<LOQ	0.74	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
36	6	<LOQ	<LOQ	0.28	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
37	16	<LOQ	<LOQ	4.58	12	<LOQ	<LOQ	2.25	12	<LOQ	<LOQ	3.47	6	<LOQ	<LOQ	0.73
38	6	<LOQ	<LOQ	0.14	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
40+41+71	10	<LOQ	<LOQ	1.26	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	1.25	8	<LOQ	<LOQ	1.3
42+59+62+75	6	<LOQ	<LOQ	0.51	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
43+73	8	<LOQ	<LOQ	1.56	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
44+47+65	12	<LOQ	<LOQ	2.73	12	<LOQ	<LOQ	5.09	14	<LOQ	<LOQ	8.02	10	<LOQ	<LOQ	4.09
45+51	8	<LOQ	<LOQ	0.82	2	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.63	2	<LOQ	<LOQ	<LOQ
46	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
48	8	<LOQ	<LOQ	0.78	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	1.08	0	<LOQ	<LOQ	<LOQ
49+69	8	<LOQ	<LOQ	1.35	16	<LOQ	<LOQ	2.79	12	<LOQ	<LOQ	3.75	12	<LOQ	<LOQ	2.1
50+53	4	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.57
52	6	<LOQ	<LOQ	3.19	6	<LOQ	<LOQ	5.73	9	<LOQ	<LOQ	21.6	6	<LOQ	<LOQ	4.6
55	6	<LOQ	<LOQ	0.42	4	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	1.51	6	<LOQ	<LOQ	0.54
56	18	<LOQ	<LOQ	2.83	18	<LOQ	<LOQ	2.85	28	<LOQ	<LOQ	3.06	18	<LOQ	<LOQ	2.39
57	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.36
58	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
60	26	<LOQ	<LOQ	1.81	18	<LOQ	<LOQ	2.34	28	<LOQ	<LOQ	2.72	16	<LOQ	<LOQ	2.33
61+70+74+76	32	<LOQ	<LOQ	17.87	10	<LOQ	<LOQ	15.05	51	7.11	<LOQ	25.52	16	<LOQ	<LOQ	19.45
63	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
64	10	<LOQ	<LOQ	1.35	8	<LOQ	<LOQ	1.5	14	<LOQ	<LOQ	2.77	8	<LOQ	<LOQ	1.36
66	50	0.94	<LOQ	7.94	38	<LOQ	<LOQ	8.57	49	<LOQ	<LOQ	6.81	35	<LOQ	<LOQ	8.6
67	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
68	0	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.4	2	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.87
72	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ

Table B7, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n =49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
77	6	<LOQ	<LOQ	1.2	10	<LOQ	<LOQ	2.14	16	<LOQ	<LOQ	7.99	16	<LOQ	<LOQ	7.87
79	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
80	6	<LOQ	<LOQ	0.29	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
82	10	<LOQ	<LOQ	1.19	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
83+99	94	3.98	0.72	10.46	58	2.57	<LOQ	9.02	86	4.23	<LOQ	11.54	51	1.86	<LOQ	6.34
84	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	3.56	6	<LOQ	<LOQ	0.91
85+116+117	16	<LOQ	<LOQ	2.1	6	<LOQ	<LOQ	1.05	19	<LOQ	<LOQ	2.21	12	<LOQ	<LOQ	1.53
86+87+97+109+119+125	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	6.28	4	<LOQ	<LOQ	<LOQ
88+91	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	1.45	6	<LOQ	<LOQ	1.05
89	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
90+101+113	4	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	8.05	6	<LOQ	<LOQ	2.52
92	8	<LOQ	<LOQ	1.1	6	<LOQ	<LOQ	0.47	9	<LOQ	<LOQ	1.51	4	<LOQ	<LOQ	<LOQ
93+100	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.77
94	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
95	4	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	12.53	4	<LOQ	<LOQ	<LOQ
96	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
98+102	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
103	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
104	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
105	32	<LOQ	<LOQ	5.47	14	<LOQ	<LOQ	5.2	44	<LOQ	<LOQ	7.34	10	<LOQ	<LOQ	4.05
107+123	16	<LOQ	<LOQ	1.04	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	1.34	0	<LOQ	<LOQ	<LOQ
108+124	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
110+115	10	<LOQ	<LOQ	12.61	12	<LOQ	<LOQ	13.29	19	<LOQ	<LOQ	11.91	10	<LOQ	<LOQ	6.55
111	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.43	0	<LOQ	<LOQ	<LOQ
112	6	<LOQ	<LOQ	0.79	6	<LOQ	<LOQ	0.65	12	<LOQ	<LOQ	1.98	8	<LOQ	<LOQ	1.17
114	24	<LOQ	<LOQ	1.07	8	<LOQ	<LOQ	0.48	12	<LOQ	<LOQ	1.03	4	<LOQ	<LOQ	<LOQ
118	84	5.35	<LOQ	17.03	42	<LOQ	<LOQ	11.27	84	6.59	<LOQ	23.11	43	<LOQ	<LOQ	10.1
120	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
121	8	<LOQ	<LOQ	0.34	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
122	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.42

Table B7, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n =49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
126	8	<LOQ	<LOQ	0.75	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
128+166	8	<LOQ	<LOQ	0.71	6	<LOQ	<LOQ	0.48	7	<LOQ	<LOQ	0.58	4	<LOQ	<LOQ	<LOQ
129+138+163	94	8.89	1.01	27.12	68	3.21	<LOQ	13.44	98	8.83	4.15	22.18	63	2.56	<LOQ	9.08
130	8	<LOQ	<LOQ	0.81	4	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.85	2	<LOQ	<LOQ	<LOQ
131	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
132	4	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	1.05	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
133	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
134+143	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
135+151	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	1.82	4	<LOQ	<LOQ	<LOQ
136	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	1.09	4	<LOQ	<LOQ	<LOQ
137+164	20	<LOQ	<LOQ	1.63	4	<LOQ	<LOQ	<LOQ	19	<LOQ	<LOQ	2.02	8	<LOQ	<LOQ	1.2
139+140	8	<LOQ	<LOQ	0.49	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
141	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
142	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
144	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
145	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.16	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
146	76	1.24	<LOQ	4.06	22	<LOQ	<LOQ	1.89	74	1.44	<LOQ	3.61	24	<LOQ	<LOQ	2.29
147+149	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	2.58	6	<LOQ	<LOQ	0.93
148	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
150	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
152	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
153+168	98	8.28	2.59	32.82	78	2.92	<LOQ	10.75	100	10.96	4.73	26.51	80	2.97	<LOQ	11.12
155	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
156+157	52	1.27	<LOQ	5.87	8	<LOQ	<LOQ	2.96	65	1.91	<LOQ	5.24	10	<LOQ	<LOQ	2.68
158	12	<LOQ	<LOQ	0.61	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.5	10	<LOQ	<LOQ	0.85
159	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
160	8	<LOQ	<LOQ	1.84	6	<LOQ	<LOQ	0.23	9	<LOQ	<LOQ	5.12	4	<LOQ	<LOQ	<LOQ
161	6	<LOQ	<LOQ	0.26	2	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.69	2	<LOQ	<LOQ	<LOQ
162	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.51
165	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ

Table B7, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n =49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
167	26	<LOQ	<LOQ	1.27	10	<LOQ	<LOQ	0.69	30	<LOQ	<LOQ	1.31	8	<LOQ	<LOQ	0.88
169	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
170	72	1.97	<LOQ	7.68	20	<LOQ	<LOQ	2.79	84	2.58	<LOQ	8.37	16	<LOQ	<LOQ	2.77
171+173	20	<LOQ	<LOQ	1.25	6	<LOQ	<LOQ	0.67	16	<LOQ	<LOQ	1.46	14	<LOQ	<LOQ	1.09
172	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	1.36	6	<LOQ	<LOQ	0.68
174	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
175	6	<LOQ	<LOQ	0.29	6	<LOQ	<LOQ	0.58	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
176	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
177	16	<LOQ	<LOQ	1.49	10	<LOQ	<LOQ	1.37	28	<LOQ	<LOQ	1.7	10	<LOQ	<LOQ	1.31
178	20	<LOQ	<LOQ	1.81	0	<LOQ	<LOQ	<LOQ	23	<LOQ	<LOQ	2.31	6	<LOQ	<LOQ	0.32
179	12	<LOQ	<LOQ	0.95	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
180+193	98	4.44	1.78	24.77	54	1.1	<LOQ	5.92	100	6.49	3.47	27.96	61	1.32	<LOQ	6.95
181	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
182	8	<LOQ	<LOQ	0.63	8	<LOQ	<LOQ	0.81	9	<LOQ	<LOQ	2.07	4	<LOQ	<LOQ	<LOQ
183+185	36	<LOQ	<LOQ	3.21	6	<LOQ	<LOQ	0.78	44	<LOQ	<LOQ	2.85	2	<LOQ	<LOQ	<LOQ
184	2	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.71	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
186	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.45	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
187	84	1.75	<LOQ	7.75	20	<LOQ	<LOQ	2.05	86	2.8	<LOQ	10.34	27	<LOQ	<LOQ	4.17
188	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
189	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
190	22	<LOQ	<LOQ	1.21	10	<LOQ	<LOQ	0.68	28	<LOQ	<LOQ	1.73	8	<LOQ	<LOQ	0.78
191	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
192	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
194	20	<LOQ	<LOQ	2.8	2	<LOQ	<LOQ	<LOQ	42	<LOQ	<LOQ	3.33	4	<LOQ	<LOQ	<LOQ
195	10	<LOQ	<LOQ	1.43	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.79	4	<LOQ	<LOQ	<LOQ
196	12	<LOQ	<LOQ	1.83	0	<LOQ	<LOQ	<LOQ	19	<LOQ	<LOQ	2.48	2	<LOQ	<LOQ	<LOQ
197+200	12	<LOQ	<LOQ	0.9	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.58
198+199	44	<LOQ	<LOQ	6.16	4	<LOQ	<LOQ	<LOQ	63	1.85	<LOQ	6.27	8	<LOQ	<LOQ	2.32
201	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
202	24	<LOQ	<LOQ	1.45	6	<LOQ	<LOQ	0.37	30	<LOQ	<LOQ	1.43	4	<LOQ	<LOQ	<LOQ

Table B7, continued

| Congener | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n =49) | | | |
	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
203	36	<LOQ	<LOQ	3.65	4	<LOQ	<LOQ	<LOQ	58	0.99	<LOQ	3.09	8	<LOQ	<LOQ	1.14
204	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
205	8	<LOQ	<LOQ	1.41	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
206	18	<LOQ	<LOQ	1.93	2	<LOQ	<LOQ	<LOQ	26	<LOQ	<LOQ	3.07	0	<LOQ	<LOQ	<LOQ
207	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
208	6	<LOQ	<LOQ	0.5	2	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.92	0	<LOQ	<LOQ	<LOQ
209	34	<LOQ	<LOQ	0.75	0	<LOQ	<LOQ	<LOQ	42	<LOQ	<LOQ	1.4	4	<LOQ	<LOQ	<LOQ
SPCBs	100	60.39	16.58	216.8	100	24.51	3.69	122.8	100	73.35	30.65	243.8	98	26.06	1.31	111.4

Note: Detections are reported as percent of the subgroup. PCBs not listed were not detected in any samples.

Table B8 Frequency of detection (Det), median (Med) and range (5th-95th percentile) of PCBs (nanograms per gram fresh weight) detected in mothers and children from East Chicago and Columbus Junction.

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
1	10	<LOQ	<LOQ	0.0031	14	<LOQ	<LOQ	0.0028	5	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.0024
2	18	<LOQ	<LOQ	0.0082	18	<LOQ	<LOQ	0.0063	9	<LOQ	<LOQ	0.0027	8	<LOQ	<LOQ	0.0019
3	12	<LOQ	<LOQ	0.022	20	<LOQ	<LOQ	0.01	2	<LOQ	<LOQ	<LOQ	10	<LOQ	<LOQ	0.005
4	10	<LOQ	<LOQ	0.0049	6	<LOQ	<LOQ	0.0016	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
5	12	<LOQ	<LOQ	0.0019	10	<LOQ	<LOQ	0.0042	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
6	16	<LOQ	<LOQ	0.0036	12	<LOQ	<LOQ	0.0046	12	<LOQ	<LOQ	0.0025	8	<LOQ	<LOQ	0.0021
7	6	<LOQ	<LOQ	0.0036	6	<LOQ	<LOQ	0.0033	7	<LOQ	<LOQ	0.0049	6	<LOQ	<LOQ	0.0044
8	20	<LOQ	<LOQ	0.015	14	<LOQ	<LOQ	0.013	14	<LOQ	<LOQ	0.011	12	<LOQ	<LOQ	0.012
9	8	<LOQ	<LOQ	0.0021	12	<LOQ	<LOQ	0.0019	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
10	10	<LOQ	<LOQ	0.0028	8	<LOQ	<LOQ	0.0016	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
11	30	<LOQ	<LOQ	0.064	34	<LOQ	<LOQ	0.057	26	<LOQ	<LOQ	0.042	16	<LOQ	<LOQ	0.039
12+13	24	<LOQ	<LOQ	0.0065	22	<LOQ	<LOQ	0.0076	14	<LOQ	<LOQ	0.0038	35	<LOQ	<LOQ	0.0043
14	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
15	24	<LOQ	<LOQ	0.018	24	<LOQ	<LOQ	0.016	19	<LOQ	<LOQ	0.009	16	<LOQ	<LOQ	0.0097
16	10	<LOQ	<LOQ	0.0048	4	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0043	4	<LOQ	<LOQ	<LOQ
17	10	<LOQ	<LOQ	0.0025	8	<LOQ	<LOQ	0.003	9	<LOQ	<LOQ	0.0064	12	<LOQ	<LOQ	0.0038
18+30	6	<LOQ	<LOQ	0.0036	6	<LOQ	<LOQ	0.0036	7	<LOQ	<LOQ	0.014	6	<LOQ	<LOQ	0.0032
19	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
20+28	54	0.017	<LOQ	0.032	38	<LOQ	<LOQ	0.025	51	0.017	<LOQ	0.048	33	<LOQ	<LOQ	0.036
21+33	14	<LOQ	<LOQ	0.02	4	<LOQ	<LOQ	<LOQ	14	<LOQ	<LOQ	0.02	0	<LOQ	<LOQ	<LOQ
22	36	<LOQ	<LOQ	0.0076	28	<LOQ	<LOQ	0.0069	33	<LOQ	<LOQ	0.0082	24	<LOQ	<LOQ	0.0061
23	10	<LOQ	<LOQ	0.0015	8	<LOQ	<LOQ	0.0021	2	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	0.0022

Table B8, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
24	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
25	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
26+29	8	<LOQ	<LOQ	0.0041	8	<LOQ	<LOQ	0.004	7	<LOQ	<LOQ	0.0038	10	<LOQ	<LOQ	0.0041
27	6	<LOQ	<LOQ	0.001	6	<LOQ	<LOQ	0.00059	5	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.0011
31	16	<LOQ	<LOQ	0.016	14	<LOQ	<LOQ	0.016	12	<LOQ	<LOQ	0.02	4	<LOQ	<LOQ	<LOQ
32	4	<LOQ	<LOQ	<LOQ	10	<LOQ	<LOQ	0.0026	7	<LOQ	<LOQ	0.0028	10	<LOQ	<LOQ	0.0023
34	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
35	8	<LOQ	<LOQ	0.0043	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
36	6	<LOQ	<LOQ	0.0017	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
37	16	<LOQ	<LOQ	0.027	12	<LOQ	<LOQ	0.0098	12	<LOQ	<LOQ	0.023	6	<LOQ	<LOQ	0.0036
38	6	<LOQ	<LOQ	0.00077	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
40+41+71	10	<LOQ	<LOQ	0.0081	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.0085	8	<LOQ	<LOQ	0.0069
42+59+62+75	6	<LOQ	<LOQ	0.0039	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
43+73	8	<LOQ	<LOQ	0.0094	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
44+47+65	12	<LOQ	<LOQ	0.019	12	<LOQ	<LOQ	0.021	14	<LOQ	<LOQ	0.055	10	<LOQ	<LOQ	0.02
45+51	8	<LOQ	<LOQ	0.0053	2	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.0049	2	<LOQ	<LOQ	<LOQ
46	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
48	8	<LOQ	<LOQ	0.0053	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0056	0	<LOQ	<LOQ	<LOQ
49+69	8	<LOQ	<LOQ	0.0094	16	<LOQ	<LOQ	0.013	12	<LOQ	<LOQ	0.025	12	<LOQ	<LOQ	0.01
50+53	4	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0025
52	6	<LOQ	<LOQ	0.019	6	<LOQ	<LOQ	0.021	9	<LOQ	<LOQ	0.13	6	<LOQ	<LOQ	0.028
55	6	<LOQ	<LOQ	0.0024	4	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0098	6	<LOQ	<LOQ	0.0026
56	18	<LOQ	<LOQ	0.015	18	<LOQ	<LOQ	0.013	28	<LOQ	<LOQ	0.019	18	<LOQ	<LOQ	0.014
57	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0017

Table B8, continued

| | | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | |
| | | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
58	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
60	26	<LOQ	<LOQ	0.0097	18	<LOQ	<LOQ	0.01	28	<LOQ	<LOQ	0.015	16	<LOQ	<LOQ	0.011
61+70+74+76	32	<LOQ	<LOQ	0.091	10	<LOQ	<LOQ	0.06	51	0.047	<LOQ	0.15	16	<LOQ	<LOQ	0.11
63	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
64	10	<LOQ	<LOQ	0.0068	8	<LOQ	<LOQ	0.0064	14	<LOQ	<LOQ	0.017	8	<LOQ	<LOQ	0.0064
66	50	0.0065	<LOQ	0.038	38	<LOQ	<LOQ	0.037	49	<LOQ	<LOQ	0.043	35	<LOQ	<LOQ	0.045
67	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
68	0	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.002	2	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.0037
72	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
77	6	<LOQ	<LOQ	0.0056	10	<LOQ	<LOQ	0.0099	16	<LOQ	<LOQ	0.05	16	<LOQ	<LOQ	0.042
79	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
80	6	<LOQ	<LOQ	0.0013	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
82	10	<LOQ	<LOQ	0.0065	4	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
83+99	94	0.024	0.0049	0.056	58	0.012	<LOQ	0.036	86	0.025	<LOQ	0.05	51	0.011	<LOQ	0.033
84	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.018	6	<LOQ	<LOQ	0.0042
85+116+117	16	<LOQ	<LOQ	0.012	6	<LOQ	<LOQ	0.0054	19	<LOQ	<LOQ	0.013	12	<LOQ	<LOQ	0.0072
86+87+97+109+119+125	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.035	4	<LOQ	<LOQ	<LOQ
88+91	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.0099	6	<LOQ	<LOQ	0.005
89	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
90+101+113	4	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.055	6	<LOQ	<LOQ	0.016
92	8	<LOQ	<LOQ	0.0071	6	<LOQ	<LOQ	0.0028	9	<LOQ	<LOQ	0.01	4	<LOQ	<LOQ	<LOQ
93+100	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.0037
94	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
95	4	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.065	4	<LOQ	<LOQ	<LOQ

Table B8, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
96	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
98+102	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
103	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
104	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
105	32	<LOQ	<LOQ	0.026	14	<LOQ	<LOQ	0.025	44	<LOQ	<LOQ	0.03	10	<LOQ	<LOQ	0.022
107+123	16	<LOQ	<LOQ	0.0063	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0076	0	<LOQ	<LOQ	<LOQ
108+124	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
110+115	10	<LOQ	<LOQ	0.066	12	<LOQ	<LOQ	0.068	19	<LOQ	<LOQ	0.07	10	<LOQ	<LOQ	0.032
111	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.0026	0	<LOQ	<LOQ	<LOQ
112	6	<LOQ	<LOQ	0.0046	6	<LOQ	<LOQ	0.0035	12	<LOQ	<LOQ	0.014	8	<LOQ	<LOQ	0.0055
114	24	<LOQ	<LOQ	0.0072	8	<LOQ	<LOQ	0.0028	12	<LOQ	<LOQ	0.0055	4	<LOQ	<LOQ	<LOQ
118	84	0.035	<LOQ	0.085	42	<LOQ	<LOQ	0.065	84	0.041	<LOQ	0.1	43	<LOQ	<LOQ	0.059
120	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
121	8	<LOQ	<LOQ	0.0021	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
122	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0019
126	8	<LOQ	<LOQ	0.005	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
128+166	8	<LOQ	<LOQ	0.0047	6	<LOQ	<LOQ	0.0022	7	<LOQ	<LOQ	0.0036	4	<LOQ	<LOQ	<LOQ
129+138+163	94	0.05	0.0085	0.14	68	0.015	<LOQ	0.062	98	0.05	0.022	0.13	63	0.016	<LOQ	0.045
130	8	<LOQ	<LOQ	0.0059	4	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0056	2	<LOQ	<LOQ	<LOQ
131	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
132	4	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0043	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
133	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
134+143	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
135+151	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.012	4	<LOQ	<LOQ	<LOQ

Table B8, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
136	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.0074	4	<LOQ	<LOQ	<LOQ
137+164	20	<LOQ	<LOQ	0.009	4	<LOQ	<LOQ	<LOQ	19	<LOQ	<LOQ	0.011	8	<LOQ	<LOQ	0.0052
139+140	8	<LOQ	<LOQ	0.0029	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
141	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
142	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
144	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
145	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.00091	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
146	76	0.008	<LOQ	0.022	22	<LOQ	<LOQ	0.0097	74	0.0078	<LOQ	0.022	24	<LOQ	<LOQ	0.012
147+149	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.013	6	<LOQ	<LOQ	0.0055
148	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
150	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
152	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
153+168	98	0.055	0.022	0.17	78	0.014	<LOQ	0.055	100	0.065	0.022	0.18	80	0.014	<LOQ	0.057
155	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
156+157	52	0.0091	<LOQ	0.034	8	<LOQ	<LOQ	0.014	65	0.011	<LOQ	0.034	10	<LOQ	<LOQ	0.014
158	12	<LOQ	<LOQ	0.0036	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.0028	10	<LOQ	<LOQ	0.0037
159	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
160	8	<LOQ	<LOQ	0.0099	6	<LOQ	<LOQ	0.001	9	<LOQ	<LOQ	0.028	4	<LOQ	<LOQ	<LOQ
161	6	<LOQ	<LOQ	0.0017	2	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0048	2	<LOQ	<LOQ	<LOQ
162	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0023
165	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
167	26	<LOQ	<LOQ	0.0074	10	<LOQ	<LOQ	0.003	30	<LOQ	<LOQ	0.01	8	<LOQ	<LOQ	0.0038
169	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
170	72	0.012	<LOQ	0.043	20	<LOQ	<LOQ	0.014	84	0.015	<LOQ	0.063	16	<LOQ	<LOQ	0.013

Table B8, continued

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
171+173	20	<LOQ	<LOQ	0.0061	6	<LOQ	<LOQ	0.0033	16	<LOQ	<LOQ	0.0097	14	<LOQ	<LOQ	0.0047
172	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	12	<LOQ	<LOQ	0.011	6	<LOQ	<LOQ	0.0031
174	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
175	6	<LOQ	<LOQ	0.0022	6	<LOQ	<LOQ	0.0025	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
176	2	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
177	16	<LOQ	<LOQ	0.008	10	<LOQ	<LOQ	0.0059	28	<LOQ	<LOQ	0.011	10	<LOQ	<LOQ	0.0056
178	20	<LOQ	<LOQ	0.01	0	<LOQ	<LOQ	<LOQ	23	<LOQ	<LOQ	0.015	6	<LOQ	<LOQ	0.0012
179	12	<LOQ	<LOQ	0.0045	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
180+193	98	0.031	0.013	0.14	54	0.0052	<LOQ	0.028	100	0.036	0.017	0.22	61	0.0065	<LOQ	0.036
181	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
182	8	<LOQ	<LOQ	0.0038	8	<LOQ	<LOQ	0.0041	9	<LOQ	<LOQ	0.014	4	<LOQ	<LOQ	<LOQ
183+185	36	<LOQ	<LOQ	0.017	6	<LOQ	<LOQ	0.0046	44	<LOQ	<LOQ	0.015	2	<LOQ	<LOQ	<LOQ
184	2	<LOQ	<LOQ	<LOQ	8	<LOQ	<LOQ	0.004	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
186	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0023	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ
187	84	0.011	<LOQ	0.041	20	<LOQ	<LOQ	0.011	86	0.018	<LOQ	0.08	27	<LOQ	<LOQ	0.018
188	0	<LOQ	<LOQ	<LOQ	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
189	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
190	22	<LOQ	<LOQ	0.007	10	<LOQ	<LOQ	0.0036	28	<LOQ	<LOQ	0.0099	8	<LOQ	<LOQ	0.0036
191	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
192	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
194	20	<LOQ	<LOQ	0.016	2	<LOQ	<LOQ	<LOQ	42	<LOQ	<LOQ	0.023	4	<LOQ	<LOQ	<LOQ
195	10	<LOQ	<LOQ	0.0077	0	<LOQ	<LOQ	<LOQ	7	<LOQ	<LOQ	0.005	4	<LOQ	<LOQ	<LOQ
196	12	<LOQ	<LOQ	0.01	0	<LOQ	<LOQ	<LOQ	19	<LOQ	<LOQ	0.015	2	<LOQ	<LOQ	<LOQ
197+200	12	<LOQ	<LOQ	0.0057	4	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	6	<LOQ	<LOQ	0.0026

Table B8, continued

| Congener | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 50) | | | | Children (n = 43) | | | | Mothers (n = 50) | | | | Children (n = 49) | | | |
	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
198+199	44	<LOQ	<LOQ	0.032	4	<LOQ	<LOQ	<LOQ	63	0.0099	<LOQ	0.04	8	<LOQ	<LOQ	0.01
201	2	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
202	24	<LOQ	<LOQ	0.0077	6	<LOQ	<LOQ	0.0019	30	<LOQ	<LOQ	0.009	4	<LOQ	<LOQ	<LOQ
203	36	<LOQ	<LOQ	0.018	4	<LOQ	<LOQ	<LOQ	58	0.0056	<LOQ	0.02	8	<LOQ	<LOQ	0.0055
204	4	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
205	8	<LOQ	<LOQ	0.0083	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
206	18	<LOQ	<LOQ	0.011	2	<LOQ	<LOQ	<LOQ	26	<LOQ	<LOQ	0.016	0	<LOQ	<LOQ	<LOQ
207	2	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ
208	6	<LOQ	<LOQ	0.0027	2	<LOQ	<LOQ	<LOQ	9	<LOQ	<LOQ	0.0061	0	<LOQ	<LOQ	<LOQ
209	34	<LOQ	<LOQ	0.0036	0	<LOQ	<LOQ	<LOQ	42	<LOQ	<LOQ	0.0093	4	<LOQ	<LOQ	<LOQ
ΣPCBs	100	0.41	0.094	1.1	100	0.11	0.017	0.5	100	0.45	0.16	1.6	98	0.11	0.0071	0.58

Note: Detections are reported as percent of the subgroup. PCBs not listed were not detected in any samples.

Table B9 Frequency of detection (Det), median (Med) and range (5th-95th percentile) of OH-PCBs (nanograms per gram fresh weight) detected in mothers and children from East Chicago and Columbus Junction.

| | East Chicago (urban) | | | | | | | | Columbus Junction (rural) | | | | | | | |
| | Mothers (n = 39) | | | | Children (n = 41) | | | | Mothers (n = 37) | | | | Children (n = 43) | | | |
Congener	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%	Det	Med	5%	95%
4'-OH-PCB107	100	0.032	0.021	0.080	95	0.032	0.017	0.071	97	0.031	0.022	0.083	98	0.026	0.018	0.046
3'-OH-PCB118	62	0.0050	<LOQ	0.051	66	0.0050	<LOQ	0.037	62	0.0037	<LOQ	0.029	58	0.0028	<LOQ	0.012
4'-OH-PCB120	38	<LOQ	<LOQ	0.073	27	<LOQ	<LOQ	0.056	32	<LOQ	<LOQ	0.087	16	<LOQ	<LOQ	0.020
4'-OH-PCB130	5	<LOQ	<LOQ	0.00092	0	<LOQ	<LOQ	<LOQ	0	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ
3'-OH-PCB138	72	0.0031	<LOQ	0.075	59	0.0023	<LOQ	0.043	78	0.0056	<LOQ	0.12	53	0.0025	<LOQ	0.029
4'-OH-PCB146	69	0.0081	<LOQ	0.048	51	0.0047	<LOQ	0.018	73	0.0097	<LOQ	0.040	42	<LOQ	<LOQ	0.018
4'-OH-PCB163	51	0.0016	<LOQ	0.013	37	<LOQ	<LOQ	0.0061	62	0.0018	<LOQ	0.014	42	<LOQ	<LOQ	0.006
4'-OH-PCB172	38	<LOQ	<LOQ	0.033	27	<LOQ	<LOQ	0.030	38	<LOQ	<LOQ	0.033	37	<LOQ	<LOQ	0.028
3'-OH-PCB180	2.6	<LOQ	<LOQ	<LOQ	2	<LOQ	<LOQ	<LOQ	5	<LOQ	<LOQ	0.0010	0	<LOQ	<LOQ	<LOQ
4'-OH-PCB187	100	0.018	0.0096	0.051	100	0.013	0.0080	0.021	100	0.020	0.0085	0.054	100	0.012	0.0064	0.022
4'-OH-PCB193	10	<LOQ	<LOQ	0.028	15	<LOQ	<LOQ	0.012	24	<LOQ	<LOQ	0.031	33	<LOQ	<LOQ	0.030
ΣOH-PCBs	100	0.11	0.046	0.30	100	0.079	0.037	0.21	100	0.12	0.038	0.31	100	0.066	0.029	0.15

Note: Detections are reported as percent of the subgroup.

APPENDIX C
SUPPLEMENTAL INFORMATION TO CHAPTER 3
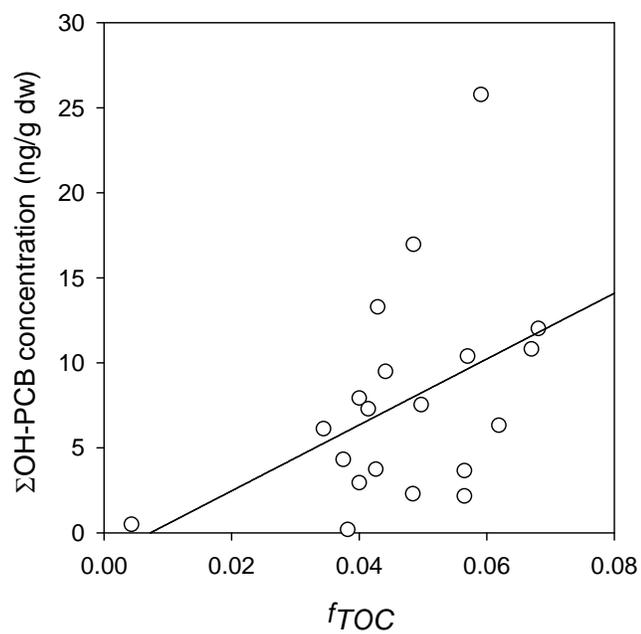
Figure C1 ΣOH-PCB increases with increasing TOC ($R^2 = 0.20$, $p = 0.048$). Each circle represents a sample. ^{f}TOC was calculated as mass of total TOC in the sample (grams) divided by mass of the sediment sample (grams).
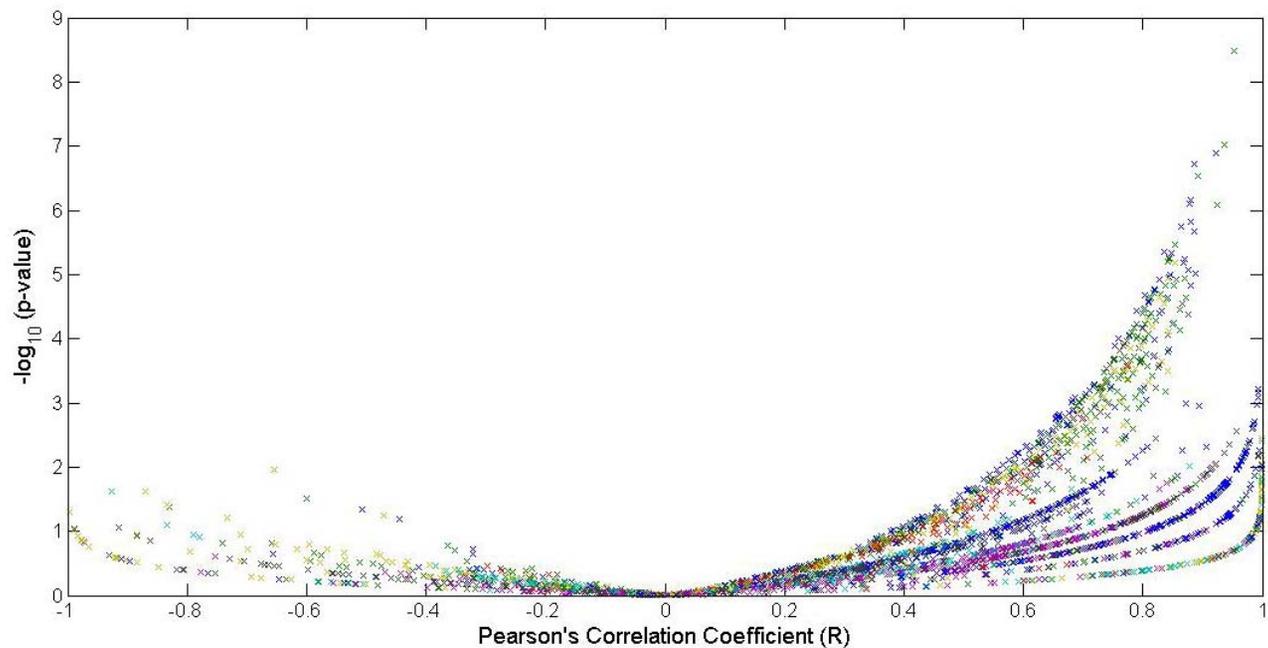
Figure C2 The Pearson's Correlation Coefficient and p-value for each OH-PCB:PCB pair. Each point on the graph represents one pair. Pairs were included only if both the OH-PCB and PCB were measured in at least 3 samples (2764 pairs). 713 pairs (26%) had significant correlations ($p < 0.05$). A positive R-value signifies a positive correlation (i.e. OH-PCB concentration increases as PCB concentration increases). Conversely, a negative R-value signifies a negative correlation (i.e. OH-PCB concentration decreases as PCB concentration increases). Of the statistically significant associations, almost all (705 pairs) were positive.
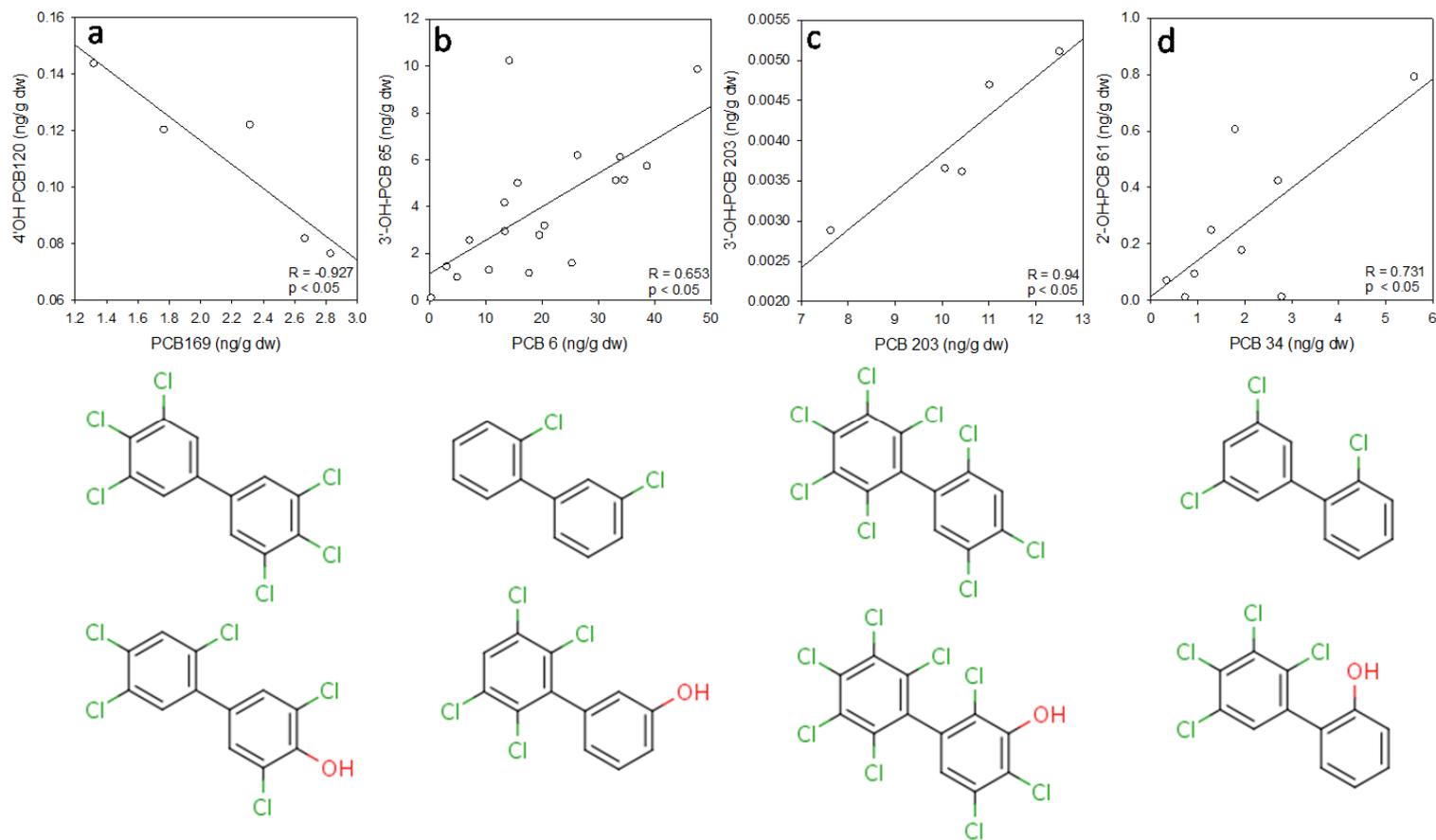
Figure C3 Significant correlations between OH-PCB:PCB pairs. Examples (a) and (b) involve OH-PCBs that were measured in both sediment and Aroclor. Assuming degradation refers to the possibility of dechlorination and insertion of an OH group but not chlorination or rearrangement of the chlorine atoms, neither OH-PCB could be formed from degradation of the PCB. Examples (c) and (d) involve OH-PCBs that were measured in sediment but not Aroclor. In example (c) the OH-PCB could be formed by degradation of the PCB but in example (d) the OH-PCB could not be formed by degradation of the PCB.

Table C1 Precursor and dominant product ions of the 65 quantitative calibration standards.

Source	Congener	Abbreviation	Homolog	Precursor	Product
AccuStd	4-methoxy-2-chlorobiphenyl	4-MeO-PCB 1	mono	218.6	174.9
AccuStd	4-methoxy-3-chlorobiphenyl	4-MeO-PCB 2	mono	218.6	174.9
AccuStd	6-methoxy-3-chlorobiphenyl	6-MeO-PCB 2	mono	218.6	168
AccuStd	4'-methoxy-4-chlorobiphenyl	4'-MeO-PCB 3	mono	218.6	174.9
AccuStd	2'-methoxy-2,3-dichlorobiphenyl	2'-MeO-PCB 5	di	253.1	201.9
AccuStd	3'-methoxy-2,5-dichlorobiphenyl	3'-MeO-PCB 9	di	253.1	152
AccuStd	4'-methoxy-2,5-dichlorobiphenyl	4'-MeO-PCB 9	di	253.1	210.9
AccuStd	2'-methoxy-3,4-dichlorobiphenyl	2'-MeO-PCB 12	di	253.1	201.9
AccuStd	4-methoxy-3,5-dichlorobiphenyl	4-MeO-PCB 14	di	253.1	210.9
AccuStd	4'-methoxy-2,2',5-trichlorobiphenyl	4'-MeO-PCB 18	tri	287.5	245
AccuStd	4'-methoxy-2,3',5-trichlorobiphenyl	4'-MeO-PCB 26	tri	287.5	245
AccuStd	6'-methoxy-2,3',5-trichlorobiphenyl	6'-MeO-PCB 26	tri	287.5	238
AccuStd	2'-methoxy-2,4,6-trichlorobiphenyl	2'-MeO-PCB 30	tri	287.5	238
AccuStd	3'-methoxy-2,4,6-trichlorobiphenyl	3'-MeO-PCB 30	tri	287.5	245
AccuStd	4'-methoxy-2,4,6-trichlorobiphenyl	4'-MeO-PCB 30	tri	287.5	245
AccuStd	3-methoxy-2,2',6,6'-tetrachlorobiphenyl	3-MeO-PCB 54	tetra	322.0	278.8
AccuStd	2'-methoxy-2,3,4,5-tetrachlorobiphenyl	2'-MeO-PCB 61	tetra	322.0	272
AccuStd	3'-methoxy-2,3,4,5-tetrachlorobiphenyl	3'-MeO-PCB 61	tetra	322.0	221.8
WellMixA	4'-methoxy -2,3,4,5-tetrachlorobiphenyl	4'-MeO-PCB 61	tetra	322.0	278.8
AccuStd	2'-methoxy-2,3,5,6-tetrachlorobiphenyl	2'-MeO-PCB 65	tetra	322.0	272
AccuStd	3'-methoxy-2,3,5,6-tetrachlorobiphenyl	3'-MeO-PCB 65	tetra	322.0	221.8
AccuStd	4'-methoxy-2,3',4,6-tetrachlorobiphenyl	4'-MeO-PCB 69	tetra	322.0	278.8
AccuStd	6'-methoxy-2,3',4,6-tetrachlorobiphenyl	6'-MeO-PCB 69	tetra	322.0	272
AccuStd	4'-methoxy-2,3',5,5'-tetrachlorobiphenyl	4'-MeO-PCB 72	tetra	322.0	278.8
WellMixB	4'-methoxy-3,3',4,5'-tetrachlorobiphenyl	4'-MeO-PCB 79	tetra	322.0	278.8

Table C1, continued

Source	Congener	Abbreviation	Homolog	Precursor	Product
AccuStd	6'-methoxy-2,2'3,3'5-pentachlorobiphenyl	6'-MeO-PCB 83	penta	356.4	305.8
AccuStd	4'-methoxy-2,2',3,4,5-pentachlorobiphenyl	4'-MeO-PCB 86	penta	356.4	312.9
AccuStd	4'-methoxy-2,2',3,5,6-pentachlorobiphenyl	4'-MeO-PCB 93	penta	356.4	312.9
WellMixG	4'-methoxy-2,2',3',4,5-pentachlorobiphenyl	4'-MeO-PCB 97	penta	356.4	312.9
WellMixB	4'-methoxy-2,2',4,5,5'-pentachlorobiphenyl	4'-MeO-PCB 101	penta	356.4	312.9
AccuStd	6'-methoxy-2,2',4,5,5'-pentachlorobiphenyl	6'-MeO-PCB 101	penta	356.4	305.8
AccuStd	6'-methoxy-2,3,3',4,5-pentachlorobiphenyl	6'-MeO-PCB 106	penta	356.4	305.8
WellMixF	4-methoxy-2,3,3',4',5-pentachlorobiphenyl	4-MeO-PCB 107	penta	356.4	312.9
WellMixE	4'-methoxy-2,3,3',4,5-pentachlorobiphenyl	4'-MeO-PCB 108	penta	356.4	312.9
WellMixC	2'methoxy-2,3,4,4',5-pentachlorobiphenyl	2'-MeO-PCB 114	penta	356.4	305.8
WellMixD	3-methoxy-2,3',4,4',5-pentachlorobiphenyl	3-MeO-PCB 118	penta	356.4	312.9
WellMixA	4'-methoxy-2,3',4,5,5'-pentachlorobiphenyl	4'-MeO-PCB 120	penta	356.4	312.9
WellMixH	4'-methoxy-3,3',4,5,5'-pentachloro-biphenyl	4'-MeO-PCB 127	penta	356.4	340.7
WellMixE	4'-methoxy-2,2',3,3',4,5'-hexachlorobiphenyl	4'-MeO-PCB 130	hexa	390.9	346.8
WellMixB	4-methoxy-2,2',3,3',5,6-hexachlorobiphenyl	4-MeO-PCB 134	hexa	390.9	346.8
WellMixD	3'-methoxy-2,2',3,4,4',5'-hexachlorobiphenyl	3'-MeO-PCB 138	hexa	390.9	346.8
AccuStd	5-methoxy-2,2',3,4,4',5'-hexachlorobiphenyl	5-MeO-PCB 138	hexa	390.9	346.8
WellMixC	4-methoxy-2,2',3,4',5,5'-hexachlorobiphenyl	4-MeO-PCB 146	hexa	390.9	346.8
WellMixA	3,3'-dimethoxy-2,2',4,4',6,6'-hexachlorobiphenyl	3,3'-diMeO-PCB 155	hexa, di MeO	420.9	376.7
WellMixG	4'-methoxy-2,3,3',4,5,5'-hexachlorobiphenyl	4'-MeO-PCB 159	hexa	390.9	346.8
WellMixI	4-methoxy-2,3,3',4',5,5'-hexachlorobiphenyl	4-MeO-PCB 162	hexa	390.9	346.8
WellMixF	4-methoxy-2,3,3',4',5,6-hexachlorobiphenyl	4-MeO-PCB 163	hexa	390.9	346.8
WellMixH	4'-methoxy-2,2',3,3',4,5,5'-heptachlorobiphenyl	4'-MeO-PCB 172	hepta	425.3	382.8
WellMixF	4-methoxy-2,2',3,3',4',5,6-heptachlorobiphenyl	4-MeO-PCB 177	hepta	425.3	382.8
WellMixB	4-methoxy-2,2',3,3',5,5',6-heptachlorobiphenyl	4-MeO-PCB 178	hepta	425.3	382.8

Table C1, continued

Source	Congener	Abbreviation	Homolog	Precursor	Product
WellMixG	3'-methoxy-2,2',3,4,4',5,5'-heptachlorobiphenyl	3'-MeO-PCB 180	hepta	425.3	382.8
WellMixC	3'-methoxy-2,2',3,4,4',5,6'-heptachlorobiphenyl	3'-MeO-PCB 182	hepta	425.3	382.8
WellMixD	3'-methoxy-2,2',3,4,4',5',6-heptachlorobiphenyl	3'-MeO-PCB 183	hepta	425.3	382.8
AccuStd	5-methoxy-2,2',3,4,4',5'6-heptachlorobiphenyl	5-MeO-PCB 183	hepta	425.3	382.8
WellMixA	3'-methoxy 2,2',3,4,4',6,6'-heptachlorobiphenyl	3'-MeO-PCB 184	hepta	425.3	382.8
WellMixE	4-methoxy-2,2',3,4',5,5',6-heptachlorobiphenyl	4-MeO-PCB187	hepta	425.3	382.8
WellMixI	4-methoxy-2,3,3',4',5,5',6-heptachlorobiphenyl	4-MeO-PCB193	hepta	425.3	382.8
WellMixD	4'-methoxy-2,2',3,3',4,5,5',6-octachlorobiphenyl	4'-MeO-PCB198	octa	459.8	416.8
WellMixE	4'-methoxy-2,2',3,3',4,5,5',6'-octachlorobiphenyl	4'-MeO-PCB199	octa	459.8	416.8
WellMixF	4'-methoxy-2,2',3,3',4,5,6,6'-octachlorobiphenyl	4'-MeO-PCB200	octa	459.8	416.8
WellMixB	4'-methoxy-2,2',3,3',4,5',6,6'-octachlorobiphenyl	4'-MeO-PCB201	octa	459.8	416.8
WellMixA	4-methoxy-2,2',3,3',5,5',6,6'-octachlorobiphenyl	4-MeO-PCB202	octa	459.8	416.8
WellMixG	4,4'-dimethoxy-2,2',3,3',5,5',6,6'-octachlorobiphenyl	4,4'-diMeO-PCB202	octa, di MeO	489.8	446.7
WellMixC	3'-methoxy-2,2',3,4,4',5,5',6-octachlorobiphenyl	3'-MeO-PCB203	octa	459.8	416.8
WellMixC	4'-methoxy 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	4'-MeO-PCB208	nona	494.2	450.7

Note: Standards were purchased from AccuStandard, Inc. (AccuStd) and Wellington Laboratories (Well).

Table C2 OH-PCB congeners and their abbreviations.

Congener	Abbreviation
4-hydroxy-2-chlorobiphenyl	4-OH-PCB 1
4-hydroxy-3-chlorobiphenyl	4-OH-PCB 2
6-hydroxy-3-chlorobiphenyl	6-OH-PCB 2
4'-hydoxy-4-chlorobiphenyl	4'-OH-PCB 3
2'-hydroxy-2,3-dichlorobiphenyl	2'-OH-PCB 5
3'-hydroxy-2,5-dichlorobiphenyl	3'-OH-PCB 9
4'-hydroxy-2,5-dichlorobiphenyl	4'-OH-PCB 9
2'-hydroxy-3,4-dichlorobiphenyl	2'-OH-PCB 12
4-hydroxy-3,5-dichlorobiphenyl	4-OH-PCB 14
4'-hydroxy-2,2',5-trichlorobiphenyl	4'-OH-PCB 18
4'-hydroxy-2,3',5-trichlorobiphenyl	4'-OH-PCB 26
6'-hydroxy-2,3',5-trichlorobiphenyl	6'-OH-PCB 26
2'-hydroxy-2,4,6-trichlorobiphenyl	2'-OH-PCB 30
3'-hydroxy-2,4,6-trichlorobiphenyl	3'-OH-PCB 30
4'-hydroxy-2,4,6-trichlorobiphenyl	4'-OH-PCB 30
3-hydroxy-2,2',6,6'-tetrachlorobiphenyl	3-OH-PCB 54
2'-hydroxy-2,3,4,5-tetrachlorobiphenyl	2'-OH-PCB 61
3'-hydroxy-2,3,4,5-tetrachlorobiphenyl	3'-OH-PCB 61
4'-hydroxy -2,3,4,5-tetrachlorobiphenyl	4'-OH-PCB 61
2'-hydroxy-2,3,5,6-tetrachlorobiphenyl	2'-OH-PCB 65
3'-hydroxy-2,3,5,6-tetrachlorobiphenyl	3'-OH-PCB 65
4'-hydroxy-2,3',4,6-tetrachlorobiphenyl	4'-OH-PCB 69
6'-hydroxy-2,3'4,6-tetrachlorobiphenyl	6'-OH-PCB 69
4'-hydroxy-2,3',5,5'-tetrachlorobiphenyl	4'-OH-PCB 72
4'-hydroxy-3,3',4,5'-tetrachlorobiphenyl	4'-OH-PCB 79
6'-hydroxy-2,2',3,3',5-pentachlorobiphenyl	6'-OH-PCB 83
4'-hydroxy-2,2',3,4,5-pentachlorobiphenyl	4'-OH-PCB 86
4'-hydroxy-2,2',3,5,6-pentachlorobiphenyl	4'-OH-PCB 93
4'-hydroxy-2,2',3',4,5-pentachlorobiphenyl	4'-OH-PCB 97
4'-hydroxy-2,2',4,5,5'-pentachlorobiphenyl	4'-OH-PCB 101
6'-hydroxy-2,2',4,5,5'-pentachlorobiphenyl	6'-OH-PCB 101
6'-hydroxy-2,3,3',4,5-pentachlorobiphenyl	6'-OH-PCB 106
4-hydroxy-2,3,3',4',5-pentachlorobiphenyl	4-OH-PCB 107
4'-hydroxy-2,3,3',4,5'-pentachlorobiphenyl	4'-OH-PCB 108
2'-hydroxy-2,3,4,4',5-pentachlorobiphenyl	2'-OH-PCB 114
3-hydroxy-2,3',4,4',5-pentachlorobiphenyl	3-OH-PCB 118
4'-hydroxy-2,3',4,5,5'-pentachlorobiphenyl	4'-OH-PCB 120

Table C2, continued

Congener	Abbreviation
4'-hydroxy-3,3',4,5,5'-pentachlorobiphenyl	4'-OH-PCB 127
4'-hydroxy-2,2',3,3',4,5'-hexachlorobiphenyl	4'-OH-PCB 130
4-hydroxy-2,2',3,3',5,6-hexachlorobiphenyl	4-OH-PCB 134
3'-hydroxy-2,2',3,4,4',5'-hexachlorobiphenyl	3'-OH-PCB 138
5-hydroxy-2,2',3,4,4',5'-hexachlorobiphenyl	5-OH-PCB 138
4-hydroxy-2,2',3,4',5,5'-hexachlorobiphenyl	4-OH-PCB 146
3,3'-dihydroxy-2,2',4,4',6,6'-hexachlorobiphenyl	3,3'-diOH-PCB 155
4'-hydroxy-2,3,3',4,5,5'-hexachlorobiphenyl	4'-OH-PCB 159
4-hydroxy-2,3,3',4',5,5'-hexachlorobiphenyl	4-OH-PCB 162
4-hydroxy-2,3,3',4',5,6-hexachlorobiphenyl	4-OH-PCB 163
4'-hydroxy-2,2',3,3',4,5,5'-heptachlorobiphenyl	4'-OH-PCB 172
4-hydroxy-2,2',3,3',4',5,6-heptachlorobiphenyl	4-OH-PCB 177
4-hydroxy-2,2',3,3',5,5',6-heptachlorobiphenyl	4-OH-PCB 178
3'-hydroxy-2,2',3,4,4',5,5'-heptachlorobiphenyl	3'-OH-PCB 180
3'-hydroxy-2,2',3,4,4',5,6-heptachlorobiphenyl	3'-OH-PCB 182
3'-hydroxy-2,2',3,4,4',5',6-heptachlorobiphenyl	3'-OH-PCB 183
5-hydroxy-2,2',3,4,4',5'6-heptachlorobiphenyl	5-OH-PCB 183
3'-hydroxy-2,2',3,4,4',6,6'-heptachlorobiphenyl	3'-OH-PCB 184
4-hydroxy-2,2',3,4',5,5',6-heptachlorobiphenyl	4-OH-PCB 187
4-hydroxy-2,3,3',4',5,5',6-heptachlorobiphenyl	4-OH-PCB 193
4'-hydroxy-2,2',3,3',4,5,5',6-octachlorobiphenyl	4'-OH-PCB 198
4'-hydroxy-2,2',3,3',4,5,5',6'-octachlorobiphenyl	4'-OH-PCB 199
4'-hydroxy-2,2',3,3',4,5,6,6'-octachlorobiphenyl	4'-OH-PCB 200
4'-hydroxy-2,2',3,3',4,5',6,6'-octachlorobiphenyl	4'-OH-PCB 201
4-hydroxy-2,2',3,3',5,5',6,6'-octachlorobiphenyl	4-OH-PCB 202
4,4'-dihydroxy-2,2',3,3',5,5',6,6'-octachlorobiphenyl	4,4'-diOH-PCB 202
3'-hydroxy-2,2',3,4,4',5,5',6-octachlorobiphenyl	3'-OH-PCB 203
4'-hydroxy-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	4'-OH-PCB 208

Table C3 Limit of Quantification (LOQ) for each OH-PCB congener in sediment in units
of nanograms per sample.

Congener	LOQ	Congener	LOQ
4-OH-PCB 1	0.36	3-OH-PCB 118	0.032
6-OH-PCB 2	0.0026	4'-OH-PCB 120	0.16
2'-OH-PCB 5	0.63	4'-OH-PCB 127	0.87
4'-OH-PCB 9 + 4-OH-PCB 14	0.26	4'-OH-PCB 130	0.28
2'-OH-PCB 12	0.00094	4-OH-PCB 134	0.039
4'-OH-PCB 18	0.2	3'-OH-PCB 138	0.068
4'-OH-PCB 26	0.047	5-OH-PCB 138	0.029
6'-OH-PCB 26	0.00062	4-OH-PCB 146	0.35
2'-OH-PCB 30	0.00034	3,3'-diOH-PCB 155	0.0050
3'-OH-PCB 30	0.026	4-OH-PCB 162	0.17
4'-OH-PCB 30	0.056	4-OH-PCB 163	0.036
3-OH-PCB 54	0.0051	4'-OH-PCB 172	0.011
2'-OH-PCB 61	0.0046	4-OH-PCB 177	0.0038
3'-OH-PCB 61	0.15	4-OH-PCB 178	0.0087
2'-OH-PCB 65 + 6'-OH-PCB 69	0.00012	3'-OH-PCB 180	0.014
3'-OH-PCB 65	0.33	3'-OH-PCB 182	0.023
4'-OH-PCB 69	0.029	3'-OH-PCB 183	0.0032
4'-OH-PCB 72	0.030	5-OH-PCB 183 + 4-OH-PCB 187	0.0055
4'-OH-PCB 79	0.028	3'-OH-PCB 184	0.012
6'-OH-PCB 83	0.00034	4-OH-PCB 193	0.0021
4'-OH-PCB 86	0.046	4'-OH-PCB 198 + 4'-OH-PCB 200 + 3'-OH-PCB 203	0.0032
4'-OH-PCB 93	0.20	4'-OH-PCB 199	0.0011
4'-OH-PCB 97	0.016	4'-OH-PCB 201	0.0022
4'-OH-PCB 101	0.011	4-OH-PCB 202	0.0013
6'-OH-PCB 101	0.00064	4,4'-diOH-PCB 202	0.0049
6'-OH-PCB 106 + 2'-OH-PCB 114	0.0017	4'-OH-PCB 208	0.0037

Table C4 Frequency of detection (Det), minimum (Min), maximum (Max), median (Med), average (Ave), and standard deviation (Stdev) of the individual and sum OH-PCBs detected in sediment (n = 20) from Indiana Harbor and Ship Canal, East Chicago, IN.

Congener	Det	Min	Max	Med	Ave	Stdev
4-OH-PCB 1	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
6-OH-PCB 2	100	0.03	3.79	0.85	1.14	1.04
2'-OH-PCB 5	10	<LOQ	1.32	<LOQ	0.10	0.33
4'-OH-PCB 9 + 4-OH-PCB 14	15	<LOQ	5.55	<LOQ	0.31	1.24
2'-OH-PCB 12	15	<LOQ	0.17	<LOQ	0.01	0.04
4'-OH-PCB 18	85	<LOQ	3.09	0.66	0.80	0.75
4'-OH-PCB 26	55	<LOQ	0.84	0.05	0.16	0.24
6'-OH-PCB 26	100	0.01	0.78	0.19	0.26	0.22
2'-OH-PCB 30	5	<LOQ	<LOQ	<LOQ	<LOQ	0.00
3'-OH-PCB 30	10	<LOQ	0.05	<LOQ	<LOQ	0.01
4'-OH-PCB 30	5	<LOQ	0.23	<LOQ	0.01	0.05
3-OH-PCB 54	35	<LOQ	0.05	<LOQ	0.01	0.01
2'-OH-PCB 61	50	<LOQ	0.79	0.01	0.13	0.23
3'-OH-PCB 61	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
2'-OH-PCB 65 + 6'-OH-PCB 69	15	<LOQ	0.01	<LOQ	<LOQ	0.00
3'-OH-PCB 65	95	<LOQ	10.24	3.08	3.79	2.91
4'-OH-PCB 69	85	<LOQ	0.86	0.12	0.21	0.23
4'-OH-PCB 72	30	<LOQ	0.21	<LOQ	0.03	0.06
4'-OH-PCB 79	30	<LOQ	0.03	<LOQ	0.01	0.01
6'-OH-PCB 83	20	<LOQ	0.05	<LOQ	<LOQ	0.01
4'-OH-PCB 86	30	<LOQ	0.29	<LOQ	0.04	0.08

Table C4, continued

Congener	Det	Min	Max	Med	Ave	Stdev
4'-OH-PCB 93	50	<LOQ	0.44	0.06	0.16	0.18
4'-OH-PCB 97	90	<LOQ	0.30	0.12	0.13	0.11
4'-OH-PCB 101	95	<LOQ	0.31	0.10	0.12	0.09
6'-OH-PCB 101	40	<LOQ	0.02	<LOQ	<LOQ	0.01
6'-OH-PCB 106 + 2'-OH-PCB 114	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
3-OH-PCB 118	10	<LOQ	0.18	<LOQ	0.01	0.05
4'-OH-PCB 120	35	<LOQ	0.14	<LOQ	0.04	0.05
4'-OH-PCB 127	25	<LOQ	1.07	<LOQ	0.17	0.34
4'-OH-PCB 130	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4-OH-PCB 134	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
3'-OH-PCB 138	10	<LOQ	0.06	<LOQ	0.01	0.02
5-OH-PCB 138	50	<LOQ	0.04	0.01	0.01	0.01
4-OH-PCB 146	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
3,3'-diOH-PCB 155	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4-OH-PCB 162	10	<LOQ	0.19	<LOQ	0.01	0.05
4-OH-PCB 163	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4'-OH-PCB 172	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4-OH-PCB 177	5	<LOQ	0.01	<LOQ	<LOQ	0.00
4-OH-PCB 178	10	<LOQ	0.01	<LOQ	<LOQ	0.00
3'-OH-PCB 180	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
3'-OH-PCB 182	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
3'-OH-PCB 183	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
5-OH-PCB 183 + 4-OH-PCB 187	10	<LOQ	0.03	<LOQ	<LOQ	0.01
3'-OH-PCB 184	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4-OH-PCB 193	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00

Table C4, continued

Congener	Det	Min	Max	Med	Ave	Stdev
4'-OH-PCB 198 + 4'-OH-PCB 200 + 3'-OH-PCB 203	30	<LOQ	0.01	<LOQ	<LOQ	0.00
4'-OH-PCB 199	25	<LOQ	0.01	<LOQ	<LOQ	0.00
4'-OH-PCB 201	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4-OH-PCB 202	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4,4'-diOH-PCB 202	0	<LOQ	<LOQ	<LOQ	<LOQ	0.00
4'-OH-PCB 208	10	<LOQ	<LOQ	<LOQ	<LOQ	0.00
ΣOH-PCB$_{58}$	100	0.19	26	6.8	7.7	6.2

Note: OH-PCBs are reported as nanograms per gram dry weight. Frequency of detection is reported as percent.

Table C5 Congener distribution as percent of ΣOH-PCB$_{64}$ for 5 Aroclors as percent.

Congener	1016	1221	1242	1248	1254
4-OH-PCB 1	0.75	14 (8.9)	0	0.18 (0.16)	0.026
4-OH-PCB 2	0	0	0	1.2 (2.0)	0
6-OH-PCB 2	0.32	5.6 (3.8)	0.69	3.0 (0.03)	0.017
4'-OH-PCB 3	0	0	0	0	0
2'-OH-PCB 5	0	0	0	0	0
3'-OH-PCB 9	0	0	0	0	0.12
4'-OH-PCB 9 + 4-OH-PCB 14	1.5	5.3 (5.6)	0	0.73 (0.26)	0.51
2'-OH-PCB 12	71	0	0	0	0.99
4'-OH-PCB 18	0	2.4 (2.1)	4.1	1.7 (0.17)	0.94
4'-OH-PCB 26	3.4	8.9 (7.2)	6.1	6.4 (0.27)	8.8
6'-OH-PCB 26	0	7.5 (4.4)	5.9	1.2 (0.12)	3.7
2'-OH-PCB 30	0	0	0	0	0
3'-OH-PCB 30	0	0	0	0	0
4'-OH-PCB 30	10	0.42 (0.72)	0	0.17 (0.086)	0
3-OH-PCB 54	2.8	0	0	0	0.15
2'-OH-PCB 61	0	0	0	0	0
3'-OH-PCB 61	0	0	0	0	0
4'-OH-PCB 61	0	0	0	1.3 (0.24)	0.82
2'-OH-PCB 65 + 6'-OH-PCB 69	0.22	0	0	1.1 (0.077)	1.5
3'-OH-PCB 65	7.6	48 (8.8)	69	50 (1.6)	42
4'-OH-PCB 69	0.82	2.0 (1.1)	6.5	4.7 (0.41)	2.9
4'-OH-PCB 72	0.98	0	0	0.13 (0.23)	0
4'-OH-PCB 79	0	0	1.1	0	0
6'-OH-PCB 83	0.003	0	0	0.1 (0.038)	1.7
4'-OH-PCB 86	0	0	0	0.89 (0.77)	0.85

Table C5, continued

Congener	1016	1221	1242	1248	1254
4'-OH-PCB 93	0.23	0	0	2.2 (0.85)	26
4'-OH-PCB 97	0.071	0	0	0.49 (0.075)	4.2
4'-OH-PCB 101	0.036	1.1 (0.1822)	0	0.66 (0.057)	0.81
6'-OH-PCB 101	0	0	0	1.1 (0.23)	0.25
6'-OH-PCB 106 + 2'-OH-PCB 114	0	0	0	0	0
4-OH-PCB 107	0.045	0.18 (0.32)	0.82	0.39 (0.089)	0.38
4'-OH-PCB 108	0	0	0	17 (0.67)	0
3-OH-PCB 118	0	0	0	0.52 (0.22)	0.21
4'-OH-PCB 120	0.092	2.6 (2.9)	5.3	2.0 (0.21)	2
4'-OH-PCB 127	0.13	0	0	2.6 (0.17)	0.59
4'-OH-PCB 130	0.015	0	0	0.067 (0.026)	0.14
4-OH-PCB 134	0.003	0	0	0	0
3'-OH-PCB 138	0	0	0	0.14 (0.033)	0.065
5-OH-PCB 138	0	0.54 (0.4650)	0	0	0.18
4-OH-PCB 146	0.047	1.3 (0.279)	0	0.17 (0.05)	0.43
3,3'-diOH-PCB 155	0	0	0	0	0
4-OH-PCB 162	0	0	0	0	0
4-OH-PCB 163	0.0043	0	0	0	0
4'-OH-PCB 172	0	0	0	0	0.009
4-OH-PCB 177	0	0	0	0	0.012
4-OH-PCB 178	0	0	0	0	0.0028
3'-OH-PCB 180	0	0	0	0	0.0049
3'-OH-PCB 182	0	0	0	0	0.097
3'-OH-PCB 183	0	0	0	0	0.013
5-OH-PCB 183 + 4-OH-PCB 187	0	0	0	0	0.047

Table C5, continued

Congener	1016	1221	1242	1248	1254
3'-OH-PCB 184	0	0	0	0	0.023
4-OH-PCB 193	0	0	0	0	0
4'-OH-PCB 198 + 4'-OH-PCB 200 + 3'-OH-PCB 203	0	0	0	0	0
4'-OH-PCB 199	0	0	0	0	0
4'-OH-PCB 201	0	0	0	0	0
4-OH-PCB 202	0	0	0	0	0
4,4'-diOH-PCB 202	0	0	0	0	0
4'-OH-PCB 208	0	0	0	0	0

Note: Values for Aroclors 1221 and 1248 are the average and (standard deviation) of 3 replicates.

APPENDIX D
PILOT STUDY OF PCB 11 AND PCB 11 METABOLITES IN THREE
HUMAN DONORS

Introduction

The primary goal of the study reported here was to determine the presence of hydroxylated metabolites of 3,3'-dichlorobiphenyl (OH-PCB11) in a large-volume blood serum sample. A secondary goal was to determine the presence of any polychlorinated biphenyls (PCBs), including PCB11, and additional hydroxylated PCBs. We hypothesized that PCB 11 may be detectable in low concentrations in humans by extracting a larger volume of serum for PCBs. Because it is likely that PCB 11, a low-chlorinated congener, is rapidly metabolized in the body, we also hypothesized that PCB 11 metabolites may be detectable in low concentrations.

Methods

Sample Extraction and Analysis

For each of the three donors, 40 g serum per donor was divided into 10 aliquots of 4 g each and spiked with PCB and OH-PCB surrogate standards, denatured with hydrochloric acid and 2-propanol, and extracted with 1:1 hexane:MTBE. The extract was washed with 1% KCl before being separated into PCB and OH-PCB fractions by liquid-liquid partitioning with KOH and hexane. The OH-PCB fraction was re-acidified with HCl (2 M) and extracted using 9:1 hexane:MTBE. OH-PCBs were derivatized to the methoxylated form (MeO-PCBs) using diazomethane. Lipids were removed from each fraction in two steps, first by mixing with concentrated sulfuric acid and then by passing the extract through a sulfuric acid-activated silica gel column. PCBs were eluted from the silica column with hexane, and MeO-PCBs were eluted with DCM. All solvents were pesticide grade quality and the water was optima quality (Fisher Scientific). PCB samples were spiked with 5 ng internal standard PCB 204and d-PCB 30 immediately prior to analysis on the instrument. A GC/MS-MS (Agilent 6890N Quattro Micro™ GC,

Micromass MS Technologies) in multiple reaction monitoring (MRM) mode was employed to analyze samples for all 209 PCBs as 159 individual or coeluting congener peaks. The GC was equipped with a Supelco SPB-Octyl capillary column with helium as the carrier gas and argon as the collision gas. MeO-PCB samples were spiked with 5 ng internal standard PCB 209 immediately prior to analysis on the instrument. Dr. Hans Lehmler of the ISRP Synthesis Core provided rough standards of the 4 PCB 11 metabolites. Both PCB and OH-PCB congener mass calculation was performed by applying a relative response factor (RRF) obtained from the calibration curve for each congener. The surrogate standards were used to adjust final concentrations to percent recovery on a per sample basis.

<div align="center">Quality Control</div>

Quality Control was assessed for every sample using blanks and surrogate standards. We also assessed the accuracy of our extraction methods and instrumental methods using NIST standard reference materials and laboratory reference materials.

A trip blank was analyzed to assess any contamination present due to sample transport and did not have any quantifiable PCB congeners. The evaporation blank, which was analyzed to assess any contamination present due to open air concentration, did not have any quantifiable congeners. The instrument blanks, which were analyzed to assess any contamination present due to the instrument, did not have any quantifiable congeners. The method blank was analyzed to assess any contamination present due to the extraction part of the method. Some PCBs and OH-PCB (as MeO-PCBs) were detected in the method blank processed with some of the sample batches, and a correction was applied to the samples based on detected peaks in the blank on a per batch basis. The correction involved a subtraction of mass from each sample analyzed in the same batch as the method blank.

Surrogate standards are used to evaluate analytical efficiency. Prior to extraction of the serum samples, each method blank and sample was spiked with surrogate standards PCB 14 (3,5-dichlorobiphenyl), d-65 (deuterium labeled 2,3,4,5-tetrachlorobiphenyl), and 166 (2,3,4,4',5,6-hexachlorobiphenyl) and 4'-OH-PCB 159 (2,3,3',4,5,5'-hexachloro-3-methoxybiphenyl. PCB and OH-PCB surrogate standard recovery for the method blanks and samples are in Table D1 and Table D2. Congener mass in each sample is corrected according to the surrogate recovery.

Table D1 Recoveries of surrogate standards PCBs 14, d-65, and 166 in method blanks and samples.

	Method Blank	Sample
Donor 1	73%, 97%, 100%	120%, 79%, 126%
Donor 2	59%, 76%, 78%	75%, 42%, 78%
Donor 3	82%, 82%, 93%	87%, 43%, 95%

Table D2 Recovery of surrogate standard 4'OH-PCB 159 in method blanks and samples

	Method Blank	Sample
Donor 1	70%	79%
Donor 2	84%	77%
Donor 3	95%	124%

Results

Our method quantitatively examined the samples for about 209 PCB congeners in about 170 individual peaks. Between the 3 donors, 51 congeners or co-eluting congeners were detected. Sum PCB concentrations ranged from 0.18 to 3.55 ng/g fresh weight. Concentrations of each congener or co-eluting congeners by donor are shown in Table D3.

Table D3 PCB congener concentration in units of nanogram per gram fresh weight by
donor.

Congener	Donor 1	Donor 2	Donor 3
3			0.0030
20+28	0.011		
21+33	0.0040	0.0070	0.0070
37	0.010	0.0090	0.010
49+69			0.0070
60		0.0070	0.017
61+70+74+76	0.033	0.11	0.094
64			0.0060
66			0.038
77	0.010	0.013	0.014
84	0.0060		0.0050
92	0.0050		0.0050
96	0.0080		
99		0.14	
107	0.0020		
110		0.036	
114		0.0080	
115	0.027		
118		0.016	
126		0.0090	
129+138+163	0.019	0.77	0.036
133		0.011	
137		0.054	
146		0.098	
153+168	0.017	0.91	0.037
170		0.23	
171+173		0.014	
172		0.018	
175	0.0050		
177		0.039	
178		0.035	
180+193	0.021	0.57	0.0080
182		0.19	
185		0.070	

Table D3, continued

Congener	Donor 1	Donor 2	Donor 3
187			0.0060
191			0.0080
198+199		0.095	
202		0.023	
203		0.071	
ΣPCBs	0.18	3.55	0.30

Note: A missing value indicates the congener was detected below the limit of quantification. Congeners not listed in the table were not detected in any of the donors.

Our method quantitatively examined the samples for four OH-PCBs. Sum of concentrations of the major OH-PCBs ranged from 0.022 to 0.31 ng/g fresh weight (Table D4). Donor 2, who had the highest sum PCB concentrations, also had the highest sum OH-PCB concentrations.

Based on a comparison of retention times between the calibration and sample, there is evidence of some PCB 11 metabolites at very low concentrations (Table D4) These concentrations are at least an order of magnitude smaller than the major human hydroxylated PCB metabolites. PCB 11 metabolite concentrations are only approximations because of the low concentrations and lack of completely characterized analytical standards. Because the Analytical Core does not have an LOQ for the PCB 11 metabolites, an Instrument Detection Limit (IDL) was used instead. Concentrations of each congener by donor are shown in Table D4.

Table D4 OH-PCB congener concentration in units of nanograms per gram fresh weight
    by donor.

Congener	Donor 1	Donor 2	Donor 3
2-OH-PCB 11	0.0060		0.0010
4-OH-PCB11		0.0030	
5-OH-PCB11			
6-OH-PCB11		0.0020	
ΣOH-PCB 11	0.0060	0.0050	0.0010
4-OH-PCB107	0.0050	0.051	0.011
3'-OH-PCB138		0.034	
4-OH-PCB146	0.0060	0.10	0.0070
4-OH-PCB187	0.011	0.12	0.010
ΣOH-PCBs (major)	0.022	0.31	0.028

Note: A missing value indicates the congener was detected below the limit of
    quantification (major OH-PCBs) or instrument detection limit (OH-PCB 11).

Summary

In this study we successfully extracted PCBs and OH-PCBs from human serum
and combined the extracts to obtain a super concentrated extract that could be analyzed
for low level PCBs and OH-PCBs. The criteria for acceptable analytical quality used by
the Analytical Core were all met.

Although donor 2 had concentrations an order of magnitude higher than the other
donors, those concentrations are still typical relative to published reports in the peer-
reviewed literature. We have also provided evidence for very low level concentrations of
PCB 11 metabolites.

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