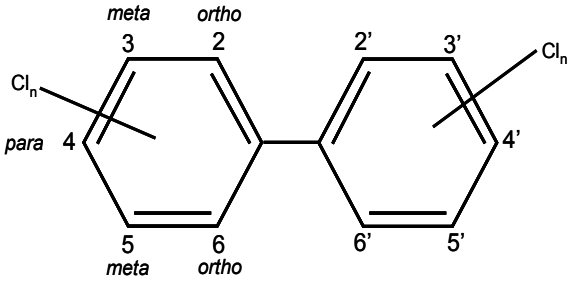
Laboratory and computational technologies to reduce the cost and improve the quality of congener-specific measurement of PCB congeners in air, water, sediments, and human blood serum

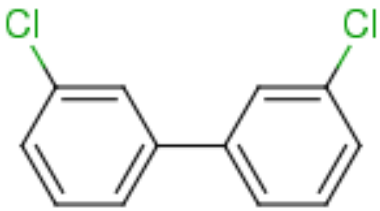
Keri C. Hornbuckle, Ph.D.

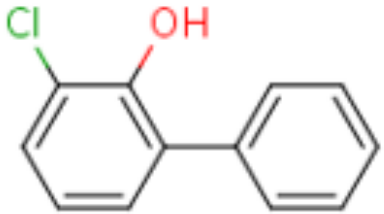
IIHR-Hydroscience and Engineering
Dept. Civil & Environmental Engineering
The University of Iowa, Iowa City, IA USA

The University of Iowa

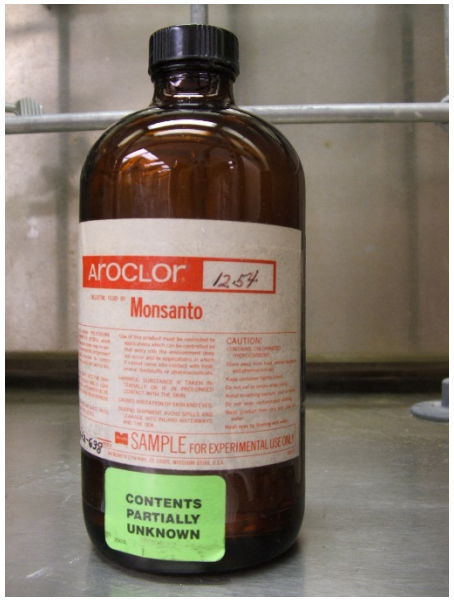
PCBs are both legacy and current, inadvertent contaminants



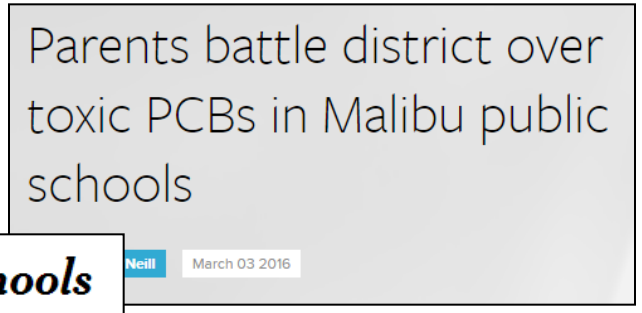


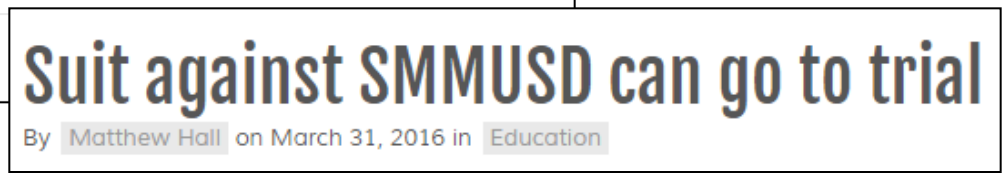


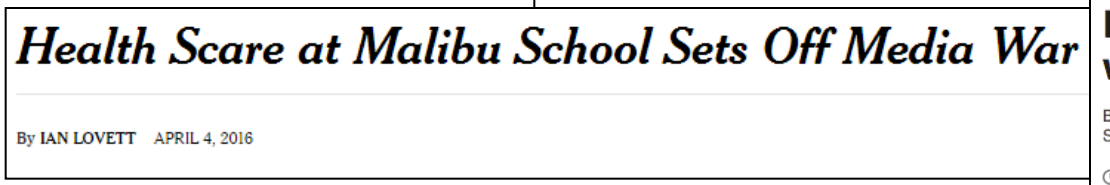
- **Aroclors** manufactured/sold until 1977
- **Current production:** inadvertently produced in low levels during pigment manufacture
- **OH-PCBs** are both metabolites and environmental contaminants
- **Exposure** from diet, dermal, inhalation
- **IARC group 1 carcinogen**, endocrine disruption, neurotoxicity



Despite PCBs being banned in 1979 by the United States Congress and in 2001 by the Stockholm Convention on Persistent Organic Pollutants, they remain relevant today.





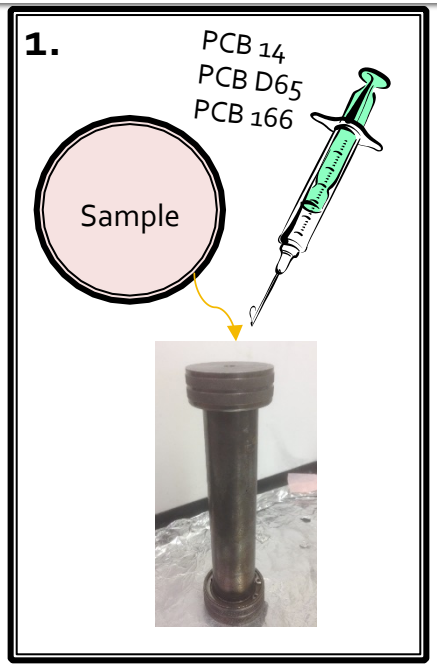


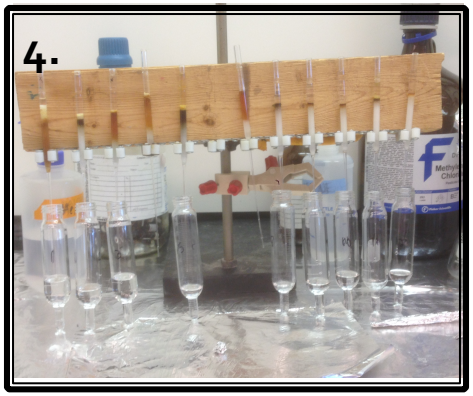
Methods

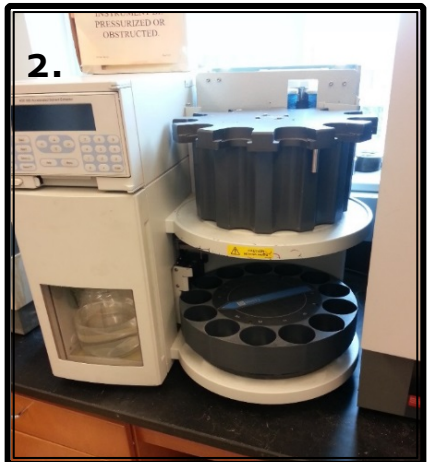
- Extraction & Cleanup of Environmental Samples
- Analysis by Triple Quadrupole GC/MS/MS
- Major Findings
- Discussion

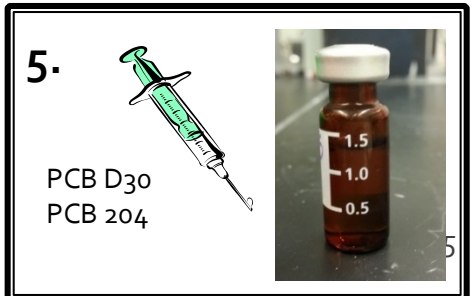
Extraction and Cleanup

1. Samples are places in ASE cell and spiked with 50 ng of Surrogate Standard
2. Samples extracted using an Accelerated Solvent Extraction (Dionex, ASE 300) with a 1:1 Hexane:Acetone mixture.
3. Samples concentrated with a Caliper Turbovap II to 0.5 mL.
4. Samples run through an acidified silica gel (2:1 silica gel:acid by weight) column eluted with 10 ml of Hexane.
5. Samples concentrated to 0.5 ml, transferred to GC vials, and spiked with internal standard.









Including OH-PCBs in Sample Analysis

- Sample Handling
  - PUF samples are acidified and extracted with hexane:acetone
  - OH-PCBs were separated from PCBs and derivatized to MeO-PCBs for GC/MS/MS analysis
  - PCB and OH-PCB fractions were cleaned using acidified silica gel columns
- SS
  - PCB and OH-PCB surrogate standards
  - Used to assess and correct recovery
- IS
  - PCB and OH-PCB internal standards
  - Used to quantify target compounds

Hornbuckle Lab Methods Compared to EPA Methods

- Pressurized fluid extraction methods using Dionex ASE 350 are identical to EPA method 3545A.
  - >100 ^{o}C
  - >1500 psi
  - 5 min static time after 5 min pre-heat equilibration
  - 60% flush volume
  - 60+ sec nitrogen purge

- Cleanup Methods are a slight variation from EPA method 3665A
  - Samples run through a cleanup column with sulfuric acid acidified silica, instead of cleanup by liquid – liquid sulfuric acid separation
  - If a sample is not fully cleaned (has color), we run it through subsequent columns, as opposed to a liquid-liquid clean up with aqueous potassium permanganate

Time and Cost Savings of Cleaning 400 air sampling media (PUF) in the ASE 350 Since January, 2017

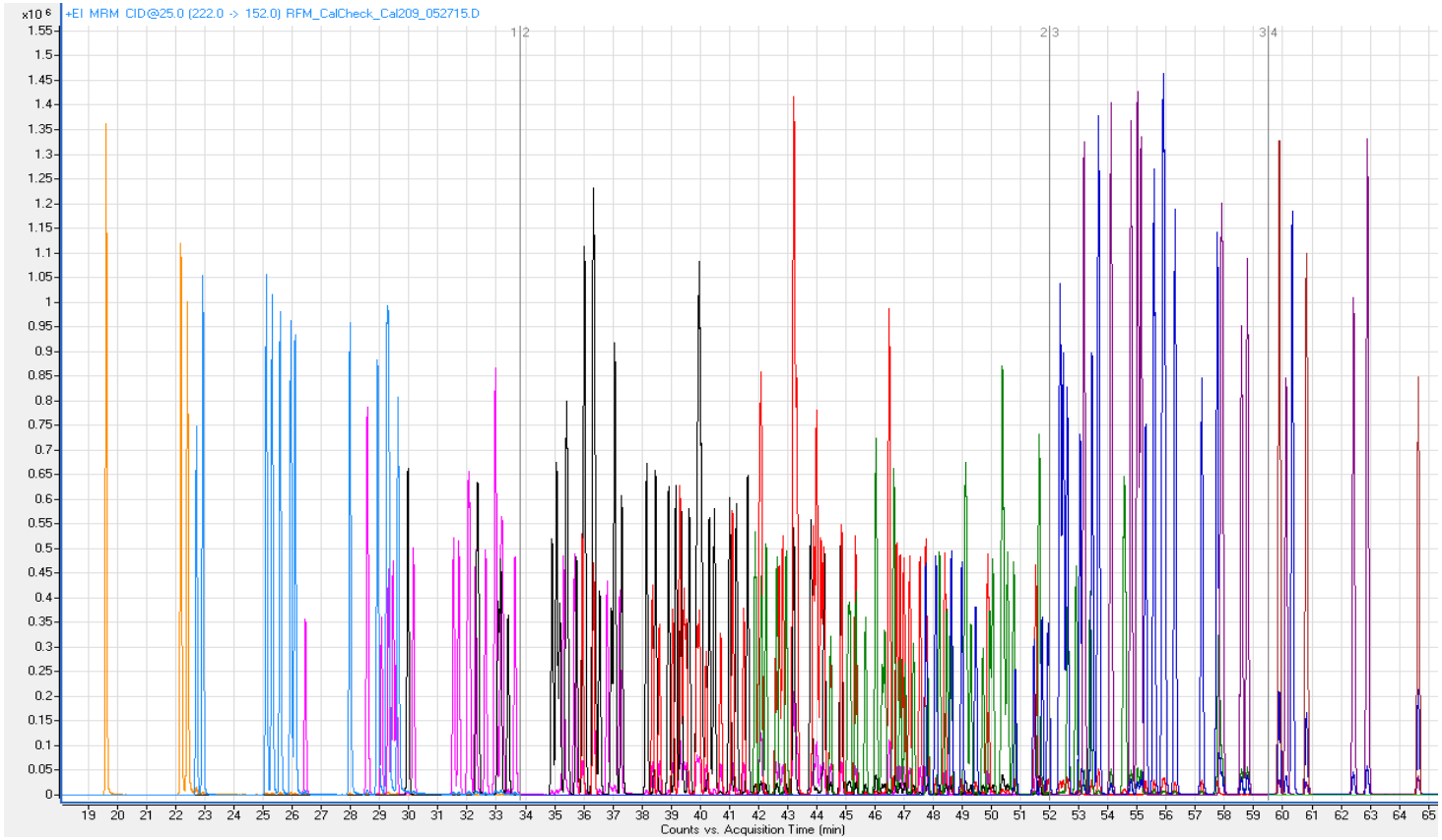
Method	Soxhlets	ASE 350
Time to clean one batch	4 days	1 day
PUF cleaned per one batch	25	50
Time required to clean 400 PUF	64 days	8 days
Solvent price per 4L bottle (variable)	~$25	~$25
Solvent volume used per batch	~10L	~4L
Batches required to clean 400 PUF	16	8
Cost to clean 450 PUF	$1000	$200

We have cut the time needed to clean PUF by a factor of 8, and the cost by a factor of 5. With the ASE, we also get:

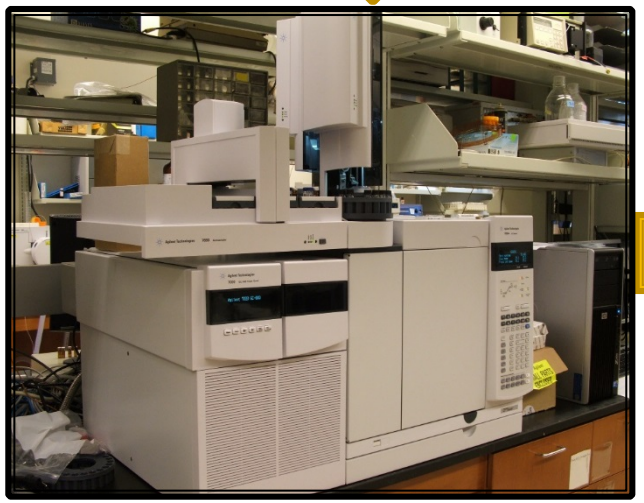
- More consistent cleaning
- More contaminant removal
- Easy QA/QC data on first and last cleaned PUF

Triple Quadrupole Tandem Mass Spectrometry

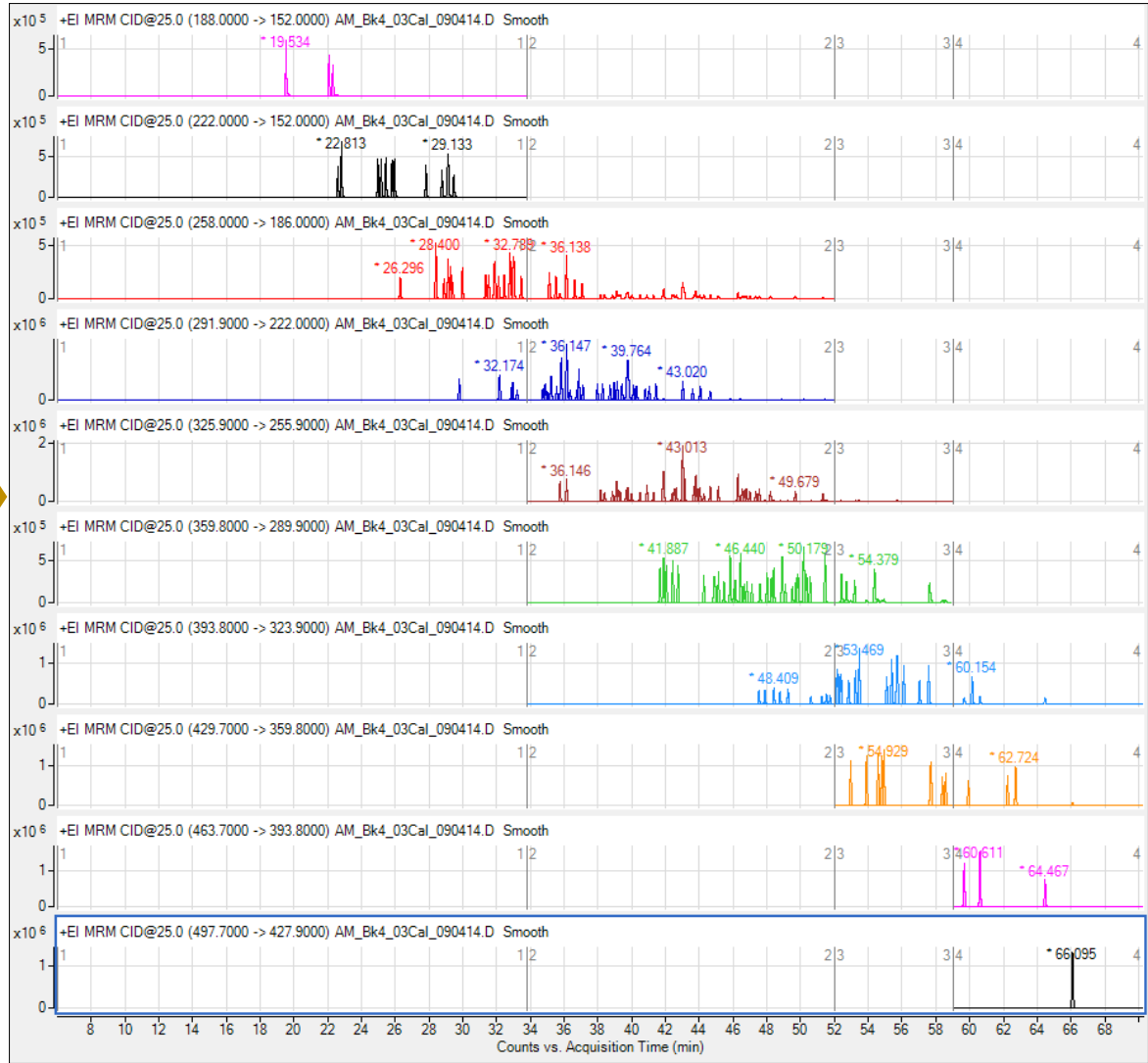
- GC-MS/MS separates congeners by retention time and mass
- 209 PCBs and 72 OH-PCBs



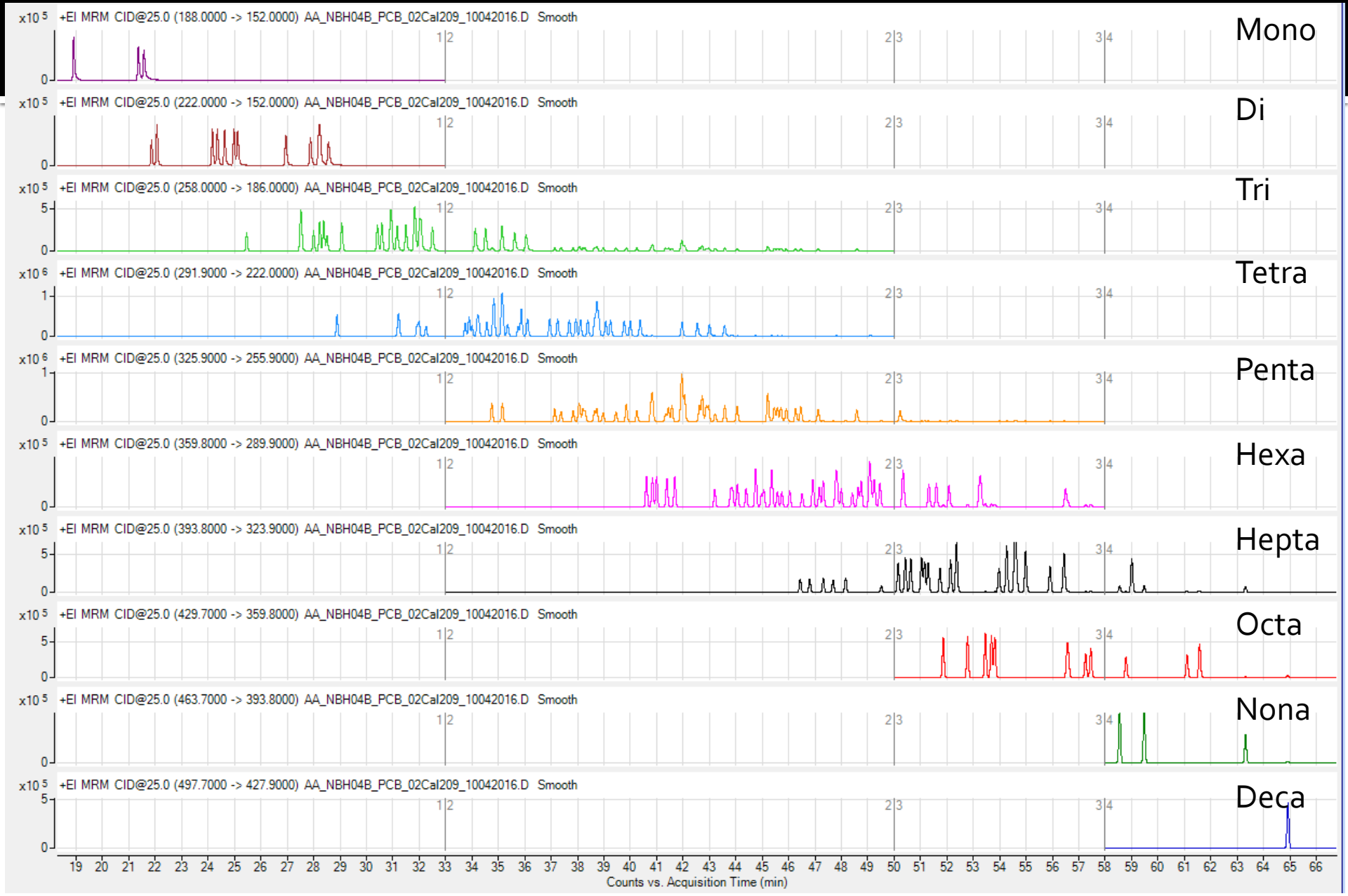
All 209 congeners represented in 176 chromatograph peaks



Samples analyzed with Gas chromatography with tandem mass spectrometry (Agilent 7000)



Ion Transitions Separate Homologs



Method	Hornbuckle Lab	EPA Method 1668c	EPA Method 8082A
Scope	Identify all 209 PCBs, individually resolving approximately 137 and the remainder as coeluting peaks	Identify all 209 PCBs, individually resolving approximately 137 and the remainder as coeluting peaks	Identify PCBs as Aroclors or as congeners, however ability to identify as congeners is limited
Instrument	GC/MS/MS	HRGC/HRMS	ECD or ELCD
Standard Reference Material (SRM)	Periodically run certified SRM as integral part of QA/QC	Include QC Check Sample with each sample batch, ideally this is a certified SRM	Provide SRM data from independent labs using method, do not require SRM as part of method
Column	Primarily SPB-octyl, also use DB-5 and DB-1701 for confirmation purposes (*SP-octyl separates the DL-PCBs*)	Primarily SPB-octyl, may employ an alternate column to resolve discrepancies, recommend DB-1	Column not specified, but states congener identification should be confirmed on a second column
Surrogate Standards	Use either a mixture of PCB 14, D65, 166, or a mixture of 10 13C-labeled PCBs, one congener from each homolog group	Uses multiple labeled PCBs for each homolog group as surrogate standards	Use PCB 209 when determining PCBs as Aroclors, Use 2,2’,4,4’,5,5’-hexabromobiphenyl or tetrachlor-m-xylene when determining PCB congeners
Quantitation	All 209 PCBS quantitated using internal standard method, using PCB D30 and PCB 204 as internal standards	PCBs are quantitated by either isotope dilution or internal standard method using labeled PCBs, depending on toxicity and elution order	PCBs are determined as congeners using PCB 209 or 2,2’,4,4’,5,5’-hexabromobiphenyl as internal standard, or as Aroclors using no internal standard

Confirmation Columns Necessary for OH-PCBs

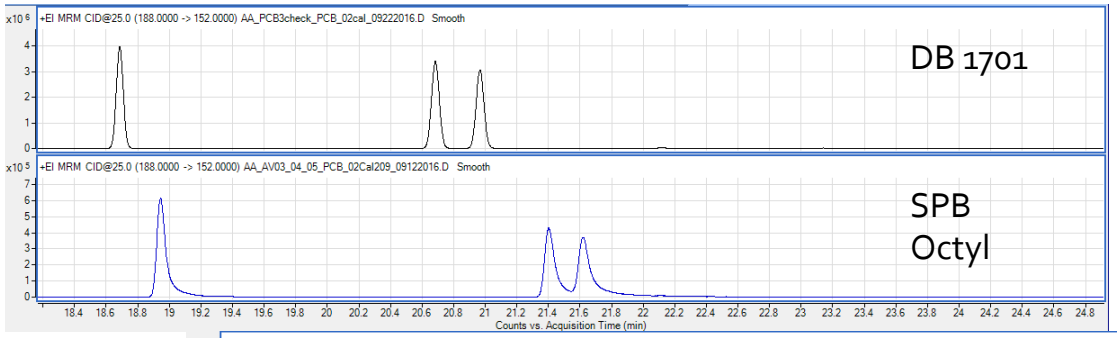
SPB Octyl

DB 1701

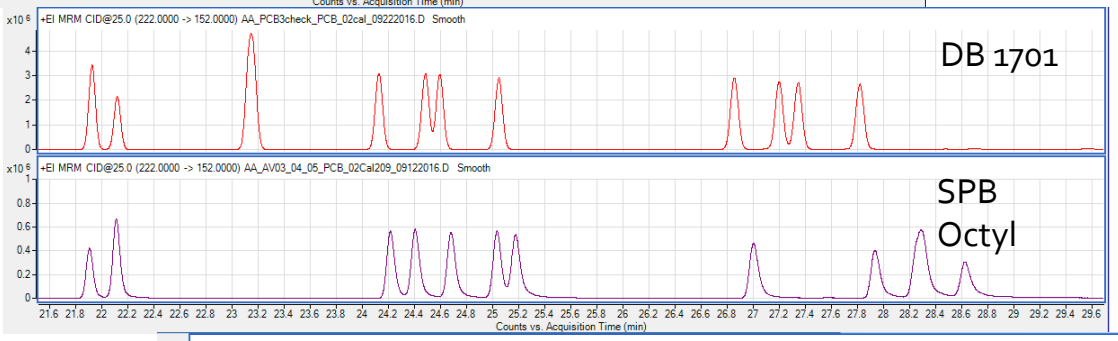
Mono Di Tri

Confirmation Columns Necessary for OH-PCBs

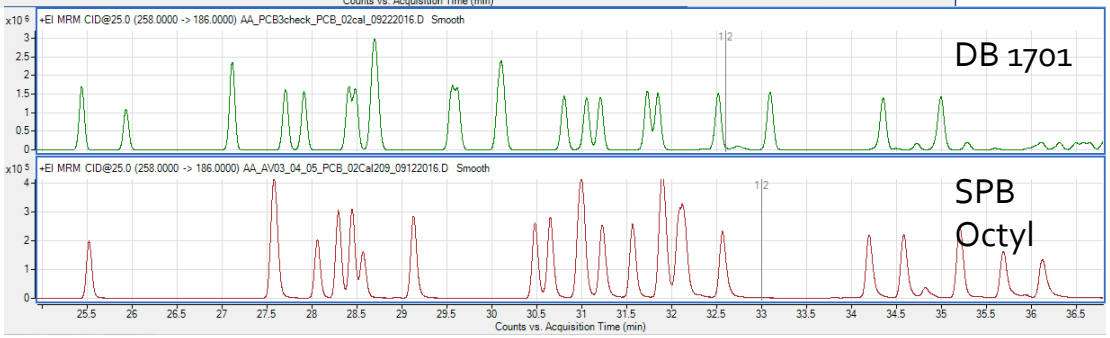
Mono



Di



Tri



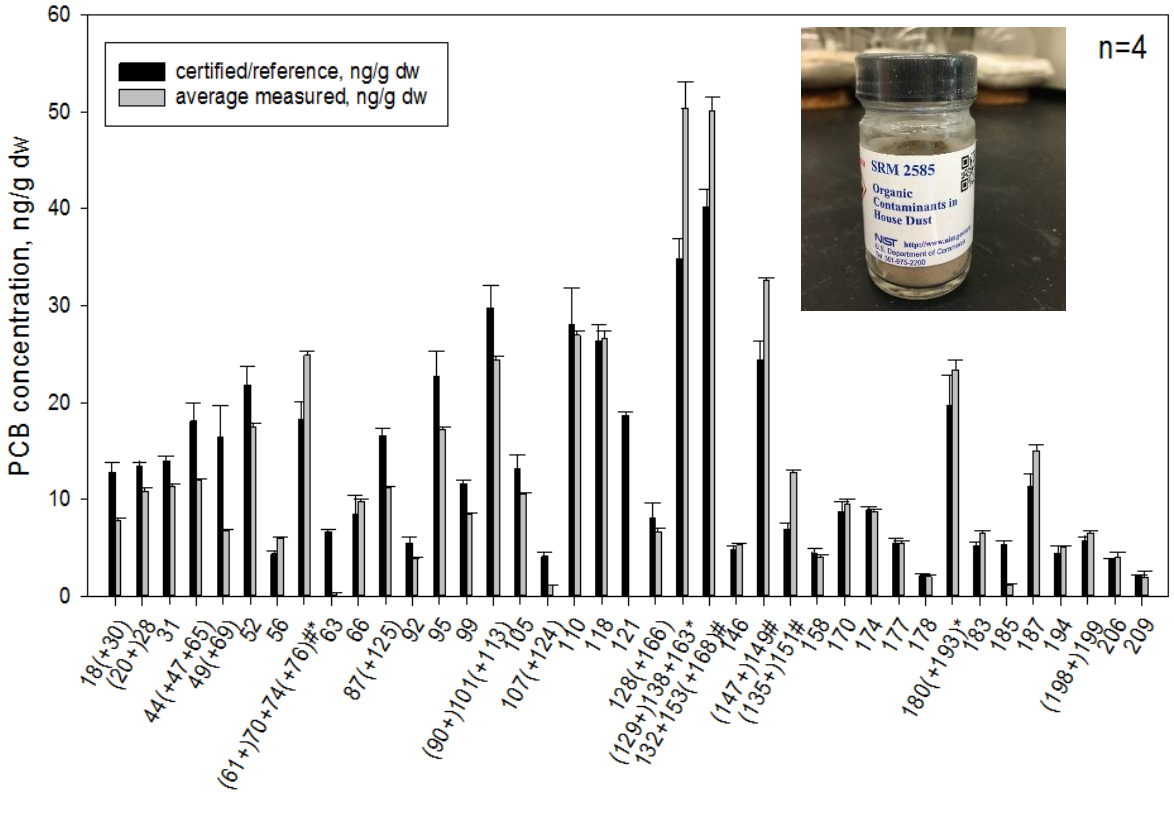
Rigorous quality control

Representativeness
- Field blanks
- Laboratory method blanks
- Instrument blanks

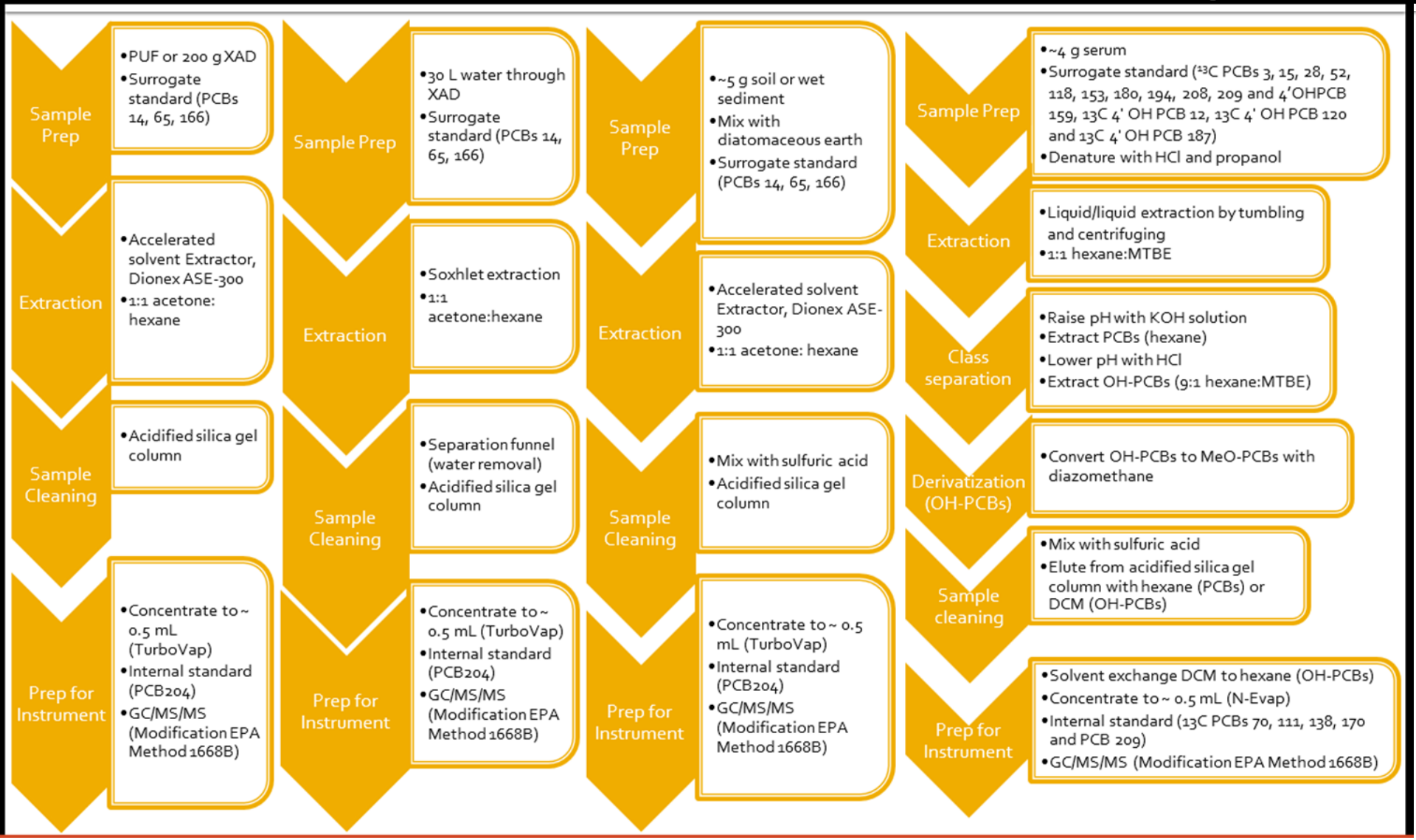
Precision
- Surrogate standard recoveries

Reproducibility & Accuracy
- NIST SRM:
- 2585 (PCBs in dust)

NIST SRM 2585: Organic contaminants in dust

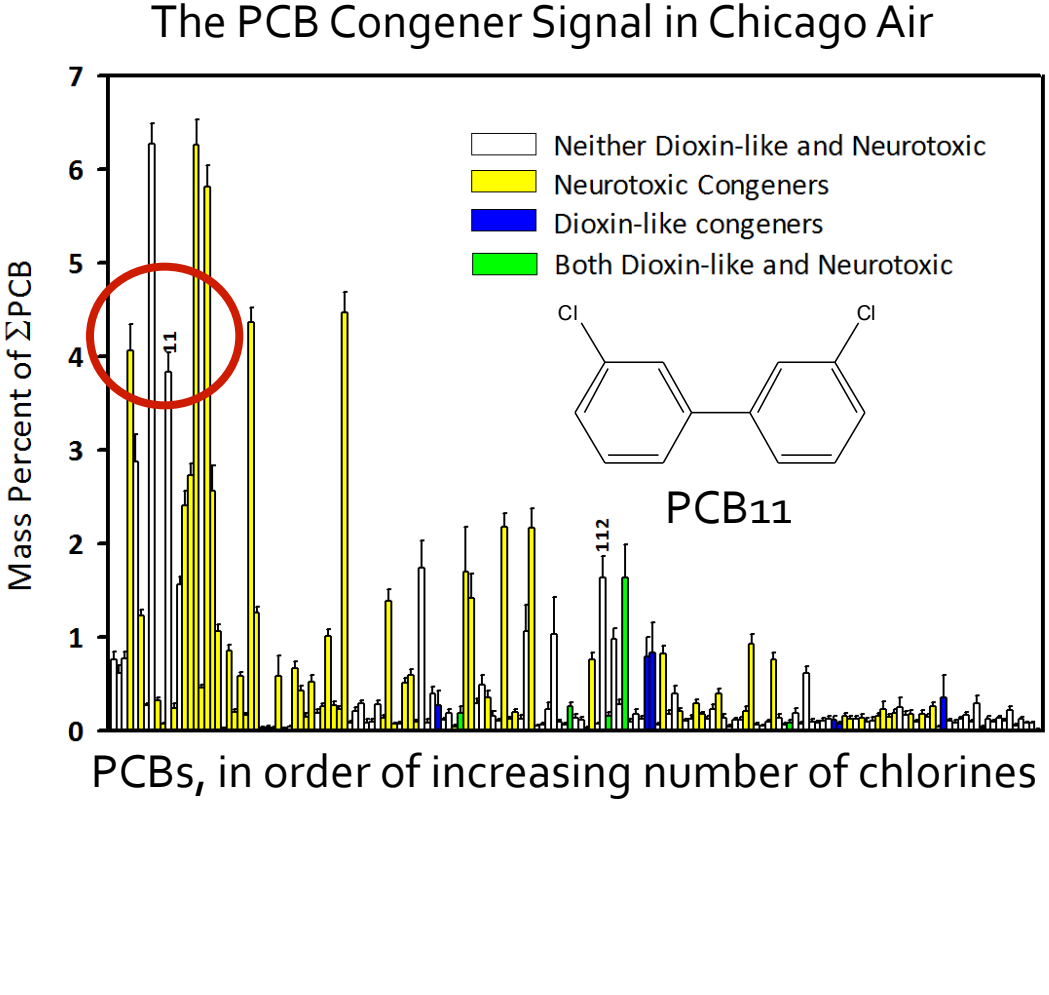


Routine methods for air, water, sediment, soil and serum



Applications

Discovery of PCB11 in Chicago Air



Research

Discovery of Non-Aroclor PCB (3,3′-Dichlorobiphenyl) in Chicago Air

DINGFEI HU, ANDRES MARTINEZ, AND KERI C. HORNBUCKLE*

Department of Civil and Environmental Engineering, IIHR-Hydroscience and Engineering, University of Iowa, Iowa City, Iowa 52242

Received July 1, 2008. Revised manuscript received August 5, 2008. Accepted August 11, 2008.

Air samples were collected in Chicago, Illinois in 2007, and 3,3′-dichlorobiphenyl (PCB11, CAS 2050-67-1) was detected and quantified using GC/MS/MS in 91% of 184 samples. To the best of our knowledge, this is the first published report of PCB11 in ambient air. This compound is ubiquitous in air throughout the city of Chicago. The annual mean concentration in air samples collected from November 2006 to November 2007 is

important impacts on regulatory decisions in th
although its source, toxicity, and potential for
exposure need further investigation.

Materials and Methods

Air Sampling. Air was sampled using high-vol
samplers (Hi-Vols) equipped with quartz fiber fil
XAD-2 resins. Hi-Vols were mounted on platforms
to the rear of two medical clinic vans (Figure 2). Th
platforms were designed to raise the sampler to th
the van for operation and lower the sampler for f
XAD replacement.

The sampling locations (Table S1) were prim
ementary schools where the mobile clinics provid
to the students and their families for diagnosis and t
of asthma and related respiratory illness. When
visited the schools for clinical service, the Hi-Vols
air samples for the 6–8 h period that the van rem
the school. The samplers were operated with the as
of the trained staff at Mobile C.A.R.E. Foundation of
(Comprehensive Care for Chicagoland's Childr
Asthma). Both vans went out for clinical service us
the same day so two samples were collected at two
sites on most sampling days. The air was pulled with a
pump through a quartz fiber filter to retain parti
then through an XAD-2 resin cartridge to collect PC

Atmospheric Environment 44 (2010) 1550–1557

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric PCB congeners across Chicago

Dingfei Hu [a], Hans-Joachim Lehmler [b], Andres Martinez [a], Kai Wang [c], Keri C. Hornbuckle

[a] Department of Civil and Environmental Engineering and IIHR-Hydroscience and Engineering, University of Iowa, Iowa City, IA 52242, USA
[b] Department of Occupational and Environmental Health, University of Iowa, Iowa City, IA 52242, USA
[c] Department of Biostatistics, University of Iowa, Iowa City, IA 52242, USA

ARTICLE INFO

Article history:
Received 11 May 2009
Received in revised form
30 September 2009
Accepted 11 January 2010

Keywords:
Spatial distribution of PCBs
Co-planar PCBs
NEQ
TEQ
Urban air toxics

ABSTRACT

We have measured PCBs in 184 air samples collected at 37 sites in the city of Chica
system of high-volume air samplers mounted on two health clinic vans. Here we desc
conducted from November 2006 to November 2007. The samples were analyzed fo
using a gas chromatograph with tandem mass spectrometry (GC–MS/MS). The ΣP
in Chicago ranged from 75 pg m^{-3} to 5500 pg m^{-3} and primarily varied as a functi
congener patterns are surprisingly similar throughout the city even though the
concentrations vary by more than an order of magnitude. The average profile resemb
1242 and Aroclor 1254, and includes many congeners that have been identified as
receptor (AhR) agonists (dioxin-like) and/or neurotoxins. The toxic equivalence
equivalence (NEQ) in air were calculated and investigated for their spatial distributio
industrial complex of Chicago. The NEQ concentrations are linearly correlated
TEQ concentrations are not predictable. The findings of this study suggest that airbo
widely present and elevated in residential communities; there are multiple sources
locations of very high emissions; the emission includes congeners associated with d
effects and congeners associated with unidentified sources.

Pigment manufacturing is an important source of PCB congeners in the environment

Environ. Sci. Technol. 2010, 44, 2822–2827

Inadvertent Polychlorinated Biphenyls in Commercial Paint Pigments†

DINGFEI HU AND KERI C. HORNBUCKLE*
Department of Civil & Environmental Engineering and IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa 52242

Received August 7, 2009. Revised manuscript received September 17, 2009. Accepted November 16, 2009.

A polychlorinated biphenyl (PCB) that was not produced as part of the Aroclor mixtures banned in the 1980s was recently reported in air samples collected in Chicago, Philadelphia, the Arctic, and several sites around the Great Lakes. In Chicago, the congener 3,3′-dichlorobiphenyl or PCB11 was found to be the fifth most concentrated congener and ubiquitous throughout the city. The congener exhibited strong seasonal concentration trends that suggest volatilization of this cc common outdoor surfaces. Due to these f compound's presence in waters that rece paint manufacturing facilities, we hypothes

Some PCB congeners, us are not present or are very unfavored or improbable f manufacturing process (*2*). P PCB congeners. In air samp 2007, we found PCB11 wide city (*4*). The compound was a in air of polar regions (*5*). Si reported in air of Philadelph Great Lakes (*7*). It appears th In addition, PCB11 was meas from paint production. Poss dechlorination is not likely t are in very low concentra widespread distribution of P elsewhere suggests volatiliz surfaces. Litten et al. report waters and effluent waste st facturing plant around New Rodenburg et al. detected it newspapers, magazines, and contain color pigments (*11*). PCB11 and other PCB conge in current commercial pigm Paint is composed of pi

Journal of Great Lakes Research 37 (2011) 359–364

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes

Dingfei Hu, Andres Martinez, Keri C. Hornbuckle *
Department of Civil & Environmental Engineering and IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, IA 52242, USA

ARTICLE INFO

Article history:
Received 11 October 2010
Accepted 31 January 2011
Available online 24 March 2011

Communicated by Erik Christensen

Index words:
PCB 11
Pigments
Paints
PCB 206
PCB 207
PCB 208
PCB 209
Sediment

ABSTRACT

Three sediment cores from Lake Ontario, Lake Erie and Indiana Harbor Ship Canal were collected, segmented and analyzed for Aroclor and non-Aroclor polychlorinated biphenyl congeners (PCBs). PCBs associated with the commercially produced Aroclor mixtures 1248 and 1254 dominate the sediment signal and the sum of all congeners (∑PCB) peaks in concentration and accumulation around 1970 in the Great Lakes. This trend is very similar to Aroclor production history. In the Indiana Harbor Ship Canal, PCBs appear around 1935 and remain at very high levels between 1940 and 1980, probably reflecting the history of use at the nearby steel mill. In contrast, the non-Aroclor PCBs in the Lake Ontario and IHSC sediment cores, including PCB11 and heavily chlorinated congeners PCB206, 207, 208 and 209 reach a peak in the 1950s, decline and peak again in the 1970s or in the early 1980s. All five congeners have been previously measured in commercial paint pigment. PCB11 was found to peak about 5 years later than ∑PCBs, and is probably associated with the production or use history of diarylide yellow pigments. The temporal distribution profiles of these non-Aroclor PCBs are well correlated with the production history of paint pigments and dyes. Although it is well known that the production of Aroclor PCBs is preserved in Great Lakes sediments, this study is the first to show that production of non-Aroclors are also preserved in the sediments as a record of long term trends in environmental exposure.

Introduction

Polychlorinated biphenyls (PCBs) have been used in an extensive variety of applications including transformer oils, hydraulic fluids, plasticizers, flame retardants, and paints due to their chemical stability, resistance to heat, low flammability, and high dielectric

determine even though congener-specific analysis has become common practice.

There are very little available data concerning emissions of inadvertent PCBs, and air emissions of inadvertent PCBs as trace by-products are poorly reported or unreported. However, in 2008 the presence 3,3′-dichlorobiphenyl (PCB11) was detected in air (Choi

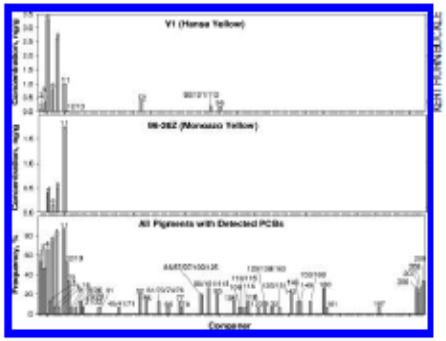
Environmental News

Researchers find little-known PCB "pretty much everywhere"

After a half-century of use in products ranging from electrical transformers to caulk to paint, PCBs were banned in the late 1970s as one of the "dirty dozen" persistent organic pollutants. But a little-known PCB is turning up in water and air in cities and watersheds in Illinois, Nova Scotia, and New Jersey. Researchers suspect the chemical is even more widespread, but do not know how—or whether—it affects human health or ecosystems.

In this issue of *ES&T*, Dingfei Hu and Keri Hornbuckle of the University of Iowa's department of civil and environmental engineering report that they found PCB 11 (3,3′-dichlorobiphenyl) "in air all over Chicago," says Hornbuckle (*Environ. Sci. Technol.* DOI

In 1998, Simon Litten, a research scientist with the New York State Department of Environmental Conservation, used a method that could detect all 209 congeners. With this technique, he found high levels of PCB 11 in wastewater in New York Harbor

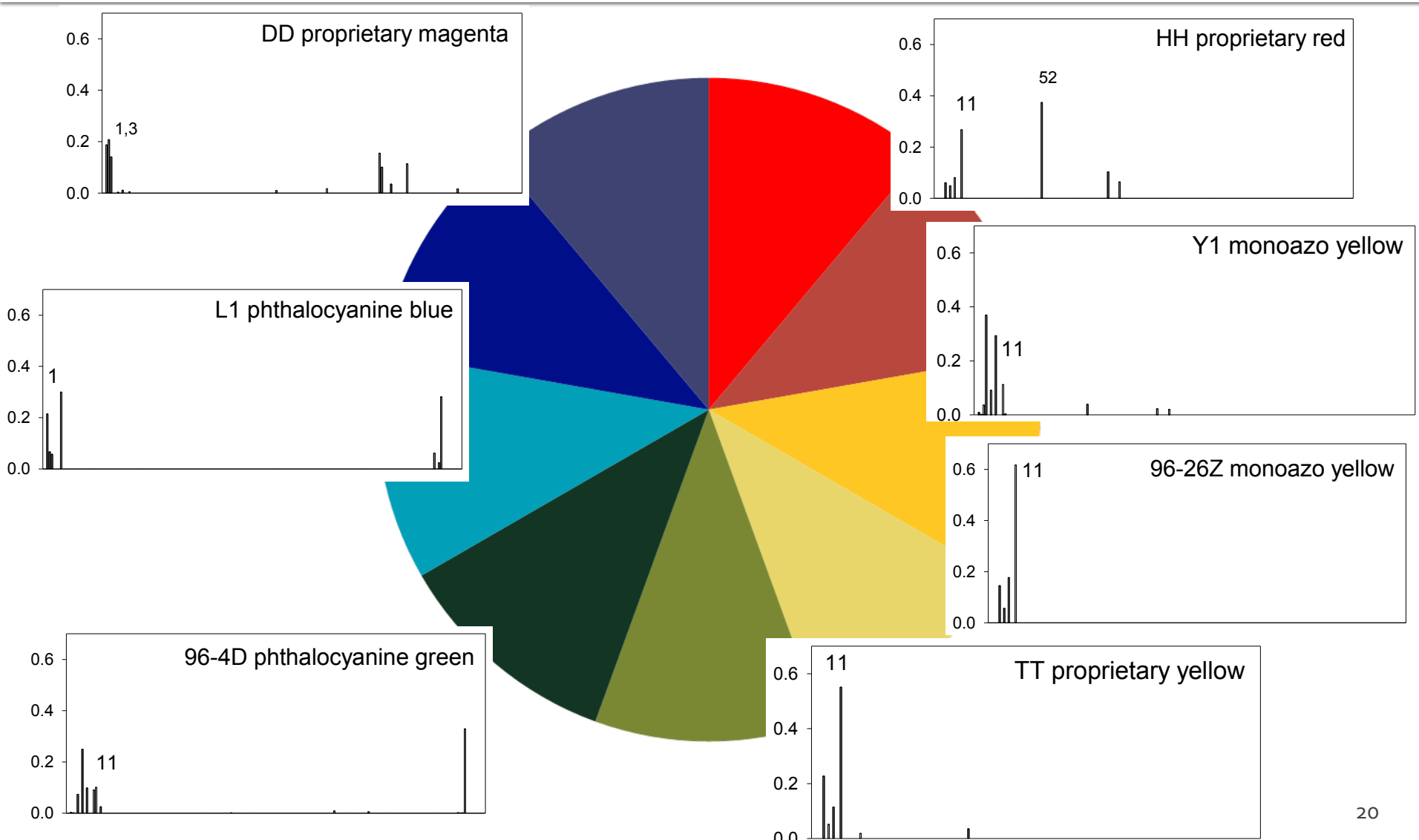


Examples of PCB profiles in paint pigments tested by Hornbuckle and Hu (top two plots), and frequency of congener detection in the 15 pigments with detected PCBs (bottom plot).

Sci. Technol. DOI es901155h). Befo their study, whic this issue, Roden leagues knew PC to the manufactu yellow coloring c pigment. Howeve prised to fin New Jersey' watershed w manufactur In their sea they discove consumer p from printe yellow cerea plastic bags ucts they te contain PCB white paper envelope.

"Once we for it, we sta pretty much Rodenburg

PCBs in Pigments



Indiana Harbor is source of PCBs to the surrounding community

Environ. Sci. Technol. **2010**, *44*, 2803–2808

Fate of PCB Congeners in an Industrial Harbor of Lake Michigan†

ANDRES MARTINEZ,‡ KAI WANG,§ AND KERI C. HORNBUCKLE*,‡

Department of Civil & Environmental Engineering, IIHR-Hydroscience and Engineering, The University of Iowa, 4105 Seamans Center, Iowa City, IA 52242, and Department of Biostatistics, The University of Iowa, Iowa City, IA 52242

Received September 24, 2009. Revised manuscript received January 4, 2010. Accepted January 22, 2010.

We have quantified the release of polychlorinated biphenyls (PCBs) from Indiana Harbor and Ship Canal (IHSC) to Lake Michigan and the atmosphere. Navigational dredging is planned for this system, and there is concern that dredging will result in releases of PCBs. We have analyzed greater than 158 PCBs in surficial sediment, water, suspended particles, and air. We predicted the release of PCBs from sediments to water and from water to air. To quantify the level of confidence in our calculations, we used a Monte Carlo simulation for each congener flux. We determined that 4 ± 0.05 kg of ∑PCBs were released from the sediment to the water and 7 ± 0.1 kg of ∑PCBs were volatilized from the water to the air annually. We measured input from the upstream regions of the canal system of 45.0 kg yr^{-1} and export to Lake Michigan of 43.9 kg yr^{-1}. The ∑PCBs mass balance accounts for nearly all the PCB inputs and losses to the navigational regions. The congener profiles in sediment, water, and air support our determination that the contaminated sediment is a major source of PCBs into the water and air above it. We have shown that the system is currently a significant source of PCBs to the air and to Lake Michigan, even under quiescent conditions.

hulled barge traffic to serve local industries, which include a major steel mill (Mittal Steel, Indiana Harbor) and a major gas refinery (BP America, Inc. in Whiting, Indiana). It has not been determined when dredging will commenc[illegible] a confined disposal facility (CDF) has been constr[illegible] to the site in East Chicago, Indiana. Despite thes[illegible] dredging, the impact of removing the contami[illegible] ments is unclear (*12*). In fact, even in the absence [illegible] the current fate of PCBs in the sediments is un[illegible]

We have previously shown that PCBs in t[illegible] sediment of IHSC resemble the commercial mixt[illegible] 1248 and are comparable in magnitude to thos[illegible] as Superfund sites by the Comprehensive Env[illegible] Response, Compensation, and Liability Act. The [illegible] tions range from 53 to 35000 ng PCB g^{-1} dry w[illegible] of sediment (*13*).

The goal of the study was to investigate t[illegible] quantify the release of PCBs from the sediments t[illegible] as well as from the waters to the air above [illegible] quantitatively evaluate the uncertainty over a w[illegible] an annual basis. We hypothesized that PCBs are c[illegible] released from the sediments to the water. Furth[illegible] hypothesized that once they are released from the [illegible] PCBs are exported from the canal into Lake Mi[illegible] also emitted to the air over the canal. To test our h[illegible] we measured PCB congeners in the air, water, a[illegible] sediment in the canal and modeled the potential [illegible] predicted the release and emission of PCB con[illegible] function of their physical–chemical properties [illegible] meteorology, and the levels of PCBs in each o[illegible] ronmental compartments. We used a Monte Carlo [illegible] approach to assess our confidence in the mode[illegible]

Methods

We conducted an intensive sampling expeditio[illegible] samples of surficial sediment, water (dissolved [illegible] suspended particles), and air (gas phase) in the [illegible] study was designed for an internally consistent ar[illegible] sample set of 158 PCB congeners quantified in

Atmospheric Environment 122 (2015) 791–798

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric dispersion of PCB from a contaminated Lake Michigan harbor

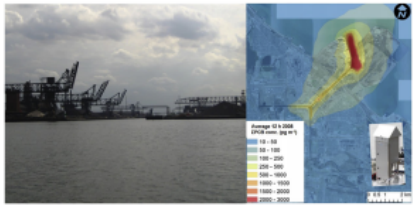
Andres Martinez [a, *], Scott N. Spak [a, b], Nicholas T. Petrich [a], Dingfei Hu [a], Gregory R. Carmichael [c], Keri C. Hornbuckle [a]

[a] *Department of Civil & Environmental Engineering, IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, IA, USA*
[b] *School of Urban and Regional Planning, Public Policy Center, The University of Iowa, IA, USA*
[c] *Department of Chemical and Biochemical Engineering, The University of Iowa, Iowa City, IA, USA*

HIGHLIGHTS

- AERMOD was used to model atmospheric dispersion of PCB emissions from IHSC.
- Emissions from IHSC contributed ca. 15% of the observed concentrations above water, and ca. 10% at a nearby school.
- Exposure estimates from annual to 24 h averages independent of data sources for observed and modeled coastal meteorology.
- Observed enriched PCB3 samples suggest a nearby non-Aroclor source.

GRAPHICAL ABSTRACT



PCB flow rates through passive samplers are a function of local meteorology

Environmental Science & Technology

Article

pubs.acs.org/est

A Model Using Local Weather Data to Determine the Effective Sampling Volume for PCB Congeners Collected on Passive Air Samplers

Nicholas J. Herkert, Andres Martinez,

Department of Civil and Environmental Engine
Iowa 52242 United States

Supporting Information

ABSTRACT: We have developed and evalua
effective sampling volumes (V_{eff}) of PCB
polyurethane foam passive air samplers (PUF-
speed, air temperature, and equilibrium partit
the samplers. The model, provided as an an
function of physical-chemical properties of
closest Integrated Surface Database (ISD) d
Centers for Environmental Information (NC
friendly, only requiring basic Matlab knowledg
we evaluated three independent data sets of a
passive and active samplers: at sites in Chicag
model provides V_{eff} values comparable to thos
average congener specific concentration metho
collected in Chicago and show that previous
long deployments, deployments conducted u

Environmental Science & Technology

Article

pubs.acs.org/est

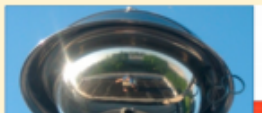
Simulating and Explaining Passive Air Sampling Rates for Semivolatile Compounds on Polyurethane Foam Passive Samplers

Nicholas T. Petrich,[†,‡] Scott N. Spak,*[,†,‡,§] Gregory R. Carmichael,[†,‡,∥] Dingfei Hu,[†,⊥] Andres Martinez,[†,⊥] and Keri C. Hornbuckle*[,†,‡,⊥]

[†]Department of Civil & Environmental Engineering, [‡]Center for Global and Regional Environmental Research, [§]Public Policy Center and School of Urban & Regional Planning, [∥]Department of Chemical & Biochemical Engineering, and [⊥]IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa 52242, United States

Supporting Information

ABSTRACT: Passive air samplers (PAS) including polyurethane foam (PUF) are widely deployed as an inexpensive and practical way to sample semivolatile pollutants. However, concentration estimates from PAS rely on constant empirical mass transfer rates, which add unquantified uncertainties



OH-PCBs are present in Aroclors, sediments and ambient air

ENVIRONMENTAL Science & Technology

Article

pubs.acs.org/est

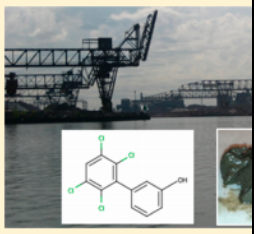
Discovery of Hydroxylated Polychlorinated Biphenyls (OH-PCBs) in Sediment from a Lake Michigan Waterway and Original Commercial Aroclors

Rachel F. Marek, Andres Martinez, and Keri C. Hornbuckle*

Department of Civil and Environmental Engineering and IIHR-Hydroscience and Engineering, The Unive
Iowa, 52242, United States

Supporting Information

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 coeluting 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
suggest PCB degradation is unlikely as a source of OH-PCBs in IHSC sediment. We are the first to report
sediment and Aroclors, and our discovery is significant because it is likely that OH-PCB contaminati
anywhere that PCB contamination from Aroclors is present.



ENVIRONMENTAL Science & Technology LETTERS

Letter

pubs.acs.org/journal/estlcu

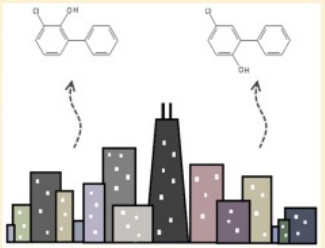
Occurrence and Distribution of Two Hydroxylated Polychlorinated Biphenyl Congeners in Chicago Air

Andrew M. Awad, Andres Martinez,* Rachel F. Marek, and Keri C. Hornbuckle*

Department of Civil and Environmental Engineering, and IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa 52242, United States

Supporting Information

ABSTRACT: We measured hydroxylated polychlorinated biphenyls (OH-PCBs) in both gas and particulate phases in 30 Chicago air samples, the first report of OH-PCBs in environmental air samples. Concentrations of 2OH-PCB2 and 6OH-PCB2 in both phases were similar to those of PCB2 measured in the same samples, from nondetect to 11 pg m^{-3} and 12 ng g^{-1} for the gas and particulate phases, respectively. We found that OH-PCB2 congeners sorbed more to particulates than did PCB2, seasonal variability was larger than spatial variability across Chicago, and partial pressure and temperature strongly correlated with the two OH-PCBs ($p < 0.0001$). Similar 6OH-PCB2:2OH-PCB2 ratios were found in our air samples and Aroclors, suggesting that Aroclors are a legacy source of OH-PCB2 congeners to the atmosphere and appear to be volatilizing proportionally to PCBs in Aroclors. Although degradation by the hydroxyl radical has been proposed as an efficient loss process for airborne PCBs, we found no evidence that this mechanism results in the formation of OH-PCB2 congeners.



INTRODUCTION

Hydroxylated polychlorinated biphenyls (OH-PCBs) are generally regarded as oxidation products of PCB metabolism in humans and other organisms;[1−5] however, they are beginning to be understood as environmental contaminants[6,7]

predicted to be quite short in comparison to those of their parent PCB compounds,[1,5,25] making them difficult to detect in the air as reaction intermediates. Still, there is no definitive information regarding the presence of OH-PCBs (or lack thereof) in environmental air samples.

The primary aim of this work was to detect and measure

Lower chlorinated PCBs are prevalent in children

Environmental Science & Technology

Article

pubs.acs.org/est

Variability in PCB and OH-PCB Serum Levels in Children and Their Mothers in Urban and Rural U.S. Communities

Rachel F. Marek,[†,‡] Peter S. Thorne,[*,†,§] Jeanne DeWall,[§] and Keri C. Hornbuckle[*,†,‡,§]

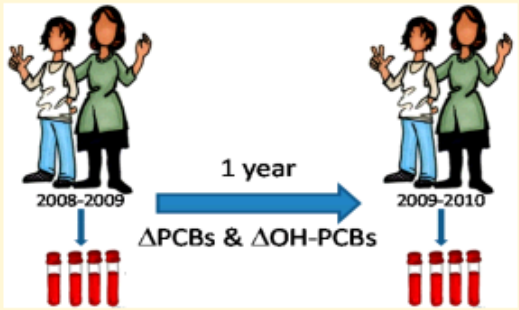
[†]Department of Civil & Environmental Engineering, The University of Iowa, Iowa City, Iowa 52242, United States

[‡]IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa 52242, United States

[§]Department of Occupational and Environmental Health, The University of Iowa, Iowa City, Iowa 52242, United States

Supporting Information

ABSTRACT: Environmental exposures that affect accumulation of polychlorinated biphenyls (PCBs) in humans are complex and not fully understood. One challenge in linking environmental exposure to accumulation is determining variability of PCB concentrations in samples collected from the same person at different times. We hypothesized that PCBs in human blood serum are consistent from year to year in people who live in the same environment between sampling. We analyzed blood serum from children and their mothers from urban and rural U.S. communities (n = 200) for all 209 PCBs (median $\sum$PCBs = 45 ng/g lw) and 12 hydroxylated PCBs (median $\sum$OH-PCBs = 0.09 ng/g fw). A subset of these participants (n = 155) also had blood PCB and OH-PCB concentrations analyzed during the previous calendar year. Although many participants had similar levels



Environmental Science & Technology

Arti

pubs.acs.or

PCBs and OH-PCBs in Serum from Children and Mothers in Urban and Rural U.S. Communities

Rachel F. Marek,[†,‡] Peter S. Thorne,[†,§,*] Kai Wang,[∥] Jeanne DeWall,[§] and Keri C. Hornbuckle[†,‡,§,*]

[†]Department of Civil & Environmental Engineering, The University of Iowa, Iowa City, Iowa, United States, 52242

[‡]IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa, United States, 52242

iversity of Iowa, Iowa City, Iowa, United States, 52242

lowa, United States, 52242

d in more East Chicago mothers and children than Columb
were enriched in lower-molecular weight PCBs. East Chica
ndividual PCBs and OH-PCBs in their blood. Concentrations
is the first temporally and methodologically consistent study

Non Aroclors and OH-PCBs are prevalent in mothers and children

Environmental Science & Technology

Article

pubs.acs.org/est

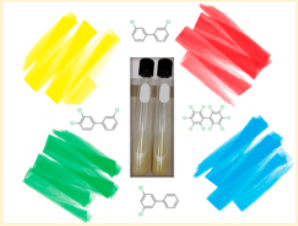
Human Serum from Urban and Rural Adolescents and Their Mothers Shows Exposure to Polychlorinated Biphenyls Not Found in Commercial Mixtures

Wen Xin Koh,[†] Keri C. Hornbuckle,*[,†,‡] and Peter S. Thorne*[,†,§]

[†]Interdisciplinary Graduate Program in Human Toxicology, [‡]Department of Civil and Environmental Engineering, and [§]Department of Occupational and Environmental Health, The University of Iowa, Iowa City, Iowa 52242, United States

Supporting Information

ABSTRACT: Although polychlorinated biphenyls are no longer sold as commercial mixtures, they are still being produced through modern manufacturing processes. We have previously shown that non-Aroclor PCB 11 is prevalent in indoor and outdoor air and sediment and detected in human serum. Here we report the prevalence of non-Aroclor PCB congeners (≤0.20 wt % in Aroclor) in human serum collected from urban and rural adolescents and their mothers. We hypothesized that additional non-Aroclor congeners are present in serum. Sera were extracted and detected for 209 PCBs using gas chromatography-tandem mass spectrometry. A list of 70 non-Aroclor PCB congeners was determined by measurement of original Aroclors. PCB 11, 14, 35, and 209 are the major dominating and most frequently detected congeners. PCB 14 and 35 have not been previously reported for environmental matrices. Adolescents have significantly lower total non-Aroclor PCB concentrations than mothers in East Chicago ($p < 0.001$) and Columbus Junction ($p = 0.008$). There are significant differences in non-Aroclor PCBs between East Chicago community and Columbus Junction community ($p < 0.001$). Non-Aroclor PCBs represent an average of 10% (and up to 50%) of total PCBs measured in serum. An average of 50% (and up to 100%) of these concentrations may be attributed to aryl azo and phthalocyanine paint pigments.



Chemosphere 147 (2016) 389–395

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Hydroxylated polychlorinated biphenyls in human sera from adolescents and their mothers living in two U.S. Midwestern communities

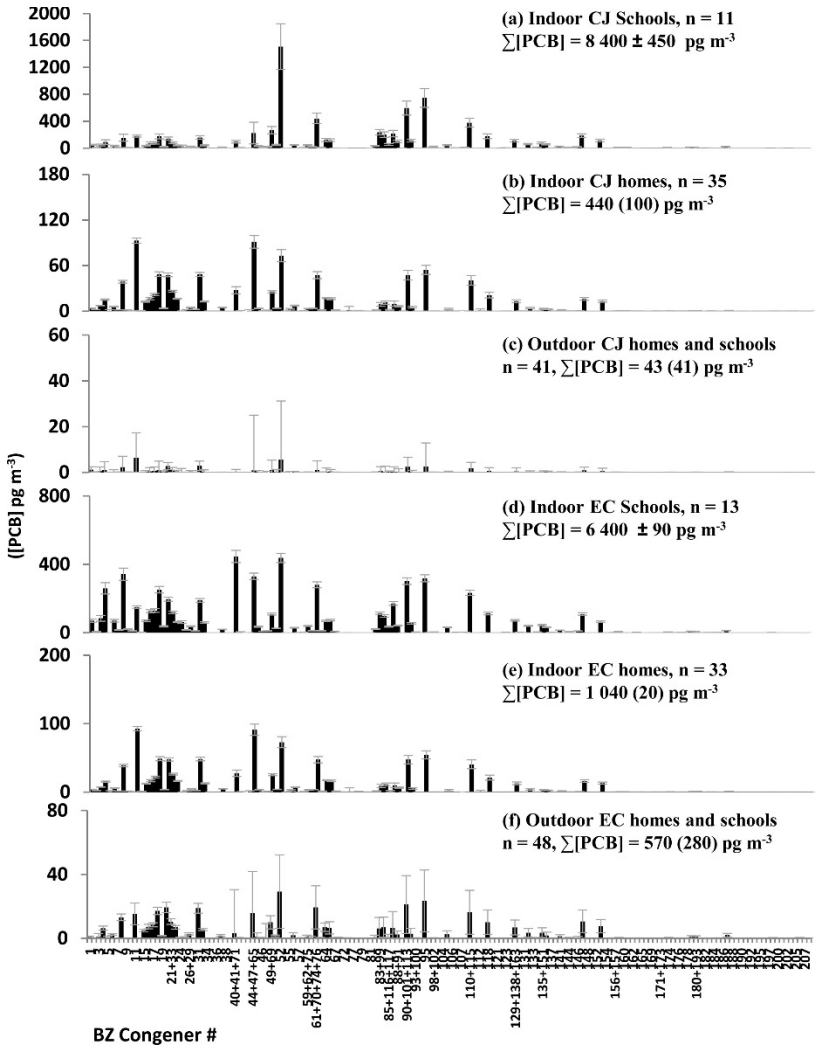
Wen Xin Koh [a], Keri C. Hornbuckle [a, b, *], Rachel F. Marek [b], Kai Wang [c], Peter S. Thorne [a, d, *]

[a] Interdisciplinary Graduate Program in Human Toxicology, The University of Iowa, Iowa City, IA 52242, United States
[b] Department of Civil and Environmental Engineering, The University of Iowa, Iowa City, IA 52242, United States
[c] Department of Biostatistics, The University of Iowa, Iowa City, IA 52242, United States
[d] Department of Occupational and Environmental Health, The University of Iowa, Iowa City, IA 52242, United States

HIGHLIGHTS

- Fifty-eight OH-PCBs were assessed in serum of 85 adolescents and 74 their mothers.
- Lower-chlorinated OH-PCBs were rarely detected in serum.
- Mothers had significantly higher total OH-PCB concentrations than their children.
- 4-OH-PCB 107 and 4-OH-PCB 187 changed significantly within subject across 3 years.
- OH-PCBs did not differ between subjects from the urban vs. the rural community.

School air is elevated in PCBs, causing elevated exposure for children



Environmental Science & Technology

Article

pubs.acs.org/est

Inhalation and Dietary Exposure to PCBs in Urban and Rural Cohorts via Congener-Specific Measurements

Matt D. Ampleman,[†,‡] Andrés Martinez,[‡,∥] Jeanne DeWall,[†] Dorothea F. K. Rawn,[§] Keri C. Hornbuckle,[*,‡,∥] and Peter S. Thorne[*,†]

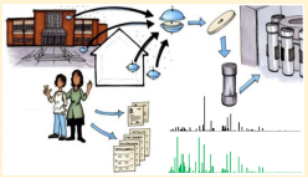
[†]Department of Occupational and Environmental Health, The University of Iowa, Iowa City, Iowa, United States, 52242

[‡]Department of Civil & Environmental Engineering, The University of Iowa, Iowa City, Iowa, United States 52242, United States

[§]Food Research Division, Health Canada, Ottawa, Ontario Canada K1A 0K9

[∥]IIHR-Hydroscience and Engineering, The University of Iowa, Iowa City, Iowa, United States, 52242

S *Supporting Information*



ABSTRACT: Polychlorinated biphenyls (PCBs) are a group of 209 persistent organic pollutants, whose documented carcinogenic, neurological, and respiratory toxicities are expansive and growing. However, PCB inhalation exposure assessments have been lacking for North American ambient conditions and lower-chlorinated congeners. We assessed congener-specific inhalation and dietary exposure for 78 adolescent children and their mothers (n = 68) in the Airborne Exposure to Semi-volatile Organic Pollutants (AESOP) Study. Congener-specific PCB inhalation exposure was modeled using 293 measurements of indoor and outdoor airborne PCB concentrations at homes and schools, analyzed via tandem quadrupole GS-MS/MS, combined with questionnaire data from the AESOP Study. Dietary exposure was modeled using Canadian Total Diet Survey PCB concentrations and National Health and Nutrition Examination Survey (NHANES) food ingestion rates. For ∑PCB, dietary exposure dominates. For individual lower-chlorinated congeners (e.g., PCBs 40+41+71, 52), inhalation exposure was as high as one-third of the total (dietary+inhalation) exposure. ∑PCB inhalation (geometric mean (SE)) was greater for urban mothers (7.1 (1.2) μg yr^{-1}) and children (12.0 (1.2) μg yr^{-1}) than for rural mothers (2.4 (0.4) μg yr^{-1}) and children (8.9 (0.3) μg yr^{-1}). Schools attended by AESOP Study children had higher indoor PCB concentrations than did homes, and account for the majority of children's inhalation exposure.

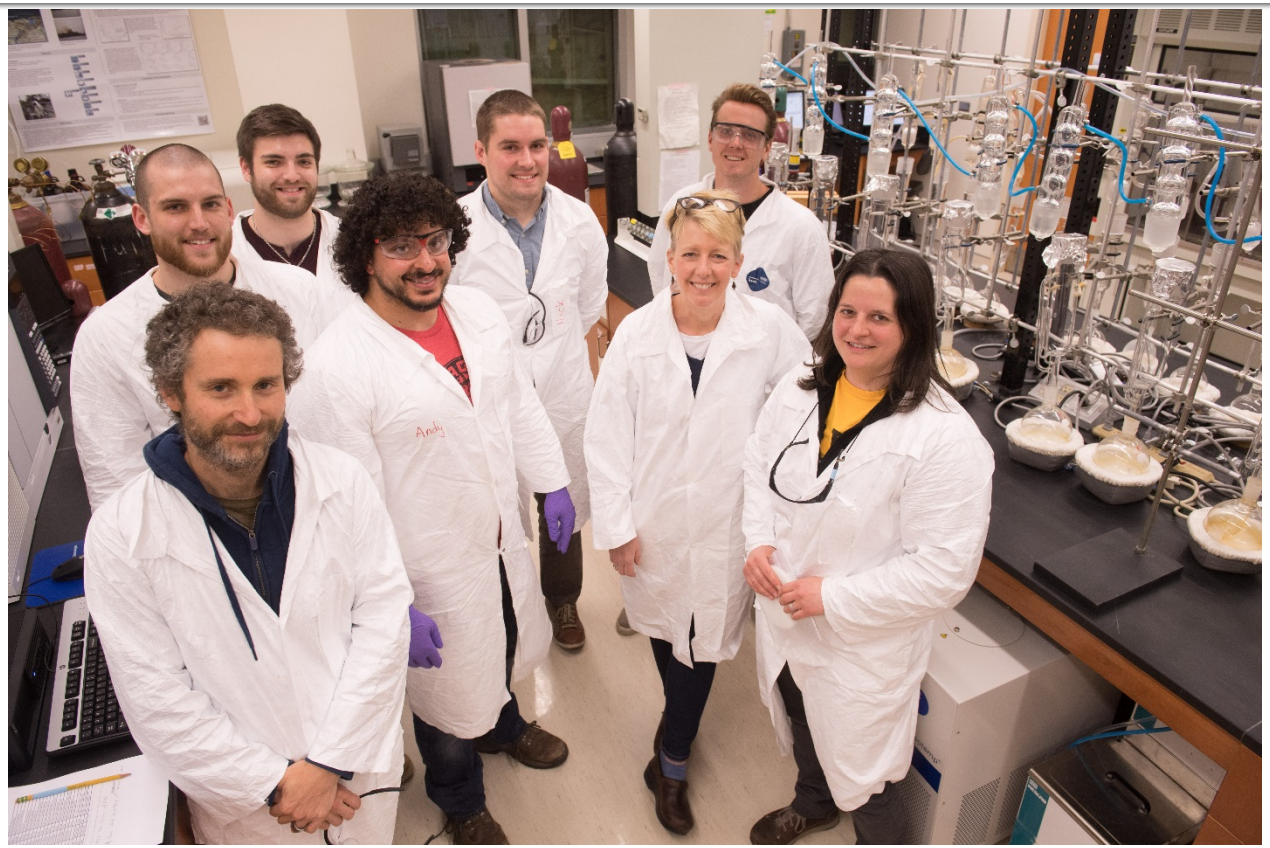
Summary

- Methods with greatest impact on quality also are most efficient and cost-effective
- GC/MS/MS provides excellent sensitivity, selectivity, reproducibility
- Pressured solvent extraction is useful for preparing sampling media as well as sample extraction
- Uniform methods allow useful comparison of congener signals across media, space, and time
- https://research.engineering.uiowa.edu/hornbuckle/

Acknowledgements

Funding sources
NIH P42 ES013661

Research Team
Rachel Marek, Ph.D.
Andres Martinez, Ph.D.
Andrew Awad, MS
Nick Herkert (Ph.D. student)
Jacob Jahnke (Ph.D. student)
Aaron Boesen, BSE
Dana Boesen



isrp iowa superfund research program

NIH National Institute of Environmental Health Sciences
Superfund Research Program