



**Please cite the Published Version**

Megson, David , Benoit, Nadine, Sandau, Courtney, Chaudhuri, Sri, Long, Tanya, Coulthard, Emma  and Johnson, Glenn (2019) Evaluation of the effectiveness of different indicator PCBs to estimating total PCB concentrations in environmental investigations. Chemosphere, 237. p. 124429. ISSN 0045-6535

**DOI:** <https://doi.org/10.1016/j.chemosphere.2019.124429>

**Publisher:** Elsevier

**Version:** Accepted Version

**Downloaded from:** <https://e-space.mmu.ac.uk/623578/>

**Usage rights:**



[Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0](#)

**Additional Information:** This is an Author Accepted Manuscript of a paper accepted for publication in Chemosphere published by and copyright Elsevier.

**Enquiries:**

If you have questions about this document, contact [openresearch@mmu.ac.uk](mailto:openresearch@mmu.ac.uk). Please include the URL of the record in e-space. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from <https://www.mmu.ac.uk/library/using-the-library/policies-and-guidelines>)

# Evaluation of the effectiveness of different indicator PCBs to estimating total PCB concentrations in environmental investigations

David Megson<sup>1,2</sup>, Nadine Benoit<sup>3</sup>, Courtney Sandau<sup>2,4</sup>, Sri Chaudhuri<sup>3</sup>, Tanya Long<sup>3</sup>, Emma Coulthard<sup>1</sup>  
Glenn Johnson<sup>5</sup>

<sup>1</sup> Manchester Metropolitan University, Manchester, UK

<sup>2</sup> Chemistry Matters Inc., Alberta, Canada

<sup>3</sup> Ontario Ministry of the Environment Conservation and Parks, Toronto, ON, Canada

<sup>4</sup> Mount Royal University, Department of Earth and Environmental Sciences, Faculty of Science and Technology, 4825 Mount Royal Gate SW, Calgary, AB, Canada

<sup>5</sup> University of Utah, Salt Lake City, UT 84108

## Abstract

Polychlorinated biphenyls (PCBs) are one of the most widely studied group of persistent organic pollutants (POPs). There are 209 different PCBs, however not all 209 can currently be individually quantified in one analytical run. This means that a subset of PCBs congeners are often determined and reported. Some of the most commonly reported subsets are the 7 indicator PCBs (28, 52, 101, 118, 138, 153 and 180) and the WHO 12 PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189). The WHO 12 congeners are co-planar ‘dioxin like’ PCBs that are effective for establishing health risks. The 7 indicator PCBs were selected as some of the most common PCBs across the compositional range of the most common technical mixtures (such as Aroclors), and are used to give an indication of the total PCB concentrations. These groups of indicator PCBs were established several decades ago. However, in the environment commercial mixtures are subject to weathering and fractionation processes, and additional sources of non-Aroclor PCBs are also becoming more important. In this manuscript we use existing large scale comprehensive congener

specific datasets to evaluate the effectiveness of indicator PCBs to predict total concentrations and establish if they are still fit for purpose. The results indicate that while these traditional indicators are a useful tool to estimate total concentrations in humans with background exposure there are many instances where they are not fit for purpose and can lead to significant under predictions in total PCB concentrations in environmental matrices.

## Keywords

Polychlorinated biphenyls, PCBs, Sediments, Water, Aroclors, Humans

## Introduction

There is no universal method for the analysis of polychlorinated biphenyls (PCBs). In fact, there are 10s to 100s of published and certified methods for PCB analysis, many of which have been summarised (Guo and Kannan, 2015, Reiner et al., 2014, Megson, 2019, Clement et al., 2012, Muir and Sverko, 2006). Methods typically involve separation by gas chromatography (GC) and detection by electron capture detectors (ECD) or using mass spectrometry (MS). One of the simplest forms of these methods is based on the approach of determining a “technical mixture equivalent total PCB value”, which employs a commercial product or mixtures of products as a standard to quantitate the matching congeners contained in the product/mixture and sample (e.g. EPA Method 8082). An intermediate method aims to measure concentrations of various PCB homologues based on the number of chlorines in the congeners (e.g. EPA Method 680), while a more detailed approach targets various individual congeners with a goal of measuring as many of them as practically possible (e.g. EPA Method 1668C) (Muir and Sverko, 2006).

In many environmental investigations a detailed approach is required, and therefore specific congeners need to be determined rather than a total PCB concentration (e.g. EU regulation 117 (2017) which requires analysis of the WHO12 congeners). The rationale for undertaking an environmental investigation should influence which PCBs are targeted. There can be many reasons for undertaking an investigation, from

commissioning brief scoping studies, to establishing potential health effects, or understanding patterns for source apportionment. The number of reported congeners in investigations can range from a few indicator (i) PCBs such as the i7 PCBs (28, 52, 101, 118, 138, 153 and 180). These have been selected as they are some of the most abundant congeners across the compositional range of the most common technical mixtures and the environment and so are often used as indicators for the magnitude of PCB contamination (Johnson et al., 2006, Battelle Memorial Institute et al., 2012). To assess human health risks, the World Health Organisation (WHO) proposes the analysis of a specific subset of 12 dioxin-like PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) (Van den Berg et al., 2006). These PCBs were selected due to their co-planar structure which results in them having the same mode of action as 2,3,7,8-TCDD against the aryl hydrocarbon receptor. Some studies aim to track sources of contamination and so they have attempted to determine as many PCBs as possible. This can result in the detection of over 130 different congeners in an environmental sample (Megson et al., 2013, Megson et al., 2018). With so many different recommendations and with analytical techniques for the analysis of one sample ranging from \$50 US to greater than \$2000 US (Reiner et al., 2014), it can be difficult to know how many and which PCBs to target, especially with such a variety of standard accredited methods (e.g. EPA 1668C) and non-accredited methods are available. It is important to note that these non-accredited methods should not always be discounted as they could provide higher quality data, although this comes at a cost (e.g through analysis by multidimensional chromatography or ultra high resolution mass spectrometry).

One of the first aims of many environmental investigations is to quantify the amount of PCBs in a given sample to establish if further work or investigation is required. It can be very time and cost intensive to accurately quantify all 209 PCBs, and equally as intensive to also process this data. Therefore, simpler screening methods such as EPA Methods 8082 and 608 are used to estimate total PCB concentrations. These involve the analysis of several individual PCBs which can then be used to calculate a total PCB concentration or estimate an Aroclor equivalent concentration. In humans, various attempts have been made to estimate total PCB concentrations from only a few congeners (Longnecker et al., 2003, Vandervan et al.,

1992, Wicklund Glynn et al., 2000, Barr et al., 2006, Needham et al., 2005, Wolff et al., 2005, Fitzgerald et al., 2005, Jain and Wang, 2010). Wicklund Glynn et al. (2000) showed that CB 153 alone was an excellent predictor for total PCB concentrations with a coefficient of determination ( $R^2$ ) value of 0.96, however this study was undertaken on a racially homogenous Swedish male sample population. Using the 2001-02 National Health and Nutrition Examination Survey (NHANES) data which represents the exposure of the United States general non-exposed population, Jain and Wang (2010) obtained an  $R^2$  value of 0.78 indicating there is more variability in a wider sample set. The i3 PCB congeners (PCB 138, 153 and 180) have been used to estimate total PCB concentrations (Wicklund Glynn et al., 2000, Barr et al., 2006, Needham et al., 2005, Jain and Wang, 2010). While these three congeners work well at predicting the total PCB concentrations for a localised population, demographic variables such as race/ethnicity can lead to poorer predictions (Jain and Wang, 2010). Similar conclusions were also reached by Gandhi et al. (2015) who investigated the use of a variety of different indicator compounds to calculate total PCB concentrations in fish. They proposed that, alternate i3 PCBs (PCB 95, 118, and 153), i4 PCBs (i3 PCBs plus 138) and i5 PCBs (i4 PCBs plus 110), and existing i6 PCBs (28, 52, 101, 138, 153 and 180) and i7 PCBs are the most optimal indicators, while use of the current i3 PCBs (PCB 138, 153 and 180) should be avoided.

While there is a lot of available literature on estimating PCB totals in animals there are less data available for matrixes such as water and sediment. Fikslin and Santoro (2003) assessed the use of a subset of 18 PCBs (proposed by the National Oceanic and Atmospheric Administration (NOAA)) to estimate total PCB concentrations in estuarine water and sediment. They concluded that total PCBs would be overestimated based on  $2\times$  the sum of the 18 congeners for effluent samples during dry weather periods and influent samples at higher PCB levels ( $>35\text{ ng L}^{-1}$ ). However, total PCB estimates for wet weather effluent concentration showed good agreement. Sediment samples show poor agreement for the  $18\text{ congener} \times 2$  estimate and clearly underestimated the total PCB value, suggesting biases in estimation of totals may be driven by environmental transformation and/or factors related to the matrix analysed.

This paper aims to evaluate the strength of commonly used indicator groups of PCBs such as CB153, i3 PCBs, i7 PCBs in providing an estimate of the total PCB concentration in different matrices. It also provides recommendations and highlights limitations of the different available methods.

## Methodology

An inherent issue with nearly all PCB datasets is that they will have already undergone some degree of “analytical filtering”. Currently, no single method can determine all 209 congeners in one run. Therefore, data analysts have to constantly deal with co-elutions (eg CB-28 and CB-31 for most methods) and data that is limited to what the authors deem as the major congeners of importance (or the ones their method targeted). This means that in many cases the total PCB concentration is not actually known as some PCBs go unrecorded or reported. In this assessment, we acknowledge this limitation and have focused our assessment on available datasets which contain as many PCBs as possible with methods targeted towards quantifying the more prevalent PCBs in that matrix. This includes congener specific PCB data from technical mixtures (Aroclors) previously quantified by Frame et al. (1996), hundreds of sediment and water samples collected from North America, and thousands of U.S. human serum samples from the National Health and Nutrition Examination Survey (NHANES). To provide a balanced assessment, samples from “background sites” and known contaminated sites were assessed separately for sediments, water and humans. These data were collated and examined using the popular PCB indicator estimation methods noted above (CB153, i3 PCBs, i7 PCBs) to predict “total PCB concentrations”. This was assessed by linear regression calculating the coefficient of determination ( $R^2$ ) along with significance testing using Spearman rank correlations (data provided in Supplementary Information, Tables S2-S7). The source of these different datasets and analytical methods used for their creation are provided in this section.

### Aroclors

Aroclor data was obtained directly from Frame (2001), which included the results from Frame et al. (1996), and used as the reference dataset for this exercise. Frame et al. (1996) diluted Aroclor standards and

120 analysed them using three high resolution gas chromatography systems with mass spectrometry. Samples  
121 covering the range of Aroclors 1221 through 1262 were analysed on 3 HRGC systems, which between them  
122 enabled unambiguous measurements of all 209 congeners. (Frame, et al., 1996; Frame, 2001).”

#### 123 Water samples – Project Trackdown

124 Two sets of water samples were collated to represent background sites and contaminated sites. All water  
125 samples were collected by the Ontario Ministry of the Environment and Climate Change (MOECC) as part  
126 of investigative monitoring programs aimed at tracking PCBs in the environment (Benoit et al., 2016). The  
127 background sites were composed of 394 samples obtained from across Ontario and the contaminated site  
128 comprised 18 samples, which were identified next to significant contamination sources. Water samples  
129 were collected in two litre glass containers and PCBs determined by congener-specific analysis using  
130 method E3459 (Ontario Ministry of the Environment, 2008). Briefly, the method identifies 75 of a possible  
131 209 PCB samples in aqueous samples using internal standard/isotope dilution. Samples were fortified with  
132 isotopically labelled PCBs and extracted by filtering through a C18 solid phase extraction disk. Particulate  
133 bound PCBs and PCBs trapped to the disc are extracted using acetone/hexane. Extracts are cleaned using  
134 silica prior to analysis with gas chromatography with high resolution mass spectrometry (GC-HRMS).

#### 135 Sediment samples

136 Two sets of sediment samples were collated to represent background sites and contaminated sites. Sediment  
137 samples that comprised the background data were collected by the MOECC as part of investigative  
138 monitoring programs in the Ontario Great Lakes Basin. Polychlorinated biphenyl concentrations were  
139 determined for 55 PCBs in 374 samples taken across Ontario’s Great Lakes Basin. Sample preparation and  
140 extraction was conducted as described in Muscalu et al. (2011). Briefly, samples were air-dried, crushed  
141 and sieved. A 5 g aliquot of sample was extracted using accelerated solvent extraction (ASE) with 25%  
142 dichloromethane/75% hexane (v/v), followed by silica cartridge clean-up, and treated with copper granules  
143 to remove sulphur interferences. Samples were analysed gas chromatography with electron capture  
144 detection (GC-ECD) as detailed in method MOE2008.

Sediment samples that comprised the contaminated data were obtained from Magar et al. (2005) and included 107 PCB congeners in more than 280 samples from 18 sediment cores and surface samples obtained from the Lake Hartwell Superfund site (Pickens County, SC). Analyses was conducted at the Battelle Ocean Science Laboratories (Duxbury, MA) using modified U.S. EPA SW-846 Method 8270. Methods are described in detail by Brenner et al. (2004) and involved extraction with hexane, clean up using alumina, granular copper and gel permeation chromatography and analysis by gas chromatography with mass spectrometry.

#### Human samples

Two data sets were collated which included a background exposure cohort and an occupationally exposed cohort. The background exposure data were retrieved from the 2003-04 United States National Health and Nutrition Examination Survey (NHANES). NHANES is a continuous survey that was designed to monitor the health of the US population through interviews, physical examination and laboratory analysis. This includes the determination of a range of contaminants including a total of 37 PCBs in serum. Data from the NHANES surveys are publicly available from the Centres for Disease Control and Prevention (CDC, 2011b). PCBs were extracted using a C18 solid phase extraction (SPE) procedure followed by extraction through neutral silica and Florisil columns with hexane and 1:1 dichloromethane/hexane. Extracts were analysed using high resolution gas chromatography / high resolution mass spectrometry (HRGC-HRMS). Further information regarding the collection and analysis of serum samples together with data quality procedures are available from the CDC (CDC, 2011a).

The data for occupationally exposed humans were obtained from a study conducted by Megson et al. (2015). This included the determination of 209 PCBs in 30 participants. PCBs were extracted using a C18 solid phase extraction (SPE) procedure and processed using EPA method 3665A sulphuric acid/permanganate clean-up followed by EPA method 3620 Florisil clean-up. Extracts were analysed using comprehensive two dimensional gas chromatography with time of flight mass spectrometry (GCxGC-ToFMS).



The full congener specific datasets for each investigation are provided for reference in the supplementary information.

## Results and Discussion

### Commercial mixtures (Aroclors)

Theoretically 209 PCBs exist, but only approximately 130 of these have been detected in commercial mixtures (Frame, 2001). Five Aroclors (A1016, A1242, A1248, A1254 and A1260) accounted for >95% of sales between 1957 and 1974 (Durfrey et al., 1976). There have been a variety of proposed methods to estimate total PCB concentrations using a subset of congeners, including the i7 PCBs, i3 PCBs and CB-153. The analysis of these congeners is often performed as an initial screening method during an environmental investigation to identify if PCBs contamination has occurred. The proportions of these groups of congeners in each of the 5 main Aroclors are presented in Table S1. The best predictor for total concentrations were the i7 PCBs although the total proportions present varied substantially between the different Aroclors. Total proportions ranged from approximately 30% of the total PCBs in the more chlorinated Aroclors (A1254 and A1260), but in A1242 nearly 90% of the total PCBs would go un-reported. The variation would be even greater for CB-153 and i3 PCBs: if only these congeners were analysed no PCBs would be detected in a technical mixture of A1016. The large variation in proportions of the indicator compounds in the different Aroclors could result in false conclusions being drawn when analysing samples that contain fresh inputs of Aroclors. No correction factors can be applied to any of the three indicators to calculate total PCB concentrations.

Most environmental samples rarely contain high proportions of fresh Aroclor inputs. They usually contain a mixture of inputs that have undergone some degree of weathering by physical, chemical and biological processes. These processes result in a relative enrichment in recalcitrant congeners including the i7 PCBs (Hansen, 1999). The relative proportions of these key congeners in water, sediment and humans was investigated along with a regression against the “total” PCB concentration.

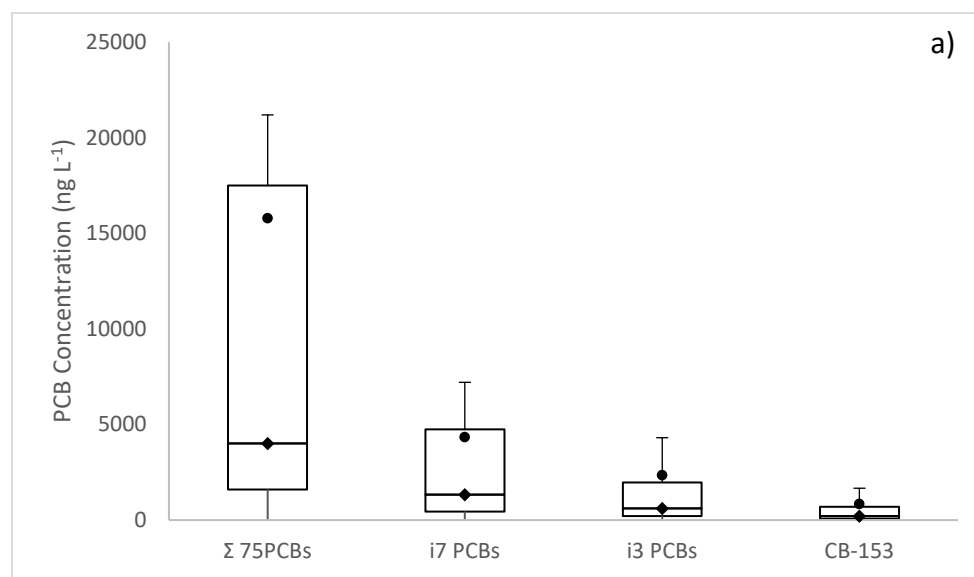
## Water samples

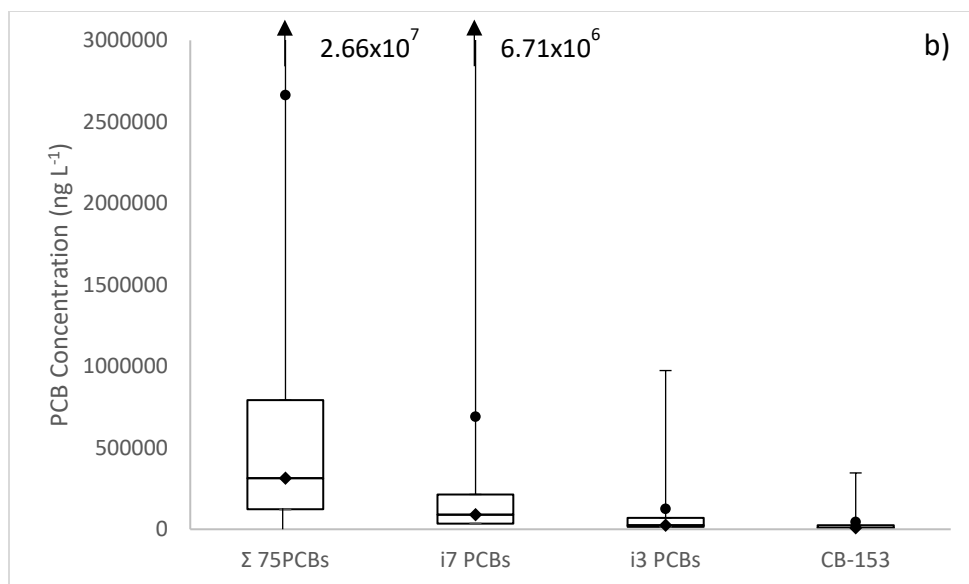
Three hundred and ninety four water samples were collected from background sites across Ontario as described in Benoit et al. (2016). The i7 PCBs accounted for approximately 28% of the total detected PCB concentrations whereas the i3 PCBs and CB-153 accounted for 15% and 5% respectively (Figure 1a). The relative proportions of the i7 PCBs, i3 PCBs and CB-153 to the total concentration all showed a relatively poor correlation to the total PCB concentration (Figure 2a). A coefficient of determination ( $R^2$ ) of approximately 0.91 was recorded for the i7 PCBs, but the i3 PCBs and CB-153 were below 0.6. The coefficient of determination was calculated for each of the 75 PCBs against the total concentration and is presented in the Supplementary Information as Table S2. The 5 PCBs with the best correlation were CB-99 ( $R^2$  of 0.81), CB-156 ( $R^2$  of 0.80), CB-110 ( $R^2$  of 0.80), CB-118 ( $R^2$  of 0.79), and CB-123 ( $R^2$  of 0.79). PCBs 99, 110 and 118 are abundant in technical PCB mixtures which may explain the good correlation for these congeners, however PCBs 156 and 123 are not as common (<0.5% of total Aroclor PCBs).

A separate targeted study was undertaken which involved the collection of eighteen water from a known contaminated site in Ontario (Figure 1b); the i7 PCBs accounted for approximately 26% of the total whereas the i3 PCBs and CB-153 accounted for 4.7% and 1.7% respectively. The relative proportions of the i7 PCBs, i3 PCBs and CB-153 had an excellent correlation with the total PCB concentration (Figure 2b), these correlations are partly attributable to a couple of samples with very high concentrations. A coefficient of determination ( $R^2$ ) of approximately 1.0 was recorded for the i7 PCBs, with the correlations for the i3 PCBs and CB-153 both greater than 0.95. The coefficient of determination was calculated for each of the 75 PCBs against the total concentration and is presented as Supplementary Information Table S3. Fifty of the 75 congeners had a  $R^2$  value of greater than 0.95 suggesting that the samples were likely from a single (or similar) sources with limited alteration/degradation).

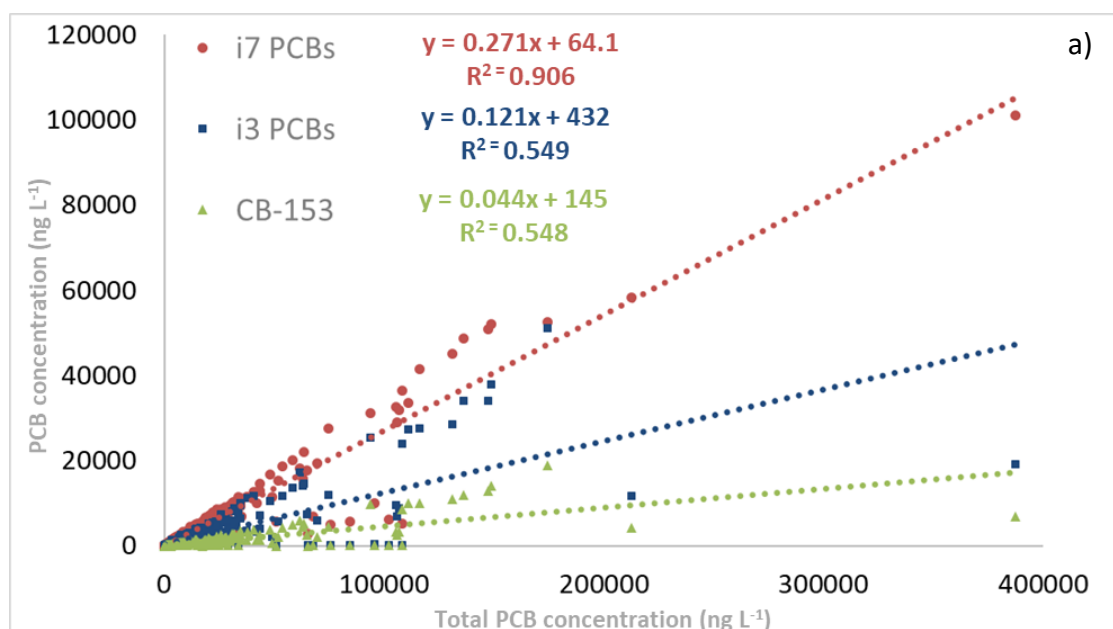
The results for the contaminated site showed the best correlation between the indicator compounds and total concentrations (Figure 2b). This strong correlation can be explained because these samples were all obtained from an area with a known source of contamination, with a relatively unaltered congener profile

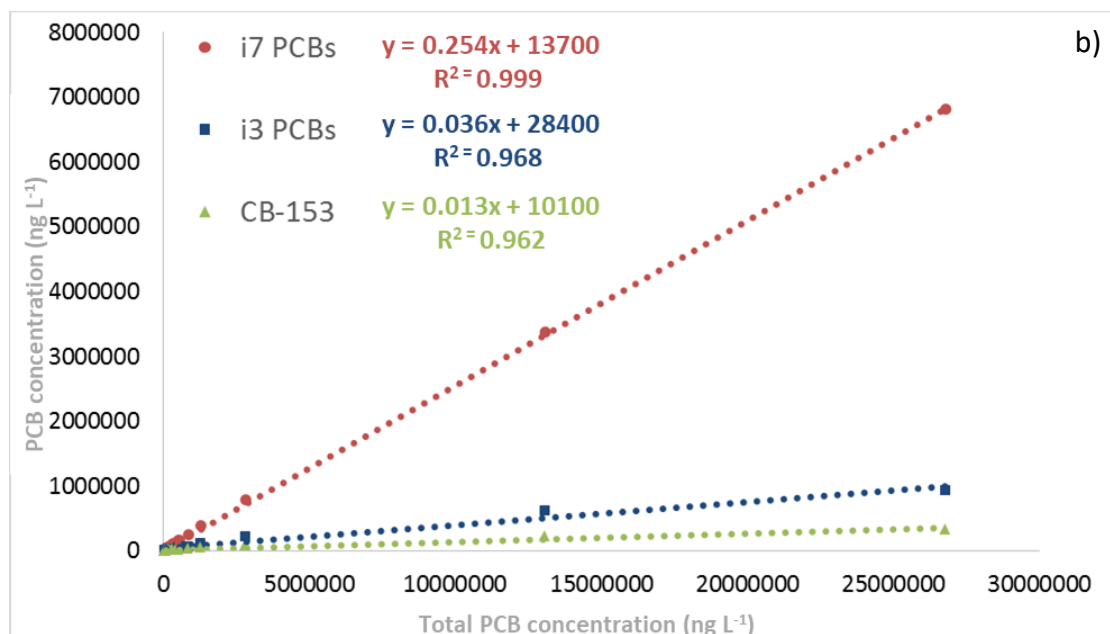
(Benoit et al., 2016). In the background sites, the PCB load will have been more impacted by post depositional factors such as areal deposition, mixing, biodegradation, volatilisation, etc. and therefore have a poorer correlation. The results indicate that the i7 PCBs, i3 PCBs and CB-153 can be good predictors for total PCBs from technical mixture sources with a relatively unaltered congener profile, but they are likely to under-predict concentrations in other environmental samples. When considering aquatic environments, the indicator compounds should not be considered in isolation. There will be partitioning between sediment, biota and the atmosphere which will alter the PCB congener profile over time (Hansen, 1999). The i3 PCBs and CB-153 have been shown to preferentially accumulate in biota and sediment and so over time, their proportions will be depleted from the aquatic environment. Therefore, when assessing PCBs from aquatic environments, care should be used when just considering a small subset of PCBs. There may be added benefit to considering an additional selection of mid and lower chlorinated congeners from the supplementary information (SI1) to estimate total PCBs.





**Figure 1.** Box and whisker diagram of PCB concentrations in of “total PCBs”, i7, PCBs, i3 PCBs and CB-153 for a) water samples obtained from streams in Ontario (n = 394) and b) water samples obtained from contaminated sites in Ontario (n = 18) Dots represent the mean value and diamonds represent the median, boxes represent the interquartile range and whiskers the minimum and maximum reported values





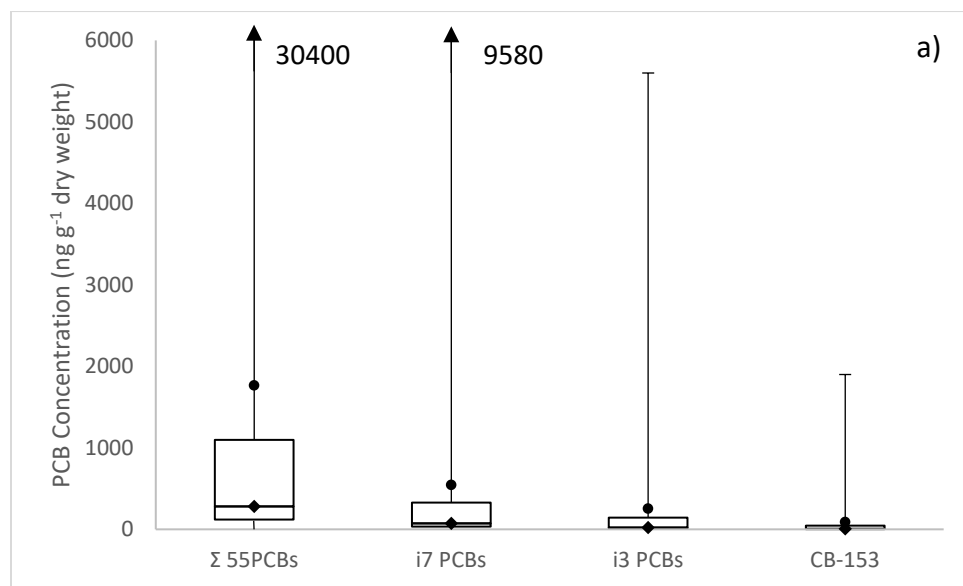
**Figure 2.** Scatter plot and regression of i7, PCBs, i3 PCBs and PCB-153 against “total PCBs ( $\Sigma 75$ )” for a) water samples obtained from waterways in Ontario (n = 394) and b) 18 water samples obtained from contaminated sites in Ontario

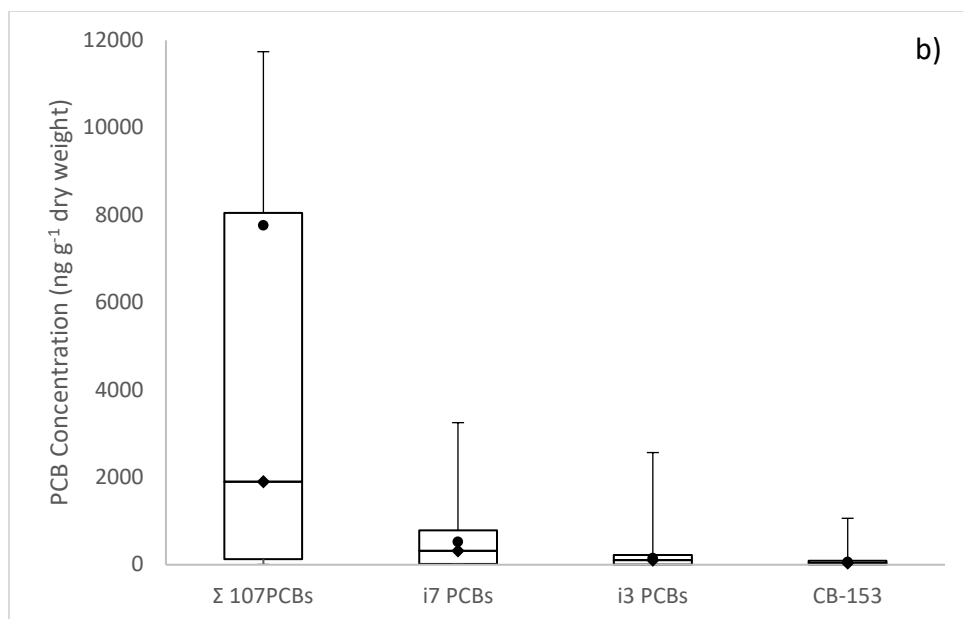
#### Sediment samples

PCB concentrations were determined in 374 sediment samples obtained from across Ontario. The i7 PCBs accounted for approximately 30%, of the total whereas the i3 PCBs and CB-153 accounted for 14% and 5% respectively (Figure 3a). The relative proportions of the i7 PCBs, to the total concentration showed a good correlation whereas the i3 PCBs and CB-153 correlation was poor. A coefficient of determination of 0.98 was recorded for the i7 PCBs, and an R<sup>2</sup> value of approximately 0.8 recorded for the i3 PCBs and CB-153 (Figure 4a). The coefficient of determination was calculated for each of the 55 PCB congeners against the total concentration and is presented as Supplementary Information Table S4. The 5 PCB congeners with the best correlation were CB-101 (R<sup>2</sup> of 0.93), CB-168 (R<sup>2</sup> of 0.91), CB-138 (R<sup>2</sup> of 0.90), CB-110 (R<sup>2</sup> of 0.87), and CB-118 (R<sup>2</sup> of 0.85). PCBs 101, 110, 118 and 138 are abundant in technical PCB mixtures

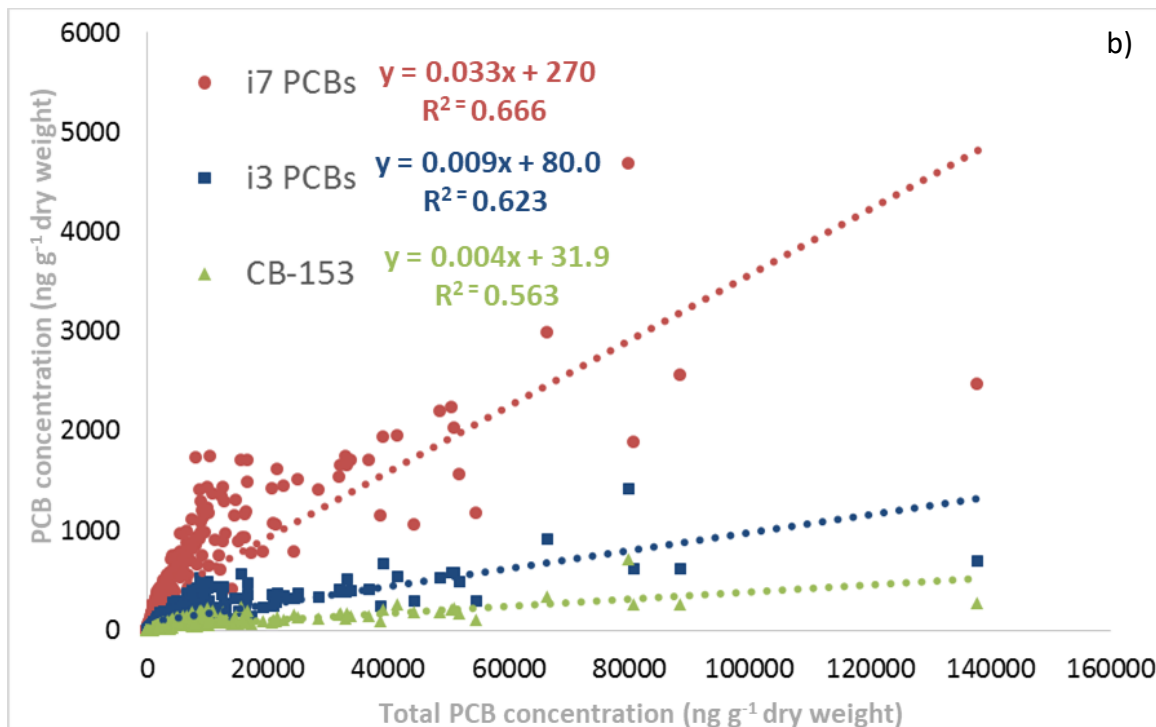
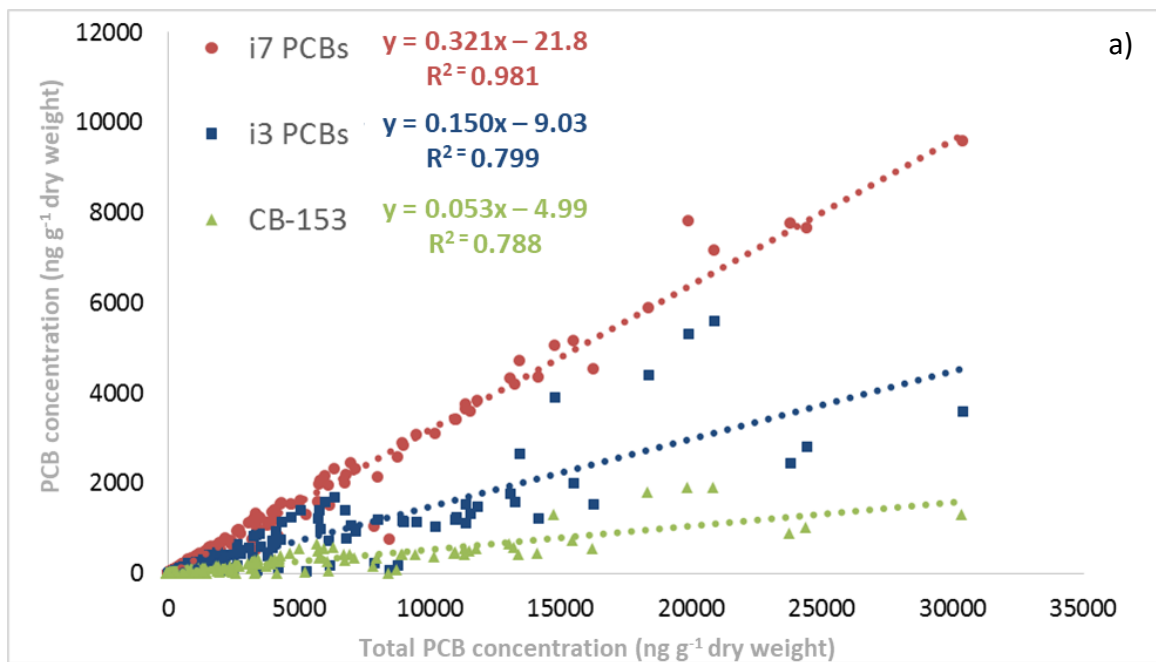
(Frame et al. (1996)) which may explain the good correlation for these congeners, however PCB 168 is not as common (<0.5% of total Aroclor PCBs).

Data for 280 sediment samples collected from the Lake Hartwell Superfund site were obtained from Magar et al. (2005). The i7 PCBs accounted for approximately 7%, of the total whereas the i3 and CB-153 accounted for 2% and 0.8% respectively. The relative proportions of the i7 PCBs, i3 PCBs and CB-153 to the total concentration all showed a very poor correlation to the total PCB concentration (Figure 4b). A coefficient of determination of less than 0.7 was recorded for the i7 PCBs, i3 PCBs and CB-153. The coefficient of determination was calculated for each of the 107 PCBs against the total concentration and is presented as Supplementary Information Table S5. The 5 PCBs with the best correlation were CB-19 ( $R^2$  of 0.97), CB-16/32 ( $R^2$  of 0.95), CB-24/27 ( $R^2$  of 0.95), CB-51 ( $R^2$  of 0.94), and CB-4/10 ( $R^2$  of 0.93).





**Figure 3.** Box and whisker diagram of PCB concentrations in of “total PCBs”, i7 PCBs, i3 PCBs and CB-153 for a) sediment samples obtained from across Ontario (n = 374) and b) sediment samples obtained from Lake Hartwell Superfund site (n = 280) (data from Magar et al. (2005)). Dots represent the mean value and diamonds represent the median, boxes represent the interquartile range and whiskers the minimum and maximum reported values



**Figure 4.** Scatter plot and regression of i7, PCBs, i3 PCBs and PCB-153 against “total PCBs” for a) sediment samples obtained from across Ontario (n = 374) and b) sediment samples obtained from Lake Hartwell Superfund site (n = 280) (data from Magar et al. (2005))



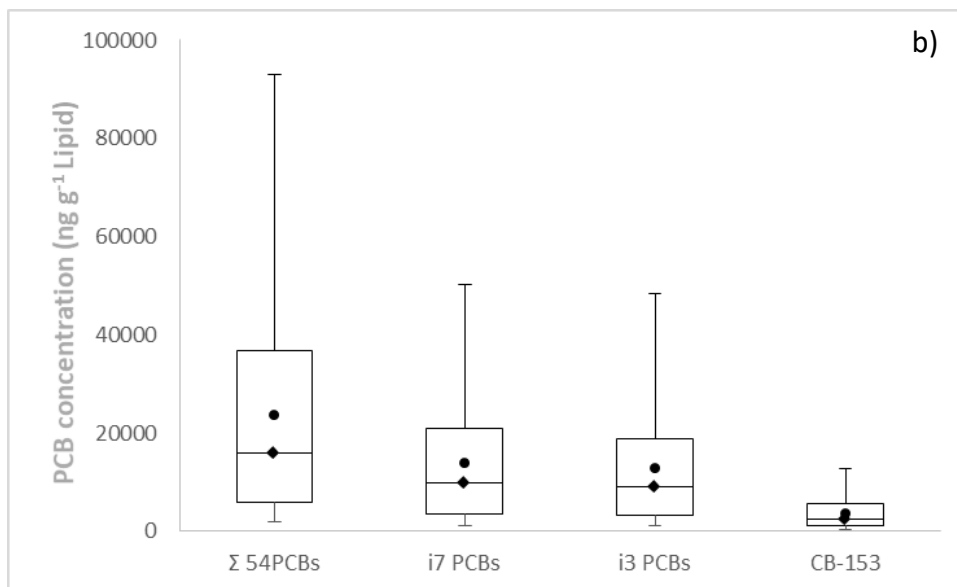
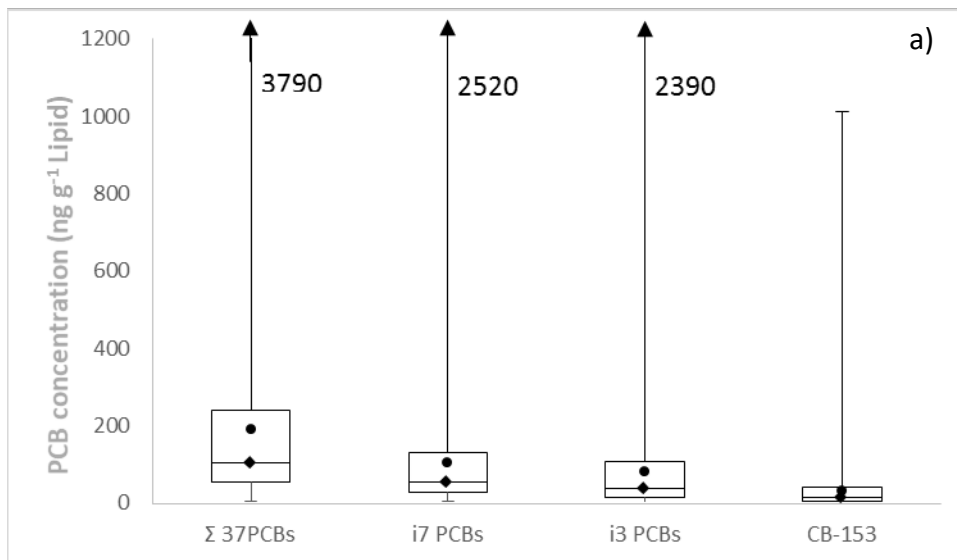
The results from the background sediments in Ontario indicate that the i7 PCBs are a fairly good predictor for total PCB concentrations. However, the results for the contaminated Superfund data set showed that the i7 PCBs, i3 PCBs and CB-153 concentrations were very poor predictors of total PCB concentrations. Unusually high concentrations of the lower chlorinated congeners were observed in the Superfund site data set. The authors noted that this was due to dechlorination from microbial degradation. The net accumulation of CB-1, the di-PCBs CB-4/10 & 5/8 and tri-PCBs CB-17/19 matched characteristic PCB dechlorination products for Processes M, Q, and C; whereas the persistence of tetrachlorobiphenyls (TeCBs) that contained 24- and 25-congener groups resembled dechlorination Processes H or H' (Magar et al., 2005, Bedard and Quensen III, 1995). Detailed discussions of these and other known dechlorination processes have been presented earlier by Bedard and Quensen (1995) and Johnson, et al. (2006). Many of these congeners show the best  $R^2$  value (Table S5) again indicating the dominance of a dechlorination pattern. Figure S1 shows the effect of the dechlorination which is targeting the i7 PCB resulting in relative decreasing concentrations of these congeners against the total. When the most dechlorinated samples were removed from the dataset the  $R^2$  value was greater than 0.95. This highlights the limitation of only using the i7 PCBs to estimate total PCB concentrations: if a correction factor was to be applied to a site where PCBs were undergoing dechlorination due to microbial activity then it would drastically under predict the total concentration.

#### Human samples

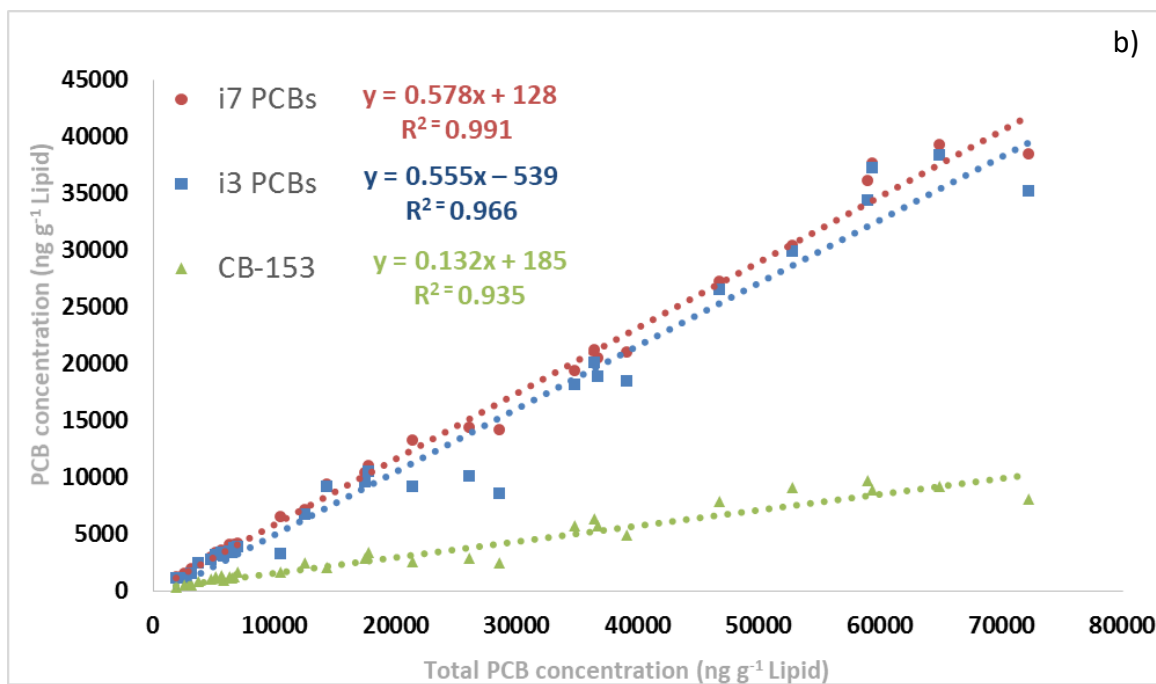
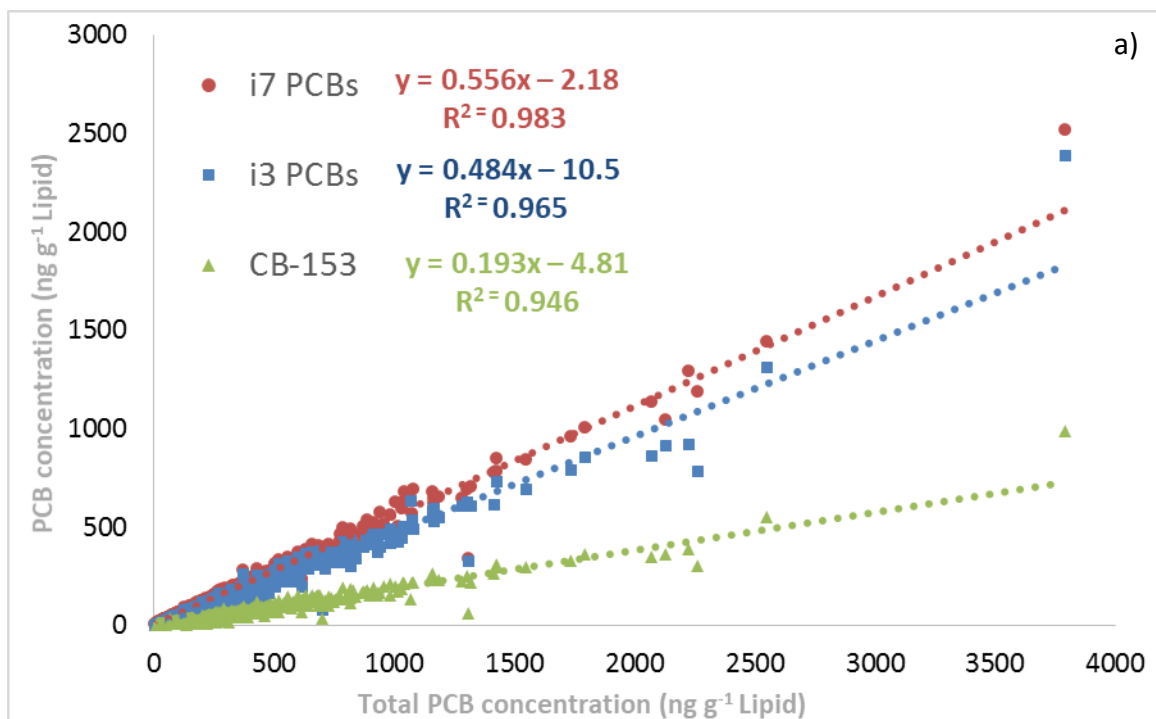
The NHANES data contains results for approximately 2000 participants and included 37 PCBs. The i7 PCBs accounted for approximately 54% of the total whereas the i3 and CB-153 accounted for 37% and 14% respectively (Figure 5a). Although Figure 5a appears to show a large range in PCB concentrations, the relative proportions of the i7 PCBs, i3 PCBs and CB-153 to the total concentration all remained relatively constant and produced a coefficient of determination ( $R^2$ ) of approximately 0.95 or greater (Figure 6a). The coefficient of determination was calculated for each of the 37 PCBs against the total concentration and is presented as Supplementary Information S6. The 5 PCBs with the best correlation were CB-153 ( $R^2$  of

0.95), CB-138 ( $R^2$  of 0.91), CB-146 ( $R^2$  of 0.88), CB-172 ( $R^2$  of 0.87), and CB-180 ( $R^2$  of 0.87). This is not surprising as all of these congeners contained chlorine substitution patterns (-234, -245, or -2345) on one or more of the phenyl rings that were shown by Megson et al. (2013) to be resistant to biotransformation and elimination in humans.

The NHANES data set represents a group of samples with predominantly background / low level PCB contamination. The data also contains fewer PCBs than the other matrixes investigated which could explain why correlations between the indicator compounds and total PCBs were so high. Data from Megson et al. (2015) was used to investigate if the indicator PCBs are still good at predicting total PCB concentrations in an exposed cohort in an investigation where all 209 PCBs were targeted. The coefficient of determination was calculated for each of the 54 PCBs detected > LOD against the total concentration and is presented as Supplementary Information S7. Figure 6b shows that the coefficient of determination for the i7 PCBs and i3 PCBs was similar in the exposed cohort as it was for the NHANES data. The  $R^2$  value for CB-153 was lower for the exposed cohort; this was likely due to a subset of the cohort being exposed to a different source of PCBs with elevated proportions of some less chlorinated PCBs including CB-28, CB-60, CB-66, and CB-74. Gandhi et al. (2015) recommended that the use of the i3 PCBs and CB-153 to calculate total PCB concentrations in fish should be avoided, however for humans they appear to be fairly good indicators for basic screening assessments to estimate total PCB concentrations. The best results were achieved using the i7 PCBs and the regression equation for Figure 6a&b was similar in each instance. The results indicate that total PCB concentrations in humans can be estimated by multiplying the i7 PCBs by a factor of 1.75. However, for more detailed assessments involving risks to human health and source tracking, the determination of more congeners (preferably all 209) is strongly recommended.



**Figure 5.** Box and whisker diagram of PCB concentrations in of “total PCBs”, i7, PCBs, i3 PCBs and CB-153 for **a)** a background cohort (n = 1900) (NHANES 2003-04 participants) (n = 1900), and **b)** an exposed cohort (n = 30) (data from Megson et al. 2015). Dots represent the mean value and diamonds represent the median, boxes represent the interquartile range and whiskers the minimum and maximum reported values



**Figure 6.** Scatter plot and regression of i7 PCBs, i3 PCBs and PCB-153 against “total PCBs” for **a)** a background cohort (n = 1900) (NHANES 2003-04 participants) and **b)** an exposed cohort (n = 30) (data from Megson et al. 2015)

The results of this investigation show large differences in correlation coefficients between the indicator PCBs investigated and total PCB concentrations in the different case studies. This highlights the limitations of relying on just a few indicator compounds to make informed decisions. There are larger groups of indicator compounds (e.g. (Ishikawa et al., 2007)) which can be used to provide a more reliable estimate of total PCBs and toxic equivalents. However, these are not flawless and so it is up to investigators to balance cost and time constraints against the quality and quantity of data they require.

### Additional (non-Aroclor) PCB sources

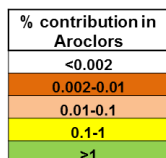
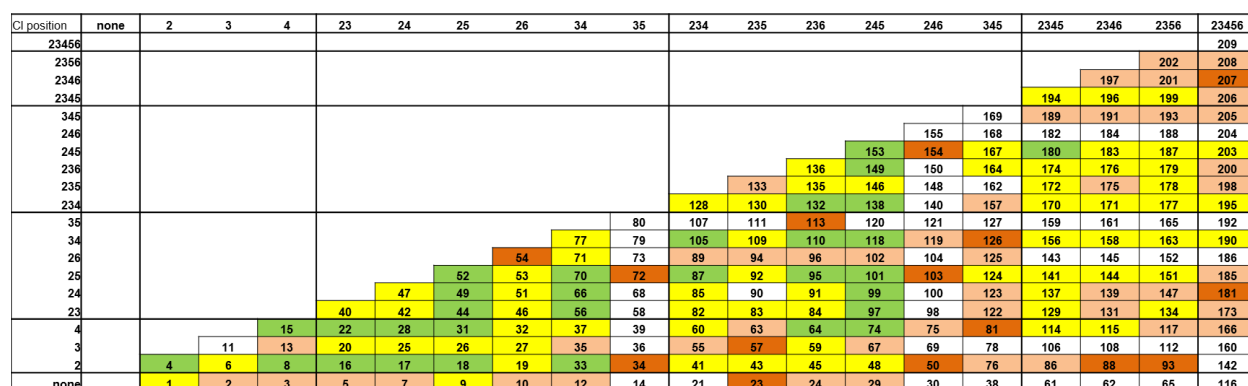
One significant limitation with the existing analytical methods that only target specific PCBs is that these methods were established to focus solely on co-planar PCBs (e.g. WHO 12) or on PCBs that are abundant in commercial PCB mixtures (e.g. i7 & i3 PCBs). Therefore, they often miss PCB contamination from non-Aroclor sources. Non-Aroclor PCBs, also referred to as non-legacy PCBs, unintentional PCBs (u-PCBs), incidental-PCBs (i-PCBs). These are PCBs that are produced inadvertently as biproducts of chemical and industrial processes and should be distinguished from secondary sources of technical mixtures (e.g. inadvertent release of PCBs from the recycling of carbonless copy paper which contained technical PCB mixtures such as Aroclor 1242). Historically, PCBs were primarily used as coolants and lubricants in electrical equipment (e.g., capacitors & transformers), however the direct production of PCBs for these or any other uses ceased in the 1970s. Since then, the importance of other sources of PCBs has increased to the extent that non-Aroclor PCBs are now considered ubiquitous contaminants in the environment (Hu et al., 2011, King et al., 2002, Hu et al., 2008, Rodenburg et al., 2010, Megson et al., 2018).

A review of the available peer-reviewed literature showed most papers focus on pigments as a source of non-legacy PCBs, with azo, phthalocyanine and titanium dioxide pigments being the main contributors. Many of these pigments are used in everyday consumer products and packaging with their impact on the environment gaining more attention. Other industrial processes that can produce unintentional PCBs include chlorinated benzenes, phenols or quinones used as solvents or reaction feeds along with the waste

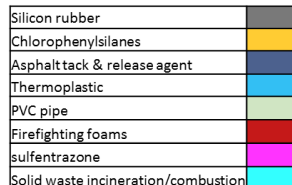
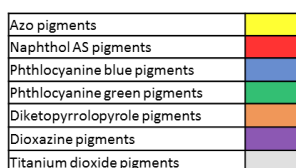
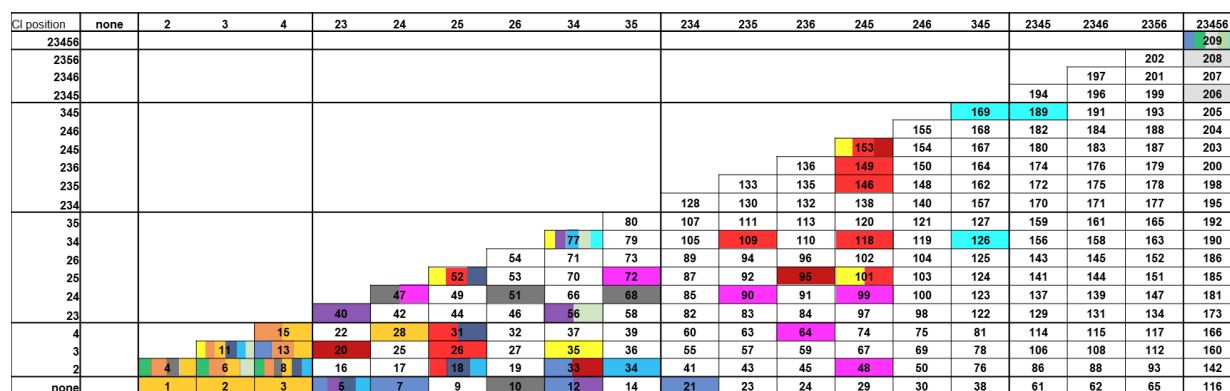
incineration industry. Most studies that identified non-legacy PCBs focused on the determination of either PCB11 or PCB209. This is likely because these two congeners were not present in detectable concentrations in many Aroclors and so their presence in environmental samples is easier to spot. There have been many instances where PCB11 was found to make up a significant portion of the total PCB concentrations in environmental samples (Hu and Hornbuckle, 2010, Law, 1995, Khairy et al., 2015, Rodenburg et al., 2010, Du et al., 2008, Vorkamp, 2016, Hu et al., 2008, King et al., 2002, Mohrherr et al., 2012, Megson et al., 2018). In several other instances PCB209 was found to contribute a significant proportion of the total PCBs in environmental samples (Hu et al., 2011, Huo et al., 2017, Martinez and Hornbuckle, 2011, Martinez et al., 2016). In these cases, the contamination was attributed to non Aroclor sources (Martinez and Hornbuckle, 2011, Martinez et al., 2016) paint pigments (Hu et al., 2011, Martinez et al., 2016) or specifically to phtalocyanine-type pigments (Huo et al., 2017). It is important to note that while Frame et al. (1996) could not measure PCB 209 in any eight Aroclors he examined, it is an important congener in three less common, more highly chlorinated Aroclors. PCB-209 is the dominant congener in Aroclors (1270 & 1271) which were produced by Monsanto from 1938 to 1949 (Hermanson et al., 2016). It also accounts for approximately 6% of Aroclor 1268(Rushneck et al., 2004) which accounted for just 0.36% of Monsanto Aroclor sales from 1957 to 1974 ((Durfree et al., 1976) Johnson, et al., 2006). As such the presence of PCB-209 in field studies does not necessarily confirm a non technical mixture source (e.g. (Hartmann et al., 2004)).

Non-Aroclor sources can contain a wider range of PCBs other than just PCB11 and PCB209 thus differentiating these from traditional commercial PCB sources in an environmental sample can be challenging. Figure 7 presents chlorine substitution matrices to allow a comparison of which of the 17 PCBs and WHO12 PCBs are present in Aroclors and a variety of non-Aroclor sources. Aroclor data was obtained from (Frame, 2001) and non-Aroclor data from the following sources: pigments (Hu and Hornbuckle, 2010, Shang et al., 2014, Anezaki and Nakano, 2014, Guo et al., 2014, Anezaki et al., 2015, Rodenburg et al., 2015, Forstinger et al., 2015, City of Spokane, 2015, Buchta et al., 1985, Rodenburg, 2012, Vorkamp,

2016), Silicone rubber (Perdih and Jan, 1994), Anezaki et al. (2015), chlorophenylsilanes (Anezaki et al., 2015), asphalt tack and release agent, Thermoplastic, PVC pipes, firefighting foams and Sulfentrazone (City of Spokane, 2015), waste incineration (Yasuhara et al., 2003, Jiang et al., 2015, Li et al., 2017, Shin et al., 2006, Anezaki et al., 2016). There is not the same level of information on the composition of PCBs in non-Aroclor sources as there are for different technical mixtures and so figure 7b is an incomplete picture. However, it is useful as it highlights the large degree of overlap between PCBs found in technical mixtures and non-Aroclor sources.



a)



b)

Cl position	none	2	3	4	23	24	25	26	34	35	234	235	236	245	246	345	2345	2346	2356	23456
23456																				209
2356																			202	208
2346																		197	201	207
2345																		194	196	206
345																169	189	191	193	205
246																155	168	182	184	204
245																153	154	167	180	203
236																136	149	150	164	200
235																133	135	146	162	198
234																128	130	132	138	195
35																107	111	113	120	192
34																77	79	105	109	190
26																54	71	73	89	186
25																49	51	66	68	185
24																47	49	51	66	181
23																40	42	44	46	173
4				15												22	28	31	32	166
3			11	13												20	25	26	27	160
2		4	6	8	16											17	18	19	33	142
none	1	2	3	5	7	9	10	12	14	21	23	24	29	30	38	61	62	65	66	116

i7 PCBs	
WHO12 PCBs	

c)

**Figure 7.** Chlorine matrices illustrating a) the PCB congeners present in Aroclors and their % abundance (taken from data from Hansen 1999 based on Aroclor production) , b) the major PCB congeners present in a variety of non-Aroclor sources and c) the i7 PCBs and WHO12 PCBs

The only PCBs that were present in non-Aroclor sources but not in Aroclors were PCBs 11, 68, 90, 189 and 209. There were 40 different PCBs that were present in both Aroclor and non-Aroclor sources and differentiating these in environmental samples may prove a significant challenge. However, Bartlett et al. (2019) did attribute unusually high levels of the indicator PCB-52 in arctic snow samples, to non-Aroclor sources. There are likely to be many similar instances where non-Aroclor sources of PCBs have been missed as they have been falsely attributed to a PCB technical mixture. The results highlight that while the i7 PCBs cover some of the most abundant PCBs in Aroclors they were only present in one third of the non-Aroclor sources investigated (Azo pigments – excluding those made with 3,3'-dichlorobenzidine, Naphthol AS pigments, chlorophenylsilanes, Asphalt tack & release agents, and firefighting foams). The i7 PCBs are therefore not an effective screening tool as they completely miss contributions from many non-Aroclor sources.

## Conclusions

When investigating commercial mixtures, the i7 PCBs, i3 PCBs and CB-153 provide different estimates for total PCB concentrations depending on the Aroclor tested. Comparing total PCBs estimated from the



indicator compounds in different sources could therefore lead to significant errors. In water, the i7 PCBs, i3 PCBs and CB-153 were all fairly poor indicators of total PCB concentrations in background environments. Where a significant, single, relatively unaltered source of PCBs was identified, the indicator compounds were good predictors. In sediment i7 PCBs, i3 PCBs and CB-153 were all poor indicators of total PCB concentrations due to microbial dechlorination biotransforming the indicator compounds into less common isomers. When the most heavily dechlorinated samples were removed from the dataset, there was a good correlation but this was because the samples were linked to a known source of PCBs. Therefore, for sediment and water samples use of indicator compounds (i7 PCBs, i3 PCBs or CB-153) to predict totals is not recommended. For humans however, the i7 PCBs proved to be excellent predictors for total PCB concentrations in those with both occupational and background exposure to PCBs. Good correlations were also observed for the i3 PCBs and individual congeners such as CB-153, and CB-180. Due to the variation in congener profiles in the different environmental samples there are no subset of indicator PCBs that can be reliably used to estimate PCB totals in every sample. Cost constraints on projects will inevitably mean that not all 209 PCBs will be analysed for every sample taken, however scientists and consultants who are relying on datasets with a reduced number of PCBs should appreciate the limitations this causes. While the use of common indicator PCBs can give unreliable estimates of total concentrations they can provide quick and useful comparisons between datasets.

Such variations in the level of prediction of the indicator PCBs underlines the need for a larger number of congeners to be analysed that represent eventual breakdown products that may improve the predictability of a subset of congeners when looking at total concentrations. When assessing human health risks, the focus is solely on the WHO12 PCBs but many of these studies include a basic screen for just the indicator compounds. This study highlights the limitations of relying on investigations that only determine the indicator PCBs alone. Under most scenarios, these compounds give a poor estimate of total PCB concentrations, and are a poor indicator to compare total PCB levels between different sources and media. They are also not an appropriate tool to identify non-Aroclor sources of PCBs.

For environmental investigations aiming to quantify total PCBs, establish sources of contamination or model fate and transport, the term “more is better” still stands. The results of this assessment show that there is not one method, or group of PCBs that can accurately predict total PCB concentrations in all matrices. Environmental samples are not well served by the indicator compounds due to complexities of weathering in the environment and the presence of non-Aroclor PCB sources. While there are obvious cost implications with performing a full comprehensive congener specific analysis the quality of data generated and the ability to identify sources of PCBs is likely to be far superior. Studies relying on only a subset of congeners need to understand the limitations and not over interpret their limited datasets.

## References

- Anezaki, K., Kannan, N. and Nakano, T. (2015) 'Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments', *Environmental Science and Pollution Research*, 22(19), pp. 14478-14488.
- Anezaki, K. and Nakano, T. (2014) 'Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments', *Environ Sci Pollut Res Int*, 21(2), pp. 998-1009.
- Anezaki, K., Nakano, T. and Kashiwagi, N. (2016) 'Estimation of Polychlorinated Biphenyl Sources in Industrial Port Sediments Using a Bayesian Semifactor Model Considering Unidentified Sources', *Environmental Science & Technology*, 50(2), pp. 765-771.
- Barr, D. B., Weihe, P., Davis, M. D., Needham, L. L. and Grandjean, P. (2006) 'Serum polychlorinated biphenyl and organochlorine insecticide concentrations in a Faroese birth cohort', *Chemosphere*, 62(7), pp. 1167-1182.
- Bartlett, P. W., Isaksson, E. and Hermanson, M. H. (2019) 'New' unintentionally produced PCBs in the Arctic', *Emerging Contaminants*, 5, pp. 9-14.
- Battelle Memorial Institute, GeoChem Metrix, I., U.S. Navy SPAWAR Systems Center and U.S. Environmental Protection Agency ORD (2012) 'A Handbook for Determining the Sources of PCB Contamination in Sediments. NAVFAC Engineering and Expeditionary Warfare Center Technical Report. Prepared under Contract N62473-07-D-4013 (DO0074). October 2012. <http://www.dtic.mil/docs/citations/ADA607839>'.
- Bedard, D. L. and Quensen III, J. F. (1995) 'Microbial Reductive Dechlorination of Polychlorinated Biphenyls', in Young, L.Y. & Cerniglia, C. (eds.) *Microbial Transformation and Degradation of Toxic Organic Chemicals*. New York: Wiley-Liss Division, Wiley & Sons, Inc.
- Benoit, N., Dove, A., Burniston, D. and Boyd, D. (2016) 'Tracking PCB Contamination in Ontario Great Lakes Tributaries: Development of Methodologies and Lessons Learned for Watershed Based Investigations', *Journal of Environmental Protection*, 7(3), pp. 390-409.
- Brenner, R. C., Magar, V. S., Ickes, J. A., Foote, E. A., Abbott, J. E., Bingler, L. S. and Crecelius, E. A. (2004) 'Long-term recovery of PCB-contaminated surface sediments at the Sangamo-Weston/Twelvemile Creek/Lake Hartwell superfund site', *Environmental Science & Technology*, 38(8), pp. 2328-2337.

- Buchta, R. C., Wyles, H. F., Hensler, C. J., Van Lenten, F. J., Westerberg, R. B. and Williams, L. A. (1985) 'Determination of polychlorinated biphenyls in copper phthalocyanine pigments', *Journal of Chromatography A*, 325, pp. 456-461.
- CDC (2011a) *National Health and Nutrition Examination Survey*. Available at: <http://www.cdc.gov/nchs/nhanes.htm> (Accessed: 21st October 2011).
- CDC (2011b) *NHANES 2003 - 2004 Laboratory Files*. Available at: [http://www.cdc.gov/nchs/nhanes/nhanes2003-2004/lab03\\_04.htm](http://www.cdc.gov/nchs/nhanes/nhanes2003-2004/lab03_04.htm) (Accessed: 21st October 2011).
- City of Spokane, Department, W.M. (2015) *PCBs in Municipal Products*. Spokane, WA.
- Clement, R. E., Reiner, E. J. and Bhavsar, S. P. (2012) 'Organohalogen contaminants of emerging concern in Great Lakes fish: a review', *Analytical and Bioanalytical Chemistry*, 404(9), pp. 2639-2658.
- Du, S., Belton, T. J. and Rodenburg, L. A. (2008) 'Source Apportionment of Polychlorinated Biphenyls in the Tidal Delaware River', *Environmental Science & Technology*, 42(11), pp. 4044-4051.
- Durfree, R. L., Contos, G., Whitmore, F. C., Barden, J. D., Hackman, E. E. I. and Westin, R. A. (1976) 'PCBs in the United States - industrial use and environmental distribution'.
- Fikslin, T. J. and Santoro, E. D. (2003) 'PCB congener distribution in estuarine water, sediment and fish samples: Implications for monitoring programs', *Environmental Monitoring and Assessment*, 87(2), pp. 197-212.
- Fitzgerald, E. F., Hwang, S. A., Lambert, G., Gomez, M. and Tarbell, A. (2005) 'PCB exposure and in vivo CYP1A2 activity among Native Americans', *Environmental Health Perspectives*, 113(3), pp. 272-277.
- Forstinger, K., Metz, H. J. and Koch, P. (2015) 'Diazo Compounds and Diazo Reactions', *Ullmann's Encyclopedia of Industrial Chemistry*: Wiley-VCH, pp. 1-22.
- Frame, G. M. (2001) 'The Current State-of-the-Art of Comprehensive, Quantitative, Congener-Specific PCB Analysis, and What We Now Know about the Distributions of Individual Congeners in Commercial Aroclor Mixtures', in Robertson, L.W. & Hansen, L.G. (eds.) *PCBs Recent Advances in Environmental Toxicology and Health Effects*: The University Press of Kentucky, pp. 3 - 9.
- Frame, G. M., Cochran, J. W. and Bowadt, S. S. (1996) 'Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis', *Hrc-Journal of High Resolution Chromatography*, 19(12), pp. 657-668.
- Gandhi, N., Bhavsar, S. P., Reiner, E. J., Chen, T., Morse, D., Arhonditsis, G. B. and Drouillard, K. G. (2015) 'Evaluation and Interconversion of Various Indicator PCB Schemes for Sigma PCB and Dioxin-Like PCB Toxic Equivalent Levels in Fish', *Environmental Science & Technology*, 49(1), pp. 123-131.
- Guo, J., Capozzi, S. L., Kraeutler, T. M. and Rodenburg, L. A. (2014) 'Global distribution and local impacts of inadvertently generated polychlorinated biphenyls in pigments', *Environ Sci Technol*, 48(15), pp. 8573-80.
- Guo, Y. and Kannan, K. (2015) 'Chapter 1 - Analytical Methods for the Measurement of Legacy and Emerging Persistent Organic Pollutants in Complex Sample Matrices', in Eddy, Y.Z. (ed.) *Comprehensive Analytical Chemistry*: Elsevier, pp. 1-56.
- Hansen, L. G. (1999) *The ortho side of PCBs*. Kluwer Academic Publishers.
- Hartmann, P. C., Quinn, J. G., Cairns, R. W. and King, J. W. (2004) 'Polychlorinated biphenyls in Narragansett Bay surface sediments', *Chemosphere*, 57(1), pp. 9-20.
- Hermanson, M. H., Hann, R. and Johnson, G. W. (2016) 'Polychlorinated Biphenyls in Tree Bark near Former Manufacturing and Incineration Facilities in Sauget, Illinois, United States', *Environmental Science & Technology*, 50(12), pp. 6207-6215.
- Hu, D. and Hornbuckle, K. C. (2010) 'Inadvertent polychlorinated biphenyls in commercial paint pigments', *Environ Sci Technol*, 44(8), pp. 2822-7.
- Hu, D., Martinez, A. and Hornbuckle, K. C. (2011) 'Sedimentary Records of Non-Aroclor and Aroclor PCB mixtures in the Great Lakes', *J Great Lakes Res*, 37(2), pp. 359-364.
- Hu, D. F., Martinez, A. and Hornbuckle, K. C. (2008) 'Discovery of Non-Aroclor PCB (3,3'-Dichlorobiphenyl) in Chicago Air', *Environmental Science & Technology*, 42(21), pp. 7873-7877.
- Huo, S., Li, C., Xi, B., Yu, Z., Yeager, K. M. and Wu, F. (2017) 'Historical record of polychlorinated biphenyls (PCBs) and special occurrence of PCB 209 in a shallow fresh-water lake from eastern China', *Chemosphere*, 184, pp. 832-840.

- Ishikawa, Y., Noma, Y., Mori, Y. and Sakai, S. (2007) 'Congener profiles of PCB and a proposed new set of indicator congeners', *Chemosphere*, 67(9), pp. 1838-1851.
- Jain, R. B. and Wang, R. Y. (2010) 'Regression models to estimate total polychlorinated biphenyls in the general US population: 2001-2002 and 2003-2004', *Chemosphere*, 79(3), pp. 243-252.
- Jiang, X. X., Liu, G. R., Wang, M. and Zheng, M. H. (2015) 'Formation of Polychlorinated Biphenyls on Secondary Copper Production Fly Ash: Mechanistic Aspects and Correlation to Other Persistent Organic Pollutants', *Scientific Reports*, 5, pp. 10.
- Johnson, G. W., Quensen III, J. F., Chiarenzelli, J. R. and Coreen Hamilton, M. (2006) 'Polychlorinated Biphenyls', in Morrison, R.D. & Murphy, B.L. (eds.) *Environmental Forensics Contaminant Specific Guide*: Academic Press.
- Khairy, M., Muir, D., Teixeira, C. and Lohmann, R. (2015) 'Spatial Distribution, Air-Water Fugacity Ratios and Source Apportionment of Polychlorinated Biphenyls in the Lower Great Lakes Basin', *Environmental Science & Technology*, 49(23), pp. 13787-13797.
- King, T. L., Yeats, P., Hellou, J. and Niven, S. (2002) 'Tracing the source of 3,3'-dichlorobiphenyl found in samples collected in and around Halifax Harbour', *Marine Pollution Bulletin*, 44(7), pp. 590-596.
- Law, R. J. (1995) '3,3'-Dichlorobenzidine: a candidate for inclusion in marine monitoring programmes?', *Chemosphere*, 30(9), pp. 1791-1797.
- Li, Q., Wang, Y., Luo, C., Li, J. and Zhang, G. (2017) 'Characteristics and potential sources of polychlorinated biphenyl pollution in a suburban area of Guangzhou, southern China', *Atmospheric Environment*, 156(Supplement C), pp. 70-76.
- Longnecker, M. P., Wolff, M. S., Gladen, B. C., Brock, J. W., Grandjean, P., Jacobson, J. L., Korrick, S. A., Rogan, W. J., Weisglas-Kuperus, N., Hertz-Picciotto, I., Ayotte, P., Stewart, P., Winneke, G., Charles, M. J., Jacobson, S. W., Dewailly, E., Boersma, E. R., Altshul, L. M., Heinzow, B., Pagano, J. J. and Jensen, A. A. (2003) 'Comparison of polychlorinated biphenyl levels across studies of human neurodevelopment', *Environmental Health Perspectives*, 111(1), pp. 65-70.
- Magar, V. S., Johnson, G. W., Brenner, R. C., Quensen, J. F., Foote, E. A., Durell, G., Ickes, J. A. and Peven-McCarthy, C. (2005) 'Long-term recovery of PCB-contaminated sediments at the Lake Hartwell superfund site: PCB dechlorination. 1. End-member characterization', *Environmental Science & Technology*, 39(10), pp. 3538-3547.
- Martinez, A. and Hornbuckle, K. C. (2011) 'Record of PCB congeners, sorbents and potential toxicity in core samples in Indiana Harbor and Ship Canal', *Chemosphere*, 85(3), pp. 542-547.
- Martinez, A., Schnoebelen, D. J. and Hornbuckle, K. C. (2016) 'Polychlorinated biphenyl congeners in sediment cores from the Upper Mississippi River', *Chemosphere*, 144, pp. 1943-1949.
- Megson, D. (2019) 'Polychlorinated Biphenyls', in Worsfold, P., Townshend, A., Poole, C. & Miró, M. (eds.) *Encyclopaedia of Analytical Science*. 3rd Edition ed: Elsevier.
- Megson, D., Brown, T. A., O'Sullivan, G., Robson, M., Ortiz, X., Worsfold, P. J., Comber, S., Lohan, M. C. and Reiner, E. J. (2018) 'Changes to polychlorinated biphenyl (PCB) signatures and enantiomer fractions across different tissue types in Guillemots', *Marine Pollution Bulletin*, 131, pp. 174-179.
- Megson, D., Focant, J. F., Patterson, D. G., Robson, M., Lohan, M. C., Worsfold, P. J., Comber, S., Kalin, R., Reiner, E. and O'Sullivan, G. (2015) 'Can polychlorinated biphenyl (PCB) signatures and enantiomer fractions be used for source identification and to age date occupational exposure?', *Environment International*, 81, pp. 56-63.
- Megson, D., Kalin, R. B., Worsfold, P., Gauchotte-Lindsay, C., Patterson Jr, D. G., Lohan, M. C., Comber, S., Brown, T. A. and O'Sullivan, G. (2013) 'Fingerprinting polychlorinated biphenyls in environmental samples using comprehensive two-dimensional gas chromatography with time-of-flight mass', *Journal of Chromatography A*, 1318, pp. 276-283.
- Mohrherr, C. J., Liebens, J. and Rao, K. R. (2012) 'Polychlorinated Biphenyl (PCB) Profiles, Degradation, and Aroclor Origin in Sediments of Escambia Bay, Florida', *Environmental Forensics*, 13(2), pp. 164-174.
- Muir, D. and Sverko, E. (2006) 'Analytical methods for PCBs and organochlorine pesticides in environmental monitoring and surveillance: a critical appraisal', *Analytical and Bioanalytical Chemistry*, 386(4), pp. 769-789.

- Muscalu, A. M., Reiner, E. J., Liss, S. N., Chen, T., Ladwig, G. and Morse, D. (2011) 'A routine accredited method for the analysis of polychlorinated biphenyls, organochlorine pesticides, chlorobenzenes and screening of other halogenated organics in soil, sediment and sludge by GCxGC-mu ECD', *Analytical and Bioanalytical Chemistry*, 401(8), pp. 2403-2413.
- Needham, L. L., Barr, D. B., Caudill, S. P., Pirkle, J. L., Turner, W. E., Osterloh, J., Jones, R. L. and Sampson, E. J. (2005) 'Concentrations of Environmental Chemicals Associated with Neurodevelopmental Effects in U.S. Population', *NeuroToxicology*, 26(4), pp. 531-545.
- Ontario Ministry of the Environment 2008. The Determination of Polychlorinated Biphenyl (PCBs) Congeners In Aqueous Samples By Gas Chromatography-High Resolution Mass Spectrometry (GC-HRMS).
- Perdih, A. and Jan, J. (1994) 'FORMATION OF POLYCHLOROBIPHENYLS IN SILICONE-RUBBER', *Chemosphere*, 28(12), pp. 2197-2202.
- Reiner, E. J., Jobst, K. J., Megson, D., Dorman, F. L. and Focant, J.-F. (2014) 'Chapter 3 - Analytical Methodology of POPs A2 - O'Sullivan, Gwen', in Sandau, C. (ed.) *Environmental Forensics for Persistent Organic Pollutants*. Amsterdam: Elsevier, pp. 59-139.
- Rodenburg, L., Guo, J. and Christie, R. (2015) 'Polychlorinated biphenyls in pigments: inadvertent production and environmental significance', *Coloration Technology*, 131(5), pp. 353-369.
- Rodenburg, L. A. 'Inadvertent PCB production and its impact on water quality'. *ECOS Annual Meeting*, Colorado Springs, CO.
- Rodenburg, L. A., Guo, J., Du, S. and Cavallo, G. J. (2010) 'Evidence for unique and ubiquitous environmental sources of 3,3'-dichlorobiphenyl (PCB 11)', *Environ Sci Technol*, 44(8), pp. 2816-21.
- Rushneck, D. R., Beliveau, A., Fowler, B., Hamilton, C., Hoover, D., Kaye, K., Berg, M., Smith, T., Telliard, W. A., Roman, H., Ruder, E. and Ryan, L. (2004) 'Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA method 1668A', *Chemosphere*, 54(1), pp. 79-87.
- Shang, H., Li, Y., Wang, T., Wang, P., Zhang, H., Zhang, Q. and Jiang, G. (2014) 'The presence of polychlorinated biphenyls in yellow pigment products in China with emphasis on 3,3'-dichlorobiphenyl (PCB 11)', *Chemosphere*, 98, pp. 44-50.
- Shin, S.-K., Kim, K.-S., You, J.-C., Song, B.-J. and Kim, J.-G. (2006) 'Concentration and congener patterns of polychlorinated biphenyls in industrial and municipal waste incinerator flue gas, Korea', *Journal of hazardous materials*, 133(1-3), pp. 53-59.
- Van den Berg, M., Birnbaum, L. S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N. and Peterson, R. E. (2006) 'The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds', *Toxicological Sciences*, 93(2), pp. 223-241.
- Vanderven, K., Vanderven, H., Thibold, A., Bauer, O., Kaisi, M., Mburu, J., Mgaya, H. N., Weber, N., Diedrich, K. and Krebs, D. (1992) 'CHLORINATED-HYDROCARBON CONTENT OF FETAL AND MATERNAL BODY-TISSUES AND FLUIDS IN FULL TERM PREGNANT-WOMEN - A COMPARISON OF GERMANY VERSUS TANZANIA', *Human Reproduction*, 7, pp. 95-100.
- Vorkamp, K. (2016) 'An overlooked environmental issue? A review of the inadvertent formation of PCB-11 and other PCB congeners and their occurrence in consumer products and in the environment', *Sci Total Environ*, 541, pp. 1463-1476.
- Wicklund Glynn, A., Wolk, A., Aune, M., Atuma, S., Zettermark, S., Mæhle-Schmid, M., Ola Darnerud, P., Becker, W., Vessby, B. and Adami, H.-O. (2000) 'Serum concentrations of organochlorines in men: a search for markers of exposure', *Science of The Total Environment*, 263(1-3), pp. 197-208.
- Wolff, M. S., Deych, E., Ojo, F. and Berkowitz, G. S. (2005) 'Predictors of organochlorines in New York City pregnant women, 1998-2001', *Environmental Research*, 97(2), pp. 170-177.
- Yasuhara, A., Katami, T. and Shibamoto, T. (2003) 'Formation of PCDDs, PCDFs, and Coplanar PCBs from Incineration of Various Woods in the Presence of Chlorides', *Environmental Science & Technology*, 37(8), pp. 1563-1567.

