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The role of soil and house dust physicochemical properties in determining the post ingestion bioaccessibility of sorbed polychlorinated biphenyls

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Abstract

Ingestion of soils and house dusts is an important pathway for children's exposure to sorbed organic pollutants such as polychlorinated biphenyls (PCBs). To reduce the uncertainty of the exposure estimates, it is important to understand the extent to which chemicals desorb and become bioaccessible following ingestion. In this study we use a three compartment in vitro digestive system to model the role of soil and house dust physicochemical properties on the post ingestion bioaccessibility of PCBs. Matched pairs (n = 37) of soil and dust were characterized for percent carbon and nitrogen, pH, moisture content, and particle size distribution. They were then fortified with a mixture of 18 PCBs and processed through the assay. The percent bioaccessibility of each PCB was calculated, then modeled using individual PCB log K_{ow} values and the soil and dust properties. The bioaccessibility of the PCBs in soil ($\bar{x}$ = 65 ± 16%) was greater ($p < 0.001$) than that of the PCBs in house dust ($\bar{x}$ = 36 ± 14%). In the soil model, carbon was the sole statistically significant predictive ($p \leq 0.05$) variable, while in house dust, both carbon and clay content were statistically significant ($p \leq 0.05$) predictors.

Graphical Abstract

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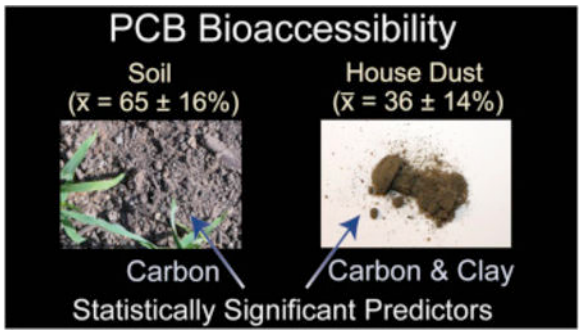

Keywords

Bioaccessibility soil; House dust; Ingestion; Physicochemical properties; Polychlorinated biphenyls

1. Introduction

Polychlorinated biphenyls (PCBs) are a group of 209 heat resistant lipophilic congeners that were primarily produced and used from the 1930's through the 1970's. Due to their widespread use, mobility, and chemical stability, the distribution of PCBs in the environment is worldwide and they continue to be important, persistent, bioaccumulative legacy pollutants. Human exposure to PCBs has been associated with a variety of health effects including; childhood leukemia (Ward et al., 2009), decreased insulin production (Jensen et al., 2014), and neurobehavioral alterations (Faroon et al., 2000).

Although PCBs were primarily used as coolants and insulating agents in transformers and capacitors, about 10% of the PCB applications in the United States were for building materials such as plasticizers in sealants for buildings containing masonry (Davies and Delistraty, 2016). Herrick et al. (2007), Kohler et al. (2005), and Priha et al. (2005)demonstrated that these exposed materials were important sources of PCBs found in nearby soils and indoor dusts and Rudel et al. (2008) found that wood floor finishes were a likely source for elevated PCBs in residential indoor dusts. Although they did not apportion sources, Orloff et al. (2003), Herrick et al. (2007), Knobeloch et al. (2012), and Wang et al. (2013) also showed that house dusts and soils located in and around residential housing may contain measurable concentrations of PCBs.

The presence of PCBs in soils and indoor dusts is of concern because children have relatively high rates of soil and dust ingestion (U.S. EPA., 2008). Further, several studies (Hack and Selenka, 1996; Oomen et al., 2000; Fries et al., 1989; Van Eijkeren et al., 2006; Fournier et al., 2012; Ertl and Butte, 2012; Feidt et al., 2013) have shown that significant amounts of sorbed PCBs are bioaccessible (desorbed and available for uptake into the circulatory system) and bioavailable (available in the circulatory system for delivery to the target organ) following soil and dust ingestion.

While these studies demonstrated that soil or dust sorption lowered PCB bioaccessibility and bioavailability, they did not determine which soil and dust characteristics were important in

reducing PCB mobilization within the digestive tract. Studies by Delannoy et al. (2014a, 2014b, 2015) indicated that soil organic matter is a key determinant of PCB desorption, but did not produce a quantitative model. To reduce the uncertainty of PCB exposure/dose estimates via the ingestion pathway, predictive models of PCB bioaccessibility for soils and house dusts are needed.

In this study, we developed quantitative post ingestion PCB bioaccessibility models using the log K_{ow} of individual PCBs and soil and house dust physicochemical properties (moisture content, pH, particle size distribution (sand, silt, and clay) and percent carbon and nitrogen). We used an in vitro three compartment (saliva/gastric/intestinal) test system to partition the PCBs between the soils/house dusts and digestive fluids. We used solid phase microextraction (SPME) and liquid extraction to measure freely dissolved, total mobilized, and residual soil/house dust (sediment) sorbed PCB concentrations, then constructed bioaccessibility models using multiple linear regression.

2. Materials and methods

2.1. Chemicals and materials

Organic solvents, including, hexane, acetone, toluene and methanol were all pesticide grade and purchased from Honeywell Burdick and Jackson (Morristown, NJ). Ethyl acetate was purchased from EMD chemicals Inc. (Gibbstown, NJ) and cyclopentane was acquired from Alfa Aesar (Ward Hill, MA). The deionized (DI) water used for this study was 18.2 MΩ resistance and purified on site. Dimethyldichlorosilane in toluene was used to deactivate all glassware and was purchased from Supelco (Bellefonte, PA). The inorganic and organic constituents of the digestive fluids were as described in the Standard Practice DIN 19738 and purchased from Sigma Aldrich (St. Louis, MO). Graphitized carbon solid phase extraction (SPE) cartridges (3 mL, 250 mg), silica gel (grade 634, 100–200 mesh, pore size 60 Å), Alumina B-super I, filtration tubes (3 mL) and 7 μm polydimethylsiloxane (PDMS, phase volume = 0.028 μL) solid phase micro-extraction (SPME) fibers were also purchased from Sigma Aldrich (St. Louis, MO). The silica gel and alumina powder were stored in a laboratory oven at 220 °C when not in use.

All labeled ($^{13}C_{12}$-PCBs, $^{13}C_{12}$ OH-PCBs), unlabeled PCBs, and OH-PCBs used in this study were purchased from Wellington Laboratories (Guelph, Canada). The PCB suite used for the bioaccessibility assay included both indicator (28, 52, 101, 138, 153, and 180) and dioxin-like (77, 81, 105, 114, 118,123, 126, 156, 157, 167, 169, and 189) PCBs. For each of the unlabeled PCBs, a structurally identical $^{13}C_{12}$-PCB was acquired for use as a surrogate standard and $^{13}C_{12}$-PCB 70 (2,3,4,5-Tetrachloro[$^{13}C_{12}$] biphenyl) was used as an internal standard. Concentrations of 4OH-PCB61, 4OH-PCB101, 4OH-PCB159, 5OH-PCB138, 4′OH-PCB 172 and 3′OH-PCB180 were measured in the digestive fluids to determine whether there was significant PCB degradation during the assay. Internal standards used for the OH-PCBs were: M4H 12 (3′,4′-Dichloro-4-[$^{13}C_{12}$] biphenylol), M4H 61 (2′,3′,4′,5′-Tetrachloro-4-[$^{13}C_{12}$] biphenylol), M4H 159 (2′,3,3′,4′,5,5′-Hexachloro-4-[$^{13}C_{12}$] biphenylol), and M4H 172 (2,2′,3,3′,4′,5,5′-Heptachloro-4-[$^{13}C_{12}$] biphenylol). The surrogate standard used for all OH-PCBs, was 2,2′,3,4,4′,5′- Hexachloro-3’-[$^{13}C_{12}$] biphenylol. The structure, log K_{ow}, molecular weight, and solubility (in DI water) of each

PCB is presented in Table S1 of the Supplemental Materials, and the relationship between the relevant PCBs and their hydroxylated degradation products is provided in Figure S1 of the Supplemental Materials.

2.2. Soil and house dust collection and characterization

The methods used to collect and characterize the soils and house dusts used for this study have been described previously (Starr et al., 2016). Briefly, 37 paired samples of soil and house dust were used. These soils and dusts were taken from archived samples that had been collected during a national survey of United States housing stock (Stout et al., 2009). The soils were collected from sites around the residences while the house dust samples were taken from used vacuum cleaner bags supplied by the study participants. The samples were sieved to <2 mm and characterized to determine percent moisture, pH, percent nitrogen, percent carbon, and percent sand (≤2.0 mm, > 0.05 mm), silt (≤0.05 mm ≥ 0.002 mm), and clay (<0.002 mm). Prior to use, the soils and house dusts were further sieved to <250 μm (soils), and <150 μm (dusts).

2.3. Screening for PCBs in soil and dust

Prior to performing the bioaccessibility assay, all soils and house dusts were screened to determine pre-existing concentrations of PCBs. To do this, 500 mg of each of the 37 soils and house dusts were extracted and analyzed using the methods described below.

2.4. Determination SPME equilibration time and K_{fw}

SPME fibers were used to measure free PCBs in digestive fluids following the bioaccessibility assay. To determine the required time for SPME equilibration, bottled replicates (n = 12), each containing 50 mL water, were spiked with 0.1 ng/mL PCBs. An SPME fiber was inserted into each bottle and the bottles were placed in a reciprocating water bath (27 °C, 100 rpm) for 24, 40, 64, or 168 h. At each time point, PCB concentrations on 3 SPME fibers and their associated water samples were measured using GC/MS. The fiber/water partition coefficients (K_{fw}) were calculated as the ratio of PCB on fiber (ng/mL) to PCB in water (ng/mL) at equilibration.

2.5. Spiking and aging of soils and house dusts with PCBs

All soil and dust samples (each in duplicate) were amended with the 18 unlabeled PCBs 1 week prior to performing the bioaccessibility assay. To do this, 500 mg soil or house dust were poured into 60 mL amber vials and the PCBs were added so that the mass of each PCB per sample was 50 ng (total solvent volume = 100 μL toluene:isooctane, v:v = 1:1). Acetone (2 mL) was then added to each bottle, then the bottles were briefly agitated to distribute the PCBs throughout the matrix. For quality control, each batch of six samples included one blank (500 mg soil or dust, spiked with 2.1 mL acetone). The uncapped samples and blank were stored in the dark at ambient conditions until used.

2.6. Bioaccessibility assay

The bioaccessibility assay was performed in duplicate on each of the 37 soil and house dust samples. The samples were grouped in batches of 6–7 (12–14 including duplicates) for the

assay and subsequent processing and analysis. The methods used to prepare the synthetic digestive fluids and perform the bioaccessibility assay (DIN, 19738) have been described previously (Starr et al., 2016). Briefly, the fortified and blank soils or house dusts were placed in amber bottles and a series of organic and inorganic compounds (dissolved in water) were added to mimic a sequential three compartment digestive model (saliva, gastric, and intestinal). For each compartment the pH was adjusted and the solution was equilibrated in a reciprocating water bath (37 °C, 200 rpm) as specified by DIN 19738 (saliva = 30 min, gastric = 2 h, intestinal = 6 h). Following the assay, the aqueous and sediment layers were removed and separated. The digestive fluids were poured back into the original bottle and SPME fibers were inserted. The sediments were dried overnight in a fume hood and the bottles were put back into the reciprocating water bath (37 °C, 100 rpm) to equilibrate the free PCBs with the SPME fibers. To monitor fiber performance, a bottle containing 50 mL water, 0.1 ng/mL each PCB and a used SPME fiber was also placed in the water bath with each batch and equilibrated with the samples.

2.7. Sample processing: PCBs in soil and house dust sediments

Surrogate standards for quality control (QC) were added to all soil and house dust sediments immediately prior to extraction. Since any hydroxylated species were expected to partition into the digestive fluids, OH-PCBs concentrations in the sediments were not measured. The steps used to extract and process the PCBs in soils and house dusts are shown in Figure S2. The PCBs were extracted using acetone: hexane (7.5:2.5, v:v) and each sample was extracted three times. For the first extraction, 5 mL of solvent was used, while 3 mL was used for both the second and third extraction. For each extraction, the samples were vortexed for 3 min, then centrifuged (2 min, 3000 rpm), and decanted into a 13 × 100 mm glass tube. The combined extracts were placed in a water bath (45 °C) and dried to near dryness under nitrogen.

After drying, 1 mL hexane was added to each tube and the tube was vortexed for 10 s. All samples were then filtered through a 0.45 μm polytetrafluoroethylene (PFTE) syringe filter and the sample tube was rinsed and filtered two additional times with 2 × 1 mL hexane. The volume of the filtered extracts was reduced to 1 mL and loaded onto 900 mg silica. The sample tubes were rinsed two times, each time with 1 mL hexane, and all rinsates were loaded onto the silica and collected. To ensure all PCBs were eluted, an additional 3 mL hexane was passed through the silica and collected.

After reducing the hexane volume to 1 mL, the samples were loaded onto alumina (1800 mg). These sample tubes were also rinsed two times, each with 1 mL hexane, and each rinsate was loaded onto the alumina. The samples were then eluted using 6 mL of 65% toluene in hexane. This eluant was reduced in a water bath (45 °C) to 500 μl. Hexane (500 μL) was added and the samples were loaded onto 250 mg graphitized carbon. The sample tubes were rinsed twice with 2 × 1 mL 65% toluene in hexane and each rinsate was loaded onto the graphitized carbon. The samples were eluted with 5 mL 65% toluene in hexane. The eluant volumes were reduced to 200 μL and 5.8 mL of 70% ethyl acetate in cyclopentane was added. The samples were passed through a styrene divinylbenzene (24 g) gel permeation, column (22.5 cm) using 70% ethyl acetate in cyclopentane as the mobile

phase. Following sample collection, 2 ng of the internal standard was added and the volume was reduced to 200 μL. The samples were transferred to autosampler vials and stored at −20 °C until analysis.

2.8. Sample processing: PCBs and OH-PCBs in synthetic digestive fluids

SPME fibers (freely dissolved PCBs) were removed from the digestive fluid and desorbed in 200 μL acetone in an autosampler vial. PCB concentrations were measured by GC/MS without additional processing.

PCBs (total PCBs) and OH-PCBs in the digestive fluids (50 mL) were extracted after removal of the SPME fiber and immediately following the addition of the surrogate standards (5 ng). The steps used to extract and process the PCBs and OH-PCBs in digestive fluids are presented in Figure S3. Methanol (20 mL) and hexane (10 mL) were added to the digestive fluid and the samples were vortexed for 0.5 min then centrifuged for 2 min at 3000 rpm. The hexane layer was transferred to a glass tube and the process was repeated two additional times. The extracts were placed in a water bath (45 °C) and dried to near dryness using nitrogen, then reconstituted to a volume of 1 mL with hexane.

The samples, in 1 mL hexane, were loaded onto 900 mg silica and the PCBs were eluted as fraction 1 using 4 mL hexane. The internal standard (2 ng) was added to fraction 1 and its volume was reduced to 200 μL. The sample was transferred to an autosampler vial and stored at −20 °C until analysis.

After replacement of the collection tube (fraction 2), the OH-PCBs were processed through the silica by first rinsing the sample tube with 2 mL of ethyl acetate and loading the rinsate onto the silica. Then, 4 mL of methanol was used to again rinse the sample tube and load OH-PCBs onto, and elute them from, the silica.

The samples (in fraction 2) were dried completely in a water bath (45 °C) using nitrogen, then re-dissolved in 2 mL methanol. The methanol (containing the OH-PCBs) was loaded onto 250 mg graphitized carbon and eluted with 4 mL of 20% toluene in methanol. The eluant was dried completely in a water bath (45 °C) using nitrogen then vortex partitioned using 1 mL of 30% methanol in water and 1 mL hexane. The hexane layer was removed and collected and the process was repeated two additional times with 1 mL fresh hexane being added prior to each partitioning. Following the final partitioning, the combined hexane layers were placed in a water bath (45 °C) and dried completely under nitrogen. The internal standards were added (50 ng) and the samples were reconstituted to 1 mL using 20% water in methanol, transferred to autosampler vials, and stored at −20 °C until analysis.

2.9. Sample analysis

Concentrations of individual PCB standards used for quantitation were 1, 10, 25, 50, 75 and 100 ng/mL. The PCBs were analyzed using an Agilent (Palo Alto, CA) model 6890N/5973 gas chromatograph/mass spectrometer (GC/MS) with a J&W Scientific (Folsom, CA) DB-5MS GC Column (30 m × 0.25 mm x 0.25 × μm). The injector temperature was 275 °C and the oven temperatures were: 120 °C for 0 min, ramped to 220 °C (50 °C/min), then ramped to 260 °C (3.5 °C/min). All chromatographic runs were 13.43 min and post run

temperatures were set to 305 °C for 2.0 min. The retention times and ions used to quantify and qualify the PCBs and PCB surrogates are presented in Table S2 of the Supplemental Materials.

OH-PCBs were analyzed using an Agilent (Palo Alto, CA) model 1100 liquid chromatograph (LC) coupled to AB Sciex (Ontario, Canada) model API4000 tandem mass spectrometer(MS/MS) with electrospray ionization. The LC-MS/MS conditions and settings used for this study are shown as in Table S3 of the Supplemental Materials.

2.10. Method validation and method limits of detection (MDL) and quantitation (MQL)

The efficiency of the methods used to extract, process, and analyze PCBs in soil and house dust, and PCBs and OH-PCBs in digestive fluid were evaluated using samples that were demonstrated during screening to be PCB and OH-PCB free. Percent recovery of PCBs from soils and house dusts was determined by spiking, eight, 500 mg samples (each matrix) with the suite of PCBs at one of two levels; four at 10 ng each PCB/g matrix, and four at 30 ng each PCB/g matrix. Percent recovery of PCBs and OH-PCBs in digestive fluid was measured by spiking four replicates of the fluid (50 mL each) with 50 ng of each of the 18 PCBs and 6 hydroxy PCBs. The samples were then extracted, processed and analyzed using the finalized methods and the percent recovery of each PCB and OH-PCB was calculated.

The MDL and MQL for each PCB was estimated using native concentrations of PCBs in 17 soil and 17 house dust samples. The samples were extracted, processed, and analyzed using the finalized method then the signal to noise ratio of each peak in each sample was measured and the concentration was calculated. For each matrix, the MDL for individual PCBs was estimated as the (sum (3 × concentration/(signal/noise))/17) and the estimated MQL for each PCB was (10 × MDL/3).

l2.11. Data analysis

The bioaccessibility of each PCB was defined as: ((mass $PCB_{digestive\ fluid}$)/(mass $PCB_{digestive\ fluid}$ + mass $PCB_{sediment}$)). For each sample, the bioaccessibility of both replicates were calculated then averaged to obtain a final value. Variables considered for inclusion into the models as bioaccessibility predictors included the soil and house dust physicochemical properties, and the log K_{ow} values of the PCBs (U.S.EPA, 2000). However, soil and dust properties were limited to only those which were individually correlated ($p \leq 0.05$) with bioaccessibility using regression Pearson product-moment correlation. Data were analyzed using SAS 9.4 (SAS Institute Inc., 2015) and the distributions of the soil and dust components were compared using a Student's t-test with significant differences noted where $p < 0.05$. The final models were constructed using stepwise multiple linear regression (PROC REG) using backward elimination that retained only variables that were statistically significant ($p < 0.05$).

3. Results and discussion

3.1. Method validation and MDL/MQL

The method validation (percent recovery from spiked matrix) and MDL/MQL results for PCBsand OH-PCBs are shown in Table S4 of the Supplemental Materials. Mean recovery (±1 standard deviation) of PCBs from soil ranged from 72 ± 4 to 88 ± 7%, and 67 ± 7 to 90 ± 7% from dust. For both soil and dust, PCB recovery improved slightly as PCB mass increased, and this was likely a result of greater evaporative loss of the lighter PCBs during the several drying steps required for sample processing. The recoveries (mean ± 1 standard deviation) of the individual PCBs from digestive fluid ranged from 74 ± 4 to 91 ± 1% and did not appear to have the mass and percent recovery association. This was probably because fewer drying steps were needed to process these samples. Mean recovery (±1 standard deviation) of the OH-PCBs from digestive fluid ranged from 73 ± 3 (4OH-PCB 101) to 103 ± 4% (3′OH-PCB 180) while The MQL's of the PCBs ranged from 0.61 ng/g (PCB 180 in soil) to 4.05 ng/g (PCB 105 in dust).

3.2. Screening for PCBs in soil and house dust stocks

Descriptive statistics for native PCBs in the stocks of soils and house dusts are presented in Table S5 of the Supplemental Materials. The PCBs were detected more frequently in dust samples (45%) than they were in the soil samples (21%), and the detection frequency of the indicator PCBs was higher in both soil (40%) and dust (85%), than it was for the dioxin-like PCBs (11% soil, 25% dust). Maximum concentrations of both indicator (177 ng/g) and dioxin-like PCBs (40 ng/g) in the house dust samples, were generally higher than in the soils where maximum concentrations of all indicator and dioxin-like PCBs were ≤6 ng/g and 2 ng/g, respectively.

3.3. Determination SPME equilibration time and K_{fw}

The log K_{fw} at 24, 40, 64, and 128 h are provided in Table 1. The PCB concentrations in water and on the SPME fibers used to calculate the log K_{fw}'s at each time point are provided in Table S6 of the Supplemental Materials. The log K_{fw} of each PCB generally increased as a function of time and at 168 h were an average of 4.6% higher than at 24 h. However, as shown in Table S6, peak fiber concentrations of individual PCBs occurred at times ranging from 24 h to 64 h, after which, their concentrations decreased. In contrast, the rate of loss of most of the PCBs from water was relatively constant. While these changes made estimation of the K_{fw}'s difficult, all PCBs had reached peak fiber concentrations by 64 h, and therefore, during the study, all SPME fibers were equilibrated for 64 h in the digestive fluids.

3.4. Soil and dust characteristics

The physicochemical properties of the soils and house dusts that were evaluated for this study have been described previously (Starr et al., 2016). The median and range for each characterized variable of the soils and dusts is provided in Table 2. Relative to the soils, the dusts were drier with a lower mean percentage of sand, while the soils had a higher mean proportion silt and were more acidic with lower percentages of carbon and nitrogen ($p \leq$

0.05). The percentages of clay (<0.002 mm) in the soil and house dust particles were not statistically different ($p \leq 0.05$).

3.5. SPME results

No measurable concentrations of PCBs were detected on any of the SPME fibers. This meant that concentrations of freely dissolved PCBs in the digestive fluid samples were ≤0.47 ng/mL (PCB 28) and ≤0.05 ng/mL (all other PCBs). The lack of freely dissolved PCBs is consistent with the results an in vitro soil bioaccessibility assay (Oomen et al., 2000) and suggests that the PCBs in the digestive fluid were sorbed to proteins or trapped in bile salt micelles. This is supported by in vitro studies of Dulfer et al. (1996), and Oomen et al. (2001)who demonstrated both bile salts and digestive proteins contribute to intestinal absorption of PCBs. According to Oomen et al. (2001), proteins and bile salt micelles function as carriers and transport, then desorb, hydrophobic compounds across the unstirred water layer that is adjacent to the enterocytes. The authors further propose that a lowering of the pH in the unstirred water layer may release the micelle trapped compounds and that protein digestion near the enterocytes may also release sorbed compounds. Bioavailability studies also indicate that the percent of desorbed PCBs entering the circulatory system is greater than would be expected given the negligible amounts that are freely dissolved. For example, Fries et al. (1989), found, that for aged PCB amended soil fed to rats, bioavailability ranged from 67 to 80%. Van Eijkeren et al. (2006), found that chickens fed contaminated soilabsorbed between 40 and 60% of the PCBs, and Delannoy et al. (2015), showed that soil sorbed PCBs fed to piglets were >45% bioavailable (relative to PCBs fed to the animals using a corn oil vehicle).

3.6. Bioaccessibility of PCBs in soil and house dust

No OH-PCBs were detected in any of the digestive fluid samples. This demonstrates that neither the method used to fortify the soils and house dusts, or the bioaccessibility assay itself, caused a measurable hydrolysis of the PCBs.

Soil and house dust data were modeled separately because their individual physicochemical properties were not correlated, and except for percent clay, were not statistically different (Starr et al., 2016). In addition, while particle size is a well-defined term in soil science, its applicability to characterization of house dust is less understood. Finally, while soil formationresults from long term environmental processes, much of the composition of house dusts is the result of short term episodic human activities.

The mean recovery of each PCB surrogate standard (by batch) is provided in Table S7 of the Supplemental materials. The mean bioaccessibility values of the 18 PCBs in individual soil and house dust samples are provided in Table S8 of the Supplemental Materials. Considering all soil and house dust samples; the bioaccessibility of the PCBs in soil ($\bar{x} = 65 \pm 16\%$) was greater ($p < 0.001$) than that of the PCBs in house dust ($\bar{x} = 36 \pm 14\%$). The mean PCB soil bioaccessibility was greater than the 35% and 9% calculated (in vitro, fasting) by Oomen et al. (2000), and Hack and Selenka (1996), respectively. The mean PCB bioaccessibility in house dust was greater than the 27% (in vitro, fasting) found by Ertl and Butte (2012).

Considering this study and the in vitro studies cited above; the constituents of the bioaccessibility test systems were similar, and probably not an important factor in explaining the differing rates of PCB mobilization. While the ratio of digestive fluid to matrix varied between the studies, higher relative proportions of digestive fluids did not correspond to increased PCB bioaccessibility. Differences in the PCB congeners used in each of the studies were also not explanatory since there was considerable overlap of the identities of the PCBs and their log K_{ow} values. Although differences in the physicochemical properties of the soils and house dusts used in each of the cited studies may have produced inter-study differences in bioaccessibility estimates, dissimilarities in the characterizations of these properties precluded an analysis of their impact.

PCB log K_{ow} did not correlate ($p > 0.05$) with PCB bioaccessibility for either the soil or house dust samples and this is consistent with the results of an in vitro PCB soil-digestive fluid partitioning study by Oomen et al. (2000). However, extrapolation of this result to other source materials may be inappropriate. Schacht et al. (2016), and Dulfer and Grovers (1995)demonstrated a positive correlation between PCB congener chlorination and partitioning from purified sorbent materials into micelle solutions and Beckingham and Ghosh (2017)showed that the extent of PCB partitioning into digestive fluids was congener specific for black carbon enriched substrates such as coal and biochar, but not for wood or plastic..

Since log K_{ow} of the individual PCBs did not explain the variability ($p > 0.05$) of either the soil or house dust data, the mean bioaccessibility of all PCBs in each sample was used to represent that sample. Individual soil and dust properties were then analyzed using simple linear regression to determine which characteristics were related to bioaccessibility, and therefore be considered for inclusion in the final statistical models. Table 3 shows the physicochemical properties of the soils and dusts that were correlated ($p \leq 0.05$) with PCB bioaccessibility and Table 4 shows the final models after elimination of collinear variables.

Of the soil physicochemical properties, percent organic carbon was the most highly correlated with bioaccessibility ($r = 0.80$, slope = −5.1). Carbon is commonly understood to sequester hydrophobic organic compounds and the negative correlation of percent carbon and PCB bioaccessibility is consistent with the results of an in vitro study (Beckingham and Ghosh (2017), and in vivo soil feeding (Delannoy et al., 2014a, 2014b, 2015) and soil sorption (Paya-Perez et al., 1991) studies. According to (Delannoy et al., 2014a, 2014b, 2015), variations in PCB bioavailability observed when using different soils may be attributable to the forms of organic carbon (diffuse or condensed) found among those soils. For example, humic acids reduce PCB bioavailability more than fulvic acids (Delannoy et al., 2014b), and it is possible that inter-soil organic matter compositional differences, which were not assessed in our study, could further explain carbon-related variability in bioaccessibility.

In soil, increases in percent nitrogen and moisture were correlated with lower PCB bioaccessibility. However, as shown in Table S9 of the Supplemental Materials, both were also correlated with carbon (nitrogen $r = 0.87$, moisture $r = 0.60$) and therefore collinear, rather than independent bioaccessibility determinants. This interdependence excluded both

variables from the final model. However, the nitrogen-carbon correlation suggests that much of the carbon in the soil samples may have been present in the form of diffuse humic materials (Paya-Perez et al., 1991; Hudson. 1994; Rawls et al., 2003) rather than more purified carbon. It also implies that nitrogen may be a suitable carbon proxy for estimation of PCB bioaccessibility in soils with high proportions of humic materials relative to condensed carbon. Use of moisture content as a carbon proxy however, should be viewed more cautiously since humic free clays can hold large amounts of water.

For house dust, simple linear regression showed a positive relationship with PCB bioaccessibility for moisture ($p = 0.0009$), pH ($p = 0.022$), and clay content ($p < 0.0001$), and a negative relationship with carbon ($p = 0.0003$), sand ($p = 0.0004$), and silt ($p = 0.035$). However, there was a high degree of collinearity ($p \leq 0.05$) among these properties (Table S9 of the Supplemental Materials). For example, the pH and the percent moisture and carbon in dust were all correlated with both percent silt and percent clay. And the pH and percent nitrogen, silt, and clay were correlated with percent carbon. In contrast to soil, nitrogen was correlated with carbon ($p = 0.007$), but not with PCB bioaccessibility ($p = 0.248$).

When analyzed using simple linear regression, PCB bioaccessibility-percent silt were inversely related ($p = 0.035$) while the PCB bioaccessibility-percent clay relationship was positive ($p < 0.0001$). This, in conjunction with the positive carbon-silt ($p = 0.025$) and negative carbon-clay ($p = 0.005$) relationships, shows that higher levels of silt were associated with increased carbon levels and reduced bioaccessibility, while higher clay content was associated with reduced carbon levels and increased bioaccessibility. This supports the importance of carbon as a central determinant of PCB bioaccessibility and is consistent with the findings of Yu et al. (2012, 2013) who evaluated the relative importance of physicochemical properties of dust collected from air conditioning filters in determining the post ingestion bioaccessibility of polybrominated diphenyl ethers.

Clay content explained a greater proportion of the bioaccessibility variability than did carbon (Table 4). Therefore, clay may have had an explanatory contribution that was independent of carbon. An inverse relationship between the relative surface area of the particle and mass of sorbed organic contaminant has been observed to occur for native pesticides and polycyclic aromatic hydrocarbons (Lewis et al., 1999). But the applicability of those results to this study is uncertain because these samples were recently fortified using an organic solvent as the delivery vehicle. It is possible that a disproportionate percentage of PCBs adhered to the clay sized fraction during the spiking procedure, but this relationship was not observed with the soil samples. Alternatively, the moisture content of the respective particle sizes may have contributed to the increase in bioaccessibility associated with the clay fraction. Percent moisture was correlated positively with PCB bioaccessibility and clay content, but had a negative correlation with silt. Therefore, compared to silt, the higher clay moisture content may have reduced the penetration of the hydrophobic PCBs into particle pores or otherwise interfered with the interaction of PCBs and available sorption sites.

The final models (Table 4) show that percent carbon is a common determinant of PCB bioaccessibility for both soil and house dust while percent clay was a significant contributor to only the dust model. This suggests that there are soil and dust commonalities but perhaps

more importantly, differences. Fergusson and Kim (1991); Calabrese and Stanek (1992); Layton and Beamer (2009) demonstrated that soils are a component of house dust, however, it is likely that there are source related differences between the particles in the different size fractions. Nearby soils and indoor sources may have contributed more to the relatively large sand fraction than to the smaller size fractions which may emanate from more distant sources. It is also important to emphasize that there are almost certainly compositional differences between soil and house dust particles in the same size fraction. This may mean that the soil clays in the study samples were significantly different than the house dust clays and these differences affected bioaccessibility.

4. Conclusion

This study demonstrated a quantitative relationship between increases in the carbon content of soils and house dusts, and reductions in PCB bioaccessibility. Since the carbon content of the house dusts was generally higher that of the soils, house dust PCB bioaccessibility was lower than that of soil. In contrast to the soils, the clay content of the house dusts was also useful in predicting PCB bioaccessibility. While these simplified models may be used to estimate PCB bioaccessibility, separate soil and house dust models should be used.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Disclaimer

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Table 1.

Equilibration of SPME fibers in DI water.

PCB	log K_{fw}			
	24 h	40 h	64 h	168 h
28	4.85 ± 0.12[a]	4.48 ± 0.39	4.40[b]	4.30[a]
52	5.49 ± 0.08	5.42 ± 0.02	5.37 ± 0.11	5.30 ± 0.21
101	5.97 ± 0.03	6.01 ± 0.05	6.05 ± 0.07	6.02 ± 0.08
81	5.70 ± 0.05	5.82 ± 0.11	5.73 ± 0.03	5.93 ± 0.04
77	5.63 ± 0.04	5.70 ± 0.09	5.63 ± 0.05	5.73 ± 0.10
123	5.89 ± 0.04	5.98 ± 0.04	5.99 ± 0.03	6.23 ± 0.09
118	5.97 ± 0.05	6.05 ± 0.02	6.08 ± 0.01	6.15 ± 0.05
114	5.95 ± 0.09	6.03 ± 0.02	6.05 ± 0.07	6.11 ± 0.08
153	6.08 ± 0.05	6.27 ± 0.07	6.37 ± 0.08	6.47 ± 0.07
105	5.89 ± 0.06	6.01 ± 0.05	6.04 ± 0.02	6.09 ± 0.19
138	6.07 ± 0.05	6.23 ± 0.05	6.31 ± 0.01	6.37 ± 0.07
126	5.88 ± 0.05	6.01 ± 0.02	6.00 ± 0.06	6.07 ± 0.09
167	6.04 ± 0.06	6.17 ± 0.03	6.27 ± 0.03	6.40 ± 0.07
156	5.99 ± 0.05	6.22 ± 0.18	6.33 ± 0.18	6.45 ± 0.16
157	6.03 ± 0.09	6.17 ± 0.05	6.26 ± 0.05	6.48 ± 0.25
180	6.10 ± 0.06	6.26 ± 0.02	6.42 ± 0.03	6.66 ± 0.14
169	5.98 ± 0.09	6.11 ± 0.06	6.16 ± 0.08	6.35 ± 0.11
189	6.09 ± 0.05	6.21 ± 0.04	6.31 ± 0.02	6.61 ± 0.10

[a] 1 standard deviation.

[b] Estimated using data from 24 to 40 h.

Table 2.

Soil and house dust physicochemical properties.

	mean ± stdev		min - max	
	soil	**dust**	**soil**	**dust**
% moisture	15 ± 8	3 ± 5	1–40	1–29
pH	6 ± 1	8 ± 2	4–8	5–12
% nitrogen	0.2 ± 0.1	6 ± 7	<0.1–0.5	0.0–45
% carbon	3 ± 2	19 ± 7	0.5–11	2–33
% sand[a]	49 ± 24	31 ± 14	6–89	4–57
% silt[b]	29 ± 19	44 ± 16	2–68	13–72
% clay[c]	22 ± 10	26 ± 19	5–47	0.0–77

[a] % particle size fraction <2.0 mm, > 0.05 mm.

[b] % particle size fraction ≤0.05 mm, ≥ 0.002 mm.

[c] % particle size fraction <0.002 mm.

Table 3.

Soil and house dust physicochemical properties correlated with PCB bioaccessibility (n = 37).

statistic	soil			dust					
	%carbon	%nitrogen	%moisture	%carbon	%sand[a]	%silt[b]	%clay[c]	%moisture	pH
r	0.81	0.74	0.49	0.56	0.55	0.35	0.70	0.52	0.37
slope	−5.1	−102	−0.9	−1.2	−0.6	−0.3	0.5	1.4	3.3
p -value	<0.0001	<0.0001	0.002	0.0003	0.0004	0.035	<0.0001	0.0009	0.022

[a] % particle size fraction <2.0 mm, > 0.05 mm.

[b] % particle size fraction ≤0.05 mm, ≥ 0.002 mm.

[c] % particle size fraction <0.002 mm.

Table 4.

Final regression model for in vitro bioaccessibility of PCB sorbed to soils and house dust.

Soil						
Variable	DF[a]	Parameter Estimate	Standard Error	t Value	Pr > |t|	Partial R^2
intercept	1	80.76	2.52	32.12	<0.0001	
%carbon	1	−5.11	0.64	−8.03	<0.0001	0.648
House dust						
Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|	Partial R^2
intercept	1	37.56	6.81	5.51	<0.0001	
%clay	1	0.41	0.10	4.36	0.0001	0.486
%carbon	1	−0.65	0.27	−2.41	0.0216	0.075

[a]Degrees of freedom.