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Sediment pore water distribution coefficients of PCB congeners in enriched black carbon sediment

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Abstract

More than 2300 sediment pore water distribution coefficients ($K_{PCBi\ ds}$) of 93 polychlorinated biphenyls (PCBs) were measured and modeled from sediments from Indiana Harbor and Ship Canal. $K_{PCBi\ ds}$ were calculated from previously reported bulk sediment values and newly analyzed pore water. PCBs in pore waters were measured using SPME PDMS-fiber and PCB ranged from 41 to 1500 ng L⁻¹. The resulting $K_{PCBi\ ds}$ were ~ 1 log unit lower in comparison to other reported values. A simple model for the $K_{PCBi\ d}$ consisted of the product of the organic carbon fraction and the octanol-water partition coefficient and provided an excellent prediction for the measured values, with a mean square error of 0.09 ± 0.06 . Although black carbon content is very high in these sediments and was expected to play an important role in the distribution of PCBs, no improvement was obtained when a two-carbon model was used.

Keywords

PCBs; Sediment pore water distribution coefficients; Organic carbon; Black carbon; Aliphatic compounds

1 Introduction

The concentration ratio of hydrophobic organic compounds (HOCs) between bulk and the freely-dissolved sediment pore water at equilibrium is the sediment pore water distribution coefficient. This parameter is used to determine bioavailability of HOCs. It is also a key component of fate and transport models of HOCs in sediment and aquatic systems, in addition to being utilized for risk assessments and remediation decisions.

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Appendix A. Supplementary Data

Supplementary data related to this article can be found, in the online version, at

Measuring the freely-dissolved sediment pore water concentration of these chemicals, especially in environmental conditions (pg L^{-1} to ng L^{-1} level) is complex. The main contributions to this complexity are very low volume of interstitial water, the presence of colloids and dissolved organic matter and low water solubility of the HOCs (Booij et al., 2003; Hermans et al., 1992; Jonker and Smedes, 2000). With the development of passive sampler techniques to measure the freely-dissolved sediment pore water concentration of HOCs, the problems mentioned above are reduced (Cornelissen et al., 2008; Gschwend et al., 2011; Hawthorne et al., 2006; Hawthorne et al., 2011; Jonker and Koelmans, 2001; Mayer et al., 2003).

Regardless of the improvement in sediment pore water distribution coefficient measurements from introduction of passive samplers, prediction models are still necessary for estimating the fate and transport of HOCs. Many sediment pore water distribution models have been developed and tested, including the two-carbon model that considers the role of both organic and black carbons. However, selecting a particular model has been shown to be challenging. For example, Werner et al. (2010) showed an improvement in the distribution coefficient prediction when a two-carbon model was used. Indeed, others have shown that black carbon in natural systems strongly affects the sediment pore water distribution of HOCs (Cornelissen et al., 2005; Jonker and Koelmans, 2002). Conversely, Hawthorne et al. (2011) concluded that the two-carbon model did not improve the prediction against the single carbon model for over more than 1900 measured sediment pore water distribution coefficients for PCBs. Hence, they did not recommend the two-carbon model to predict the sediment pore water distribution coefficients.

The purpose of the current work was to determine the best model for the sediment pore water distribution coefficients of PCB congeners from the Indiana Harbor and Ship Canal (IHSC) sediments, an industrial harbor of Lake Michigan that is currently undergoing navigational dredging. Previous work has shown that the contaminated sediments are a source of PCBs into the overlying water ($\sim 4 \text{ kg yr}^{-1}$ of PCB) (Martinez et al., 2010). The sediment pore water distribution coefficient is a key parameter used to estimate the soluble release of PCBs from the sediment into the water.

To determine the distribution coefficients, poly-dimethylsiloxane (PDMS) coated fibers were used as passive samplers to extract freely-dissolved PCB congeners from sediment pore water. Bulk PCB sediment concentrations were already determined (Martinez and Hornbuckle, 2011). Several published sediment pore water distribution coefficient models were tested against the measured values. Due to the high values of black carbon found in the sediments ($\sim 30\%$ of total organic carbon), special attention was given to the role of black carbon in the sediment pore water partitioning. Therefore and in addition to using published black carbon normalized partition coefficient models, a set of experiments was developed to directly measure and model the black carbon normalized partition coefficients from these sediments. The best performing models were calibrated with the IHSC's data to observe the effect of site-specificity in the models' prediction.

2 Materials and Methods

2.1 Sediment Locations and Sampling

Two 4-meter sediment cores were collected from IHSC in East Chicago, Indiana in May 2009. Core 1 was segmented every 0.15 m and Core 2 every 0.31 m. Details on the sampling and handling, as well as the concentration of PCBs in the bulk sediment ($C_{PCB_{i,s}}$), total organic carbon (TOC), organic carbon (OC) and black carbon (BC) measurements have been previously reported in Martinez and Hornbuckle (2011). Briefly, $C_{PCB_{i,s}}$ ranged from 1700 to 90 000 (ng g^{-1} dw), TOC from 7% to 24%, OC from 4% to 15% and BC from 3%

to 10%. These parameters are presented in Table S1, Supplementary Data. In addition, the oxidation reduction potential (ORP) was measured in the field for each sediment section using a Hanna Instruments Redox/pH combination meter (Table S1).

2.2 Freely-Dissolved Sediment Pore Water Determination

New glass fibers manufactured by Fiberguide Industries, Inc. (Stirling, NJ) with a 210 μm inner diameter and a 10 μm coating of PDMS were used as passive samplers to measure PCB freely-dissolved sediment pore water concentrations ($C_{PCBi\ pw}$) (Lu et al., 2011; Mayer et al., 2000). Prior to any experiment, the fiber was cleaned by sonication in hexane for at least 45 min, followed by four rinses with acetone and then rinsed with deionized water (Lampert et al., 2011). Each slice from both cores was manually homogenized and a subsample of ~ 15 g of wet sediment was used to determine the PCB freely-dissolved sediment pore water concentration. Thirty pieces of clean PDMS coated fiber, each 0.01 m long, were placed in a clean 25 mL glass vial with Teflon liner cap, with sediment and deionized water (~ 5 g), and tumbled (8 rpm and 25 $^{\circ}\text{C}$) for at least 12 days.

Preliminary uptake experiments from sediments were used to ensure that 12 days was sufficient to achieve equilibrium between pore water and PCBs in the fibers, at least for PCB congeners up to PCBs180+193 ($\log K_{PCBi\ 180+193\ OW} = 7.36$, Hawker and Connell (1988)) (Figure S1). PCB mass as well as individual congeners in the fiber were used as indicator of equilibrium. No significant differences ($p < 0.05$) were found for the total and individual PCB masses between day 8 and day 32 of the uptake experiments. Freely-dissolved sediment pore water concentration of PCBs (ng L^{-1}) was determined according to $C_{PCBi\ pw} = m_{PCBi\ f} / (V_f \times K_{PCBi\ f/w})$, where $m_{PCBi\ f}$ is the mass in the fiber for the i^{th} PCB (ng), V_f is the polymer fiber volume (L) and $K_{PCBi\ f/w}$ is the fiber–water equilibrium partitioning coefficient for the i^{th} PCB (dimensionless). The latter was obtained from Lu et al. (2011) ($\log K_{PCBi\ f/w} = 1.06 \times \log K_{PCBi\ OW} - 1.16$, $R^2 = 0.94$), where the octanol-water partition coefficients ($K_{PCBi\ OW}$) were from Hawker and Connell (1988).

2.3 PCB Analysis

After the fibers were removed from the sediment, the fiber was rinsed and wiped with a laboratory tissue to remove any particles, placed into a GC vial with an insert, and 100 μL of hexane was added. A mass of 50 ng of PCB14 (3,5-dichlorobiphenyl), 20 ng of PCB30-d5 (2,4,6-trichlorobiphenyl-2',3',4',5',6'-d5, deuterated), 50 ng of PCB65-d5 (2,3,5,6-tetrachlorobiphenyl-2',3',4',5',6'-d5, deuterated), 50 ng of PCB166 (2,3,4,4',5,6-hexachlorobiphenyl) and 20 ng of PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) were added as internal standards. PCB calibration standards were purchased from AccuStandard (New Haven, USA) and deuterated compounds from CDN Isotopes (Quebec, Canada). PCB quantification was carried out using a modification of US EPA method 1668C (USEPA, 2010) with a tandem mass spectrometer GC/MS/MS (Quattro Micro GC, Micromass MS Technologies) in multiple reaction monitoring mode, detecting all 209 congeners in 161 individual or coeluting congener peaks.

2.4 Distribution Models

A set of distribution models for predicting the sediment pore water distribution coefficient ($K_{PCBi\ d}$, L kg^{-1}) was tested against the values measured in this study. We prioritized models that have been used for PCBs and some of them specifically tested in anthropogenically impacted sediments. In addition, we selected models with diverse chemical sorbents and different sorption theory behind them. We also looked at the effect of using TOC or OC as the phase of interest (Arp et al., 2009). Thus we calculated the distribution coefficient for both OC and TOC and then multiplied by the respective phase of interest (e.g. $K_{PCBi\ d} = K_{PCBi\ OC} \times f_{OC}$), except for Raoult's law, where OC was not

considered. For the purpose of simplicity, only the organic carbon normalized partition coefficient relationships are shown below in the equations. Some of the models were also used to predict the black carbon normalized partition coefficients.

- i. One-parameter linear free energy relationships (OP-LFERs). This model assumes that the majority of the sorption is due to the presence of organic carbon in the sediment/soil. We tested the following models:

$$\log K_{PCBi\ OC} = 0.94 \times \log K_{PCBi\ OW} - 0.42 \quad (1)$$

$$\log K_{PCBi\ OC} = 0.74 \times \log K_{PCBi\ OW} + 0.15 \quad (2)$$

where $K_{PCBi\ OC}$ is the organic carbon normalized partition coefficient for the i^{th} PCB ($\text{L kg}^{-1} \text{ oc}$), $K_{PCBi\ OW}$ is the octanol-water partition coefficient for the i^{th} PCB (L kg^{-1}). The first model was developed from sediment/soil that did not show high sorption contribution from black carbon (Nguyen et al., 2005). Conversely, the second model published by Schwarzenbach et al. (2003) has been used in sediments with high values of BC (Hawthorne et al., 2011) or with an important BC sorption contribution (Werner et al., 2010). To model the black carbon normalized partition coefficient ($K_{PCBi\ BC}$) we used the OP-LFER published by Werner et al. (2010):

$$\log K_{PCBi\ BC} = 0.91 \times \log K_{PCBi\ OW} + 1.4 \quad (3)$$

- ii. Poly-parameter linear free energy relationships (PP-LFERs) which account for specific and non-specific interactions between the chemical and the sorbent phase were also tested. The general PP-LFER equation is:

$$\log K_{PCBi\ OC} = e \times E + s \times S + a \times A + b \times B + v \times V + c \quad (4)$$

where E , S , A , B , and V are the compound specific parameters, and e , s , a , b , v and c depend on the difference in chemical properties between water and the sorbents (Arp et al., 2009; Endo et al., 2008; Nguyen et al., 2005). Eleven carbonaceous phases were tested. The PP-LFER models were also used to predict the black carbon normalized partition coefficient.

- iii. Raoult's law has also been used to determine the partition coefficient of PCBs from TOC and coal tar (Arp et al., 2009; Endo et al., 2008; Hawthorne et al., 2011):

$$\log K_{PCBi\ TOC} = -\log(S_L^* \times MW_{TOC}) \quad (5)$$

where S_L^* is the subcooled saturated molar water solubility for the i^{th} PCB ($\text{mol L}_{\text{water}}^{-1}$), and MW_{TOC} is the molar weight of the sediment's total organic phase ($\text{g}_{\text{TOC}} \text{ mol}^{-1}$). The subcooled saturated molar water solubilities were obtained from van Noort et al. (2010). A value of $223 \text{ g}_{\text{TOC}} \text{ mol}^{-1}$ was employed (Arp et al., 2009; Hawthorne et al., 2011).

- iv. To investigate only the molecular structure and size of the PCB effect on the partition coefficients, a quantitative-structure activity relationship (QSAR) that only included the number and position of the Cl groups from the PCB molecule were tested (Arp et al., 2009; Hawthorne et al., 2011):

$$\log K_{PCBi\ OC} = 0.53 \times (N_{Cl} - 0.5 \times N_{ortho-Cl}) + 5.00 \quad (6)$$

where N_{Cl} is the total number of chlorines and $N_{ortho-Cl}$ is the number of ortho-chlorines. Black carbon normalized partition coefficients were also predicted using this model.

- v. Two-carbon model. This model considers the partition into organic carbon together with adsorption onto black carbon (Accardi-Dey and Gschwend, 2002):

$$K_{PCBi\ d} = f_{OC} \times K_{PCBi\ OC} + f_{BC} \times K_{PCBi\ BC} \times C_{PCBi\ pw}^{(n_{Fi} - 1)} \quad (7)$$

where f_{OC} is the OC fraction (kg OC kg^{-1}), f_{BC} is the BC fraction (kg BC kg^{-1}), $K_{PCBi\ BC}$ is the BC-normalized partition coefficient for the i^{th} PCB ($\text{ng g}^{-1}_{\text{BC}}$) (ng mL^{-1}) $^{-n_{Fi}}$, $C_{PCBi\ pw}$ is the freely-dissolved sediment pore water concentration for the i^{th} PCB (ng L^{-1}) and n_{Fi} is the Freundlich exponent for adsorption onto BC for the i^{th} PCB. The $K_{PCBi\ BC}$ values were obtained from Eqs (3), (4) and (6), as well as the models developed here.

2.5 Black Carbon Sediment Experiments

In addition to using different published BC-normalized partition coefficients for PCBs ($K_{PCBi\ BC}$) in the two-carbon model (Eq (7)), a set of experiments were carried out to directly measure $K_{PCBi\ BC}$ s. Details of the experiments, quality assurance and control (QA/QC) and results are described in the Supporting Data. Briefly, sediment was chemically oxidized removing the OC fraction, while preserving the BC fraction. This chemical method has been used to measure BC in sediments (Grossman and Ghosh, 2009; Werner et al., 2010) as an alternative method to the thermal oxidation methods (Gustafsson et al., 1997). However, this chemical method has not been used previously to determine the $K_{PCBi\ BC}$. Bulk as well as freely-dissolved pore water concentrations were measured in the treated sediments. These measurements enabled us to determine $K_{PCBi\ BC}$ s.

2.6 Data and Statistical Analyses

Mean square error (MSE) and individual differences between measured and predicted log $K_{PCBi\ d}$ were used to evaluate the distribution models. Prediction error was defined as the difference between the measured and the predicted values. MSE was calculated when congeners were present in more than 3 samples in both the bulk and the pore water of the same sediment core section (Matlab R2012a).

2.7 QA/QC

For every 10 pore water samples, a blank sample was included that consisted of a clean fiber (30 pieces of 0.01 m) and deionized water. Congeners PCB68, PCBs85+116+117 and PCB209 were detected in those blanks and were removed from further consideration in the dataset. Triplicates of five different sediment sections of freely-dissolved pore water concentrations yielded a relative standard deviation of 19%.

Sixteen sediment sections from Core 1 and all 15 sections from Core 2 were used for determination of $K_{PCBi\ d}$. Ninety-three individual/coeluting congeners were evaluated, all of which were detected at a frequency of 25% or greater. This subtraction only reduced the total $C_{PCBi\ pw}$ by < 7%. In total, 2326 $K_{PCBi\ ds}$ values were measured and compared with the different models.

3 Results and Discussion

3.1 Freely-Dissolved Sediment Pore Water Concentrations

Freely-dissolved sediment pore water concentrations of 93 PCB congeners were measured in 31 sediment samples. All PCB congeners were not detected in every sample. The pore water

PCB concentrations ranged from 63 to 1500 ng L and 41 to 800 ng L⁻¹ for cores 1 and 2, respectively (Figure 1). Mono- to hepta- chlorinated congeners were detected (PCB1 to PCB187). Individual or coeluting congeners ranged from 0.0 to 240 ng L⁻¹. Individual concentrations of each congener are shown in Table S2. A very similar pattern in vertical distribution was found for C_{PCBs} and $C_{PCB\ pw}$ in both cores. Indeed, both the linear and loglog correlations between PCBs in bulk sediment and pore water for each core yielded $R^2 > 0.92$. Both cores showed higher concentrations at depth, presumably associated with active sources in the past, with lower concentrations at the surface. The near surface concentrations were largely independent of depth in the core, suggesting either vertical mixing in the surface layer or continuing low level sources.

3.2 Measured Sediment Pore Water Distribution Coefficient

At least 7 $K_{PCBi\ ds}$ were measured for each congener, with a mean per congener of 25 values. Individual log $K_{PCBi\ d}$ values ranged from 2.0 to 4.0, 6.2 to 7.1 for PCB2 and PCBs180+193, respectively. A unique characteristic of our measured values is that they are ~1 log unit lower than Arp et al. (2009), Hawthorne et al. (2011) and Werner et al. (2010) have reported. This finding is quite unexpected because of the high carbon content for these sediments, which initially would have suggested higher $K_{PCBi\ ds}$. Log $K_{PCBi\ ds}$ of selected congeners from cores 1 and 2 are plotted in Figure 1.

Interestingly, we found a strong log-log correlation between the individual measured $K_{PCBi\ d}$ and $K_{PCBi\ OW}$ ($R^2 = 0.86$, $p < 0.001$) (Figure 2).

3.3 Sediment Pore Water Distribution Coefficient Models

We evaluated each of the models described with Equations (1) through (7) above. The OP-LFERs and PP-LFERs models yielded lower MSE values when OC was used as the phase of interest, except for the QSAR relationship, where a lower MSE was obtained when TOC was used as the phase of interest. A summary of the minimum, maximum, mean and standard deviation of MSEs and the frequency in the prediction error for each of the models tested are showed in Table 1. In detail, OP-LFER reported by Nguyen et al. (2005) performed better than the model by Schwarzenbach et al. (2003) (MSEs of 0.60 ± 0.15 versus 2.00 ± 0.30 , respectively). This finding is unexpected because Eq (1) was developed from low BC sediment content, and our sediments present high values of BC. However, both models still predict an error of the $K_{PCBi\ d}$ within a factor of 5, 60% and 96% of the time, respectively.

Interestingly, the best fit using the PP-LFERs was found when both aliphatic compounds hexadecane and n-octanol were employed as sorbent ($MSE = 0.21 \pm 0.072$ and 0.18 ± 0.062 , respectively). A prediction error of the $K_{PCBi\ d}$ within a factor of 5 was only found 11% and 10% of the time, respectively. These findings suggest the presence of aliphatic compounds in the sediment, which is consistent with an oil refinery that operated until the 1970's adjacent to IHSC. Perhaps the anoxic conditions found in these sediments (−10 to −400 mV) prevent the decay of these compounds. Indeed, aliphatic compounds degrade very slowly under anaerobic conditions (Chandra et al., 2013; Rajasekar et al., 2012).

Raoult's Law did not perform as well as the other models described before, with an MSE of 2.20 ± 0.33 , and with a prediction error of a factor 5, 99% of the time. This overestimation

could just be because this model was calibrated for TOC (~90% of coal tar) as a sorbent, which resulted in a MW_{TOC} of 223 g_{TOC} mol⁻¹ (Arp et al., 2009). Coal tar, hexadecane and n-octanol as sorbents did not improve the predictions.

The QSAR developed by Arp et al. (2009) and calibrated by Hawthorne et al. (2011) resulted in not a very good fit to the measured values ($MSE = 1.3 \pm 0.23$), with a prediction error of a factor of 5, 78% of the time. This model performed very similar to PP-LFERs for coal tar.

The two-carbon model, independent of the model used to predict the $K_{PCBi BC}$ (Eqs (3), (4) or (6)) and where η_{Fi} was changed from 0.7 to 1.0, performed similar to the OP-LFER from Nguyen et al. (2005), but better than the OP-LFER from Schwarzenbach et al. (2003), Raoult's Law and QSAR, but not as well as the PP-LFERs (hexadecane and n-octanol). For example, employing OP-LFER from Werner et al. (2010) to determine the $K_{PCBi BC}$ and a $\eta_{Fi} = 1$ (best fit), a MSE of 0.47 ± 0.21 , with a prediction error of a factor of 5, 35% of the time were obtained.

Different calibration methods of the models already tested were carried out. This allowed us to see the effect of site-specificity in the prediction of the $K_{PCBi d}$. We included the weathering factor (WF, Table S1) developed by Hawthorne et al. (2011) but calculated using our data, into the PP-LFERs and Raoult's Law relationships. A better $K_{PCBi d}$ prediction was found when the WF was included, although it did not improve the fit by much. For example, a MSE of 0.16 ± 0.05 , with a prediction error within a factor of 5, 6% of the time resulted when the PP-LFER with n-octanol as sorbent was used (without WF, a MSE of 0.18 ± 0.062 , a factor of 5, 10% of the time).

The QSAR relationship was also reconstructed through a least squares regression, and a new equation was obtained:

$$\log K_{PCBi OC} = (0.59 \pm 0.007) \times (N_{Cl} - N_{ortho-Cl}) + (4.7 \pm 0.02) \quad (R^2=0.84, \quad p<0.001) \quad (8)$$

We noted that the best fit was obtained with $N_{Cl} - N_{ortho-Cl}$ and not $N_{Cl} - 0.5 \times N_{ortho-Cl}$ as suggested by Arp et al. (2009). Here, the prediction really improved, from a MSE of 1.30 ± 0.23 to 0.17 ± 0.08 , and the prediction error of a factor of 5, decreased from 78% to 6% of the time.

Because a strong relationship between $K_{PCBi d}$ and $K_{PCBi OW}$ was found (Figure 2), we explored the possibility of a simpler model. Our data indicate that the $K_{PCBi d}$ is roughly 10% of the $K_{PCBi OW}$, which could also be determined as the organic carbon fraction in the sediment. Thus, the following relationship was developed:

$$K_{PCBi d} = f_{OC} \times K_{PCBi OW} \quad (9)$$

which surprisingly yielded a MSE of 0.09 ± 0.06 , and a prediction error of a factor of 5, 3% of the time. No calibration was needed. It is possible that the organic carbon fraction is an ideal surrogate for n-octanol in this system.

Because $K_{PCBi OW}$ was shown to play an important role in the distribution of PCBs in these sediments, we performed a sensitivity analysis on $K_{PCBi OW}$. An error of ± 0.5 log units was added into this parameter to observe the effect on our estimations. We decided to investigate two models, the OP-LFER from Nguyen et al. (2005) and our developed model (Eq (9)), mainly because $K_{PCBi OW}$ is a key parameter in these two models. No significant effect was found in the two models after $K_{PCBi OW}$ was modified, as is shown in Table 1. Changing

$K_{PCBi\ OW}$ will not only modify the outcome from the model, but also will change the sediment pore water concentration calculations, which at the end will change the measured sediment pore water distribution coefficient.

3.4 BC-Normalized Partition Coefficient Measurements and Models

Although the chemical method consisted of the application of a strong oxidant, it was still possible to measure 19 PCB congeners in the bulk as well as in the freely-dissolved pore water concentrations. Those 19 congeners were not destroyed or extracted by the oxidant but could be detected in all the treated sediment samples. This allowed us to measure the respective $K_{PCBi\ BCs}$ (Figure 3, tables S3 and S4). To our knowledge, these are the first published values of $K_{PCBi\ BC}$ derived from measurements of both native PCBs and BC. Other reports represent determination of the partitioning by calculation (Kupryianchyk et al., 2012; Lohmann et al., 2005; Moermond et al., 2005) or from measurements of different carbonaceous materials spiked with non-native PCBs (Bucheli and Gustafsson, 2003; Jonker and Koelmans, 2002). Our values are in the same range of other reported values ($\sim \pm 1$ log unit), with some remarkable agreements (e.g. PCB52) (Table S4). We noted that the BC spiked experiments could result in more than an order of magnitude of our measured $K_{PCBi\ BCs}$, because of structural differences in the various types of BC.

Previous models (Eqs (3), (4) (coal tar) and (6) effectively predicted the measured values of our $K_{PCBi\ BCs}$ (Figure 3, MSE < 0.15, Table S5). For example, the OP-LFER (Eq (3)) published by Werner et al. (2010) yielded a MSE of 0.06. The measured $K_{PCBi\ BCs}$ were used to reconstruct Eq (3) and a modification of Eq (6) (likewise Eq (8)). Thus, least squares regressions were performed between the measured log $K_{PCBi\ BCs}$ against the log $K_{PCBi\ OW}$ and $N_{Cl} - N_{ortho-Cl}$ values. A good correlation was found for both models:

$$\log K_{PCBi\ BC} = (1.05 \pm 0.13) \times \log K_{PCBi\ OW} + (0.55 \pm 0.70) \quad (R^2=0.81, \quad p<0.001) \quad (10)$$

$$\log K_{PCBi\ BC} = (0.54 \pm 0.07) \times (N_{Cl} - N_{ortho-Cl}) + (5.5 \pm 0.14) \quad (R^2=0.78, \quad p<0.001) \quad (11)$$

As expected, these models predicted the measured $K_{PCBi\ BCs}$ very well, with MSEs of 0.06 and 0.04, respectively, very similar to what was obtained using the model developed by Werner et al. (2010) (Table S5).

These two new models Eqs (10) and (11) were also included in the two-carbon model (Eq (7)). However, the inclusion of these 2 calibrated models did not provide substantial improvement in the overall $K_{PCBi\ d}$ predictions compared to Werner et al. model (Table 1).

4 Conclusions

The sediment pore water distribution coefficients of 93 PCB congeners measured from the IHSC sediments are likely to be the lowest values to have been published for anthropogenic impacted sediments (Arp et al., 2009; Hawthorne et al., 2011; Werner et al., 2010). The anoxic conditions found in these sediments may have prevented the degradation of petroleum residues (sorbents), and therefore, it could play an important role in the distribution of HOCs in these sediments.

Five published models were tested against the measured $K_{PCBi\ d}$. Despite the enrichment of black carbon in the sediment, the two-carbon model did not yield the best fit. Moreover, when the models were calibrated with the data, no important improvement in the prediction

was obtained. Conversely, a simple model ($K_{PCBi\ d} = f_{OC} \times K_{PCBi\ OW}$) was found to fit the data very well. This simple model will improve the ability to predict the risks of exposing deep sediment in the IHSC. The model reported here can be used to predict PCB bioaccumulation in benthic organisms as well as potential release when deeper sediments are dredged.

We caution readers that sediment pore water distribution coefficients for PCBs can be site-specific and it is necessary to perform a few measurements to confirm or develop a new model for each site. However, if measured $K_{PCBi\ ds}$ from other locations are in the range of our values, it is possible that our model could work better than the rest of the models. It could also be interesting to measure the redox potential in the sediment to see if they follow the distribution found in IHSC sediment or these sediments are unique.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Capsule

The organic carbon fraction times the octanol-water partition coefficient yielded the best prediction model for the sediment pore water distribution coefficient of PCBs.

HIGHLIGHTS

- PCB sediment-pore water distribution coefficients were measured and modeled.
- Distribution coefficients were lower in comparison to other reported values.
- Organic carbon fraction times the K_{OW} yielded the best prediction model.
- The incorporation of black carbon into a model did not improve the results.

Figure 1.

Vertical profiles of PCB bulk, PCB freely-dissolved pore water concentrations and measured log sediment pore water distribution coefficients for selected individual PCB congeners in cores 1 (top panel) and 2 (bottom panel). Error bars in freely-dissolved pore water concentration plots represent one standard deviation ($n=3$ analytical quantification).

Figure 2.

Measured sediment pore water distribution coefficients of 93 PCB congeners versus the octanol-water partition coefficient (Hawker and Connell, 1988). A strong correlation was found between these two parameters ($R^2 = 0.86$, $p < 0.001$).

Figure 3.

$\log K_{PCBi BC}$ measured values for 19 PCB congeners (○). Error bars in $\log K_{PCBi BC}$ represent one standard deviation (5th, 6th and 19th from the left to the right). $K_{PCBi BC}$ models are described with different line types. Models from Eqs (3), (4) and (6) were not calibrated, but 12 and 13 were calibrated with the measurement values. Triangles (△) are from Lohmann et al. (2005).

Table 1

Mean square error (MSE) and frequency of five prediction factor errors for six sediment pore water distribution coefficient models. Best model performance is in bold.

Models		MSE				Prediction factor error (frequency)				
		min	max	mean	stdev	× 2	× 3	× 5	× 10	× 30
OP-LFERS	$K_{PCBI\ OC}$ (Eq (1))	0.33	1.00	0.60	0.15	94%	86%	60%	12%	0%
	(Eq (1), + 0.5 log unit to $K_{PCBI\ OW}$)	0.36	1.10	0.67	0.16	95%	89%	67%	17%	0%
	(Eq (1), - 0.5 log unit to $K_{PCBI\ OW}$)	0.29	0.95	0.54	0.14	93%	84%	52%	9%	0%
PP-LFERS (Eq (4))	$K_{PCBI\ OC}$ (Eq (2))	1.30	2.90	2.00	0.30	99%	98%	96%	88%	41%
	Coal tar	1.9	0.94	1.4	0.23	98%	95%	80%	55%	17%
	Peat (low)	4.2	2.8	3.5	0.4	100%	99%	98%	91%	65%
	Peat (high)	0.43	0.15	0.25	0.073	50%	30%	14%	5%	1%
	Lignite	3.7	2.4	3	0.36	100%	100%	99%	93%	63%
	Sedimentary NOM	1.4	0.54	0.91	0.19	93%	85%	71%	40%	4%
	Leonardite	11	7.1	9	0.67	100%	100%	100%	100%	99%
	Hexadecane	0.45	0.11	0.21	0.072	44%	26%	11%	4%	0%
	Diesel	0.88	0.29	0.49	0.13	76%	57%	33%	13%	2%
	n-octanol	0.4	0.1	0.18	0.062	42%	22%	10%	2%	0%
	Gac (low)	26	22	24	1.1	100%	100%	100%	100%	100%
	Gac (high)	2.4	1.3	1.7	0.27	100%	99%	94%	71%	27%
	n-octanol (TOC)	0.54	0.13	0.29	0.1	57%	36%	18%	7%	1%
Raoult's Law (Eq (5))	Hexadecane (WF)	0.08	0.27	0.15	0.04	44%	20%	6%	1%	0%
	n-octanol (WF)	0.09	0.29	0.16	0.05	47%	24%	6%	1%	0%
	TOC	1.60	2.90	2.20	0.33	100%	100%	99%	93%	42%
QSAR (Eq (6))	TOC (WF)	1.20	2.30	1.70	0.29	100%	100%	97%	79%	21%
	TOC	1.20	2.30	1.70	0.30	99%	96%	87%	70%	29%
	OC	0.88	1.90	1.30	0.23	96%	89%	78%	55%	16%
	TOC (Eq (8))	0.06	0.30	0.13	0.06	31%	12%	5%	3%	1%
	OC (Eq (8))	0.07	0.42	0.17	0.08	47%	23%	6%	1%	0%
2 carbon model ($n_{FI} = 1.0$) (Eq (7))	$K_{PCBI\ BC}$ (Eq (3))	0.13	0.92	0.47	0.21	90%	69%	35%	11%	2%

Models		MSE				Prediction factor error (frequency)					
		min	max	mean	stdev	$\times 2$	$\times 3$	$\times 5$	$\times 10$	$\times 30$	
	$K_{PCBI, BC}$ (coal tar PP-LFERS, Eq (4))	0.19	1.40	0.75	0.36	90%	78%	60%	32%	9%	
	$K_{PCBI, BC}$ (Eq (6))	0.19	1.30	0.71	0.33	85%	76%	59%	32%	7%	
	$K_{PCBI, BC}$ (Eq (10))	0.16	0.99	0.51	0.22	95%	77%	40%	11%	2%	
	$K_{PCBI, BC}$ (Eq (11))	0.10	0.85	0.42	0.18	78%	53%	26%	9%	3%	
$K_{PCBI, OW} \times f_{OC}$	(Eq (9))	0.03	0.31	0.09	0.06	19%	8%	3%	1%	0%	
	(Eq (9), + 0.5 log unit to $K_{PCBI, OW}$)	0.02	0.29	0.08	0.05	18%	7%	3%	1%	0%	
	(Eq (9), - 0.5 log unit to $K_{PCBI, OW}$)	0.03	0.31	0.09	0.06	19%	8%	3%	1%	0%	