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Fate of PCB congeners in an Industrial Harbor of Lake Michigan

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Abstract

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

INTRODUCTION

Indiana Harbor and Ship Canal (IHSC) is one of the most heavily polluted water systems in the United States. It is contaminated with polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons, chlorinated solvents, volatile organic compounds, heavy metals, and is home to a former lead smelter (1). The IHSC discharges water to Lake Michigan and may be one of the largest sources of many of these chemicals to the freshwater lake, one of the largest in the world. This is certainly the case for PCBs (2–4). This is a major environmental threat because of PCBs' known toxicity (5–7) and very strong bioaccumulation potential in the aquatic food web (8, 9). As a result of PCB contamination of fish, consumption advisories are still necessary in Lake Michigan (10).

The sediments of IHSC are to be dredged for navigational purposes within the next few years (11), allowing deep-hulled barge traffic to serve local industries, which include a major steel mill (Mittal Steel Indiana Harbor) and a major gas refinery (BP America Inc. in Whiting, Indiana). It has not been determined when dredging will commence, although a

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Brief: Kilograms of PCBs are released from the sediments of Indiana Harbor and Ship Canal annually, even during quiescent conditions.

SUPPORTING INFORMATION AVAILABLE

Three figures and three tables are included as Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

confined disposal facility (CDF) has been constructed close to the site in East Chicago, Indiana. Despite these plans for dredging, the impact of removing the contaminated sediments is unclear (12). In fact, even in the absence of dredging, the current fate of PCBs in the sediments is unknown.

We have previously shown that PCBs in the surficial sediment of IHSC resemble the commercial mixture Aroclor 1248 and are comparable in magnitude to those identified as Superfund sites by the Comprehensive Environmental Response, Compensation, and Liability Act. The concentrations range from 53 to 35,000 ng PCB g⁻¹ dry weight (d.w.) of sediment (13).

The goal of the study was to investigate the fate and quantify the release of PCBs from the sediments to the water, as well as from the waters to the air above it, and to quantitatively evaluate the uncertainty over a week and on an annual basis. We hypothesized that PCBs are continuously released from the sediments to the water. Furthermore, we hypothesized once they are released from the sediments, PCBs are exported from the canal into Lake Michigan and also emitted to the air over the canal. To test our hypotheses, we measured PCB congeners in the air, water, and surficial sediment in the canal and modeled the potential release. We predicted the release and emission of PCB congeners as a function of their physical-chemical properties, the local meteorology and the levels of PCBs in each of the environmental compartments. We used a Monte Carlo simulation approach to assess our confidence in the model results.

METHODS

We conducted an intensive sampling expedition to collect samples of surficial sediment, water (dissolved-phase and suspended particles), and air (gas-phase) in the IHSC. The study was designed for an internally consistent and matched sample set of 158 PCB congeners quantified in those four environmental compartments. This dataset is the basis for the determination of the potential movement of PCB congeners between sediment, water, and air.

Sampling Methods

During the second week of August 2006, samples were collected in IHSC (Figure 1) from aboard the U.S. Environmental Protection Agency's *R/V Mudpuppy*. Details of sampling methods are provided in the Supporting Information. Meteorological data such as wind speed, atmospheric pressure, water and air temperatures were obtained from the National Oceanic and Atmospheric Administration (NOAA), Calumet Harbor, IL, Station. Daily average volumetric flows from IHSC were obtained from U.S. Geological Survey (USGS). Figure 2 depicts the wind speed, air and water temperatures and water flows for 2006.

Analytical Methods and Quality Assurance and Control

The extraction method of PCBs in bulk sediment and airborne PCBs sorbed to XAD-2 resin required pressured fluid extraction with acetone and hexane and has been described in detail elsewhere (13). Extraction of water-borne PCBs collected on glass fiber filters and XAD-2 resin required Soxhlet apparatus, also refluxed with acetone and hexane (14). PCB quantification was carried out employing a modification of USEPA method 1668a (15). Tandem Mass Spectrometry GC/MS/MS (Quattro MicroTM GC, Micromass MS Technologies) in multiple reaction monitoring mode was utilized to quantify all 209 congeners in 158 individual or coeluting congener peaks (see congener order in Table S1), of which PCB14 (3,5-dichlorobiphenyl), PCB65 (2,3,5,6-tetrachlorobiphenyl) and PCB166 (2,3,4,4',5,6-hexachlorobiphenyl) are surrogate standards and PCB204 (2,2',3,4,4',5,6,6'-

octachlorobiphenyl) is internal standard (see Supporting Information for additional details and QA/QC).

Mathematical Approach

The mathematical structure of the mass transfer phenomena used in this study is well established and has been used and described in numerous papers and textbooks (16–20). Our study applied this structure using the most accurate, recently reported, and/or well characterized parameters. In all cases, we used data specific to each PCB congener and the local environment. The sediment/water and air/water interfacial boundary layer coefficients were determined from reported experimental and modeling studies. Figure S1 depicts the equations utilized in this model.

Sediment/water exchange

A theoretical resistance-in-series model between two phases was utilized to model the water-sediment exchange (19). Fluxes were computed for each congener or coeluting congeners, and equilibrium between sediment and porewater concentrations were assumed (Eq. 1)

$$F_{PCBi\ s/w} = k_{fPCBi} \times (C_{PCBi\ pw} - C_{PCBi\ w}) \quad (1)$$

where $F_{PCBi\ s/w}$ is the flux between sediment and water for the i^{th} PCB ($\text{ng m}^{-2} \text{day}^{-1}$), k_{fPCBi} is the solubilization mass transfer coefficient for the i^{th} PCB (m day^{-1}), $C_{PCBi\ pw}$ is the concentration in the porewater for the i^{th} PCB (ng m^{-3}), and $C_{PCBi\ w}$ is the concentration in the water column for the i^{th} PCB (ng m^{-3}). A positive flux value indicates a flux from the sediment into the water. This model assumes the process of PCBs solubilization from the surficial sediment bed to the water column, and resuspension is not included. Even though solubilization of hydrophobic compounds is a slower process in comparison to resuspension, recent studies have shown that the resuspension phenomenon balanced by deposition and is a less significant process than solubilization in terms of net release of contaminants into the water column (21, 22). The solubilization mass transfer coefficient (k_{fPCBi}) was developed by Thibodeaux (19) and tested in different studies (17, 21, 22). It lumps both bioturbation and chemical sorption/desorption processes (Eq. 2).

$$k_{fPCBi} = \frac{1}{\beta_{PCBi} + \frac{z}{D_b \times K_{PCBi\ oc} \times f_{oc} \times \rho}} \quad (2)$$

where β_{PCBi} is the benthic boundary layer coefficient for the i^{th} PCB (m day^{-1}), z is the bioturbated depth (m), D_b is the biodiffusion coefficient ($\text{m}^2 \text{day}^{-1}$), $K_{PCBi\ oc}$ is the organic carbon base partition coefficient corrected by water temperature for the i^{th} PCB ($\text{L kg}^{-1} \text{oc}$), f_{oc} is the total organic carbon fraction (kg oc kg^{-1}) and is the bulk dry density of the bed (kg L^{-1}).

Parameter estimation: Sediment/water

The parameters used in the sediment/water exchange model were chosen based on their applicability to IHSC. Details are provided in the Supporting Information and briefly summarized here. We used the congener-specific octanol-water equilibrium coefficient, $K_{PCBi\ ow}$ (23) with water temperature correction (24, 25). A one-parameter linear free energy relationship (op-LFER) (26) was employed to calculate $K_{PCBi\ oc}$. The β_{PCBi} were computed using a relationship between the water-to-bed friction velocity and the Schmidt number. The water-to-bed friction velocity was calculated from the mean flow velocity, a

coefficient of roughness, mean hydraulic radius, the water depth and the gravitational acceleration constant (19). The bioturbation component of the solubilization mass transfer coefficient was computed using values from literature (17, 21). The biodiffusion coefficient was selected from a seasonal range and the lowest value was considered for the calculation because we did not observe any evidence of macro-fauna during our sampling of the surficial sediments.

Air/water exchange

We calculated the direction and magnitude of air/water exchange of each PCB congener using the gradient-flux law, i.e. a mass transfer velocity multiplied by a concentration gradient (Eq. 3) (18)

$$F_{PCBi\ a/w} = V_{PCBi\ a/w} \times (C_{PCBi\ w} - C_{PCBi\ w}^{eq}) \quad (3)$$

where $F_{PCBi\ a/w}$ is the flux between air and water for the i^{th} PCB ($\text{ng m}^{-2} \text{day}^{-1}$), $V_{PCBi\ a/w}$ is the air-water exchange velocity for the i^{th} PCB (m day^{-1}), $C_{PCBi\ w}$ is the concentration in the water column for the i^{th} PCB (ng m^{-3}), and $C_{PCBi\ w}^{eq}$ is the concentration in water in equilibrium with the gas-phase for the i^{th} PCB (ng m^{-3}). A positive flux value indicates a flux from the water into the atmosphere. The air/water exchange velocity was separated into velocities for the compounds in air and water using diffusivity ratios between a known chemical and the congeners. Once both terms are computed, the air/water exchange velocity is calculated from Eq. 4

$$\frac{1}{V_{PCBi\ a/w}} = \left(\frac{1}{V_{PCBi\ w}} \right) + \left(\frac{1}{V_{PCBi\ a} \times K_{PCBi\ a/w}} \right) \quad (4)$$

where $V_{PCBi\ w}$ is the water exchange velocity for the i^{th} PCB (m day^{-1}), $V_{PCBi\ a}$ is the air exchange velocity of the i^{th} PCB (m day^{-1}), and $K_{PCBi\ a/w}$ is the equilibrium air-water partition constant (nondimensional Henry's Law constant) for the i^{th} PCB corrected by air and water temperatures. The aqueous concentration in equilibrium with the atmospheric concentration for each congener ($C_{PCBi\ w}^{eq}$) was obtained from the division of the gas-phase concentration and $K_{PCBi\ a/w}$. This is a well accepted approach for determining volatilization flux potentials (20, 27, 28).

Parameter estimation: Air/water

The choice of Henry's Law constant in $\text{Pa m}^3 \text{mol}^{-1}$ (HLC_{PCBi}) affects the direction and magnitude of the PCB flux and many studies have reported different values for congener HLC_{PCBi} (25, 29–31), although the differences are most pronounced for the highest molecular weight PCBs. The selection of HLC_{PCBi} has been source of considerable discussion in the literature (32, 33). For this study, the internal consistency of the measurements and availability of the measurement's uncertainty is most important factor. We chose the values from Dunnivant et al. ($R = 0.95$, standard error = 0.66 or 1.9% of the mean value) (31). Temperature correction for $K_{PCBi\ a/w}$ was carried out using van't Hoff equation (24), where the $\Delta U_{PCBi\ a/w}$ was from Li et al. (25) (Eq. 5).

$$K_{PCBi\ a/w(T_2)} = K_{PCBi\ a/w(T_1)} \times e^{\left(-\frac{\Delta U_{PCBi\ a/w}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right)} \quad (5)$$

where $K_{PCBi\ a/w(T_2)}$ and $K_{PCBi\ a/w(T_1)}$ are the nondimensional Henry's Law constant at temperatures T_2 and T_1 (K) for the i^{th} PCB, $\Delta U_{PCBi\ a/w}$ is the internal energy for the transfer of water to air transfer for the i^{th} PCB (J mol^{-1}) and R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) (more details in Supporting Information).

Annual emissions

Because sediment, water and air concentrations were measured only in August, we estimated concentrations over the rest of the year as follows. We assumed that the bulk sediment PCB concentration was constant during the entire year. However, porewater concentration of PCBs varied during the year due to temperature difference in the water which modifies the octanol-water equilibrium coefficient. Total water concentrations (dissolved-phase + suspended particulates) were assumed to be the same as measured from June to September but 2.5 times higher during the rest of the year. We made this assumption due to two pieces of information. First, Offenberg and Baker (34) measured total water concentrations in the southern Lake Michigan region (Chicago, IL and Gary, IN) and found that total concentration of total PCBs were 2.5 higher in January than in July. Second, USEPA measured total water concentrations (dissolved-phase + suspended particulates) in IHSC from August 1994 to September 1995 and found a similar trend of 1.3 to 2.7 times higher levels during winter and spring months than the rest of the year (3, 4). The ratio between dissolved-phase and suspended particulates was assumed to be constant for the whole year, but a 20% error in the dissolved-phase concentration was included in the Monte Carlo simulation.

Air concentrations increase as a function of air temperature: we assumed that gas-phase PCBs in IHSC varied as a function equivalent to what we have observed in the City of Chicago of the same 158 congeners in 184 air samples collected in Chicago, IL (35). The resulting extrapolation predicted Σ PCBs in summer are about three times larger than in winter. All physical-chemical parameters as well as mass transfer coefficients were corrected for meteorological and hydraulic conditions obtained from NOAA and USGS, respectively. Emissions were calculated in a monthly basis and then added for the entire year. Emissions were calculated as flux multiplied by the total water surface area of IHSC ($1,300,000 \text{ m}^2$).

Monte Carlo simulation

We evaluated the precision of the calculated fluxes and emissions by considering the frequency distribution for each model parameter instead of single average values. These frequency distributions were determined from the original reports of the parameter's confidence intervals or standard deviations. Some estimate of uncertainty was available for all the parameters. Wind speed, HLC_{PCBi} and $K_{PCBi\ ow}$ were described as lognormal distributions and the rest of the parameters as normal distributions (more details in Supporting Information). The Monte Carlo simulation then randomly probes the distributions to generate a set of input parameter values from which fluxes were computed. This was repeated 10,000 times and provided a frequency distribution of PCB congener fluxes. From the frequency distribution, we determined the arithmetic mean, the standard error, and the 95% confidence intervals. This Monte Carlo simulation procedure was applied to each congener flux and emission for the air/water and sediment/water exchanges. It was a powerful method to assess the variability of the flux results as a function of the variability in the independent variables.

RESULTS AND DISCUSSION

Air, water and sediment total concentrations

The concentrations of Σ PCBs in gas-phase, dissolved-phase and suspended particulates, and sediments are presented in Figure S2. The Σ PCBs average gas-phase concentration during the sampling period was $4,500 \pm 1,800 \text{ pg m}^{-3}$ ($n=16$). Dissolved Σ PCB water phase concentrations averaged $33 \pm 16 \text{ ng L}^{-1}$ ($n=10$). The particulate water phase samples averaged $20.0 \pm 8.5 \text{ ng L}^{-1}$ ($n=7$). The dissolved-phase represents 61% of Σ PCB in water (all samples). Similar dissolved/particulate PCB distributions have been reported by many studies in different locations (34, 36). Surficial sediment Σ PCB concentrations have been previously reported (13) and ranged from 53 to 35,000 ng g^{-1} d.w. ($n=60$) with an arithmetic mean of $7,400 \pm 6,700 \text{ ng g}^{-1}$ d.w. The three sites with concentrations above the 95th percentile were not considered in the model simulation, resulting in an arithmetic mean of $5,900 \pm 1,200 \text{ ng g}^{-1}$ d.w. Total organic carbon fraction (*foc*) in the sediments ranged from 0.43% to 7%, with an arithmetic mean of $4.6 \pm 1.5\%$ kg oc kg^{-1} sediment. The concentration of each PCB congener in the sediment, dissolved-phase and the gas-phase used to compute the week fluxes are presented in Table S1.

It is difficult to compare PCB levels in heterogeneous systems between different studies, but Table S2 provides some perspective to the level of contamination in IHSC. It is especially difficult to compare airborne PCBs concentrations because the variation and seasonal time periods collection, site location, wind direction, analytical methods and quantity of congeners analyzed can significantly impact the results. For example, airborne PCB measurements by USACE (37) and Hsu et al. (38) indicate concentrations were 1/10 to 1/100 times (lower) than our results (Table S2). Our samplers were located directly over the water while the other samplers were located on land. The air directly over the IHSC water is enriched in PCBs, as has been reported for air over other contaminated waters (20, 27).

The congener distributions in the IHSC (Figure S3) are quite similar and their similarity is consistent with the strong potential for chemical fluxes from sediment to water to air. As expected, the gas-phase and dissolved water profiles are slightly skewed to less chlorinated congeners while the sediment and suspended particulate profiles are skewed toward the more chlorinated congeners. Nevertheless, the profiles in the sediment and gas phases are remarkably similar as indicated by linear ($R^2 = 0.69$ and $s = 0.0061$) and non-linear correlations ($\cos \theta = 0.81$ (39, 40)). Indeed, the difference between each congener fraction (congener mass to total congeners mass ratio) in the gas-phase and sediment is less than 5%. The same analyses of the sediment/water and air/water profiles (compared as averages or pairs) are even stronger. Overall, these findings are consistent with our model that predicts the sediments are one of the major sources of waterborne and atmospheric PCBs.

Flux: Sediment/water

The Σ PCBs net sorption/desorption flux yielded $9,700 \pm 130 \text{ ng m}^{-2} \text{ day}^{-1}$, and ranged from -7 ± 2.3 to $800 \pm 210 \text{ ng m}^{-2} \text{ day}^{-1}$, for PCB192 and PCBs61/70/74/76, respectively. Figure 3 depicts the average flux of each congener, including the 97.5th percentile. Gross desorption from the sediment to the water yielded a flux of $10,300 \pm 140 \text{ ng m}^{-2} \text{ day}^{-1}$ and gross sorption from water to sediment yielded a flux of $-610 \pm 7 \text{ ng m}^{-2} \text{ day}^{-1}$. To illustrate how the independent parameters affect each congener fate, Figure 4 shows the probability distribution of PCB52 and PCB205 for the simulated fluxes during the sampling period, including the 95% CI. All the fluxes calculated for PCB52 are positive, thus the net flux of PCB52 is from sediment to water. PCB205, on the other hand, exhibited negative flux values and is predicted to sorb or desorb into the sediment. Our study results indicate that

70% of congeners or coeluting congeners are desorbing and 5% are sorbing. The net direction of flux cannot be identified within a 95% CI for the other 25% of congeners.

Flux: Air/water

The Σ PCB net volatilization/gas absorption flux yielded $6,800 \pm 100 \text{ ng m}^{-2} \text{ day}^{-1}$, and ranged from -1.4 ± 1.6 to $730 \pm 230 \text{ ng m}^{-2} \text{ day}^{-1}$ for PCB141 and PCBs18/30, respectively. Figure 3 depicts the average flux of each congener, including the 97.5th percentile. The total net average flux is at least 3 times higher than total fluxes for Lake Michigan or the Delaware River (16, 20, 27, 28), where they employed a similar flux model. Gross gas absorption yielded a total flux of $-220 \pm 2.4 \text{ ng m}^{-2} \text{ day}^{-1}$ and gross volatilization resulted in $7,100 \pm 110 \text{ ng m}^{-2} \text{ day}^{-1}$.

Figure 4 shows the probability distribution of PCB52 and the coeluting PCBs147/149 for the simulated fluxes during the sampling period. Because all the fluxes within the 95% CI are positive, PCB52 will volatilize from water to air. However, PCB147/149 does not behave as PCB52 and we cannot state with the same level of confidence that PCB147/149 will volatilize. Our study results indicate that 64% of congeners or coeluting congeners are volatilizing from the water and no congeners are absorbing into the water. The net direction of flux cannot be identified within a 95% CI for the other 36% of congeners.

Annual release of PCBs from IHSC

The 2006 gross emissions in kg per year are presented as part of the steady state mass budget (Figure 5). The mass balance includes annual gross desorption, sorption, volatilization and gas absorption emissions, input from upstream flow, and direct discharge to Lake Michigan. To calculate the annual emissions, we used monthly mean values for parameters that had known seasonal variability. For example, Figure 2 shows the seasonal variation for air ($V_{PCB52 a}$), water ($V_{PCB52 w}$), air-water exchange ($V_{PCB52 a/w}$) velocities, benthonic boundary layer (β_{PCB52}) and the solubilization mass transfer coefficient (k_{fPCB52}) for PCB52. For gas-phase, dissolved-phase and sediment porewater PCB concentrations, water flow, and temperature, we used monthly averages and calculated monthly emissions. The emissions and uncertainties were determined using the same congener-specific and Monte Carlo methods described above. Net desorption of Σ PCBs from IHSC sediment was determined to $4 \pm 0.05 \text{ kg yr}^{-1}$ and net volatilization of Σ PCBs from IHSC water was determined to be $7 \pm 0.1 \text{ kg yr}^{-1}$. The input from upstream flow was calculated using water samples collected in the middle of the canal (45.0 kg yr^{-1}). The direct discharge to Lake Michigan was calculated using water samples collected near the lake side of the harbor. Both mass flows assumed the same monthly USGS water flow rates and considered PCBs sorbed to suspended particles as well as in the dissolved-phase. The downstream PCB flow to Lake Michigan equals a net load of $43.9 \text{ kg PCB yr}^{-1}$. This finding is somewhat higher than the $29.86 \text{ kg PCB yr}^{-1}$ determined in the mid-1990s by the USEPA (2). Although each term of the mass balance is determined independently, the inputs and losses nearly balance. We conclude that the approach we used to extrapolate from August measurements to the rest of the year is reasonable and representative of the major processes controlling PCB fate in IHSC.

Implications

The approach we used to determine that the sediments are one of the major sources of PCBs to the overlying water could be used to determine emissions of PCBs if the dredging at IHSC exposes sediments that are more contaminated than the surficial sediments we sampled. If the underlying sediment is three times more concentrated than the surficial sediment, and all other things remain equal, then the gross annual desorption fluxes and volatilization fluxes increase by a factor of three.

The IHSC sediments are an indirect source of PCBs to the atmosphere. Our value, $7 \pm 0.1 \text{ kg yr}^{-1}$, is lower than estimated from the municipal sludge drying beds from Stickney and Calumet ($\sim 90 \text{ kg yr}^{-1}$) and insignificant to the 70 kg day^{-1} of ΣPCBs emission estimated for Chicago (38, 41). However, if we consider just the immediate community of East Chicago, the emissions may account for a significant fraction of the gas-phase PCBs in the local community. Despite the lack of information available and the many assumptions made to develop this model, we believe the approach undertaken and the information resulted from this investigation could be used in other similar places to assess the fate of not just PCBs, but other persistent organic pollutants around the world. Moreover, POPs are dispersed worldwide from their original emission sites to vulnerable regions the world. The findings of this study may also be used to more accurately determine the impact of local decisions on global emissions of POPs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Indiana Harbor and Ship Canal, East Chicago, Indiana. The blue circles (O) and red diamonds (◇) represent the sites where sediment and water samples, respectively, were collected.

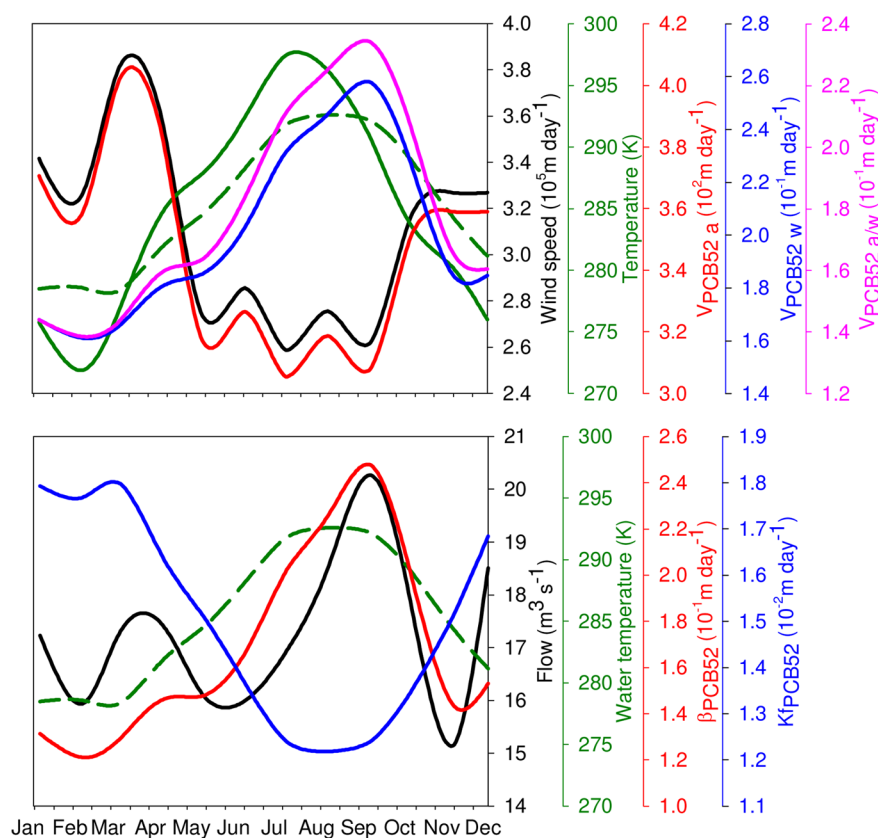


Figure 2. Seasonal variation of meteorological and hydraulic conditions, and transfer coefficients for PCB52. Top plot depicts air-water coefficients and bottom one, sediment-water coefficients. Note the difference in scale on the right for each parameter. The green lines on the top plot describe the air and water temperatures (dash line), respectively. Transfer coefficients are strongly dependent on the congener. See text for abbreviations.

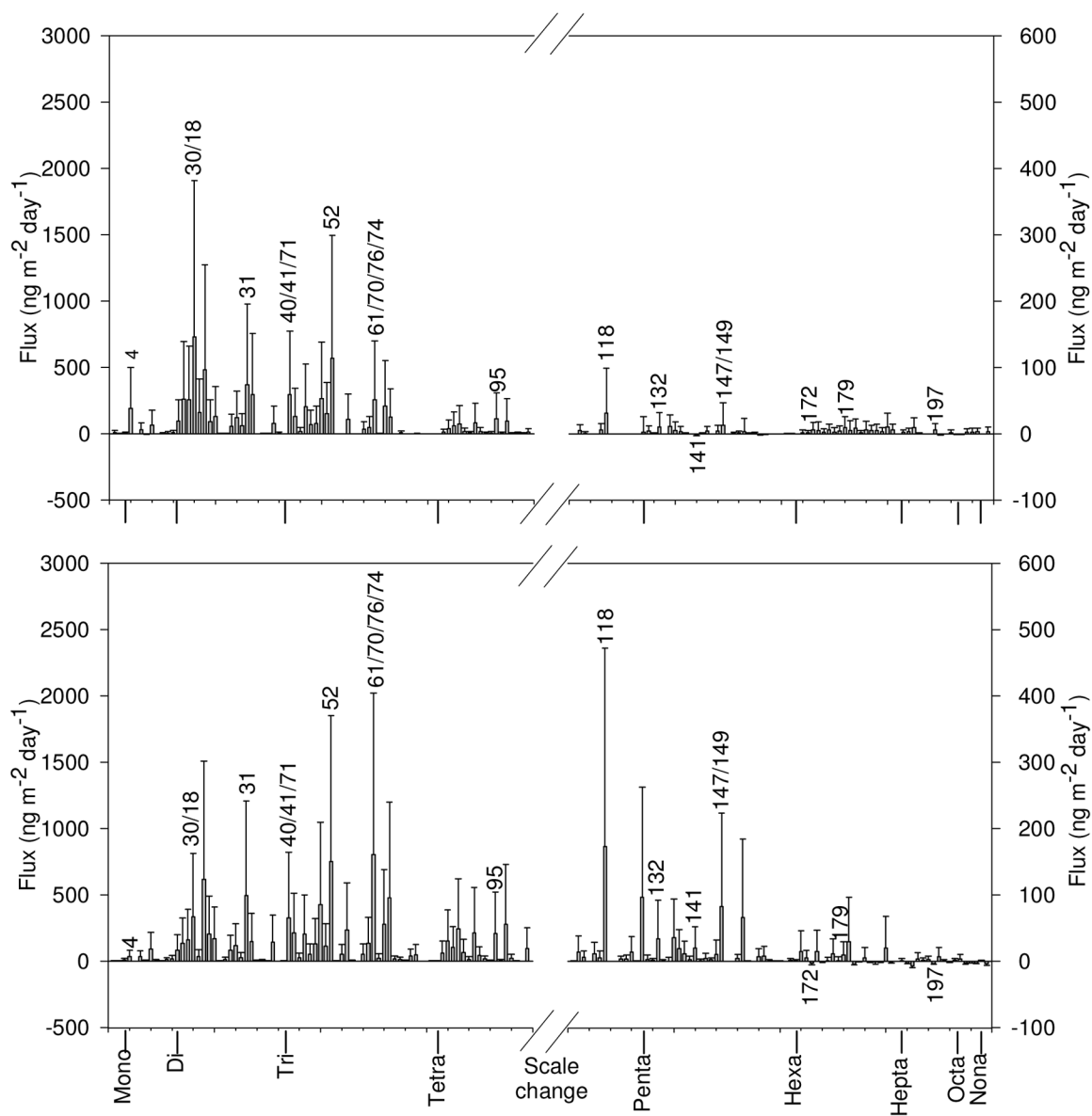


Figure 3. The top plot is the net air/water flux and the bottom plot is the net sediment/water flux for PCB congeners in IHSC. The bars represent the arithmetic average and the error bars represent the 97.5th percentile. Note the different scales for the vertical axes.

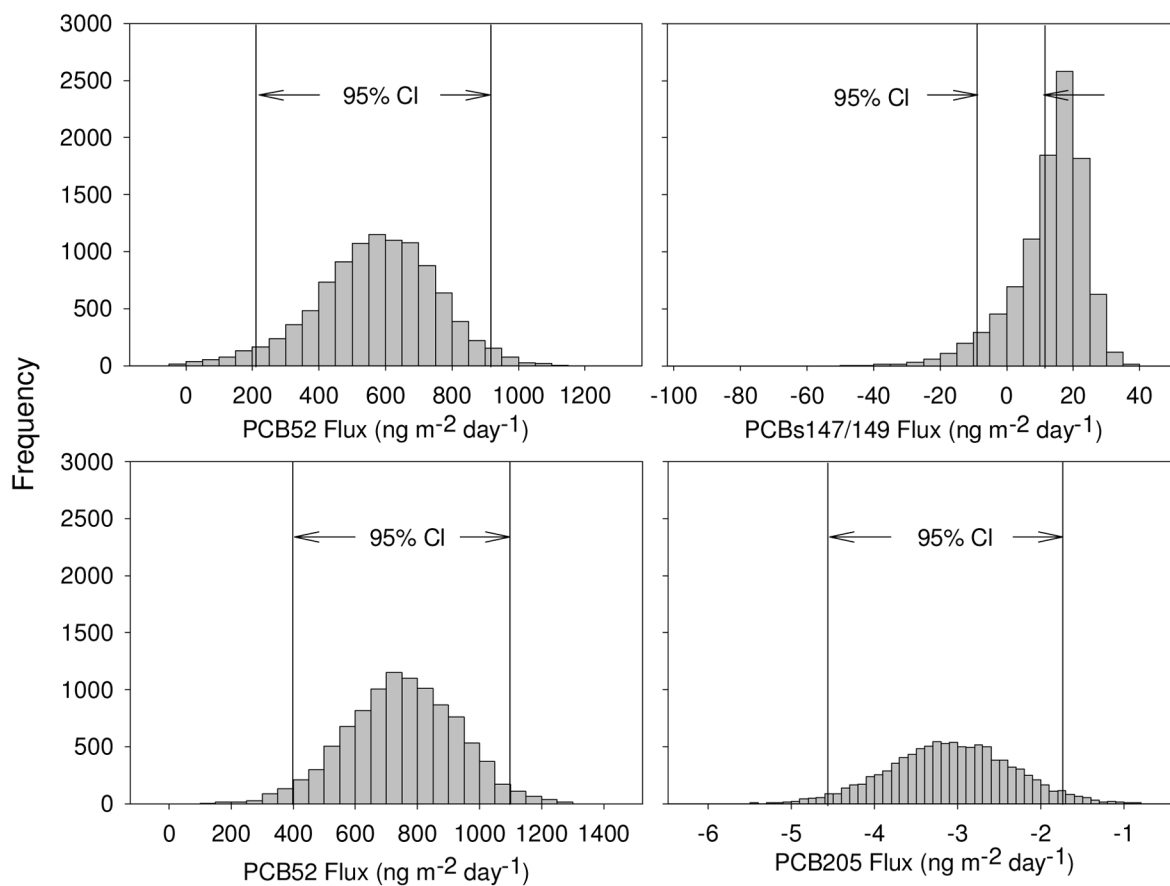


Figure 4.

Histograms of simulated PCB fluxes during the sampling period for three congeners. Top left plot depicts PCB52 and top right depicts PCBs147/149 (coeluting congeners) for the air/water interface. Bottom left plot depicts PCB52 and bottom right depicts PCB205 for the sediment/water (bottom plots) interface.

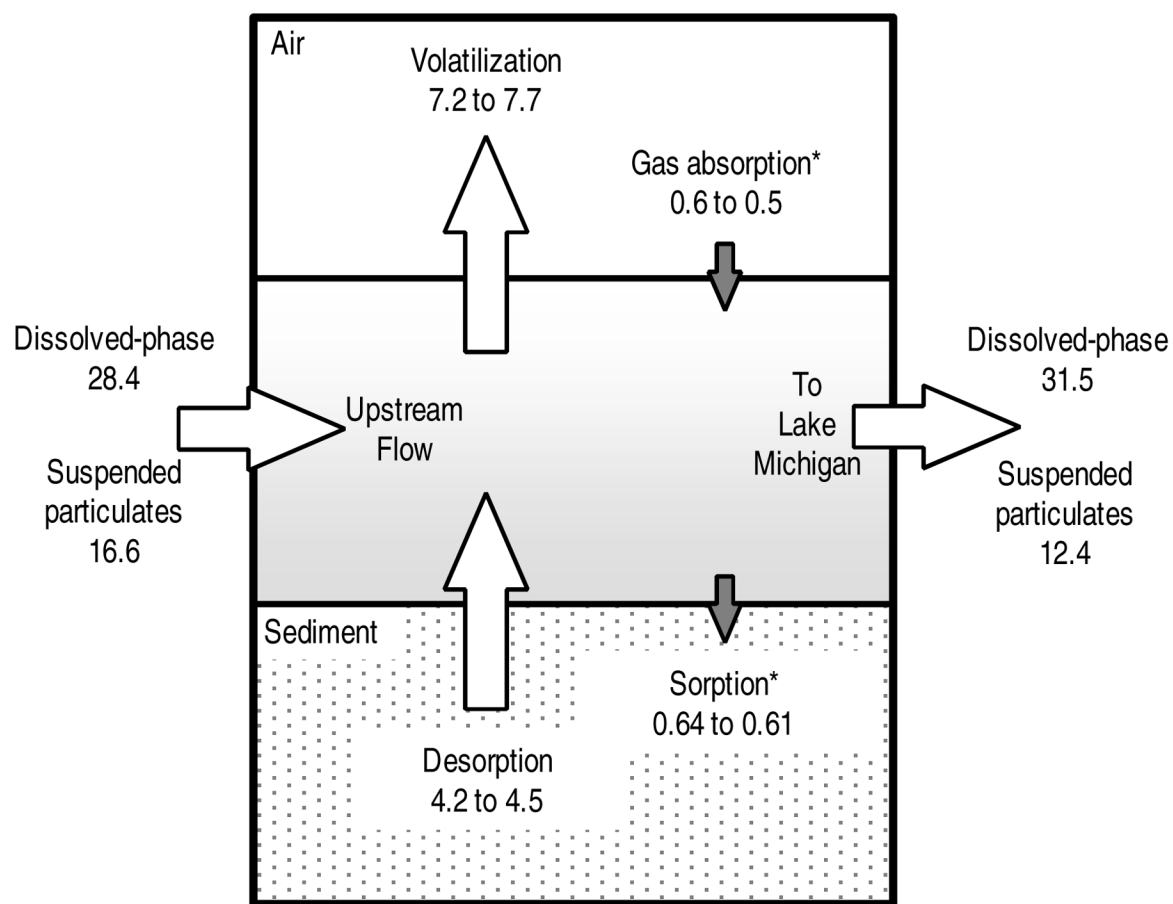


Figure 5. The steady state mass budget for total PCBs in IHSC for 2006 in kg per year. The ranges shown for sediment, water and air fluxes are the 2.5th and 97.5th percentiles. Asterisk (*) means negative values.