Supporting Information

Fate of PCB congeners in an Industrial Harbor of Lake Michigan

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Sampling Methods. During the second week of August 2006, surficial sediment, water, and air were collected in IHSC from aboard the U.S. Environmental Protection Agency's R/V Mudpuppy. Surficial sediment samples were collected using a standard ponar dredge sampler (top 10 cm layer) as described previously (1). Water samples were collected using a submersible pump that pushed water from approximately 1 meter below the surface. The water was pushed at a rate of approximately 150 mL min^{-1} through a stainless steel pentaplate that held five 0.293 cm glass fiber filters (GFF) in parallel. The filtered water was collected in stainless steel tanks that were covered at the water surface by precleaned aluminum foil. The filtered water was then pulled at a rate of approximately 150 mL min-1 through 3 cm I.D. x 30 cm long glass columns packed with a water slurry of XAD-2 resin. An average volume of 30 L of water was collected in this manner at each of 10 sites. Air samples were collected using two high volumetric air samplers (Hi-Vol) mounted to the roof of the vessel. The Hi-Vols pulled air through a 20.3 cm x 25.4 cm GFF and then through 40 g XAD-2 resin at a rate of ~0.4 m^3 min^{-1}. QFF samples were archived and not used for this study. The samplers were operated continuously while water and sediment was being collected. The average sampling time for the air samples collected during the week was 7 hrs. In summary, this study collected 60 bulk sediment samples, 10 XAD water samples (operationally defined as dissolved-phase), 7 GFF water samples (operationally defined as suspended particles), and 17 XAD air samples (operationally defined as gas-phase), throughout the harbor and canal. In relation to the water samples, 4 samples were paired and 3 of suspended particles came from composite of 2 dissolved-phase samples.

Analytical Methods. Surficial sediment analysis is described in (1) and is briefly summarized here. Samples were dehydrated using combusted diatomaceous earth, then extracted with hexane in an accelerated solvent extraction (ASE 300, Dionex, Sunnyvale, CA). Prior to extraction, PCB14 (3,5-dichlorobiphenyl), PCB65 (2,3,5,6-tetrachlorabiphenyl) and PCB166 (2,3,4,4′,5,6-hexachlorobiphenyl) were injected and employed as surrogate standards. The resulting solution was again shaken with potassium hydroxide and sulfuric acid. The solution was then passed through Pasteur pipettes filled with combusted and acidified silica gel and eluted with hexane. The solution was reduced to approximately 0.5 mL and PCB204 (2,2′,3,4,4′,5,6,6′-octachlorobiphenyl) was spiked as internal standard.

XAD resin or fiber glass filters were extracted individually in a Soxhlet apparatus for 16 hrs using 500 mL of acetone/hexane (1:1 v/v) solution (2). Surrogate standards – PCB14, PCB65 and PCB166 – were spiked before extraction. Excess water and acetone was removed by liquid - liquid extraction. After concentration, the sample extract in hexane was eluted through Pasteur pipettes filled with combusted and acidified silica gel. The final 10 mL solution was again concentrated and PCB204 was spiked as internal standard.

Air samples were analyzed as described in Hu et al. (3). Briefly, samples were extracted in ASE 300 with acetone/hexane (1:1, v/v). Prior to extraction air samples were injected with surrogate standards PCB14, PCB65 and PCB166. The resulting extracts were further reduced to about 500 µL by a Turbovap concentration workstation, and the final solutions were injected with the internal standard PCB204.

Sediment, water, suspended water particles, and air samples were all analyzed for all 209 PCB congeners in 158 individual or coeluting congener using Tandem Mass Spectrometry

GC/MS/MS (Quattro MicroTM GC, Micromass MS Technologies). The instrument was operated in multiple reaction monitoring mode (MRM) and we used the following pairs of parent/daughter ions to identify the PCBs: mono- to deca- homologs were 188/152, 117 222/152.10, 255.96/186, 291.92/222, 325.88/255.90, 359.84/289.90, 393.80/323.90, 118 427.76/357.80, 461.72/391.83, 497.68/427.70, respectively.

Quality Assurance and Control. Percentage recovery of PCB14 and PCB166 for gas phase samples were 60 ± 20% and 78 ± 19%, respectively (n=16). Dissolved water samples yielded a percentage recovery of PCB14 and PCB166 of 59 ± 12% and 76 ± 12%, respectively (n=10). In the case of particulate in water, percentage recovery of PCB14 and PCB166 were 66 ± 11% and 97 ± 11%, respectively (n=7). Percentage recovery for sediment was 93 ± 36% and 85 ± 16% for PCB14 and PCB166, respectively (n=80). PCB65 acquired high values due to coelution issues and was not used for correction. Percentage recovery of PCB14 was used to correct mass congeners of PCB1 to PCB39 and PCB166 percentage recovery for PCB40 till PCB209. Field and lab blanks were analyzed. No mass correction was made from blanks, which were insignificant. In addition, Standard Reference Material 1944 was analyzed, showing acceptable results (4). Total organic carbon (TOC) was analyzed by Minnesota Valley Testing Laboratories. Inc (SW-846 Method SW 9060).

Monte Carlo parameters. The input parameters were wind speed (u_{10}), air (T_a) and water (T_w) temperatures, atmospheric pressure (P), water flow (Q), water depth of the canal (h), total organic carbon fraction (f_{oc}), air ($C_{PCBi\ a}$), water ($C_{PCBi\ w}$) and sediment ($C_{PCBi\ s}$) concentrations, Henry's law constant (HLC_{PCBi}) (5), octanol-water equilibrium coefficient ($K_{PCBi\ ow}$) (6), the parameters obtained from linear regressions use to calculate the internal energy for the transfer of water to air and octanol to air (7), and the parameters from the one-parameter linear free energy relationship (op-LFER) used to obtain the octanol-water equilibrium coefficients and the ($K_{PCBi\ oc}$) (8).

The frequency distribution for each parameter was determined as follows: histograms were plotted and the distribution was obtained for wind speed, air and water temperatures, atmospheric pressure, water flow and water depth of the canal. Total organic carbon fraction, air, water and sediment concentrations were considered as normal distribution. If the parameters were obtained from linear regressions such as the parameters obtained from linear regressions use to calculate the internal energy for the transfer of water to air and octanol to air, and the parameters from the one-parameter linear free energy relationship (op-LFER) used to obtain the octanol-water equilibrium coefficients and the ($K_{PCBi\ oc}$), the distribution was determined as normal and if the regression was logarithmic such as octanol-water equilibrium coefficient ($K_{PCBi\ ow}$) and Henry's law constant (HLC_{PCBi}), the distribution was considered lognormal. In summary, for this simulation, wind speed, HLC_{PCBi} and $K_{PCBi\ ow}$ were described as lognormal distribution and the rest of the parameters as normal distributions.

Parameter estimation and Assumptions

Sediment-water. We used the congener-specific $K_{PCBi\ ow}$ reported by Hawker and Connell (6) with water temperature correction from Goss (9) and Li et al. (7). The relationship between octanol-water equilibrium coefficients and the $K_{PCBi\ oc}$ controls the solid-water distribution coefficient which may vary with the quantity of the organic matter and the chemical nature of the organic matter (10). We used a one-parameter linear free energy relationship (op-LFER) developed by Nguyen et al. (8) to calculate $K_{PCBi\ oc}$ ($R^2 = 0.97$ and an absolute average value of the difference between measured and fitted values of 0.21). In addition, we estimated $K_{PCBi\ oc}$ (= C_{PCBi} particulate $\bullet foc^{-1} \bullet C_{PCBi\ \mathrm{dissolved}}{}^{-1}$) for each congener and compared with $K_{PCBi\ ow}$. We evaluated and found a weak relationship between both coefficients, suggesting that not all the organic carbon is acting as sorbent, i.e. presence of other types of carbons, kinetic problems (e.g. not at equilibrium), and presence of colloids in the dissolved measured phase (10-12). These findings do not significantly reduce the value of the model or our findings.

The mean flow velocity and mean hydraulic radius were calculated from the field conditions, i.e. flow, wide and water depth of the canal. The bioturbation component of the solubilization mass transfer coefficient was computed using values from literature, i.e. bioturbated depth and biodiffusion coefficient from Erickson et al. (13) and the solids concentration of sediment from Birdwell and Thibodeaux (14).

Air-water. Diffusivity of PCBs in air was computed using water vapor as reference substance. Water vapor diffusivity was calculated as a function of air temperature and atmospheric pressure (10). Air exchange velocity for each congener was obtained from the ratio of PCB and water vapor diffusivity in air and the velocity of water in air, which is function of wind speed measured at 10 m above the water surface (10). One of the key parameters involved in the water exchange velocity calculation is the gas transfer velocity of CO_2 or k_{600} (k at 20°C in freshwater, i.e. k at a Schmidt number of 600). This parameter is not easy to measure or to estimate because it depends on the system (e.g. lakes, oceans, streams and estuaries), wind speed, rain fall, formation of thin layers and the roughness of the water surface (during sampling days the wind speed was narrow, ranging from 0 to 5.7 m s^{-1}). In the case of shallow stream and rivers, the k_{600} is influences by the stream depth and flow velocity, and not the wind speed (15, 16). Therefore, we employed that relationship to estimate the k_{600} for the different scenarios, as function of the stream depth and the flow velocity. The kinematic viscosity (i.e. viscosity to density ratio) was computed for each air and water temperature scenarios.

Mathematical Approach.
Air -water exchange equations

$$F_{PCBi\,a/w} = V_{PCBi\,a/w} \times \left(C_{PCBi\,w} - C^{eq}_{PCBi\,w}\right)$$

$$C^{eq}_{PCBi\,w} = \left(\frac{C_{PCBi\,a}}{K_{PCBi\,a/w}}\right)$$

$$K_{PCBi\,a/w} = K_{PCBi\,a(T_a)/w(T_w)} = K_{PCBi\,(a/w)(T_w)} \times \frac{T_w}{T_a}$$

$$K_{PCBi\,(a/w)(T_w)} = K_{PCBi\,(a/w)(T_{std})} \times e^{\left(-\frac{\Delta U_{PCBi\,a/w}}{R} \times \left(\frac{1}{T_w} - \frac{1}{T_{std}}\right)\right)}$$

$$K_{PCBi\,(a/w)(T_{std})} = HLC_{PCBi} \times \left(\frac{1}{R \times T_{std}}\right)$$

$$HLC_{PCBi} = f(PCB_i)$$

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

$$V_{PCBi\,w} = V_{CO_2} \times \left(\frac{Sc_{PCBi\,w}}{Sc_{CO_2 w}}\right)^{-0.5} \times (0.24 \frac{h\,m}{day\,cm})$$

$$Sc_{PCBi\,w} = \left(\frac{\nu_{water}}{D_{PCBi\,w}}\right)$$

$$D_{PCBi\,w} = D_{CO_2\,w} \times \left(\frac{MW_{PCBi}}{MW_{CO_2}}\right)^{-0.5}$$

$$D_{CO_2\,w} = f(T_w)$$

$$\nu_{water} = f(T_w)$$

$$V_{CO_2} = 1.72 \times \left(\frac{\nu_x}{h}\right)^{0.5}$$

$$\nu_x = \frac{Q}{A} \times \left(100 \frac{cm}{m}\right)$$

$$A = w \times h$$

$$Sc_{CO_2\,w} = \left(\frac{\nu_{water}}{D_{CO_2\,w}}\right)$$

$$V_{PCBi\,a} = V_{water\,a} \times \left(\frac{D_{PCBi\,a}}{D_{water\,a}}\right)^{0.67}$$

$$D_{PCBi\,a} = D_{water\,a} \times \left(\frac{MW_{PCBi}}{MW_{water}}\right)^{-0.5}$$

$$D_{water\,a} = f(T_a, P)$$

$$V_{water\,a} = 0.2 \times u_{10} + 0.3$$

Sediment-water exchange equations

$$F_{PCBi\,w/s} = k_{f\,PCBi} \times \left(C_{PCBi\,pw} - C_{PCBi\,w}\right)$$

$$\left\{\begin{array}{l}
C_{PCBi\,pw} = \left(\frac{C_{PCBi\,s}}{K_{PCBi\,d(T_w)}}\right)\times\left(10^{6}\,\frac{g\,L}{kg\,m^{3}}\right)
\left\{\begin{array}{l} K_{PCBi\,d(T_w)} = \\ = f_{oc}\times K_{PCBi\,oc\,(T_w)} \end{array}\right.
\left\{\begin{array}{l} \log\left(K_{PCBi\,oc(T_w)}\right) = \\ = a\times\log\left(K_{PCBi\,ow(T_w)}\right) - b \end{array}\right.
\left\{\begin{array}{l} K_{PCBi\,ow(T_w)} = \\ = K_{PCBi\,ow(T_{std})}\times e^{\left(-\frac{\Delta U_{PCBi\,ow}}{R}\times\left(\frac{1}{T_w}-\frac{1}{T_{std}}\right)\right)} \end{array}\right.
\left\{ K_{PCBi\,ow(T_{std})} = f(PCB_i) \right.
\\[2em]
K_{f\,PCBi} = \left(\frac{1}{\frac{1}{\beta_{PCBi}} + \frac{z}{D_b\times K_{PCBi\,oc(T_w)}\times f_{oc}\times\rho}}\right)
\left\{\begin{array}{l}
\beta_{PCBi} = \left(\frac{0.114\times\upsilon}{\left(Sc_{PCBi\,w}\right)^{2/3}}\right)
\left\{\begin{array}{l}
\upsilon = \frac{v_x\times n}{\left(r_H\right)^{2/3}}\times\sqrt{h\times g}
\left\{\begin{array}{l} v_x = \frac{Q}{A} \\ r_H = \frac{A}{P_w} \end{array}\right.
\left\{\begin{array}{l} A = w\times h \\ P_w = w + 2h \end{array}\right.
\\[1em]
Sc_{PCBi\,w} = \left(\frac{\nu_{water}}{D_{PCBi\,w}}\right)
\left\{\begin{array}{l}
D_{PCBi\,w} = \\ = D_{CO_2\,w}\times\left(\frac{MW_{PCBi}}{MW_{CO_2}}\right)^{-0.5}
\left\{ D_{CO_2\,w} = f(T_w) \right.
\\ \nu_{water} = f(T_w)
\end{array}\right.
\end{array}\right.
\\[1em]
\log\left(K_{PCBi\,oc(T_w)}\right) = \\ = a\times\log\left(K_{PCBi\,ow(T_w)}\right) - b
\left\{\begin{array}{l} K_{PCBi\,ow(T_w)} = \\ = K_{PCBi\,ow(T_{std})}\times e^{\left(-\frac{\Delta U_{PCBi\,ow}}{R}\times\left(\frac{1}{T_w}-\frac{1}{T_{std}}\right)\right)} \end{array}\right.
\left\{ K_{PCBi\,ow(T_{std})} = f(PCB_i) \right.
\end{array}\right.
\end{array}\right.$$

Figure S1. Equations developed for the flux calculations.

Definition of Terms

The equations in the top half of Figure S1depict the equations used for the air-water PCB exchange model. The equations in the bottom half depict the equations used for the sediment-water exchange model. The definitions and sources of parameters are defined as follows:

$F_{PCBi\ a/w}$ is the flux between air and water for the i^{th} PCB (ng m^{-2} day^{-1}) (10).
$C_{PCBi\ w}$ is the concentration in the water column for the i^{th} PCB (ng m^{-3}).
$C^{eq}_{PCBi\ w}$ is concentration in water in equilibrium with the gas phase for the i^{th} PCB (ng m^{-3}).
$V_{PCBi\ a/w}$ is the air –water exchange velocity of the i^{th} PCB (m day^{-1}) (10).
$C_{PCBi\ a}$ is the concentration in the gas phase for the i^{th} PCB (ng m^{-3}).
$K_{PCBi\ a/w}$ or $K_{PCBi\ a(Ta)/w(Tw)}$ is the temperature corrected nondimensional Henry's law constant of the i^{th} PCB (5, 7, 9).
T_w is the water temperature (K).
T_a is the air temperature (K).
$K_{PCBi\ a/w(Tw)}$ is the nondimensional Henry's law constant of the i^{th} PCB corrected by water temperature (9).
$K_{PCBi\ a/w(Tstd)}$ is the nondimensional Henry's law constant of the i^{th} PCB at standard temperature (5).
$\Delta U_{PCBi\ a/w}$ is the internal energy for the transfer of water to air transfer for the i^{th} PCB (J mol^{-1}) (7).
R is the ideal gas constant (8.3144 J mol^{-1} K^{-1} or 8.3144 Pa m^3 mol^{-1} K^{-1}).
T_{std} is the standard temperature (298.15 K).
HLC_{PCBi} is the Henry's law constant for the i^{th} PCB (Pa m^3 mol^{-1}) (5).
$V_{PCBi\ a}$ is the air exchange velocity of the i^{th} PCB (m day^{-1}) (10).
$V_{water\ a}$ is the water vapor exchange velocity in air (m day^{-1}) (10).
$D_{PCBi\ a}$ is the diffusivity in air for the i^{th} PCB (cm^2 s^{-1}) (10).
$D_{water\ a}$ is the water diffusivity in air corrected by air temperature and atmospheric pressure (cm^2 s^{-1}) (10).
P is the atmospheric pressure (mbar).
MW_{PCBi} is the molecular weight for the i^{th} PCB (g mol^{-1}).
MW_{CO2} is the molecular weight of CO_2 (44.0094 g mol^{-1}).
u_{10} is the wind speed measured at 10 above the water surface (m day^{-1}).
$V_{PCBi\ w}$ is the water exchange velocity of the i^{th} PCB (m day^{-1}) (10).
V_{CO2} or k_{600} is the CO_2 gas transfer velocity in water (cm h^{-1}) (15, 17, 18).
$Sc_{PCBi\ w}$ is the Schmidt number in water for the i^{th} PCB (10).
$Sc_{PCBi\ CO2\ w}$ is the Schmidt number in water for CO_2 (10).
v_{water} is the kinematic viscosity of water corrected by water temperature (cm^2 s^{-1}).
$D_{PCBi\ w}$ is the diffusivity in the water for the i^{th} PCB (cm^2 s^{-1}) (10).
$D_{CO2\ w}$ is the CO_2 diffusivity in water corrected by water temperature (cm^2 s^{-1}) (19).
v_x is the flow velocity (cm s^{-1}).
h is the water depth (m).
Q is the water flow (m^3 s^{-1}).
w is the wide of the canal (75 m).
A is the sectional canal area (m^2).

$F_{PCBi\ w/s}$ is the flux between water and sediment for the ith PCB (ng m^{-2} day^{-1}) (20).
$k_{f\ PCBi}$ is the sediment/water mass transfer coefficient for the ith PCB (m day^{-1}) (20).
$C_{PCBi\ pw}$ is the porewater concentration in the sediment for the ith PCB (ng m^{-3}).
$C_{PCBi\ w}$ is the concentration in the water column for the ith PCB (ng m^{-3}).
$C_{PCBi\ s}$ is the sediment concentration for the ith PCB (ng g^{-1} d.w.).
$K_{PCBi\ d}$ or $K_{PCBi\ d(Tw)}$ is the solid-water distribution coefficient corrected by water temperature for the ith PCB (L kg^{-1}) (10).
foc is the organic carbon fraction (kg oc kg^{-1}).
$K_{PCBi\ oc\ (Tw)}$ is the organic carbon base partition coefficient corrected by water temperature for the ith PCB (L kg^{-1} oc) (8).
a is 0.94 ± 0.02 (8).
b is -0.42 ± 0.12 (8).
$K_{PCBi\ ow\ (Tw)}$ is the octanol-water partition coefficient corrected by water temperature for the ith PCB (L kg^{-1}) (7, 9).
$K_{PCBi\ ow\ (Tstd)}$ is the octanol-water partition coefficient at standard temperature for the ith PCB (Lkg^{-1}) (6).
$\Delta U_{PCBi\ o/w}$ is the internal energy for the transfer of octanol-water for the ith PCB (J mol^{-1}) (7).
R is the ideal gas constant (8.3144 J mol^{-1} K^{-1} or 8.3144 Pa m^{3} mol^{-1} K^{-1}).
T_w is the water temperature (K).
T_{std} is the standard temperature (298.15 K).
β_{PCBi} is the benthic boundary layer coefficient for the ith PCB (m day^{-1}) (13).
z is the bioturbated depth (0.1 m) (13).
D_b is the biodiffusion coefficient (3.36 x 10^{-7} m^{2} day^{-1}) (13).
ρ is the solids concentration of sediment (0.6 kg L^{-1}) (14).
ν is the water-to-bed friction velocity (m day^{-1}) (20).
ν_x is the flow velocity (m s^{-1}).
n is the coefficient of roughness (0.025 s m$^{-0.33}$) (20).
r_H is the mean hydraulic radius (m).
h is the water depth (m).
g is the gravitational acceleration constant (847,324.8 m day^{-2}).
Q is the water flow (m^{3} s^{-1}).
A is the sectional canal area (m^{2}).
P_w is the wet perimeter (m).
w is the wide of the canal (75 m).
$Sc_{PCBi\ w}$ is the Schmidt number in water for the ith PCB (10).
ν_{water} is the kinematic viscosity of water corrected by water temperature (cm^{2} s^{-1}).
$D_{PCBi\ w}$ is the diffusivity in the water for the ith PCB (cm^{2} s^{-1}) (10).
$D_{CO2\ w}$ is the CO$_2$ diffusivity in water corrected by water temperature (cm^{2} s^{-1}) (19).
MW_{PCBi} is the molecular weight for the ith PCB (g mol^{-1}).
MW_{CO2} is the molecular weight of CO$_2$ (44.0094 g mol^{-1}).

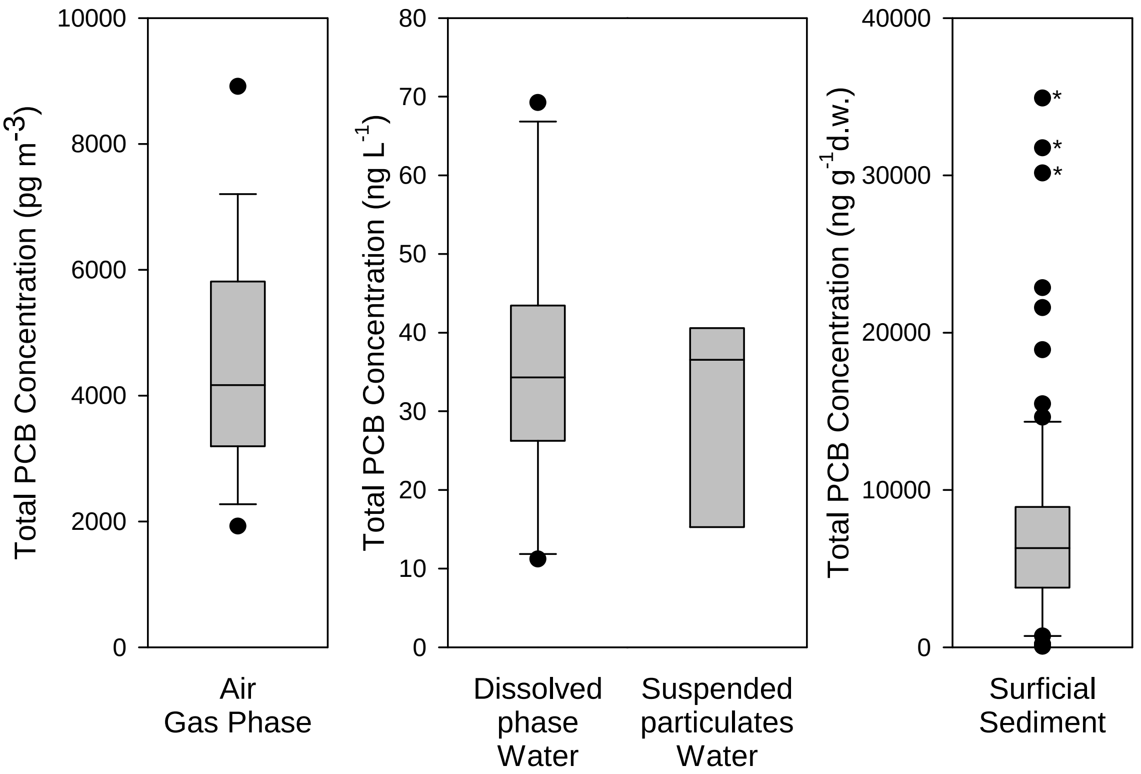

Figure S2. Total PCB concentrations measured in IHSC.
Air n=16, dissolved-phase water n=10, suspended particulates water n=7 and sediment n=60. Asterisk (*) in the surficial sediment samples means that those samples are above the 95th percentile.

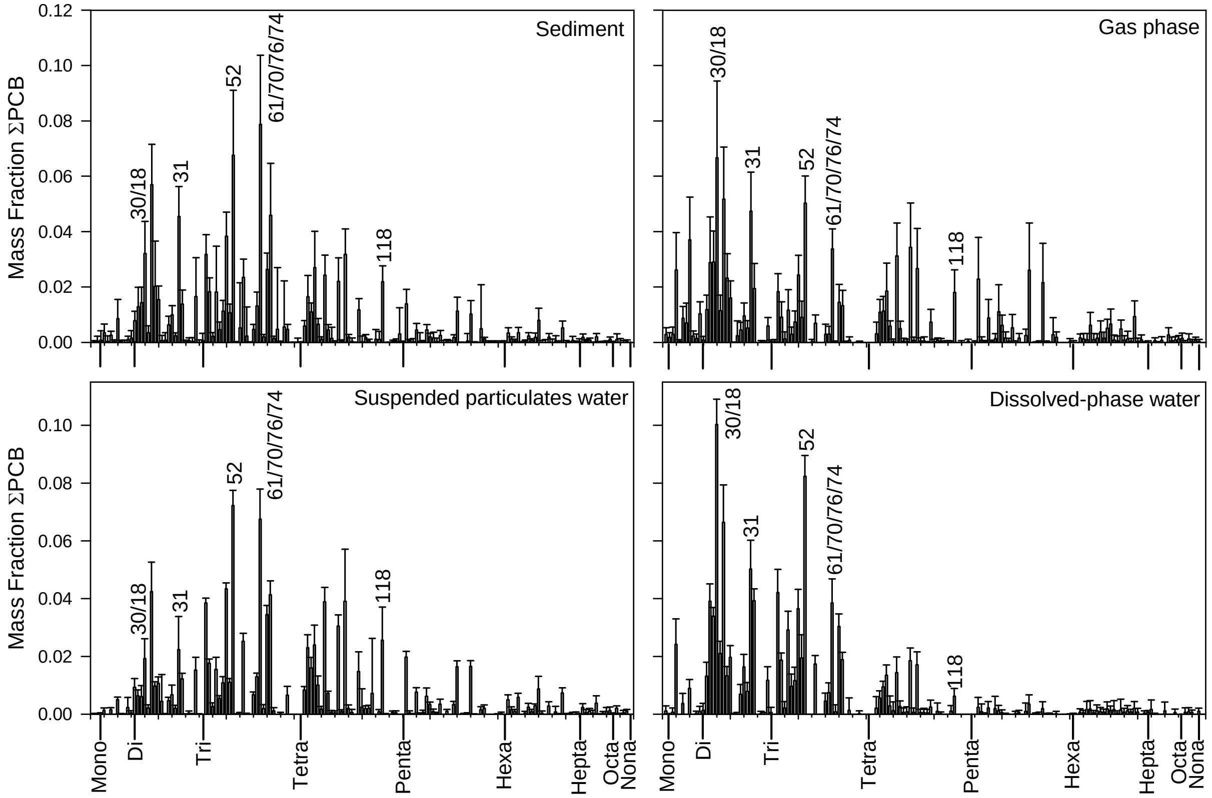

Figure S3. Congener profile distributions in the IHSC.

The congeners in each sample was normalized to its total concentration, and the error bars represents one standard deviation about mean (sediment n=60, air gas phase n=16, suspended particulates water n=7 and dissolved-phase water n=10). Congeners are ordered by “IUPAC” nomenclature (21)

Table S1. Sediment, dissolved-phase and gas phase concentrations of individual congeners measured in IHSC.

These values were applied to the flux calculation and Monte Carlo simulation of the five day period in August 2006. Congeners are ordered by "IUPAC" nomenclature (21).

Congener	Sediment Concentration (ng g^{-1} d.w.)	Dissolved-phase concentration (ng m^{-3})	Gas phase concentration (ng m^{-3})
1	1.200	38.000	0.014
2	1.100	4.200	0.008
3	4.500	23.000	0.012
4	17.000	850.000	0.120
5	0.390	0.000	0.002
6	16.000	140.000	0.043
7	1.500	0.000	0.034
8	46.000	310.000	0.180
9	2.300	0.000	0.011
10	0.860	15.000	0.006
11	5.700	29.000	0.045
12+13	9.200	42.000	0.005
15	43.000	450.000	0.055
16	71.000	1200.000	0.140
17	85.000	1200.000	0.130
18/30	180.000	3400.000	0.310
19	19.000	710.000	0.052
20+28	340.000	2300.000	0.240
21+33	110.000	460.000	0.110
22	90.000	660.000	0.075
23	1.100	3.600	0.000
24	6.200	6.700	0.011
25	43.000	260.000	0.022
26+29	63.000	570.000	0.045
27	15.000	270.000	0.023
31	270.000	1800.000	0.220
32	80.000	1300.000	0.086
34	1.400	0.000	0.000
35	3.100	9.900	0.001
36	0.970	6.800	0.001
37	79.000	390.000	0.027
38	0.380	19.000	0.002
39	0.920	0.000	0.001
40+41+71	190.000	1400.000	0.079
42	120.000	630.000	0.040
43	14.000	87.000	0.004
45+51	110.000	950.000	0.050

46	29.000	320.000	0.012
48	72.000	380.000	0.032
49+69	240.000	1300.000	0.100
50+53	63.000	690.000	0.036
52	420.000	2700.000	0.220
54	0.580	0.000	0.000
55	29.000	0.000	0.002
56	140.000	580.000	0.028
57	1.800	0.000	0.000
58	0.190	0.000	0.000
59+62+75	30.000	170.000	0.012
60	78.000	250.000	0.013
61+70+74+76	480.000	1300.000	0.150
63	13.000	8.800	0.001
64	160.000	1000.000	0.064
66	290.000	640.000	0.058
67	9.200	0.000	0.001
68	7.400	39.000	0.004
72	1.400	0.000	0.000
73	21.000	0.000	0.000
77	30.000	5.500	0.000
78	0.014	0.000	0.000
79	0.110	0.000	0.000
80	1.100	0.000	0.000
81	0.490	0.000	0.000
82	36.000	68.000	0.011
83+99	98.000	200.000	0.047
84	62.000	310.000	0.050
85+86+87+109+115+116+117+119+125	150.000	420.000	0.080
88+91	39.000	76.000	0.026
89	8.000	36.000	0.001
90+101+113	140.000	440.000	0.140
92	27.000	87.000	0.022
93+100	8.900	19.000	0.002
94	1.600	28.000	0.002
95	130.000	590.000	0.150
96	3.300	23.000	0.003
97+110	190.000	520.000	0.110
98+102	12.000	18.000	0.003
103	1.100	20.000	0.002
104	0.018	15.000	0.000
105	70.000	81.000	0.031
106	0.170	0.000	0.001
107	11.000	28.000	0.003

108+124	4.500	7.000	0.002
111	0.002	0.000	0.000
112	7.100	0.000	0.000
114	4.700	32.000	0.001
118	140.000	210.000	0.077
120	0.037	0.000	0.000
121	0.090	0.000	0.001
122	2.200	0.000	0.000
123	2.600	0.000	0.002
126	11.000	0.000	0.000
127	0.260	0.000	0.000
129+138+160+163	79.000	55.000	0.098
130	3.500	25.000	0.004
131	1.100	3.400	0.001
132	25.000	65.000	0.039
133	0.890	0.000	0.001
134+143	2.300	57.000	0.007
135+151	26.000	35.000	0.049
136	11.000	22.000	0.026
137+164	8.900	2.600	0.007
139+140	2.000	0.000	0.002
141	15.000	0.000	0.023
142	0.810	2.600	0.001
144	3.800	22.000	0.007
145	1.300	0.000	0.000
146	11.000	27.000	0.011
147+149	63.000	95.000	0.110
148	0.110	0.000	0.000
150	0.013	5.200	0.000
152	2.400	8.000	0.001
153+168	59.000	48.000	0.093
154	0.310	2.700	0.001
155	0.001	4.600	0.000
156+157	7.100	0.000	0.012
158	7.600	2.700	0.008
159	0.900	0.000	0.000
161	0.250	0.000	0.000
162	0.270	0.000	0.000
165	0.009	0.780	0.001
167	1.800	2.500	0.001
169	1.000	0.000	0.000
170	19.000	14.000	0.008
171+173	6.500	11.000	0.006
172	3.200	38.000	0.004
174	19.000	40.000	0.028

175	0.340	15.000	0.004
176	2.400	30.000	0.006
177	13.000	20.000	0.017
178	3.800	24.000	0.007
179	9.500	53.000	0.021
180+193	45.000	46.000	0.029
181	0.062	45.000	0.004
182	0.031	9.700	0.002
183	10.000	40.000	0.020
184	0.068	26.000	0.004
185	2.500	30.000	0.004
186	0.420	19.000	0.002
187	29.000	66.000	0.040
188	0.032	29.000	0.001
189	0.220	0.000	0.004
190	3.200	13.000	0.000
191	0.320	19.000	0.001
192	0.380	50.000	0.000
194	10.000	3.500	0.003
195	3.000	0.000	0.000
196	4.800	0.000	0.003
197	0.150	32.000	0.000
198+199	12.000	0.000	0.012
200	0.830	0.000	0.002
201	1.000	13.000	0.004
202	1.700	0.000	0.006
203	6.500	0.000	0.006
205	0.140	18.000	0.001
206	4.100	20.000	0.005
207	0.390	18.000	0.002
208	0.960	0.000	0.003
209	1.100	24.000	0.001

Table S2. Summary of air and water ΣPCB concentrations reported in this study and others.

Location	Air – gas phase (pg m^{-3})	Water – dissolved (ng L^{-1})	Water – particulate (ng L^{-1})	Reference
IHSC (August, 2006)	1900 – 9000	10 - 70	11 - 36	This work
IHSC (summers, 2003 – 2004)	190 - 310			(22)
Southern Baltic Sea (March, May, June, 1999)	10	0.008 – 0.016		(23)
New York – New Jersey Harbor Estuary (July, 1998)	1000 – 3100	1.4 – 4.2	2.3 – 5.2	(11)
IHSC (August, 1998)	1.34 – 1.61			(24)
Chicago (1996 – 2003)	100 – 9500			(25)
Southern Lake Michigan (May and July, 1994 and January, 1995)	132 – 1120	0.039 – 0.23		(26)
Green Bay (June to October, 1989)	250 - 2300	0.46 – 8	0.13 – 33.5	(12)

Table S3. Examples of arithmetic average of air-water and sediment-water parameters for PCB homolog groups calculated for the sampling period.
Parameters were calculated using equations and constants described in Figure S1, and the following environmental and hydraulic conditions. Homolog groups are ordered by "IUPAC" nomenclature (21).

T_w = 291.97 K
T_a = 296.78 K
P = 1018.77 mbar
u_{10} = 103,680 (m day^{-1})
Q = 18.97 (m^3 s^{-1})
h =5 (m)
$D_{water\ a}$=0.271 (cm^2 s^{-1})
$D_{CO2\ w}$=0.0000162 (cm^2 s^{-1})
v_{water} = 0.0104 (cm^2 s^{-1})

PCB homolog group	Air-water exchange velocity $V_{PCBi\ a/w}$ (m day^{-1})	Schmidt number in water $Sc_{PCBi\ w}$	Solid-water distribution coefficient corrected by water temperature $K_{PCBi\ d}$ (L kg^{-1})	Benthic boundary layer coefficient β_{PCBi} (m day^{-1})	Solubilization mass transfer coefficient $k_{f\ PCBi}$ (m day^{-1})
Monochlorobiphenyls	0.247	1330.000	0.268	0.268	0.001
Dichlorobiphenyls	0.237	1450.000	0.254	0.254	0.003
Trichlorobiphenyls	0.227	1550.000	0.242	0.242	0.008
Tetrachlorobiphenyls	0.213	1650.000	0.232	0.232	0.021
Pentachlorobiphenyls	0.200	1750.000	0.223	0.223	0.044
Hexachlorobiphenyls	0.194	1840.000	0.216	0.216	0.073
Heptachlorobiphenyls	0.185	1930.000	0.210	0.210	0.110
Octachlorobiphenyls	0.164	2010.000	0.204	0.204	0.148
Nonachlorobiphenyls	0.158	2090.000	0.199	0.199	0.166
Decachlorobiphenyls	0.145	2160.000	0.194	0.194	0.178

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