Global Biogeochemical Cycles

Supporting Information for:

A global 3-D ocean model for polychlorinated biphenyls (PCBs): Benchmark compounds for understanding the impacts of global change on neutral persistent organic pollutants

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Introduction

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Table S1. Air-sea exchange parameterization.

Variable (Units)	Description	Equation	Reference
F (mol m^{-2} sec^{-1})	flux of gas across the air-sea interface	$F = K_w(C_a/K_H - C_w)$	1
C_a (mol m^{-3})	Air concentration	GEOS-Chem atmospheric simulation	2
C_w (mol m^{-3})	Water concentration	MITgcm ocean simulation	This work
K_H	dimensionless gas-over-liquid Henry's law constant	$K_H = C_a / C_w$	--
--	Temperature dependence of K_H	$K_H = K_{H0}$ *exp($-\Delta H/R$ * $(1/T - 1/T_0)$)	3
T_0 (Kelvin)	Standard temperature	25 °C = 298.15 K	--
T (Kelvin)	Temperature of seawater	MITgcm ocean simulation	This work
K_{H0}	Dimensionless gas-over-liquid Henry's law constant at standard temperature and pressure (1 atm)	See Table S2	--
ΔH (J mol^{-1})	Enthalpy of solution	See Table S2	--
R (J K^{-1} mol^{-1})	Universal gas constant	8.314	--
K_w (m sec^{-1})	Total water-side transfer velocity	$K_w = (1 - f_{ice})*[1/k_w + 1/(k_a K_H)]^{-1}$	4
k_a (m sec^{-1})	Single-phase air-side transfer velocity	$k_a = 1 \times 10^{-3} + \frac{u_*}{13.3 {S_{c,a}}^{0.5} + {C_D}^{-0.5} - 5 + \frac{\ln(S_{c,a})}{2\kappa}}$	5
k_w (cm h^{-1})	Single-phase water-side transfer velocity	$k_w = (0.222 u_{10}^2 + 0.333 u_{10})*(S_{c,w} / S_{c,CO2})^{-0.5}$	6
f_{ice} (0 to 1)	Grid box sea ice fraction	MITgcm ocean simulation	This work
$S_{c,CO2}$	Schmidt number of CO_2 at 20 °C in freshwater	600	4
$S_{c,w}$	Schmidt number for the PCB of interest	$S_{c,w} = \mu_w / D_w = \eta_w / (\rho_w D_w)$	4
μ_w (units)	Kinematic viscosity of water	--	--

D_w (in cm^2 sec^{-1})	Diffusivity of the gas-phase PCB in water	$D_w = \frac{7.4 \times 10^{-8} T \sqrt{\Phi M_s}}{\eta_s {V_b}^{0.6}}$	7
η_w (kg m-1 s-1)	Dynamic viscosity of water	$\eta_w = \frac{t + 246}{0.05594t^2 + 5.2842t + 137.37} 1 \times 10^{-3}$	8
ρ_w (kg m^{-3})	Density of sea water	1.03	4
t (°C)	Seawater temperature	MITgcm ocean simulation	This work
V_b (cm^3 mol^{-1})	Liquid molar volume	See Table S2	--
η_s (kg m^{-1} s^{-1})	Dynamic viscosity of seawater at 15°C	1.219	9
M_s	Relative molecular mass of the solvent	18.01 for water	7
Φ	Association factor of the solvent	2.6 for water	7
u_* (m s^{-1})	Description of u_{star}	$u_* = u_{10}\ sqrt(\ 6.1 \cdot 10^{-4} + u_{10}\ 6.3 \cdot 10^{-5}\ )$	5
u_{10} (m s^{-1})	10-meter wind speed	Provided by ERA Re-analysis data	
C_D	Drag coeffcient	$C_D = 6.1 \cdot 10^{-3} + 6.3 \cdot 10^{-5}\ u_{10}$	10
κ	von Karman constant	0.4	4
$S_{c,a}$	Schmidt number in air	$S_{c,a} = \mu_a / D_a = \eta_a / (\rho_a D_a)$	4
μ_a (units)	Kinematic viscosity of air	--	--
D_a (units)	Diffusion coefficient in air	$D_a = 0.001 T^{1.75} \frac{{M_r}^{0.5}}{P[{V_a}^{1/3} + {V_b}^{1/3}]^2}$	11
η_a (kg m^{-3})	Dynamic viscosity of water (air)	$\eta_a = S_{V0} + S_{V1}t + S_{V2}t^2 + S_{V3}t^3 + S_{V4}t^4$	12
ρ_a (kg m^{-3})	Density of air	$\rho_a = S_{D0} + S_{D1}t + S_{D2}t^2 + S_{D3}t^3$	12
S_V and S_D	Constants	*values*	12
P	Atmospheric pressure	1 atm	--
V_a (cm^3 mol^{-1})	Molar volume of air	20.1	13
M_r (units)	Description	$M_r = (M_a + M_b) / (M_a M_b)$	4
M_a (g mol^{-1})	Molar mass of air	28.97	--
M_b (g mol^{-1})	PCB molar mass	See Table S2	--

(1) *Liss and Slater* [1974]; (2) *Friedman and Selin* [2015]; (3) *Sander* [1999]; (4) *Johnson* [2010]; (5) *Duce et al.* [1991]; (6) *Nightingale et al.* [2000]; (7) *Wilke and Chang* [1955]; (8) *Laliberté* [2007]; (9) *ITTC* [2006]; (10) *Smith* [1980] (11) *Fuller et al.* [1966]; (12) *Tsilingiris* [2008]; (13) *Tucker and Nelken* [1990].

Table S2. Physicochemical properties of PCBs.

	CB-28	**CB-101**	**CB-153**	**CB-180**	**Reference**
molar mass, M_b (g mol^{-1})	257.54	326.43	360.88	395.32	1
molar volume, V_b (cm^3 mol^{-1})	169.14	193.62	205.86	218.1	2
log K_{OW} (unitless)	5.92	6.76	7.31	7.66	3
log K_H (unitless)	-1.93	-2.08	-2.13	-2.51	3
log K_{OC}* (unitless)	6.99	7.79	8.32	8.65	3, 4
enthalpy of air-water exchange, ΔH (kJ mol^{-1})	51.8	65.2	68.2	69.0	3
Degradation half-life, $t_{1/2}$ (hours)	5 500	31 000	55 000	55 000	5

(1) *Li et al.* [2003]; (2) *Schwarzenbach et al.* [2003]; (3) *Schenker et al.* [2005]; (4) *Sobek et al.* [2004]; (5) *Wania and Daly* [2002]

*Calculated using the relationship from *Sobek et al.* as follows: $logK_{OC} = (0.88 \pm 0.07)logK_{OW} + (0.90 \pm 0.47)$ [2004].

Table S3. Modeled and measured dissolved seawater concentrations.

Ocean Basin	Surface ocean (<10 m) Observed median/ percentiles (pg/L)		Modeled median/ percentiles (pg/L)
CB-28			
Arctic Ocean	0.18 (0.03. 0.57)	(n=41)	0.29 (0.16, 0.54)
North Atlantic	0.41 (0.13, 2.33)	(n=11)	0.09 (0.02, 0.18)
South Atlantic	0.16 (0.06, 1.04)	(n=14)	<0.02
Eq. and S. Pacific	0.76 (0.33, 2.45)	(n=16)	<0.01
Southern Ocean	0.045 (0.024, 0.158)	(n=17)	0.003 (0.002, 0.009)
Mediterranean Sea	0.51 (0.18, 3.93)	(n=16)	0.09 (0.06, 0.16)
Global Mean	**0.23 (0.03-2.21)**		**0.09 (0.06, 0.16)**
CB-101			
Arctic Ocean	0.040 (0.018, 1.549)	(n=38)	0.038 (0.022, 0.076)
North Atlantic	0.39 (0.05, 0.61)	(n=15)	0.02 (0.01, 0.05)
South Atlantic	0.33 (0.05, 0.52)	(n=54)	<0.02
Eq. and S. Pacific	1.54 (0.26, 6.35)	(n=10)	<0.005
Southern Ocean	0.38 (0.10, 0.91)	(n=19)	<0.001
Mediterranean Sea	0.76 (0.39, 1.89)	(n=7)	0.05 (0.03, 0.06)
Global Mean	**0.30 (0.03, 1.78)**		**0.01 (<0.06)**
CB-153			
Arctic Ocean	0.039 (0.005, 1.425)	(n=18)	0.142 (0.097, 0.352)
North Atlantic	0.14 (0.02, 1.06)	(n=7)	0.11 (0.07, 0.46)
South Atlantic	0.040 (0.009, 0.200)	(n=8)	0.009 (<0.071)
Southern Ocean	0.068 (0.035, 0.347)	(n=19)	0.001 (<0.004)
Mediterranean Sea	1.17 (0.13, 5.54)	(n=20)	0.36 (0.18, 0.45)
Global Mean	**0.082 (0.010, 1.766)**		**0.122 (<0.427)**
CB-180			
Arctic Ocean	0.020 (0.004, 0.193)	(n=16)	0.008 (0.006, 0.024)
North Atlantic	0.080 (0.045, 0.244)	(n=4)	0.022 (0.010, 0.045)
South Atlantic	0.032 (0.028, 0.053)	(n=4)	0.001 (<0.003)
Southern Ocean	0.012 (0.002, 0.117)	(n=18)	<0.0003
Mediterranean Sea	0.35 (0.06, 5.81)	(n=22)	0.04 (0.01, 0.44)
Global Mean	**0.053 (0.04, 0.603)**		**0.008 (<0.041)**

	Epi- and Mesopelagic Zone (top 1000 m)		Bathypelagic Zone (> 1000 m)	
Ocean Basin	**Observed median/ percentiles (pg/L)**	**Modeled median/ percentiles (pg/L)**	**Observed median/ percentiles (pg/L)**	**Modeled median/ percentiles (pg/L)**
CB-28				
Arctic Ocean	0.19 (0.03, 0.57) (n=43)	0.29 (0.15, 0.54)	0.22 (0.12, 0.30) (n=3)	1.49 (0.72-2.04)
North Atlantic	0.42 (0.13, 2.40) (n=13)	0.09 (0.02, 0.18)	NA	
South Atlantic	0.12 (0.01, 1.00) (n=18)	<0.30	0.49 (n=1)	2.55
Eq. and S. Pacific	0.76 (0.33, 2.45) (n=16)	<0.01	NA	
Southern Ocean	0.045 (0.024, 0.158) (n=17)	0.003 (0.002, 0.009)	NA	
Global Mean	**0.24 (0.03, 2.27)**	**0.08 (<0.43)**	**0.26 (0.12, 0.49)**	**1.76 (0.72, 2.55)**
CB-101				
Arctic Ocean	0.040 (0.018, 1.458) (n=40)	0.037 (0.014, 0.076)	0.08 (0.03, 0.14) (n=3)	0.04 (0.02, 0.06)
North Atlantic	0.39 (0.05, 0.60) (n=20)	0.02 (0.01, 0.03)	0.27 (0.11, 0.70) (n=7)	0.22 (0.05, 0.43)
South Atlantic	0.35 (0.06, 1.54) (n=58)	<0.01	2.50 (n=1)	0.39
Eq. and S. Pacific	1.54 (0.26, 6.35) (n=10)	<0.01	NA	
Southern Ocean	0.38 (0.10, 0.91) (n=19)	<0.001	NA	
Global Mean	**0.33 (0.03, 2.19)**	**0.01 (<0.06)**	**0.24 (0.04, 2.23)**	**0.25 (0.02, 0.39)**
CB-153				
Arctic Ocean	0.049 (0.005, 1.419) (n=20)	0.138 (0.058, 0.352)	0.004 (0.004, 0.150) (n=3)	0.114 (0.071, 0.161)
North Atlantic	0.10 (0.02, 0.14) (n=12)	0.07 (0.05, 0.11)	0.22 (0.07, 0.82) (n=10)	0.85 (0.29, 5.85)
South Atlantic	0.062 (0.010, 3.470) (n=12)	0.016 (<0.184)	2.6 (n=1)	0.94
Southern Ocean	0.068 (0.035-3.47) (n=19)	0.001 (<0.004)	NA	
Global Mean	**0.13 (0.01, 3.05)**	**0.13 (<0.42)**	**0.19 (<1.90)**	**0.77 (0.09, 5.85)**
CB-180				
Arctic Ocean	0.020 (0.004, 0.192) (n=16)	0.008 (0.006, 0.024)	NA	NA
North Atlantic	0.06 (n=1)	0.01	0.06 (0.03-0.29) (n=8)	0.20 (0.02-1.10)
South Atlantic	0.13 (0.03, 0.32) (n=8)	<0.01	0.34 (n=1)	0.08
Southern Ocean	0.012 (0.002, 0.117) (n=18)	<0.0003	NA	NA
Global Mean	**0.086 (0.004, 0.703)**	**0.008 (<0.041)**	**0.060 (0.031, 0.338)**	**0.079 (0.034, 1.072)**

Modeled concentrations were compared to measurements collected between 2000 and 2015 and matched by year. Measurements included cover the Arctic Ocean [*Booij et al.*, 2014; *Galbán-Malagón et al.*, 2012; *Gioia et al.*, 2008a; *Gustafsson et al.*, 2005; *Sobek and Gustafsson*, 2014], the North Atlantic [*Galbán-Malagón et al.*, 2012; *Gioia et al.*, 2008b; *Gioia et al.*, 2008a; *Lohmann et al.*, 2012; *Sun et al.*, 2016], the South Atlantic [*Booij et al.*, 2014; *Gioia et al.*, 2008b; *Lohmann et al.*, 2012; *Sun et al.*, 2016], the Pacific Ocean [*Zhang and Lohmann*, 2010], the Indian Ocean [*Booij et al.*, 2014], and the Southern Ocean [*Galbán-Malagón et al.*, 2013].

Figure S1. Modeled vertical profiles from five sensitivity simulations**.** Panel a shows vertical profiles of CB-28 with uniform degradation (orange), photolytic degradation (green) and combined photolytic and biotic degradation (blue). Panel b shows vertical profiles of CB-153 using log K_{OC} of 5.82 (pink), 7.64 (dark blue) and 8.32 (dark-green).

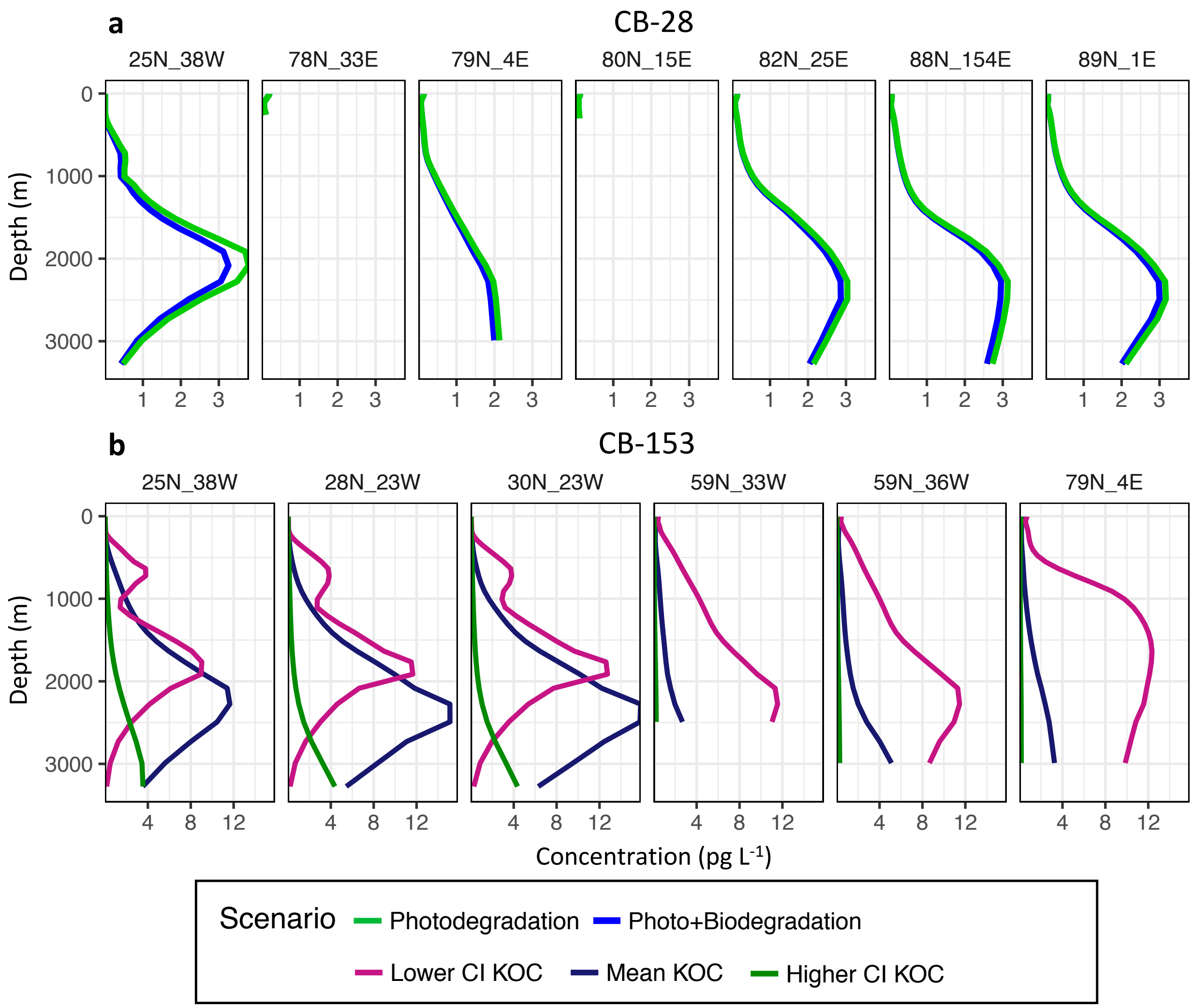

Figure S2. Measured PCB depth profiles of a) CB-28, b) CB-101, c) CB-153 and d) CB-180. Profiles are from the Tropical Atlantic [*Booij et al.*, 2014; *Sun et al.*, 2016], the North Atlantic [*Booij et al.*, 2014] and the Arctic Ocean [*Gustafsson et al.*, 2005; *Sun et al.*, 2016]. Concentrations at depth exceed the surface concentrations wherever surface concentrations exist and peak between 40 and 2500 m. Reported maximum concentrations are 1.30 pg CB-28 L^{-1}, 3.3 pg CB-101 L^{-1}, 3.5 pg CB-153 L^{-1} and 0.34 pg CB-180 L^{-1}.

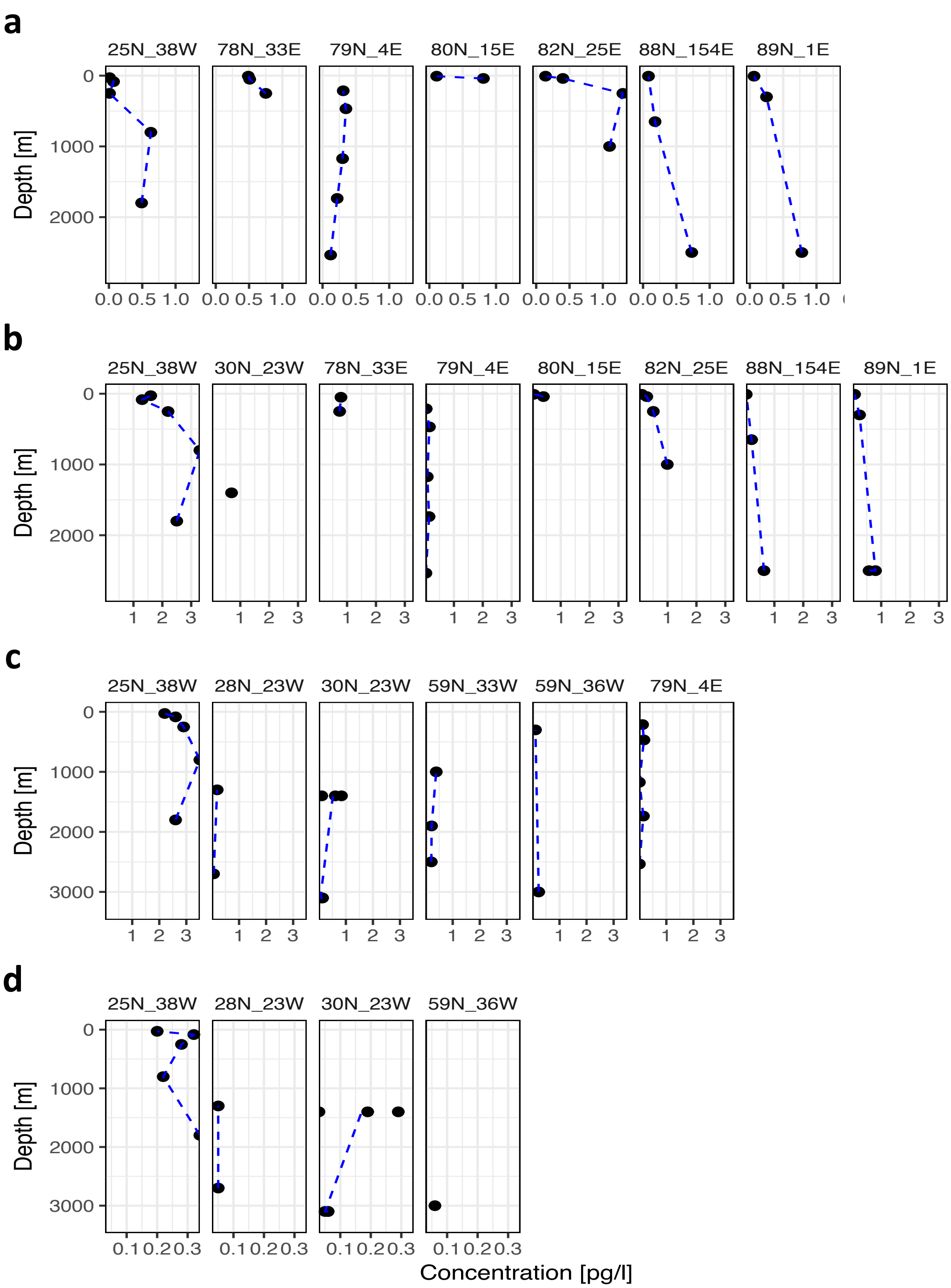

Figure S3. Changes in PCB residence times in the upper 1000 m between 1970-2015.

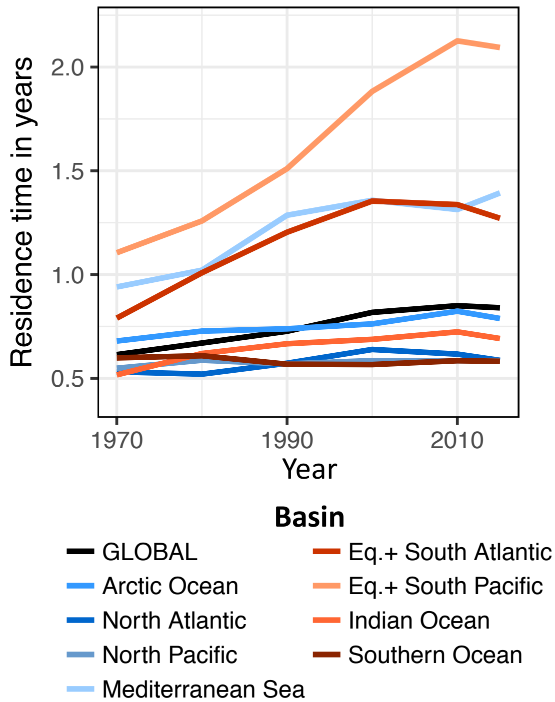

Figure S4. Changes in CB-101 and CB-180 mass distribution between 1930-2015. Northern Hemisphere basins are shades of blue and Southern Hemisphere basins are shades of red/orange.

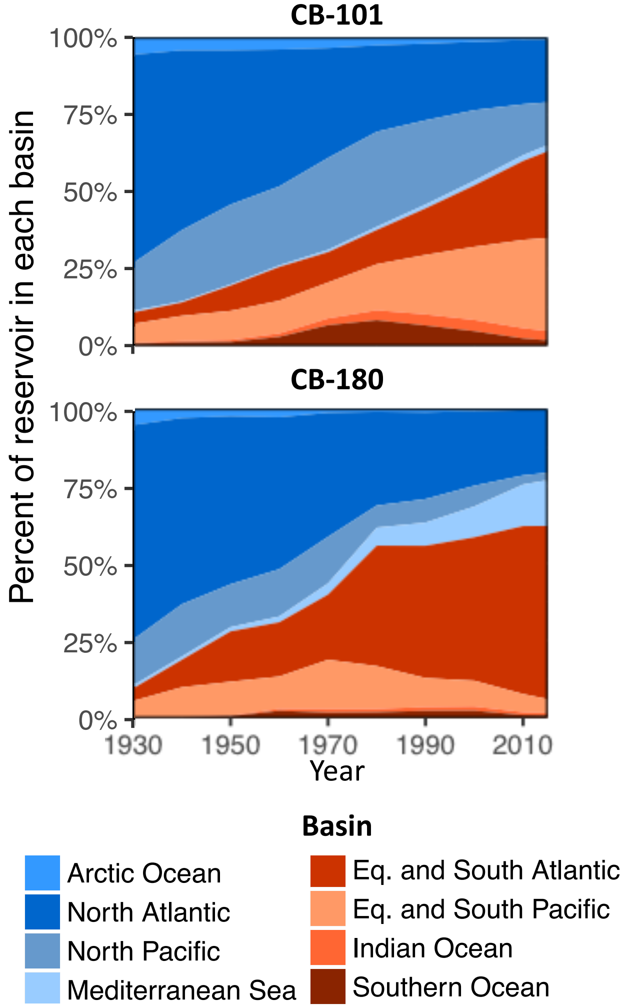

Table S4. Modeled best estimate for 2015 PCB reservoir (kg) and mass flows (kg yr^{-1}) in the upper ocean (top 1000 m) using high K_{OC} and a combination of photolytic and biotic degradation.

	CB-28	**CB-101**	**CB-153**	**CB-180**
Arctic Ocean				
Reservoir	**1 089**	**99**	**1 047**	**98**
Atm. deposition	752	129	1 935	193
Upward/downward vert. transport[a]	103/-85	5/-4	18/-16	1/-1
Hor. Transport[b]	-45	-2	-3	0
Particle sinking	-174	-43	-622	-64
Burial	-151	-51	-944	-96
Degradation	-82	-1	-4	0
Evasion	-369	-31	-163	-8
North Atlantic				
Reservoir	**2 905**	**404**	**3 467**	**339**
Atm. deposition	2 356	418	5 658	623
Upward/downward vert. transport[a]	192/-227	20/-22	106/-142	9/-13
Hor. transport	-1 108	-275	-933	-106
Particle sinking	-525	-220	-3 593	-419
Burial	-225	-78	-1 395	-163
Degradation	-803	-37	-137	-9
Evasion	-907	-113	-645	-40
North Pacific				
Reservoir	**1 644**	**272**	**2 161**	**181**
Atm. deposition	1 846	424	4 520	409
Upward/downward vert. transport[a]	29/-31	3/-3	13/-20	1/-2
Hor. transport	-10	-1	-1	0
Particle sinking	-690	-286	-3 439	-318
Burial	-156	-49	-714	-67
Degradation	-492	-23	-39	-2
Evasion	-607	-75	-236	-10
Mediterranean Sea				
Reservoir	**363**	**244**	**1 257**	**117**
Atm. deposition	309	66	688	87
Upward/downward vert. transport[a]	14/-14	23/-21	76/-71	4/-4
Hor. transport	0	-1	-17	-3
Particle sinking	-9	-26	-282	-41
Burial	-10	-14	-232	-34
Degradation	-238	-24	-108	-9
Evasion	-69	-22	-161	-13
Eq. and South Atlantic				
Reservoir	**1 707**	**329**	**1 540**	**142**
Atm. deposition	438	102	894	98
Upward/downward vert. transport[a]	41/-56	7/-5	24/-17	2/-2

Hor. transport	871	171	446	20
Particle sinking	-72	-44	-486	-64
Burial	-10	-7	-94	-11
Degradation	-315	-33	-135	-11
Evasion	-99	-38	-255	-20
Eq. and South Pacific				
Reservoir	**1 357**	**252**	**992**	**73**
Atm. deposition	485	145	983	97
Upward/downward vert. transport[a]	54/-33	15/-13	30/-24	2/-1
Hor. transport	25	-2	-5	0
Particle sinking	-144	-77	-782	-85
Burial	-5	-6	-69	-8
Degradation	-355	-39	-87	-5
Evasion	-117	-50	-186	-10
Indian Ocean				
Reservoir	**247**	**75**	**353**	**34**
Atm. deposition	266	77	527	58
Upward/downward vert. transport[a]	23/-14	4/-2	14/-10	1/-1
Hor. transport	59	26	135	24
Particle sinking	-39	-42	-373	-45
Burial	-4	-6	-65	-8
Degradation	-183	-16	-45	-3
Evasion	-57	-19	-86	-6
Southern Ocean				
Reservoir	**753**	**119**	**889**	**95**
Atm. deposition	680	177	1 729	197
Upward/downward vert. transport[a]	265/-188	17/-13	77/-71	7/-7
Hor. transport	208	85	377	66
Particle sinking	-418	-153	-1 620	-188
Burial	-22	-7	-73	-8
Degradation	-102	-2	-3	0
Evasion	-243	-19	-49	-3

[a]Upward/downward vert. transport denotes gross upward/downward and includes advective and diffusive vertical transport.
[b]Hor. transport denotes net horizontal diffusion and advection.