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Supplement of

PCBs in the Arctic atmosphere: determining important driving forces using a global atmospheric transport model

C. L. Friedman and N. E. Selin

Correspondence to: C. L. Friedman (carey.friedman@mma.edu)

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Modeling surface media and air-surface exchange PCB dynamics
The descriptions of surface media modules given below are for use with MERRA meteorological datasets. Slight variations exist when the GEOS5 dataset is employed due to lack of certain variables compared to MERRA (e.g., no sea ice). Within each surface medium, concentrations within a given gridbox for the current time step are calculated, and then masses lost due to various processes are estimated. Losses are subtracted from the current mass and either lost from the medium as ultimate model sinks (e.g., deposition of PCBs to sediments in lakes and oceans), passed to other media (e.g., PCBs lost from snow in meltwater can be passed to soils, lakes, or oceans), or passed back to the atmosphere as re-emissions. All degradation rates and partition coefficients are temperature-corrected using the van't Hoff equation. References provided within each section were used for parameterization of the surface medium module and for coefficient or rate values.

Vegetation
The fractional coverage of a grid box by vegetation is estimated by first determining whether the leaf area index (LAI) within the grid box is greater than zero. If LAI > 0, then a fraction of vegetation (f_{VEG}) is calculated by multiplying the fraction of soil in the grid box (f_{SOIL}) by a "vegetation greenness fraction" (GRN).

$$f_{VEG} = f_{SOIL} \times GRN$$

If LAI is less than or equal to zero, f_{VEG} is set to zero.

The mass of PCB incorporated into vegetation is equal to 100% of the dry deposition to f_{VEG} plus 10% of the wet deposition to f_{VEG}. The other 90% of wet deposition is assumed to wash directly from vegetation into soil (see below).
To calculate PCB concentrations within vegetation, we assume all vegetation has a thickness (L_{VEG}) of ~0.01 m (0.01 m reservoir thickness plus 2×10^{-6} m surface thickness). While GRN is used to estimate fractional coverage of vegetation within a gridbox, LAI is used to estimate concentration. I.e., the volume of vegetation in a grid box is (V_{VEG}; m^3)

$$V_{VEG} = A_{GB} \times LAI \times L_{VEG} \times f_{SOIL}$$

where A_{GB} is the area of the grid box. Thus, the concentration in vegetation (C_{VEG}; mol/m^3) within a grid box is

$$C_{VEG} = \frac{(m_{VEG,P} + m_{VEG,C})}{(MW \times V_{VEG})}$$

where $m_{VEG,P}$ is the mass of PCB already accumulated in vegetation within a gridbox and $m_{VEG,C}$ is the deposited mass for the current time step (both in kg) and MW with the molar mass of the of the PCB in kg/mol.

Concentrations are then converted to fugacities for the sake of calculating diffusive gradients and loss rates, and for ease of comparison to other POP models, which generally tend to be multimedia fugacity models. The fugacity in vegetation, F_{VEG}, is determined by dividing C_{VEG} by the fugacity capacity (Z_{VEG})

$$F_{VEG} = \frac{C_{VEG}}{Z_{VEG}}$$

where F_{VEG} is in units of Pa, equivalent to partial pressure, and Z_{VEG} is in units of mol m^{-3} Pa^{-1}. Z_{VEG} is a combination of the Z values of the surface and reservoir compartments of the vegetation

$$Z_{VEG} = (f_{SURF} \times f_{OCT,SURF} \times Z_{OCT}) + (1 - f_{OCT,SURF}) \times (f_{H2O,RES} \times Z_{H2O} + f_{OCT,RES} \times Z_{OCT})$$

where f_{SURF} is the fraction of the total leaf volume that is the surface layer (2×10^{-4}), $f_{OCT,SURF}$ is the fraction of octanol-like material within the surface layer (0.8), Z_{OCT} is the fugacity capacity of octanol (mol m^{-3} Pa^{-1}), $f_{H2O,RES}$ is the fraction of reservoir volume that is water (0.7), Z_{H2O} is the fugacity capacity of water (mol m^{-3} Pa^{-1}), and $f_{OCT,RES}$ is the fraction of octanol-like material in the reservoir (0.02). Z_{OCT} and Z_{H2O} are determined as follows

$$Z_{OCT} = \frac{Z_{AIR}}{K_{OA}}$$

$$Z_{H2O} = \frac{1}{(K_{AW} \times R \times T_{SURF})}$$

where Z_{AIR} is the fugacity capacity of air (mol m^{-3} Pa^{-1}), K_{OA} is the dimensionless octanol-air partition coefficient, K_{AW} is the dimensionless air-water partition coefficient, R is the gas constant, and T is the ground surface temperature (K). Z_{AIR} is defined as

$$Z_{AIR} = \frac{1}{R \times T_{AIR}}$$

where T_{AIR} is the temperature of the surface layer of air (K).

Re-emissions (passed to atmosphere)
The vegetation re-emission rate (E_{VEG}; kg/s) is calculated as follows

$$E_{VEG} = \frac{FLUX_{VEG} \times MW \times A_{GB} \times LAI}{3600}$$

where $FLUX_{VEG}$ (mol hr^{-1} m^{-2}) is the flux of PCB across the air-vegetation boundary and is calculated as follows

$$FLUX_{VEG} = DLA(F_{VEG} - F_{AIR})$$

F_{AIR} is the fugacity in air (Pa), calculated from the concentration in the air (C_{AIR}; mol/m3)

$$F_{AIR} = \frac{C_{AIR}}{Z_{AIR}}$$

DLA is the overall transfer coefficient for PCBs in vegetation (mol hr^{-1} Pa^{-1} m^2):

$$DLA = \frac{1}{\frac{1}{DC} + \frac{1}{DABF}}$$

DC and DABF are the transfer coefficients for cuticle and boundary layer diffusions, respectively (mol hr^{-1} Pa^{-1} m^2).

$$DC = UC{\times}Z_{VEG}$$

$$DABF = UABF{\times}Z_{AIR}$$

where UC is the cuticle mass transfer coefficient (m/h) and UABF is the mass transfer coefficient for the vegetation surface-air boundary layer diffusion (set to 9 m/h).

$$UC = 3600{\times}PC{\times}\frac{1}{K_{AW}}$$

PC is the cuticle permeance (m/s) and is given by

$$\begin{aligned}&\log(PC)\\&= \frac{(0.704{\times}\log(K_{OW}) - 11.2) + (-3.47 - 2.79{\times}\log(MW) = 0.970{\times}\log(K_{OW}))}{2}\end{aligned}$$

Degradation (ultimate sink)
The degradation rate in vegetation (DEG_{VEG}; kg/s) is calculated as

$$DEG_{VEG} = D_{RXN}{\times}F_{VEG}{\times}MW/3600$$

where D_{RXN} (mol hr^{-1} Pa^{-1}) is the degradation mass transfer coefficient

$$D_{RXN} = DEG_R{\times}V_{VEG}{\times}Z_{VEG}$$

where DEG_R is the temperature-corrected decay rate (hr^{-1}) based on the PCB half-life in vegetation ($t_{1/2}$; hr)

$$DEG_R = \frac{0.693}{t_{1/2}}$$

Litter loss (passed to soil)
The litter loss rate ($LITR_{VEG}$; kg/s) is calculated as

$$LITR_{VEG} = D_{LITR} \times F_{VEG} \times MW / 3600$$

where D_{LITR} is the litter loss mass transfer coefficient (mol hr^{-1} Pa^{-1}) assuming an average leaf cycle of 1 year

$$D_{LITR} = \frac{D_{LITR} \times Z_{VEG} \times V_{VEG}}{24 \times 365}$$

All loss rates in kg/s are multiplied by f_{SOIL}, LAI, and time to calculate final loss quantities in kg within a model time step. We multiply by f_{SOIL} as all vegetation volume is assumed to exist over the portion of the grid box that is soil.

References for vegetation module: Cousins and Mackay, 2000, 2001; Mackay, 2001; Mackay and Paterson, 1991

Soil
The fractional coverage of a grid box by soil (f_{SOIL}) is estimated by subtracting the fraction of snow (f_{SNOW}) from the fraction of land (f_{LAND}), which is obtained from the meteorological data and does not include lakes or land ice:

$$f_{SOIL} = f_{LAND} - f_{SNOW}$$

The mass of PCB incorporated into soils is equal to total deposition delivered to vegetation-free soil (i.e., f_{SOIL}-f_{VEG}) plus 90% of the wet deposition to vegetation, plus litter losses from vegetation, plus losses from melting snow (discussed below).
To calculate soil concentrations, we assume PCBs distribute through only the top 5 cm of soil (i.e., soil depth, L_{SOIL}, is equal to 0.05 m). Hence, soil volume (V_{SOIL}; m³) is

$$V_{VEG} = A_{GB} \times L_{SOIL} \times f_{SOIL}$$

The concentration in soil (C_{SOIL}; mol/m³) within a grid box is then

$$C_{SOIL} = \frac{(m_{SOIL,P} + m_{SOIL,C})}{(MW \times V_{SOIL})}$$

where $m_{SOIL,P}$ is the mass of PCB already accumulated in soils within a gridbox and $m_{SOIL,C}$ is the mass deposited from the sources listed above for the current time step (both in kg). Air and soil concentrations are converted to fugacities (see above for air):

$$F_{SOIL} = \frac{C_{SOIL}}{Z_{SOIL}}$$

where Z_{SOIL} is the fugacity capacity in soil (mol m⁻³ Pa⁻¹), calculated as

$$Z_{SOIL} = \frac{K_{SA}}{R \times T_{SURF}}$$

where K_{SA} is a temperature-dependent dimensionless soil-air partition coefficient. K_{SA} is estimated from the K_{OW}

$$K_{SA} = 1.5 \times f_{OC} \times K_{OW}$$

where f_{OC} is the fraction of organic carbon in the soil. f_{OC} is generated with a version of the CASA biogeochemical model previously coupled to GEOS-Chem (Smith-Downey et al., 2010) at latitudes between 60N and 60S; at the poles, a mean Arctic tundra lowlands soil carbon content (15.1 kg C/m²) from the organic-enriched surface horizon (Ping et al., 2008) is used to estimate f_{OC}, as f_{OC} is not well defined by CASA in seasonally ice-covered regions.

Re-emissions (passed to atmosphere)
The soil re-emission rate (E_{SOIL}; kg/s) is calculated as follows

$$E_{SOIL} = \frac{FLUX_{SOIL} \times MW \times A_{GB} \times f_{SOIL}}{3600}$$

where $FLUX_{SOIL}$ (mol hr^{-1} m^{-2}) is the flux of PCB across the air-soil boundary and is calculated as follows

$$FLUX_{SOIL} = DS(F_{SOIL} - F_{AIR})$$

DS is the overall mass transfer coefficient for soil-air diffusion (mol m^{-2} hr^{-1} Pa^{-1}) and is given by

$$DS = \frac{1}{\frac{1}{DSA} + \frac{PL}{DAD + DWD}}$$

DSA is the air-side boundary layer diffusion parameter (mol m^{-2} hr^{-1} Pa^{-1}), PL is the soil diffusion path length, set to one half the soil depth (i.e., 0.025 m), DAD is the diffusion parameter between soil particles and interstitial soil air (mol m^{-1} hr^{-1} Pa^{-1}), and DWD is the diffusion parameter between soil particles and porewater (mol m^{-1} hr^{-1} Pa^{-1}).

$$DSA = KSA \times Z_{AIR}$$

$$DAD = BA \times Z_{AIR}$$

$$DWD = BW \times Z_{H2O}$$

where KSA (1 m/h), BA is the molecular diffusivity in air (0.04 m^2/hr), and BW is the molecular diffusivity in water (4x10^{-6} m^2/hr).

Degradation (ultimate sink)
The degradation rate in soil (DEG_{SOIL}; kg/s) is calculated as

$$DEG_{SOIL} = D_{RXN} \times F_{SOIL} \times MW / 3600$$

where D_{RXN} (mol hr^{-1} Pa^{-1}) is the degradation mass transfer coefficient

$$D_{RXN} = DEG_R \times V_{SOIL} \times Z_{SOIL}$$

where DEG_R is the temperature-corrected decay rate (hr^{-1}) based on the PCB half-life in soil ($t_{1/2}$; hr)

$$DEG_R = \frac{0.693}{t_{1/2}}$$

Water runoff (ultimate sink)
The dissolved PCB runoff rate from soils (W_{RATE}; kg/s) is calculated as

$$W_{RATE} = D_{WROFF} \times F_{SOIL} \times MW / 3600$$

where D_{WROFF} (mol hr^{-1} Pa^{-1}) is the mass transfer term, calculated as

$$D_{WROFF} = A_{GB} \times 0.3 \times W_{ROFF} \times Z_{H2O}$$

where 0.3 is the fractional volume of water in soil and W_{WROFF} (m/h) is the water runoff rate, set to 40% of the precipitation rate

$$W_{ROFF} = 0.4 \times P$$

where P is the precipitation rate (m/hr) provided by meteorological data.

Solids runoff (ultimate sink)
The runoff rate for PCBs associated with soil solids (S_{RATE}; kg/s) is calculated as

$$S_{RATE} = D_{SROFF} \times F_{SOIL} \times MW / 3600$$

where D_{SROFF} (mol hr^{-1} Pa^{-1}) is the mass transfer term, calculated as

$$D_{SROFF} = A_{GB} \times 0.3 \times S_{WROFF} \times Z_{SOIL}$$

where $S_{WRUNOFF}$ is the solids runoff rate, set to 2×10^{-8} m/hr .

Leaching (ultimate sink)
The leaching rate of PCBs from soil (L_{RATE}, kg/s) is calculated as

$$L_{RATE} = D_{LCH} \times F_{SOIL} \times MW / 3600$$

where D_{LCH} is the leaching transfer coefficient (mol hr^{-1} Pa^{-1}), equal to D_{WROFF} above.

All loss rates in kg/s are multiplied by $f_{SOIL,}$ and time to calculate final loss quantities in kg within a model time step.

References for soil module: Mackay, 2001; Mackay and Paterson, 1991; Ping et al., 2008; Potter et al., 1993; Ribes et al., 2003; Smith-Downey et al., 2010

<u>Oceans/lakes</u>
The fractional coverage of a grid box by lakes (f_{LAKE}) is given by the meteorological data. The fractional coverage of open ocean (f_{OCEAN}) is estimated from the total ocean coverage ($f_{TOTOCEAN}$) and the fraction of sea ice (f_{SEAICE}), both of which are provided by MERRA:

$$f_{OCEAN} = f_{TOTOCEAN} - f_{SEAICE}$$

The mass of PCB accumulated in oceans and lakes is equal to total deposition delivered to each as well as PCBs delivered from ice/snow melt water.
To calculate concentrations, we assume PCBs distribute through the entire volume of water. Volume (m³) is calculated as follows (designated with the subscript "water" as a general reference to either lakes or oceans), with the depth of the ocean (L_{OCEAN}) assumed to be 1000 m and the depth of lakes (L_{LAKE}) assumed to be 10 m.

$$V_{WATER} = A_{GB} \times L_{WATER} \times f_{WATER}$$

The concentrations in water (C_{WATER}; mol/m³) within a grid box are then

$$C_{WATER} = \frac{(m_{WATER,P} + m_{WATER,C})}{(MW \times V_{WATER})}$$

where $m_{WATER,P}$ is the mass of PCB already accumulated in water in a gridbox and $m_{WATER,C}$ is the mass deposited from the sources listed above for the current time step (both in kg). Concentrations are converted to fugacities

$$F_{WATER} = \frac{C_{WATER}}{Z_{WATER}}$$

where in this case, Z_{WATER} accounts for the fugacity capacity of both the aqueous and particle solid phases.

$$Z_{WATER} = \frac{1}{K_{AW} \times R \times T_{SURF}} + (10^{-6} \times \frac{K_{SA}}{R \times T_{SURF}})$$

10^{-6} is the assumed volume fraction of particles in water. For K_{SA} (defined above), we assume the f_{OC} in aqueous particles is 0.2.

Re-emissions (passed to atmosphere)
The re-emission rate from water bodies (E_{WATER}; kg/s) is calculated as follows

$$E_{WATER} = \frac{FLUX_{WATER} \times MW \times A_{GB} \times f_{WATER}}{3600}$$

where FLUX$_{WATER}$ (mol hr^{-1} m^{-2}) is the flux of PCB across the air-water boundary and is calculated as follows

$$FLUX_{WATER} = KOL(F_{WATER} - F_{AIR})$$

where KOL (mol hr^{-1} Pa^{-1}) is the overall mass transfer coefficient across the air-water boundary, calculated as

$$KOL = \cfrac{1}{\cfrac{1}{KA \times A_{GB} \times Z_{AIR}} + \cfrac{1}{KW \times A_{GB} \times Z_{AIR}}}$$

where KA and KW are the air- and water-side mass transfer coefficients (m/hr), respectively. KA is calculated as

$$KA = \frac{KA_{H2O}(\frac{DA}{DA_{H2O}})^{0.67}}{100} \times 3600$$

where DA is the diffusivity of the PCB in air (cm^2/s), DA$_{H2O}$ is the diffusivity of water in air, and KA$_{H2O}$ is the exchange velocity of water in air (cm/s).

$$DA = 10^{-3} \times \frac{T_{AIR}^{1.75} \times \left(\left(\frac{1}{MW_{AIR}}\right) + \left(\frac{1}{MW \times 10^3}\right)\right)^{0.5}}{P\left(V_{AIR}^{0.33} + V_{PCB}^{0.33}\right)^2}$$

$$DA_{H2O} = 10^{-3} \times \frac{T_{AIR}^{1.75} \times \left(\left(\frac{1}{MW_{AIR}}\right) + \left(\frac{1}{MW_{H2O}}\right)\right)^{0.5}}{P\left(V_{AIR}^{0.33} + V_{H2O}^{0.33}\right)^2}$$

$$KA_{H2O} = 0.2u_{10} + 0.3$$

where MW$_{AIR}$ is the molar mass of air (28.97 g/mol), V$_{AIR}$ is the average molar volume of air (20.1 cm^3/mol), V$_{PCB}$ is the PCB molar volume (cm^3/mol), MW$_{H2O}$ is the molar mass of water (18.1 g/mol), V$_{H2O}$ is the average molar volume of water (16.73 cm^3/mol), P is the air pressure (atm), and u$_{10}$ is the wind speed at 10 m (m/s). The latter two variables are obtained from meteorological data.

KW is calculated as

$$KW = \frac{KW_{CO2}(\frac{Sc_{PCB}}{Sc_{CO2}})^{-\alpha}}{100} \times 3600$$

where KW_{CO2} is the mass transfer coefficient of CO_2 in water (cm/s), Sc_{PCB} is the Schmidt number for the PCB (unitless), Sc_{CO2} is the Schmidt number of CO_2, and α is an exponent derived from observations. KW_{CO2} and α depend on the wind speed as follows

if u_{10} <= 4.2 then
$$KW_{CO2} = 0.65 \times 10^{-3}$$
$$\alpha = 0.67$$
if $4.2 < u_{10}$ <= 13 then
$$KW_{CO2} = (0.79 \times u_{10} - 2.68) \times 10^{-3}$$
$$\alpha = 0.5$$
if $13 < u_{10}$ then
$$KW_{CO2} = (1.64 \times u_{10} - 13.69) \times 10^{-3}$$
$$\alpha = 0.5$$

The Schmidt numbers are estimated by

$$Sc_{PCB} = \frac{\upsilon_{H2O}}{DW}$$

$$Sc_{CO2} = \frac{\upsilon_{H2O}}{DW_{CO2}}$$

where υ_{H2O} is the temperature-dependent kinematic viscosity of water (cm^2/s), DW is the diffusivity of the PCB in water (cm^2/s), and DW_{CO2} is the diffusivity of CO_2 in water (cm^2/s). The diffusivities are given by

$$DW = \frac{13.26 \times 10^{-5}}{(\upsilon_{H2O} \times 100)^{1.14} (V_{PCB})^{0.589}}$$

$$DW_{CO2} = \frac{13.26 \times 10^{-5}}{(\upsilon_{H2O} \times 100)^{1.14} (V_{CO2})^{0.589}}$$

where V_{CO2} is the molar volume of the CO_2 (cm^3/mol).

Degradation (ultimate sink)
The degradation rate in water (DEG$_{WATER}$; kg/s) is calculated as

$$DEG_{WATER} = D_{RXN} \times F_{WATER} \times MW / 3600$$

where D_{RXN} (mol hr^{-1} Pa^{-1}) is the degradation mass transfer coefficient

$$D_{RXN} = DEG_R \times V_{WATER} \times Z_{WATER}$$

where DEG_R is the temperature-corrected decay rate (hr^{-1}) based on the PCB half-life in water ($t_{1/2}$; hr)

$$DEG_R = \frac{0.693}{t_{1/2}}$$

Deposition to sediment (ultimate sink)
The deposition rate of PCBs (DEP_{RATE}; kg/s) is calculated as

$$DEP_{RATE} = DDX \times F_{WATER} \times MW / 3600$$

where DDX is the mass transfer coefficient for particle settling (mol hr^{-1} Pa^{-1}) , given by

$$DDX = \frac{UDX \times A_{GD} \times Z_{PART}}{365 \times 24}$$

where UDX is a velocity for the deposition of suspended particles to the sediment bed (assumed to be 4x10^{-4} m/yr) and Z_{PART} is the fugacity capacity of the particles, given by

$$Z_{PART} = \frac{K_{SA}}{R \times T_{SURF}}$$

All loss rates in kg/s are multiplied by f_{WATER} and time to calculate final loss quantities in kg within a model time step.

References for oceans/lakes modules: Mackay, 2001; Mackay and Paterson, 1991; Schwarzenbach et al., 2003

Snow/Ice

The fractional coverage of a grid box by snow or ice (f_{SNOW}), assumed to be one substance and henceforth referred to as "snow", is given by

$$f_{SNOW} = \min (f_{SNOW} + f_{SEAICE} + f_{LANDICE}, 1)$$

where the fractional values on the right-hand side of the equation are provided by MERRA. The mass of PCB accumulated in snow is equal to total deposition delivered directly to the snow. To calculate concentrations, we assume PCBs distribute through the entire volume of snow. Volume (m³) is calculated using a snow depth (L_{SNOW}; m) that is also given by the meteorological data. To avoid dividing by small numbers, when snow is present its depth is set to a minimum of 10 mm.

$$V_{SNOW} = A_{GB} \times L_{SNOW} \times f_{SNOW}$$

The concentrations in snow (C_{SNOW}; mol/m³) within a grid box are then

$$C_{SNOW} = \frac{(m_{SNOW,P} + m_{SNOW,C})}{(MW \times V_{SNOW})}$$

where $m_{SNOW,P}$ is the mass of PCB already accumulated in snow in a gridbox and $m_{SNOW,C}$ is the mass deposited from the sources listed above for the current time step (both in kg). Concentrations are converted to fugacities

$$F_{SNOW} = \frac{C_{SNOW}}{Z_{WATER}}$$

where Z_{SNOW} accounts for the fugacity capacity of interstitial air, water, meltwater at the interface (Z_{INTER}), and organic matter in the snow (Z_{OM}), all in mol m⁻³ Pa⁻¹

$$Z_{SNOW} = (Z_{AIR} \times V_{AIR-SNOW}) + (Z_{WATER} \times V_{WATER-SNOW}) + Z_{INTER} + (Z_{OM} \times V_{OC-SNOW})$$

where $V_{AIR-SNOW}$, $V_{WATER-SNOW}$, and $V_{OM-SNOW}$ are the volume fractions of air, water, and organic matter in the snow. $V_{OM-SNOW}$ is assumed to be 4×10^{-7}, while $V_{AIR-SNOW}$ and $V_{WATER-SNOW}$ are given by

$$V_{AIR-SNOW} = POR - V_{WATER-SNOW}$$

If T_{SURF} <= 248.15 K then
$$V_{WATER-SNOW} = 10^{-4}$$
if 248.15 K <= T_{SURF} < 273.15 K then
$$V_{WATER-SNOW} = 0.004 \times T_{SURF} - 0.99$$
if T_{SURF} >= 273.15 K then
$$V_{WATER-SNOW} = 0.1$$

where POR is the porosity of the snow (unitless), given by

$$POR = \frac{(\rho_{ICE} - \rho_{SNOW})}{\rho_{SNOW}}$$

where ρ_{ICE} and ρ_{SNOW} are the densities of ice and snow, respectively. ρ_{ICE} is assumed to be 917 kg/m³, while ρ_{SNOW} (kg/m³) is calculated as

$$\rho_{SNOW} = 350.29(e^{-0.0162 \times SSA_t})$$

where SSA_t is the time- and temperature-dependent snow specific surface area (m²/kg), given by

$$SSA_t = SSA_0(e^{-\alpha t})$$

where SSA_0 is the initial snow specific surface area (40 m²/kg), α is the snow settling rate (d⁻¹), and t is time (d). α is given by

$$\alpha = (8.87 \times 10^{-4})e^{1708/T_{SURF}}$$

Z_{INTER} and Z_{OM} are given by

$$Z_{INTER} = \frac{K_{CA}}{R \times T_{SURF}}$$

$$Z_{OM} = \frac{K_{OA}}{R \times T_{SURF}}$$

where K_{CA} is a dimensionless temperature-dependent snow-air adsorption coefficient, adjusted using the van't Hoff equation from $K_{CA\text{-}266}$ (m), the snow-air adsorption coefficient at 266 K, as follows

$$K_{CA} = SSA_T \times \rho_{SNOW} \times K_{CA-266} e^{(\frac{-\Delta H_{IA}}{R}(\frac{1}{T_{SURF}} - \frac{1}{T_{266}}))}$$

where ΔH_{IA} is the enthalpy of sorption at the liquid-air interface (J/mol), given by

$$\Delta H_{IA} = (-5.07 \log(K_{IA-288}) - 108) \times 1000$$

where $K_{IA\text{-}288}$ is the water-air adsorption coefficient at 15 C (m), and is given by

$$\log(K_{IA-288}) = 0.635 \times \log(L16) + (5.11 \times SUM_\beta) + (3.6 \times SUM_\alpha) - 8.47$$

similarly, $K_{CA\text{-}266}$ is given by

$$\log{(K_{CA-26})} = 0.639 \times \log(L16) + (3.38 \times SUM_{\beta}) + (3.53 \times SUM_{\alpha}) - 6.85$$

L16 is the hexadecane-air partition coefficient, taken from (Abraham and Al-Hussaini, 2005), while SUM_{β} and SUM_{α} are the overall electron acceptor and donor (respectively) strengths for the partitioning.

Re-emissions (passed to atmosphere)
The re-emission rate from snow (E_{SNOW}; kg/s) is calculated as follows

$$E_{SNOW} = \frac{FLUX_{SNOW} \times MW \times A_{GB} \times f_{SNOW}}{3600}$$

where $FLUX_{SNOW}$ (mol hr^{-1} m^{-2}) is the flux of PCB across the air-snow boundary and is calculated as follows

$$FLUX_{SNOW} = DSP_A(F_{SNOW} - F_{AIR})$$

where DSP_A is the transfer coefficient for snow-air diffusion (mol hr^{-1} Pa^{-1})

$$DSP_A = \frac{A_{GB}}{\frac{1}{USA_{BL} \times Z_{AIR}} + \frac{1}{WPF \times USA_{PS} \times Z_{AIR}}}$$

where USA_{BL} is the air-side exchange velocity over snow (m/hr), WPF is a wind pumping factor for ventilating interstitial air (unitless), and USA_{PS} is the mass transfer coefficient for air-filled pore space (m/hr). USA_{BL} is given by

$$USA_{BL} = \frac{k^2 \times u_{10}}{\ln\left(\frac{Z_W}{Z_0}\right) \ln\left(\frac{Z_{REF}}{Z_0}\right)}$$

where k is the von Karman constant (0.4, unitless), Z_w is the height of the wind (10 m), Z_0 is the surface roughness for snow (0.001 m), and Z_{REF} is the reference height (10 m).

USA_{PS} is given by

$$USA_{PS} = \frac{BA(1 - \frac{\rho_{SNOW}}{\rho_{ICE}})^{1.5}}{0.693 \times L_{DEPTH}}$$

where BA is the molecular diffusivity of the PCB in air, set to 0.04 m^2/hr.

Degradation (ultimate sink)
The degradation rate in snow (DEG_{SNOW}; kg/s) is calculated as

$$DEG_{SNOW} = D_{RXN} \times F_{SNOW} \times MW / 3600$$

where D_{RXN} (mol hr^{-1} Pa^{-1}) is the degradation mass transfer coefficient

$$D_{RXN} = DEG_R \times V_{SNOW} \times Z_{SNOW}$$

where DEG_R is the temperature-corrected decay rate (hr^{-1}) based on the PCB half-life in snow ($t_{1/2}$; hr)

$$DEG_R = \frac{0.693}{t_{1/2}}$$

Meltwater runoff (passed to soils, lakes, and oceans, depending on what other media are present in a given grid box)
The runoff rate of PCBs in meltwater (MW_{SNOW}; kg/s) is given as

$$MW_{SNOW} = D_{MLT} \times F_{SNOW} \times MW / 3600$$

where D_{MLT} (mol hr^{-1} Pa^{-1}) is the transfer coefficient for meltwater runoff, given by

$$D_{MLT} = V_{WATER-SNOW} \times A_{GB} \times L_{SNOW-MAX} \times Z_{WATER} \times K_{MLT}$$

where $L_{SNOW-MAX}$ is the maximum snow height (set to 4 m) and K_{MLT} is a melting rate (set to 0.0013 hr^{-1}).

Particle flush loss (ultimate sink)
The rate of PCBs lost with particle flushing (P_{FLUSH}; kg/s) is given by

$$P_{FLUSH} = \frac{D_{FLUSH} \times F_{SNOW} \times MW}{3600}$$

where D_{FLUSH} is the particle transfer coefficient (mol hr^{-1} Pa^{-1}), given by

$$D_{FLUSH} = V_{ORG} \times Z_{OM} \times K_{MELT}$$

where V_{ORG} (m^3) is the volume of organic matter in the snow, which we estimate by

$$V_{ORG} = V_{OC-SNOW} \times A_{GB} \times L_{SNOW}$$

All loss rates in kg/s are multiplied by f_{SNOW} and time to calculate final loss quantities in kg within a model time step.

References for snow/ice module: Abraham and Al-Hussaini, 2005; Daly and Wania, 2004; Hansen et al., 2006; Roth et al., 2004; Stocker et al., 2007

Table S1. Physicochemical parameters used in GEOS-Chem model, including new surface media routines

Physicochemical parameter	Units	CB 28	CB 52	CB 101	CB 118	CB 138	CB 153	CB 180	Ref
Molar mass	kg/mol	0.25754	0.29199	0.32643	0.32643	0.36088	0.36088	0.39532	a
K_{OA}	unitless	7.24E+07	1.66E+08	6.76E+08	2.75E+09	4.68E+09	2.82E+09	1.48E+10	b
k_{OH}	cm^3/s	1.10E-12	9.55E-13	5.89E-13	5.89E-13	3.63E-13	3.63E-13	2.24E-13	c
K_{AW}	unitless	1.17E-02	1.10E-02	8.32E-03	4.37E-03	1.07E-02	7.41E-03	3.09E-03	b
ΔH_{vap}	J/mol	78400	81300	84400	89800	86.9	94800	95200	b
ΔH_{sol}	kJ/mol	51.8	53.8	65.2	65.2	64.7	68.2	69	b
Soil $t_{1/2}$	hr	55000	55000	55000	55000	55000	55000	55000	d
E_{act} for degradation in air	J/mol	10000	10000	10000	10000	10000	10000	10000	e
E_{act} for degradation in all surface media	J/mol	30000	30000	30000	30000	30000	30000	30000	e
Molar volume	cm^3/mol	169.14	181.38	193.62	193.62	205.86	205.86	218.1	f
Water $t_{1/2}$	hr	17000	55000	55000	55000	55000	55000	55000	d
Vegetation $t_{1/2}$	hr	550	1700	1700	1700	5500	5500	5500	d
Log L16 (hexadecane-air partition coef. for snow routine)	unitless	7.9	8.1	8.9	9.4	9.8	9.6	10.4	g
Σ_{alpha} (electron acceptor for snow routine)	unitless	0	0	0	0	0	0	0	g
Σ_{beta} (electron donor for snow routine)	unitless	0.15	0.15	0.13	0.11	0.11	0.11	0.09	g
Snow $t_{1/2}$	hr	17000	55000	55000	55000	55000	55000	55000	d

References: (a) Li et al., 2003, (b) Schenker et al., 2005, (c) Anderson and Hites, 1996; CB28 k_{OH} was determined experimentally, - all other congener k_{OH} values were determined using the following relationship derived within: log k = -0.21(#Cl) – 11.18, where k is in units of 10^{-12} cm^3/s, (d) Mackay et al., 2006, (e) chosen to be consistent with Lamon et al., 2009 and Gouin et al., 2013, (f) Schwarzenbach et al., 2003, (g) Abraham and Al-Hussaini, 2005.

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