Global transport of POPs: the role of aerosol particles

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Persistent Organic Pollutants

Organic chemical compounds and mixtures that include industrial chemicals like PCBs, pesticides like DDT HCH and wastes like dioxins.

- Volatile and semi-volatile
- Long life time in the atmosphere
Grasshopper Effect
Global Emissions of $\alpha$-HCH and Arctic Concentrations

(Li and Bidleman, 2003)
Cycles of POPs in the Atmosphere

Atmospheric Processes
- Partitioning
- Dry and Wet Removals
- Chemical Degradation

Atmospheric Transports

Exchanges/Emissions

Atmospheric Particle Surface and Particle Removal

\[ \text{Soil} \rightarrow C_S \rightarrow F_S \rightarrow \text{Water} \rightarrow C_W \rightarrow F_W \rightarrow \text{Anthropogenic} \rightarrow F_A \rightarrow \text{Atmosphere} \]
Transport Model
Modeling System

CANadian Model for POPs

- CAN/POPs Framework
  - Transport Models
  - Emissions
  - Exchange Modules
  - Aerosol Module
- PCB Simulation Results
Transport Model - GEM
Global Environment Model

Canadian Weather Forecast Model

Global Uniform
400x200 ~ 90 km

Variable Global
Focused ~ 25 km

Limited Area
~ 200 m
Properties by Transport Model

• Advection
• Vertical Mixing
• Metrological Parameters
  Wind speed, clouds, precipitation, T, P, RH ....
Exchanges/Emissions
Air/Water Exchange

**Flux (mol/m²/s)**

\[ F_W = K_{TA} (C_W \cdot K_{AW} - C_G) \]

**Mass transfer coefficient** \( K_{TA} \) (s/m)

\[ 1 / K_{TA} = 1 / k_A + K_{AW} / k_w \]

- **a)** in water (Wanninkhof, 1992)
  \[ k_w = [2.5 \ (0.5246 + 1.6256 \times 10^{-2} \cdot T + 4.9946 \times 10^{-4} \ T^2) + 0.3u_{10}^2] \cdot (Sc/660)^{-1/2} \]

- **b)** in air (Mackay et al., 1983)
  \[ k_A (m/s) = 10^{-3} + 4.62 \times 10^{-4} \times (6.1 + 0.63u_{10})^{0.5} \cdot u_{10} \cdot [Sc_{pcb,air}]^{-0.67} \]

**Boundary layers**

- AIR
- WATER

- 30 > H (for PCB’s) > 0.1
- 0.01 > \( K_{AW} \) > 10⁻⁵
**Air/Soil Exchange**

- **Flux** (mol/m²/s)
  \[ F_S(0, t) = \frac{1}{R_T} (C_{G, soil}(0, t) - C_{G, air}(0, t) K_{SA}) \left[ 1 - \exp\left(\frac{-L^2}{4D_{ES}t}\right) \right] \]

- **Total resistance** (s/m)
  \[ R_T = \left[ K_{SA} R_A + r_s \right] \]

\( K_{SA} \) the soil-air equilibrium coefficient and \( D_{ES} \) (m²/s) the effective diffusivity of the chemical in the soil matrix.
Anthropogenic PCB

Estimated cumulative global usage of PCBs (T)
Breivik (2001)
PCB Atmospheric Processes
Removals

- Dry deposition
  - Water, Snow and Vegetation
- Scavenging
  - by Snow and Rain
- OH Reaction
Junge-Pankow Partition
(Junge, 1997; Pankow, 1987)

\[ \Phi = \frac{c \cdot \Theta}{P_L^0 + c \cdot \Theta} = \frac{C_P}{C_P + C_G} \]

\( \Theta \) - the aerosol surface area available for adsorption \( (\text{m}^2 \text{ aerosol}/\text{m}^3 \text{ air}) \),
\( P_L^0 \) - the liquid-phase saturation vapour pressure of pure compound \( \text{(Pa)} \),
\( c \) - a parameter that depends on the thermodynamics of the adsorption process and surface properties of the aerosol \( \text{(Pa.cm)} \).
PCBs partitioned to aerosol particles will be removed from the atmosphere by the same mechanism as the aerosol particles by dry deposition, in-cloud and below-cloud removals.
Global Aerosol Distributions

(courtesy of S. Kinne MPI, Hamburg, Germany)
Types of Aerosol Emissions

- **Anthropogenic**
  - SOx, NOx, VOC, BC/OC
  - Bio-mass burning emission
  - Governmental (or private) statistics
  - Meteorology redistributed

- **Natural**
  - Sea-salt, DMS, biomass burning, soil dust
  - Nature
  - Meteorology driven, surface features
Wet Processes

- Below-Cloud Scavenging of Aerosols
  Rain or Snow (Washout)
- Aerosol Activation
  CCN
- Evaporation of Clouds to Aerosols
  Bi-modal Formation
- Precipitation Removals
  Rain or Snow (Rainout)
- Cloud Chemistry
  CTM
Global Aerosol Surface Areas
Simulation Results
Model Configurations

- Meteorology - Year 2000
- $2^\circ \times 2^\circ$ resolution
- 20 minute integration time
- GEIA Emissions for aerosols
- PCB emissions (Breivik et al. 2001)
- Initial atmospheric, soil and water PCB concentrations from MSC-E modeling results.
PCB 28

Date: 05JAN2000; Pentad: 1

ng m⁻²
PCB 180

Date: 05JAN2000; Pentad: 1

ngm^-2
Roervik

Monthly PCB 153 vs PCB 180
Daily PCB 153 vs PCB 180

Kosetice

![Graphs showing daily PCB concentrations for PCB 153 and PCB 180 over Julian Day with observations and model predictions.](image-url)
PCB 153 vs PCB 180

Spitsbergen

Observations vs Model for PCB 153 and PCB 180 concentrations over Julian Day.
PCB 153 vs PCB 180

Arctic Alert

PCB 153

PCB 180

Observation Yr 2000
Model
Observation Yr 1992
Vertical Profiles

ng m⁻³
Vertical Profiles

ng m$^{-3}$
Intercontinental Transports

PCB28

Particle/Gas
kg/year

PCB180

Atlantic

~0/~0

505/4430

64W,30N

27/364

14W,60N

91/446

16/0.5

277/50

14W,60N

7/6

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Intercontinental Transports

PCB28

Particle/Gas kg/year

132/4867

66E,60N

~0/~0

14W,30N

-53/1034

Europe

675/6948

PCB180

88/10

66E,60N

~0/~0

14W,30N

14/31

Europe

71/7
Intercontinental Transports

PCB28

Particle/Gas kg/year

PCB180

Asia

675/6948
66°E, 30°N
18/406

658/5010

260/656
146°E, 60°N

1/-0.4

146°E, 60°N

71/7

29/3

2/5

66°E, 30°N

Asia
Intercontinental Transports

PCB28

Particle/Gas kg/year

PCB180

Pacific

102/188

658/5010

126W,60N

2/1

29/3

4/1

1/2

77/347

289/1149

146E,30N

126W,60N

Pacific
Global transport patterns of POPs vary greatly by their chemical and physical properties.

Aerosol particles play an important role in the global transport of POPs for semi volatile POPs.

Heavy PCBs are transported through particle phases while lighter PCBs through gas phases.

Lighter PCBs transport longer distances than heavy PCBs.

Inter-continental transports of PCBs are dominated by light PCBs.
Future Works

- More accurate emissions of POPs are needed.
- Comparison of model results with observations of network monitoring needs to be done to validate model results.
- For some persistent POPs, a global survey of the soil concentrations is needed due to its function as a dominant source of POPs.
- Seasonal and inter-annual variability of inter-continental transports need further study.