POP intercontinental transport: main processes

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POPs

Persistent Organic Pollutants are multi-phase, long-lived toxic chemicals which have a tendency to partition between air, water and organic phases

POPs – pollutants of global concern

Regional and International Programmes:

EMEP, HELCOM, OSPAR, GLBTS, AMAP, UNEP, OECD

Regional and global international agreements:

Protocol on POPs **UN ECE**

Stockholm Convention **UNEP**

Traditional POPs and new substances

POPs considered within existed international agreements:

HCB, HCHs, PCBs, Dioxins & Furans, PAHs, ...

New substances – candidates for POPs (Task Force on POPs):

Polybrominated diphenyl ethers (PBDEs)
Hexachlorobutadien (HCBD)
. . .

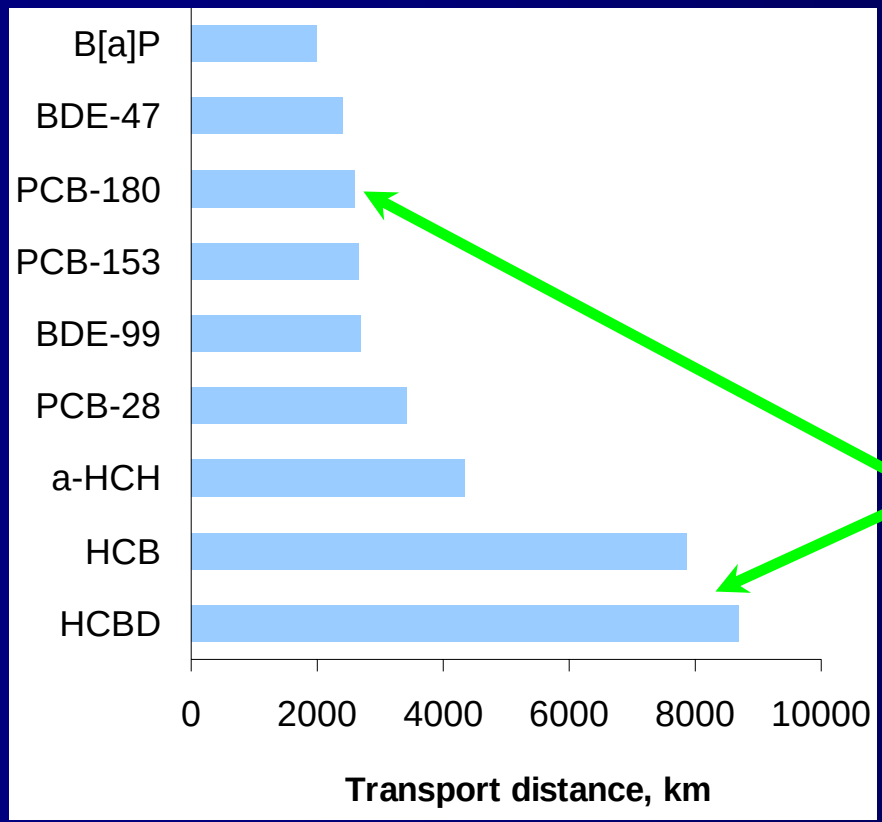
POP long-range transport

Long-range transport of POPs is determined by :

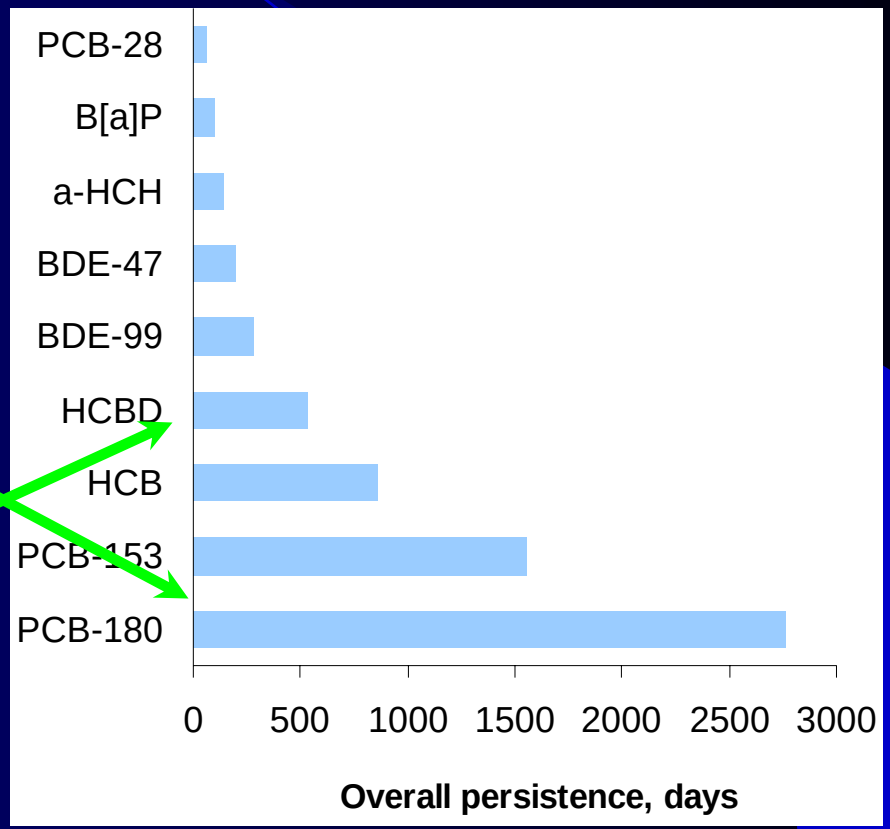
- **Physical-chemical properties of POPs**
  vapor pressure,
  partitioning between air-water,
  solubility, degradation rates, ...
- **Variation of environmental properties in time and space**
  temperature, ...

POP physical-chemical properties

Long-range transport

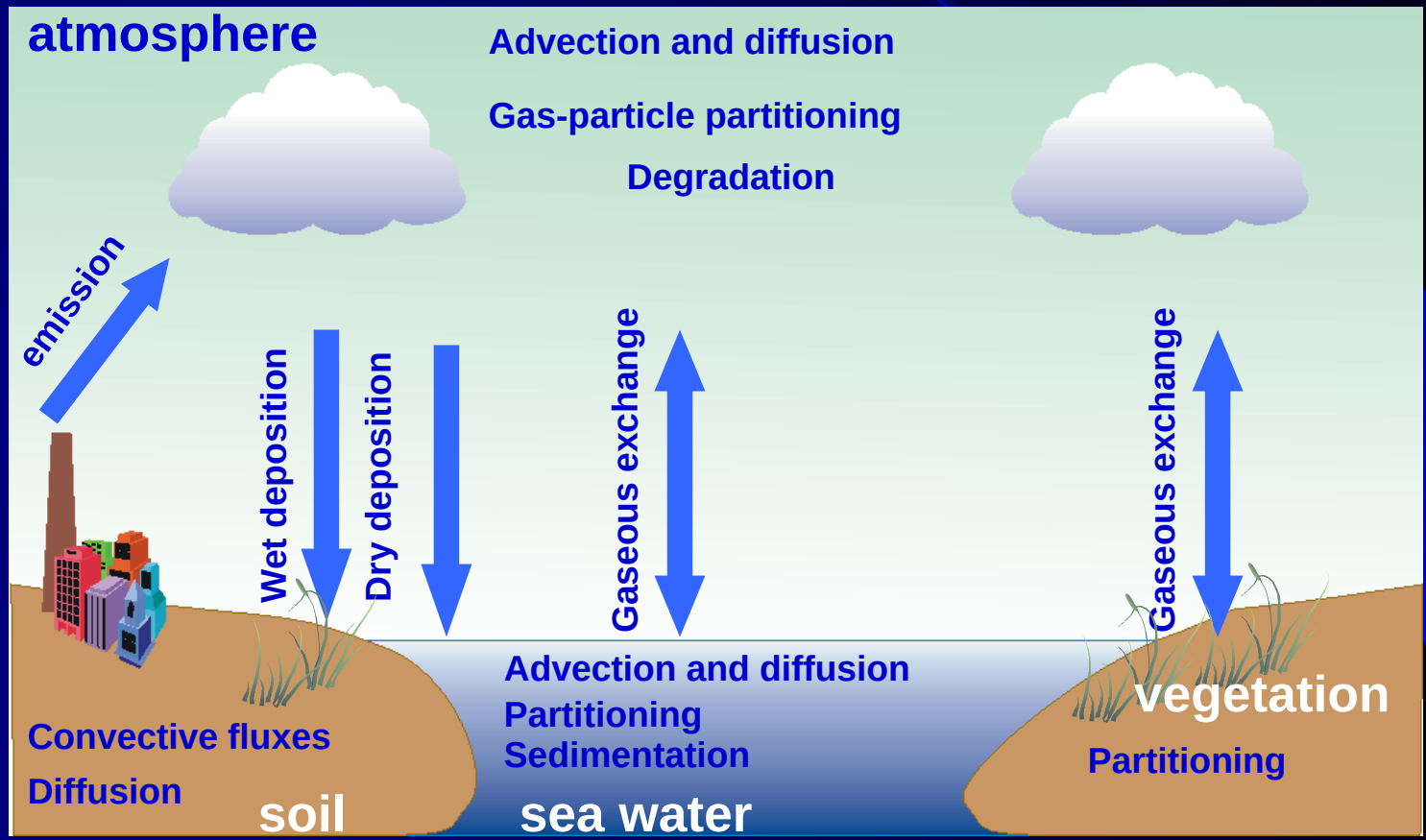


Persistence in the environment



- **What processes of POP environmental behavior should be taken into account while modeling POP long-range transport?**

Processes governing POP fate in environment



Main transport pathways

- Atmospheric transport
- Oceanic transport
- Riverine transport
- Transport with ice drift

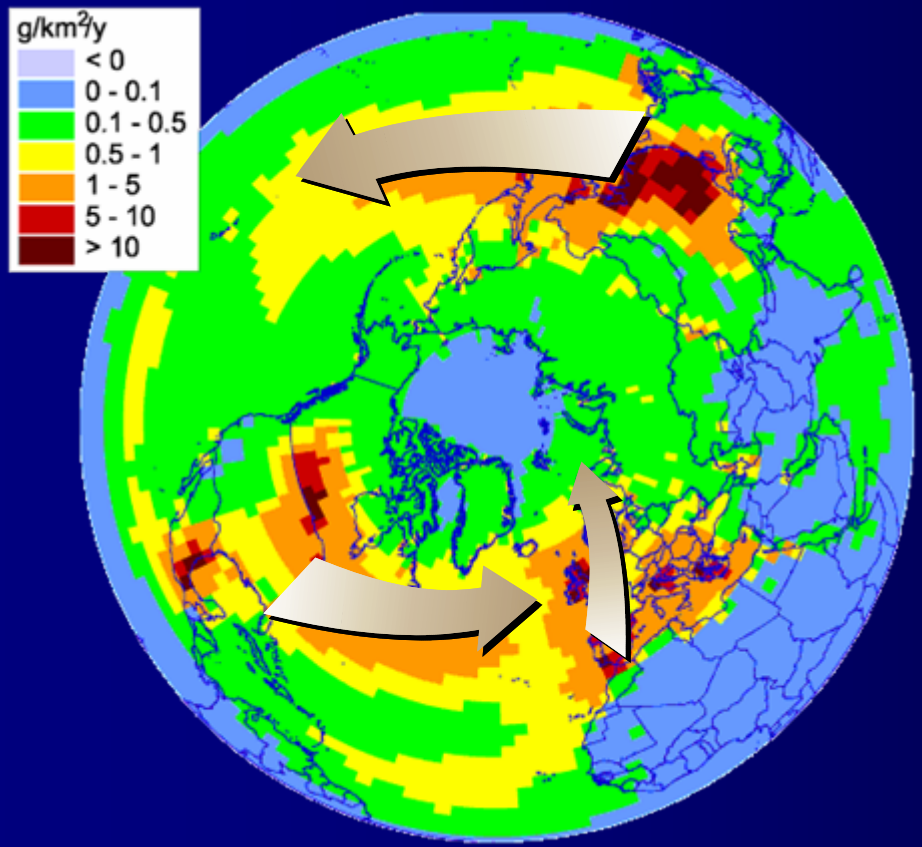
POP atmospheric transport

Processes:

- advective transport and turbulent diffusion
- gas-particle partitioning
- degradation
- wet deposition of POPs in gas and particulate phase
- dry deposition of POPs in particulate phase
- gaseous exchange with underlying surface

POP atmospheric transport

γ-HCH



Transatlantic transport

Transport to the Arctic

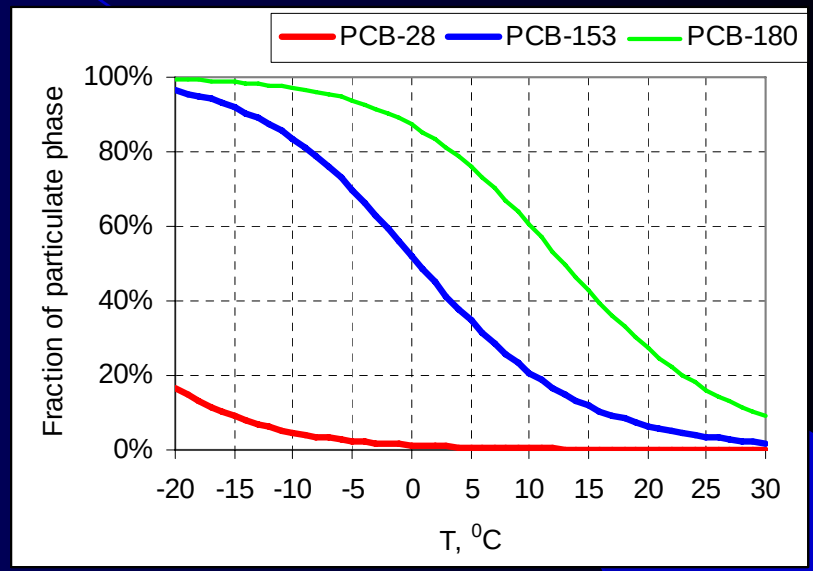
Transpacific transport

Total annual depositions (MSCE-POP model)

Gas-particle partitioning of POPs

Adsorption model of gas-particle partitioning of POPs [Junge, 1977; Pankow, 1987] :

$$\varphi = \frac{c \cdot \theta}{p_L + c \cdot \theta}$$



c = 0.17 Pa·m

p_L – subcooled liquid vapour pressure, Pa

θ – specific surface of aerosol particles (m^2/m^3)

spatial and temporal distribution of specific aerosol surface is required

Gas-particle partitioning of POPs

Absorption model of gas-particle partitioning of POPs

[*Finizio et al.*, 1997; *Falconer and Harner*, 2000] :

$$\varphi = \frac{K_{PA} \cdot TSP}{K_{PA} \cdot TSP + 1}$$

$$\log K_{PA} = m_r \log K_{OA} + \log f_{om} - 11.91$$

m_r – slope of regression relation (~1)

K_{oa} – octanol-air partition coefficient

TSP – total suspended particulate matter concentrations

f_{om} – fraction of organic matter in the particles ?

Degradation of POPs in atmosphere

POPs in gaseous phase - reaction with OH radicals

$$dC_a/dt = -k_d^2 \cdot [^{\bullet}OH] \cdot C_a,$$

C_a – air concentration in gaseous phase, ng/m^3

[$^{\bullet}$OH] – concentration of OH-radical, molec/m^3

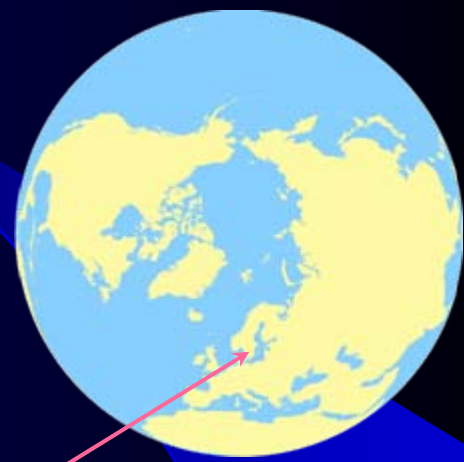
k_d^2 – degradation rate constant, m^3/molec/s.

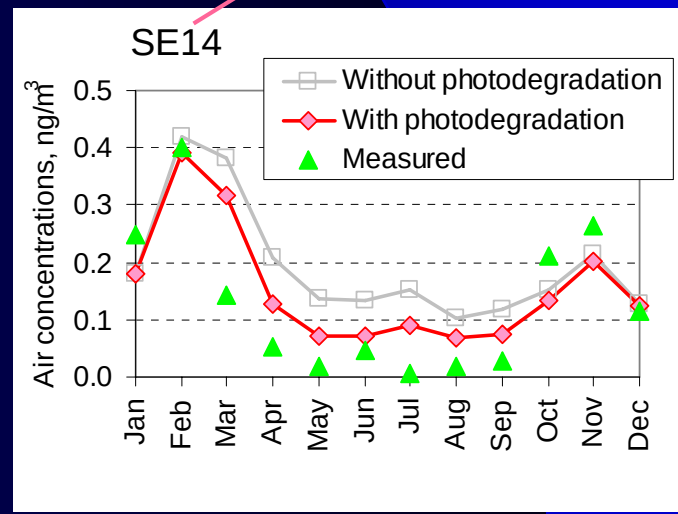
POPs in particle-bound phase

Photodegradation of POPs on particle surface

[Kamens et al., 1988, Valerio et al., 1984, Behymer and Hites, 1988, Chen et al., 2001]

Reactions with other radicals ?





Monthly mean B[a]P in air

Deposition of POPs with precipitation

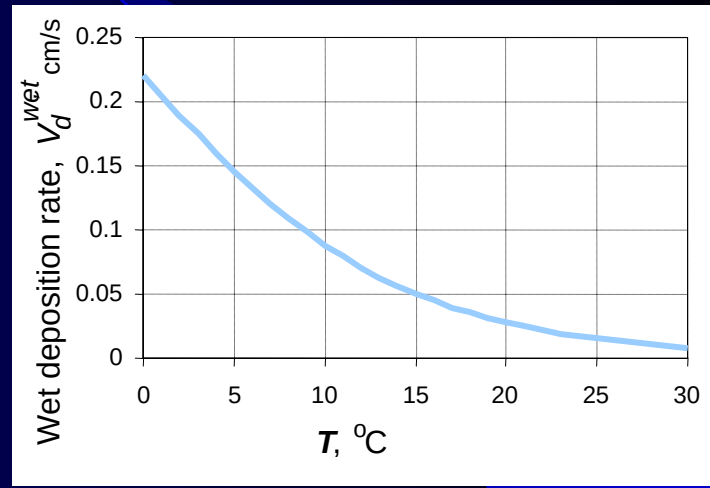
Scavenging of POPs from the atmosphere with precipitation:

$$W_T = W_P \cdot \varphi + W_G \cdot (1 - \varphi)$$

φ – fraction of POP in particulate phase

W_P – washout ratio for POP particulate phase

W_G – washout ratio for POP gaseous phase



$$W_G = \frac{R \cdot T}{H}$$

H – Henry's Law Constant

T – temperature

R – universal gas constant

Deposition of POPs with precipitation

Scavenging of POPs with snow:

$$W_G = K_{IA} \cdot A \cdot \rho$$

ρ – density of snow meltwater, g/m^3

A – specific snow surface area, m^2/g

K_{IA} – ice-air sorption coefficient

[Wania et al., 1999]

Can be essential removal process for northern areas (Arctic region)

Gaseous exchange with underlying surface

Gaseous exchange:

- direct gaseous flux to underlying surface (soil, seawater, vegetation)
- volatilization from environmental media (re-emission)

Gaseous exchange with underlying surface

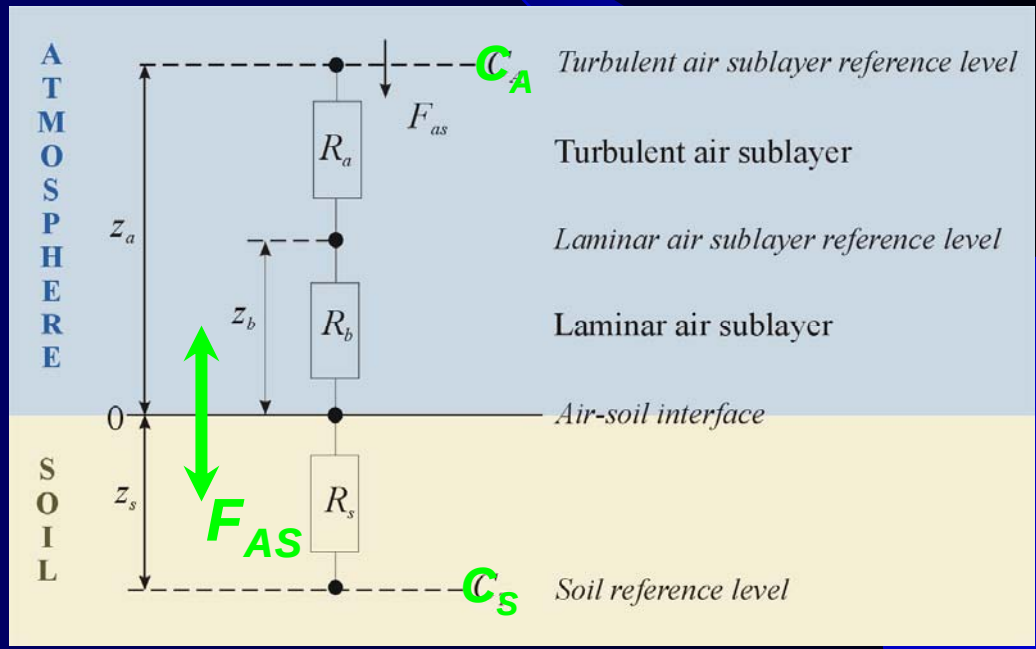
Net gaseous exchange flux between soil and the atmosphere:

$$F_{as} = \frac{C_a - C_s / K_{as}}{R_a + R_b + R_s}$$

C_A – POP air concentrations

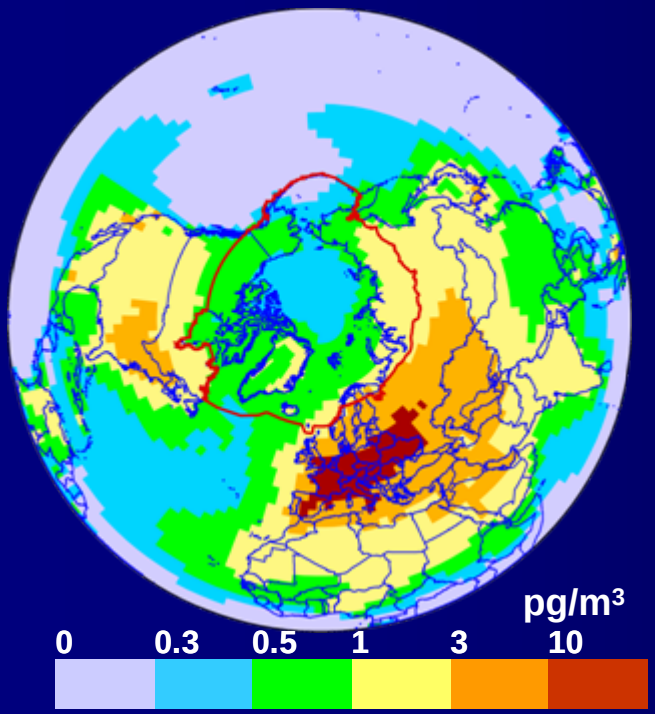
C_S – POP soil concentration

K_{AS} – effective air-soil distribution coefficient

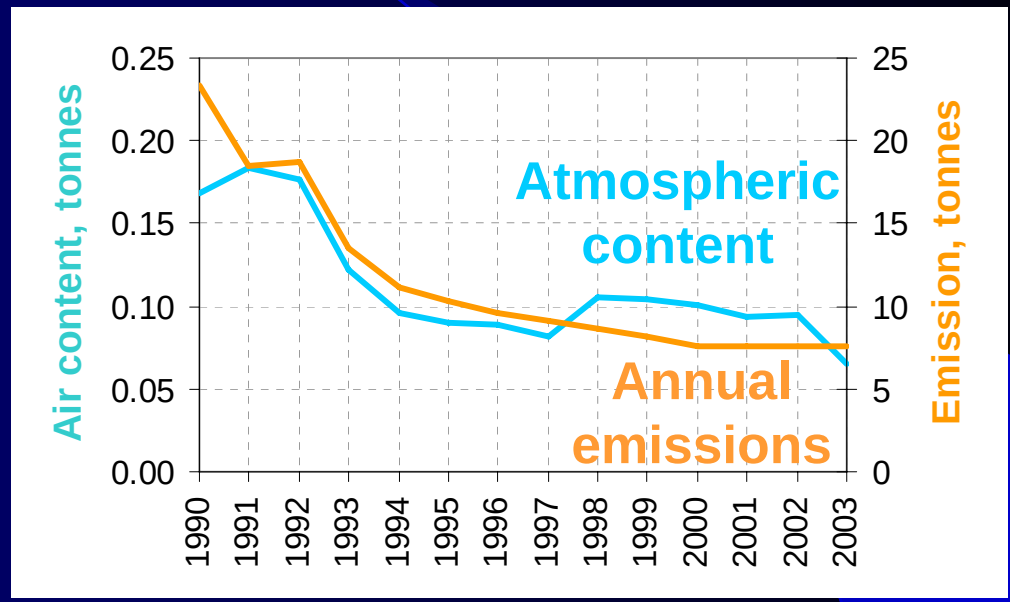


Resistant analogy

Gaseous exchange with underlying surface

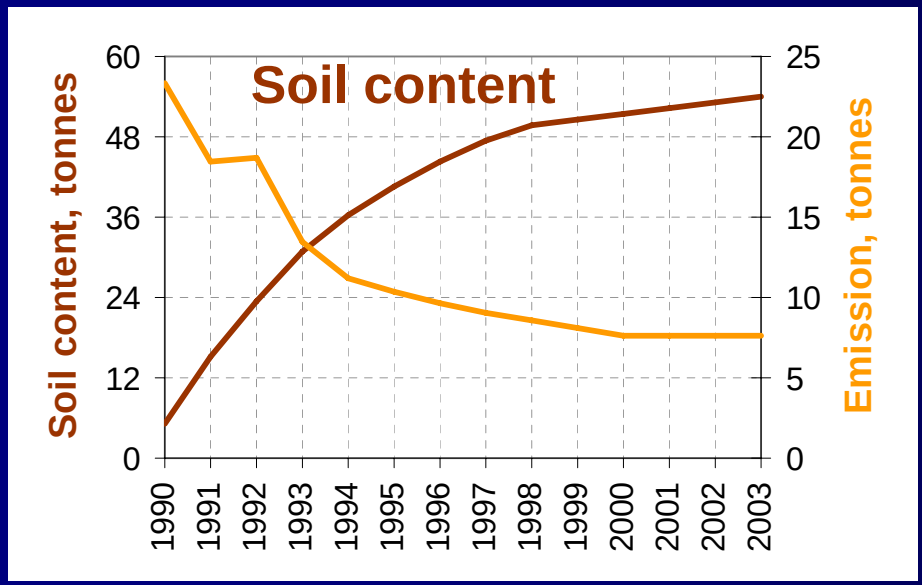


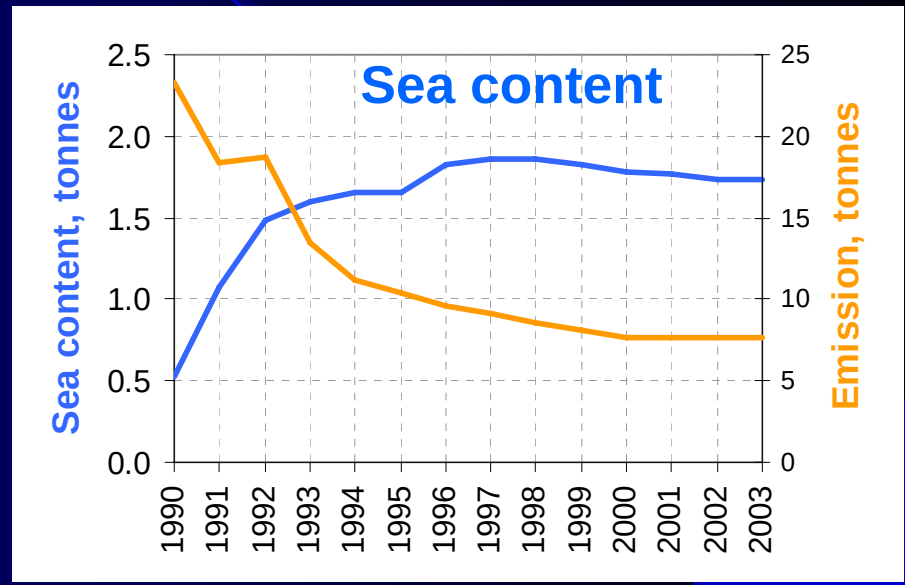
PCB-153 annual mean air concentrations



Variation of annual emissions and atmospheric content of PCB-153

Gaseous exchange with underlying surface

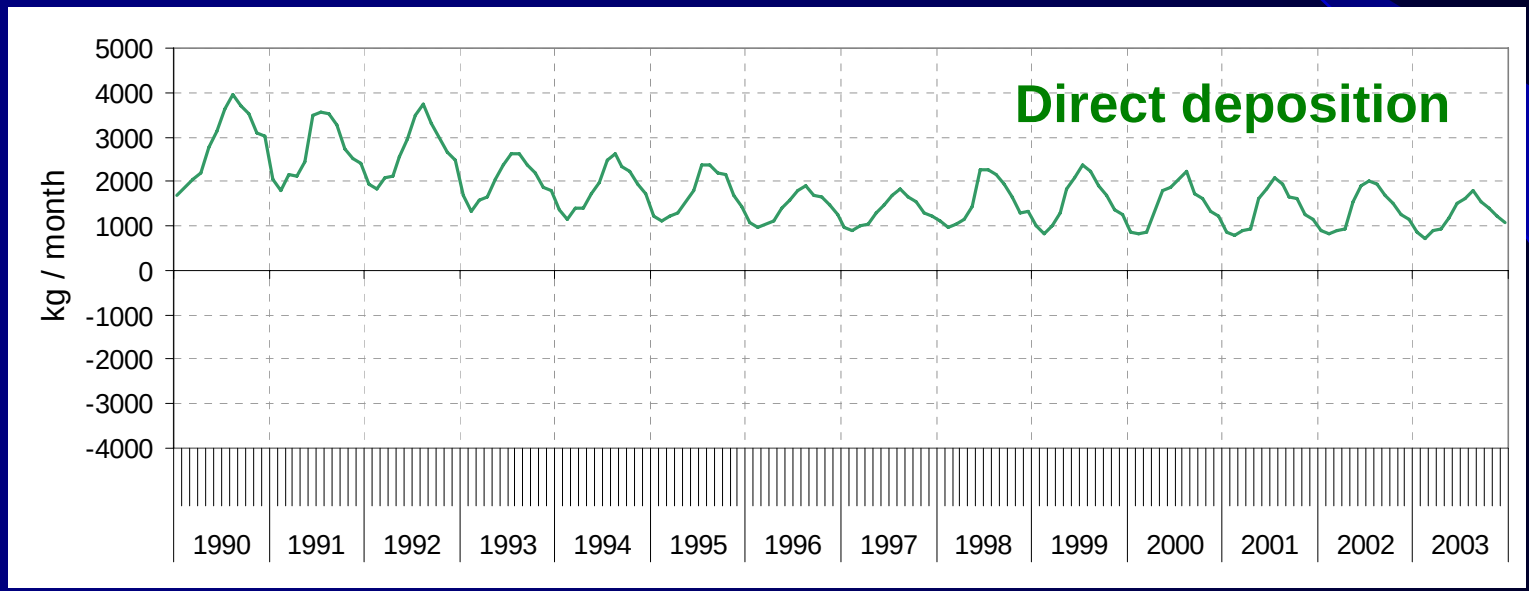




Temporal variations of of PCB-153 content in soil and seawater

Gaseous exchange with underlying surface

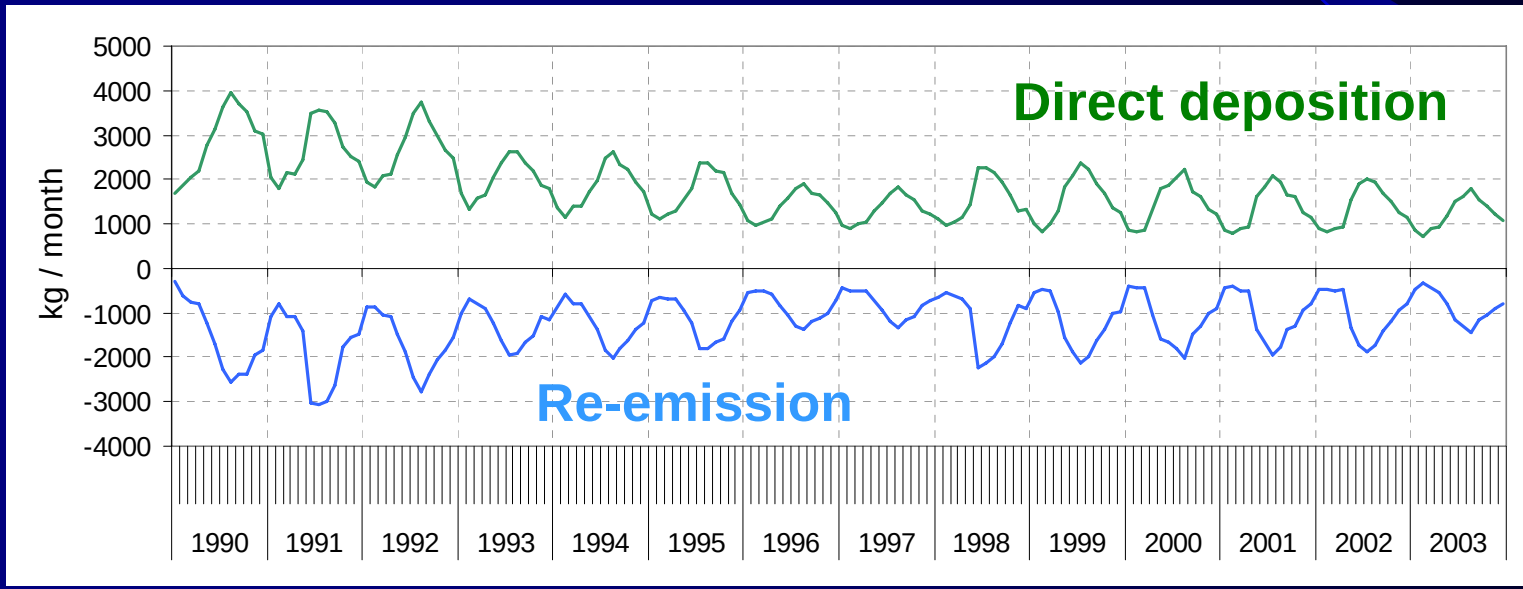
Direct gaseous flux of PCB-153 to underlying surface



Direct deposition

Gaseous exchange with underlying surface

Re-emission and direct gaseous fluxes of PCB-153

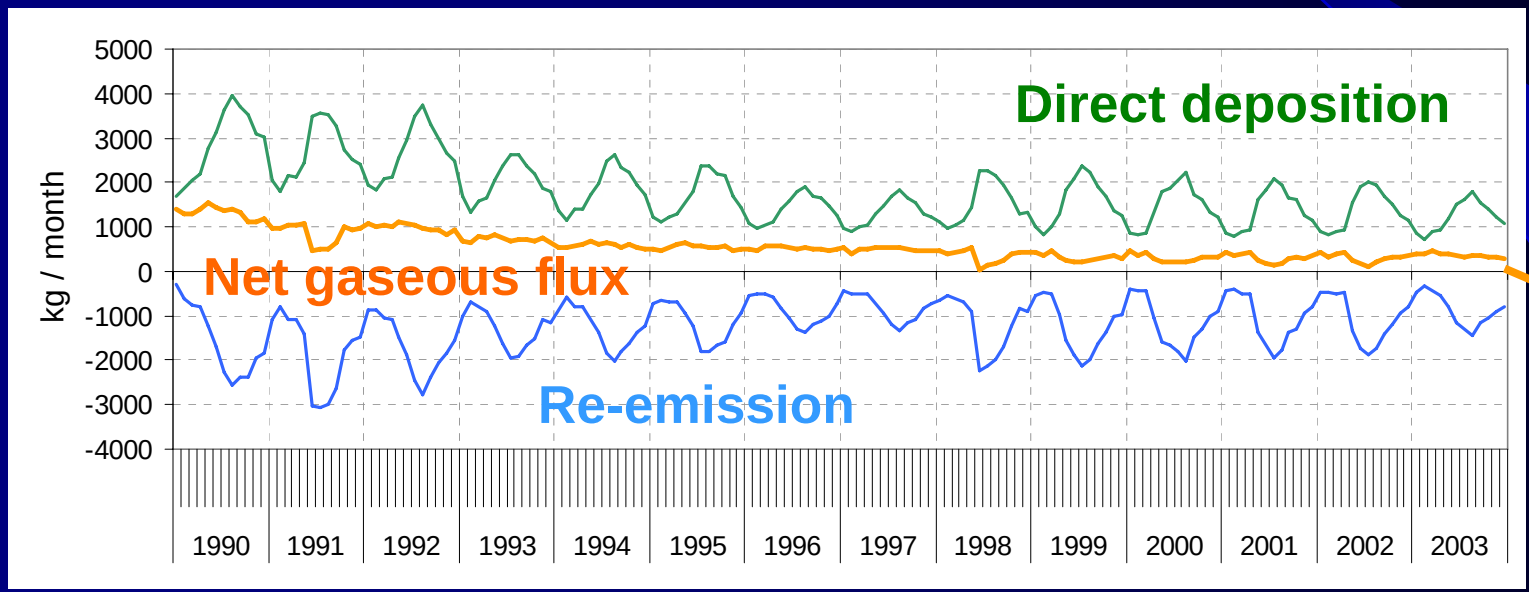


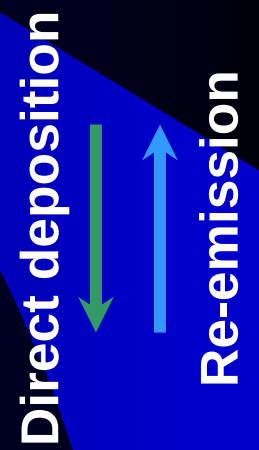
Direct deposition

Re-emission

Gaseous exchange with underlying surface

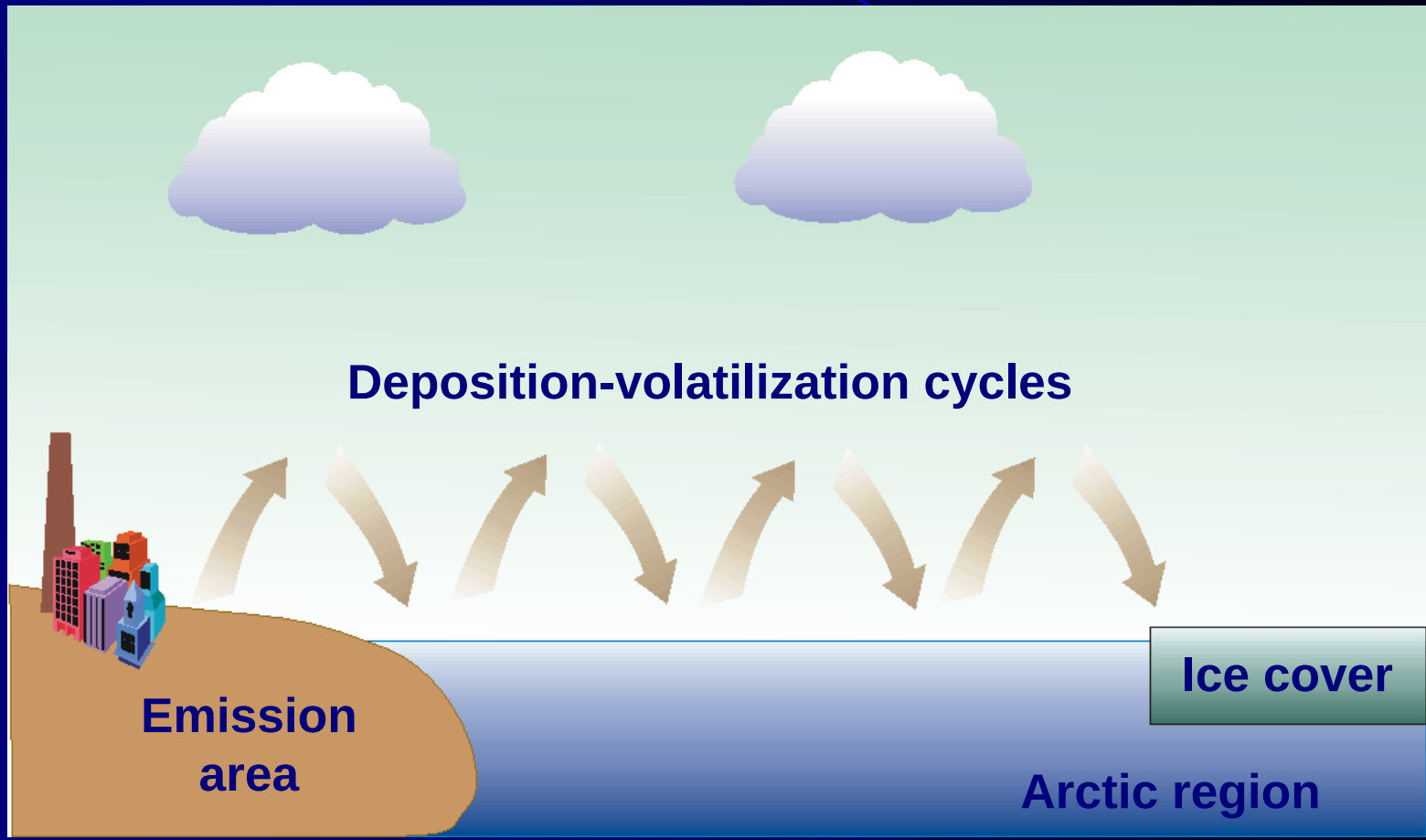
Re-emission and net gaseous exchange fluxes of PCB-153



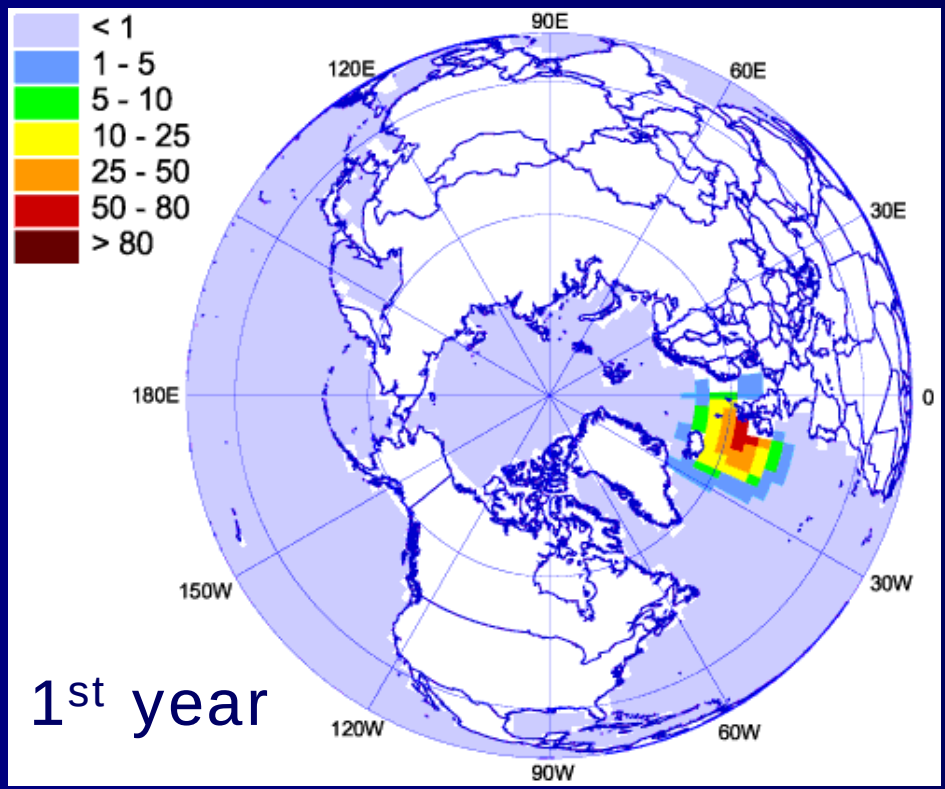


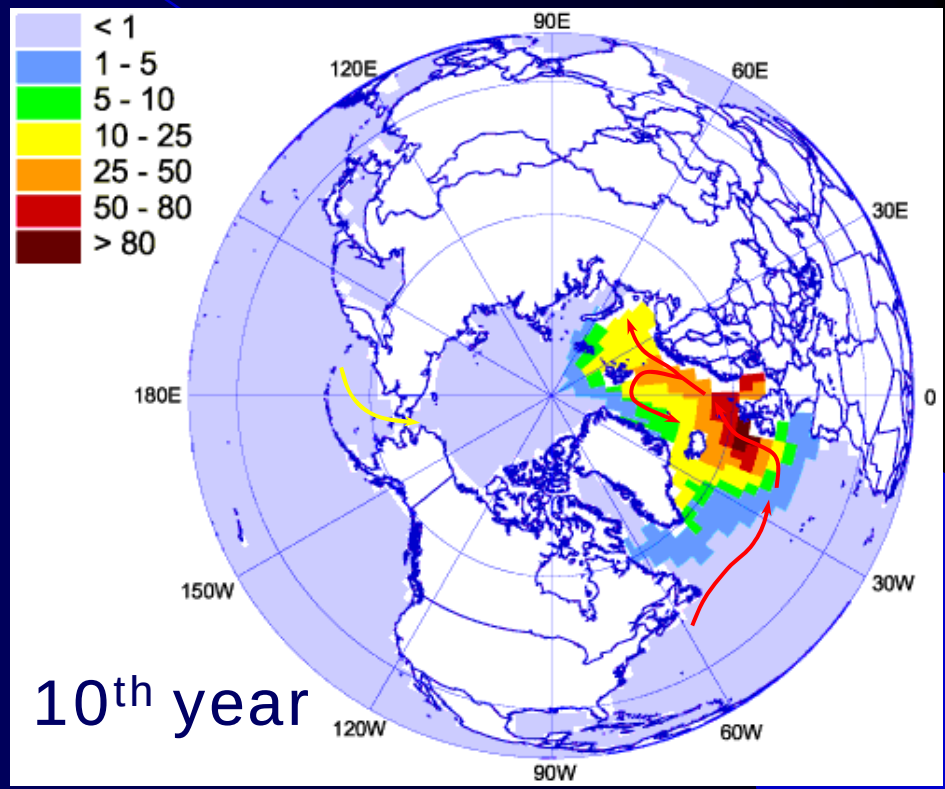
Net gaseous flux is the sum of wet and dry deposition and re-emission fluxes

Multi-hop transport of POPs



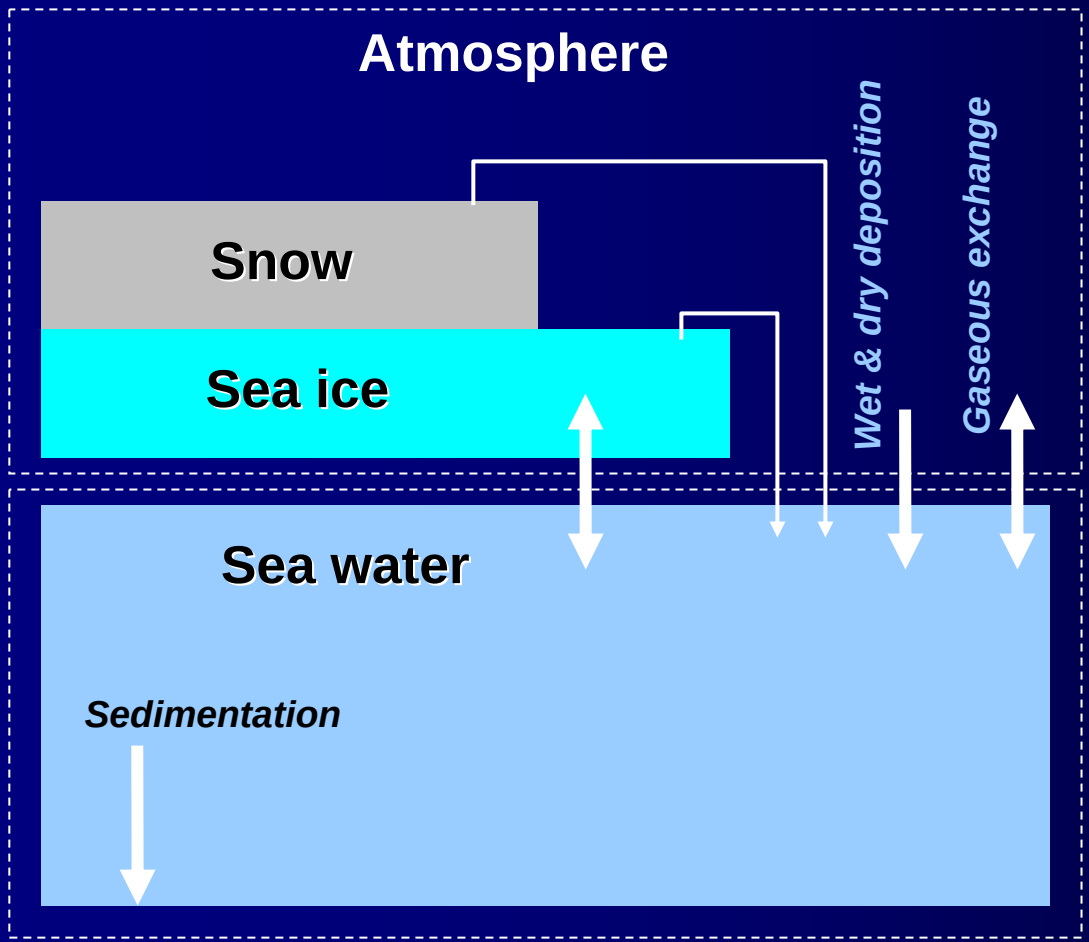
POP transport with sea currents





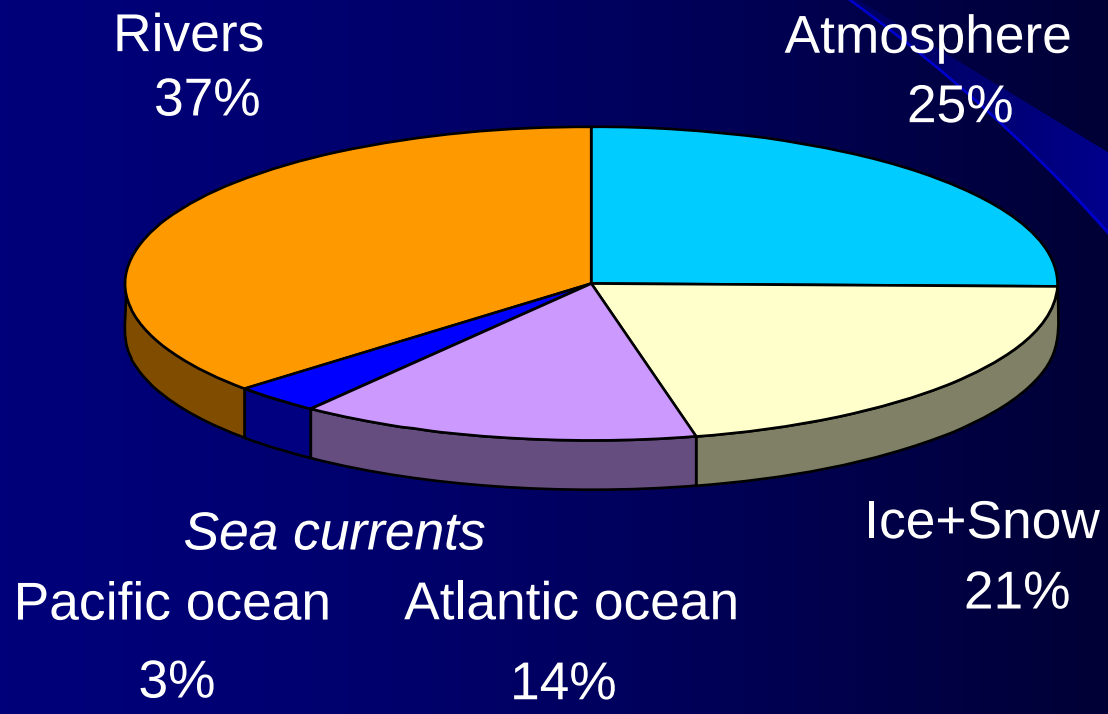
Changes of concentrations of PCB-153 in seawater during 10 years, in %

POP transport with sea currents (Northern hemisphere, Arctic region)



- Advective transport with sea currents
- Turbulent diffusion within seawater
- Partitioning of POPs between dissolved phase and phases sorbed on particles and dissolved organic matter
- Sedimentation with particles
- Degradation of POPs

Model experiments: Input of γ-HCH into the Arctic Ocean for 1996



Input of γ-HCH from Russian rivers in 1990-1996 based on [*Alexeeva et al.*, 2001]

Concluding remarks

- For most of the POPs the atmospheric transport pathway is the most essential for the consideration of their intercontinental transport.
- Intercontinental transport of POPs is significantly influenced by their **gas-particle partitioning** and **gaseous exchange with underlying surface**.
- Further studies of POP **gaseous exchange** processes with different types of underlying surface (soil, sea water, fresh water, vegetation), accumulation, and subsequent re-volatilization are of importance.
- **Gas-particle partitioning** and its temperature dependence is significant factor for the intercontinental transport of POPs.
- Refinement of the description of gas-particle partitioning requires the information on spatial distribution, temporal variations, and organic matter content of aerosol particles.

Concluding remarks (2)

- **Degradation rates** for gaseous phase POPs due to reactions with atmospheric radicals with regard to their spatial and temporal variations should be refined.
- In contrast to the atmospheric transport **migration** of POPs with **oceanic currents** is comparatively slow. However for highly persistent POPs and long-term scales this transport pathway can be of importance.
- Studies of Arctic pollution by POPs require further investigations of the processes of POP fate taking into low temperatures, seasonal variation of solar radiation, presence of ice cover, etc.