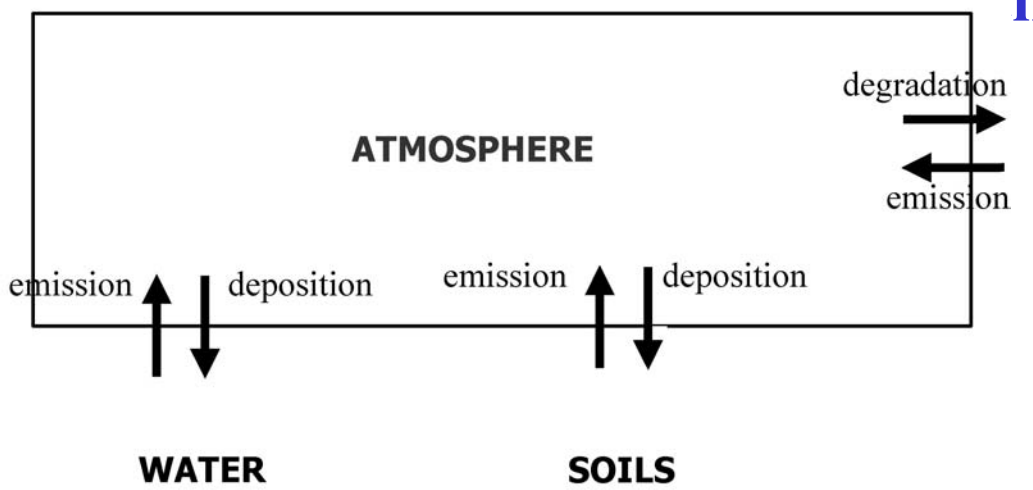
4 Trace substance mass budgets, surface cycling: Emissions, deposition, re-volatilisation ime



$$-dm_i/dt = \text{sources} - \text{sinks} = E - S = E - (k_{degrad}^{(1)} + k_{dep}^{(1)})\, m_i = m_i/\tau \; [g/s]$$

$$-dc_i/dt = E - S = F_{em}/h - (k_{degrad}^{(1)} + k_{dep}^{(1)})\, c_i = c_i/\tau_{air} \qquad [g/m^3/s]$$

- Chemical loss processes of i are 1st order in c_i
- Source processes of i are 0th order in c_i

Depositional loss processes are here expressed as 1st order in c_i for simplicity

For $dm_i/dt = 0$, the system is called to be chemically in a steady state

Variability and atmospheric residence time:

$dm_i/dt = F_{i\,in} + F_{i\,out} + E_i + S_i$;

with: $F_{i\,in}$, $F_{i\,out}$ = fluxes over boundary

E_i, S_i = internal sources and sinks

$m_i = M_i/M_{air} \langle x_i \rangle m_{trop}$

M_i, M_{air} = molar masses (M_{air} = 29 g/mol)

$\langle x_i \rangle$ = spatial average of mixing ratio

m_{trop} = mass of tropospheric air = 4.25×10^{15} t

$S_i = (\Sigma_j\, k_{ij}^{(2)}\, N_j/V + j_i^{(1)})\, N_i/V = k_V^{(1)}\, N_i/V$

with: $k_{ji}^{(2)}$, $j_i^{(1)}$= rate coefficients, photolysis rates

N_i/V, N_j/V = reaction partner number concentrations

$k_V^{(1)}$ = tropospheric average chemical sink rate coefficient

If well mixed or almost well mixed: advective losses $F_{i\,out}$

$F_{i\,out} \sim m_i = k_F\, m_i$; with: k_F = empiric parameter

$dm_i/dt = F_{i\,in} + E_i + (k_F + k_V^{(1)})\, m_i$

$\tau_i = (k_F + k_V^{(1)})^{-1}$; with: τ_i = residence time (*not equal to but < ‚lifetime'!*)

assuming (in 1st approx.) that $k_V^{(1)} \neq f(m_i)$, i.e. no chemical feedbacks leading to $N_j/V = f(N_i/V)$

Averaging over long times (> mixing times)
steady state-assumption holds: $dm_i/dt = \langle F_{i\,in} \rangle + \langle Q_i \rangle - (k_F + k_V^{(1)})\, m_i \approx 0$

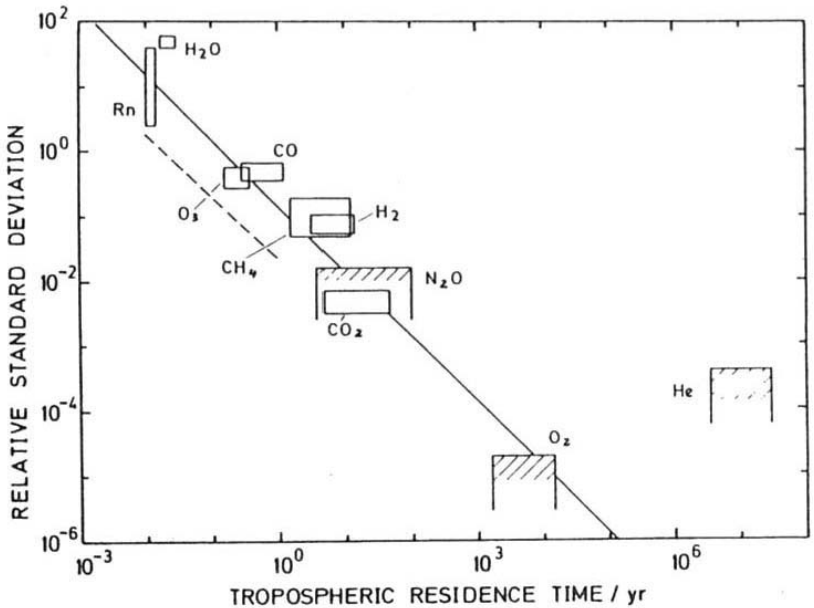
$N_i/V = \langle N_i/V \rangle + (N_i/V)'(x, y, z, t)$;

with: $\langle N_i/V \rangle$ = temporally and spatially mean number concentration
$(N_i/V)'$ = local and temporal number concentration
x, y, z = space coordinates

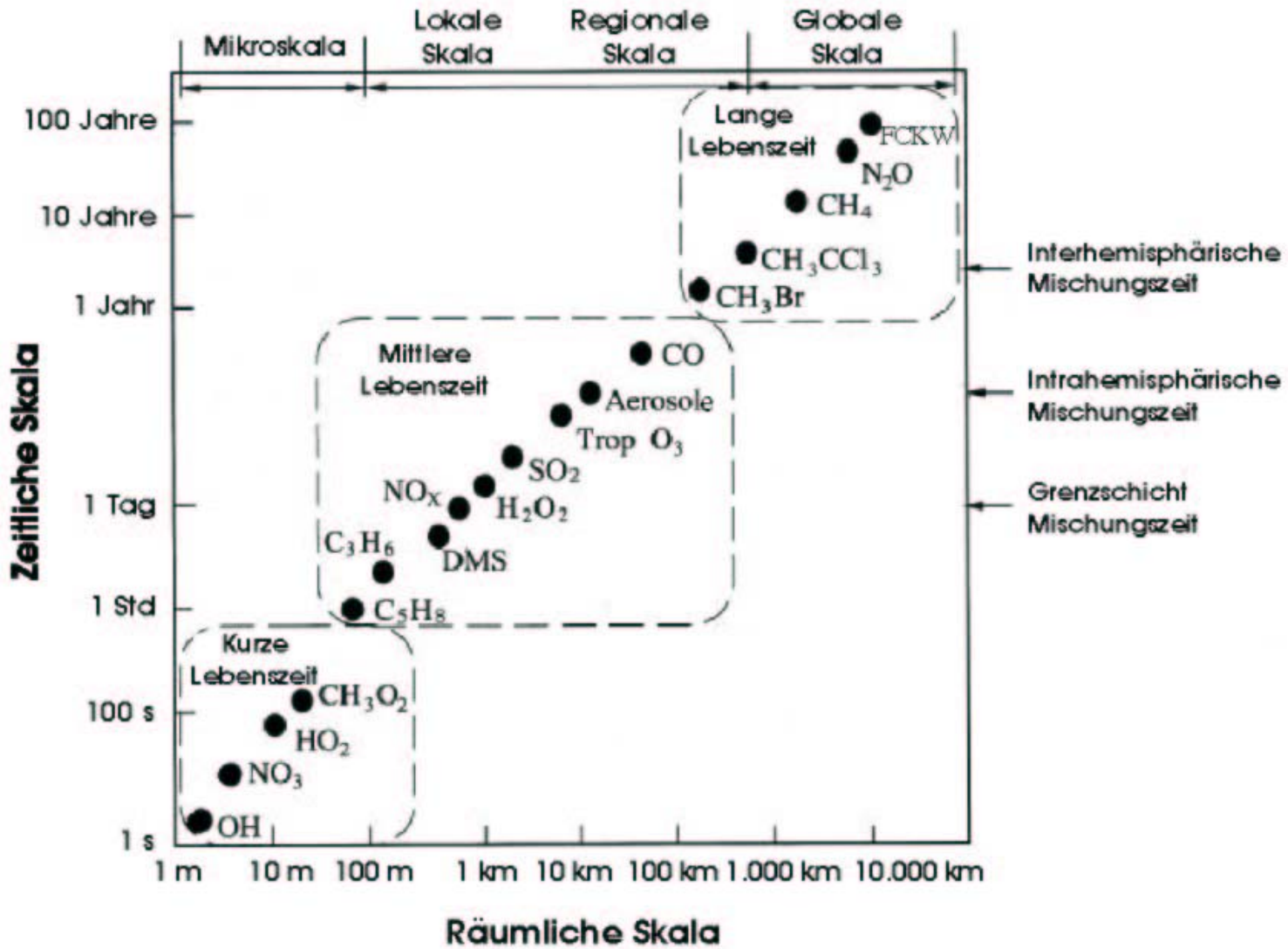
Empiric finding (*Junge, 1974*) for the relative standard deviation
$\sigma_i = \sigma_i^* ((N_i/V)') / \langle N_i/V \rangle = 0.14/\tau_i$

with: σ_i^* = absolute standard deviation of $(N_i/V)'$

→ The residence time, τ_i, can be infered from variability, as $\sigma_i = f(\tau_i)$



Atmospheric residence times, mixing and transport times



4.2 Emissions

- location: mostly from ground, from stacks, from aircrafts
- temporal profile, e.g. diel, weekly, seasonal, historical trends
- spatial distributions

Example: non-methane hydrocarbons (NMHC)

Global budget	**(Tg/a)**	
Natural	1150	terrestrial vegetation
	2	marine biosphere
Anthropogenic	120	of which are:

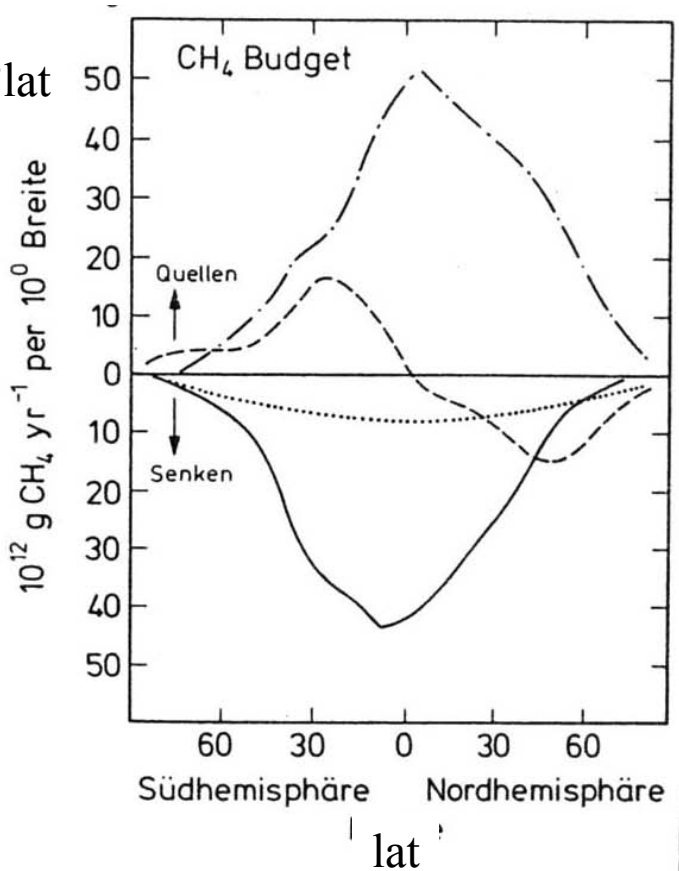
52 % transport
7 % fossil fuels, stationary
5 % chemical, petrochemical industries
9 % oil and gas production
27 % solvents

(Ehhalt, 1986; Guenther et al., 1996)

Emissions, CH_4

Global Model results

Tg/10°lat



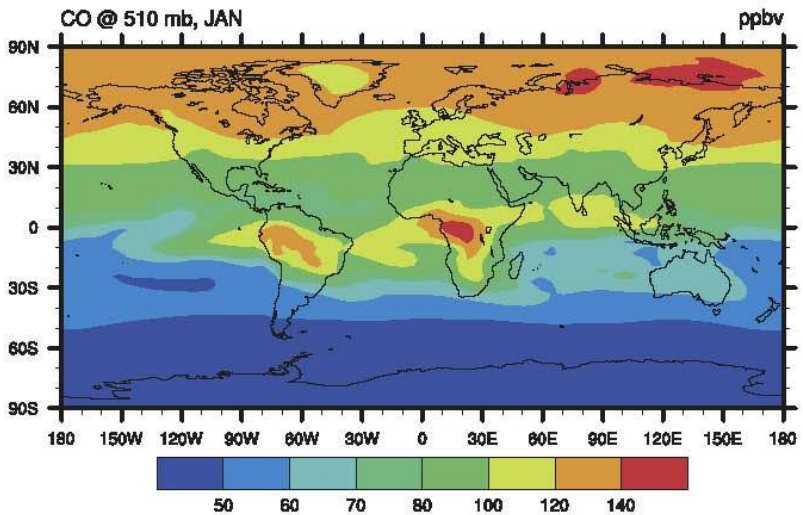
Legende	Global	Prozeß
– – – –	$\pm 71 \times 10^{12}$	Transport
.....	87×10^{12}	CH_4 Zunahme
———	-322×10^{12}	CH_4 + OH Oxidation
—·—·—	409×10^{12}	Quellenverteilung

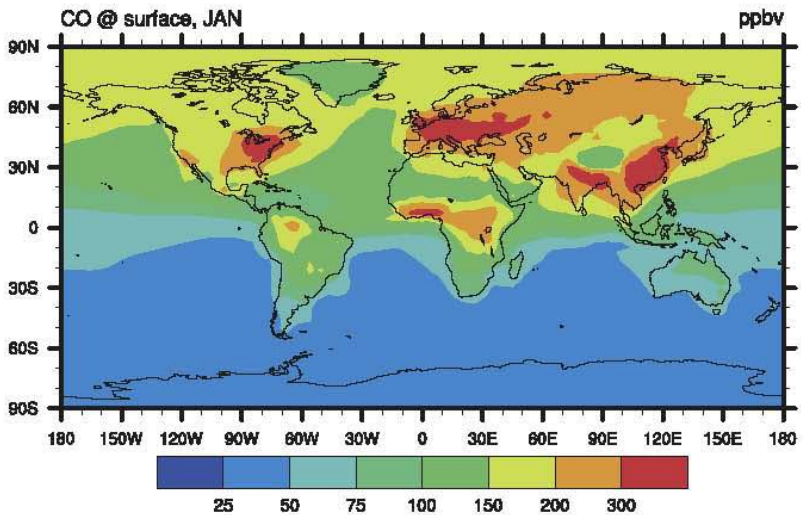
increase sources

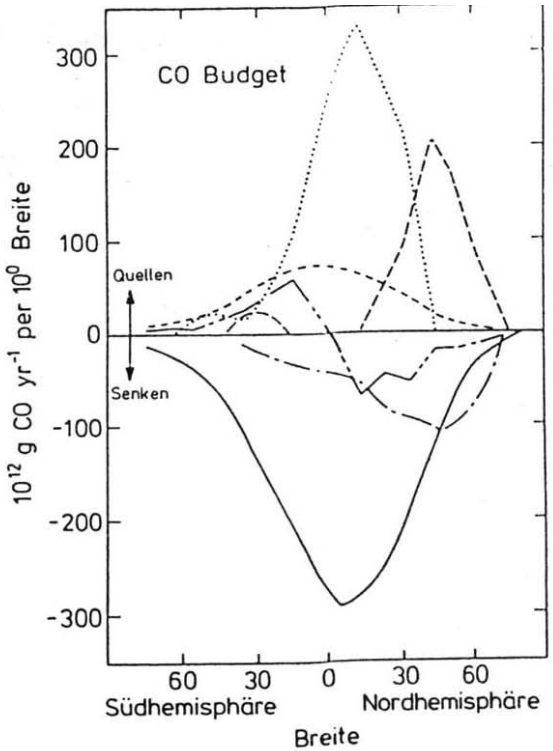
(Crutzen & Gidel, 1983)

Distributions – spatial, seasonal

Global distributions CO (ppbv) @ 970 and 510 hPa, monthly mean





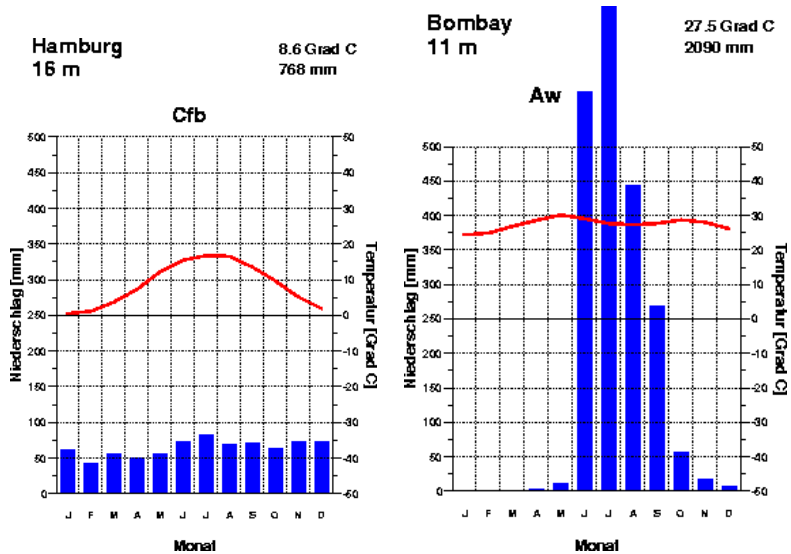


Legende	Global	Prozeß
------	643×10^{12}	Technologische Quellen
—·—	-636×10^{12}	Deposition am Boden
———	-2054×10^{12}	CO + OH Oxidation
------	566×10^{12}	CH_4 + OH Oxidations - Quellen
— — —	$\pm 194 \times 10^{12}$	Transport
.....	1483×10^{12}	Tropische Quellen

(Model results: *Horowitz et al., 2003; Crutzen & Gidel, 1983*)

4.3 Deposition
4.1 Wet deposition

- temporal profile, seasonal, interannual variability
- spatial distributions



Simplified rate (pseudo-1st order):

$$-dc_i/dt = k_{rain}^{(1)}\ \varepsilon\ c_i\ ;\ \tau_{rain} = (k_{rain}^{(1)})^{-1}$$

$$\tau_{cloud} = [(1-\theta)\ \varepsilon_{gas}\ r + \theta\ \varepsilon_{part}\ r]^{-1}$$

r = rain repetition rate, below cloud, in cloud (s^{-1}), ε = scavenging coefficient

(dependent on Henry coefficient K^H, partcile size D, type of precipitation)

Occult deposition / fog droplet impaction:

can significantly contribute to total wet (= precipitation + occult) deposition of pollutants in sub-alpine mountain ridges which are frequently within clouds (fog)

(Kroll & Winkler, 1989; Klemm et al., 2005)

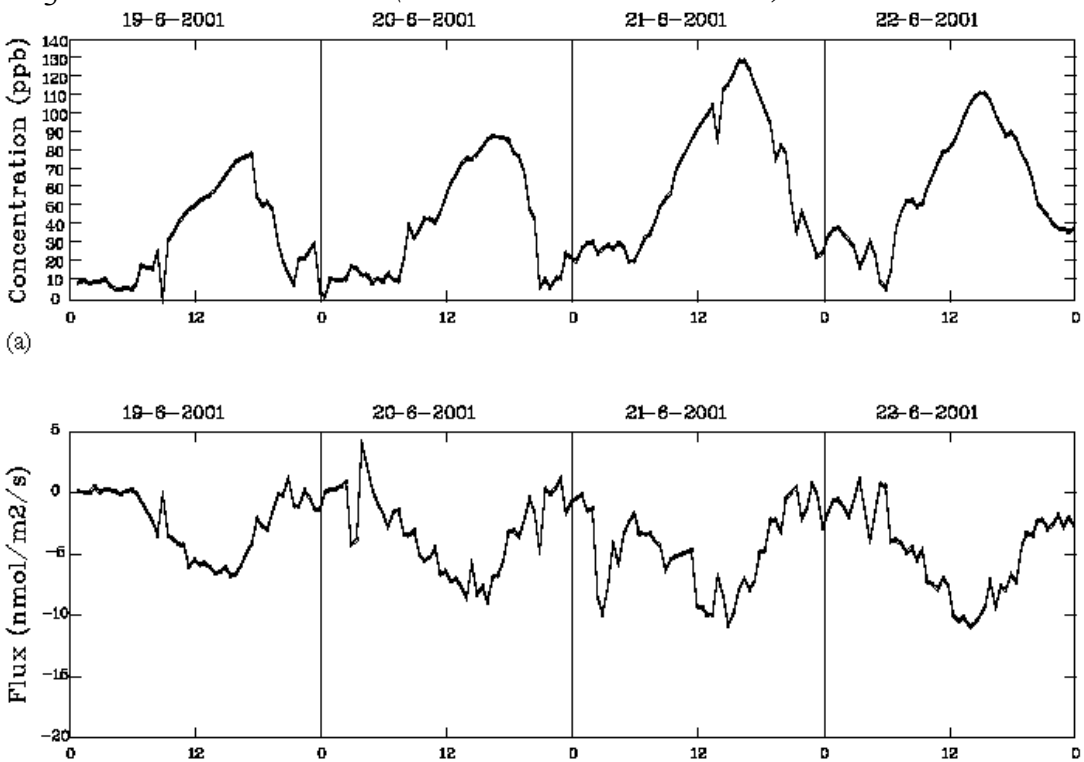
4.3.2 Dry deposition

upon reactivity on or absorption into surfaces

$v_{dep\ i}$ = 0.1-1.0 cm/s

Deposition velocity: = number with units of velocity that when multiplied by the mean concentration of i (gaseous) yields the vertical flux of i ($F_i = c_i\ v_{dep\ i}$), or: measure for depletion due to loss at the ground

Example: Water-insoluble gas, no sources, but destruction on soil:
O_3 over wheat field *(Gerosa et al., 2002)*



v_{dep} shortterm variability

Dry deposition

$v_{dep}(g) = F / c$, varies with atmospheric turbulence, canopy structure (terrain), surface chemical properties, plant physiological status (stomata resistance)

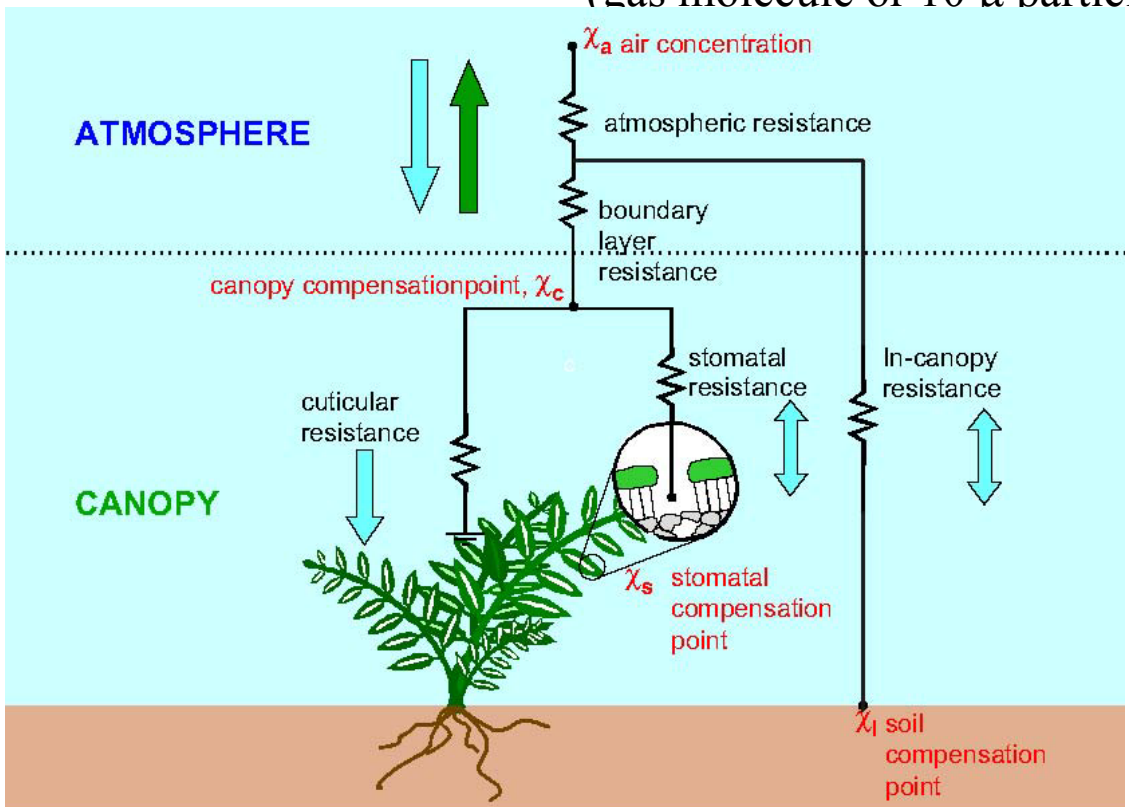
Description: multiple-resistance analog model of transports and interfacial transfer (*Sheih et al., 1979; Wesely & Hicks, 1977; Slinn, 1983*)

Transport across:

Ekman layer or boundary layer: 1 km, (turbulent) mixing time 10^2-10^5 s

Viscous sublayer: 0.05 km, mixing time 10^{-1}-1

(gas molecule or 10 μ particle) - 10^3 s (0.1 μm particle)



(Sutton et al., 2007)

$r_{aerodyn.}$ to overcome by atmospheric turbulence
$r_{boundary\ layer}$ (quasi laminar) to overcome by diffusivity of molecule or particle
$r_{surface}$ to overcome by reaction (kinetics)

Gases: $$V_{d,gas} = \left(R_a + R_b + R_s\right)^{-1}$$

Particles: $$V_{d,part,i} = \left(R_a + R_b + R_a R_b V_{f,i}\right)^{-1} + V_{f,i}$$

Resistances in air, R_a, R_b

Aerodynamic resistance

$$R_a = \frac{\int_{z_{0,q}}^{z_r} \phi_h \frac{dz}{z}}{k u_*}$$

Resistance to diffusion in laminar sublayer

$$R_b = \ln\left(\frac{z_{0,m}}{z_{0,q}}\right) \frac{(\mathrm{Sc}/\mathrm{Pr})^{2/3}}{k u_*}$$

Particle and gas Schmidt numbers, Prandtl number

$$\mathrm{Sc}_{pi} = \frac{\nu_a}{D_{pi}} \qquad \mathrm{Sc}_q = \frac{\nu_a}{D_q} \qquad \mathrm{Pr} = \frac{\eta_a c_{p,m}}{\kappa_a}$$

u* = friction velocity

Surface resistance, R_s , s = vegetation

$$R_s = \left(\frac{1}{R_{stom} + R_{meso}} + \frac{1}{R_{cut}} + \frac{1}{R_{conv} + R_{exp}} + \frac{1}{R_{canp} + R_{soil}} \right)^{-1}$$

Stomatal resistance

Resistance to entering openings in leaf surfaces

$$R_{stom,q} = R_{min} \left[1 + \left(\frac{200}{S_f + 0.1} \right)^2 \right] \frac{400}{T_{a,c}\left(40 - T_{a,c}\right)} \frac{D_v}{D_q}$$

Leaf mesophyll resistance

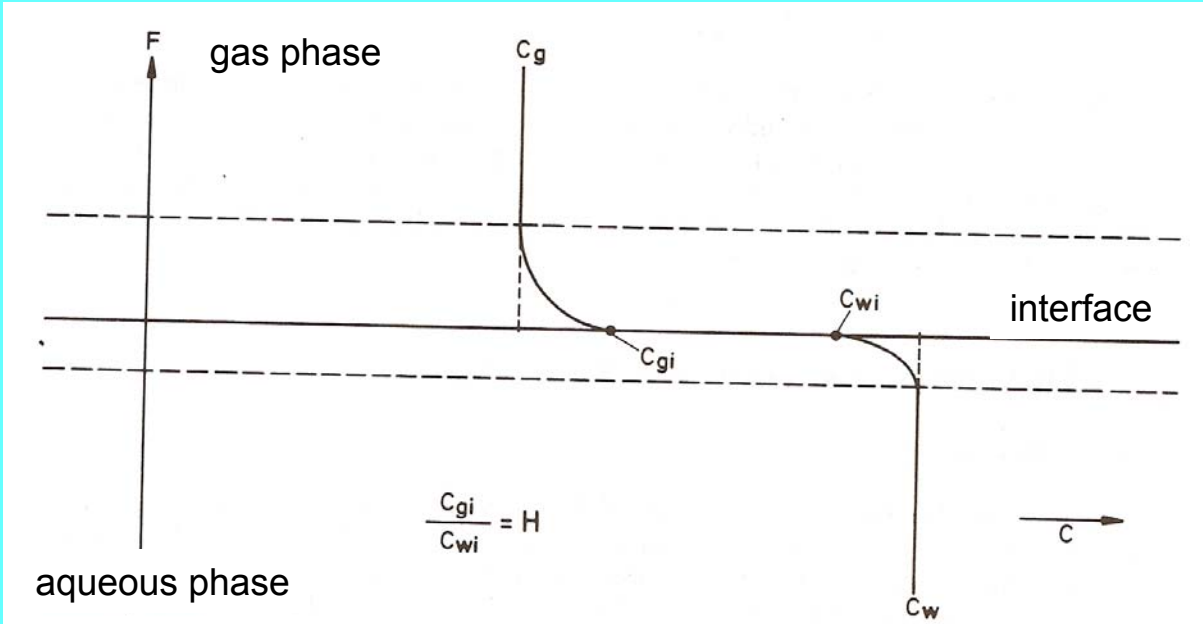
Resistance to dissolving in or reacting with water within leaves

$$R_{meso,q} = \left(\frac{H_q^*}{3000} + 100 f_{0,q} \right)^{-1}$$

3.2.4 Gas exchange, re-volatilisation
3.2.4.1 Atmosphere/ocean

Two film model

- existence of 2 stagnant layers on either side of the interface (fictitious dimensions)
- provide resistance additively *(Liss & Slater, 1974; Schwartzenbach et al., 2002)*



- equilibrium established at the interface itself
- gas flux through interface $F = -k_w (c_w - c_{wi}) = -k_g (c_{gi} - c_g)$ [mol/m²/s]

$c_{gi} = K_{aw}\, c_{gi}$

with bulk (c_w, c_g) and equilibrium (c_{wi}, c_{gi}) concentrations in water and air and transfer coefficients (k_w, k_g [cm/s] ,piston velocity,) in boundary layers (determined by diffusion and turbulence within the 2 layers), expressed empirically in most models

- defined positive for flux from air to water
- consideration of 1 side sufficient for most gases

$dc_w/dt = k_{net}\,(c_w - c_g/K_{aw})$ [mol/s]

$R = 1/k_{net} = 1/k_w + 1/(k_a K_{aw})$ [s/cm]

From known examples to formula for unknown molecule i, M_{gi}:

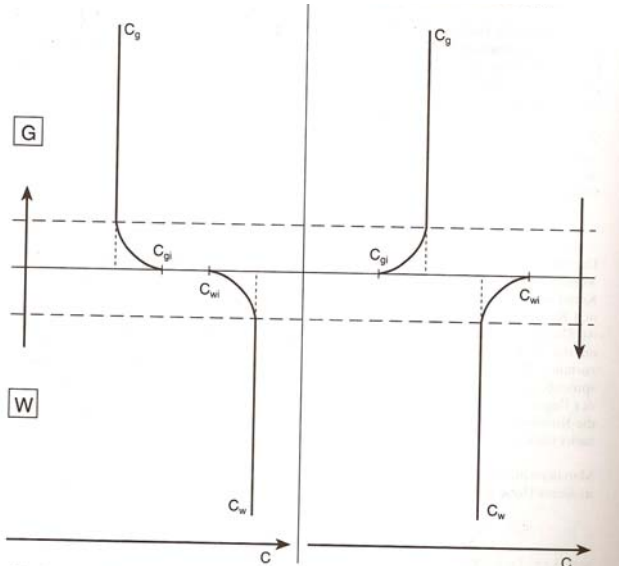
$k_{g\,H2O} = 0.83$ cm/s $\rightarrow$ $k_{g\,i} = 0.83\,(18/M_{gi})^{0.5}$ cm/s

$k_{w\,CO2} = 0.0056$ cm/s $\rightarrow$ $k_{w\,i} = 0.0056\,(44/M_{gi})^{0.5}$ cm/s

Wind dependence:

$k_{w\,CO2}(u) = 0.31\,u^2\,(Sc/660)^{0.5}$ cm/s *(Wanninkhoff, 1992)*

Volatilisation (left) and dry deposition (right) result from and correspond to opposite signs of $(c_g - c_w K_{aw})$.



General concept for all interfaces:

Fugacity of substance i, f_{ij}: = escaping tendency from a phase j ([Pa] or [N/m²])

f/p describes deviation from ideal behaviour, similar to a/c.

(example: Molar free enthalpy $\mu = \mu^0 + RT \ln(p/p^0) \rightarrow \mu = \mu^0 + RT \ln(f/p^0)$)

Mass flow direction is from phase with higher to phase with lower fugacity.

Fugacity capacity Z_{ij}: $f_{ij} = c_{ij}/Z_{ij}$

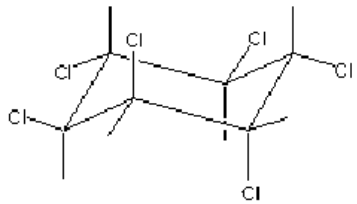
$K_{i\,12} = c_{i1}/c_{i2} = Z_{i1}i1_{)}/Z_{i2}f_{i2}$ *(Paterson & Mackay, 1985)*

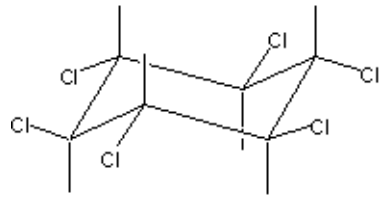
Air: $c_g = n/V = p/RT \rightarrow c_g = f_g/RT$, $Z_g = (RT)^{-1}$, $f_g = c_g RT$

Fugacity capacity of seawater: $Z_w = c_w/p = 1/H'$, Henry coefficient H' [Pa m³/mol]

$f_w = c_w/Z_w = H'c_w$

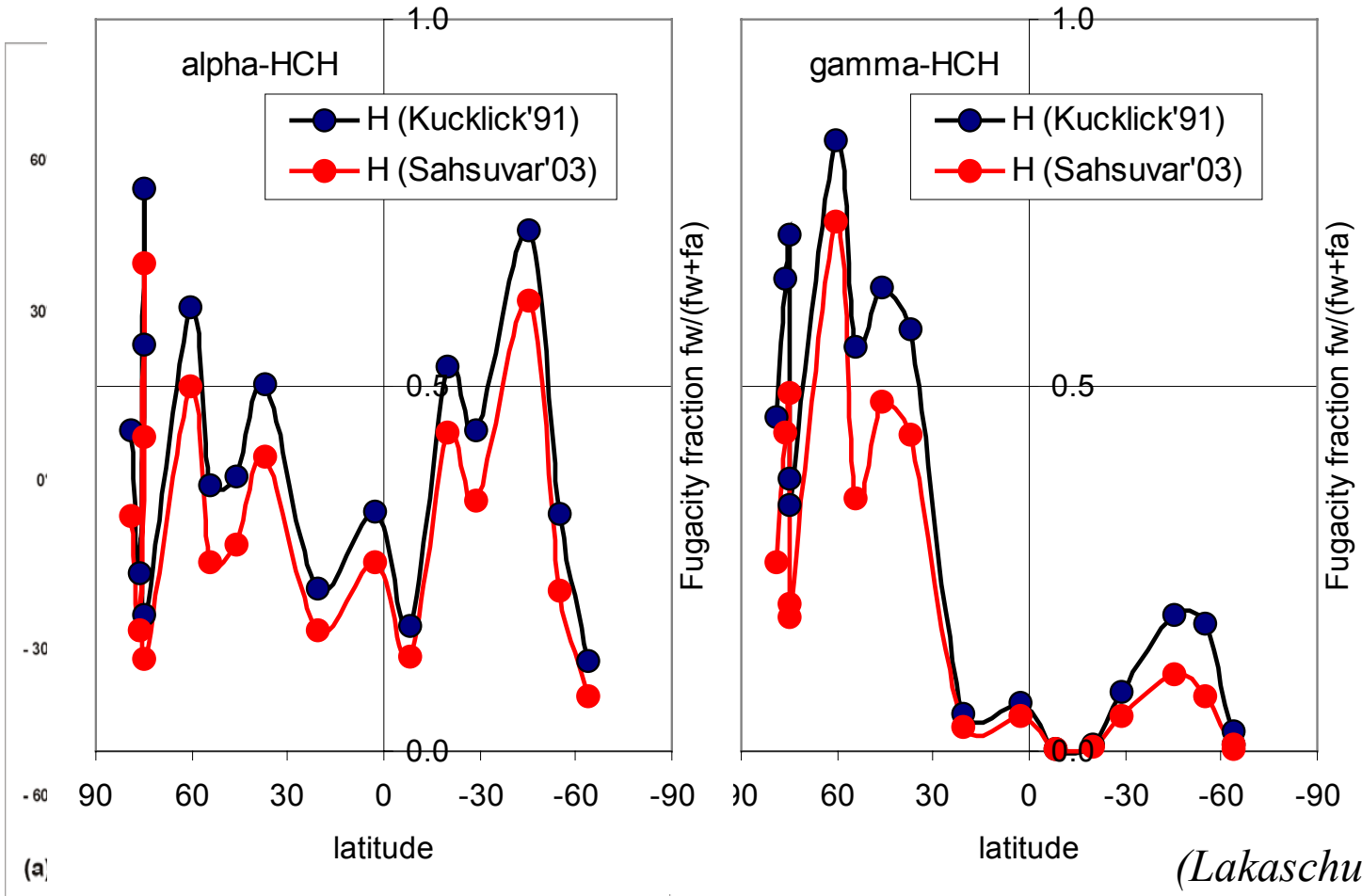
($H' = RTK_{aw}$ as: $K_{aw} = c_g/c_w = Z_g f_g / Z_w f_w$)





Fraction of fugacity from seawater = $f_w / (f_w + f_g)$

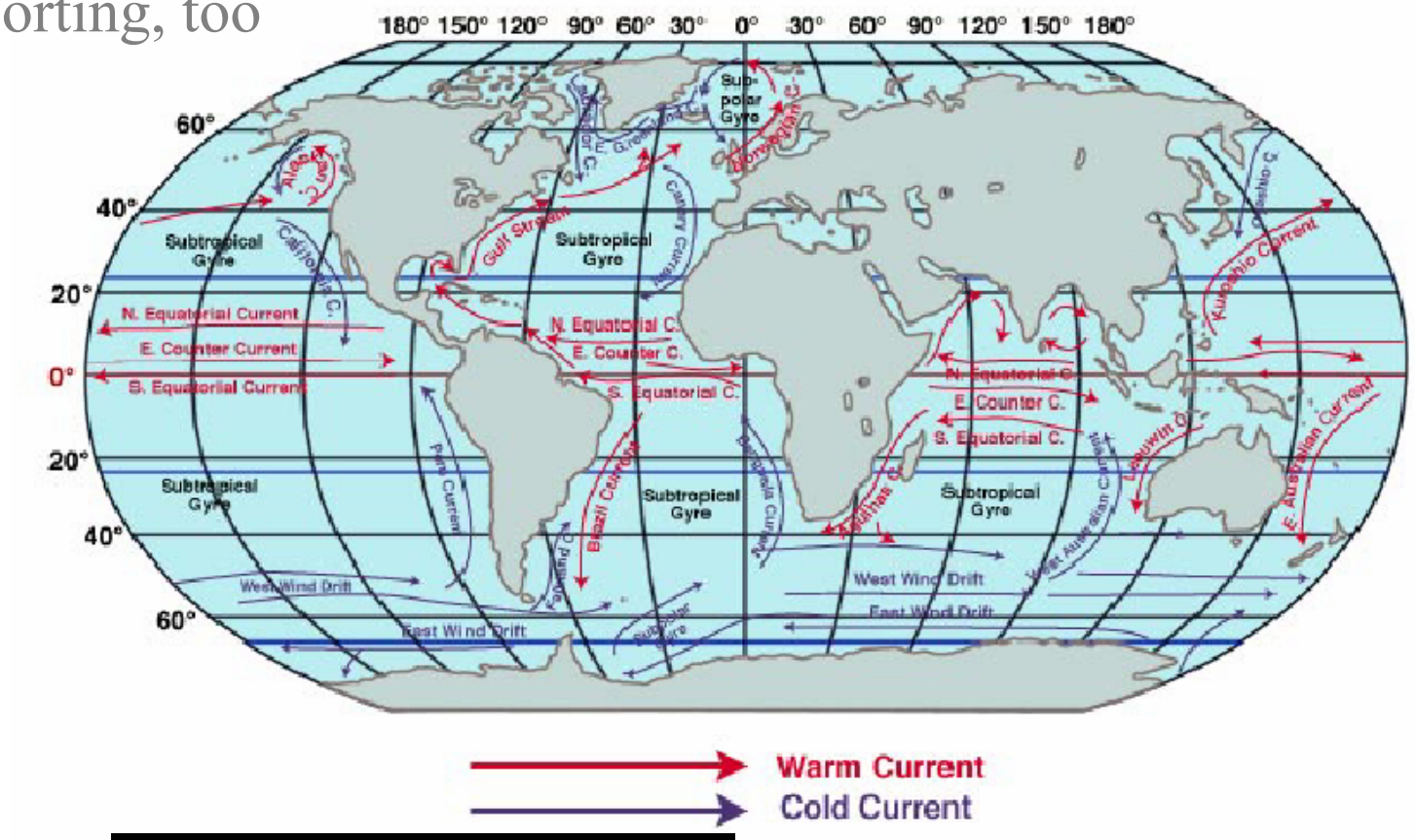
α- and γ-hexachlorocyclohexane along a N-S-transect 1999/2000



(Lakaschus et al., 2002)

The sea is transporting, too

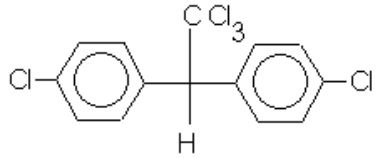
Wind driven



Salinity driven

ocean currents

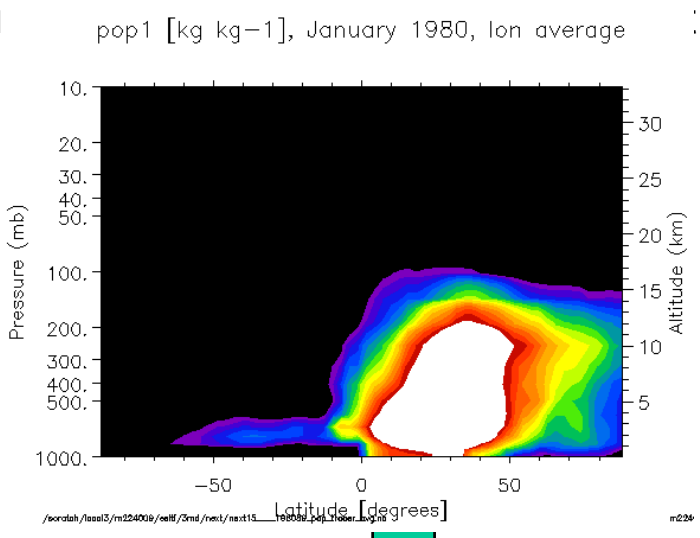
Budget atmospheric and oceanic transports separately



Environmental cycling of a SOC, DDT:

- Fictitious release into the ocean surface layer off the coast of the SE USA
- Labelli : seq

ATMOSPHERE (kg/kg)



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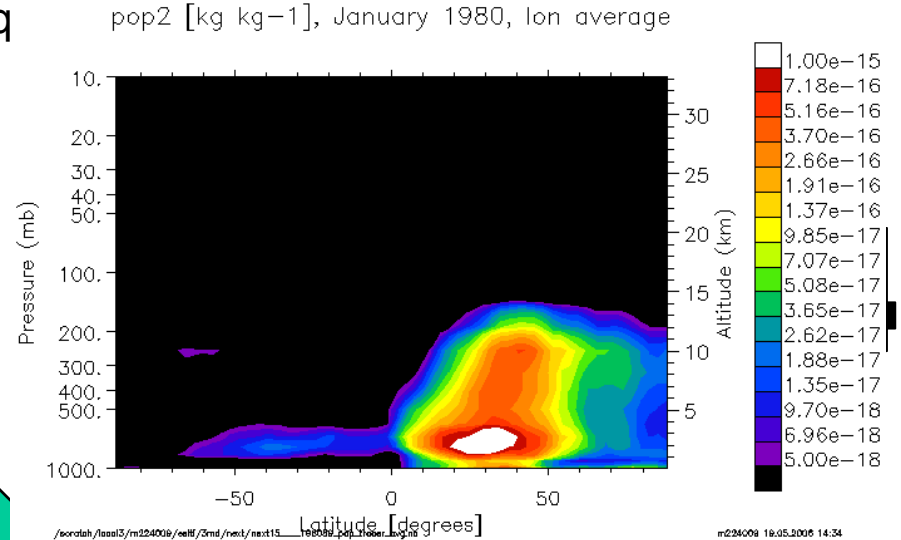
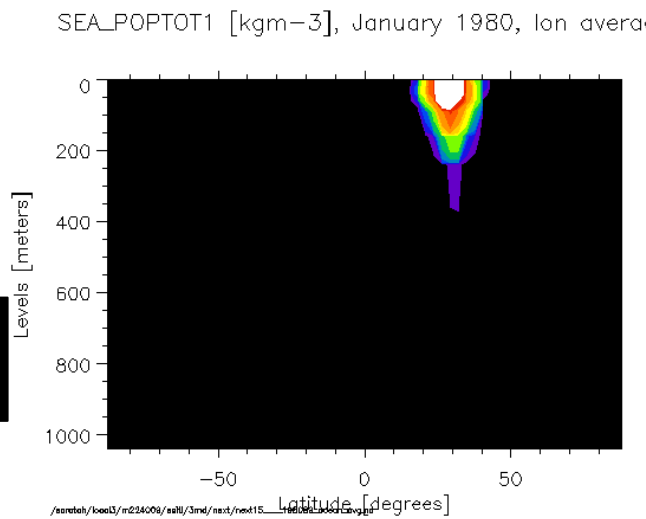


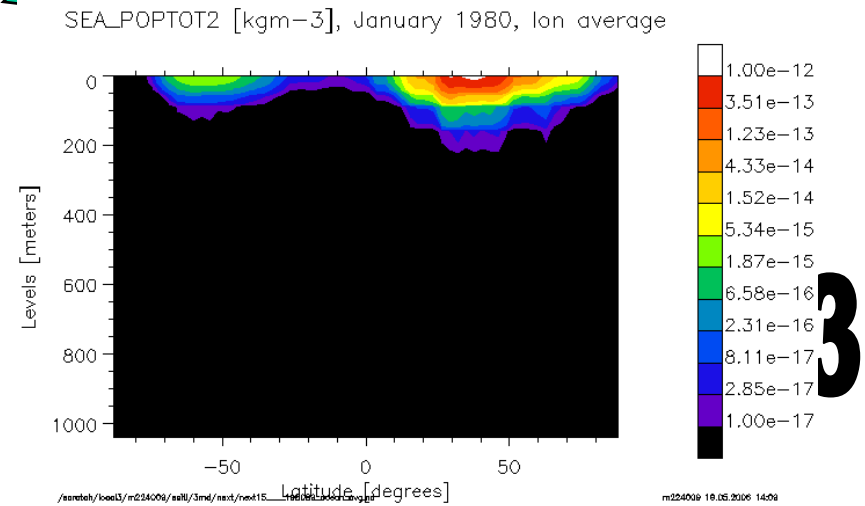
1st cycle:

multiple cycles:

OCEAN (kg/m^3)



1



3

10 years of simulation, monthly means, longitudinal averages

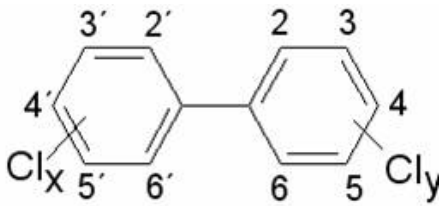
(Guglielmo et al., 2005)

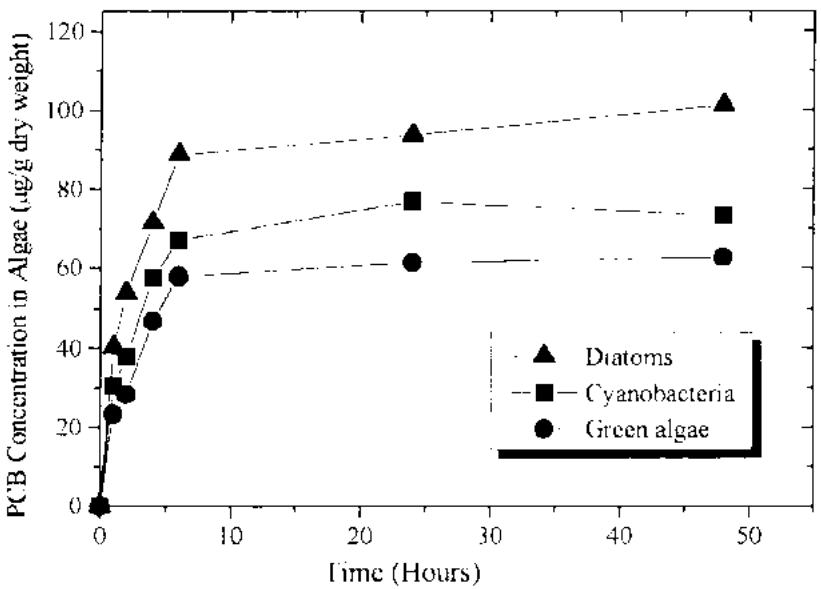
4.4.2 Vegetation and air

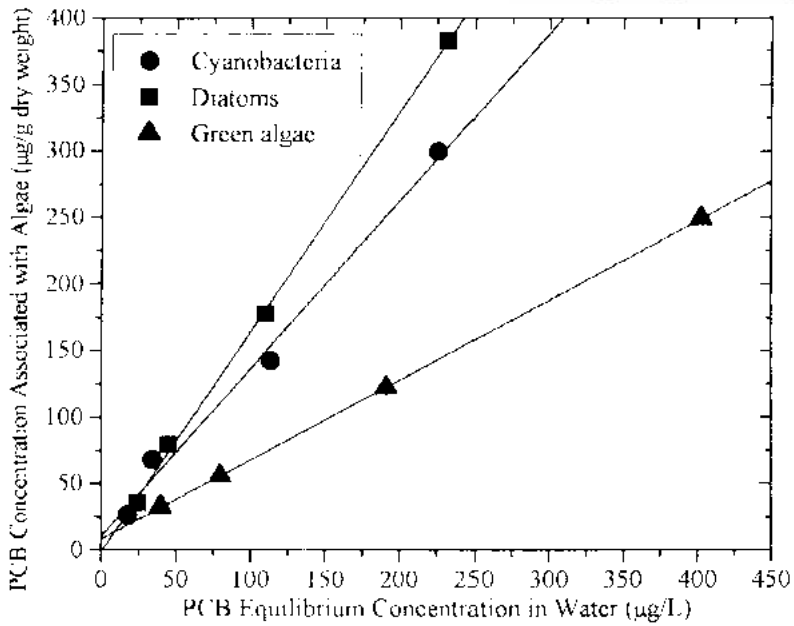
Bioaccumulation in an aqueous system:

Bioconcentration factor BCF:= $c_{i\ biota}/c_{i\ w}$ [ ]

Uptake of polychlorinated biphenyls (PCB; 0.1 mg/l) in 3 algae species: Kinetics, inter-species variability *(Wang et al., 1999)*







Air and plants

Uptake of neutral organic substances in leaves/needles from the gas phase:

- primarily via (wax covered) cuticulae, not stomatae (which enable gas exchange of small, inorganic molecules), distribution within the plant largely unknown

-partitioning determined by lipophilicity (expressed as the octanol-water partitioning coefficient K_{ow}), diffusion driven (*Tolls & McLachlan, 1994*, besides others):

$$F = v\,(a_{inside} - a_{outside})$$

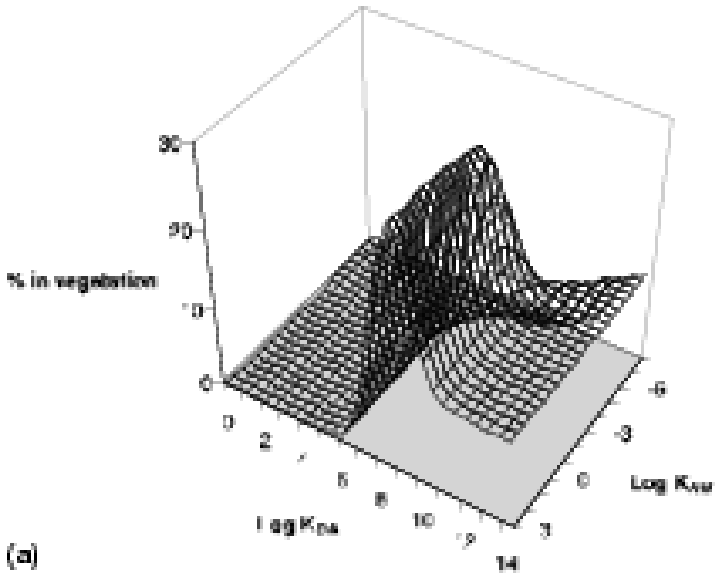
$$\log v_{membrane} = 1.2 \log K_{ow} - 7.5 \quad (\textit{Grayson \& Kleier 1990})$$

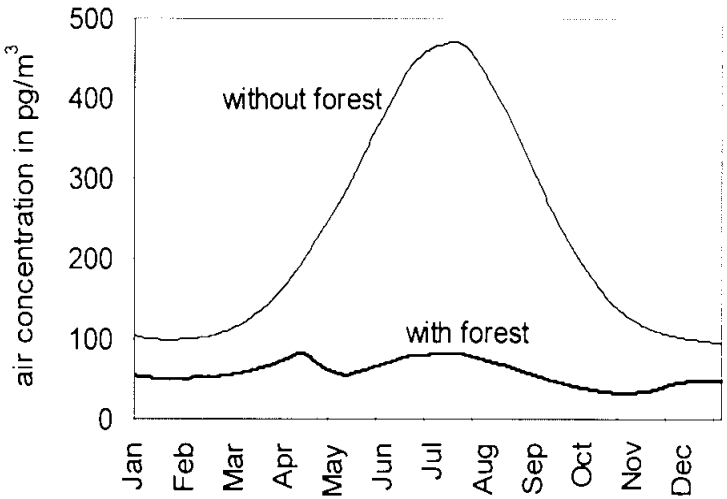
$$v = D\,K_{av} / \Delta x$$

$$\log v_{membrane} = \log K_{ow} - 6.7$$

F = flux ($g/m^2/s$), v = permeability (m/s), a = activity (g/m^3),
D = diffusion coefficient ≈ 10-14 m^2/s for organics, K_{av} = air/veg. partitioning coefficient,
Δx = membrane thickness ≈ 0.05 mm

Flux from air to vegetation controlled by (specific) surface, boundary layer resistance (atmospheric turbulence)



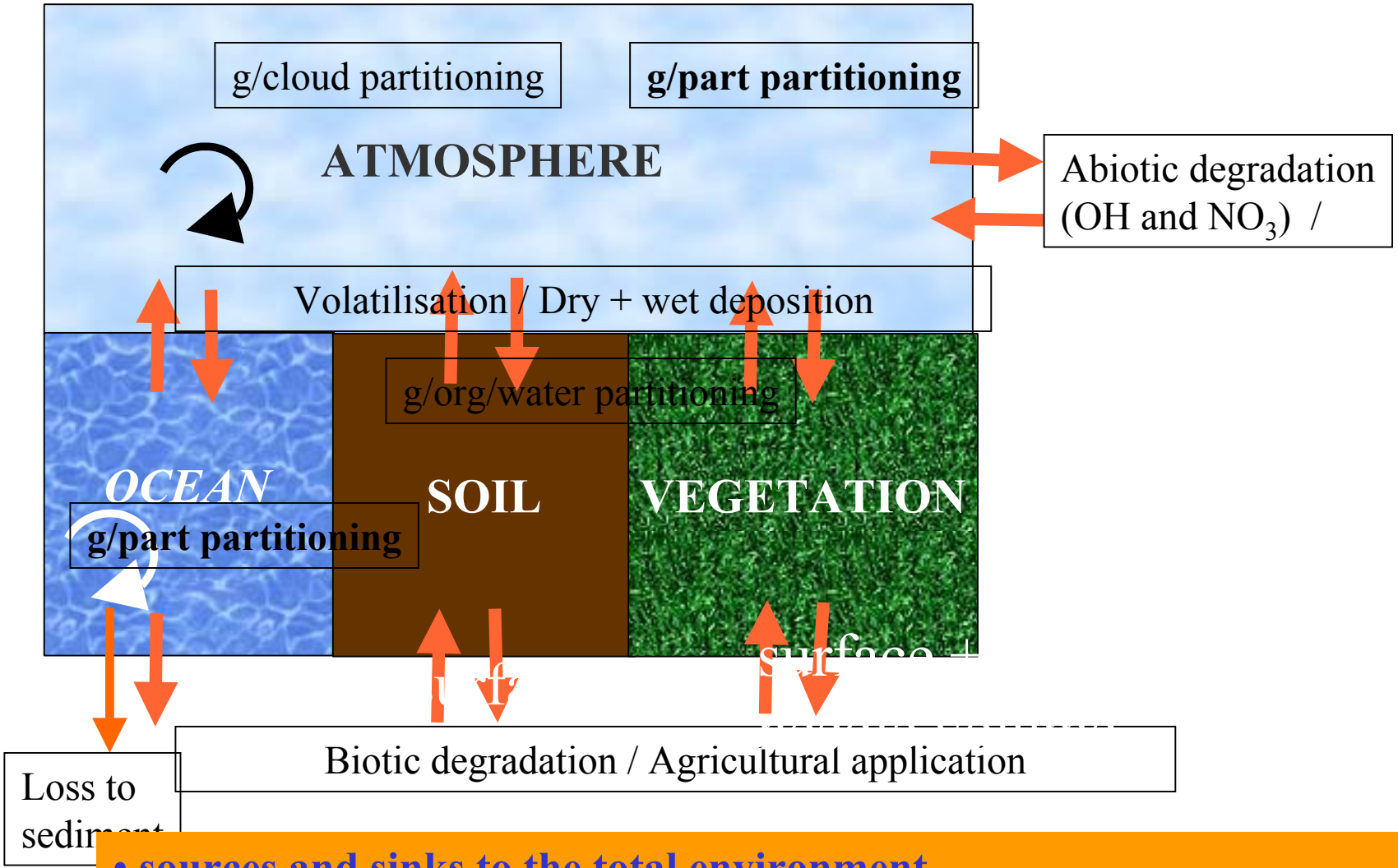


Plant uptake from atmospheric dry gas species deposition for hypothetical substances
(K_{oa} > 7: no net effect compared to bare soil)

Simulated atmospheric concentrations of a persistent chemical with log K_{OW} 7 and log K_{AW} –2.5 in a hypothetical environment with and without forest cover for the year 1999. The strong uptake of chemical in the forest canopy during the spring results in a double-peak behaviour with two air concentration maxima, one in early spring and one in summer.

(Wania & McLachlan, 2001)

4.5 Multicompartmental chemistry

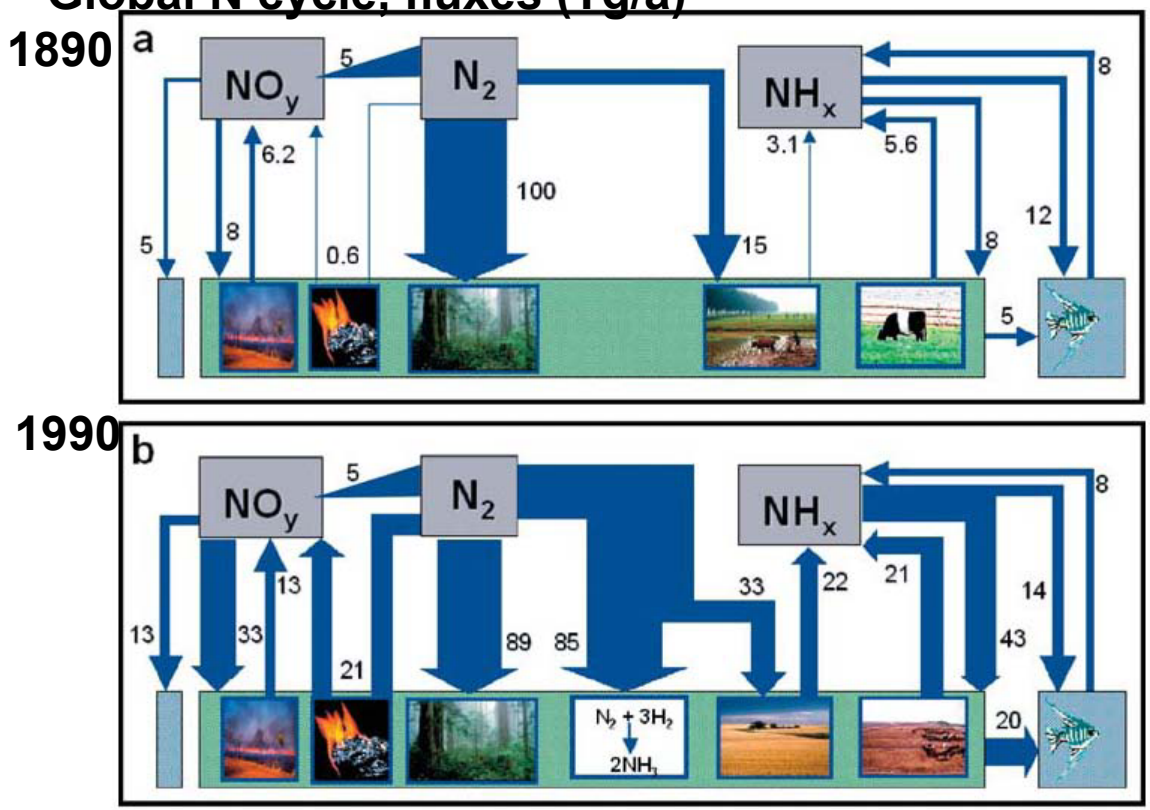


- **sources and sinks to the total environment**
- **transport in and mass exchange between compartments**
- **partitioning between phases within and at interfaces between compartments**

4.5.1 Emissions to the multicompartmental system

• **receptor (‚mode of entry'): air, surface waters, cropland, seawater**

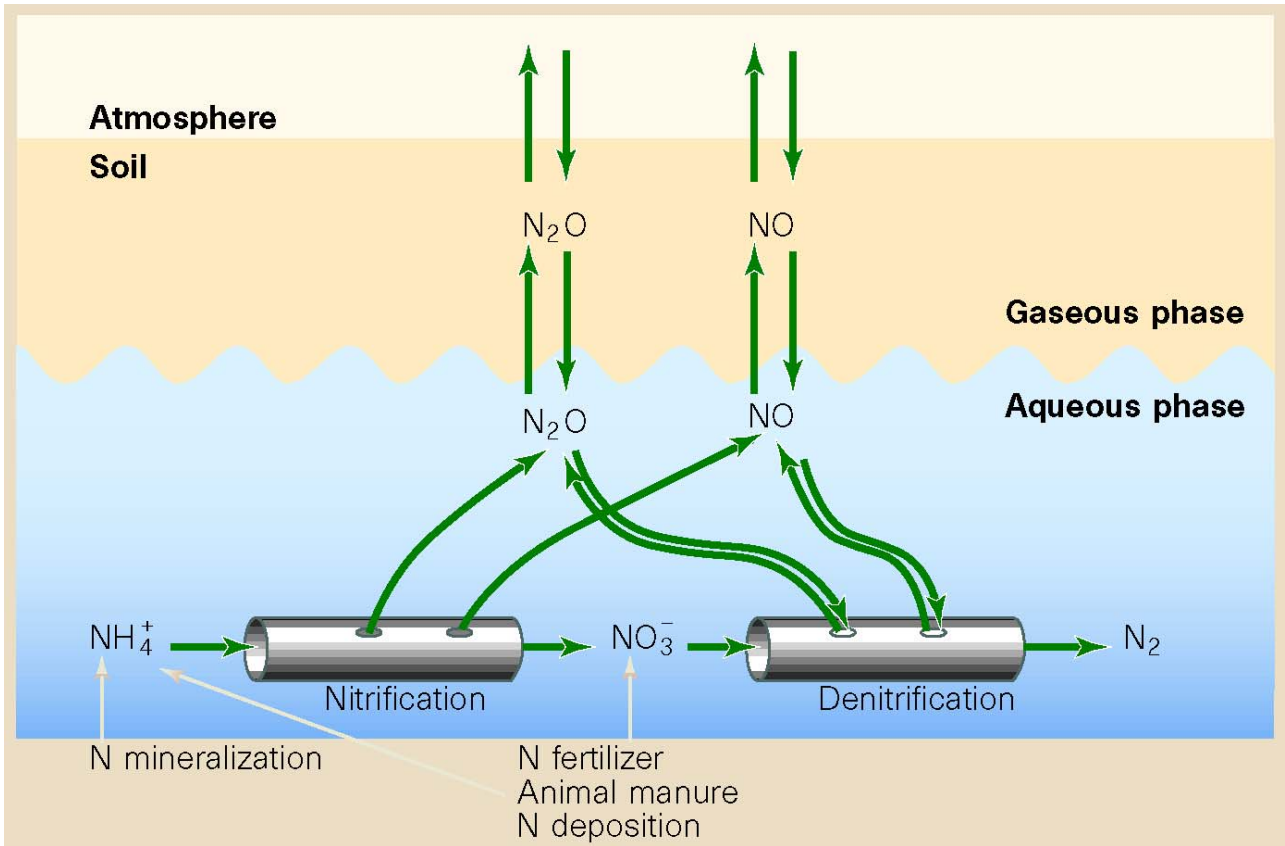
Global N cycle, fluxes (Tg/a)



into soils upon application as fertilizer or pesticide

(Hibbard et al., 2006)

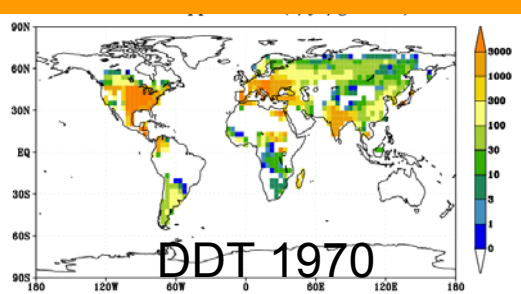
Role microbiology and fungi:

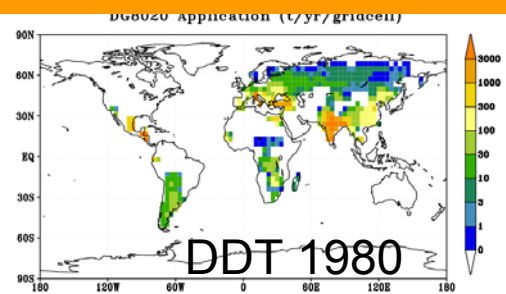


‚Hole in the pipe model': Leakage of NO and N_2O from nitrification and denitrification. Usage in denitrification.

(Davidson, 1991)

- temporal profile, e.g. diel, weekly, seasonal, historical trends
- spatial distributions





(Semeena & Lammel, 2003)

4.5.2 Total environmental residence time

Residence time of substance i in **1** compartment j:

$dc_i/dt = - k_j c_i$: $c / c_0 = e^{-k_j \Delta t}$

$\tau_{ij} = [k_{ij} c_j]^{-1} = t_{1/2} / \ln(2)$

half time $t_{1/2}$

time elapsed until $c^0 \rightarrow c(t) = c^0/2$

However, usage of term ‚residence time' is not totally consistent.

example: j = soil

concept from biochemistry: substrate decay upon reagent supply

$k_{soil} = k_{degrad} + k_{vol} + k_{chemisorption} + \ldots$

$\Leftrightarrow$ *$t_{1/2}$ includes all apparent loss processes*

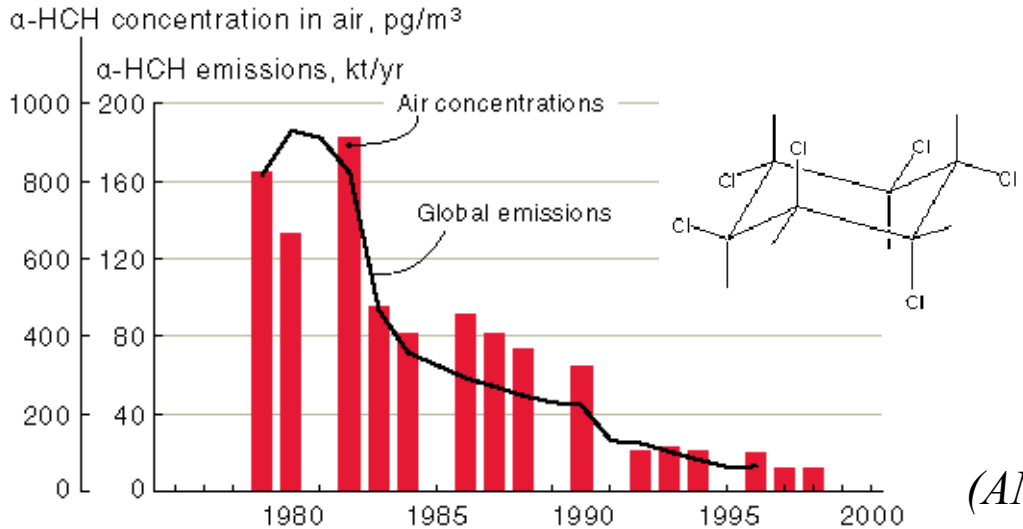
example: j = sediment

Sometimes the corresponding Δt in the gradient $c_{sed}(z)$, if decaying, is called ‚halflife' implying that source was historically constant over time

$\Leftrightarrow$ *$t_{1/2}$ includes all apparent loss processes and ignores input variation*

Residence time of substance i in the mulicompartmental system, so-calle overall residence time $\tau_{overall\ i}$:

upon cease of emissions ⇔ ‚life' of a chemical on earth



(AMAP, 2004)

$dc/dt = - k_{overall} c$: $\quad c / c_0 = e^{-k_{overall}\Delta t}$

$$\tau_{overall\ i} = k_{overall}^{-1} = [\sum_j (x_{ij} / \tau_{ij})]^{-1} = \infty \text{ for } \tau_{ji} = \infty$$

(Klöpffer, 1994)

example: i = DDT, $\tau_{i\ air} = (4.8 \times 10^{-12} \times 1 \times 10^{6})^{-1} s = 2.4$ d,

$\tau_{i\ soil} = (3.5 \times 10^{-9})^{-1} s = 9$ a, $\tau_{i\ ocean}$ = infinite

$\tau_{overall\ i} = 1$ a ($x_{iair}/x_{isoil}/x_{iocean} = 0.005/0.1/0.895$)

$\tau_{overall\ i} = 24$ d ($x_{iair}/x_{isoil}/x_{iocean} = 0.1/0.1/0.8$)

$\tau_{overall\ i} = 12$ d ($x_{iair}/x_{isoil}/x_{iocean} = 0.2/*/*$)

During continuous emissions:

$dc/dt = - k_{overall}c + E$

under steady state conditions ($dc/dt=0$):

$$\tau_{overall\ i} = m_i(t)/F_{em\ i}(t) = m_i(t)/F_{sink\ i}(t)$$

in general: $(c - Q/k_{overall})/(c_0 - Q/k_{overall}) = e^{-k_{overall}\Delta t}$

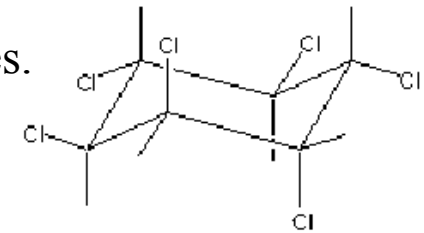
Approximated by: $\Delta m_i/\Delta t \approx F_{em\ i}(t) - m_i(t)/\tau_{overall\ i}$

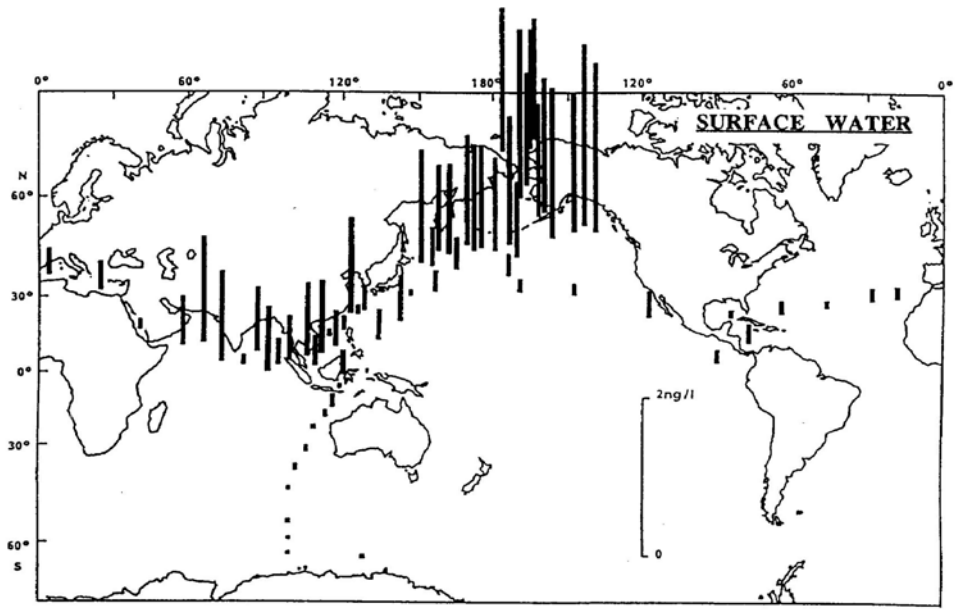
$$\tau_{overall\ i}(t) \approx m_i(t)/[\Delta m_i/\Delta t - F_{em\ i}(t)]$$

(Leip & Lammel, 2004)

4.5.3 Global distribution of re-volatilising substances, grasshopper effect

Persistent organic substances are accumulating in high latitudes.
Example α-hexachlorocyclohexane (*α*-HCH)





Higher levels in the N Pacific *(Iwata et al., 1993)*

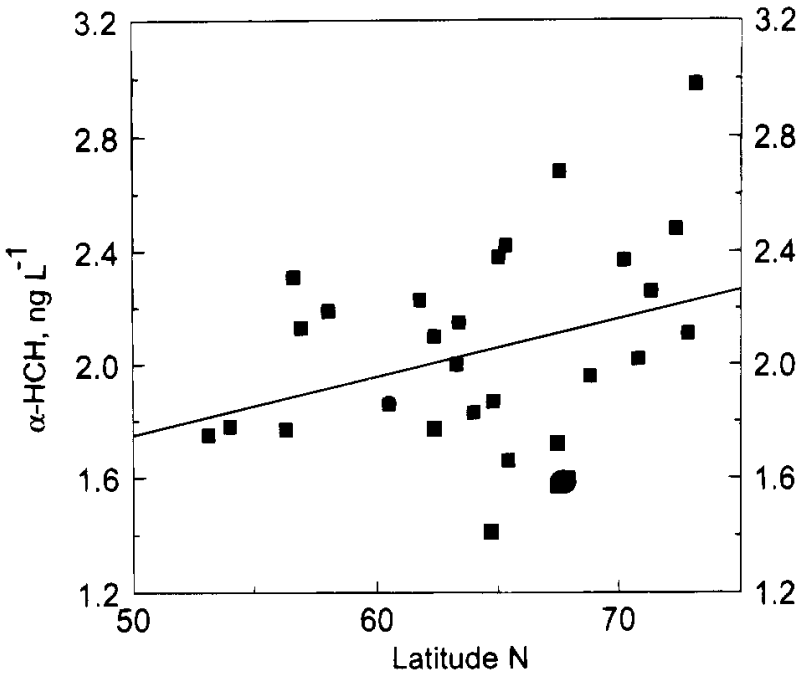
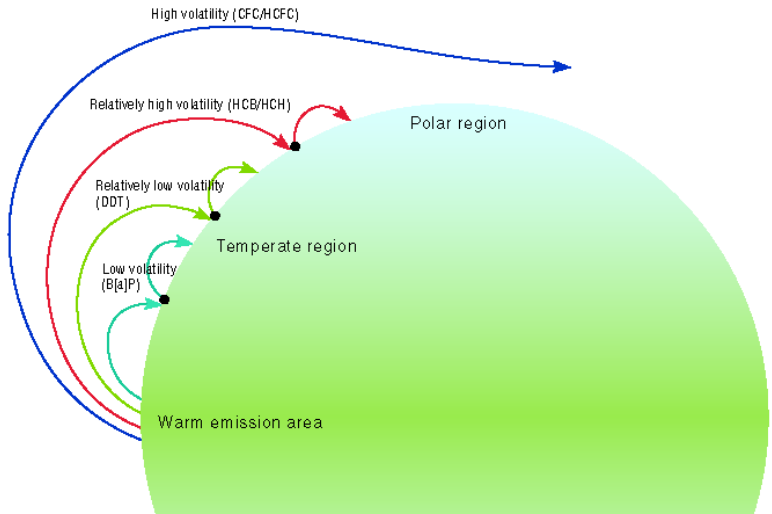


FIGURE 2. Variation in the concentration of α-HCH in the upper water column with latitude: α-HCH (ng L^{-1}) = 0.0206 × latitude + 0.72 (r^2 = 0.11).

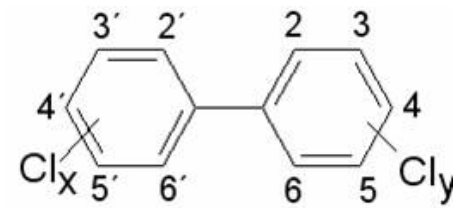
N-S gradient in the Bering and Chukchi Seas
(Jantunen & Bidleman, 1995)

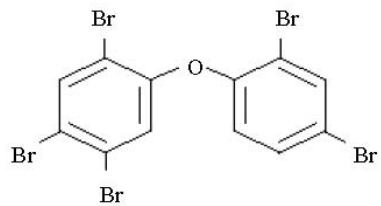
What drives accumulation in high latitudes ? (and high altitudes ?)



Re-volatilising substances: Hypothesis of a global scale (i.e. meridional) and local scale (i.e. altitudina distillation mechanism (‚global distillation‘;
Wania & Mackay, 1993)

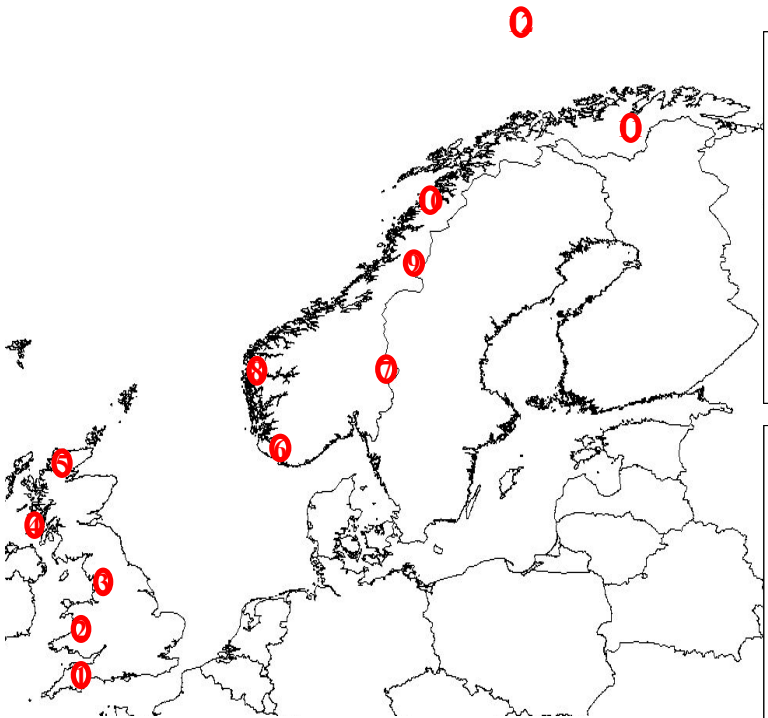
Observations:
- Accumulation of heavier vs. lighter polychlorinated biphenyls (PCB) and polybrominated diphenylethers (PBDE) in high latitudes
- Accumulation in alpine areas (e.g. in fish of alpine lakes, in top soil of the Alps)

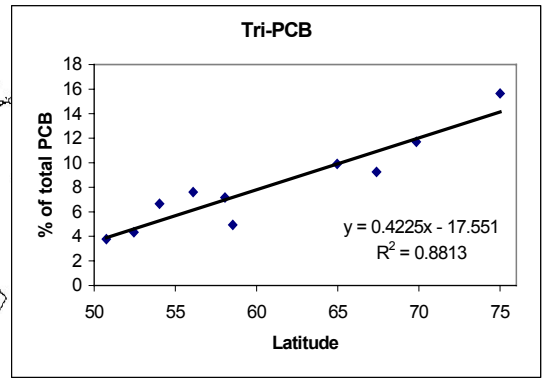


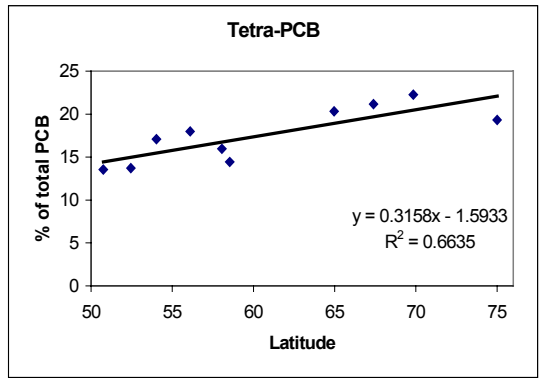


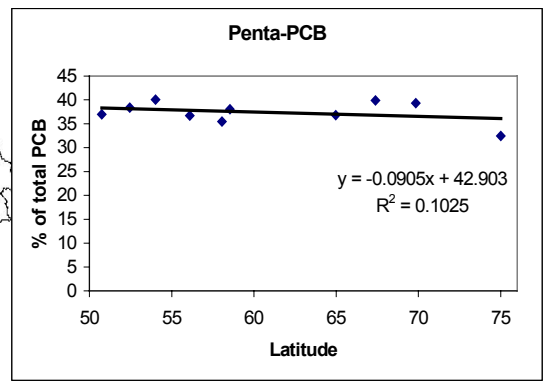
However:
- Also single hopping trace substances accumulate in alpine areas (as a consequence of mountain specific advection and deposition processes)
- on-going emissions of most relevant substances make inter-pretation difficult
- distribution patterns in biota are difficult to interprete (dynamics of individual organisms and of the ecosystem)

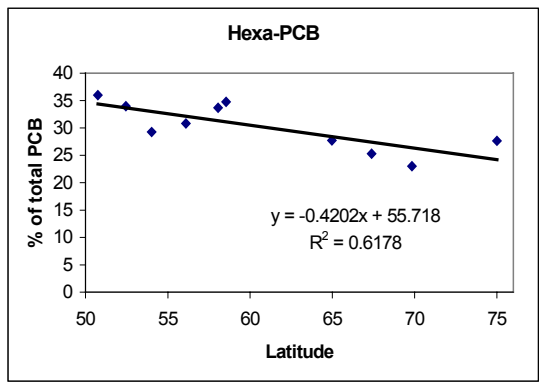
S-N transect (air, passive sampling) 1994-1996 and 1998-2000

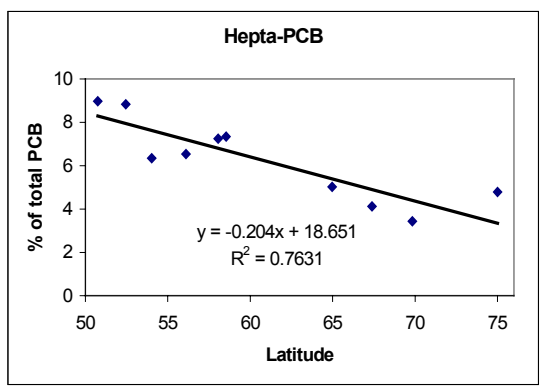


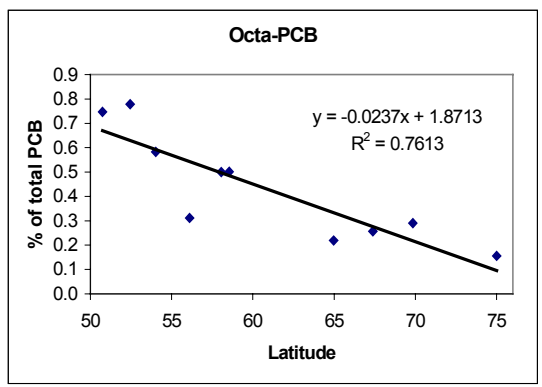












Global fractionation supported

(Meijer et al., 2002)