

Gerhard Lammel: "Trends and Advances in Atmospheric and Environmental Chemistry"

Budgeting atmospheric processes

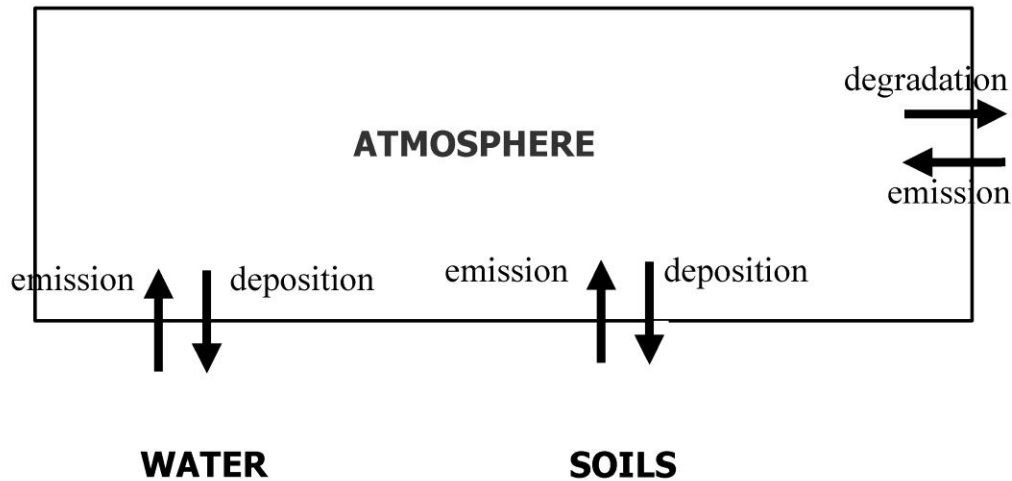
Halogenated SOCs and multicompartamental substances

Air-surface mass exchange processes

4 Trace substance mass budgets, surface cycling:

Emissions, deposition, re-volatilisation

4.1 Mass budget equation, residence time



$$\frac{dm_i}{dt} = \text{sources} - \text{sinks} = E_i - S_i = E_i - (k_{i \text{ degrad}}^{(1)} + k_{i \text{ dep}}^{(1)}) m_i = m_i / \tau$$

[g/s]

$$\frac{dc_i}{dt} = E_i - S_i = F_{i \text{ em}}/h - (k_{i \text{ degrad}}^{(1)} + k_{i \text{ dep}}^{(1)}) c_i = c_i / \tau_{\text{air}} \quad [\text{g/m}^3/\text{s}]$$

- 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:

$$dm_i/dt = (F_{i \text{ in}} + E_i) - (F_{i \text{ out}} + S_i)$$

with:

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

E_i, S_i = internal sources and sinks

$m_i = M_{g \text{ i}}/M_{g \text{ air}} \langle x_i \rangle m_{\text{trop}}$

$M_{g \text{ i}}, M_{g \text{ air}}$ = molar masses ($M_{\text{air}} = 29 \text{ g/mol}$)

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

m_{trop} = mass of tropospheric air = $4.25 \times 10^{15} \text{ t}$

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

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 $F_{i \text{ out}}$

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

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

$\tau_i = (k_F + k_V^{(1)})^{-1}$; 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: $dm_i/dt = \langle F_{i\text{ in}} \rangle + \langle E_i \rangle - (k_F + k_V^{(1)}) m_i \approx 0$

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

with: $\langle N_i/V \rangle =$ temporally and spatially mean number concentration

$(N_i/V)' =$ local and temporal number concentration

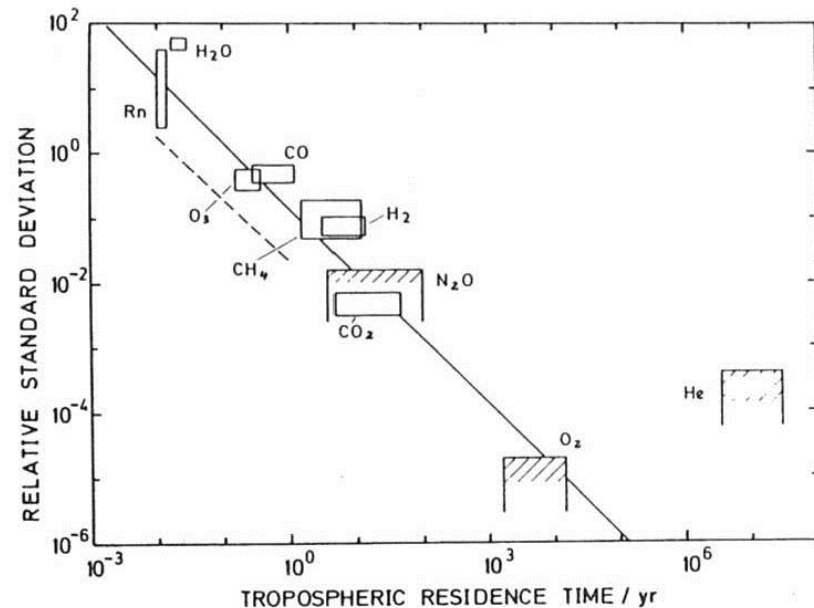
x, y, z = space coordinates

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: $\sigma_i^*((N_i/V)') =$ absolute standard deviation of $(N_i/V)'$

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



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:
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52 % transport

7 % fossil fuels, stationary

5 % chemical, petrochemical industries

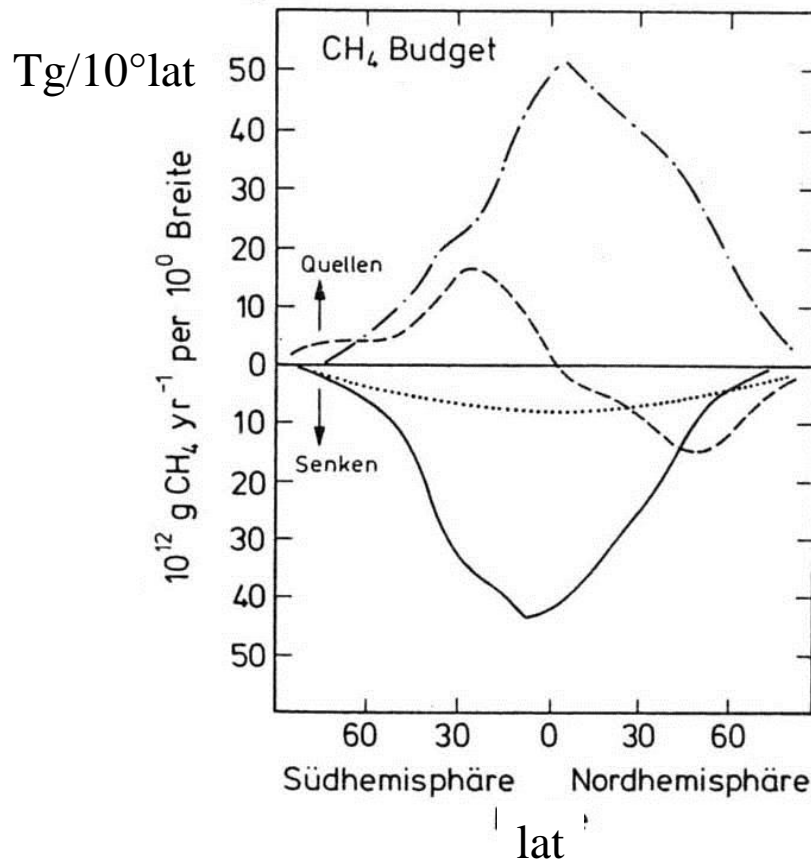
9 % oil and gas production

27 % solvents

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

Emissions, CH₄

Global Model results



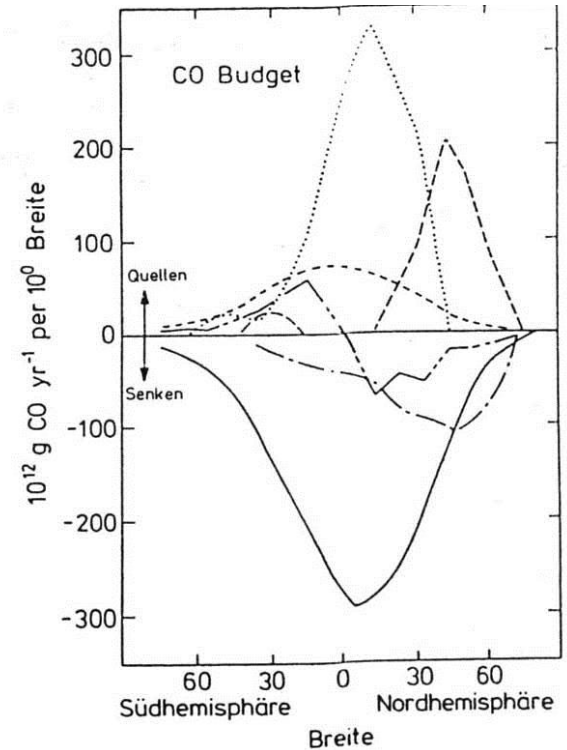
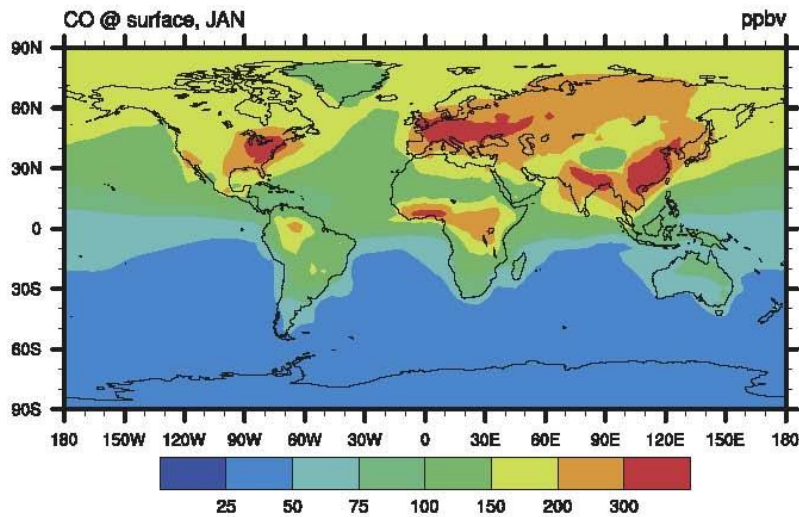
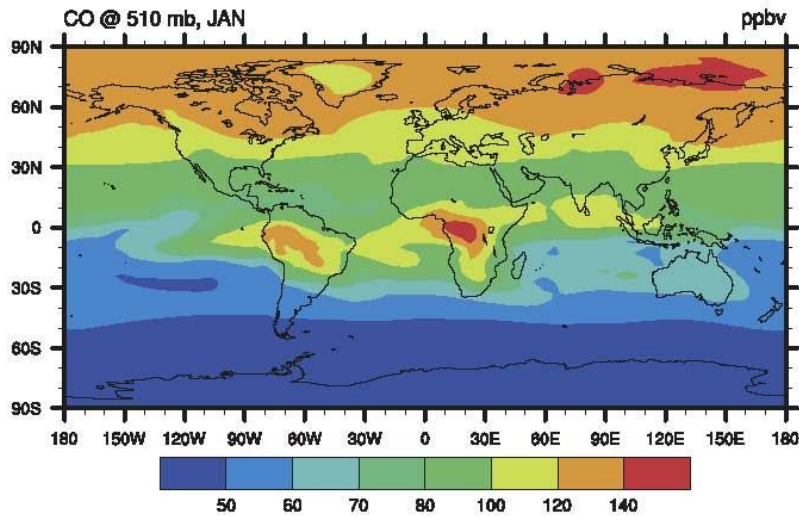
Legende	Global	Prozess
-----	$\pm 71 \times 10^{12}$	Transport
.....	87×10^{12}	CH ₄ Zunahme
————	-322×10^{12}	CH ₄ + OH Oxidation
- · - · -	409×10^{12}	Quellenverteilung

increase
sources

(Crutzen & Gidel, 1983)

Distributions – spatial, seasonal

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

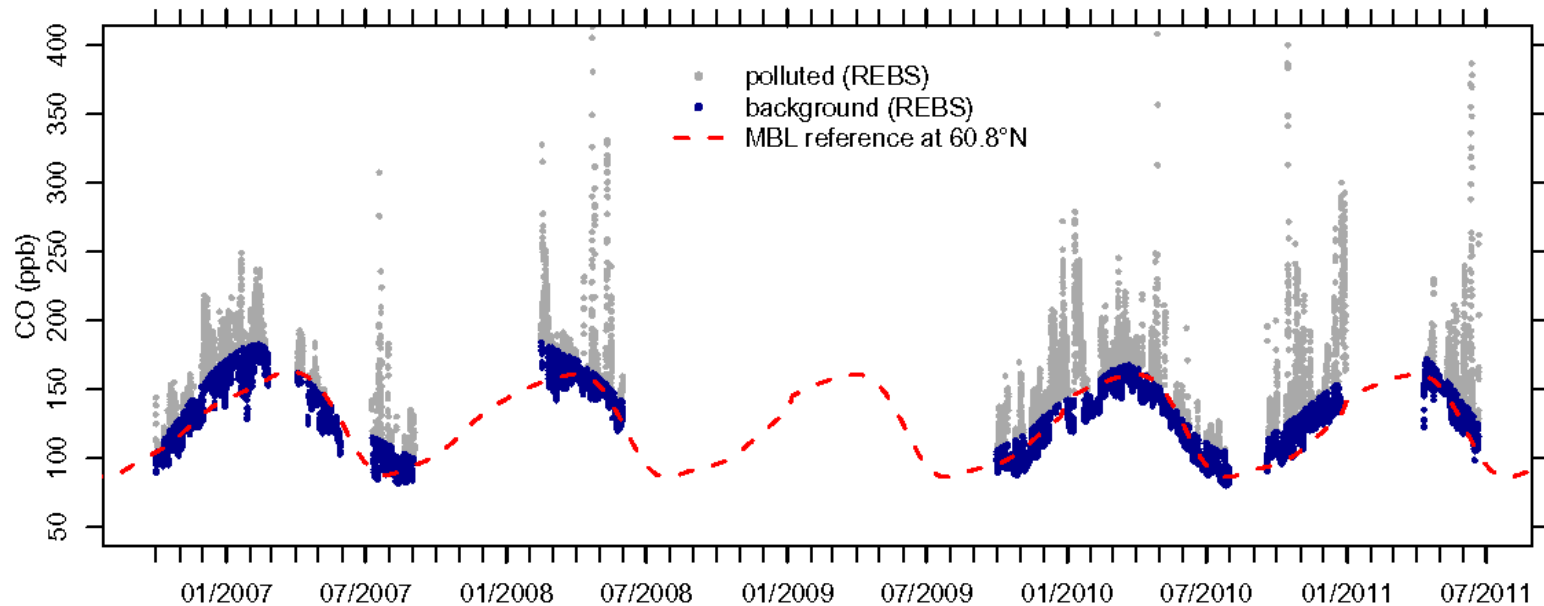


Legende	Global	Prozeß
-----	643×10^{12}	Technologische Quellen
-----	-636×10^{12}	Deposition am Boden
-----	-2054×10^{12}	CO + OH Oxidation
-----	566×10^{12}	CH ₄ + OH Oxidations - Quellen
-----	$\pm 194 \times 10^{12}$	Transport
.....	1483×10^{12}	Tropische Quellen

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

Distributions – spatial, seasonal

Regional distribution CO (ppbv) @ 300 m 60°N/90°E (ZOTTO)



Measurements:

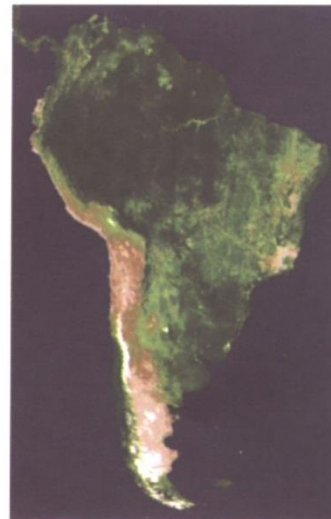
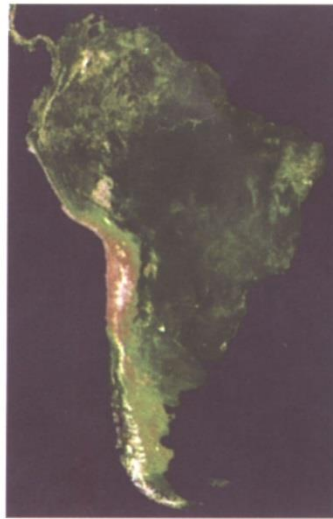
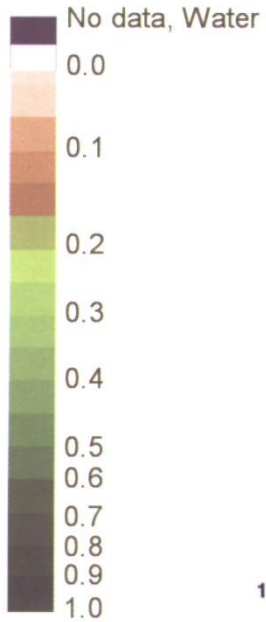
polluted air masses

background

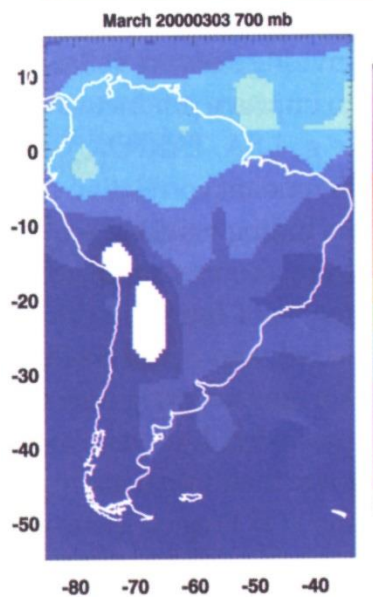
background in the marine boundary layer 60°N

(courtesy of *Chi & Andreae 2013*)

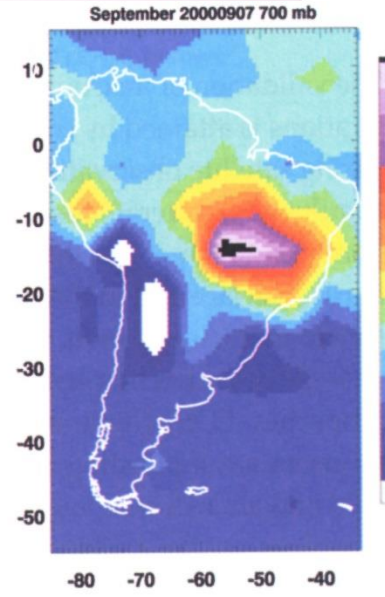
Land use and atmosphere in South America



Difference Vegetation Index



wet season

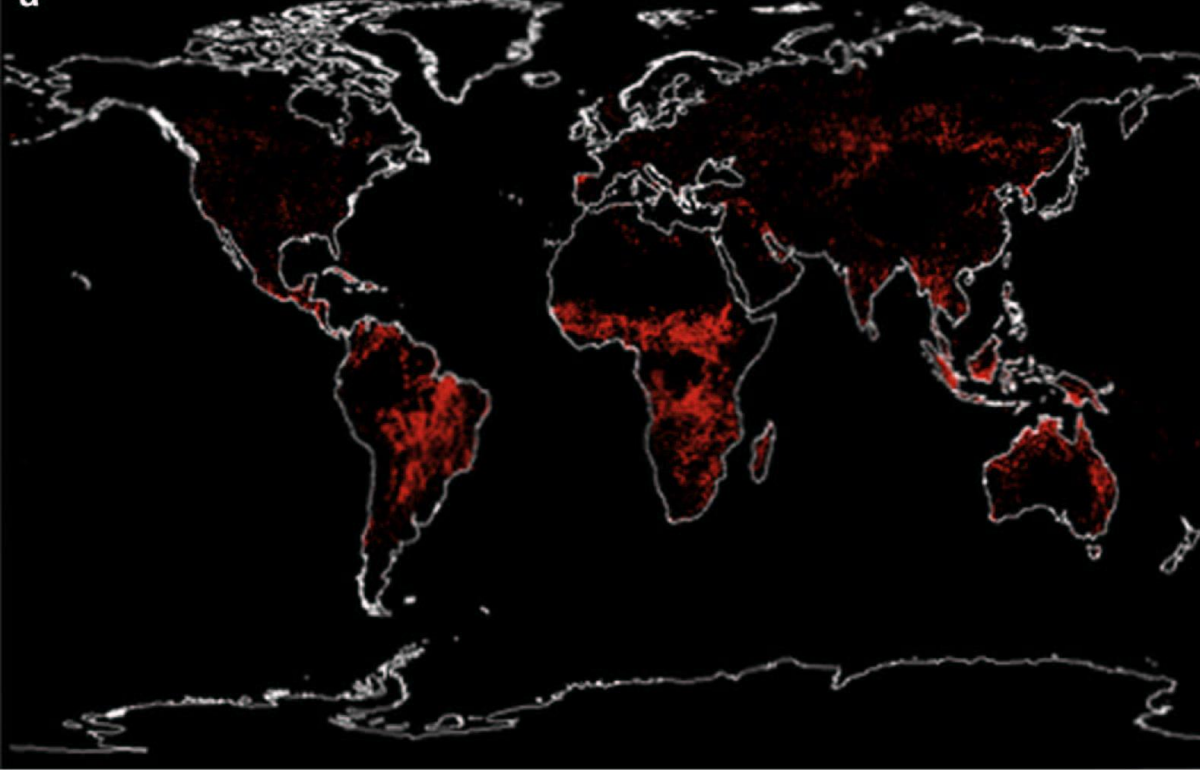


dry season

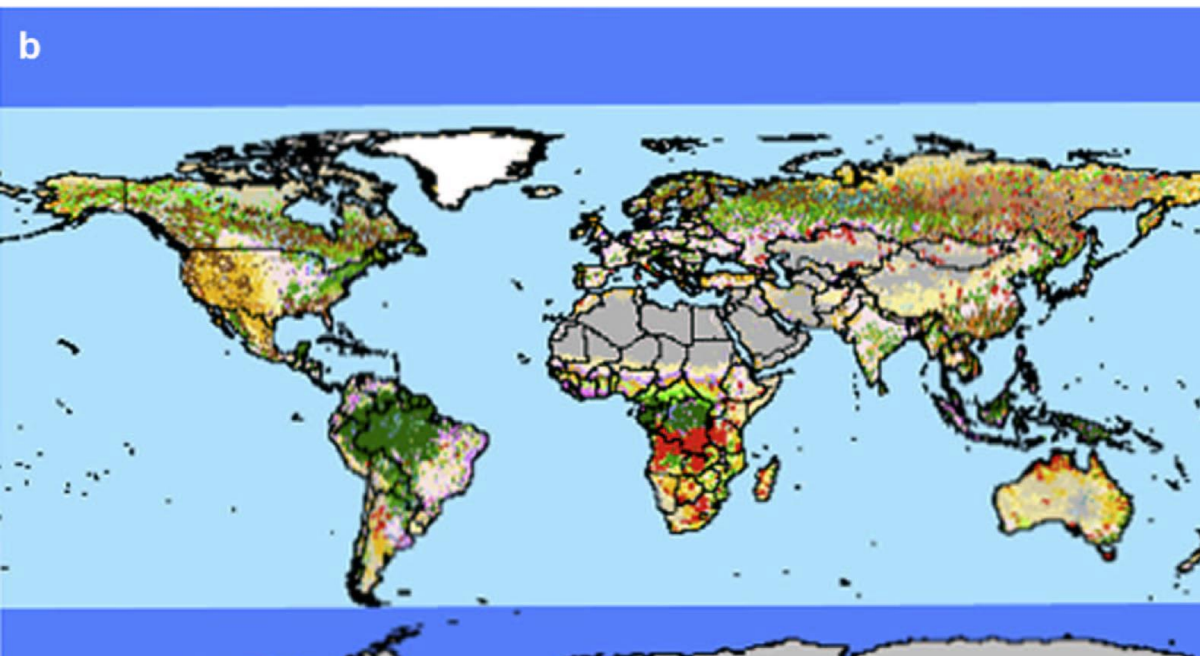
CO column density

(Ranson & Wickland, 2001)

Biomass burning



Example of the spatial distribution of nighttime active fires given by the ATSR satellite sensor

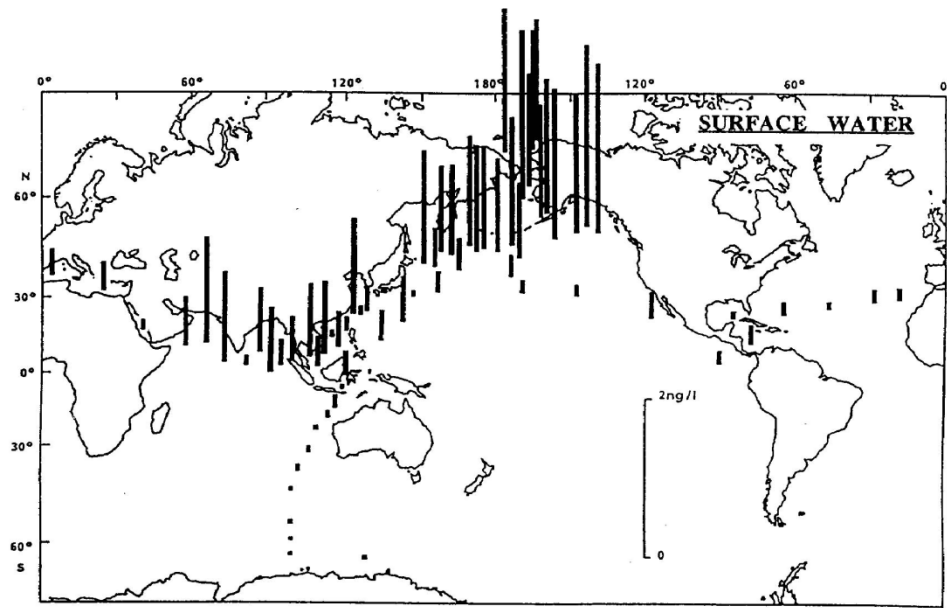


example of burnt area provided by the GBA-2000 product
(*Tansey et al., 2008*)

Halogenated SOCs and multicompartmental substances

Introduction: concerns persistence, bioaccumulation and effects

Many (most) semivolatile and persistent organic substances are accumulating in high latitudes (despite source distribution). Example α -hexachlorocyclohexane (α -HCH)



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

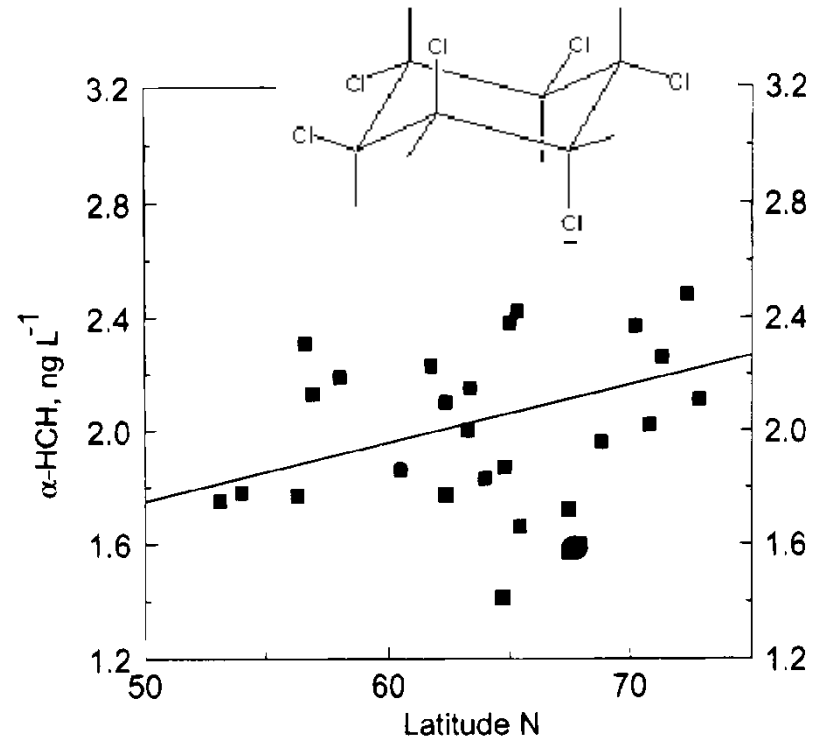
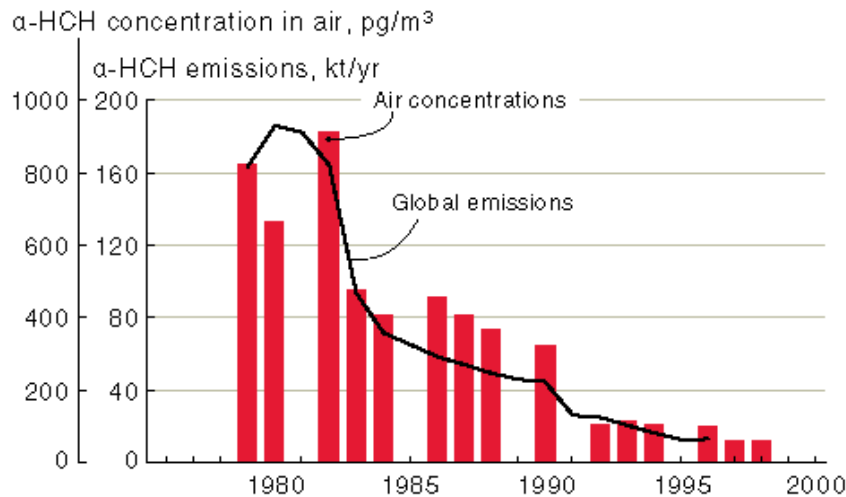


FIGURE 2. Variation in the concentration of α -HCH in the upper water column with latitude: $\alpha\text{-HCH (ng L}^{-1}\text{)} = 0.0206 \times \text{latitude} + 0.72$ ($r^2 = 0.11$).

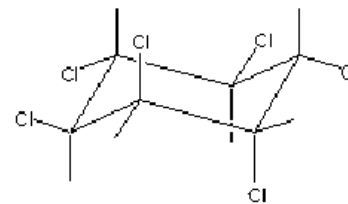
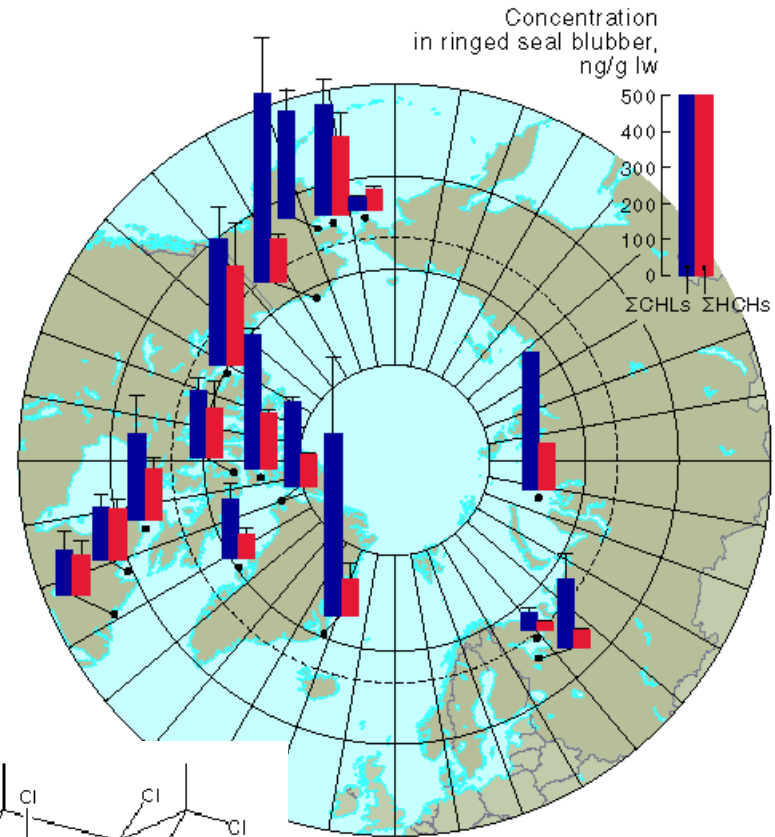
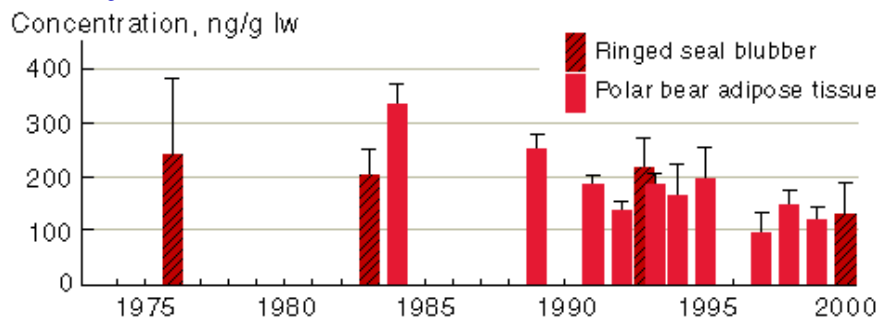
N-S gradient in the Bering and Chukchi Seas (*Jantunen & Bidleman, 1995*)

Decreasing trends in air and water not necessarily followed in organisms:

Bioaccumulation along food chains



Decreasing trends in air, water and sediments not found in biota:



(AMAP, 2004)

6.2.2.2 SOCs surface exchange

6.2.2.2.1 Air-sea exchange

= volatilisation and dry deposition of (gaseous) molecules

- gas flux through interface $F = -v_{wg} (c_w - c_{wi}) = -v_{gw} (c_{gi} - c_g)$ [mol/m²/s]

with $c_{wi} = c_g / K_{aw}$

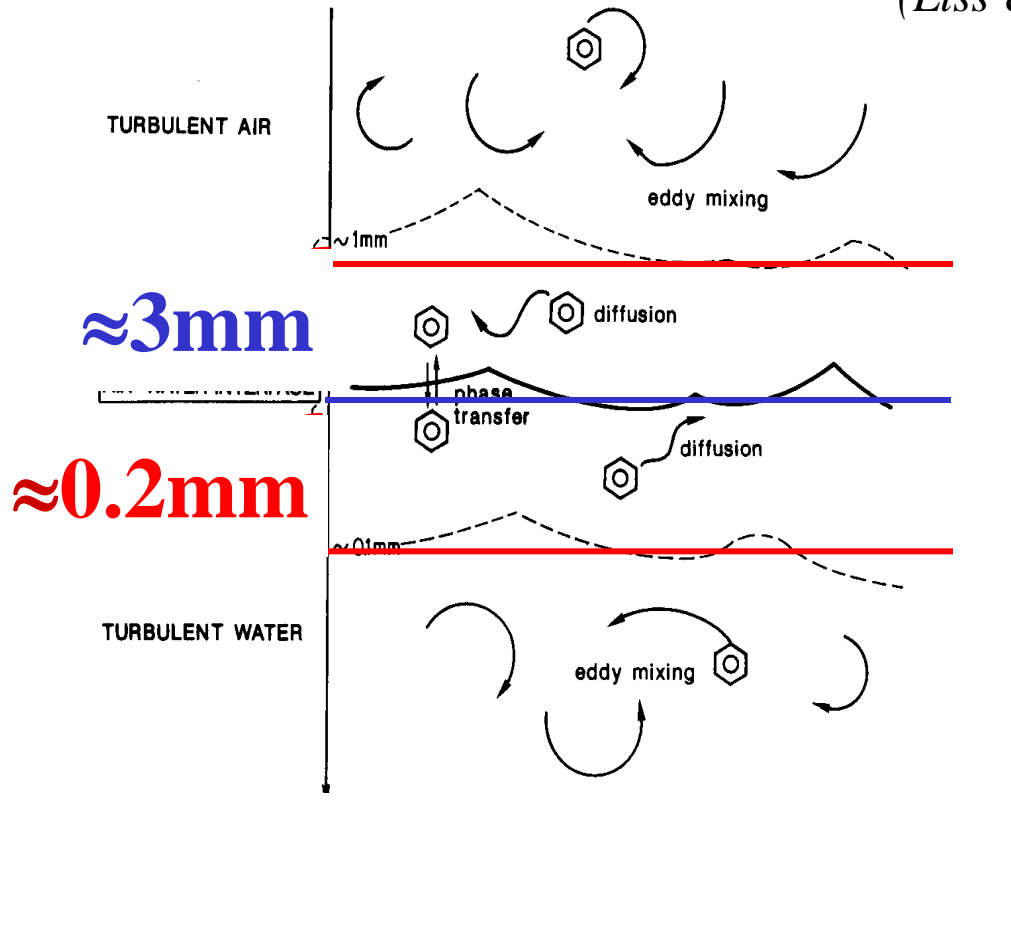
- all physics hidden in v ; equilibrium established at the interface itself

Two film model (or: two film theory of gas absorption)

- existence of 2 stagnant layers on either side of the interface = transition zone from fully turbulent to molecular conditions

- provide resistance additively $R_{aw} = R_a + R_w \Leftrightarrow 1/v_{aw} = 1/v_w + 1/(v_a K_{aw})$

(Liss & Slater, 1974; Schwarzenbach et al., 2002)



$$F_{aw} = k_{mt} (c_w - c_a / K_{aw})$$

Mass transfer coefficient k_{mt} (often K_{ol})

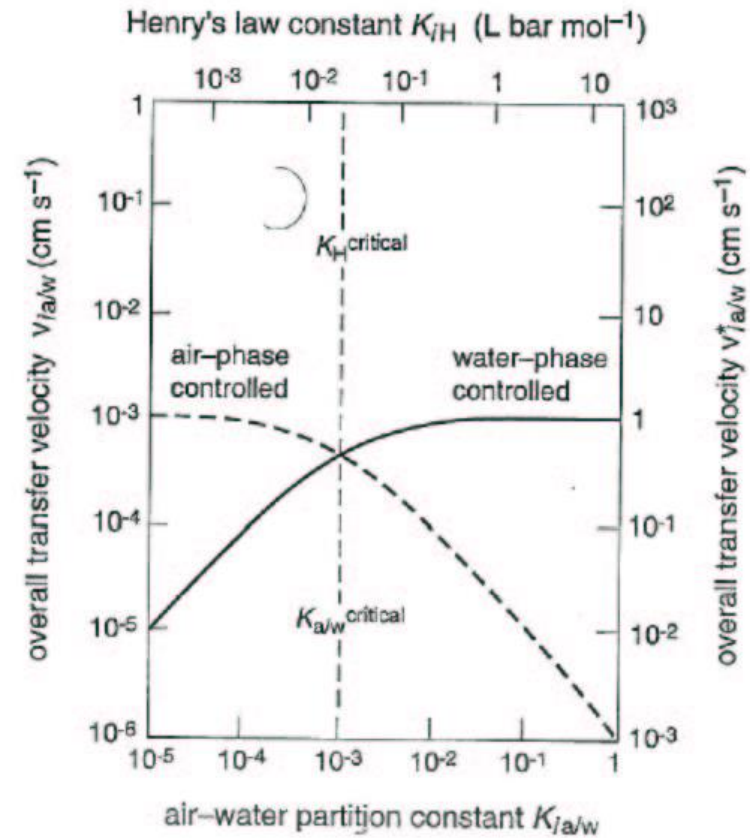
H' = dimensionless Henry coefficient K_{aw}

(courtesy of M. Tsapakis)

Two film model (followed)

- there is a water-phase and an air-phase controlled regime existing

- $1/v_{aw} = 1/v_w + 1/(v_a K_{aw})$ means that in the water-phase controlled regime the overall transfer velocity is independent, in the air-phase related regime linearly dependent of K_{aw} . This asymmetry, however, is only related to the decision to relate all concentrations to the reference phase water.



Schematic of overall air-water exchange velocity v_{aw} as a function of the air-water partition coefficient K_{aw} .

Symmetry as equally frequent renewed surfaces are assumed (not realistic).

$$F = -k_{mt\ w} (c_w - c_{wi}) = -k_{mt\ a} (c_{ai} - c_a) \text{ [mol/m}^2\text{/s]}$$

defined positive for flux from air to water

$$c_{ai} = K_{aw} c_{wi}$$

with actual bulk (c_w, c_a) and equilibrium (c_{wi}, c_{ai}) concentrations in water and air

$$F = -k_{mt\ net} [c_w - c_a R_g T / (c_w H(T,s))] \quad ; \text{ salinity } s, H \text{ [Pa m}^3\text{/mol)},$$

$$R_g = 8.206 \text{ m}^3\text{Pa/K/mol}$$

$$H(T,s) = R_g T K_{aw}(T,s) = R_g T K_{aw}(T) \times 10^{K_s c_s} \quad ; \text{ Setschenow constant } K_s \text{ [L/mol]}$$

$$K_s = 0.04 \log K_{ow} + 0.114 \text{ (Ni \& Yalkowsky, 2003)}$$

Resistance by boundary layers:

reciprocal transfer coefficients (, piston velocity' $k_{mt\ w}, k_{mt\ g}$ [m/s])

$$R = 1/k_{mt\ net} = 1/k_{mt\ w} + R_g T / (k_{mt\ g} H(T,s)) \text{ [s/m]}$$

consideration of 1 side sufficient for most gases

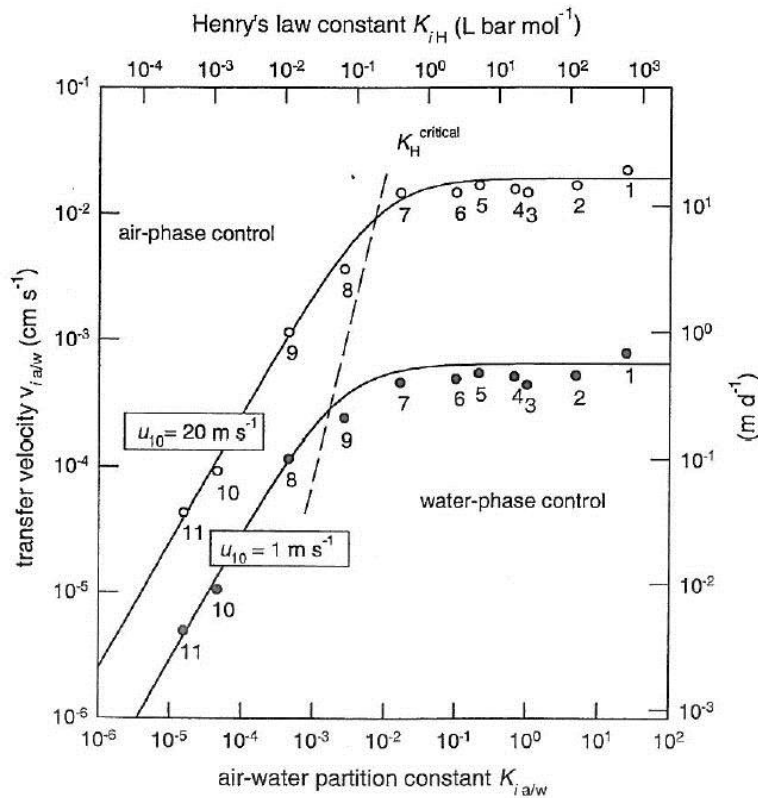
However:

Stagnant film model (which ignores non-diffusive mass transport) implies $F = (D/z)\Delta c$ with diffusion layer thickness z (can be estimated). $F \sim D$ is not really true.

Other existing conceptual models of air-sea mass exchange:

- Surface renewal model (interface periodically renewed by turbulence eddies) implies $F = 2(D/t_a\pi)^{0.5}\Delta c \sim D^{0.5}$. However, the model is not useful, as the characteristic surface renewal time, t_a , is not known or experimentally accessible.
- Turbulent fluid flow based model
- Turbulence enhancement by bubbles model: bubbles are created by breaking waves ($u > 13$ m/s)
- Surface film effects: no direct inhibition but indirect (hydrodynamic: wave dampening ($3.6 < u < 13$ m/s), suppression of surface renewal...) effects

These conceptual models are not predictive / fail as they are limited to individual processes which in reality combine



Overall air-water transfer velocity as a function of Henry's law coefficient for 2 very different wind regimes.

Result: magnitude of air-water transfer velocity v is determined mainly by wind speed, less by substance (Henry coefficient)

Result of lab and field measurements: v_w is positively correlated with wind speed, faster for $u_{10} > 10 \text{ m s}^{-1}$

→ Parameterisations in models are empirically based.

Wind dependence:

- 3 linear regimes for the piston velocity k_w
- quadratic $k_w \text{ CO}_2(u) = 0.31 u^2 (\text{Sc}/660)^{0.5} \text{ cm/s}$

(Liss & Merlivat, 1986)

(Wanninkhoff, 1992)

Empiric relationships to for H₂O, CO₂, and derived for unknown molecule i:

$$k_{mt\ a\ H_2O} = 0.83\ \text{cm s}^{-1} \rightarrow k_{mt\ g\ i} = 0.83\ (18/M_{gi})^{0.5}\ \text{cm s}^{-1} ; \text{molecular mass } M_{gi} \\ (\text{g/mol})$$

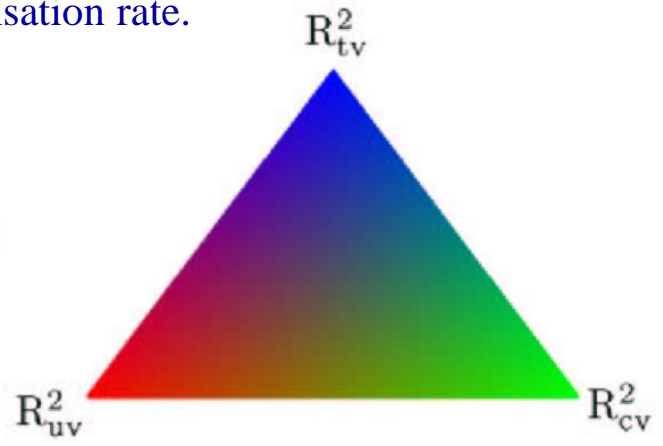
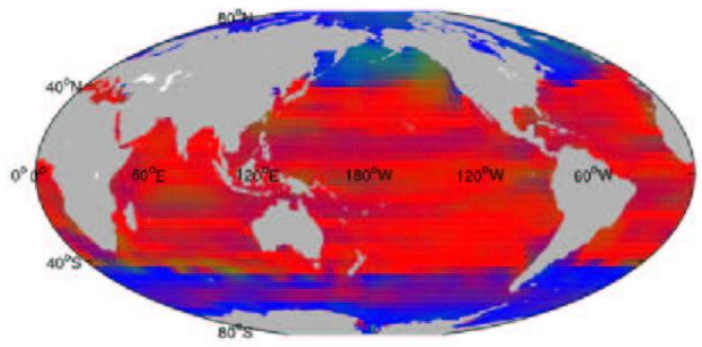
$$k_{mt\ w\ CO_2} = 0.0056\ \text{cm s}^{-1} \rightarrow k_{mt\ w\ i} = 0.0056\ (44/M_{gi})^{0.5}\ \text{cm s}^{-1} \\ (\text{Atlas \& Giam, 1986})$$

$$k_{mt\ a\ H_2O} = 0.2\ u_{10} + 0.23 \rightarrow k_{mt\ g\ i} = (D_{gi}/D_{g\ H_2O})^{0.67}\ v_{g\ H_2O} \\ (\text{Mackay \& Yeun, 1983})$$

$$k_{mt\ w} = 36 \times (0.2\ u_{10} + 0.3) \times (D_{i\ g}/D_{H_2O\ g})^{0.61} ; \text{wind velocity in 10 m height } u_{10} \\ k_{mt\ a} = 0.01 \times (0.45\ u_{10}^{1.64}) \times (Sc_i/Sc_{CO_2})^{-0.5} ; \text{Schmidt number } Sc := v/D$$

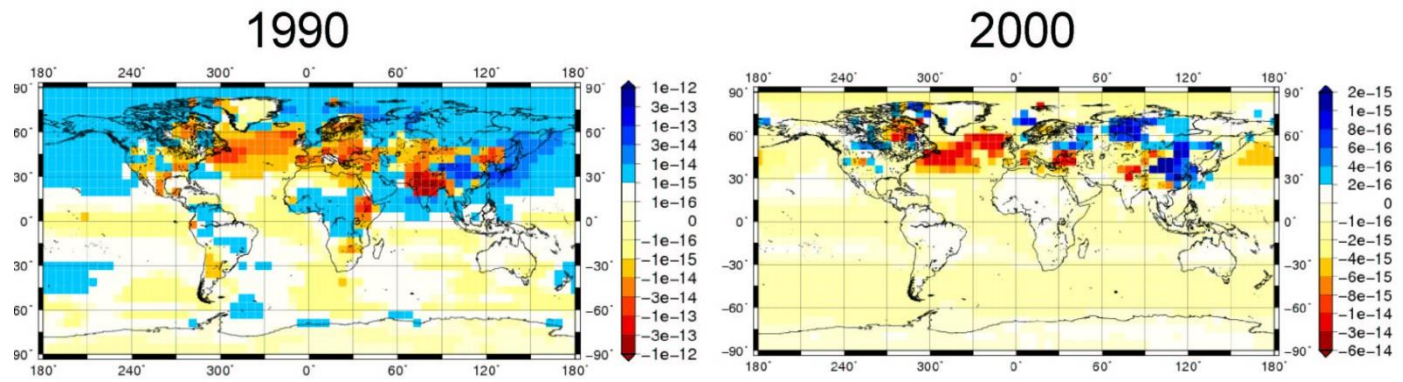
Kinematic viscosity $v := \text{fluid viscosity } \mu / \text{fluid density } \rho$
(Murphy, 1995)

Volatilisation rate v determined by sea surface temperature t , wind speed u and concentration in seawater c . Here: $p(T)$, $H(T)$, K_{ow} , $k_{oc}(T)$ and c of DDT
 Coefficients of determination R^2 (linear correlation) used to find out which of the parameters explains most of the variance of the volatilisation rate.



Model experiment with transient historic emissions 1950-1990 *(Stemmler & Lammel, 2011)*

Net-deposition = Deposition – Volatilisation ($\text{kg}/\text{m}^2/\text{s}$)



$[\text{kg}/\text{m}^2/\text{s}]$

(Stemmler & Lammel, 2009)