

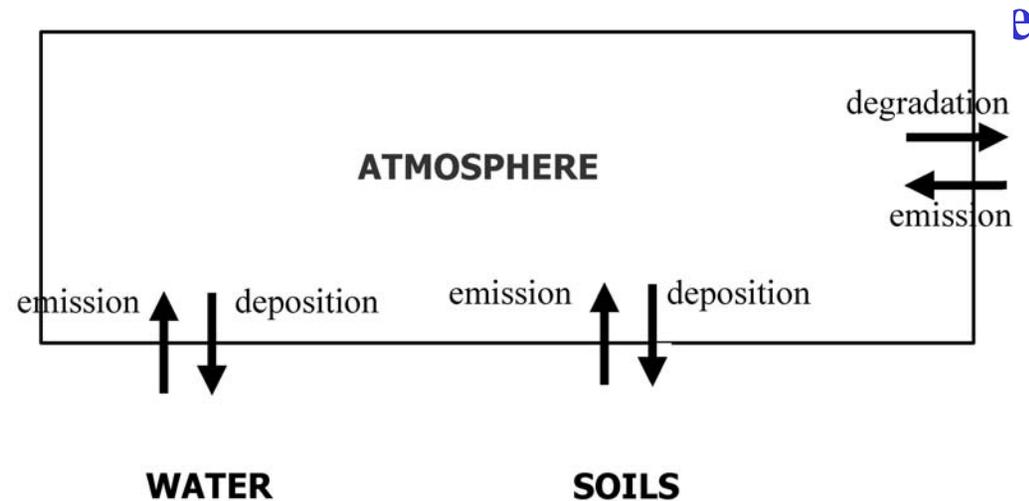
# **Gerhard Lammel: “Trends and Advances in Atmospheric and Environmental Chemistry”**

**Budgeting atmospheric processes**

**Halogenated SOCs and multicompartmental substances**

**Air-surface mass exchange processes**

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



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

[g/s]

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

- Chemical loss processes of  $i$  are 1<sup>st</sup> order in  $c_i$
- Source processes of  $i$  are 0<sup>th</sup> order in  $c_i$

Depositional loss processes are here expressed as 1<sup>st</sup> 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

$m_{\text{trop}}$  = 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:  $\tau_i$  = residence time (*not equal to but < ,lifetime'!*)

assuming (in 1<sup>st</sup> 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:  $dm_i/dt = \langle F_{i\text{ in}} \rangle + \langle Q_i \rangle - (k_F + k_V^{(1)}) m_i \approx 0$

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

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

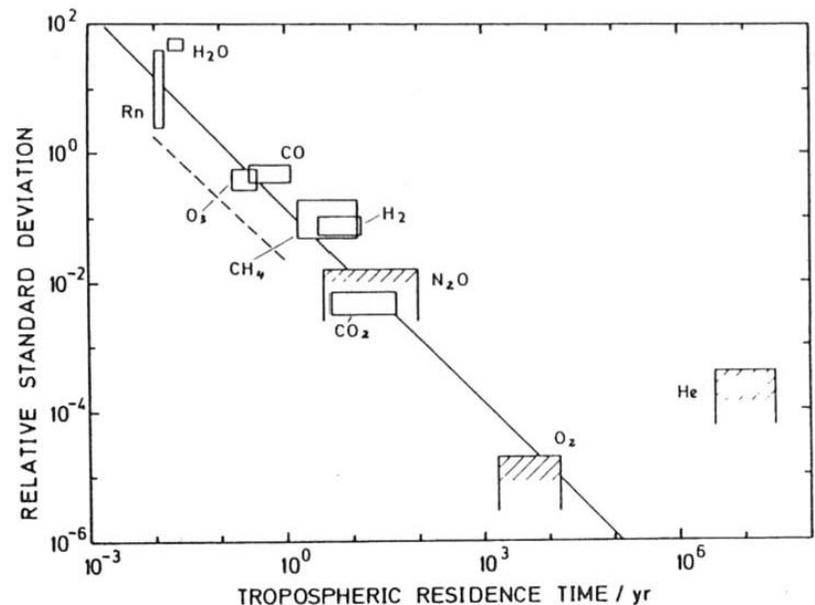
Empiric finding (*Junge, 1974*) for the relative standard deviation

$$\sigma_i = \sigma_i^* ((N_i/V)') / \langle N_i/V \rangle = 0.14 / \tau_i$$

with:  $\sigma_i^* =$  absolute

standard deviation of  $(N_i/V)'$

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



# 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)

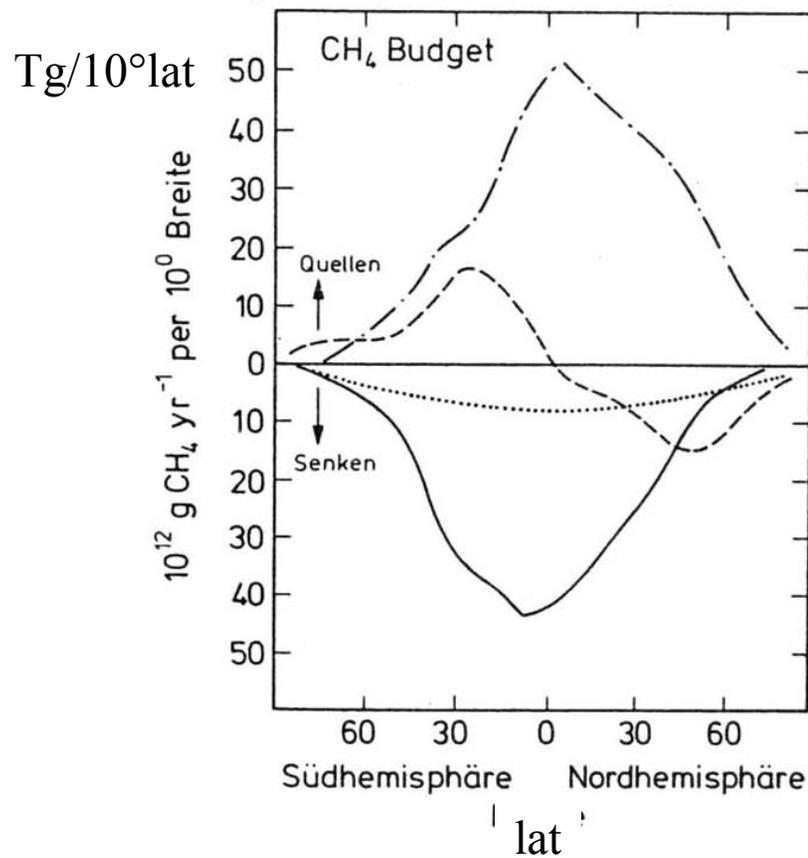
### Global budget (Tg/a)

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<sub>4</sub>

## Global Model results



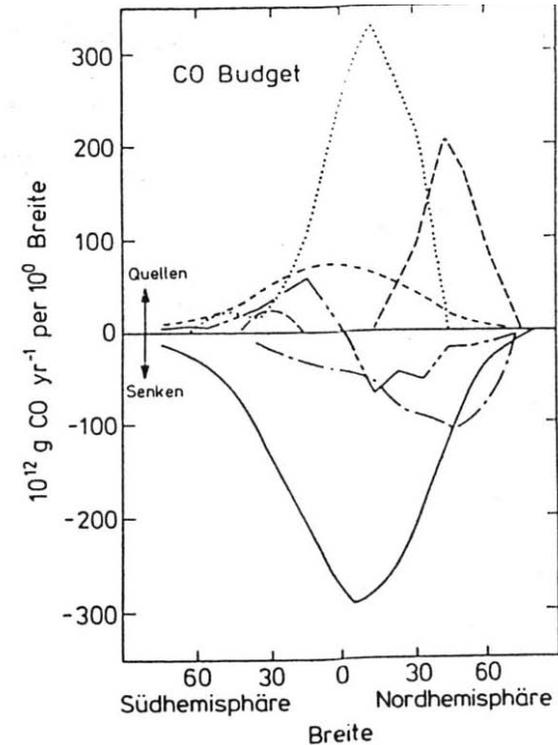
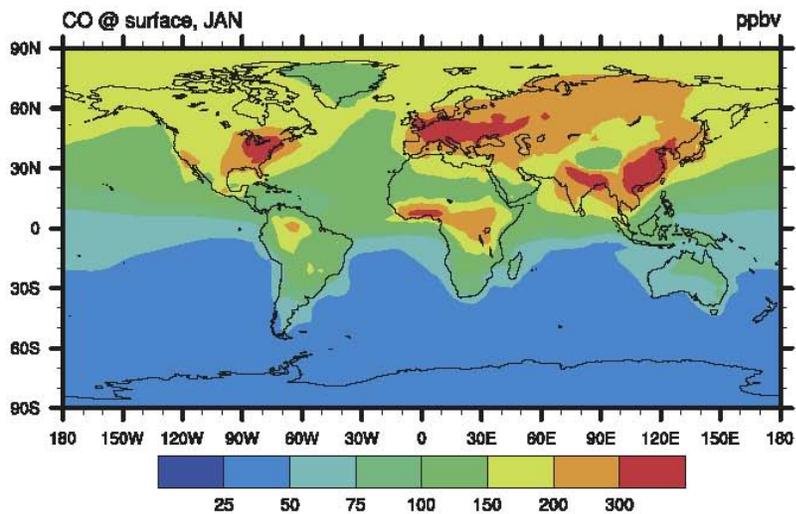
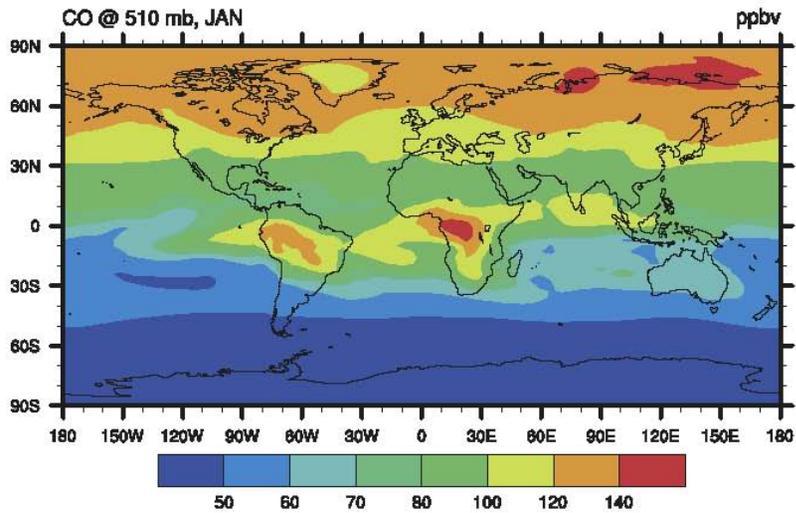
Legende	Global	Prozess
-----	$\pm 71 \times 10^{12}$	Transport
.....	$87 \times 10^{12}$	CH <sub>4</sub> Zunahme
————	$-322 \times 10^{12}$	CH <sub>4</sub> + OH Oxidation
- · - · -	$409 \times 10^{12}$	Quellenverteilung

increase  
sources

(Crutzen & Gidel, 1983)

# Distributions – spatial, seasonal

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



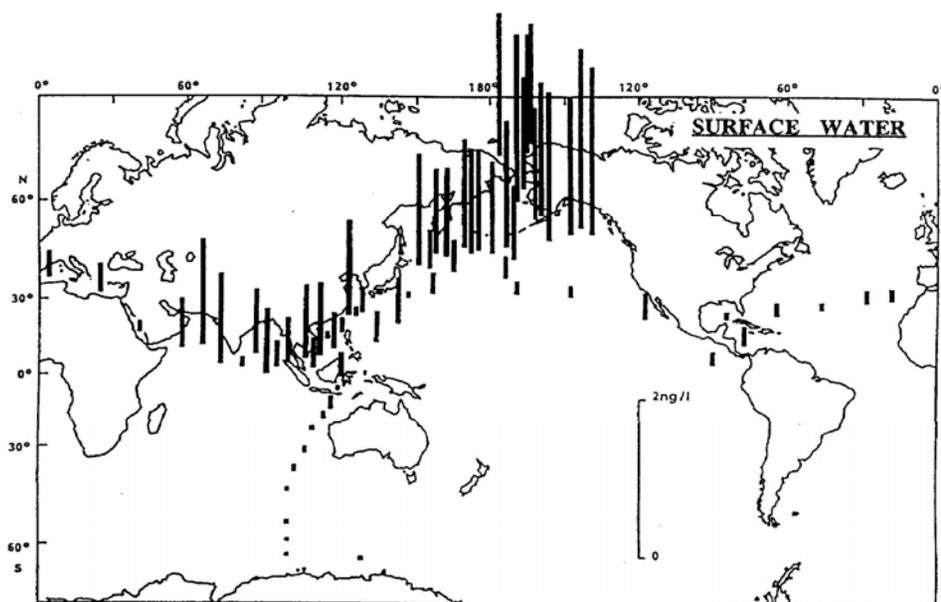
Legende	Global	Prozess
-----	643 × 10 <sup>12</sup>	Technologische Quellen
-----	-636 × 10 <sup>12</sup>	Deposition am Boden
-----	-2054 × 10 <sup>12</sup>	CO + OH Oxidation
-----	566 × 10 <sup>12</sup>	CH <sub>4</sub> + OH Oxidations - Quellen
-----	±194 × 10 <sup>12</sup>	Transport
.....	1483 × 10 <sup>12</sup>	Tropische Quellen

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

# Halogenated SOC and multicompartamental substances

## Introduction: concerns persistence, bioaccumulation and effects

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



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

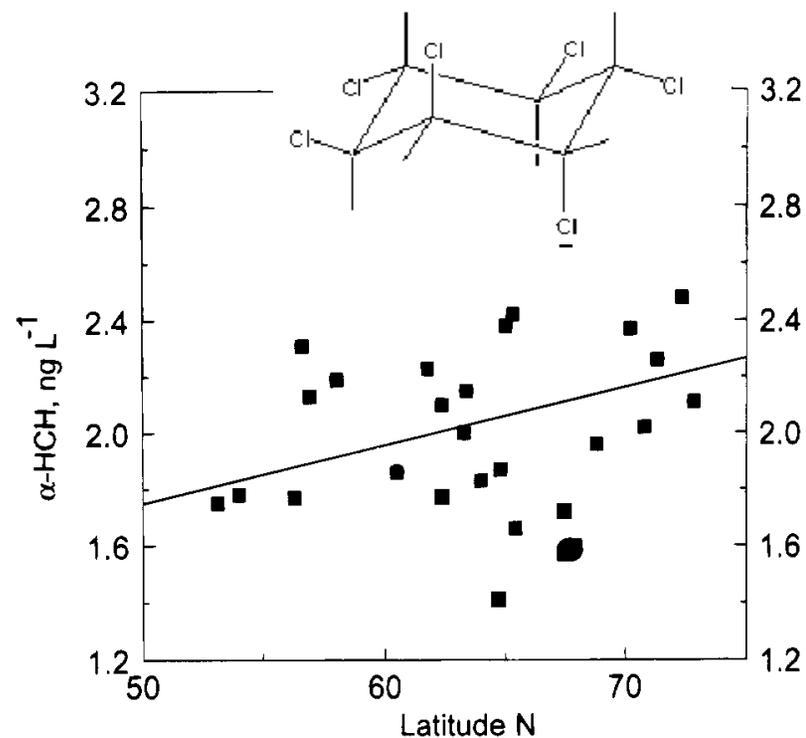
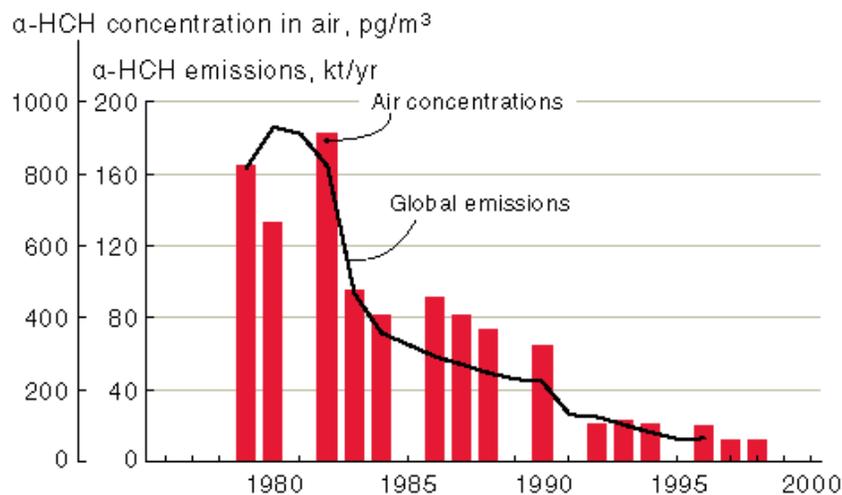


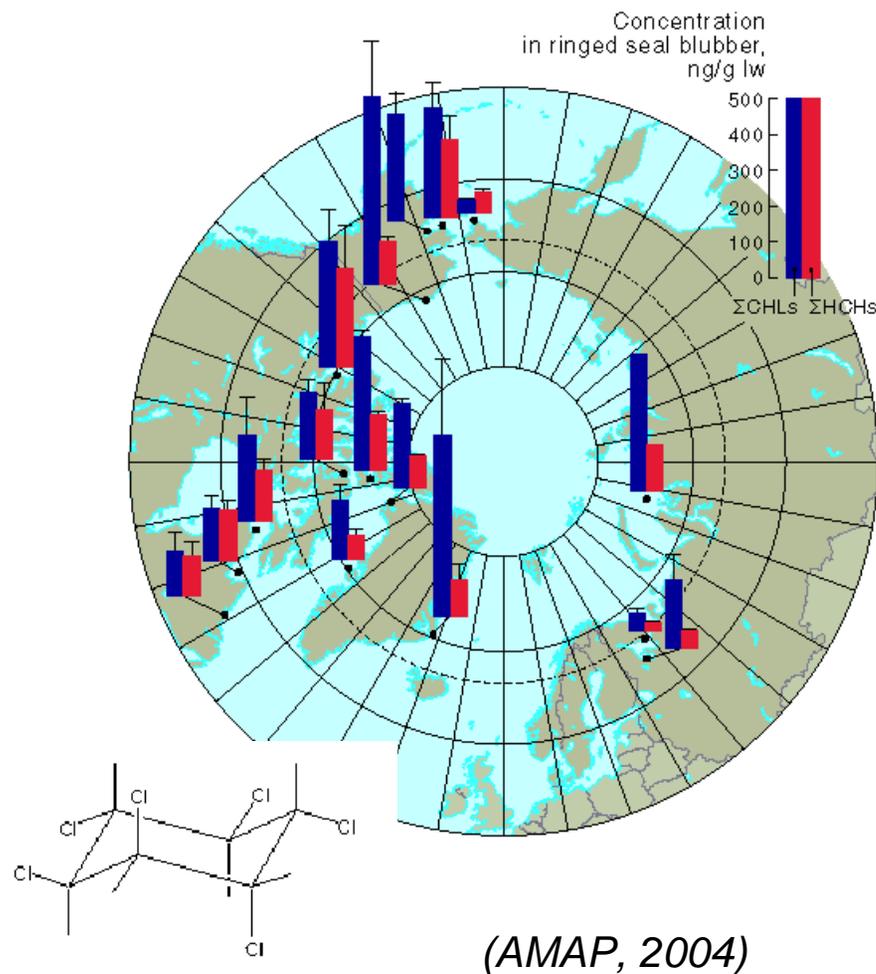
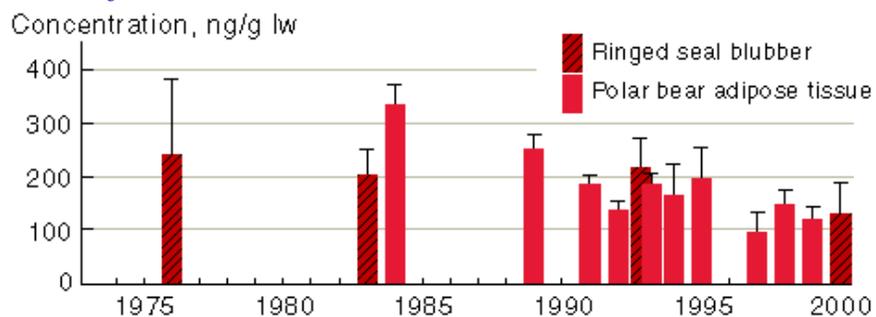
FIGURE 2. Variation in the concentration of  $\alpha$ -HCH in the upper water column with latitude:  $\alpha$ -HCH (ng L<sup>-1</sup>) = 0.0206 × latitude + 0.72 ( $r^2 = 0.11$ ).

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:*



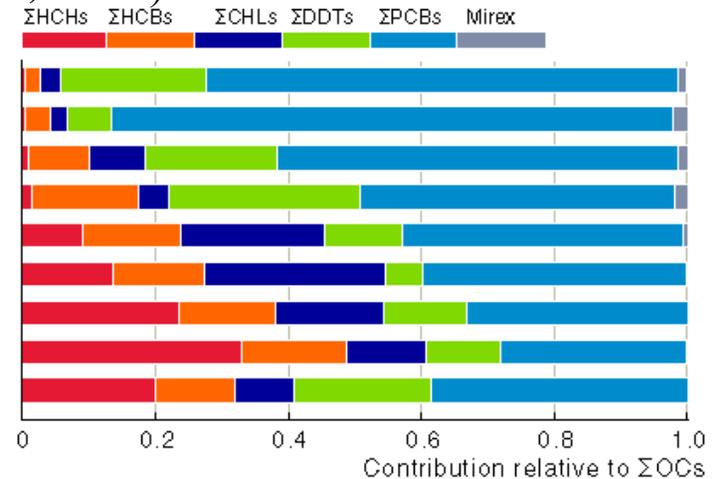
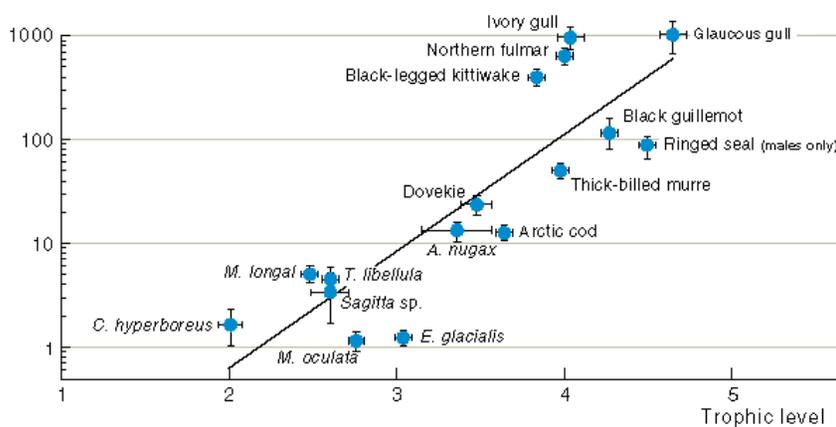
## Bioaccumulation, marine foodweb

Table 4-10. Biomagnification factors determined for key fauna in the marine food webs of the Barents Sea and northern Baffin Bay. Biomagnification factors are based on lipid corrected concentrations. Biomagnification factors for Baffin Bay were corrected to one full trophic level based on trophic levels derived from stable nitrogen isotopes.

Predator/prey	Site	HCb	ΣHCHs	ΣCHLs	<i>p,p'</i> -DDE	ΣPCBs
Amphipod/copepod	Barents Sea	1.5	1.3	1.9	0.4	1.1
	Baffin Bay	3.8	4.5	26.5	16	4.6
Arctic cod/amphipod	Barents Sea	2.0	1.2	3.5	1.7	2.2
	Baffin Bay	6.1	1.1	1.6	3.1	0.9
Thick-billed murre/Arctic cod	Barents Sea	15	1.3	2.6	62	17
	Baffin Bay	10.9	2.1	1.8	19	8.2
Black guillemot/Arctic cod	Barents Sea	8.6	1.1	3.9	40	19
	Baffin Bay	5.0	3.5	4.0	18.5	8.9
Black-legged kittiwake/Arctic cod	Barents Sea	22	1.2	5.9	70	164
	Baffin Bay	21.6	4.2	11.6	56	60.5
Glaucous gull/Arctic cod	Barents Sea	105	6.8	73	2299	1144
	Baffin Bay	6.7	5.2	80	49	28
Ringed seal/Arctic cod	Baffin Bay	0.5	2.0	2.4	7.0	5.5
Food web biomagnification factor (BMF)		4.1	2.7	7.0	14	4.6

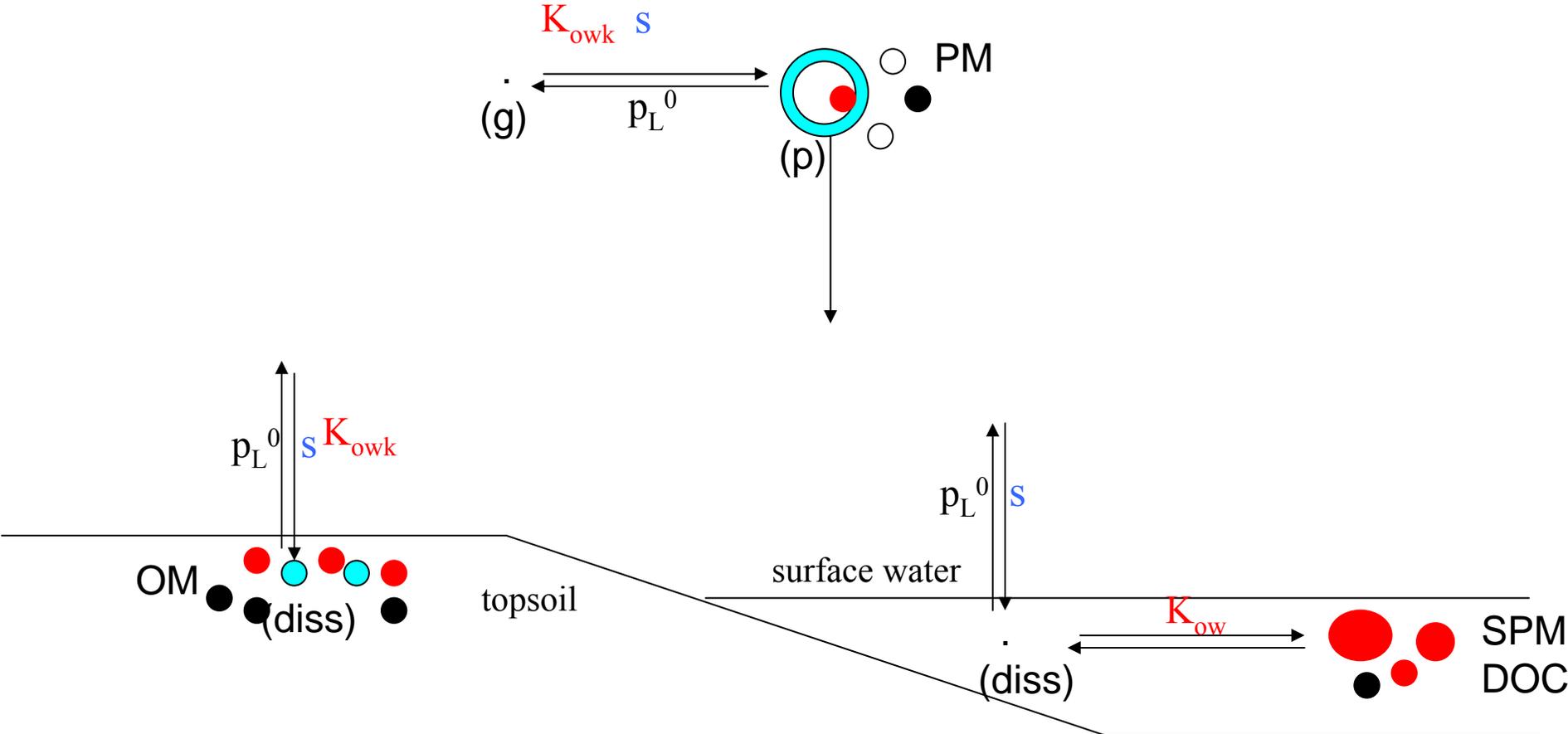
$$\log K_{ow} = 5.3 \quad 3.6-3.8 \quad 5-7$$

## PCB-180 in Northwater Polynya foodweb (Fisk et al., 2001)



## Relative proportions of halogenated SOCs in the Barents Sea foodweb (Borga et al., 2001)

# Processes of SOC<sub>s</sub>



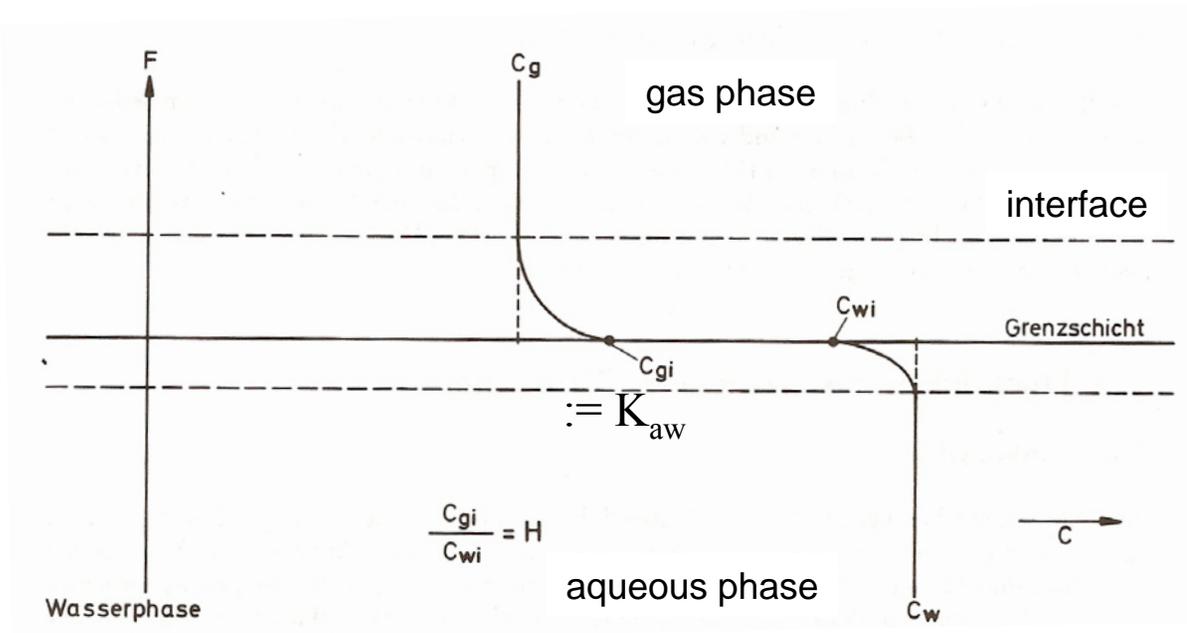
# SOCs surface exchange

## Air-sea exchange

= volatilisation and dry deposition of (gaseous) molecules

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

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



- equilibrium established at the interface itself
- gas flux through interface  $F = -k_{mt w} (c_w - c_{wi}) = -k_{mt g} (c_{gi} - c_g)$  [mol/m<sup>2</sup>/s]

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

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

with bulk ( $c_w, c_g$ ) and equilibrium ( $c_{wi}, c_{gi}$ ) concentrations in water and air

Resistance by boundary layers: reciprocal transfer coefficient (‘piston velocity’  $k_{mt\ w}$ ,  $k_{mt\ g}$  [cm/s])

- defined positive for flux from air to water

- consideration of 1 side sufficient for most gases

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

$$R = 1/k_{mt\ net} = 1/k_{mt\ w} + 1/(k_{mt\ w} K_{aw}) \text{ [s/cm]}$$

Parameterisations in models are empirically based.

From known examples to formula for unknown molecule  $i$  (molecular mass  $M_{gi}$ ):

$$K_{mt\ g\ H_2O} = 0.83 \text{ cm/s} \rightarrow k_{mt\ g\ i} = 0.83 (18/M_{gi})^{0.5} \text{ cm/s}$$

$$K_{mt\ w\ CO_2} = 0.0056 \text{ cm/s} \rightarrow k_{mt\ w\ i} = 0.0056 (44/M_{gi})^{0.5} \text{ cm/s}$$

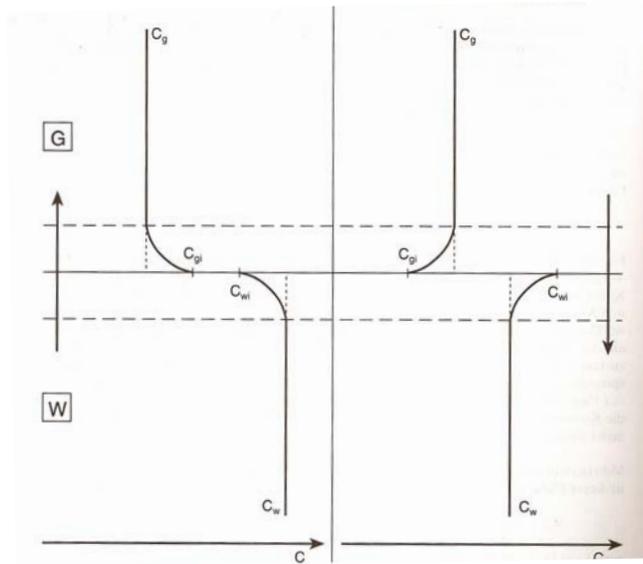
*(Atlas & Giam, 1986)*

Wind dependence:

$$k_{w\ CO_2}(u) = 0.31 u^2 (Sc/660)^{0.5} \text{ cm/s}$$

*(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:

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

**Fugacity of substance i,  $f_{ij}$ :** = escaping tendency from a phase j ([Pa] or [N/m<sup>2</sup>])

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

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

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

$$K_{i12} = c_{i1}/c_{i2} = Z_{i1}f_{i1}/(Z_{i2}f_{i2})$$

(Paterson & Mackay, 1985)

$f_{ij}$  [Pa]

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

Partitioning coefficients, e.g.  $K_{aw} = c_g / c_w = Z_g f_g / Z_w f_w$

Examples

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

Seawater:  $Z_w = c_w/p = 1/H'$ ,

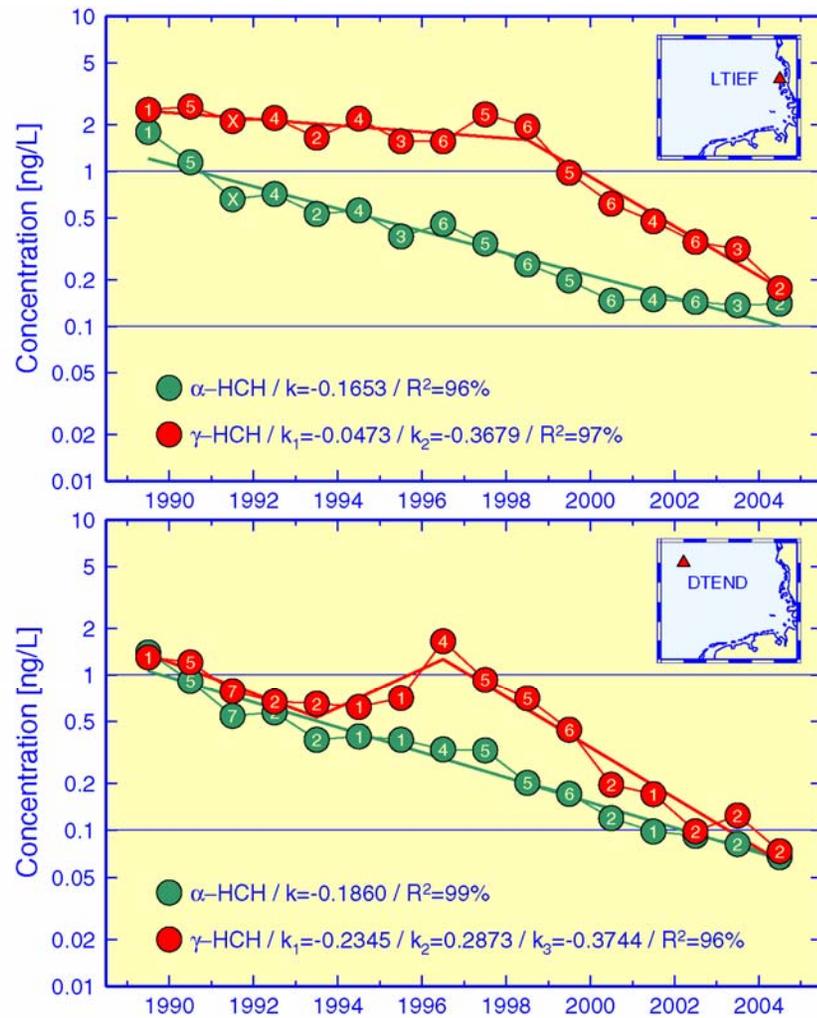
with Henry coefficient  $H' = RTK_{aw}$  [Pa m<sup>3</sup>/mol] = 10<sup>-2</sup>/K<sup>H</sup>[M/at]

$$f_w = c_w / Z_w = H' c_w$$

Air-sea exchange: Fraction of fugacity from seawater =  $f_w / (f_w + f_g)$

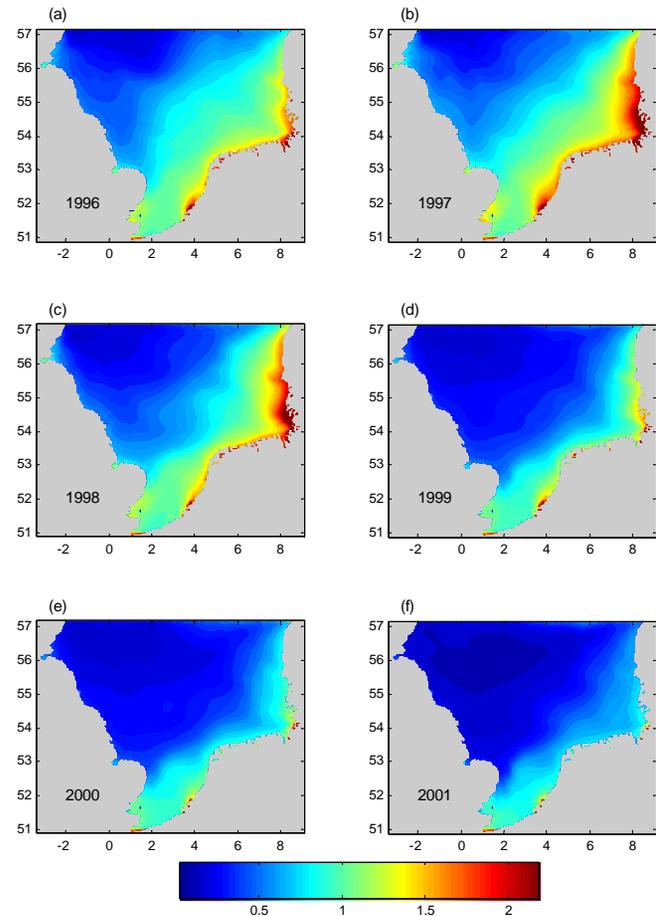
# Cycling of HCH in the North Sea: Dry deposition vs. volatilisation ?

Observation: declining local emissions



(BSH, 2006)

Dry deposition vs. volatilisation of HCH in the North Sea  
 Under declining local emissions net-deposition of  $\gamma$ -HCH, net-volatilisation in the German Bight (*Ilyina et al., 2006*)



Sea region	$\gamma$ -HCH				Vertically integrated annual mean concentrations of $\gamma$ -HCH (ng/l)			
	Southern North Sea		German Bight					
Year	1996	2001	1996	2001				
Burden (Sensitivity)	3.03 (13%)	1.39 (5%)	0.31 (40%)	0.18 (27%)				
Wet deposition	5.47	1.67	0.35	0.11				
Dry deposition	8.85	2.34	0.76	0.21				
Volatilisation	3.42	1.59	0.61	0.33				
Degradation	0.002	0.001	0.0002	0.0001	0.003	0.001	0.0002	0.0001
Sedimentation	1.96	0.98	0.06	0.03	0.97	0.39	0.03	0.01
Resuspension	0.21	0.10	0.007	0.003	0.05	0.02	0.002	0.001

## Dry deposition vs. volatilisation of HCH in the Bering and Chukchi seas

The isomer  $\alpha$ -HCH, upon accumulation since the 1950s, turned net-volatilisation in the early 1990s. (Jantunen & Bidleman, 1995)

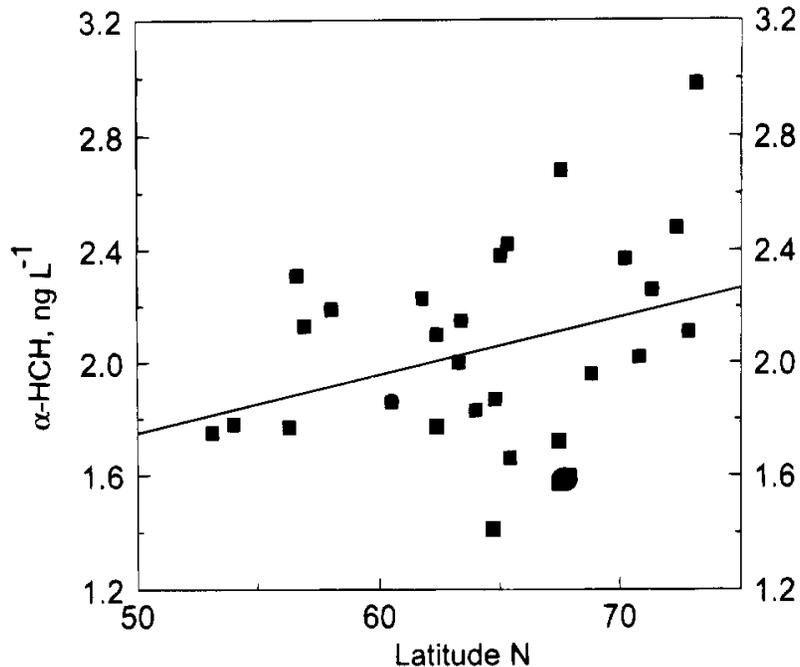


FIGURE 2. Variation in the concentration of  $\alpha$ -HCH in the upper water column with latitude:  $\alpha$ -HCH (ng L<sup>-1</sup>) = 0.0206 × latitude + 0.72 ( $r^2 = 0.11$ ).

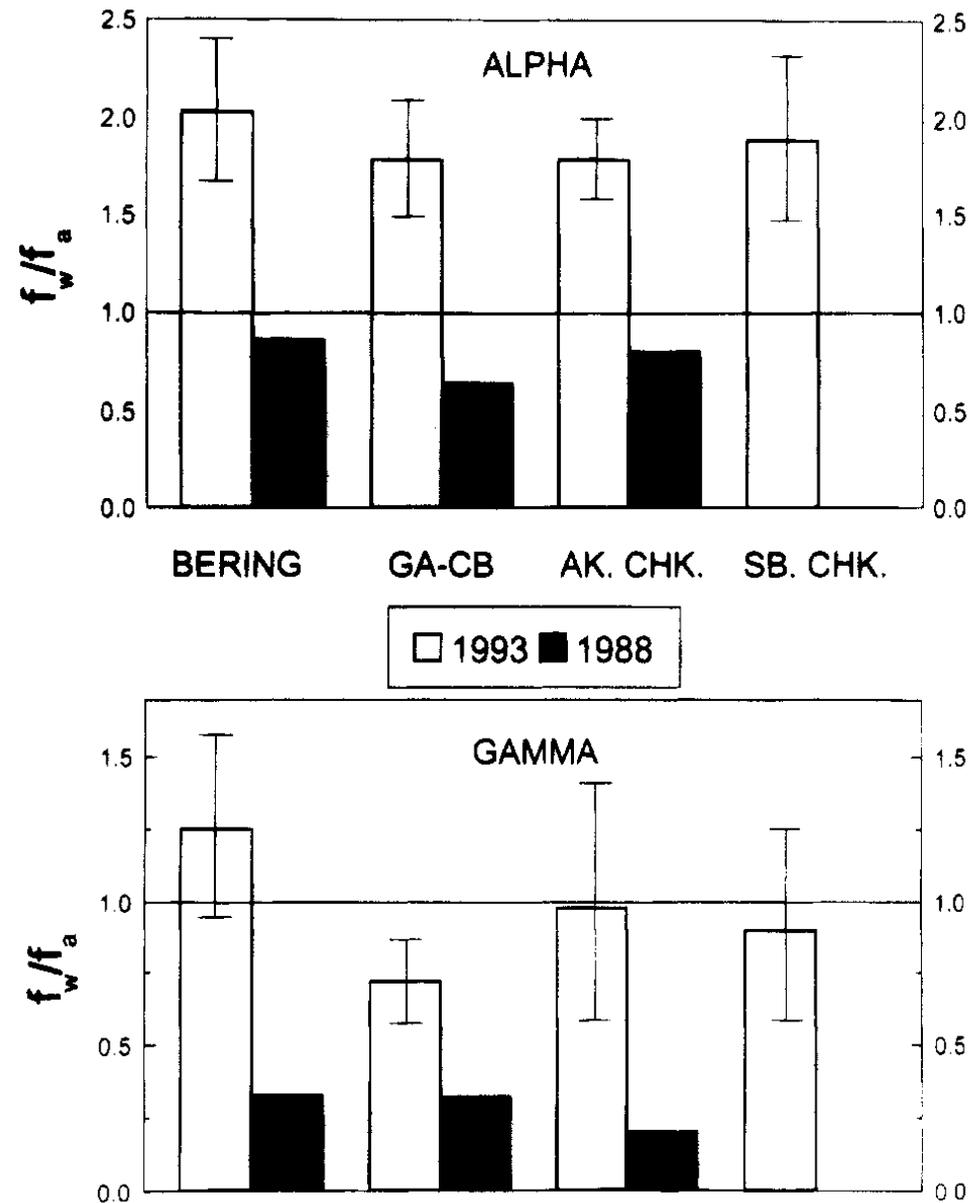
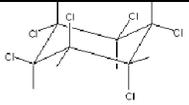
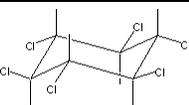
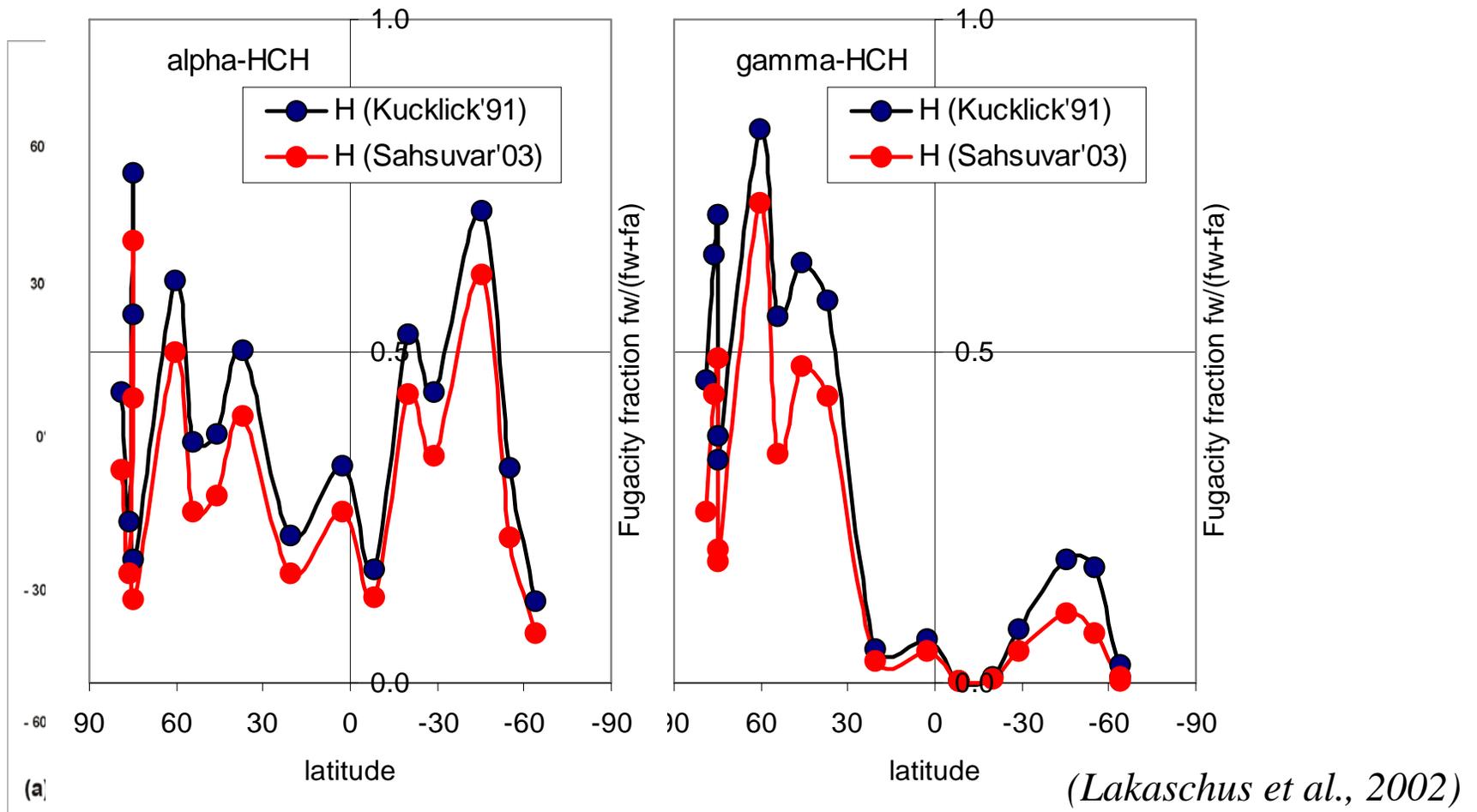


FIGURE 4. Water/air fugacity ratios ( $f_w/f_a$ ) on BERPAC-93 and BERPAC-88 in the Bering Sea south of 61° (Bering), Gulf of Anadyr–Chirikov Basin region (GB-CB), Alaskan Chukchi (AK CHK), and Siberian Chukchi (SB CHK). Error bars refer to standard deviations.

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

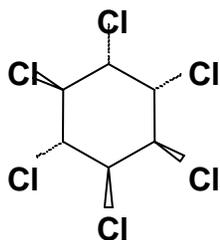
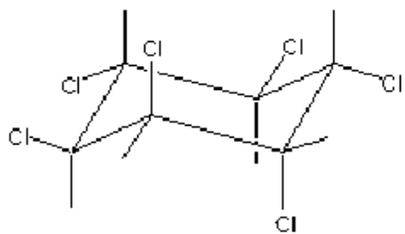
	$\alpha$ -HCH	$\gamma$ -HCH
		
H'(T) [Pa m <sup>3</sup> /mol] (Kucklick <i>et al.</i> , 1991)	$10^{(9.31-2810/T)}$	$10^{(7.54-2382/T)}$
H'(T) [Pa m <sup>3</sup> /mol] (Sahsuvar <i>et al.</i> , 2003)	$10^{(10.13-3098/T)}$	$10^{(10.14-3208/T)}$

### $\alpha$ - and $\gamma$ -hexachlorocyclohexane along a N-S-transect 1999/2000

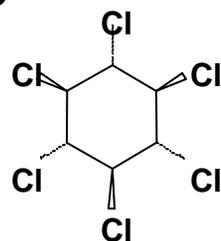
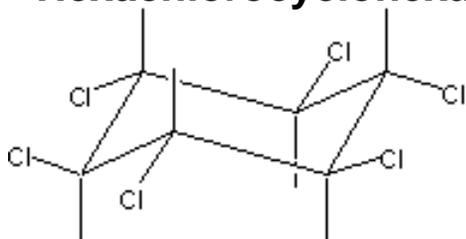


## Isomers

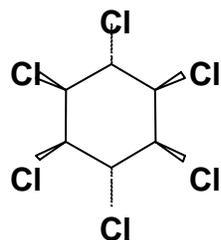
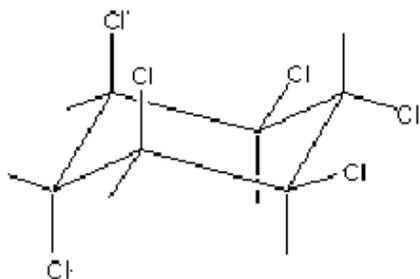
### $\alpha$ -1,2,3,4,5,6-Hexachlorocyclohexane



### $\beta$ -1,2,3,4,5,6-Hexachlorocyclohexane



### $\gamma$ -1,2,3,4,5,6-Hexachlorocyclohexane

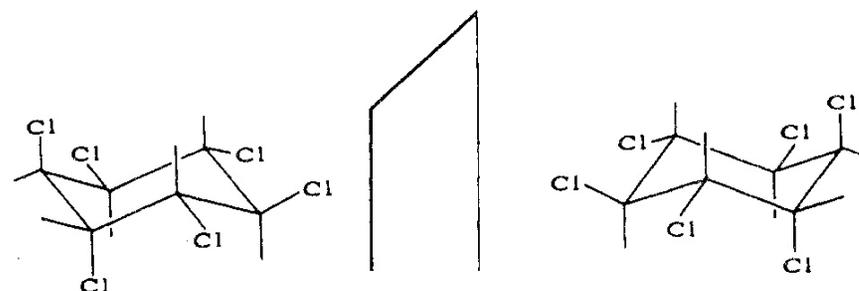


## Terminology:

- Congeners: compounds of similar but not identical elemental composition
- Isomers: compounds of same elemental composition but different structure
- Conformational isomers: Isomers which can be converted into each other without cleavage of bonds
- Enantiomers: chiral isomers,

## Enantiomers

### $\alpha$ -1,2,3,4,5,6-Hexachlorocyclohexane



*An assignment of the absolute structure to (+)- and (-)-enantiomers is not (yet) possible.*

Manufacture of all chiral compounds is as racemic mixture, (as long as no enzymatic processes are involved).

## Using enantiomeric signatures to study SOC cycling

Enzymatic processes are enantioselective.

→ Degradation of chiral substances often takes place enantioselectively, yielding nonracemic residues (enantiomeric ratio  $ER \neq 1.00$ ). The distinct enantiomeric signatures of these residues can be used as markers to follow environmental transport and fate processes:

Fraction emitted from one source, A, of 2 possible sources, A, B:

$$f_A = (ER_{A \text{ and } B} - ER_B) \times (ER_A + 1) / [(ER_A - ER_B) \times (ER_{A \text{ and } B} + 1)]$$

*(Bidleman & Falconer, 1999)*

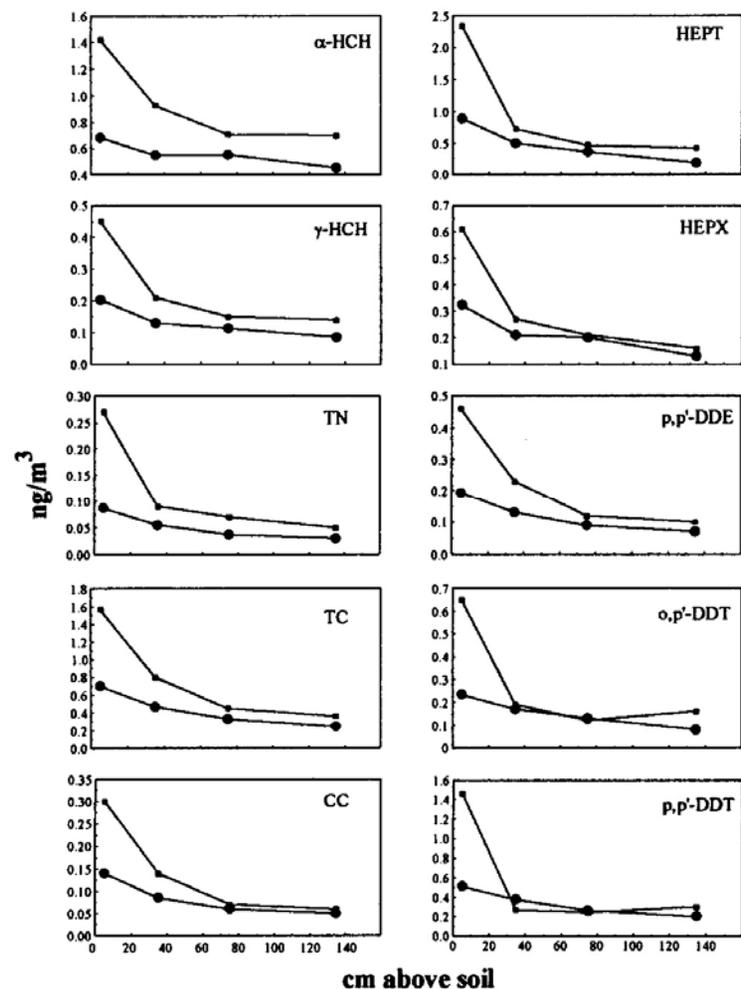
Examples:

ER of (+)- $\alpha$ -HCH/(-)- $\alpha$ -HCH =  $0.85 \pm 0.03$  in Baltic Sea and  $0.87 \pm 0.05$  in North Sea waters, because microbial degradation prefers (+)- $\alpha$ -HCH, (while photolytic degradation is not enantioselective). It seems that part of the  $\alpha$ -HCH is formed from (slow, non-enantioselective) isomerization from  $\gamma$ -HCH. (*Hühnerfuss et al., 1992*)

Observation in North Sea air:  $ER = 0.95 \rightarrow f_{vol} = 0.37$  and  $f_{adv} = 0.63$  for A = volatilization, B = advection, and with  $ER_{vol} = 0.87$ ,  $ER_{adv} = 1.00$

## Using enantiomeric signatures

Similar air-soil exchange (Fraser Valley, Canada, 1995): Determination of the fraction volatilizing from contaminated soil vs. advected.



$$ER = f(z):$$

Table 4. Enantiomer Ratios of Chiral Pesticides in Soil and Overlying Air

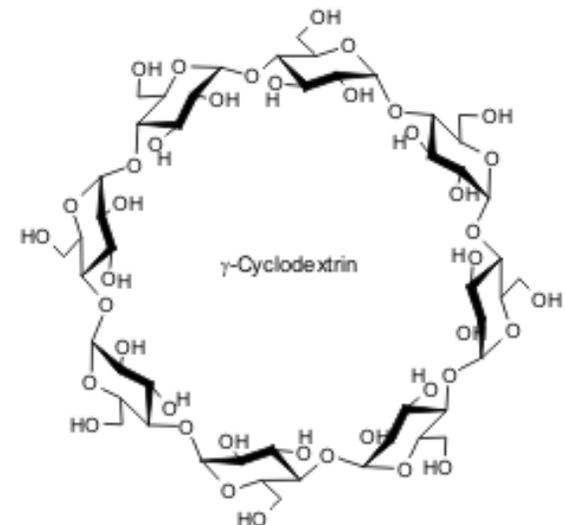
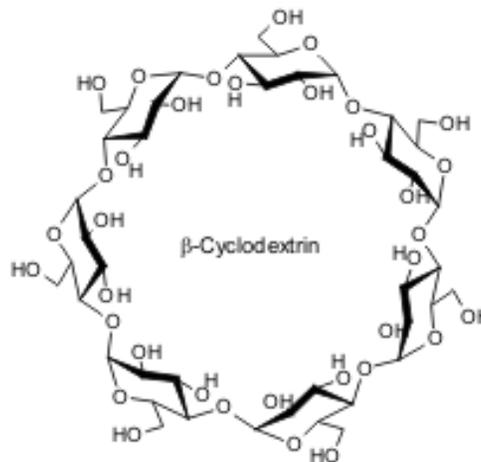
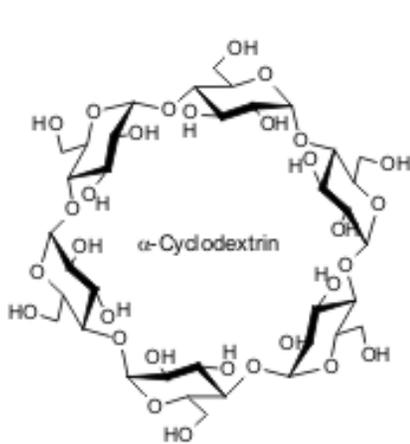
Compound	Soil <sup>a</sup>	5 cm <sup>c</sup>	35 cm <sup>c</sup>	75 cm <sup>c</sup>	140 cm <sup>c</sup>
α-HCH	1.38	1.35	1.28	1.23	1.19
Heptachlor	1.03	1.05	1.05	1.09	1.09
Hept. epoxide	1.39	1.45	1.45	1.42	1.41
o,p'-DDT	1.03	1.02	1.03	1.01	1.06

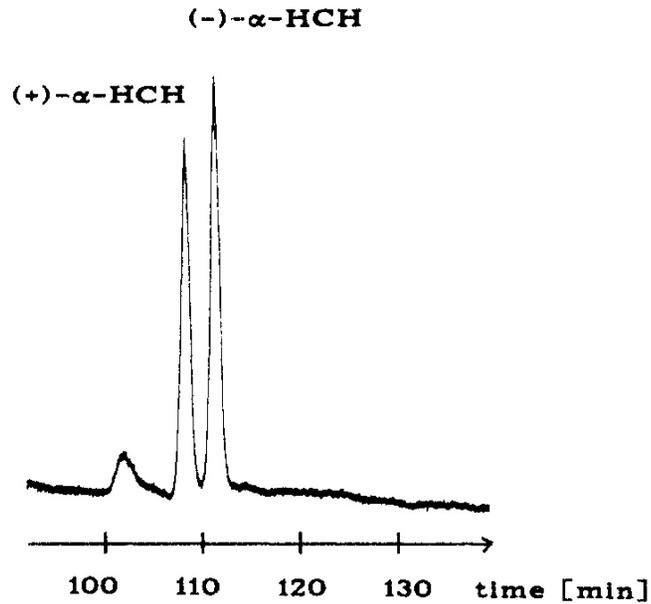
$$c_{\text{air}} = f(z) \text{ (Finizio et al., 1998)}$$

Enantioselective degradation of (+) or (-) *o,p'*-DDT in soil was accompanied by enrichment or depletion of the corresponding enantiomers in the overlying air (*Bidleman & Leone, 2004*).

## 9.2.1.5 Enantioselective chromatography

- Most volatile chiral compounds can be separated in their enantiomers using cyclodextrin-based capillary GC columns (*König, 1984; König et al., 1988*).
- Cyclodextrin is a cyclic, chiral, torus shaped macromolecule which contains D(+)-glucose residues bonded through (1-4)glycosidic linkages. The common cyclodextrins used in chromatography are the  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins which contain 6, 7 and 8 glucose units, respectively. Inside the ring is hydrophobic, outside hydrophilic.
- Substance classes: mono- and sesquiterpenes, pharmaceuticals, biphenyls and polychlorinated biphenyls (PCBs), besides other.





GC using an enantioselective chromatographic column:

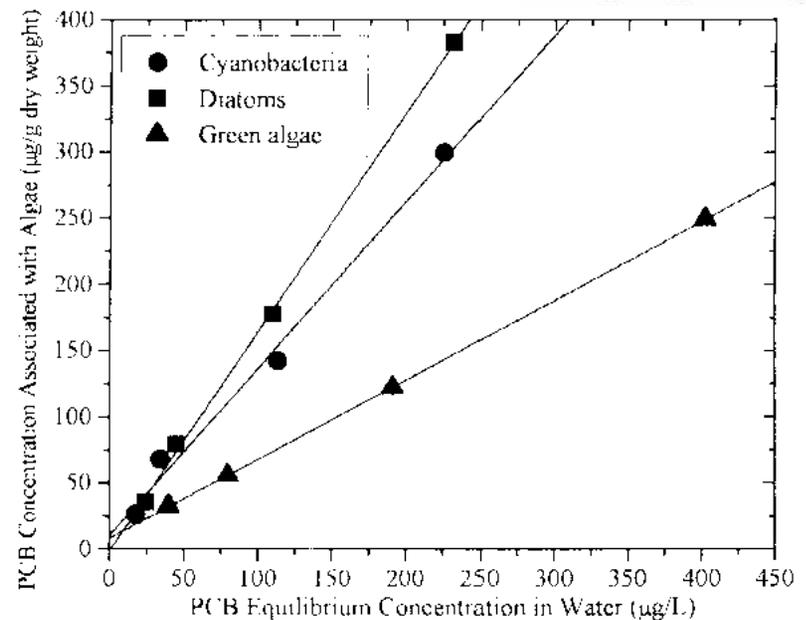
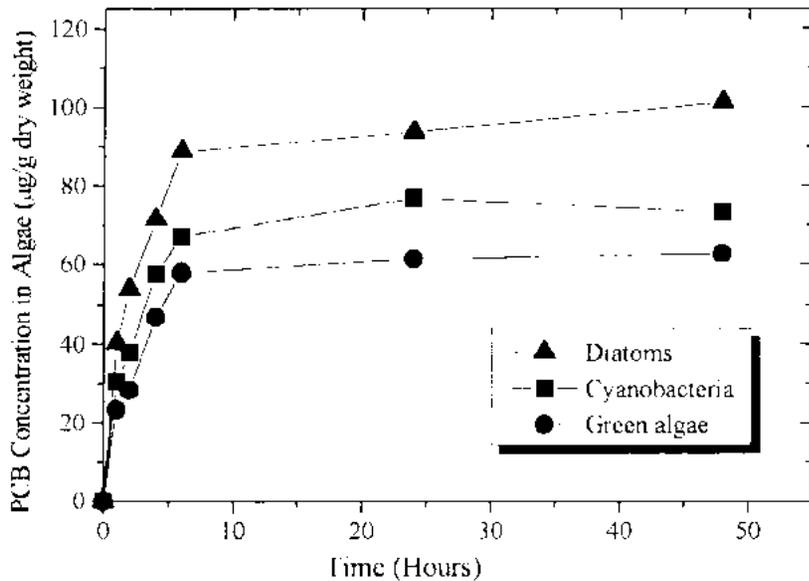
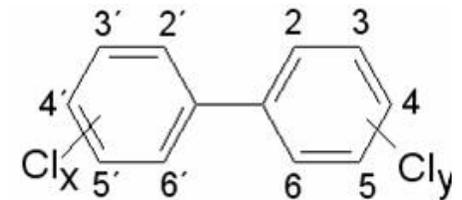
Fused-silica capillary, coated with 50% heptakis(2,3,8-tri-n-pentyl)- $\beta$ -cyclodextrin and 50% polysiloxane (high polarity, OV1701), ECD detection (*Hühnerfuss & Kallenborn, 1992; Hühnerfuss et al., 1992*)

# Vegetation and air

Start with (easier!): bioaccumulation in the *aqueous system*:

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

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



## 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):

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

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

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

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

$F$  = flux ( $\text{g}/\text{m}^2/\text{s}$ ),  $v$  = permeability ( $\text{m}/\text{s}$ ),  $a$  = activity ( $\text{g}/\text{m}^3$ ),

$D$  = diffusion coefficient  $\approx 10\text{-}14 \text{ m}^2/\text{s}$  for organics,  $K_{av}$  = air/veg. partitioning coefficient,

$\Delta x$  = membrane thickness  $\approx 0.05 \text{ mm}$

## Uptake (continued): Kinetic limitations

- For plants with little permeability equilibrium distribution not achieved within one vegetation period

$$F = A^{-1} \frac{dm}{dt} = v \Delta c$$

$$A = V / \Delta x$$

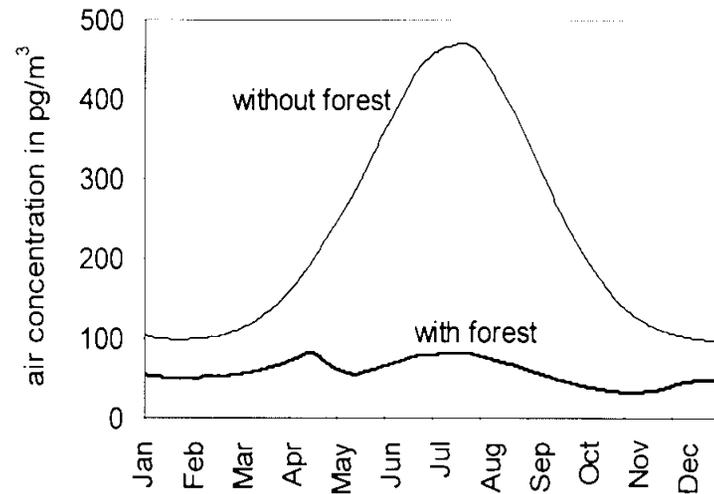
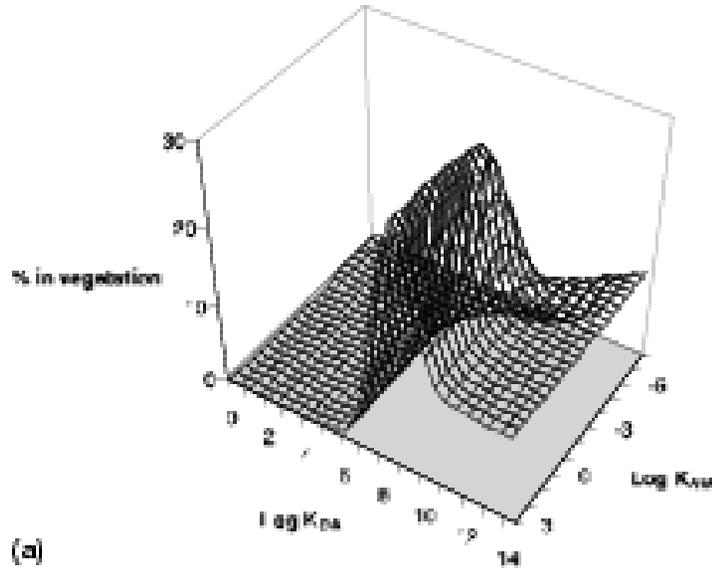
$$V^{-1} \frac{dm}{dt} = \frac{dc_{i(\text{veg})}}{dt} = \Delta x k_{\text{mt}}^{(1)} (c_{i(\text{g})}/K_{\text{leaf/air}} - c_{i(\text{veg})})$$

$$k_{\text{mt}}^{(1)} = k_{\text{mt}}^{\prime(1)} K_{\text{leaf/air}} / (S/V)$$

$S/V$  = leave surface/vol., exchange coefficient  $K_{\text{leaf/air}}$  (can vary by several orders of magnitude for various species, as a function of wax, phyto structure), clearance rate  $k^{\prime(1)}$  (determined by volatilisation during photodegradation, degradation slow, for example  $< 5\%$ /vegetation period for PCB)

- ,Kinetically‘ limited due to delays caused by the turbulence of the atmospheric layers near to the ground and the canopy (for  $\log K_{\text{ow}} > 8.2$ ), limited by particle processes if  $\log K_{\text{ow}} > 11$  (McLachlan *et al.*, 1995; McLachlan, 1996; Böhme *et al.*, 1999)

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



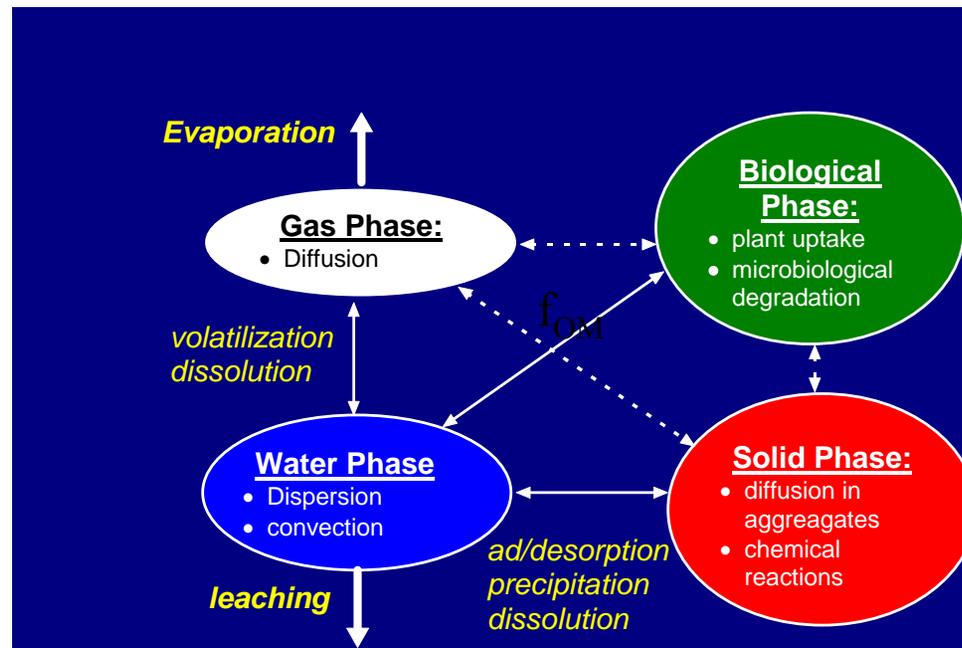
Plant uptake from atmospheric dry gaseous deposition for hypothetical substances  
( $\log K_{oa} < 5$ : no net effect compared to bare soil)

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)*

# Air-soil exchange

## Multiphase system soil



Upward:

- Gas-phase diffusion within soil pore space
- Aqueous phase diffusion in soil water
- Co-evaporation with water vapour
- Turbulent flow in capillaries

(Jury et al., 1983)

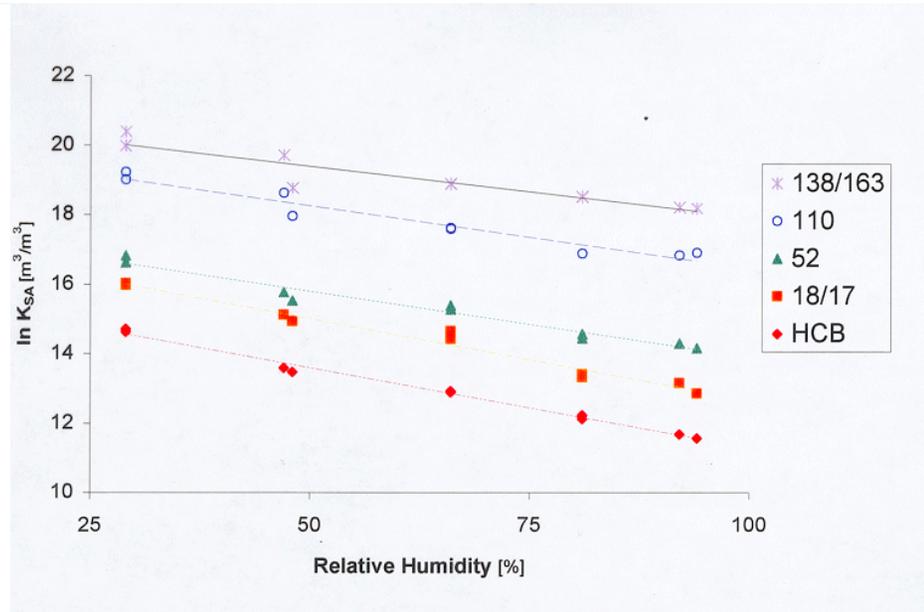
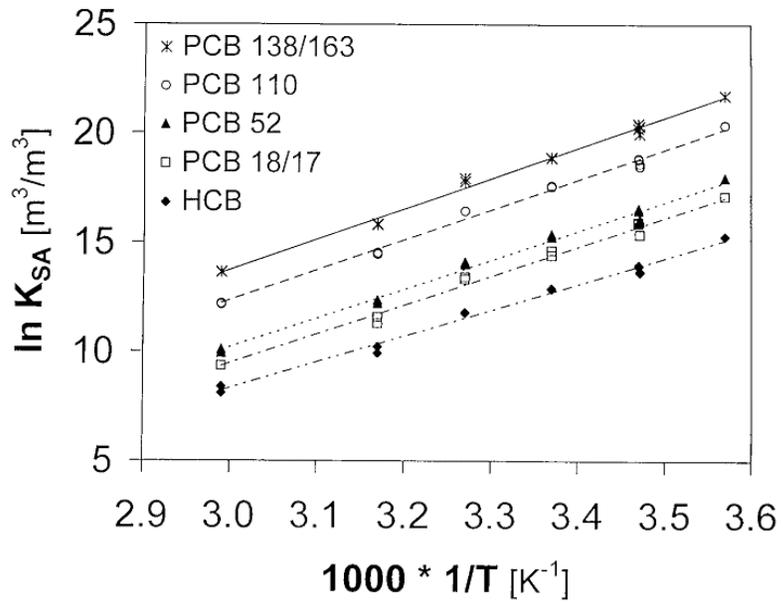
Downward:

- Dry deposition, limited by uptake in soil multiphase system (water, OM, solid surfaces)

$$F_z = v_{\text{dep}}(z) (c(z) - c^0)$$

# Air-soil partitioning = f(T, rh)

Soil-air partitioning coefficient  $K_{SA} = c_S / c_A$

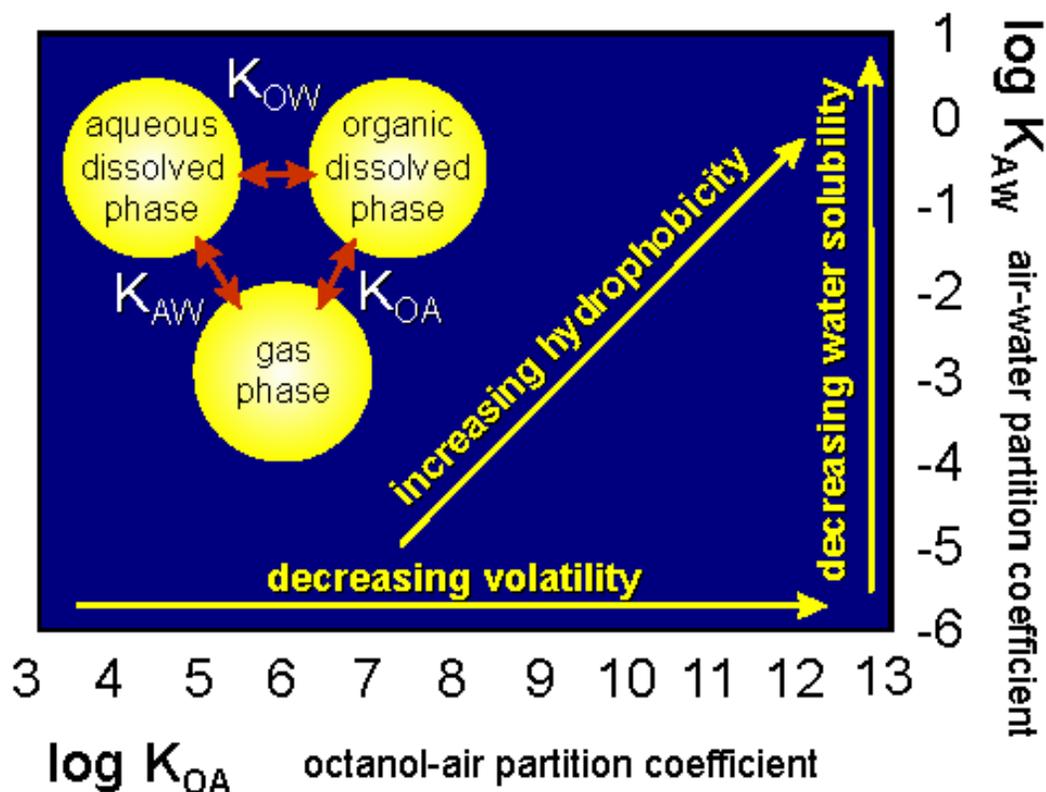


(McLachlan, 2001)

# Multicompartmental modelling approaches

## Multicompartmental distribution

Multicompartmental distribution when phase equilibria were established in the environment:  $f(K_{AW}, K_{OW}, K_{OA})$



adopted from Wania, 1999