



cetocoen



Research centre
for toxic compounds
in the environment

Fate of toxic compounds in the environment

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**SC Regional POPs Centre
for Central and Eastern Europe**





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Research centre for toxic compounds in the environment



EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND
INVESTING IN YOUR FUTURE



OP Research and
Development for Innovations

RECETOX research team



15 teachers and professors

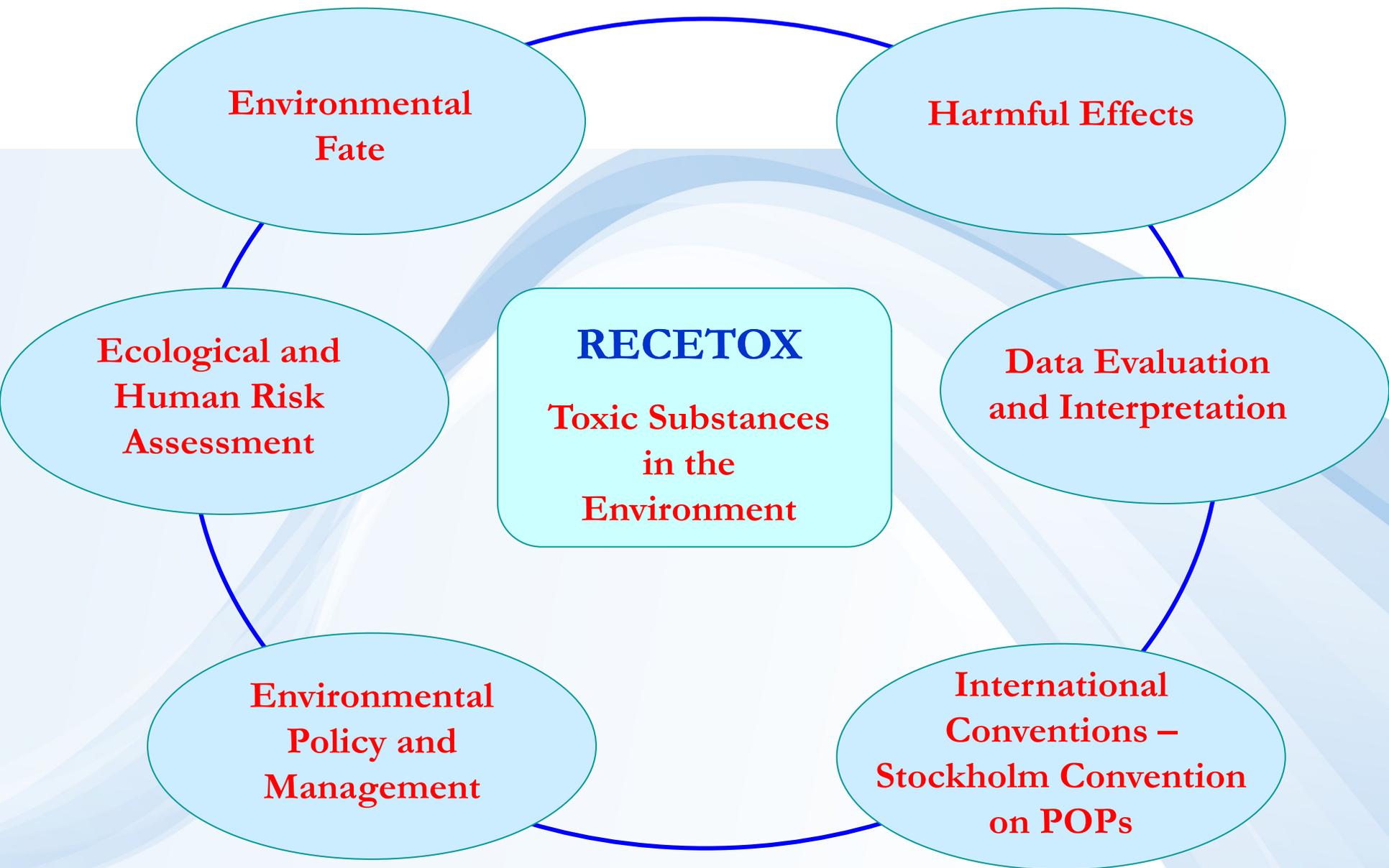
20 Ph.D. researchers

50 Ph.D. students

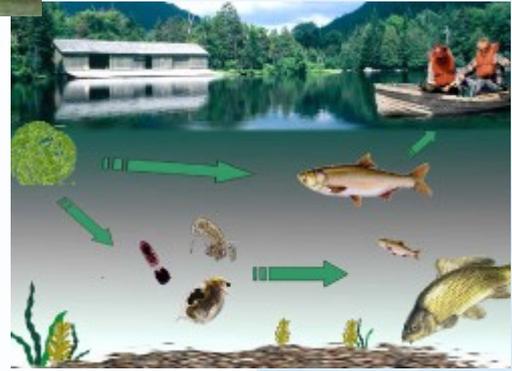
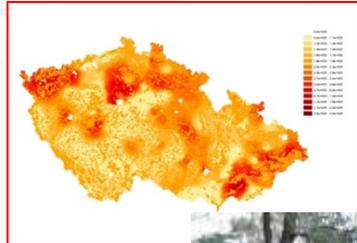
10 senior researchers and post-docs

6 technical and administrative stuff

<http://recetox.muni.cz>



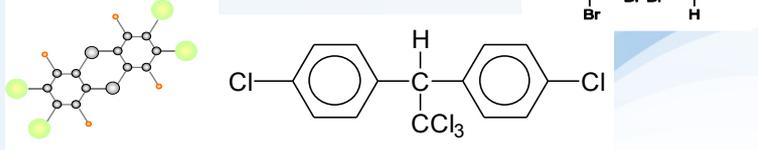
Study of the fate and harmful effects of environmental toxic compounds



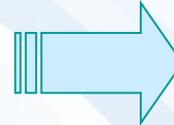
Persistent organic pollutants



Persistent



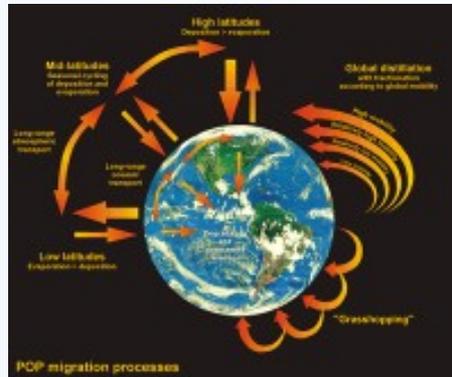
Bioaccumulation



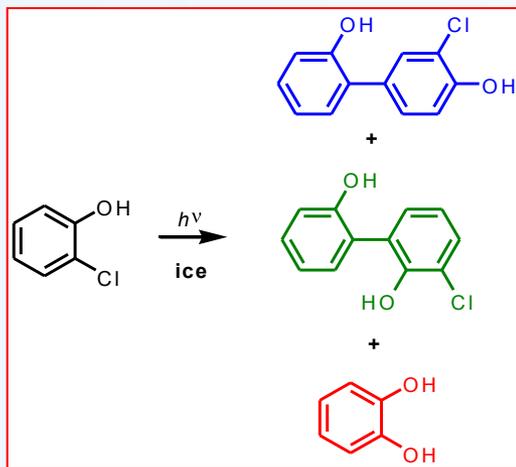
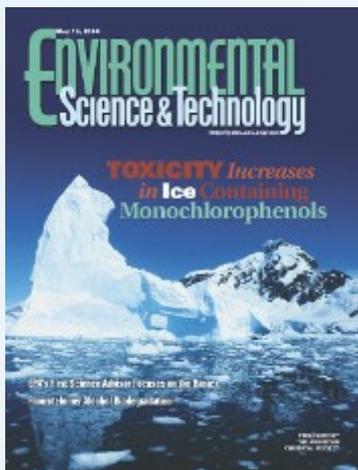
Toxicity



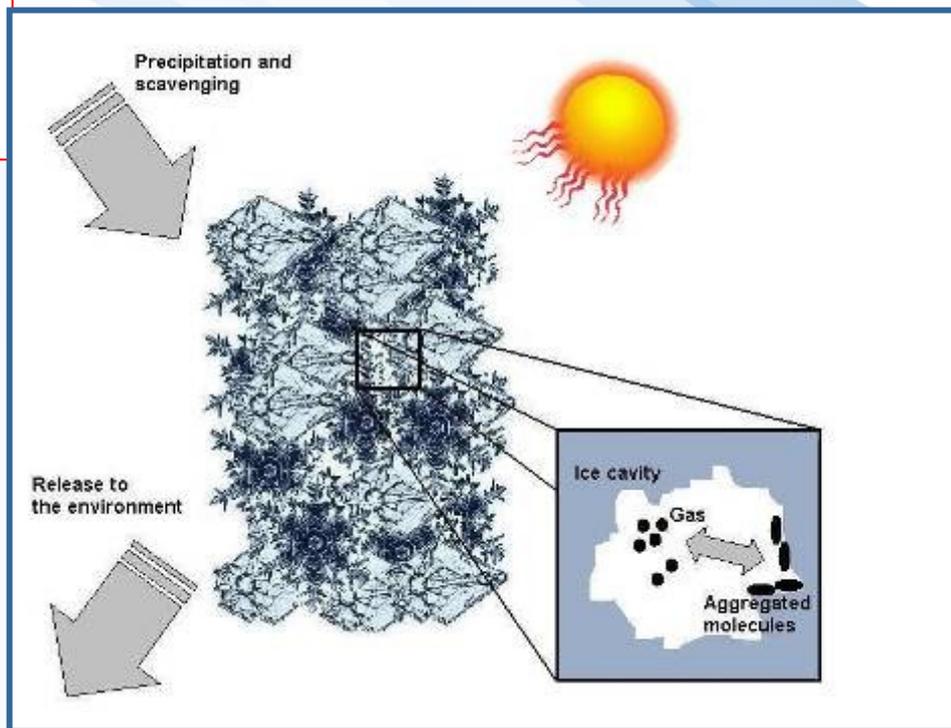
Long-range transport



Study of impacts of global changes to the fate and effects of toxic environmental pollutants

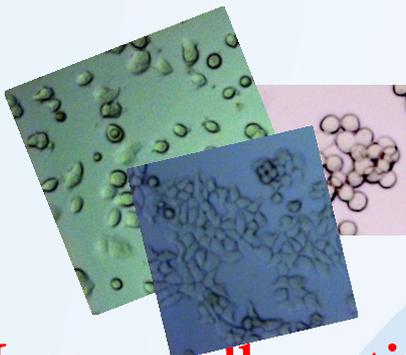


Photochemistry and fate of POPs polar areas

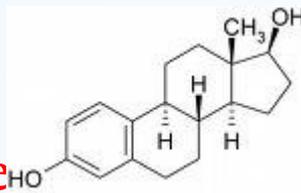


Ecotoxicology and harmful effects of pollutants

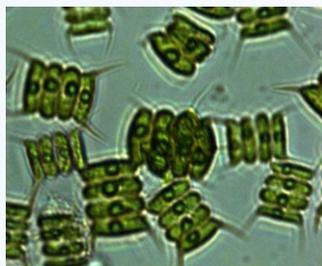
Bioassays for acute and chronic toxicity – air, water, soil



Hormonally active xenobiotics in waste waters



Blue-green algal (cyanobacte



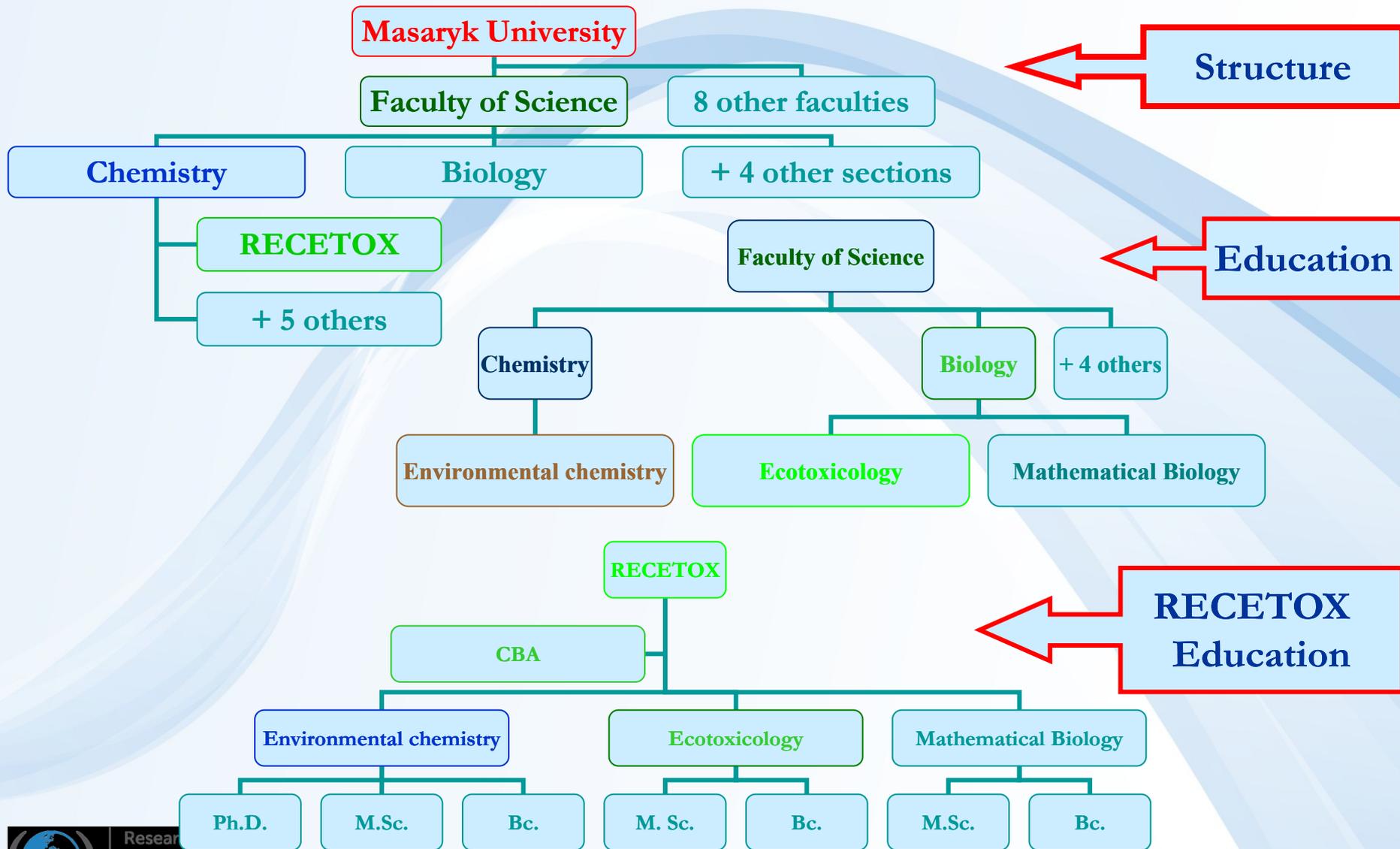
RECETOX activities



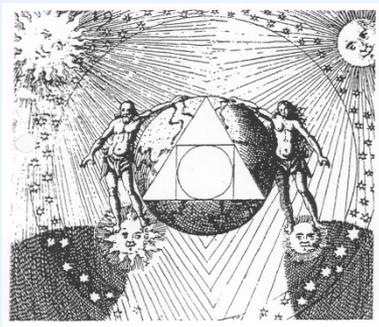
**Persistent, bioaccumulative and toxic substances
– Relationship between their environmental
levels and their biological effects – ecological
risk assessment**

- ↗ **International conventions and programmes**
- ↗ **Monitoring on the regional and local scales**
- ↗ **Environmental chemistry and ecotoxicology**
- ↗ **Human and ecological risk assessment**
- ↗ **Co-operation with government, regional and local
authorities and industry**
- ↗ **Educational activities**

RECETOX Educational programme



RECETOX Conceptual approaches



Ecological risk
assessment

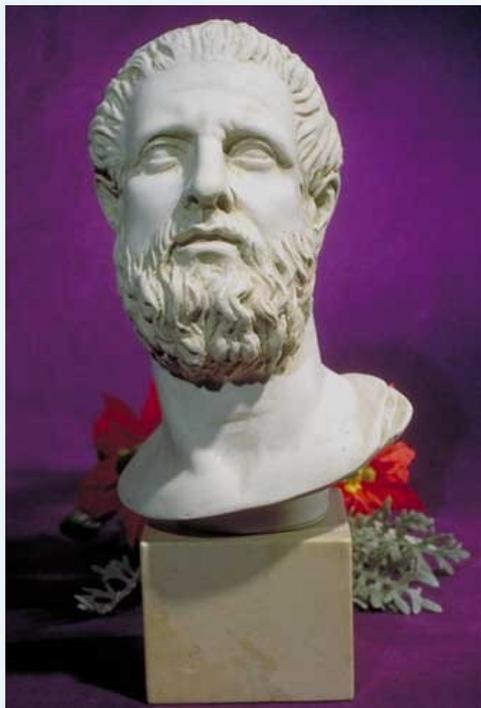
Environmental
chemistry

Ecotoxicology

Fate of toxic compounds in the environment

- ↪ Fate concept: physical, chemical, biological mechanisms
- ↪ Properties, abiotic & biotic degradation mechanisms

Chemicals in the environment: nothing new....



Hippocrates (460-377 BC)

“Whoever wishes to investigate medicine properly should proceed thus... We must also consider the qualities of the waters, for they differ from one another in taste and weight, so also do they differ much in their quality”

So... Hippocrates appreciated the significance of human health in context of the characteristics of the natural environment

Cause - effect paradigm: nothing new....

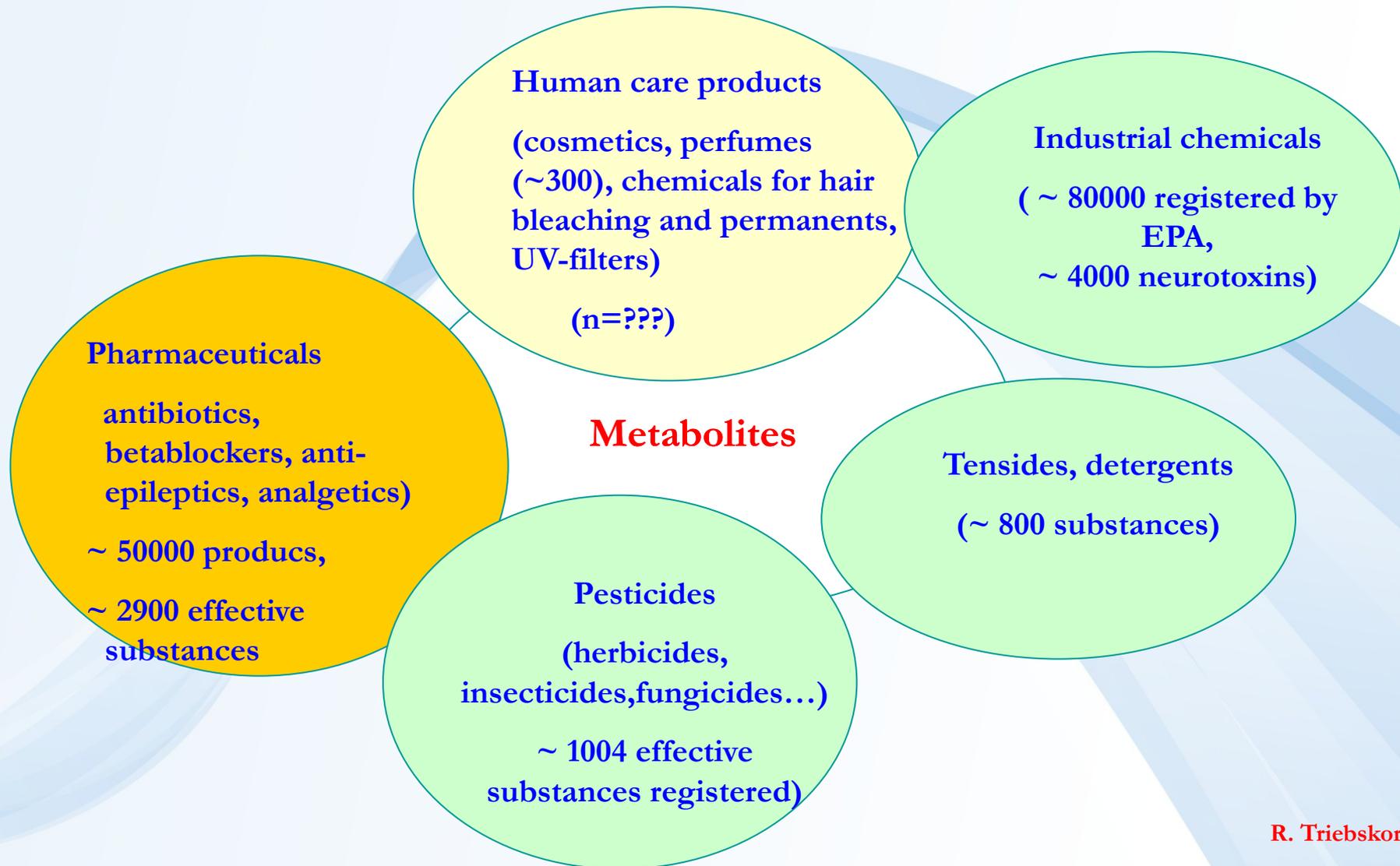


Paracelsus (1493 - 1541)

What is there which is not a poison?

- ↪ All things are poison and nothing without poison.
- ↪ Solely the dose determines that a thing is not a poison.'

Nowdays environmental chemicals



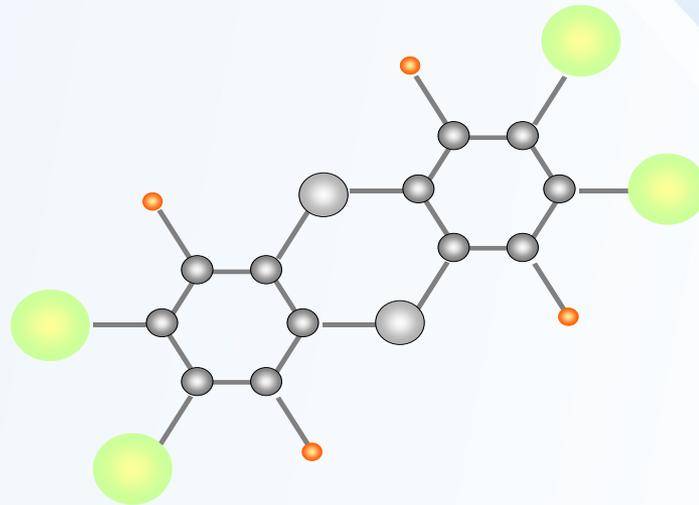
R. Triebskorn

Subject of interest

PTS= Persistent toxic substances

PBTs = Persistent, bioaccumulative and toxic substances

POPs = Persistent organic pollutants



POPs (Persistent organic pollutants)

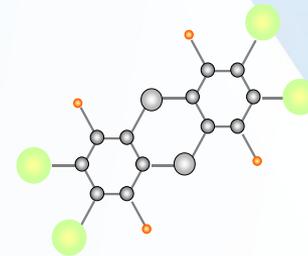
☺ The group of most fascinating pollutants (Kevin C. Jones)



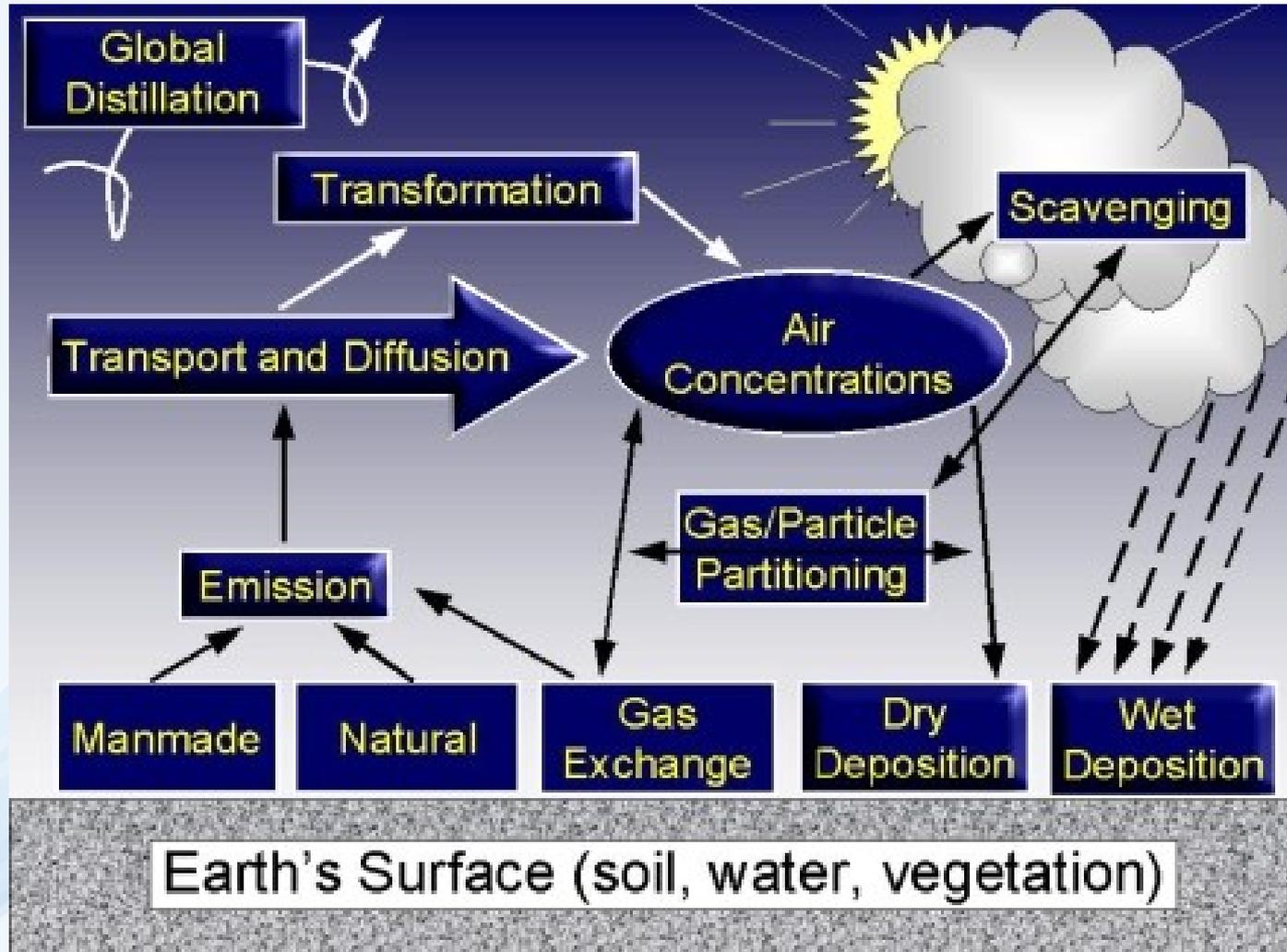
☹ Ghost of the past (Terry Bidleman)



God created 90 elements, man round 17, but Devil only 1 – chlorine (Otto Hutzinger)



Environmental fate of chemicals



Environmental chemistry and photochemistry

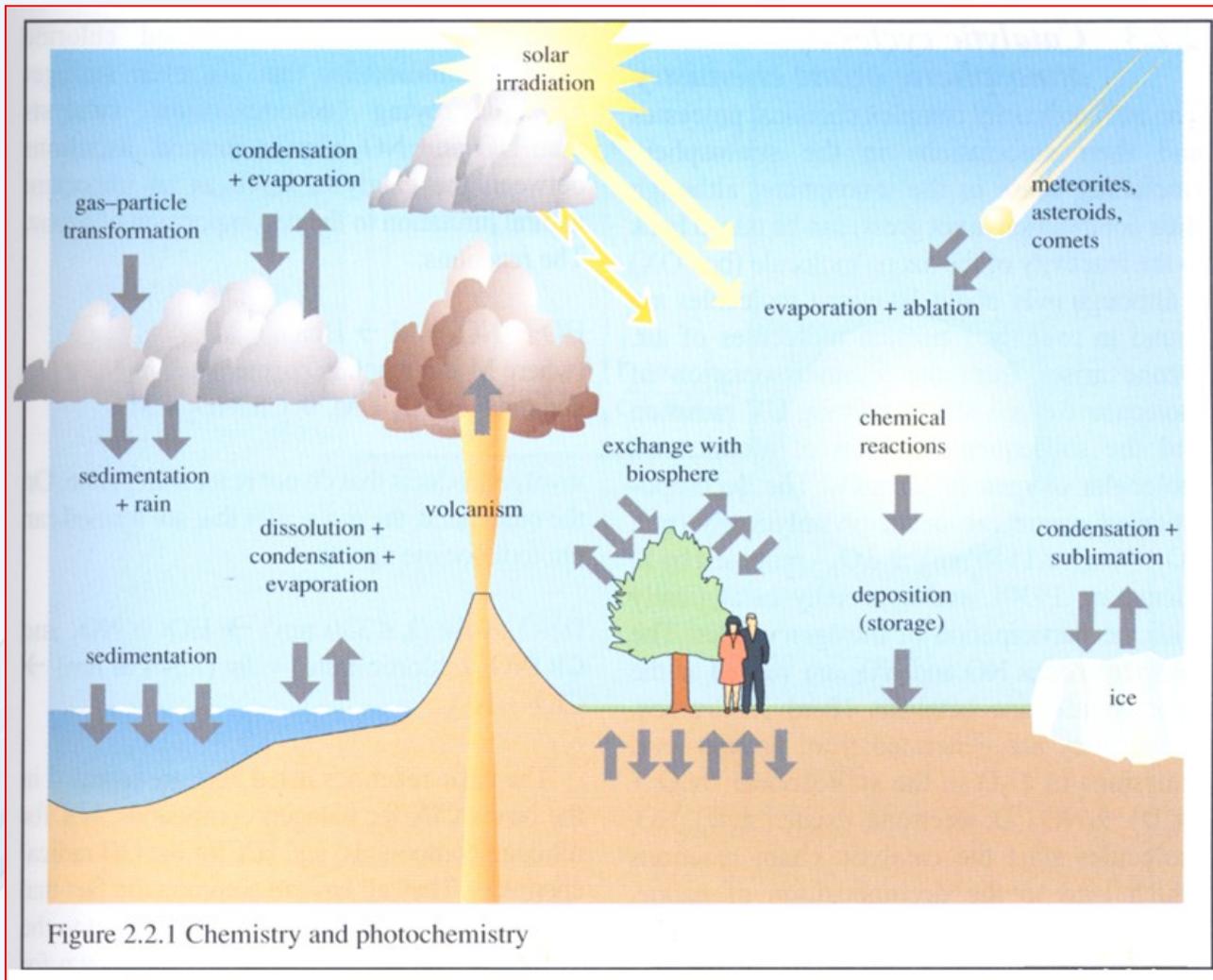


Figure 2.2.1 Chemistry and photochemistry

Environmental interface

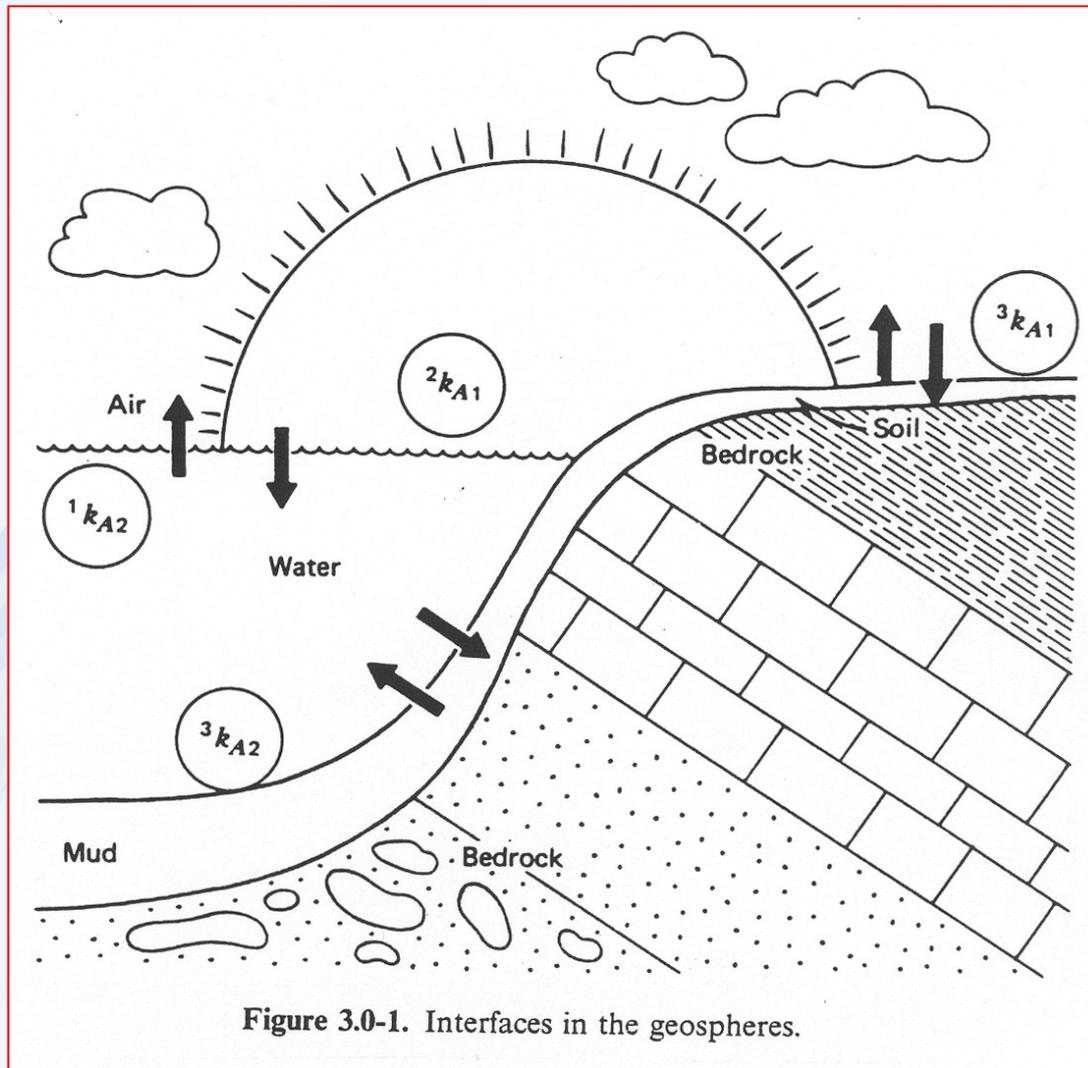
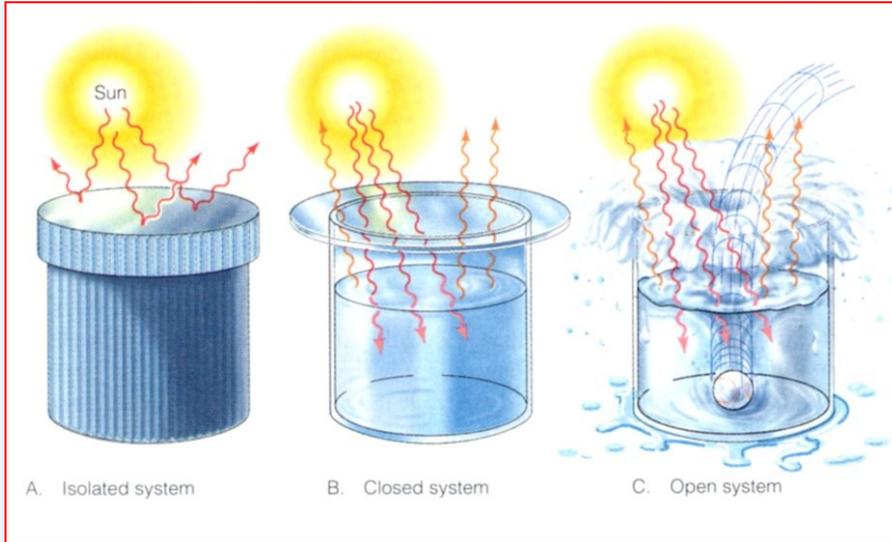
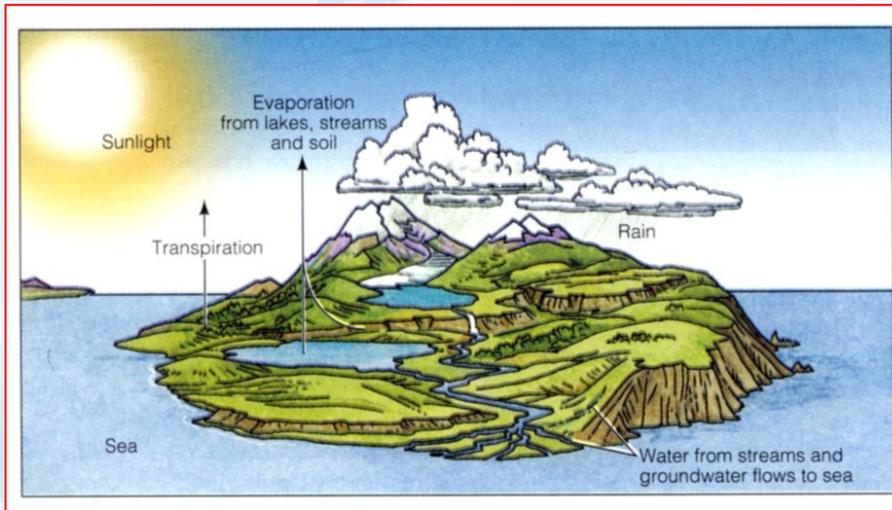


Figure 3.0-1. Interfaces in the geosphere.

Systems, environmental system



↪ Isolated
↪ Closed
↪ Opened



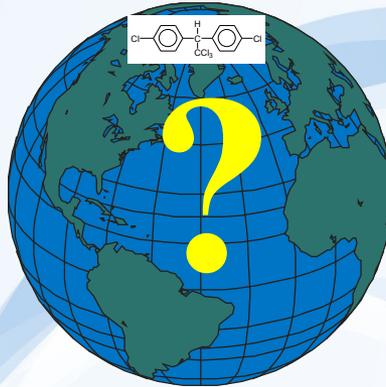
↪ Opened

Environmental fate of POPs



How well do we understand the fate of POPs ?

Environmental fate of POPs

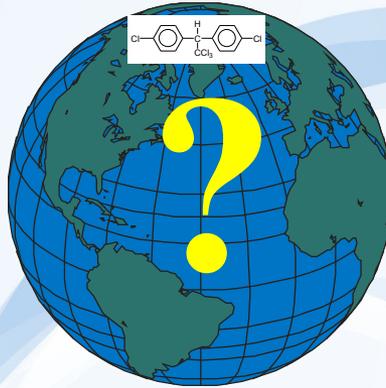


Fate of POPs – environmental transport and transformations

Study of environmental processes:

- ↪ **Physical-chemical properties of POPs**
- ↪ **Environmental properties**
- ↪ **Environmental distribution**

Environmental fate of POPs



Fate of POPs – environmental transport and transformations

Study of environmental processes:

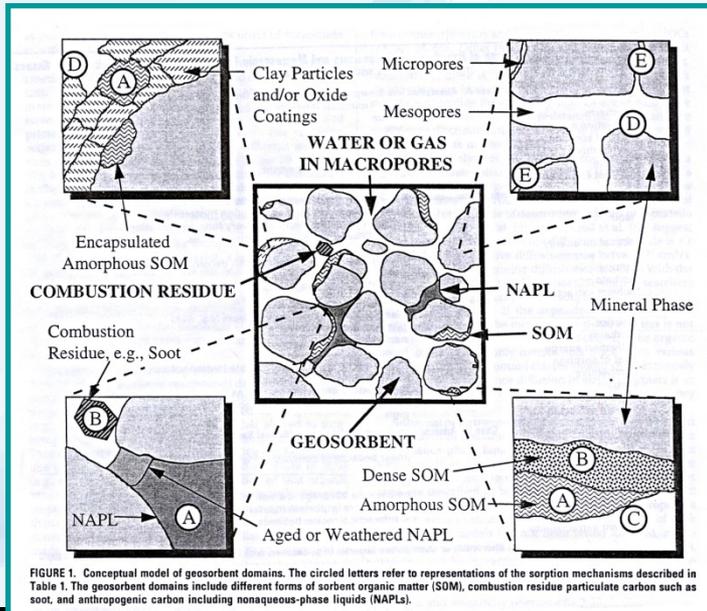
- ↪ **Laboratory experiments**
- ↪ **Field experiments**
- ↪ **Monitoring**
- ↪ **Modelling**

Soil can be a source or sink of POPs

Direct applications

Air-surface exchange

'Occlusion'



Biodegradation

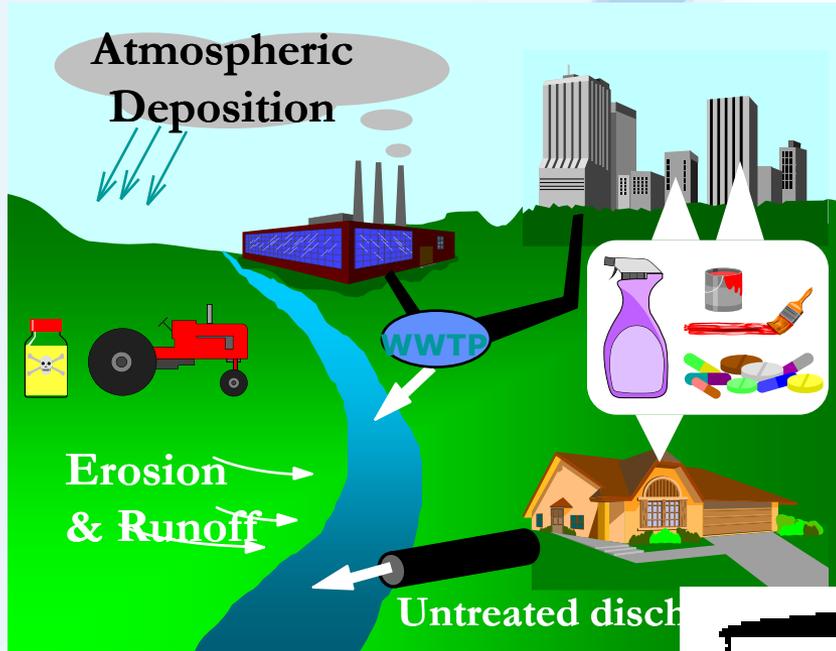
Physical mixing – 'dilution' with depth

K. C. Jones

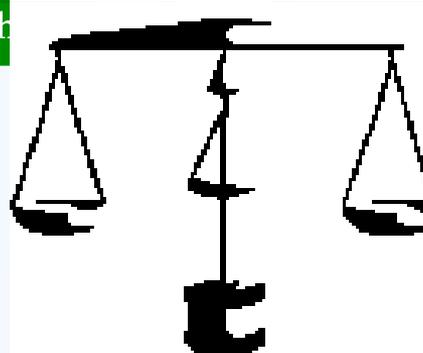
Risk assessment

Exposure

Effects



Laboratory (and field) studies
Ecotoxicity tests



Predicted Exposure Concentration (PEC)

Predicted No Effect Concentration (PNEC)

Three Types of Processes



Phase partitioning:

- ◆ Described by partition coefficients (Henry's law constant, octanol-water partition coefficient, etc.) and intermedia mass transfer coefficients



Degradation:

- ◆ Described by first-order rate constants, representing biological and chemical degradation



Transport:

- ◆ Described by air and water flow velocities or macroscopic eddy diffusion coefficients

Phases in the Atmosphere

What phases do organic chemicals associate with in the atmosphere?

- ↗ Gas phase
- ↗ Particulate matter
- ↗ Water
- ↗ Ice/Snow

Surfaces in the environment

Which surfaces are important for exchange of organic chemicals with the atmosphere?



Water



Soil



Vegetation



Snow/Ice

Environmental persistence

Velocity of losses of the chemical in environmental compartments can be described by the equation of the 1. order:

$$d[A] / dt = - k_T * [A]$$

c_A after time t

c_A in time $t = 0$

$$\ln [A_0] / [A] = k_T * t$$

If $[A_0] / [A] = 2$, $t = \text{const.}$, then:

$$t_{1/2} = \ln 2 / k_T$$

Half life – characteristics of the pollutant persistence in environmental compartments under specific conditions

Environmental persistence

The ability to resist degradation in various media, e.g. air, soil, water, sediment, measured as half-life of the substance in the medium.

Persistence reflects the ability of the substance to resist physical, chemical or biological degradation.

The overall persistence of a chemical in the environment depends on how it is emitted to the environment (i.e. to air, water, or soil) and on how it subsequently migrates between media.

The implication is that a substance may be quite short-lived if discharged to air, but long lived if it is discharged to water.

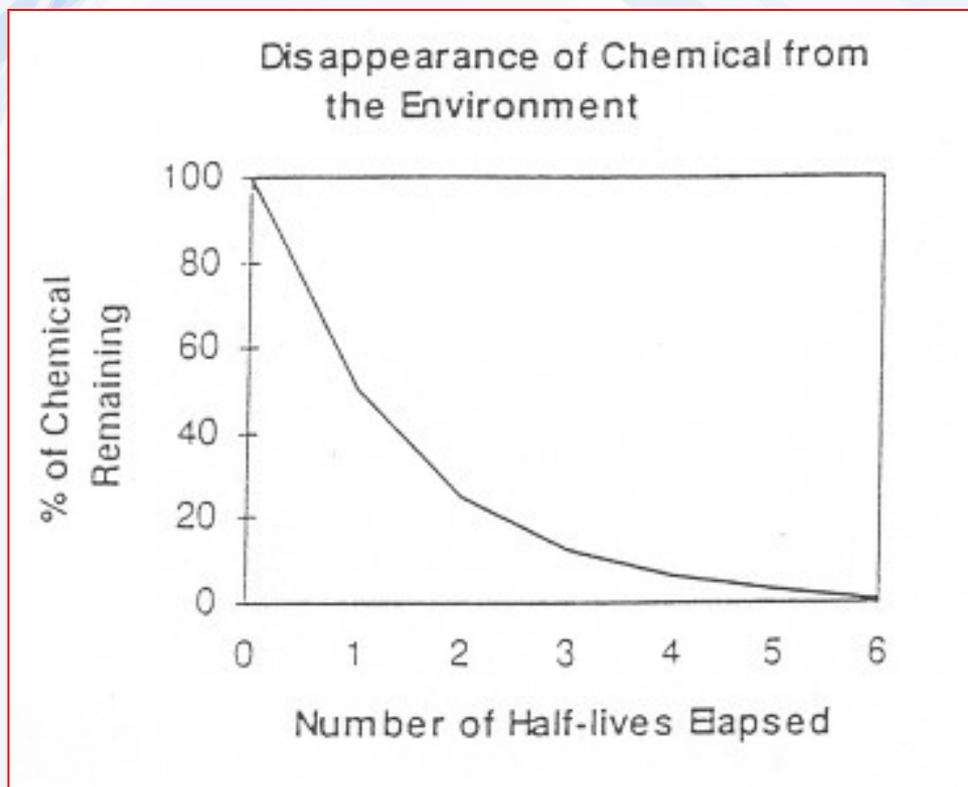
Furthermore, a long half-life in a medium may be relatively inconsequential if the substance is not emitted to that medium or is likely to transfer to it.

For example, an accurate half-life for reaction in air may not be needed for a relatively involatile chemical which is unlikely to evaporate into the atmosphere.

Environmental persistence

Persistence is described by half-life ($t_{1/2}$), when the concentration of compound decreases on the half of original amount in given environmental compartments – after 5 cycles the level decreased on 3 %

Waters - $t_{1/2} = 6$ days – during 1 months; if $t_{1/2} = 70$ days, removal during ca 1 year



Environmental persistence

Persistence under environmental conditions depends:

- ↪ **properties of compound**
- ↪ **properties of environmental compartments:**
 - **sun irradiation**
 - **concentrations of OH radicals**
 - **composition of microbial communities - temperature**

Volatility

Chemicals with a volatility of less than 1000 Pascals are considered as a POPs.

The volatility criterion is applied together with persistence in air, and/or data on presence in remote regions.

It should be noted that even chemicals with a low to very low volatility may be transported over long distances in sufficient quantities to cause risks to human health and the environment in remote regions.

Velocity of volatilization – V_v [$\text{mol.l}^{-1}.\text{hod}^{-1}$]:

$$V_v = dC_w / dt = k_{vw} * C_w$$

Water concentration
[mol.l^{-1}]

Velocity constant of
volatilization [hod^{-1}]

Henry's Law Constant

$$H = p/C_w$$

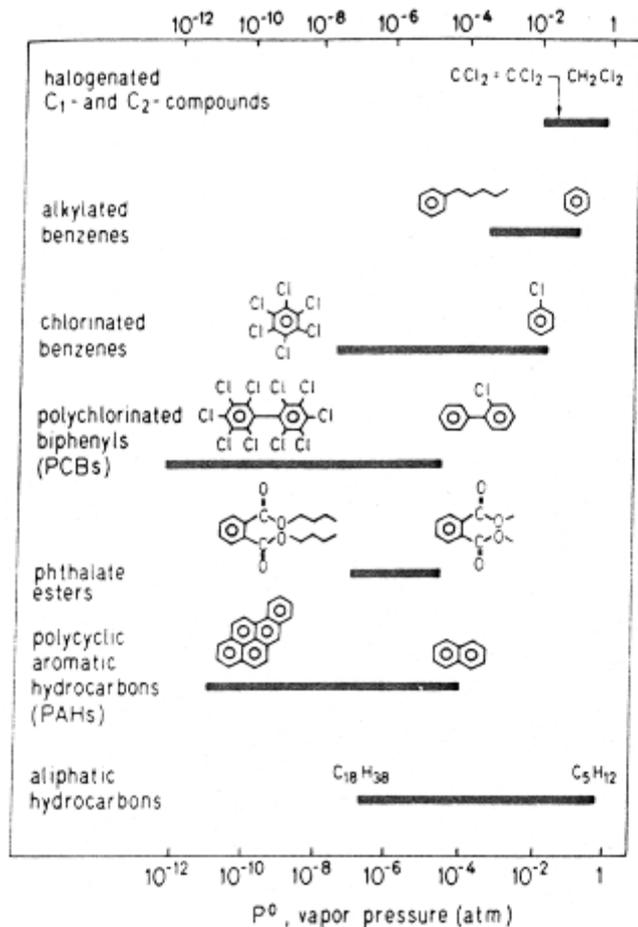
P = partial pressure, Pa

C_w = water concentration, mol/m³

$$K_{AW} = C_A/C_w = \text{air-water partition coefficient} = H/R*T$$

Sometimes K_{AW} is called the dimensionless Henry's Law constant, H'

Vapour pressure (VP)



4.1 Ranges at 25°C in saturation vapor pressure (P^0) values for some important classes of organic compounds.

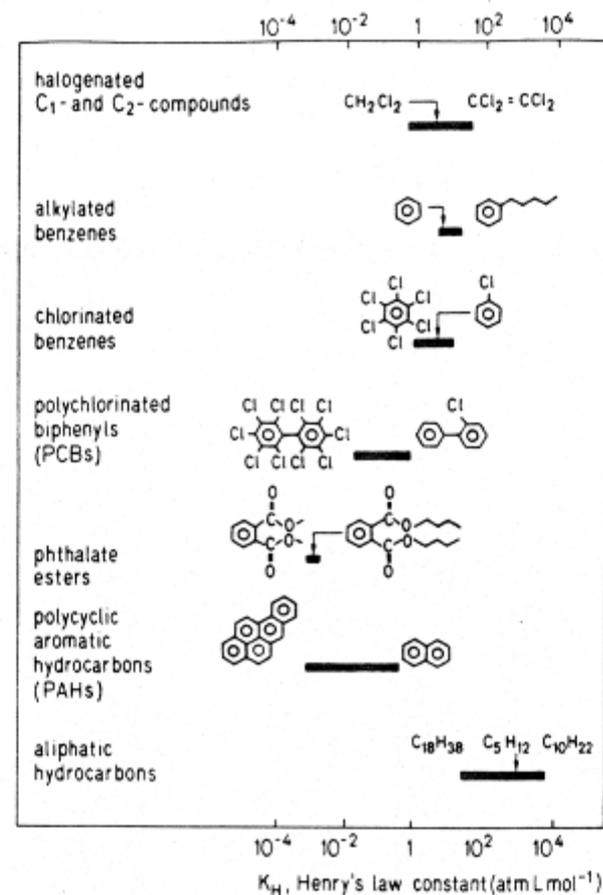


Figure 6.2 Ranges in Henry's Law constants (K_H) for some important classes of organic compounds.

Water solubility (WS, S)

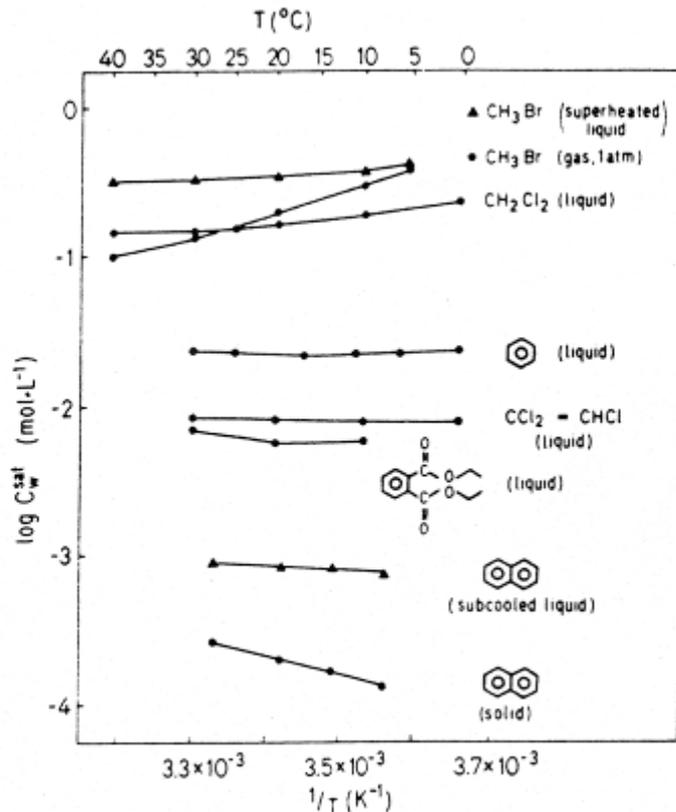


Figure 5.6 Solubility in water as a function of temperature for various compounds.

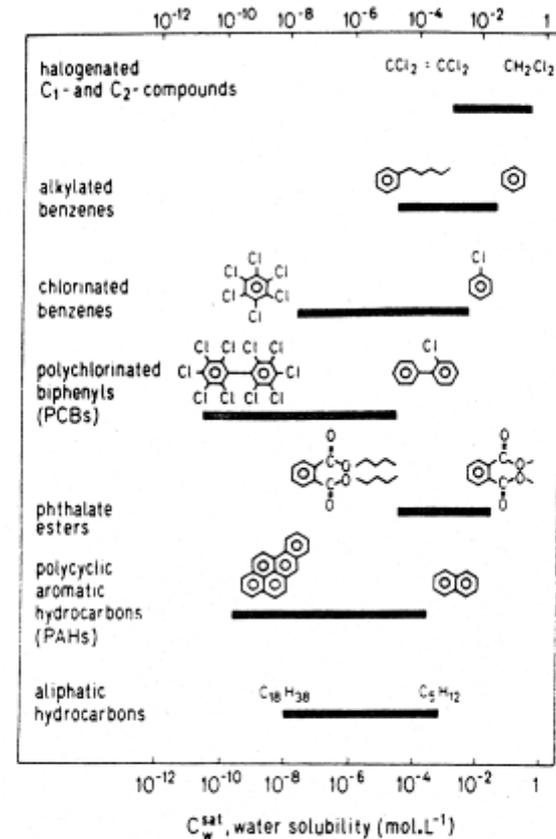


Figure 5.1 Ranges in water solubilities (C_w^{sat}) of some important classes of organic compounds.

Partition coefficient n-octanol-water (K_{OW} , P)

Partition coefficient n-octanol-water K_{OW} – the ratio of the concentration of a solute between water and octanol as a model for its transport between phases in a physical or biological system:

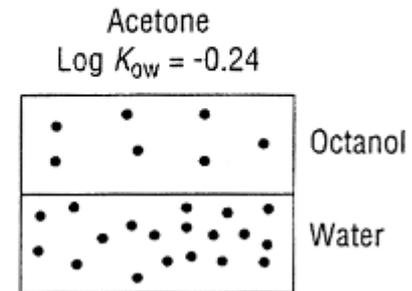
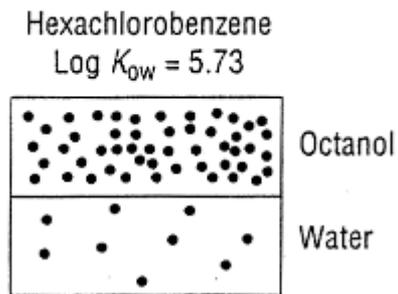
$$K_{OW} = C_{OW} / C_W$$

Because the n-octanol is a good surrogate phase for lipids in biological organisms, a K_{OW} represents how a chemical would thermodynamically distribute between the lipids of biological organisms and water.

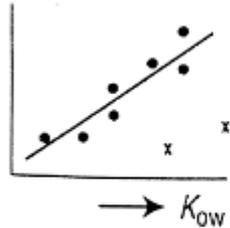
It further represents the lipophilicity and the hydrophobicity of the chemicals.

Partition coefficient n-octanol-water (K_{OW} , P)

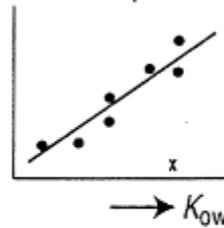
$$K_{OW} = (X)_{\text{octanol}} / (X)_{\text{water}}$$



Bioconcentration factor



Soil sorption



LC50

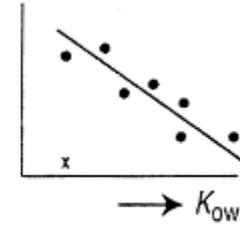


Figure 7.6. The octanol-water partition coefficient (K_{OW}) is defined as the ratio of the concentrations of a chemical in octanol and in the aqueous phase at steady-state. It can be measured, for example, by the shake-flask procedure. K_{OW} is often used for the estimation of bioconcentration, sorption and toxicity.

Partition coefficient n-octanol-air (K_{OA})

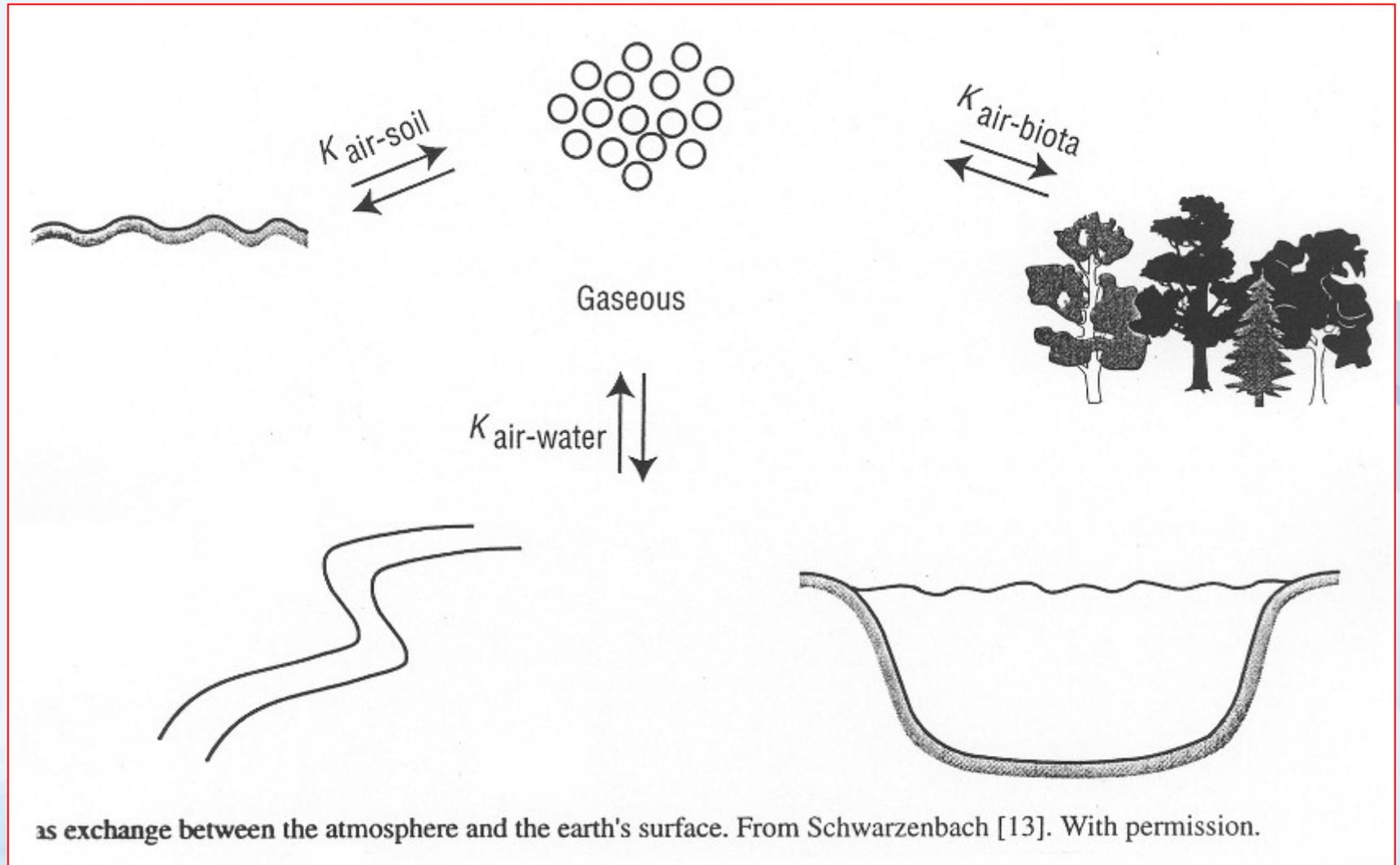
Transfer of compound cross the interface octanol – air can be described by Whitman two-resistance coefficient of mass transfer (MTC), which used the conception of two resistance – in boundary layers of octanol and air.

Mass transfer if directed by molecular diffusion and the result is slower diffusion.

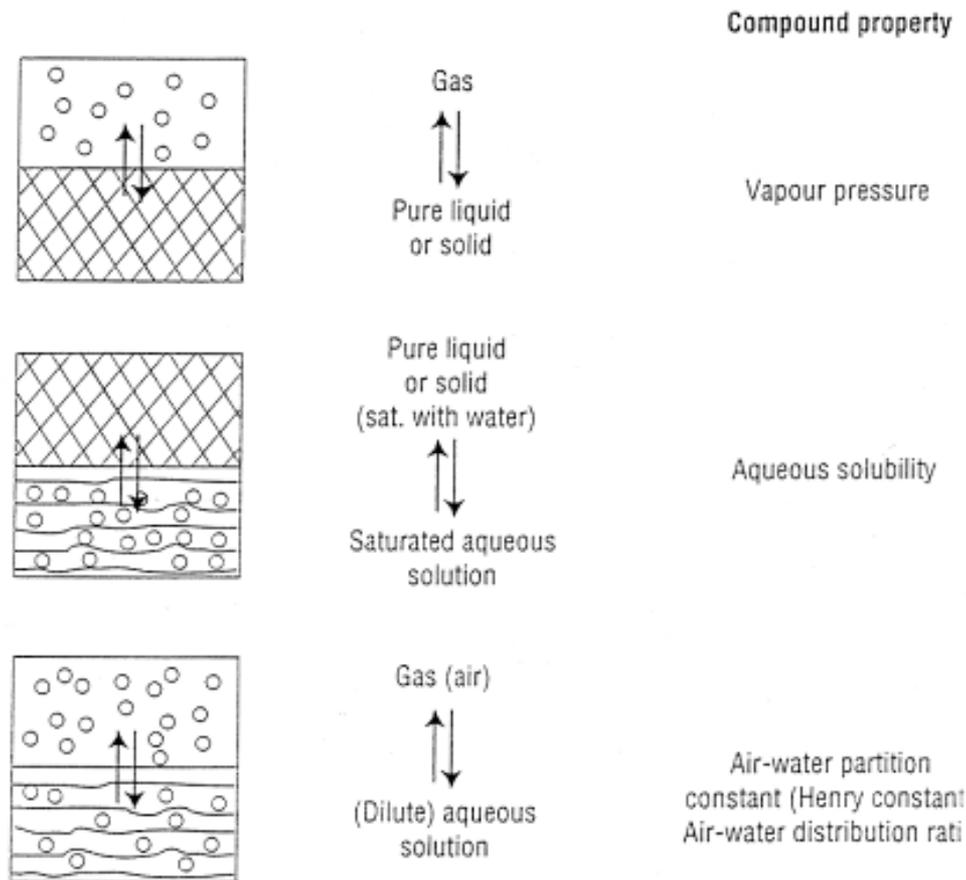
Overall mass transfer coefficient derived from particular MTC:

$$1 / k = 1 / k_A + 1 / (k_O * K_{OA})$$

Environmental equilibria



Environmental equilibria



Important compound properties showing the equilibrium partitioning between two phases.

$$C_1/C_2 = \text{constant} = K_{12}$$

Equilibrium air - water

Processes Resulting in Emissions and/or Depositions at the Air/Water Interface

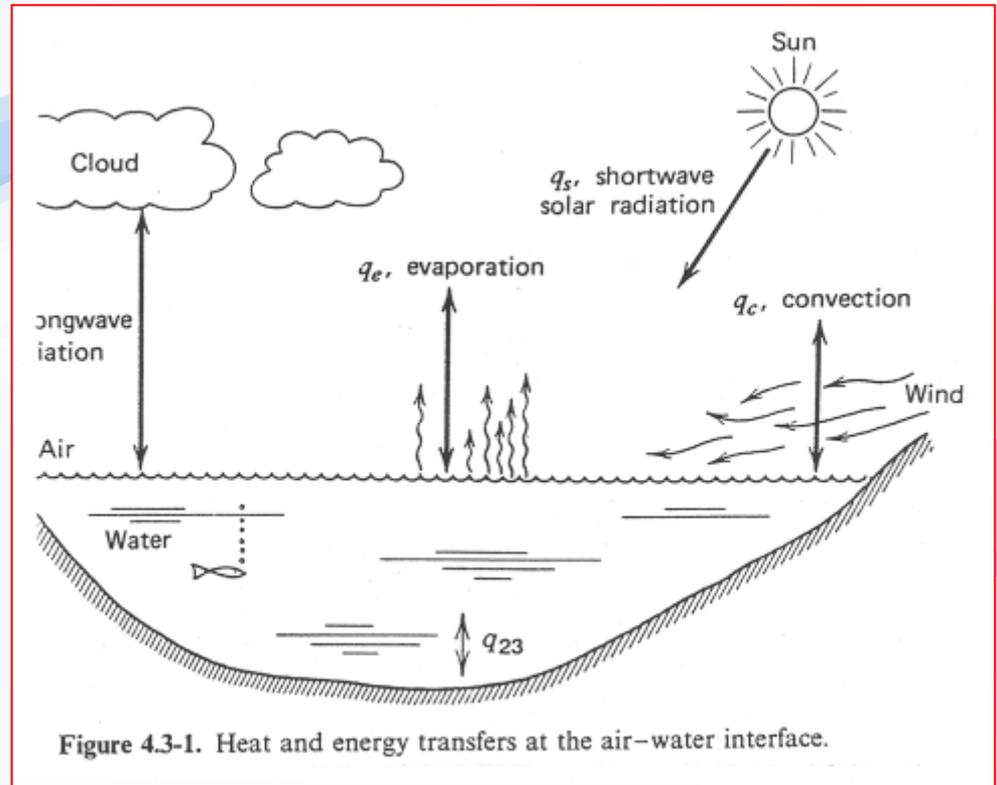
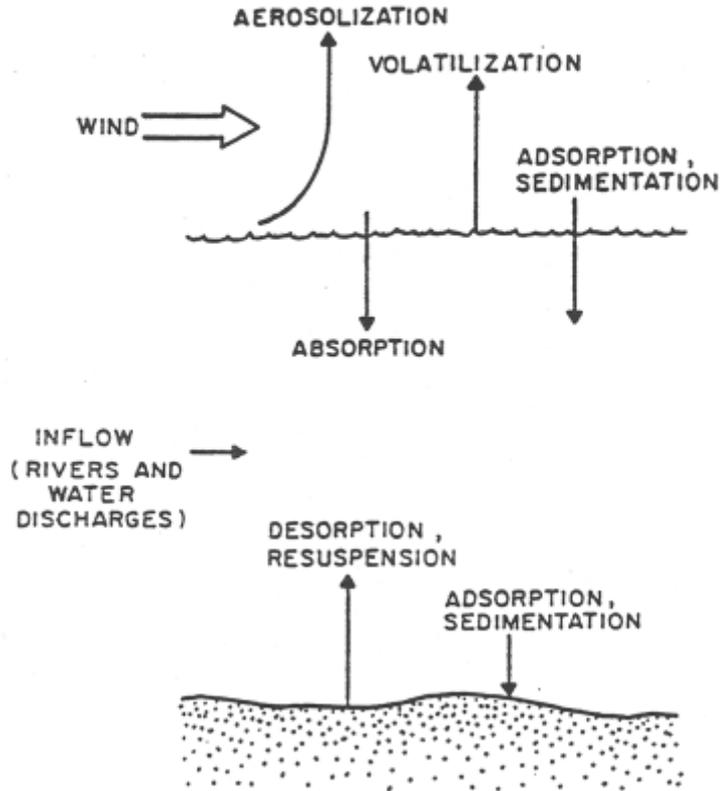


Figure 4.3-1. Heat and energy transfers at the air-water interface.

Exchange Processes

What processes can transfer organic chemicals from the atmosphere to surfaces?

- ↗ **Deposition of water (wet deposition of dissolved chemical)**
- ↗ **Deposition of ice/snow**
- ↗ **Wet deposition of particulate matter**
- ↗ **Dry deposition of particulate matter**
- ↗ **Gaseous deposition**

Exchange Processes

What processes can transfer organic chemicals from surfaces to the atmosphere?

- ↗ **Aerosol generation**
- ↗ **Volatilisation**

Phase Distribution in the Atmosphere

Between the gas phase and water:

- ↪ According to the Henry's Law constant ($K_{AW} = H/RT$)
- ↪ Dependent on temperature
- ↪ Equilibrium generally reached, but perhaps not locally
- ↪ Surface adsorption can contribute to levels in very small water droplets (fog)

Phase Distribution in the Atmosphere

Between the gas phase and particulate matter:

- ↪ Combination of dissolution, surface adsorption, and absorption in organic matter
- ↪ Absorption believed to dominate for POPs, described by:

$$K_{PA} = V_P * f_{OC} * K_{OC}/K_{AW}$$

- ↪ Temperature dependent
- ↪ Equilibration believed to be rapid, but not much experimental evidence

Phase Distribution in the Atmosphere (III)

Between the gas phase and snow:

- ↪ Surface adsorption
- ↪ Dependent on surface area of snow (0.01-0.1 m²/g)
- ↪ Little experimental evidence on magnitude and kinetics of partitioning

Two resistant concept of mass transfer of a chemical between air and water

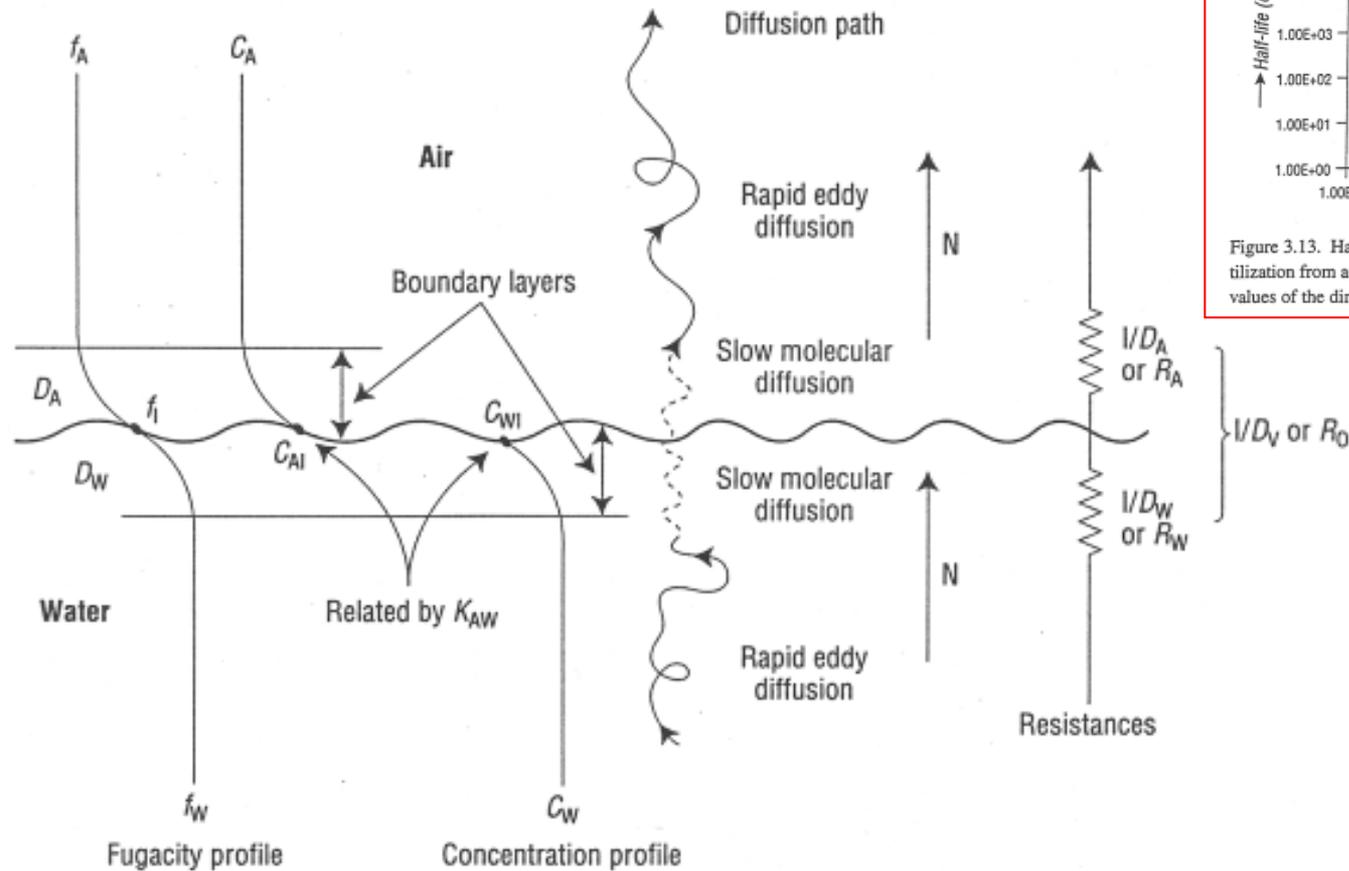


Figure 3.12. Mass transfer of a chemical between two phases, air and water, according to the two resistances concept described by Mackay [1]. Reprinted by permission of Lewis Publishers, an imprint of CRC Press, Boca Raton, Florida.

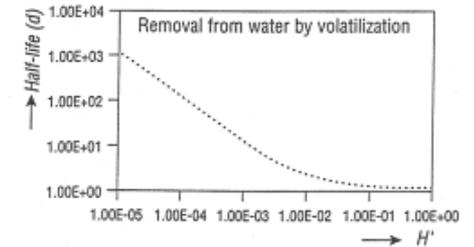
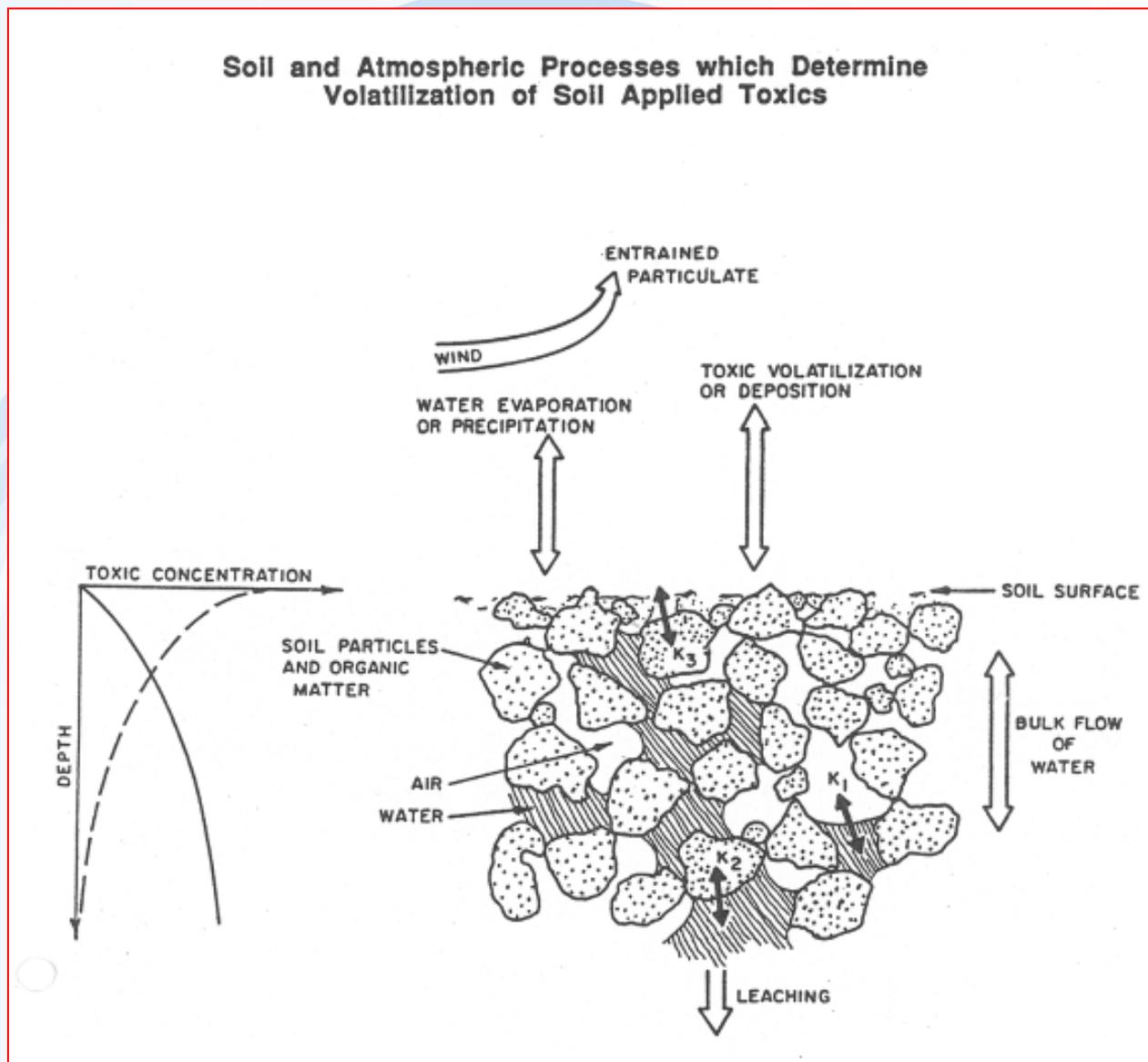


Figure 3.13. Half-lives for the removal of a substance by volatilization from a body of water (depth 2 m), plotted for different values of the dimensionless Henry's law constant.

Soil and atmospheric processes which determine volatilization of soil applied chemicals

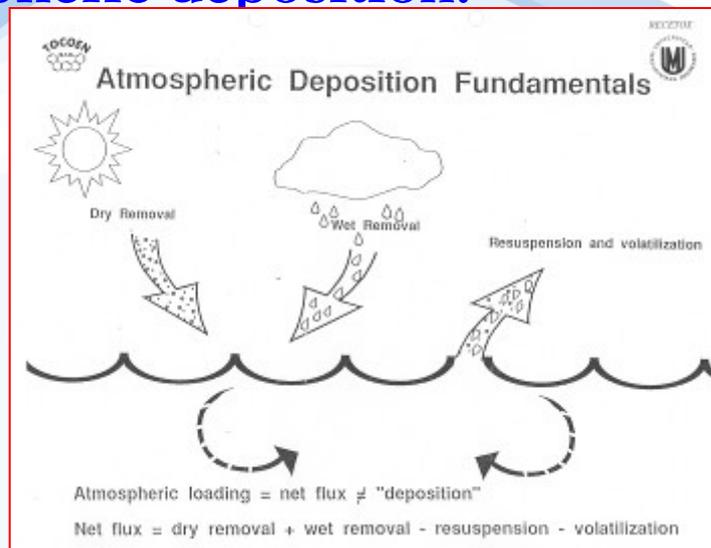


Dry and wet atmospheric deposition

Chemical compounds are transported from the atmosphere on water or soil by atmospheric deposition.

Atmospheric deposition:

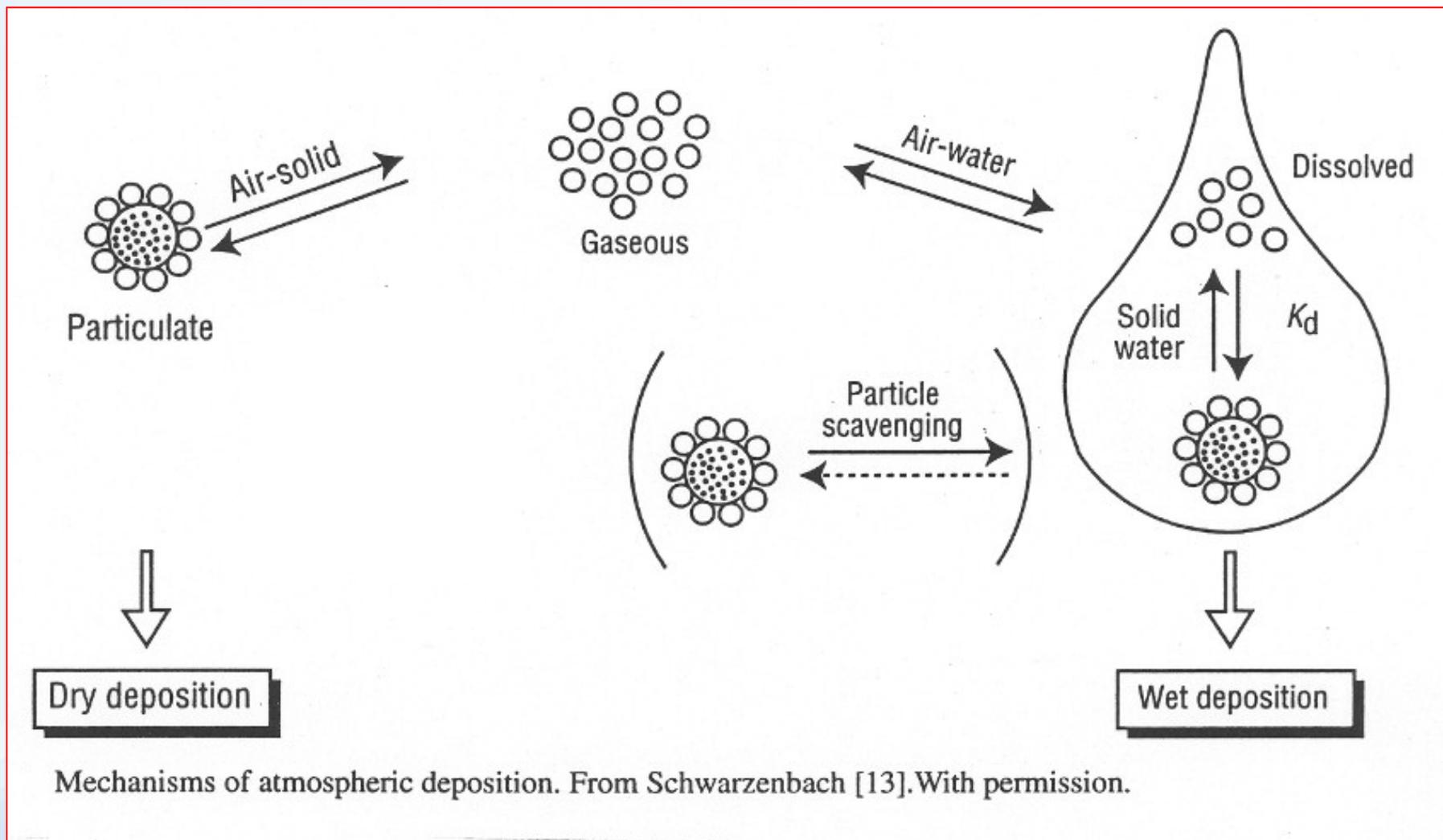
- ↪ wet
- ↪ dry



Wet atmospheric deposition – sum of rain washing (rain out) a washout (under clouds) process.

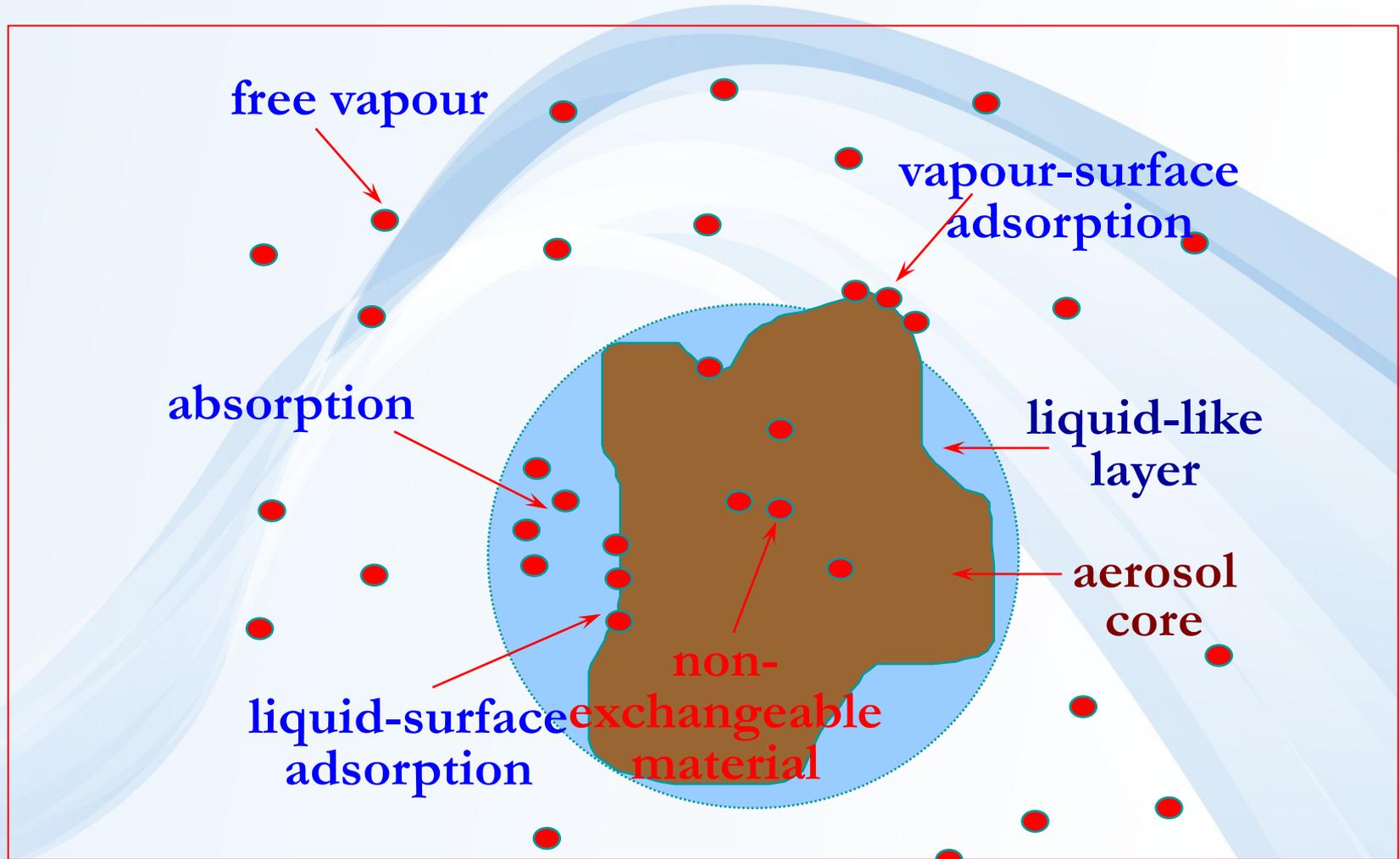
Dry atmospheric deposition – sum of aerosol deposition and gas absorption.

Dry and wet atmospheric deposition

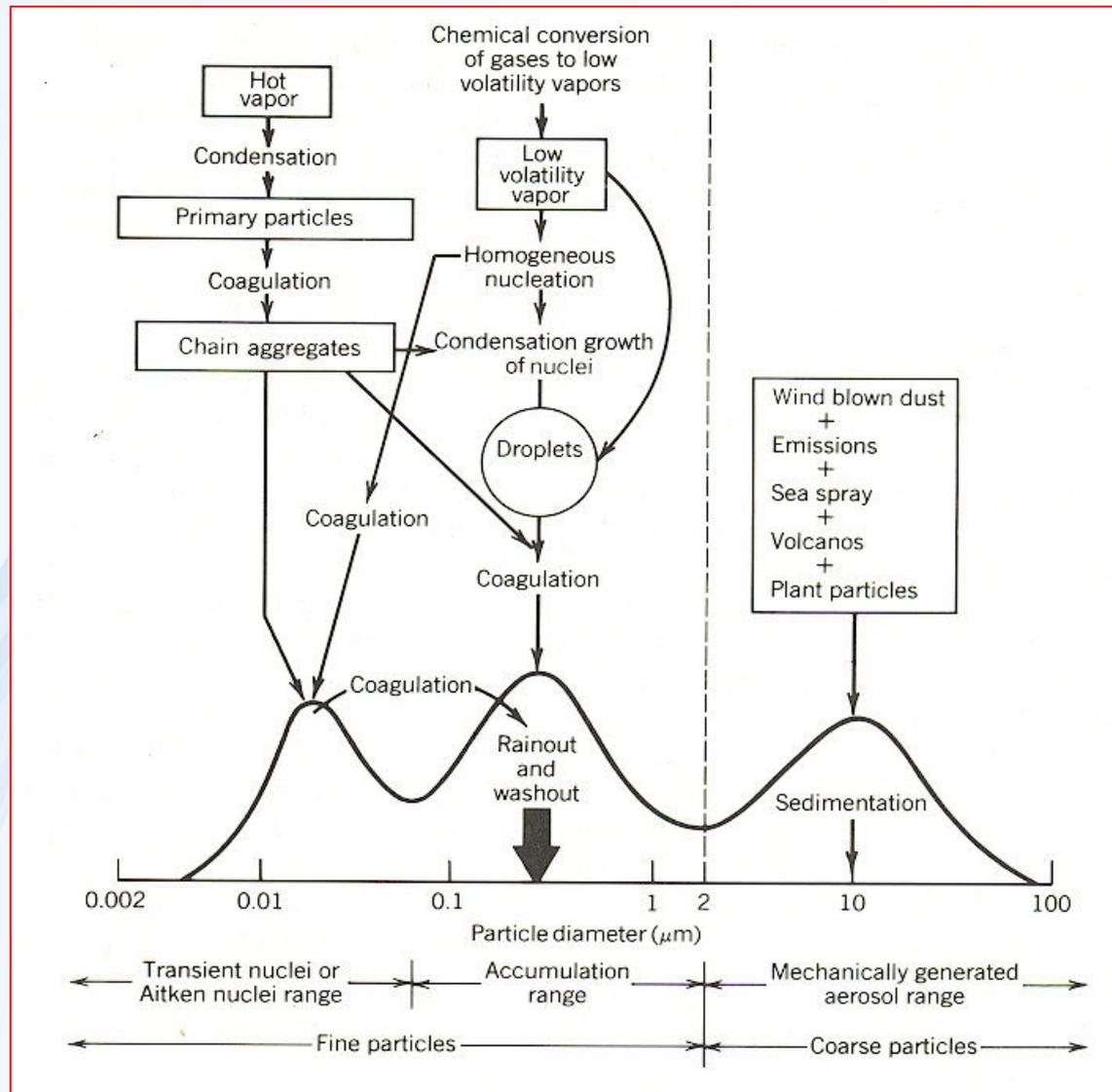


Mechanisms of atmospheric deposition. From Schwarzenbach [13]. With permission.

Particle - gas interactions



Particles in the Atmosphere



Whitby, K., Sverdrup, G., Adv. Environ. Sci. Technol. 10, 477 (1980)

Dry and wet atmospheric deposition

Rainout, washout and aerosol deposition – one direct advection transport processes – chemicals are removed from atmosphere to waters and soils – this mechanism is realized if compound has a higher fugacity in water or soil.

Absorption of gases has a diffusive mechanism – absorption of compound from gaseous phase by water or soil is realized in the fugacity of chemical is higher in air than in water or soil.

If the fugacity in water or soil is higher, the result is a opposite – the volatilization is coming.

Dry atmospheric deposition

Transport of chemical compounds from air to the waters and soils by dry deposition can be described resistance.

Velocity of deposition v_d indirectly depends on the three resistances which represent three various steps of process:

$$v_d = 1 / (r_a + r_b + r_c)$$

Where:

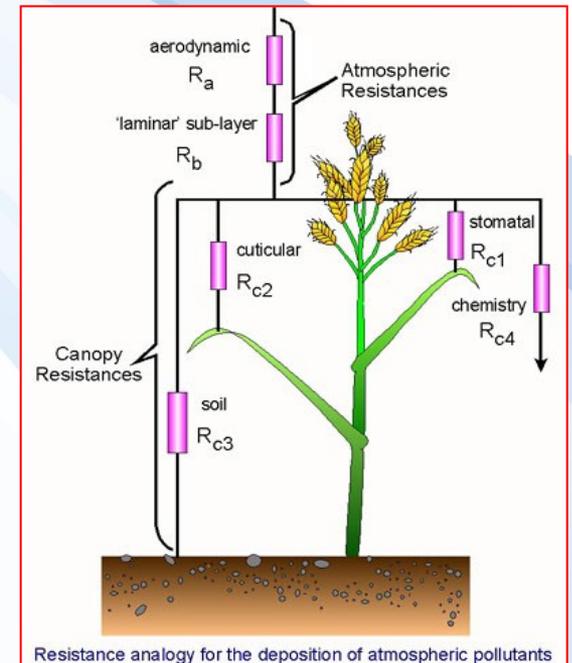
r_a = atmospheric resistance

r_b = resistance of laminar layer

r_c = resistance of surface covering

r_a, r_b – depend on atmospheric stability

r_c - depends on chemical composition and physical structure of acceptor surface and deposited material.



Sorption

In the interface of two phases the transition area is created the concentrations of individual components are generally different than inside the phases.

The different properties if inter-phase are done by the existence of inter-surface powers.

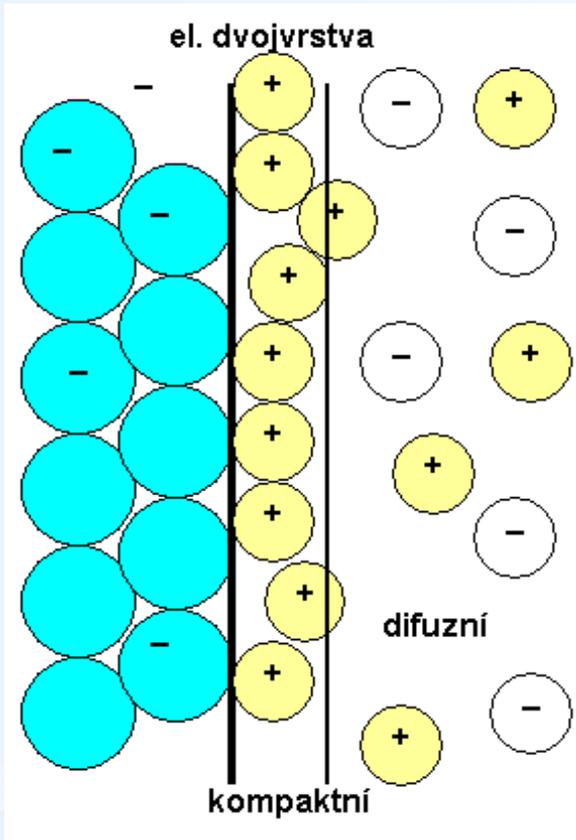
If based on the effect of these powers, the concentration of one component increased in the comparison with the concentrations inside the phase – this cummulation is described as a sorption.

The contact of gases or solutions with solid phase is described as adsorption.

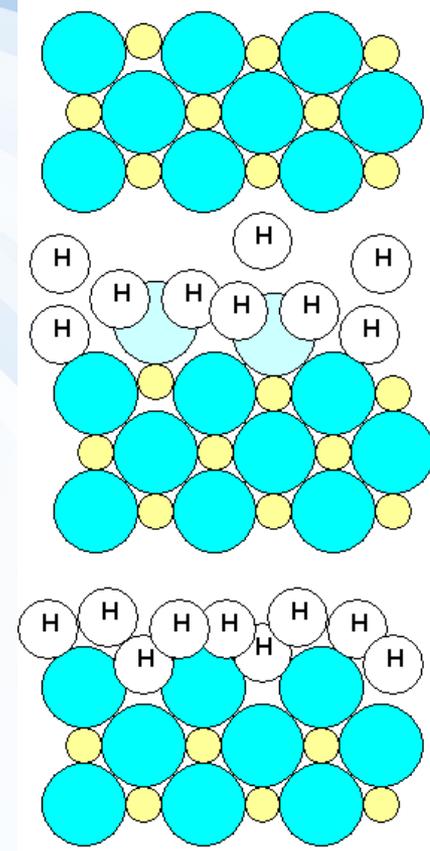
Adsorbent – adsorbate.

Surfaces

Electric double-layer



Iont exchange



Physical sorption

Two types of adsorption:

Physical – van der Waals intermolecular powers act between the solid phase and molecules of adsorbate:

- ↪ Bond is relatively weak, reversible
- ↪ Consists from more than 1 layers
- ↪ Adsorption energy - $0,3 - 3 \text{ kJ}\cdot\text{mol}^{-1}$
- ↪ Adsorption equilibrium is constituted relatively quickly
- ↪ Example: adsorption of gases on active carbon

Chemical sorption

Chemical – nature are powers much more stronger, comparable with the powers which are leading to the production of chemical compounds:

- ↪ Production of surface compound
- ↪ One layer
- ↪ Adsorption energy – $40 - 400 \text{ kJ}\cdot\text{mol}^{-1}$
- ↪ In the range of low temperature – mostly irreversible, we need for removal chemisorbed gas from the surface higher temperature
- ↪ Adsorption of ions – electrostatic powers – electro-adsorption.

Adsorption is not a simple process – combination of interactions.

Adsorption isotherms

Freundlich isotherm:

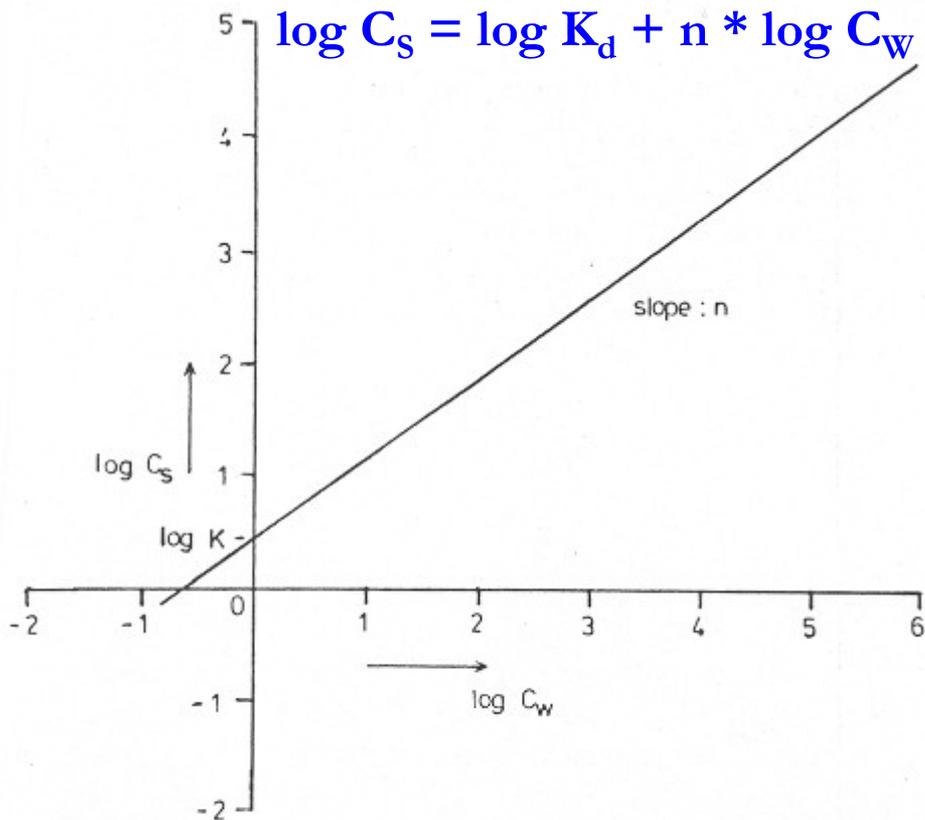


Figure 8. Typical Freundlich adsorption isotherm C_s = concentration on the adsorbent; C_w = concentration in the water; $0 < n \leq 1$. $C_s = K C_w^n$ or $\log C_s = n \log C_w + \log K$.

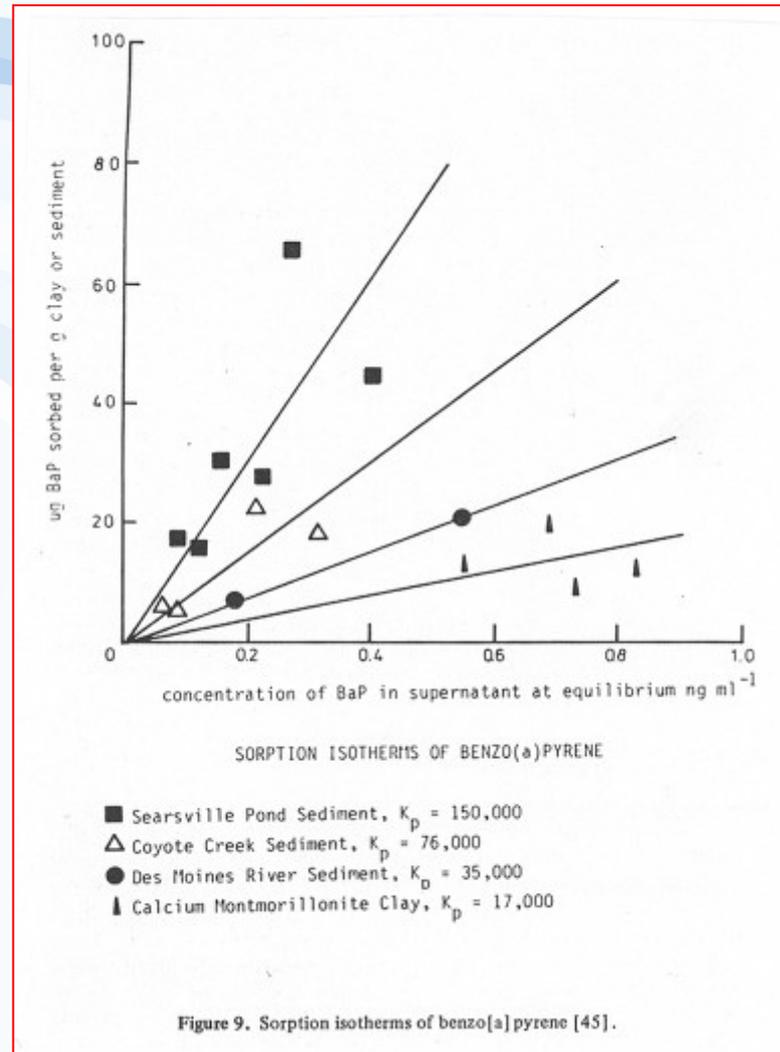
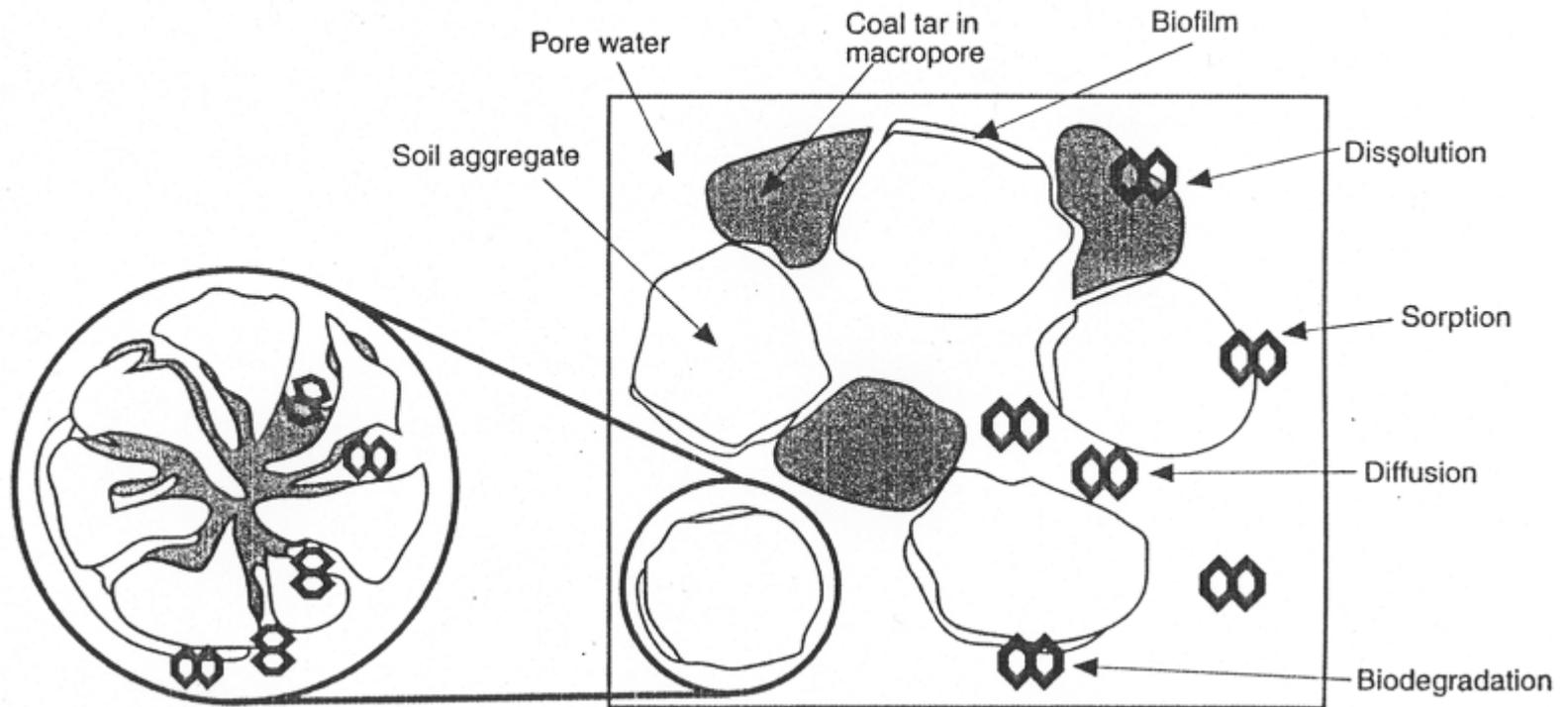


Figure 9. Sorption isotherms of benzo[a]pyrene [45].

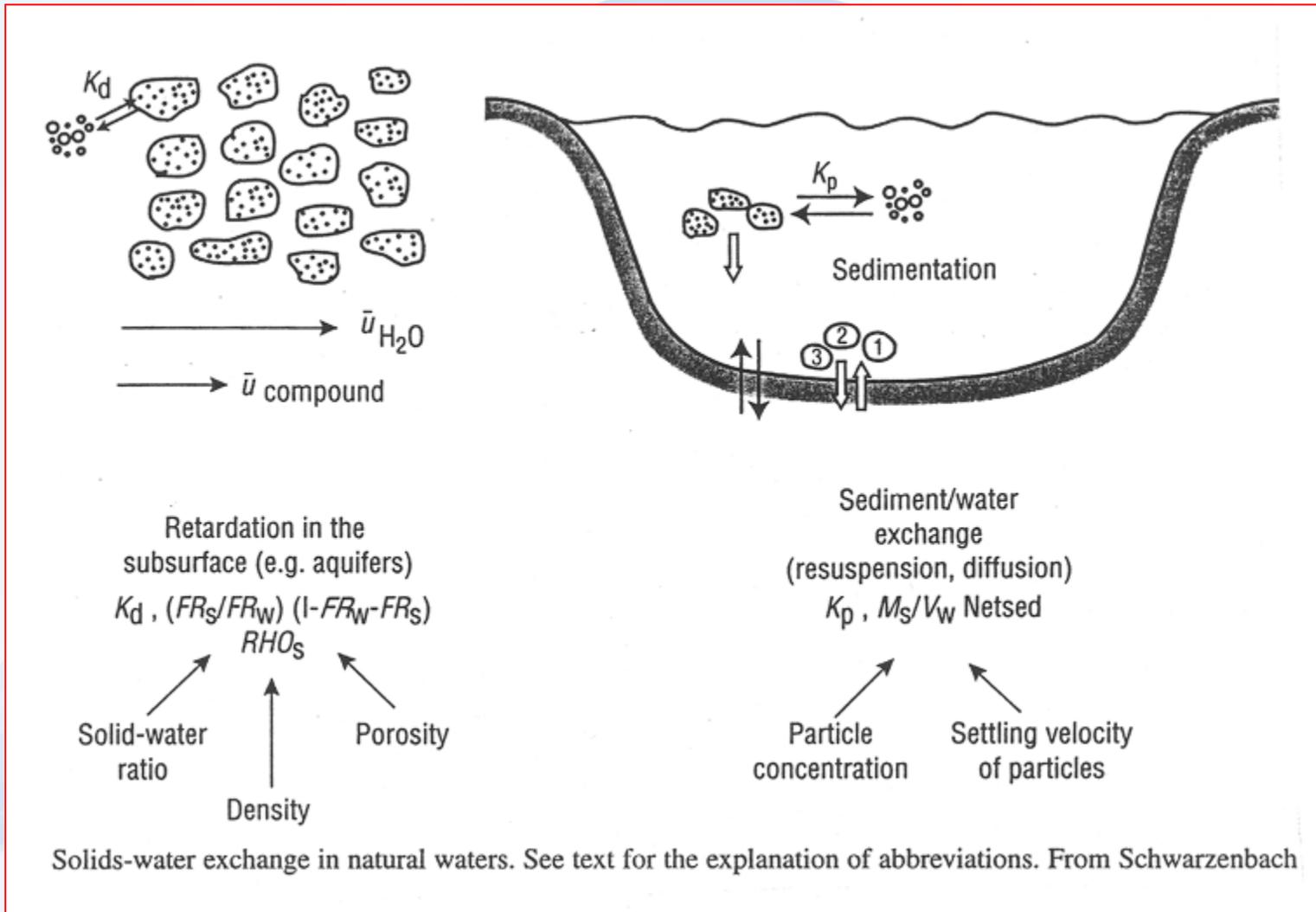
Sorption

FIGURE 2

Schematic showing mass transfer and microbial degradation of solutes from nonaqueous-phase liquid in porous media (not to scale)



Equilibrium water – solid phase (sediments, suspended sediments, soils)



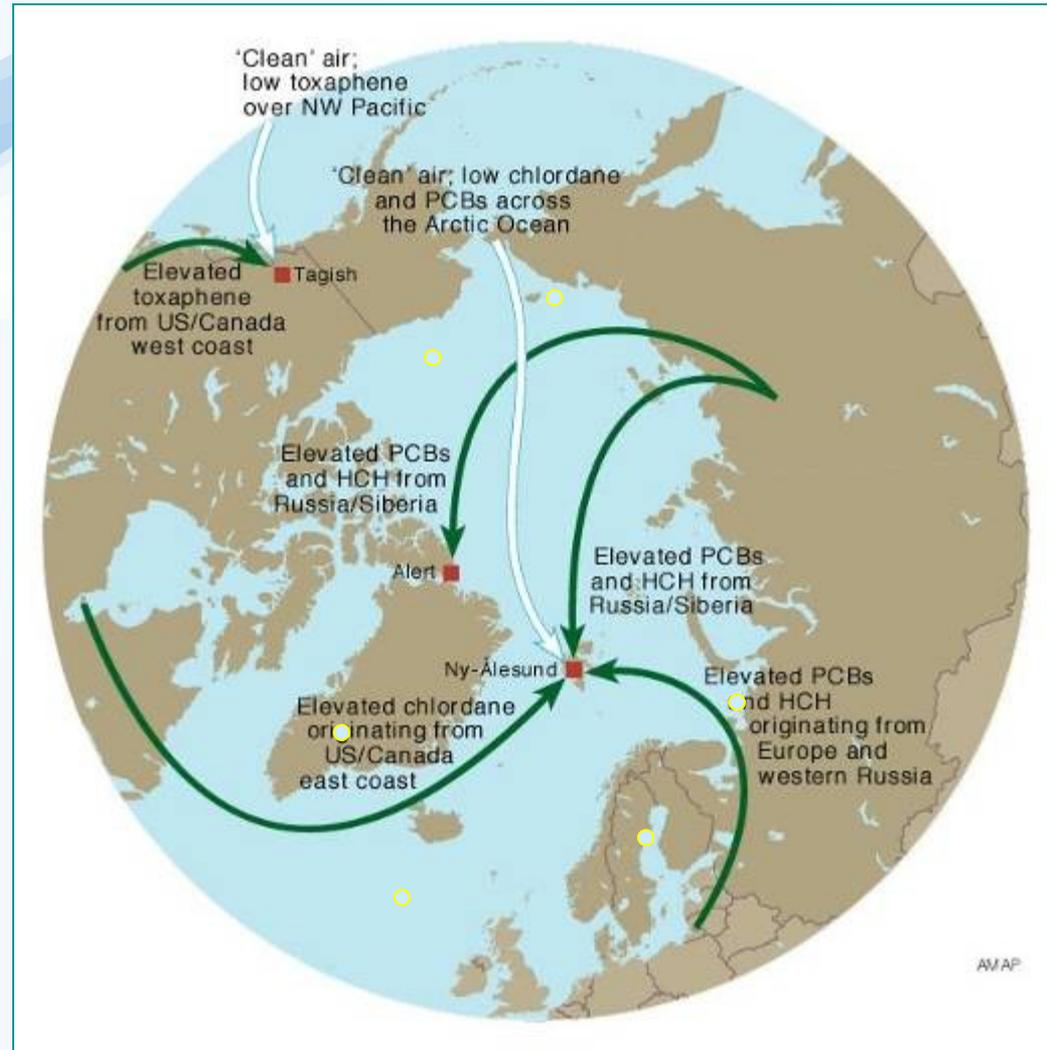
Atmospheric transport

- ↪ Substantial transport of the volatile and semi-volatile POPs
- ↪ Significant seasonal variations for some POPs reflecting differences in usage, transport mechanisms and degradation (*e.g. trans-chlordane, γ -HCH*)
- ↪ Change in congener/isomer distribution due to differences in deposition and photo-chemical processes (*e.g. PCB, HCH and chlordane profiles*)

Long-range atmospheric transport

Persistent Organic Pollutants (POPs)

Mainly due to LRT, but also some regional use and releases of pesticides and industrial chemicals (e.g. PCBs and HCB)



Principles and consequences of long-range transport

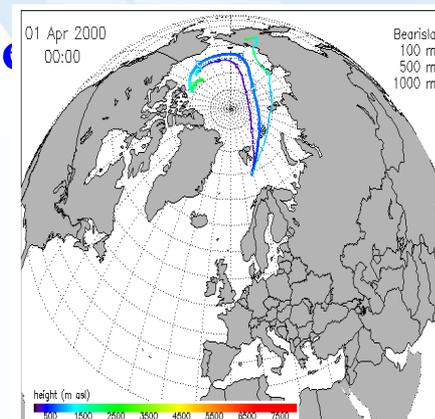
- ↪ Distribution and transport of stable contaminants across long distances
- ↪ Major distribution routes: atmosphere, oceans, rivers and sea ice
- ↪ Transport and accumulation in pristine ecosystems
- ↪ Ultimately, significant impact on indigenous people



Long-range transport elucidation

Evaluation tools

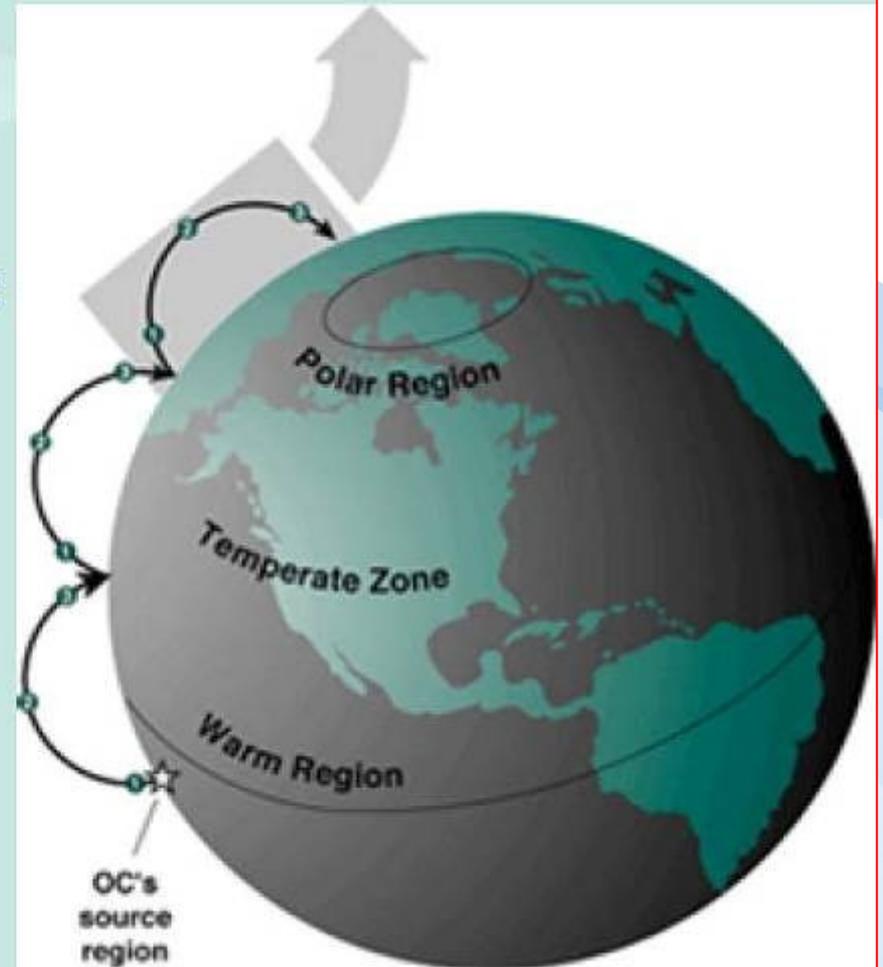
- ↪ Estimation of **meteorological, hydrological, oceanographic conditions** during the transport event (e.g, air mass back trajectories)
- ↪ **Physico-chemical properties and characterisation**
- ↪ **Compound pattern elucidation**
- ↪ **Assessment of concentration levels including ratio evaluation between different contaminant types**
- ↪ **Transport and fate modeling**



The „Grasshopper Effect“

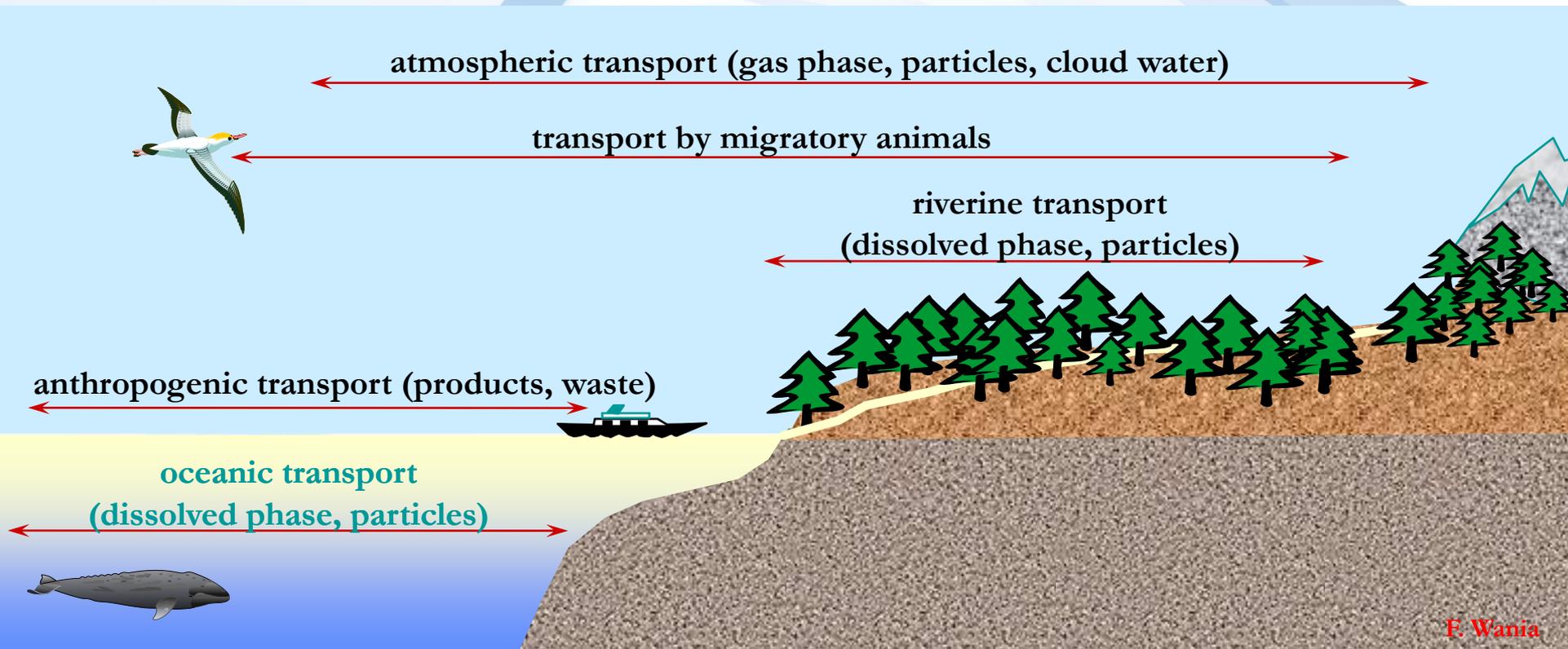
Steps

1. Volatilization
2. Long-range transport
3. Condensation



PTS Transport Pathways

- ↗ persistence increases the relative importance of transport relative to transformation in controlling a contaminant's fate
- ↗ distribution characteristics leading to significant presence in different environmental media (air, water, soil)

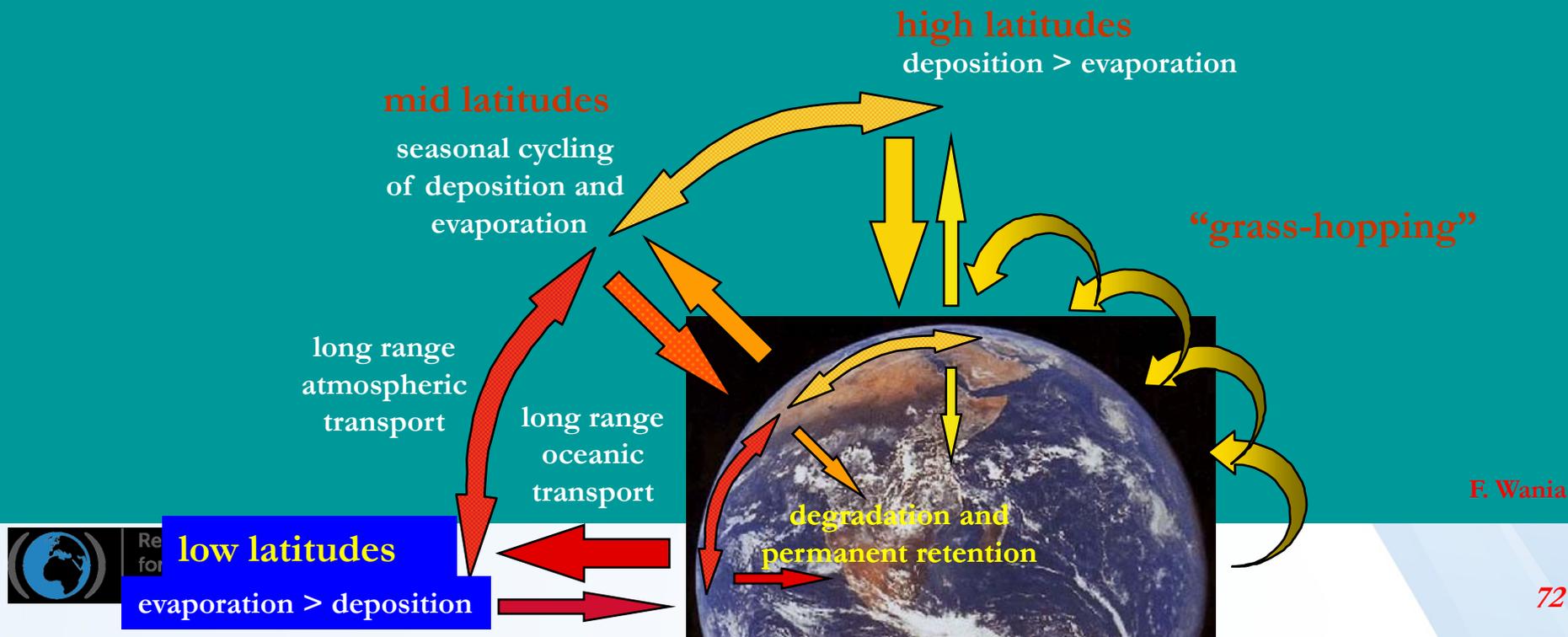
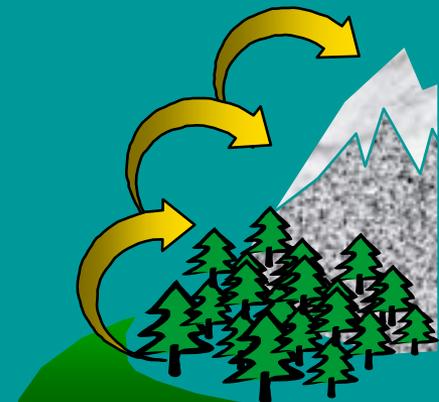


F. Wania

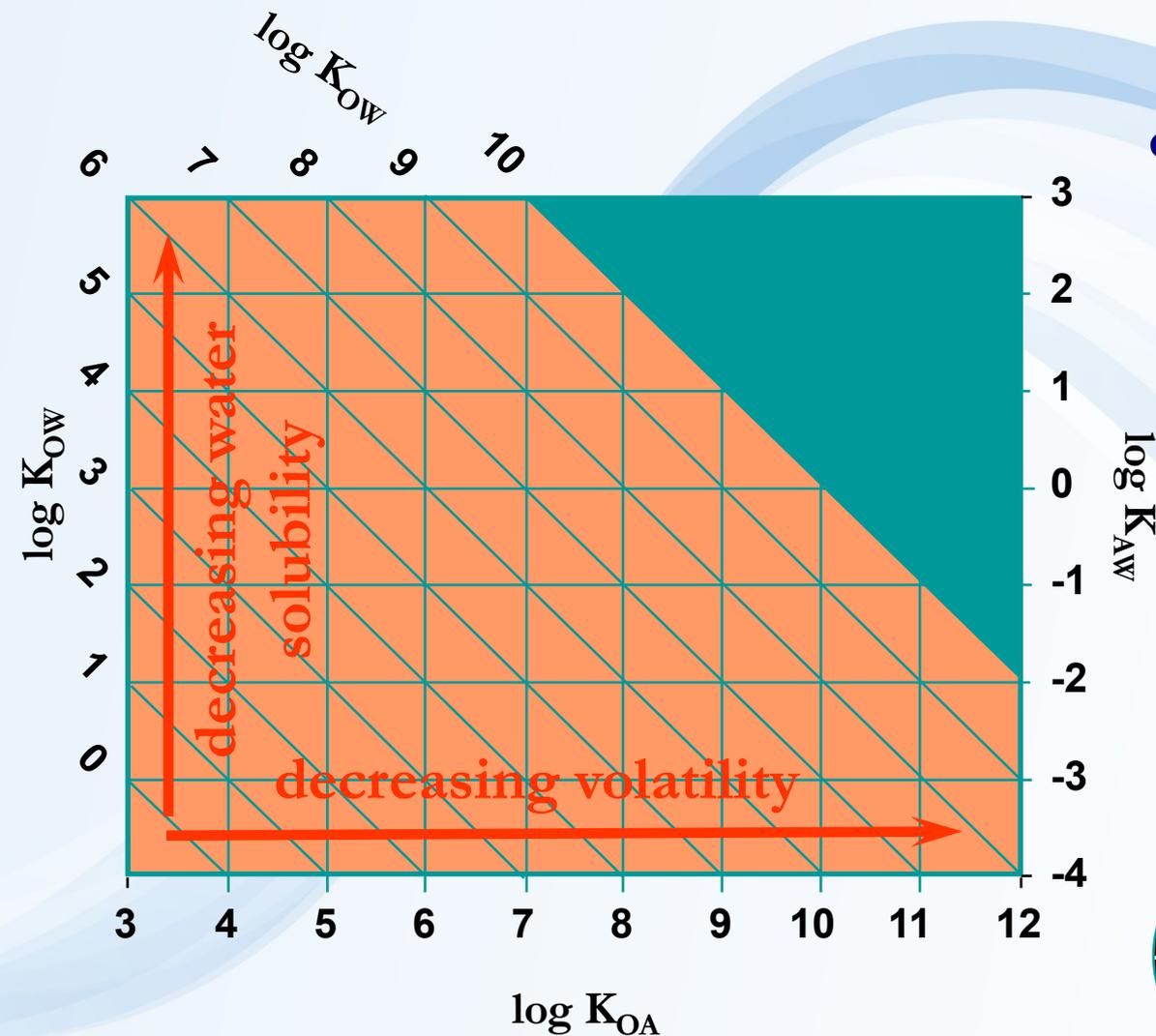
Long-range transport of PTS, e.g. HCB

Because rates of deposition and evaporation are temperature-dependent, hopping is enhanced by periodic temperature changes

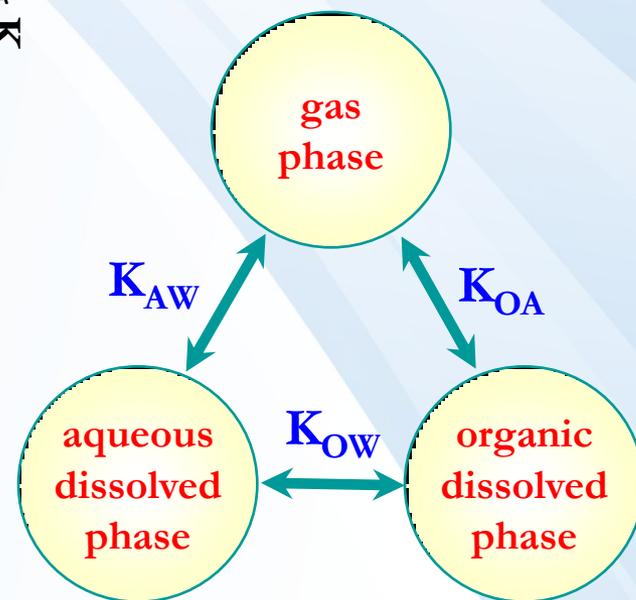
Temperature gradients in space in combination with atmospheric mixing will favour gradual transfer from warm to cold regions on both global and regional scales



The Chemical Partitioning Space



defined by equilibrium phase partition coefficients between air, water and octanol



Biaccumulation – basic definitions

The **process** by which the chemical concentration in an (aquatic) organism achieves **a level that exceeds** that in the water (soil), as a result of chemical uptake **through all possible routes of chemical exposure** (dietary absorption, transport across the respiratory surface, dermal absorption, inhalation).

Bioaccumulation takes place under field conditions.

It is a combination of chemical **bioconcentration** and **biomagnification**.

Biaccumulation

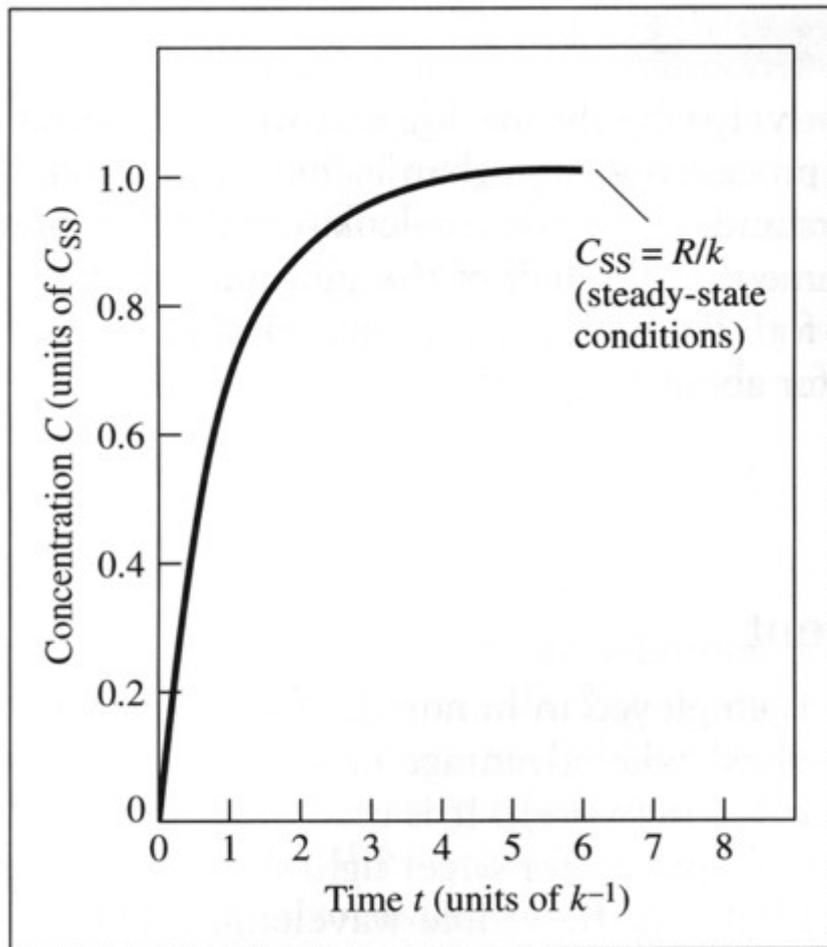


Figure 7-1
Increase in metal concentration with time to reach the steady-state value, C_{ss} .

Bioconcentration – basic definitions

The **process** in which the chemical concentration in an (aquatic) organism **exceeds that in water (soil)** as a result of chemical exposure to (water)borne chemical.

Bioconcentration refers to a condition, usually achieved under laboratory conditions, where the chemical is absorbed only from the water (soil) via the respiratory surface (e.g. gills) and/or the skin.

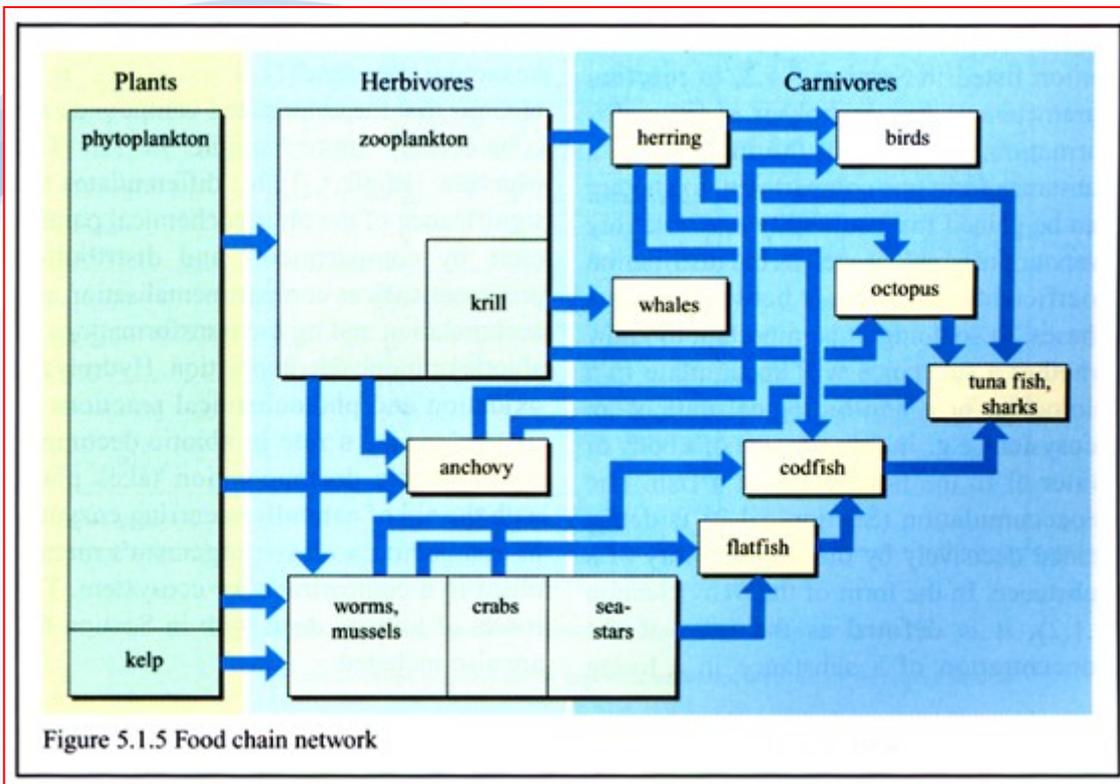
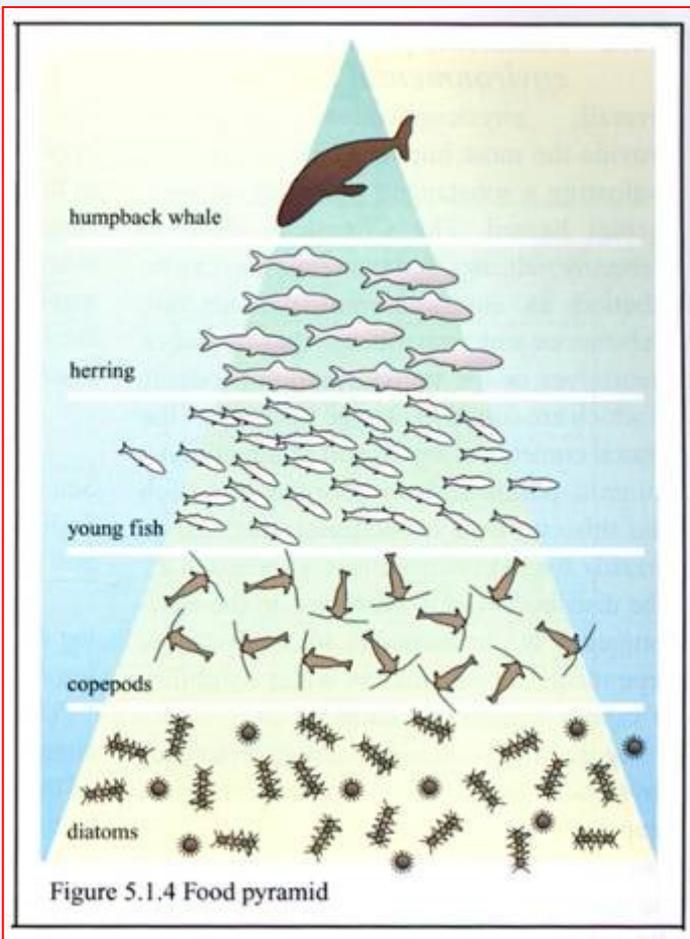
Biomagnification – basic definitions

The **process** in which the chemical concentration in an (aquatic) organism **exceeds that in the organism s diet**, due to dietary absorption.

The **extent of chemical biomagnification** in an organism is best determined under laboratory conditions, where organisms are administered diets containing a known concentration of chemical, and there is no chemical uptake through other exposure routes (e.g. Respiratory surface, dermis).

Biomagnification also can be determined **under field conditions**, based on chemical concentrations in the organism and its diet.

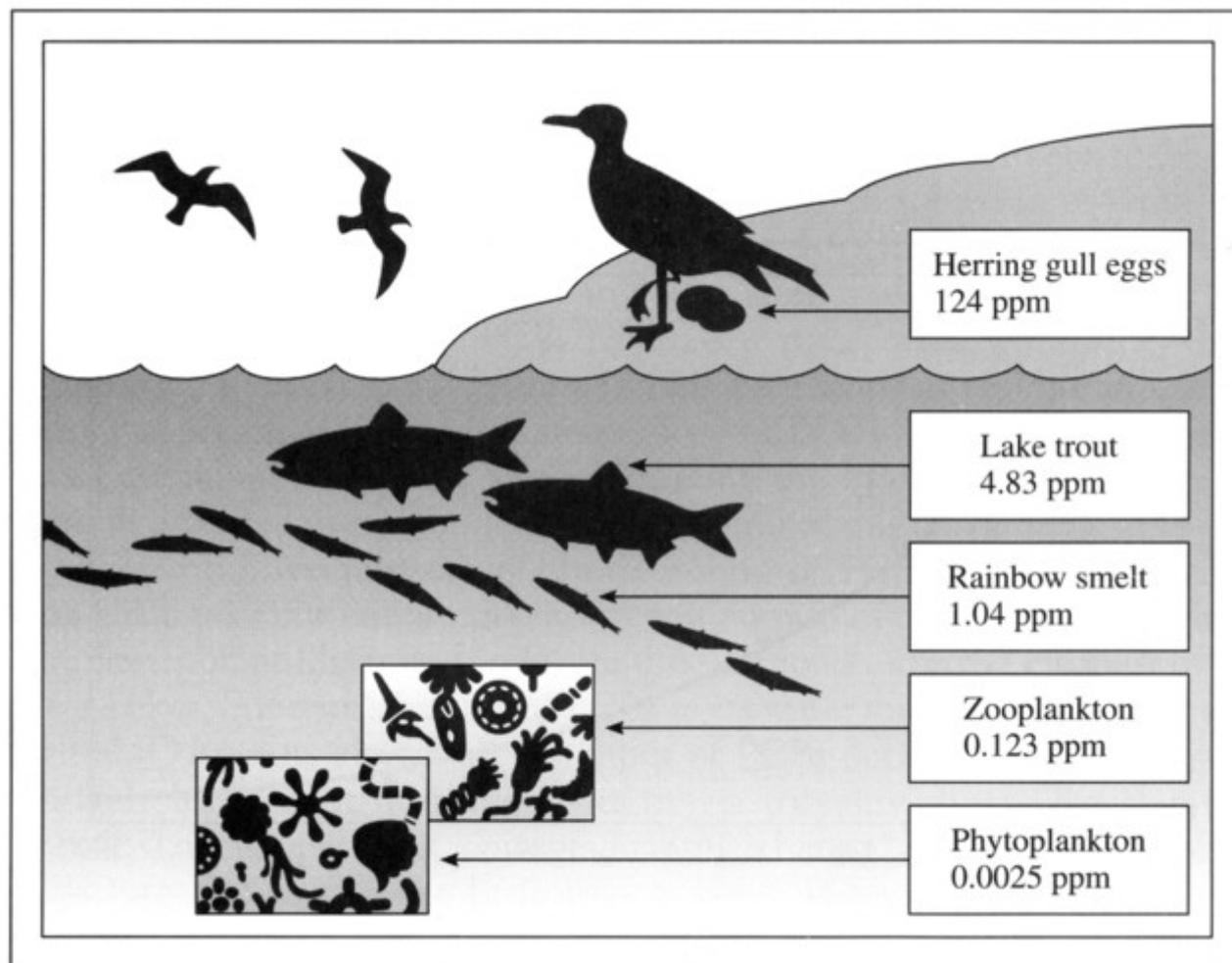
Biomagnification



Bioaccumulation

Figure 6-7

The bioaccumulation and biomagnification of PCBs in the Great Lakes aquatic food chain. (Source: *The State of Canada's Environment*. 1991. Ottawa: Government of Canada.)



Bioaccumulation

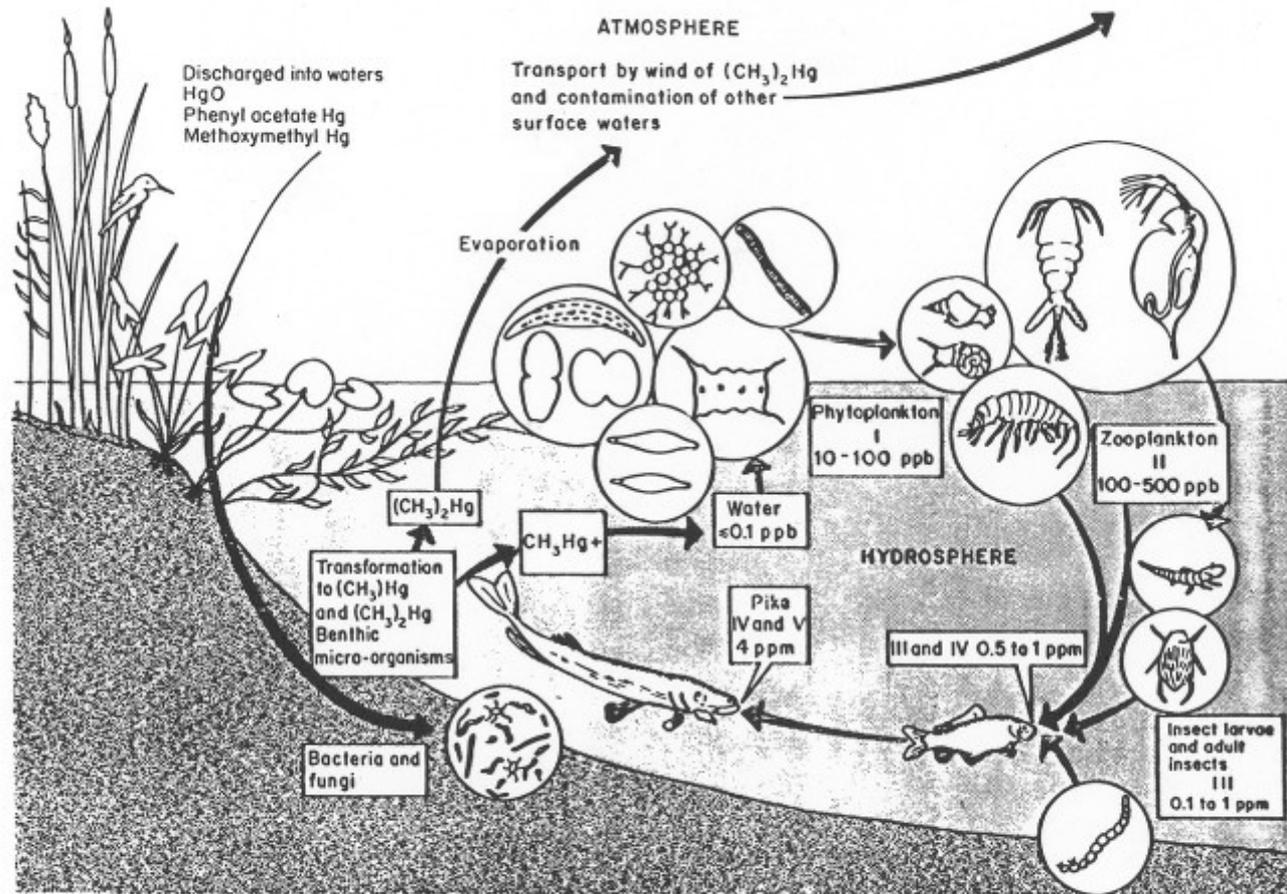


Fig. 3.24 Contamination of the food chain of the pike in Sweden (this diagram has been based on one by Duvigneaud (1974) and on analytical data on mercury contamination from various Swedish researchers). (In Ramade, 1982. Reproduced by permission of McGraw-Hill)

Bioaccumulation, biomagnification

Elimination process

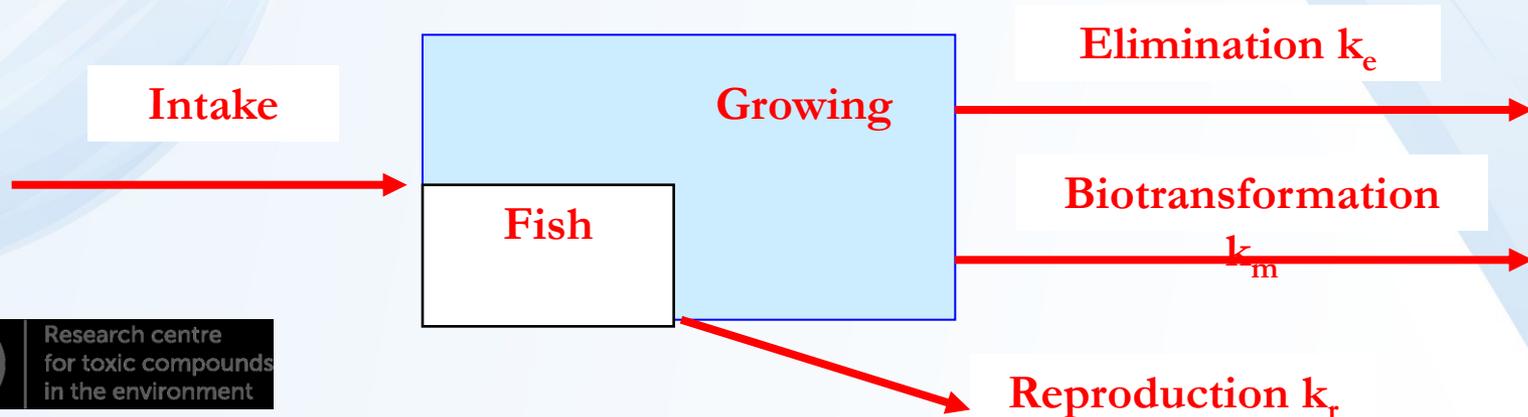
Analogically of the process of intake also the process of elimination can be directed mainly by passive diffusion and active transport.

Main part of hydrophobic compounds are eliminated by passive diffusion to water or excrements.

Concentration of compound is also diluted by the process of organism growing.

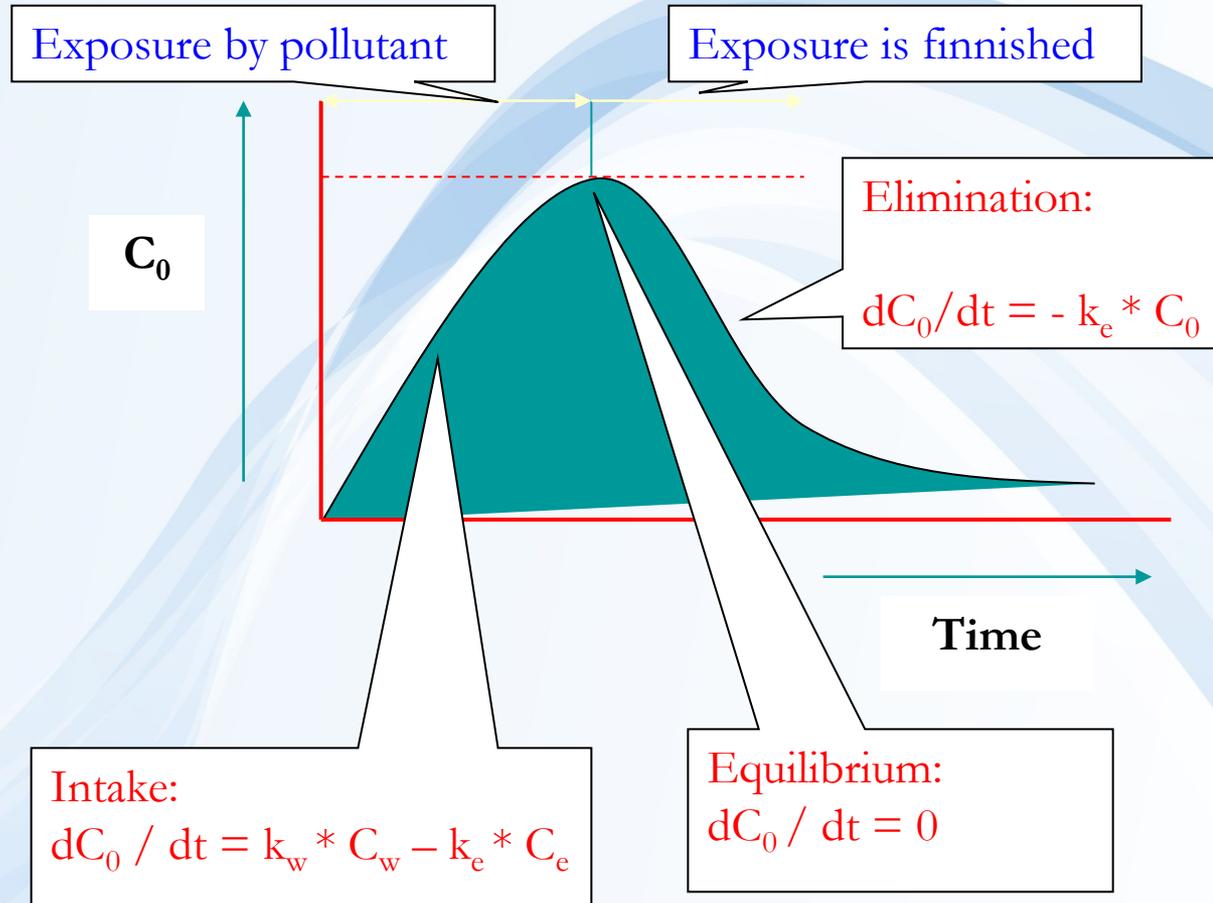
Other possible elimination process is breathing or transfer of chemicals to the eggs.

Biotransformations, especially of more hydrophilic compounds is other possible process of elimination of compound from organism.



Bioaccumulation, biomagnification

Intake and elimination of compounds by aquatic organism:



Bioaccumulation

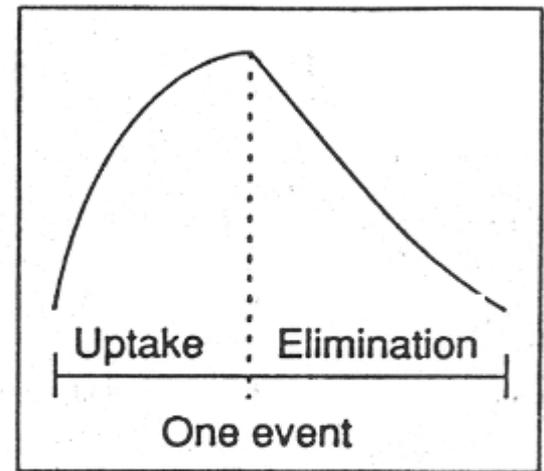
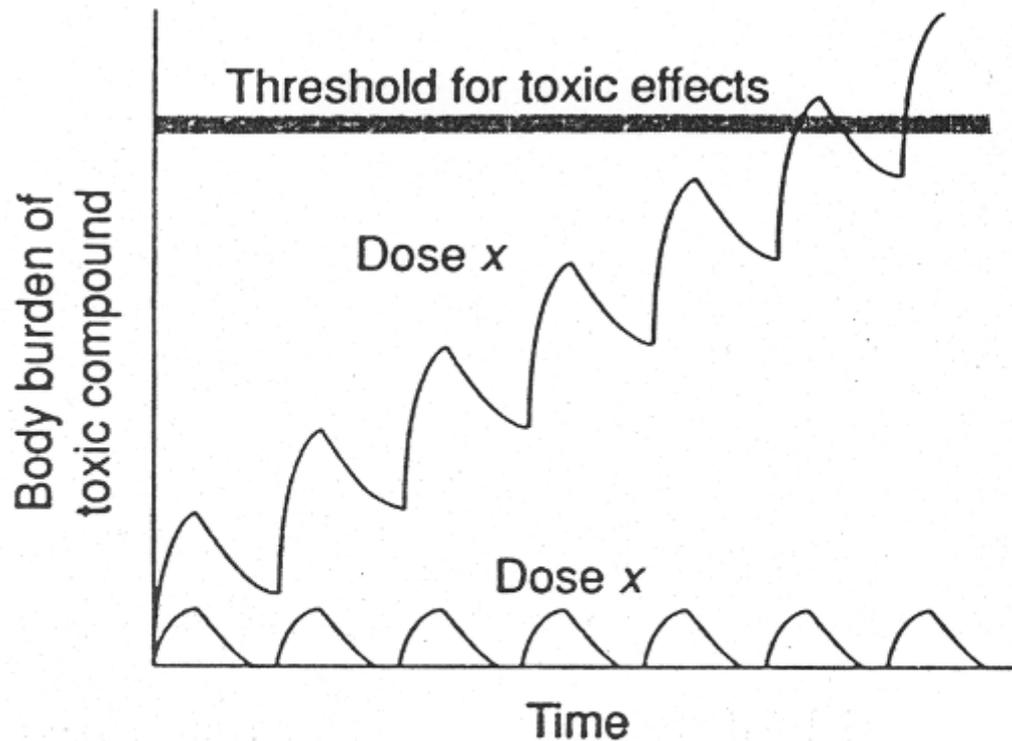


FIGURE 5-5

Effect of dose fractionalization on accumulation of a toxic compound.

Bioaccumulation factor

Bioaccumulation factor (BAF) is the ratio of the chemical concentration in an organism (C_B) to the concentration in water (C_W):

$$\text{BAF} = C_B / C_W$$

Because chemical sorption to particulate and dissolved organic matter in the water column can reduce substantially the fraction of chemical in water that can be absorbed by aquatic organisms, the BAF also can be expressed in terms of the **freely dissolved chemical concentration (C_{WD})**:

$$\text{BAF} = C_B / C_{WD}$$

Bioconcentration factor

Bioconcentration factor (BCF) is the ratio of the chemical concentration in an organism (C_B) to the concentration in water (C_W):

$$BCF = C_B / C_W$$

BCF, like the BAF, also can be expressed in terms of the dissolved chemical concentration (C_{WD}):

$$BCF = C_B / C_{WD}$$

The exposure under steady state conditions is considered.

Biomagnification factor

Biomagnification factor (BMF) is the ratio of the chemical concentration in an organism (C_B) to the concentration in the organism's diet (C_D):

$$BMF = C_B / C_D$$

Relationship between BCF and $\log K_{ow}$

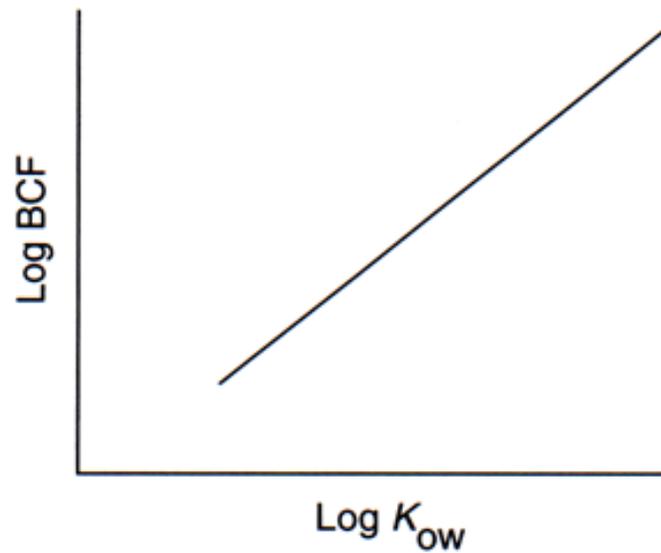
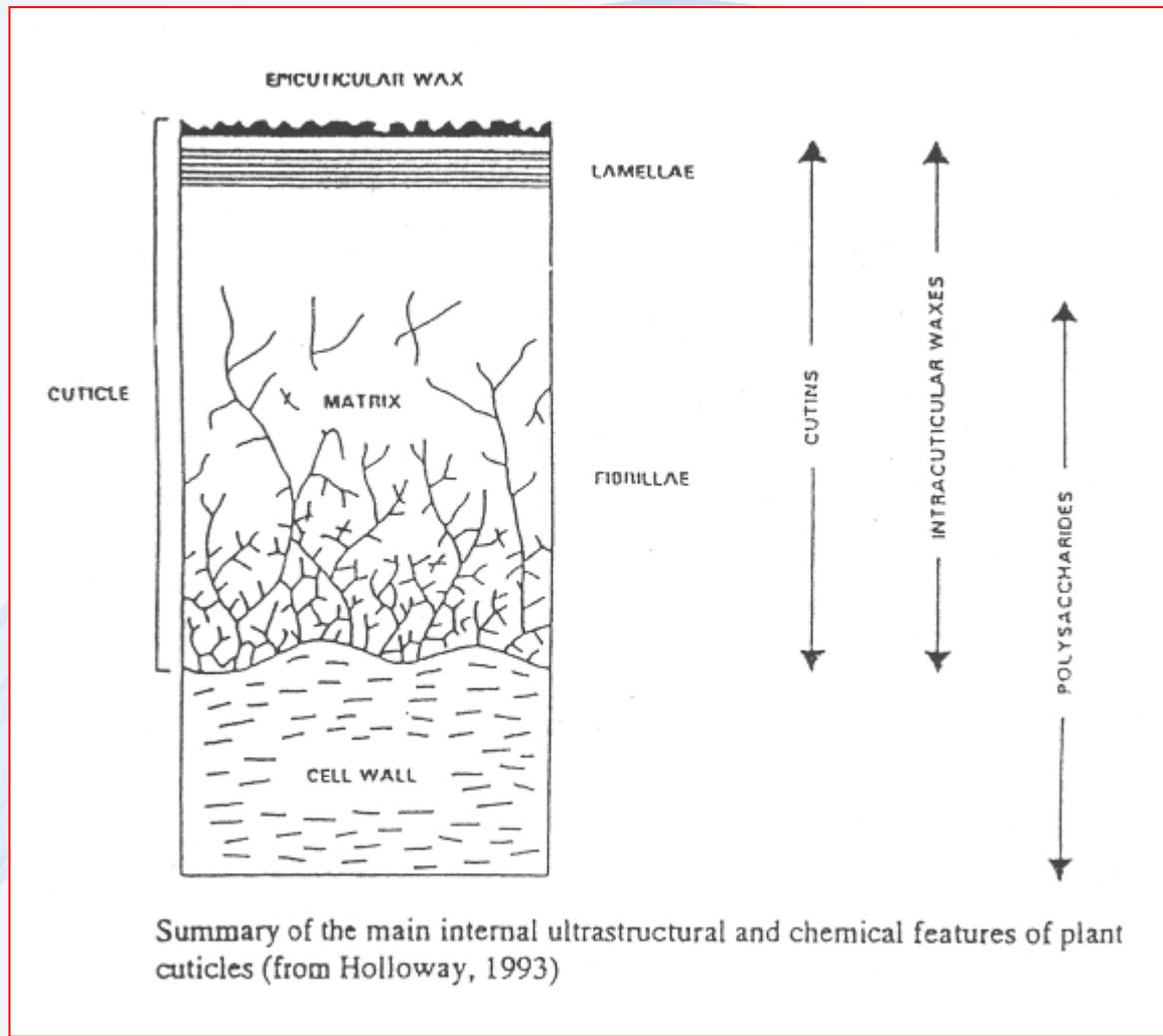


FIGURE 4.1 *Relationship of BCF to $\log K_{ow}$.*

Bioaccumulation in terrestrial vegetation

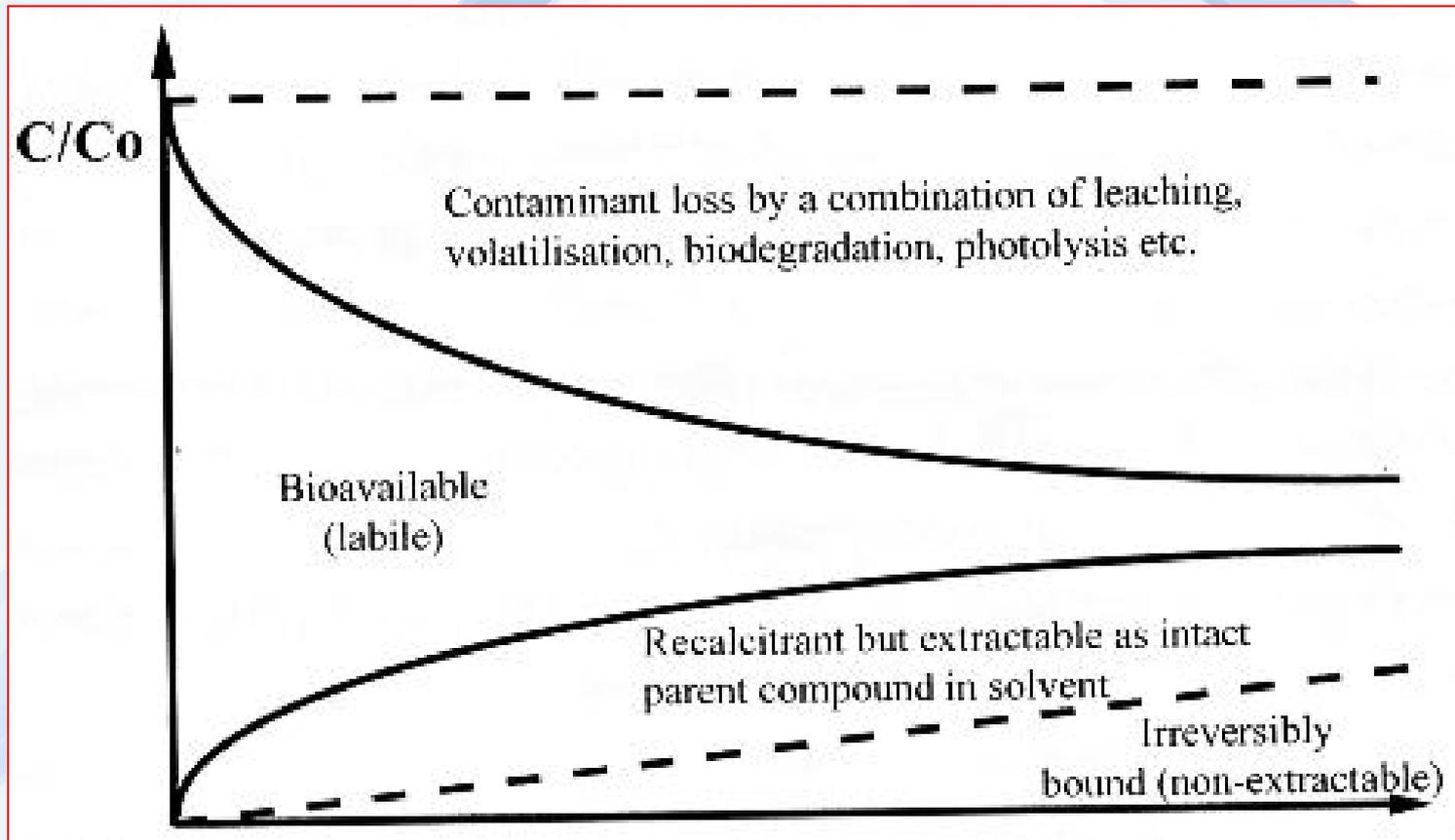


Relationships among the environmental parameters

Compartment	Parameter	Compartment
Water (more mobile)	K_{OW} →	Soil, sediment, animals (less mobile)
	K_{OC} →	
	K_D →	
	BCF →	
	WS ←	
Water	H →	Air
	VP →	

Bioavailability – key issue

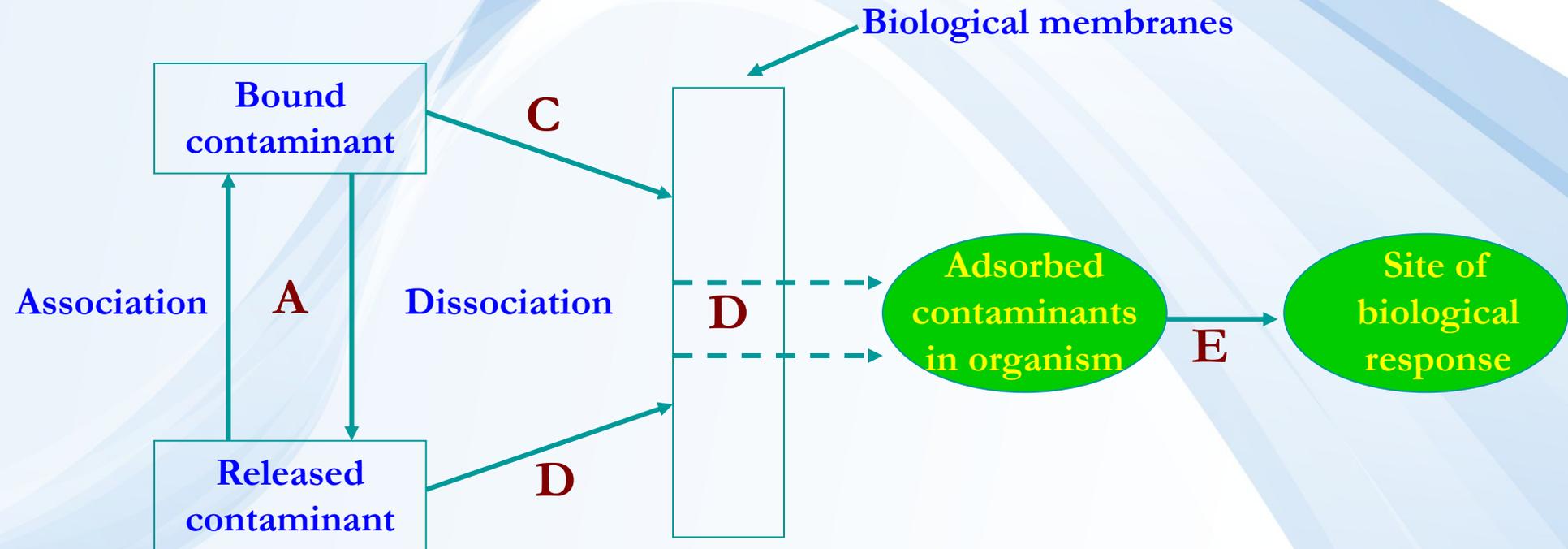
Bioavailability processes can be defined as the individual physical, chemical and biological interactions that determine the exposure of organisms to chemicals associated with soils and sediments.



K. Semple

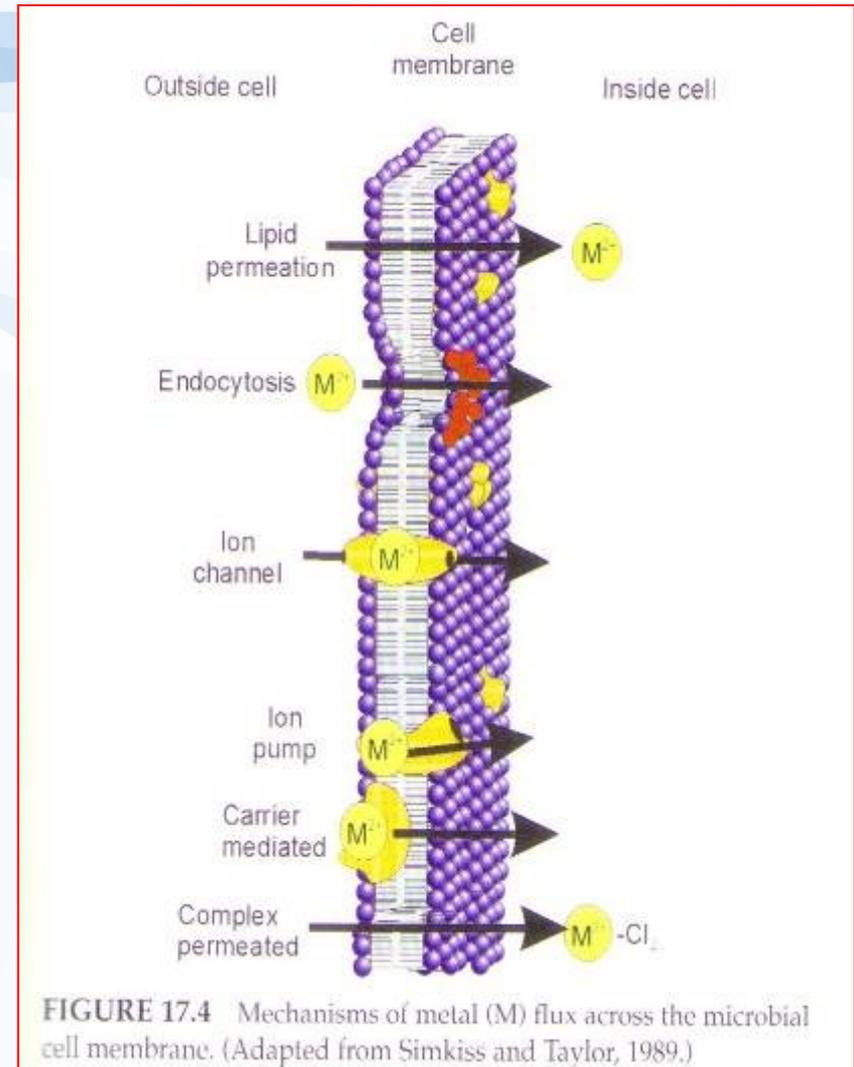
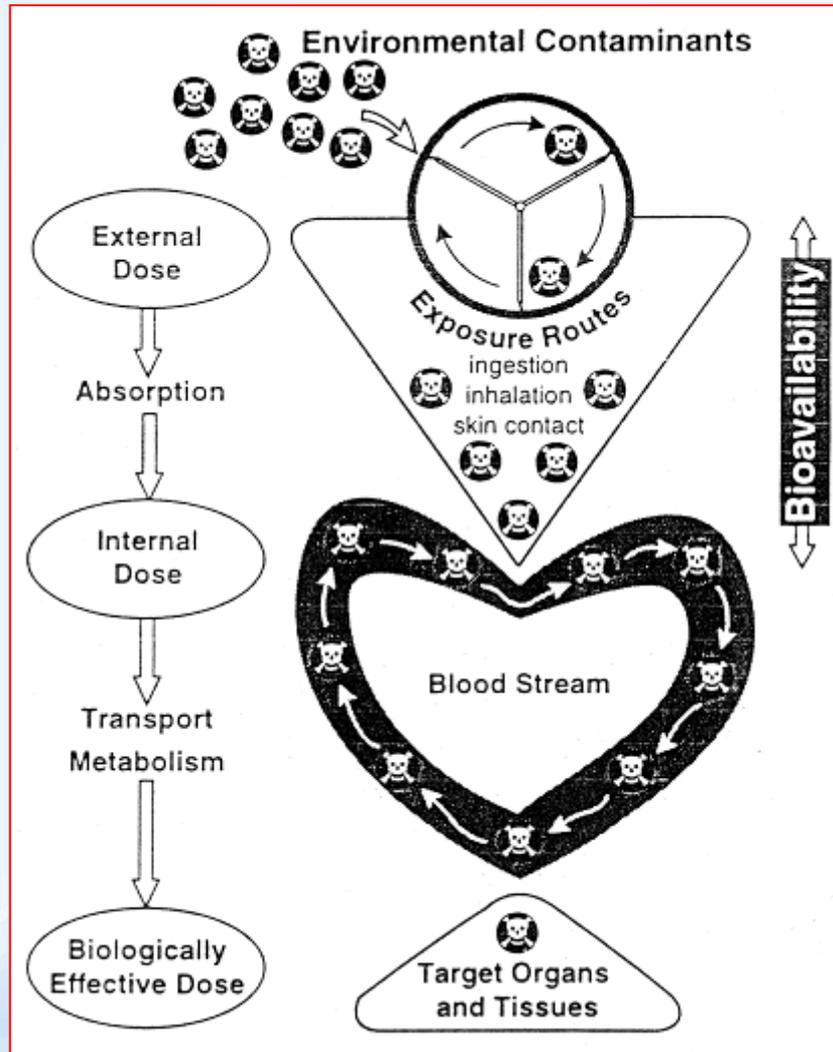
Bioavailability

In both soil and sediment, processes that determine exposure to contamination include release of a solid-bound contaminant (A) and subsequent transport (B), transport of bound contaminants (C), uptake across a physiological membrane (D), and incorporation into a living system (E). (A, B, C, D – bioavailability processes)

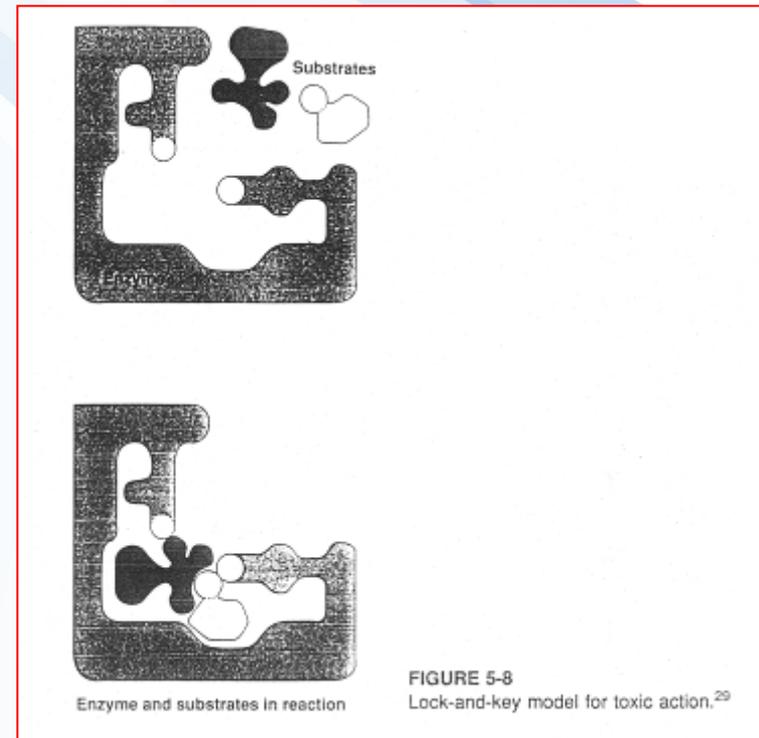
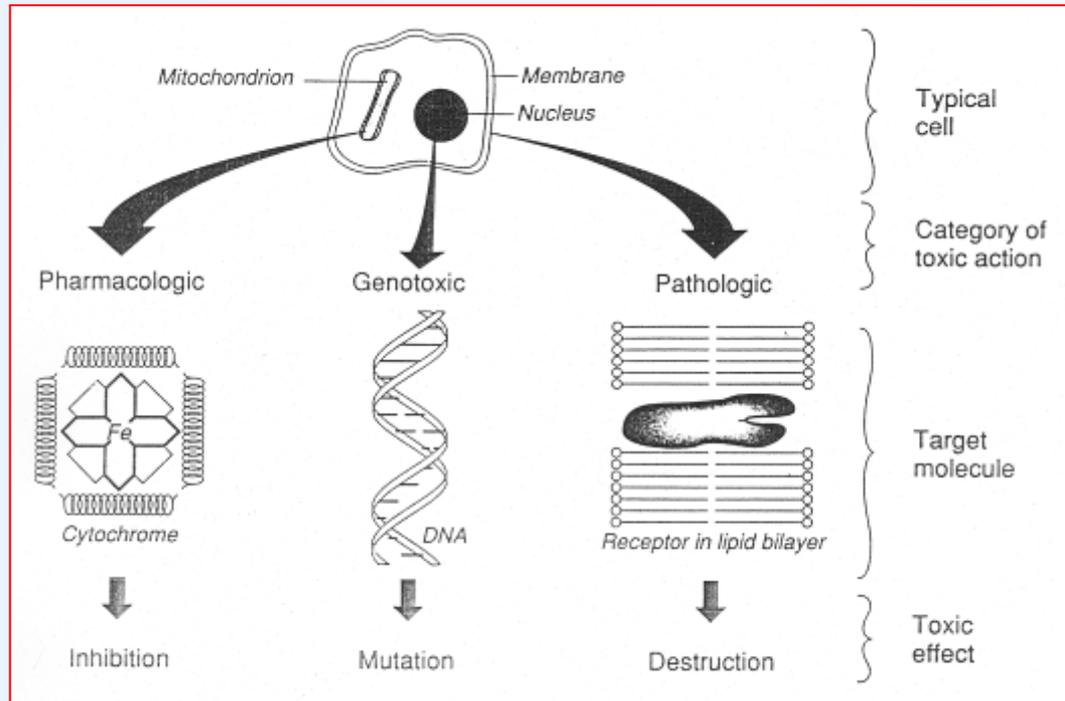


Ehlers and Luthy, 2003

Chemicals in the living organisms



Toxic effects of chemical compounds



Environmental transport and transformation processes

Chemodynamics

vapour pressure,
vaporisation rate

solubility,
diffusion

adsorption,
desorption

transport in
biological systems

Chemical and biochemical transformations

photochemical
reactions

redox reactions
(abiotic, biotic)

hydrolysis reactions

microbial transformations
(enzymatic)

Figure 5.1.2 Basic principles of pollutant distribution and transformation

Chemical transformation processes

Processes – reactions, when attend to the disappearance of chemical bonds and origin of new ones:

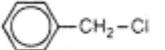
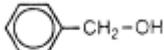
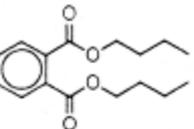
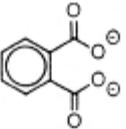
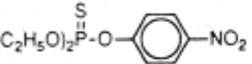
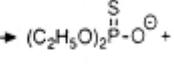
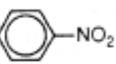
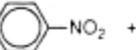
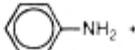
↪ **Abiotic** (without present living organisms) – the result is a new compound:

- **chemical** (redox, hydrolysis),
- **photochemical**:
 - **direct** photolysis (direct absorption of light)
 - **indirect** photolysis (reaction with reactive particles – free radicals, singlet oxygen)

↪ **Biotic**:

- **biological (microbial degradation)** – it can leads to the environmental mineralisation.

TABLE 12.1 Examples of Environmentally Relevant Chemical Reactions

Reactants	Products	Equation Number
Nucleophilic substitution		
 + H ₂ O	 + H ⁺ + Cl ⁻	(12-1)
Benzyl chloride	Benzyl alcohol	
CH ₃ Br + H ₂ O	CH ₃ OH + H ⁺ + Br ⁻	(12-2)
Methyl bromide	Methanol	
CH ₃ Br + SH ⁻	CH ₃ SH + Br ⁻	(12-3)
Methyl bromide	Methyl mercaptan	
Elimination		
Cl ₂ HC-CHCl ₂ + OH ⁻	ClHC=CCl ₂ + Cl ⁻ + H ₂ O	(12-4)
1,1,2,2-Tetrachloroethane	Trichloroethene	
Ester hydrolysis		
 + 2 OH ⁻	 + 2 HO-C ₄ H ₉	(12-5)
Dibutyl phthalate	Phthalate	Butanol
 + OH ⁻	 + HO- 	(12-6)
Parathion	O,O-Diethylthiophosphoric acid	p-Nitrophenol
Oxidation		
2 CH ₃ SH + 1/2 O ₂	H ₃ C-S-S-CH ₃ + H ₂ O	(12-7)
Methyl mercaptan	Dimethyl disulfide	
Reduction		
 + "reduced species" + 6H ⁺	 + "oxidized species" + 2H ₂ O	(12-8)
Nitrobenzene	Aniline	

Chemical transformation processes

Chemical transformation processes

- ↪ One or more reactions of given compound is ongoing under given environmental conditions and what reaction products can be expected ?
- ↪ What is a kinetic of different reactions ?
- ↪ How is a effect of important environmental variables such as a temperature, pH, redox conditions, ionic power, presence of other dissolved compounds or concentration and type of solid phases on the behaviour of given compound during the transformation process ?

For answering of these questions - we need to the reaction mechanism of compound transformation.

Chemical transformation processes – reaction kinetics

Reaction of the first order:

Velocity constant of the 1. order

$$d[A] / dt = -k * [A]$$

Integration from $[A] = [A]_0$ in time $t = 0$ to $[A] = [A]_t$ in time $t = t$:

$$[A]_t = [A]_0 * e^{-kt}$$

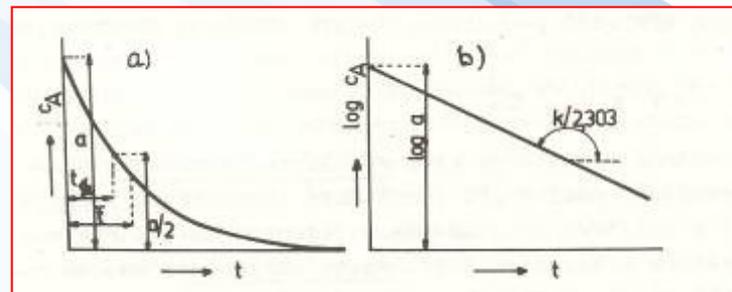
Half-life of the 1.st order reaction:

$$t_{1/2} = \ln 2 / k = 0,693 / k$$

Reaction of the second order:

$$d[A] / dt = -k * [A] * [B]$$

$t_{1/2}$ for losses of compound A = $\ln 2 / k [B]$



Hydrolysis

Nucleophilic substitution of halogens on the saturated C atom

S_N2 mechanism

S_N1 mechanism

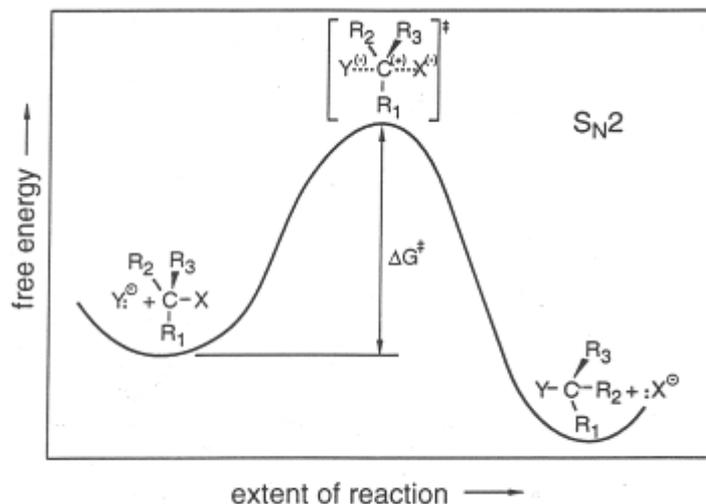


Figure 12.3 Two-dimensional portrayal of relative free energies exhibited by the educts, activated complex, and products of an S_N2 reaction.

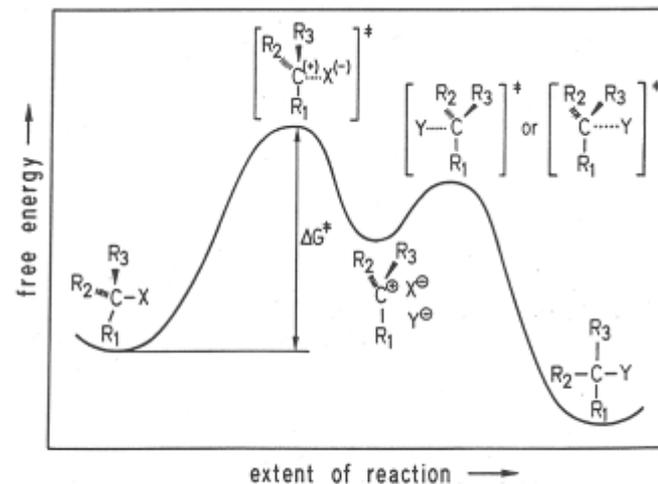


Figure 12.4 Two-dimensional portrayal of the relative free energies exhibited by educt, activated complexes, an intermediate, and product of an S_N1 reaction.

Oxidation

Process, where electron-deficient particle (oxidant) receives electrons from substance, which is oxidized.

Examples of oxidants present under environmental conditions in sufficient high concentrations and react quickly with organic substances:

- ↪ alkoxy radicals ($\text{RO}\bullet$)
- ↪ peroxy radicals ($\text{ROO}\bullet$)
- ↪ hydroxyl radicals ($\text{OH}\bullet$)
- ↪ singlet oxygen ($^1\text{O}_2$)
- ↪ ozone (O_3)

Most of these oxidants are directly or indirectly generated from compounds after interaction with sun light via excited form of molecule (photochemical excitation).

Oxidation is a main transformation process for the most or organics in troposphere and surface waters.

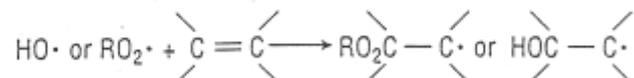
Oxidation

(1) H-atom transfer



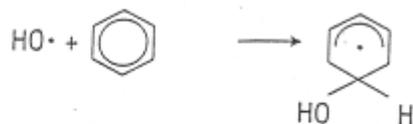
R = alkyl or H; n = 1 or 2

(2) Addition to double bonds



R = alkyl or H

(3) HO· addition to aromatics



(4) RO₂· transfer of O-atoms to certain nucleophilic species



Figure 3.31. The general reaction pathways for environmental oxidation. From Mill [49]. With permission.

Table 3.10. Half-lives (d) for tropospheric oxidation of various classes of organic compounds in the northern hemisphere

Alkanes	1 - 10
Alcohols	1 - 3
Aromatics	1 - 10
Olefins	0.06 - 1
Halomethanes	100 - 47,000

Reduction

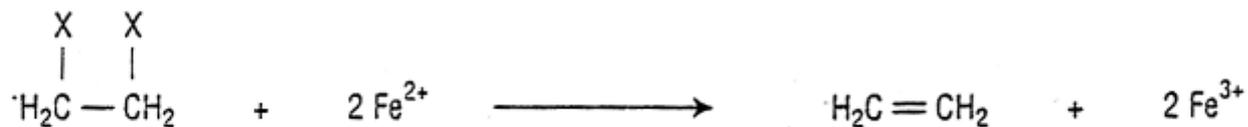
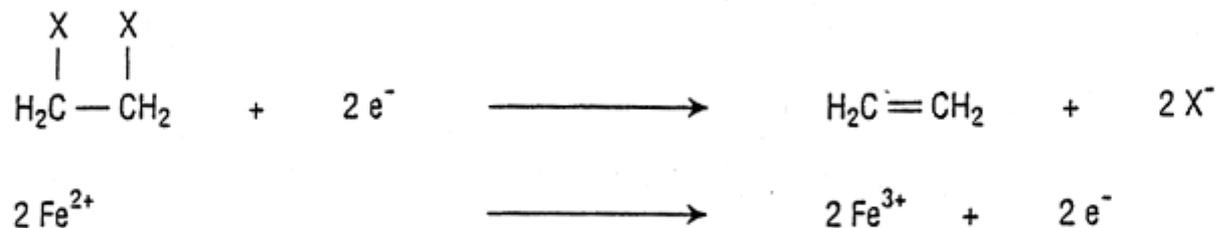
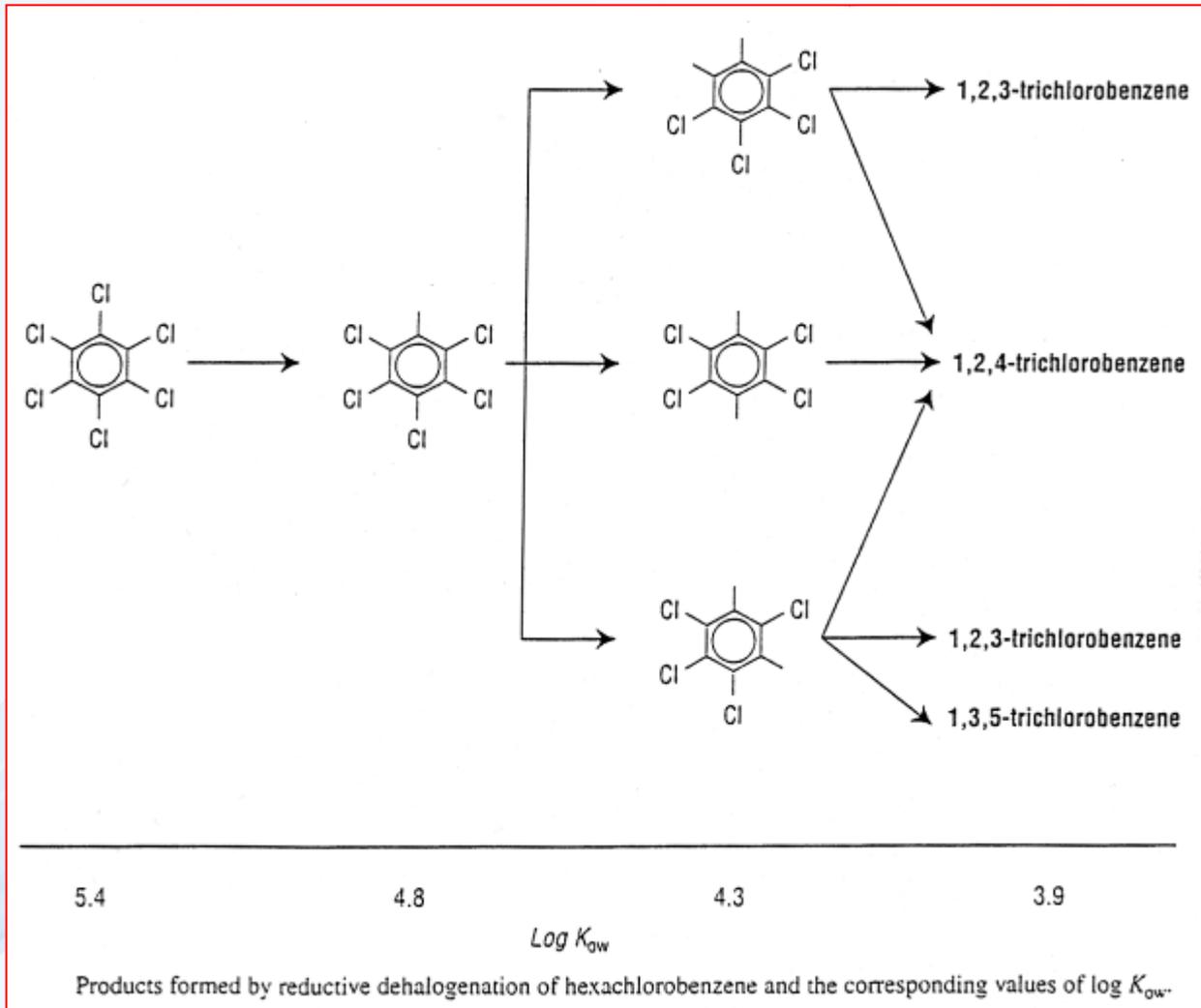
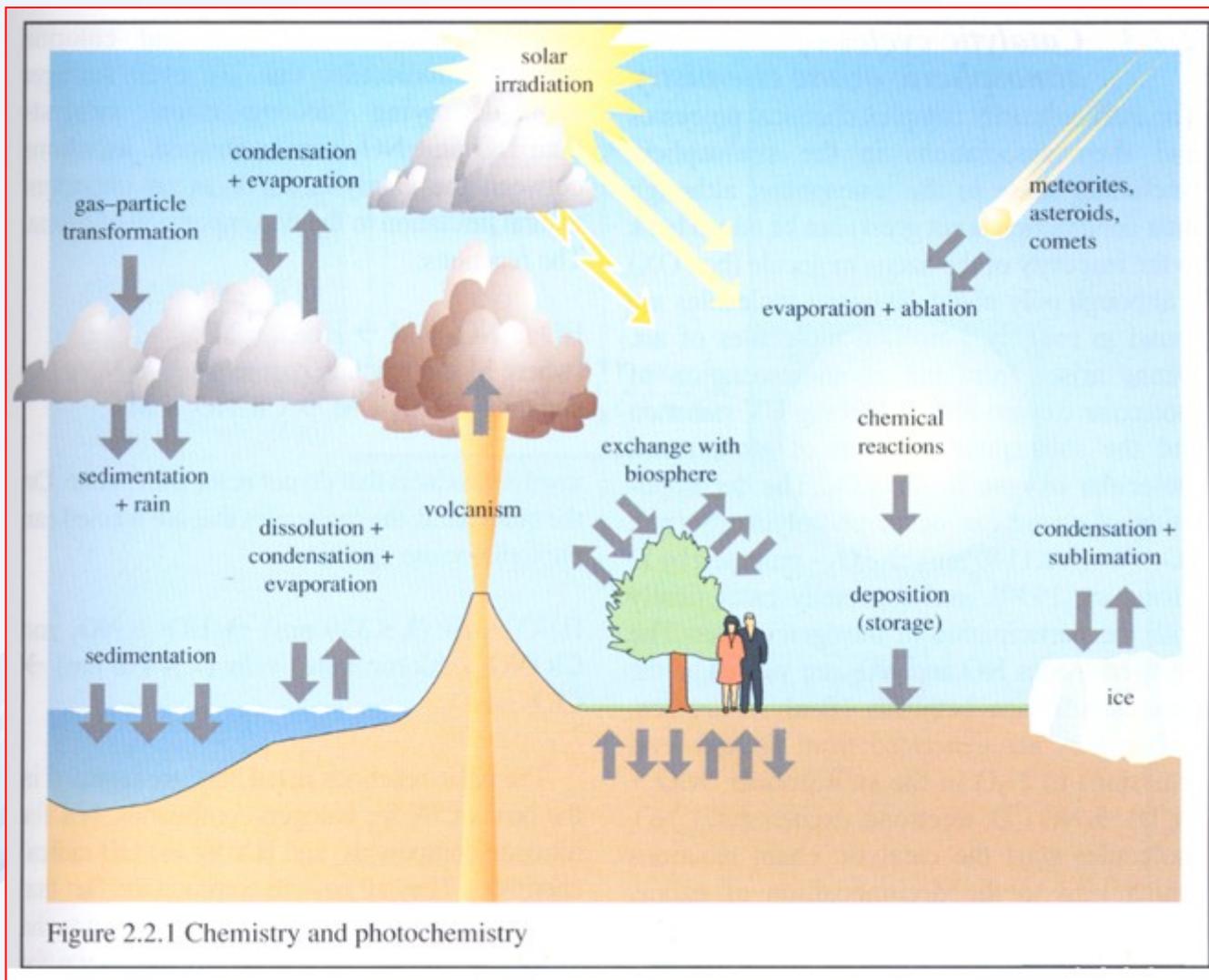


Figure 3.32. Example of a reductive transformation: electron transfer from Fe^{2+} to 1,2-dihalogen substituted ethane (X denotes a halogen atom).

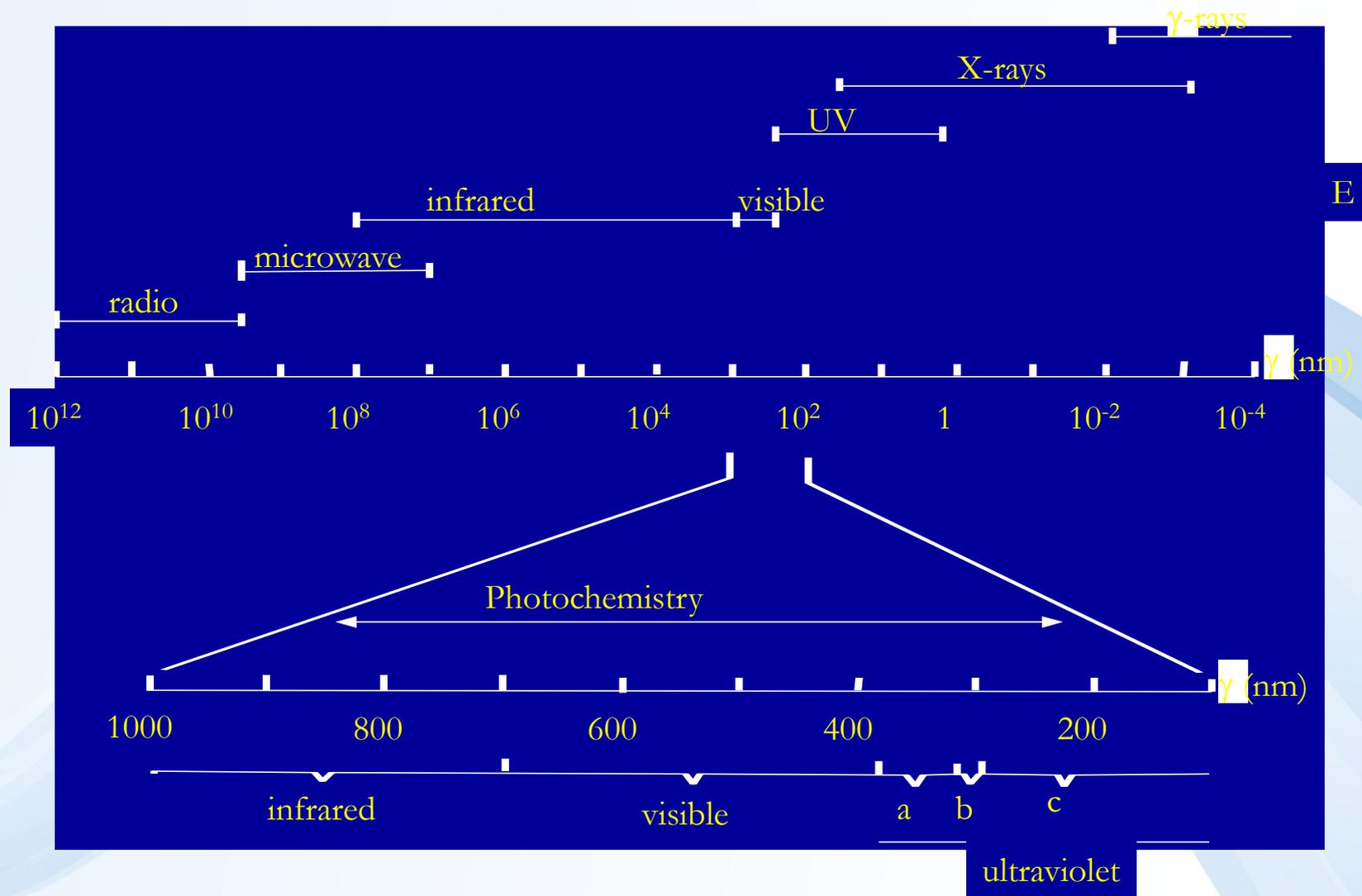
Reduction



Photochemical transformation processes



Photochemical transformation processes



Photochemical transformation processes

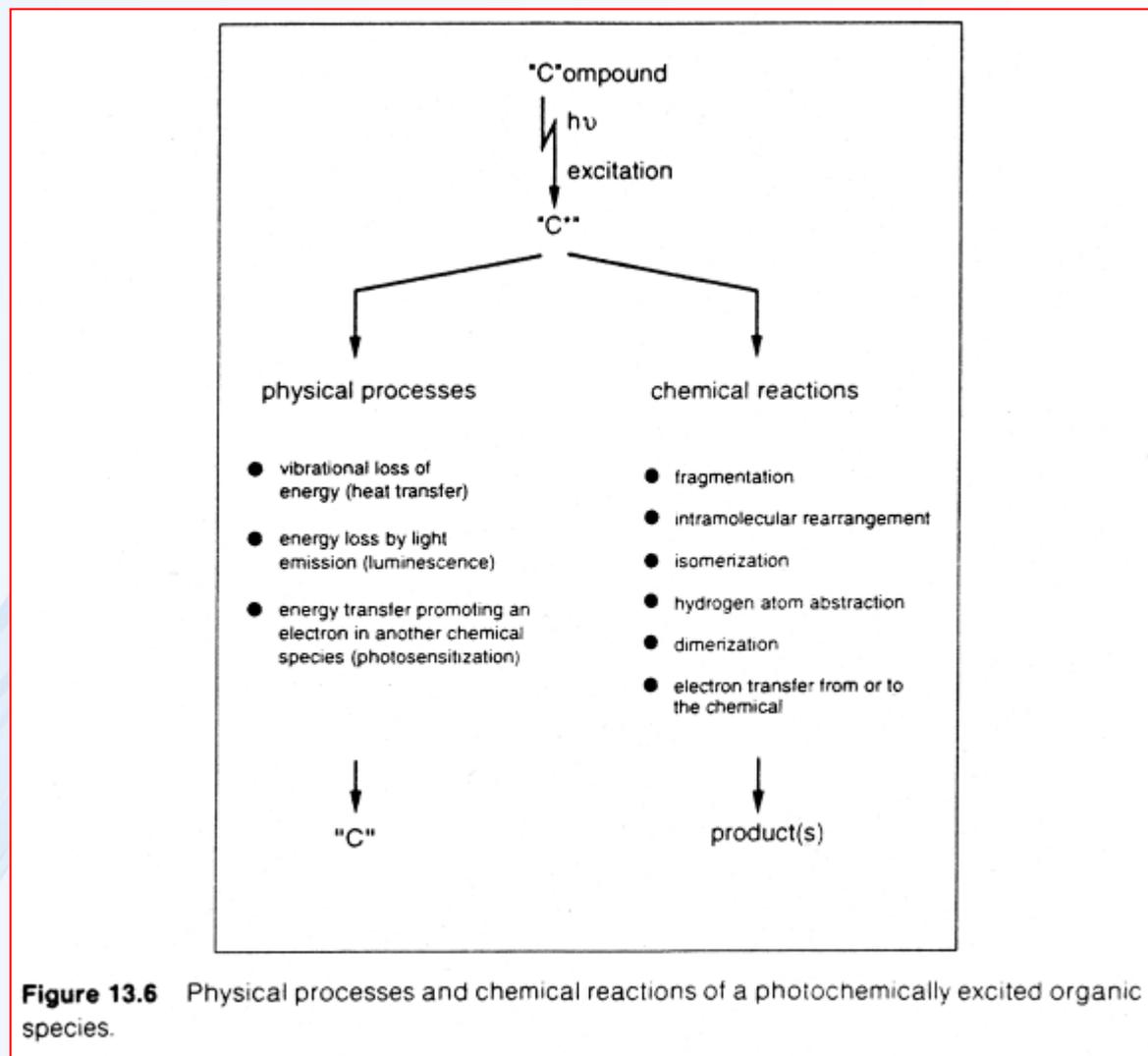
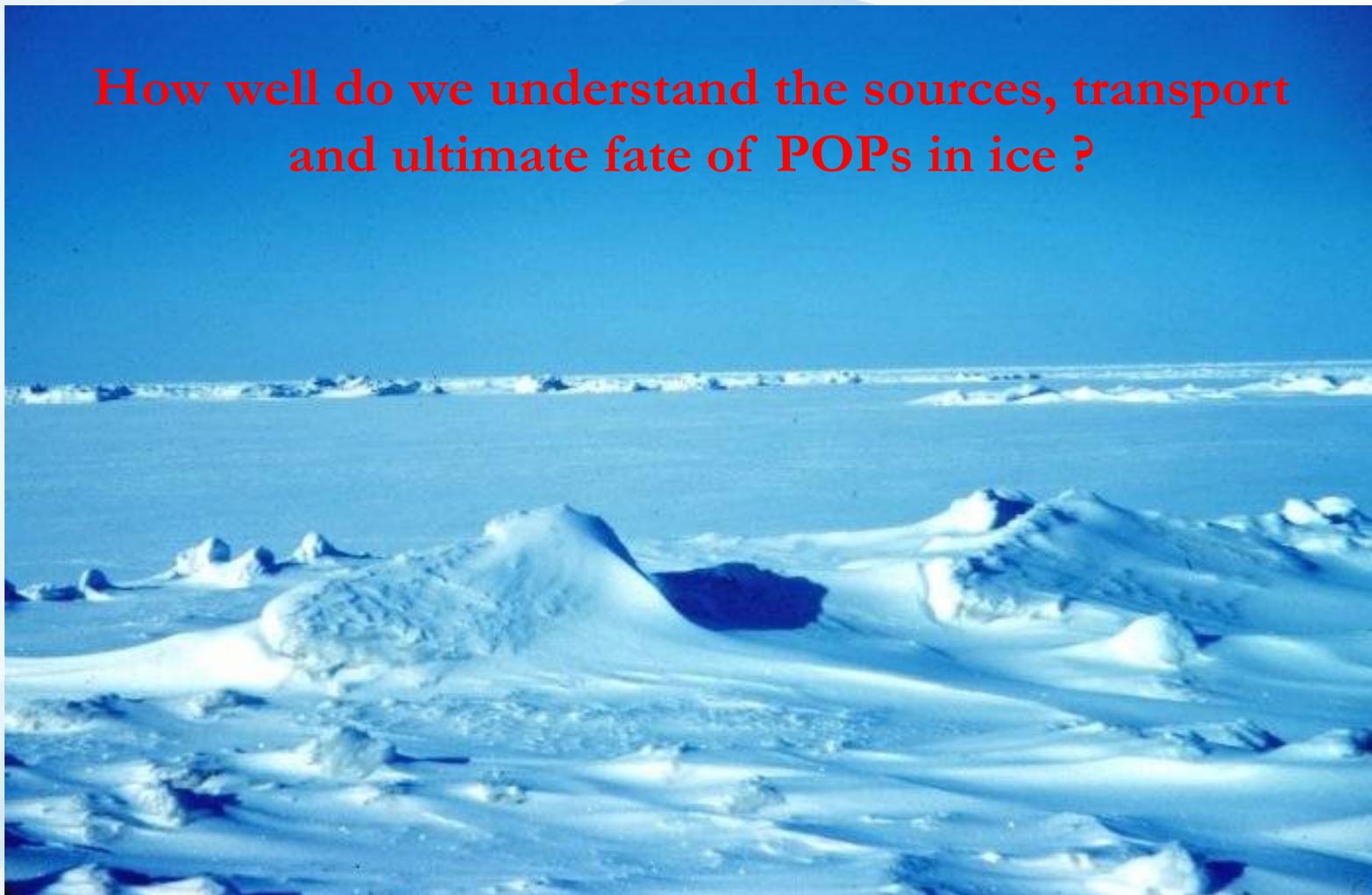


Figure 13.6 Physical processes and chemical reactions of a photochemically excited organic species.

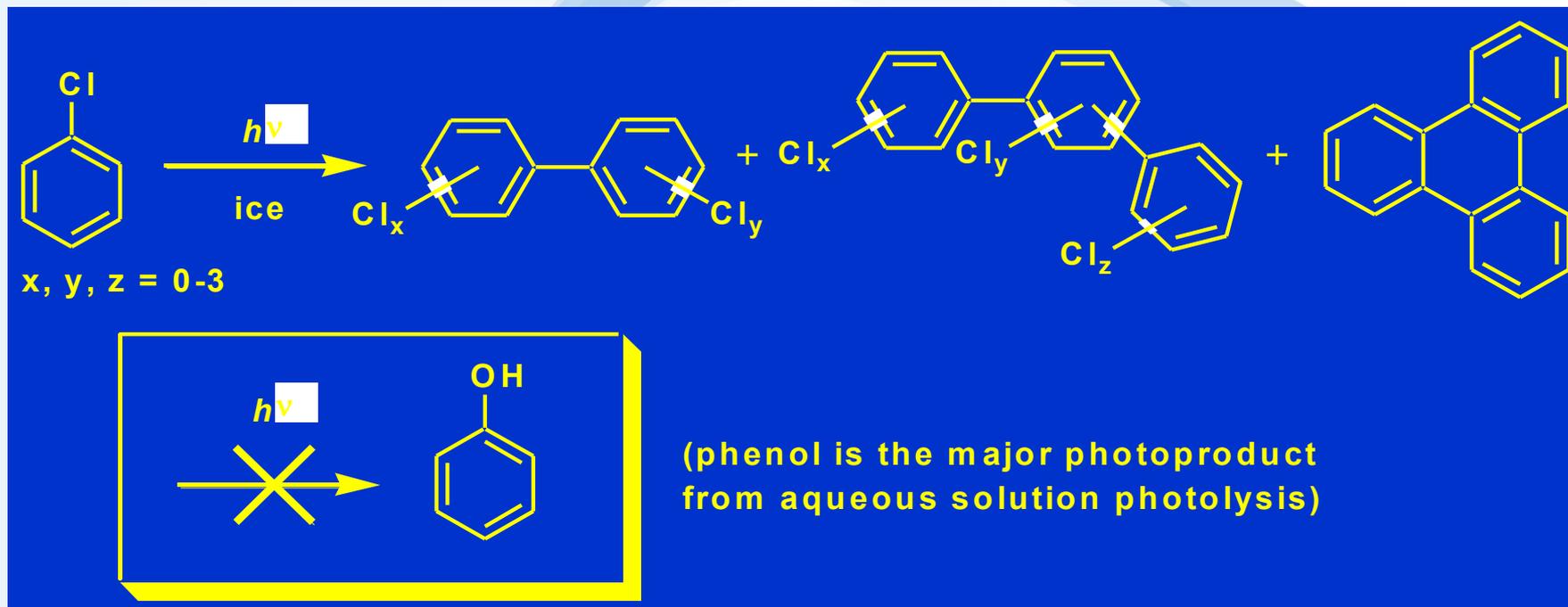
Photochemistry of organic pollutants in solid matrices

How well do we understand the sources, transport and ultimate fate of POPs in ice ?



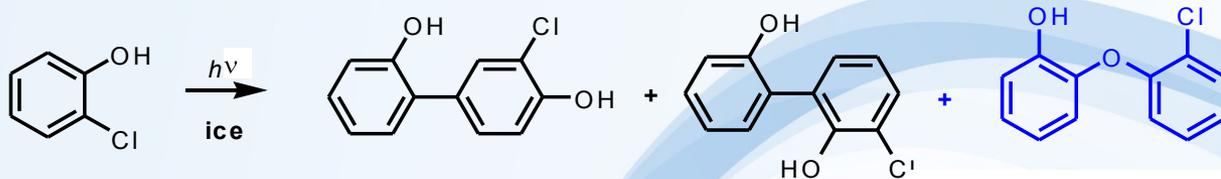
Ice Photochemistry of organic pollutants

Chlorobenzene - unique transformation pathways in ice matrix

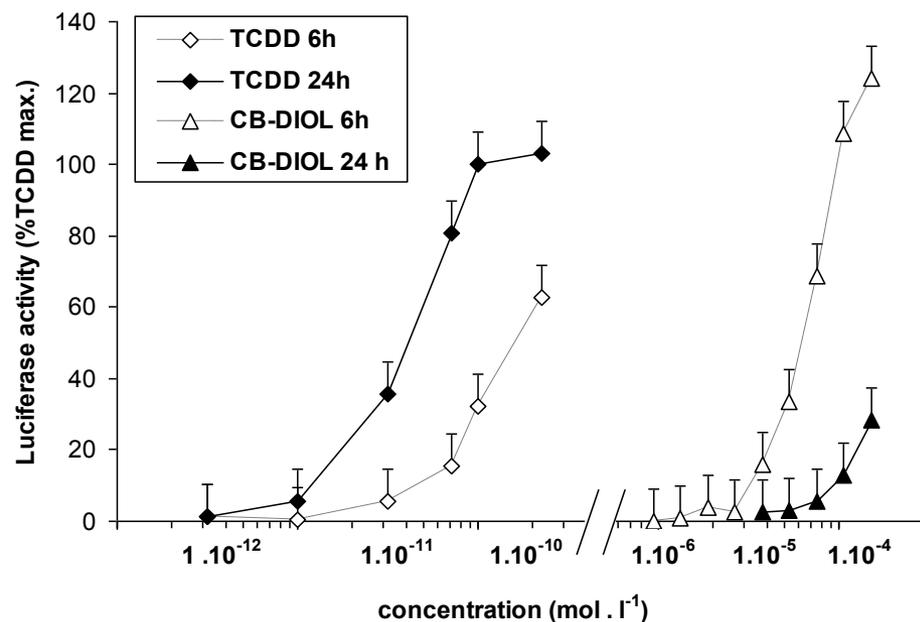
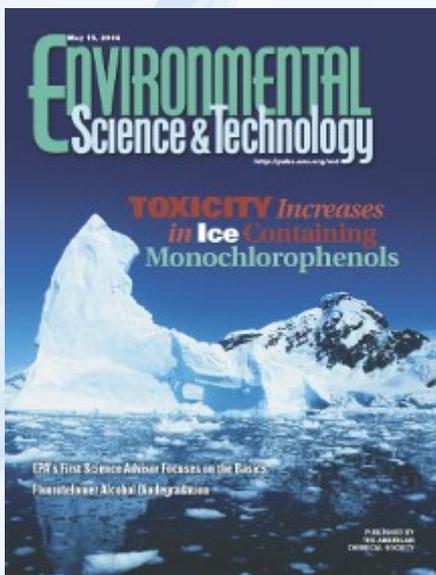


Klán P., Ansorgová A., Del Favero D., Holoubek I. *Tetrahedron Lett.* **2000**, 41, 7785-7789.

Toxicity increases in ice upon photolysis



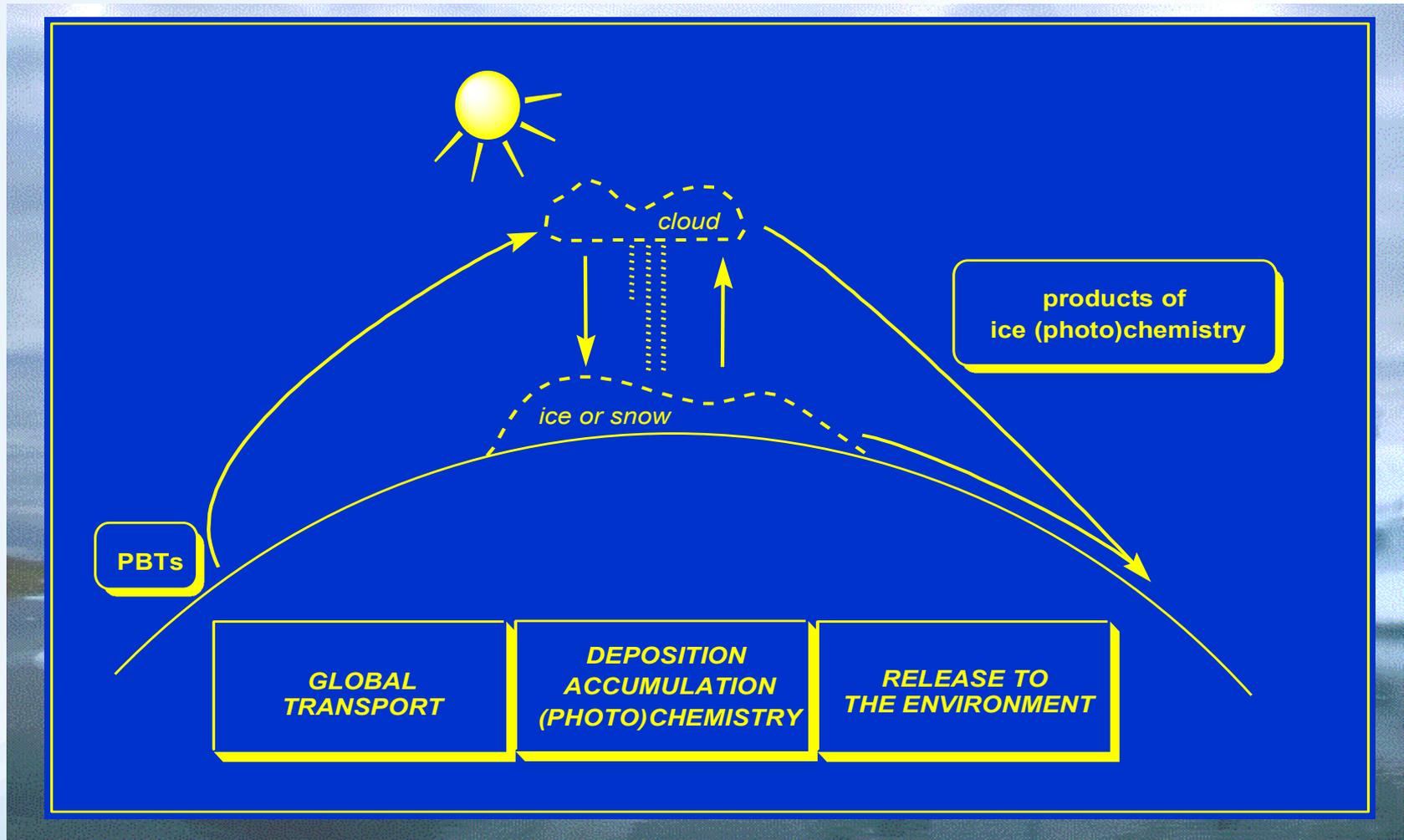
no photosolvolyis:



Induction of dioxin-like toxicity by photoproducts of *p*-chlorophenol in water ice (comparison with the toxic potency of 2,3,7,8-TCDD)

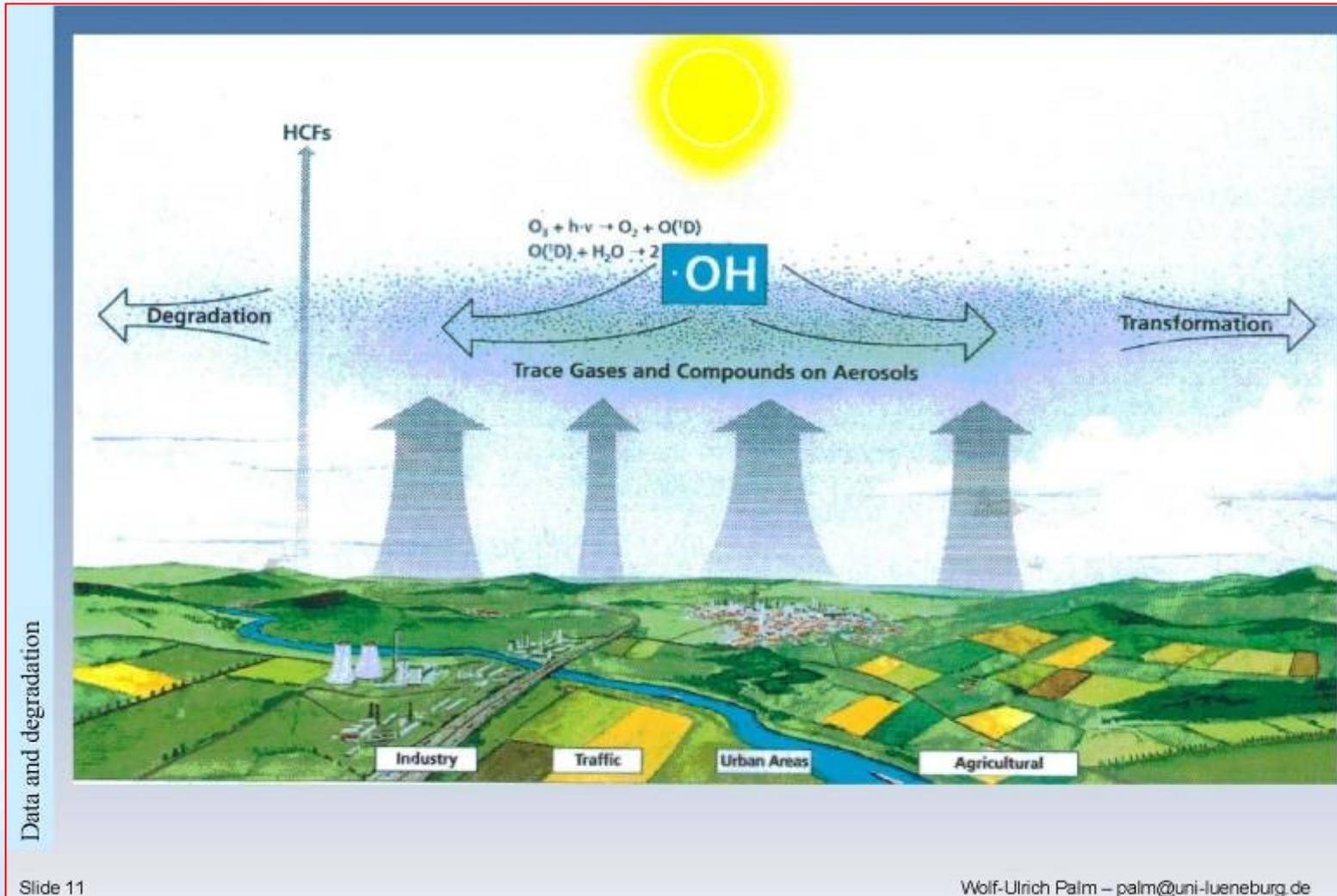
Blaha et al., 2004

Environmental consequences



Klán P., Holoubek I.: Chemosphere, 2002, 46, 1201-1210

OH radicals in the atmosphere



Biodegradation

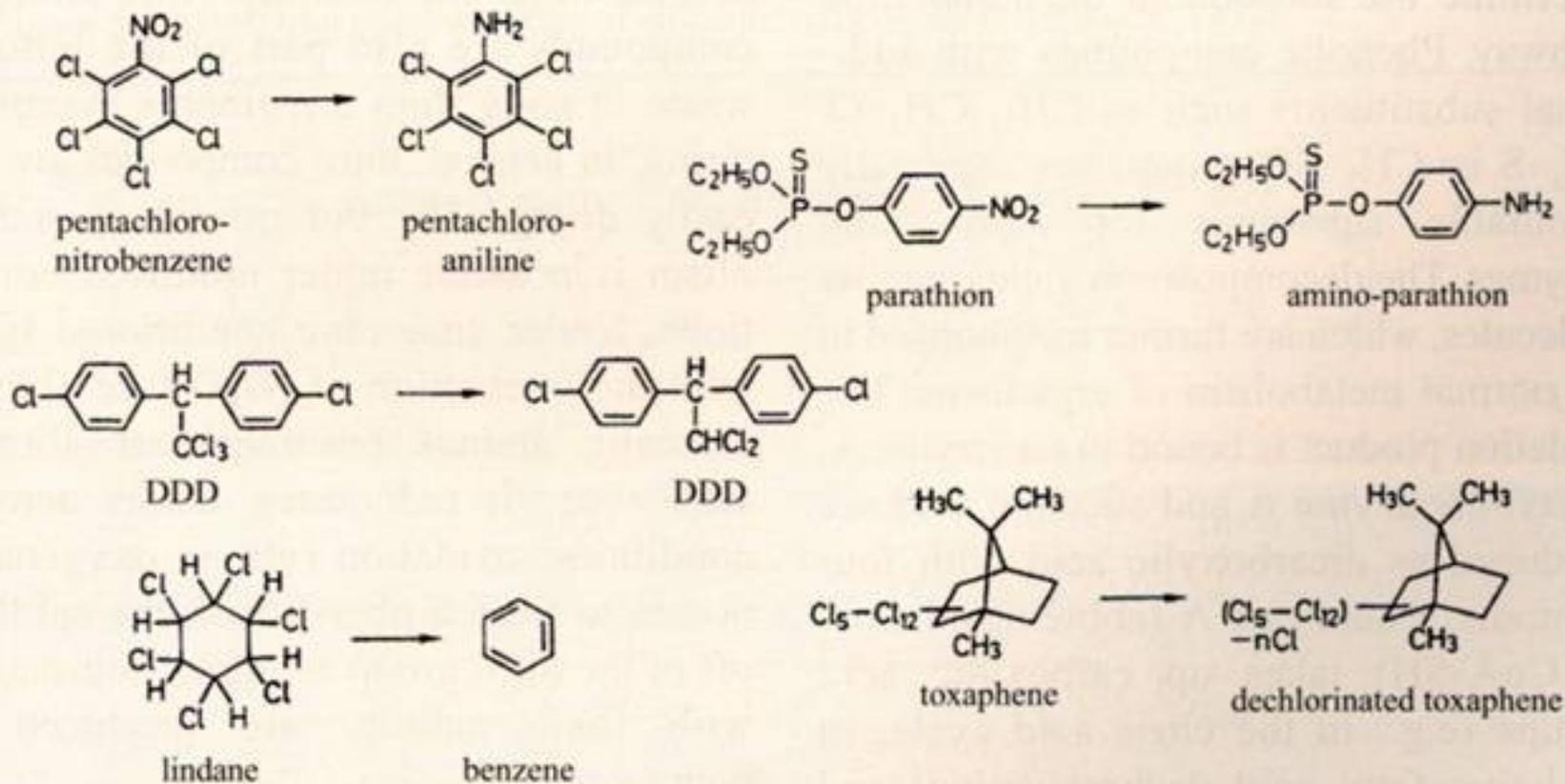


Figure 5.2.2 Reductive (anaerobic) reactions of xenobiotics

Biodegradation

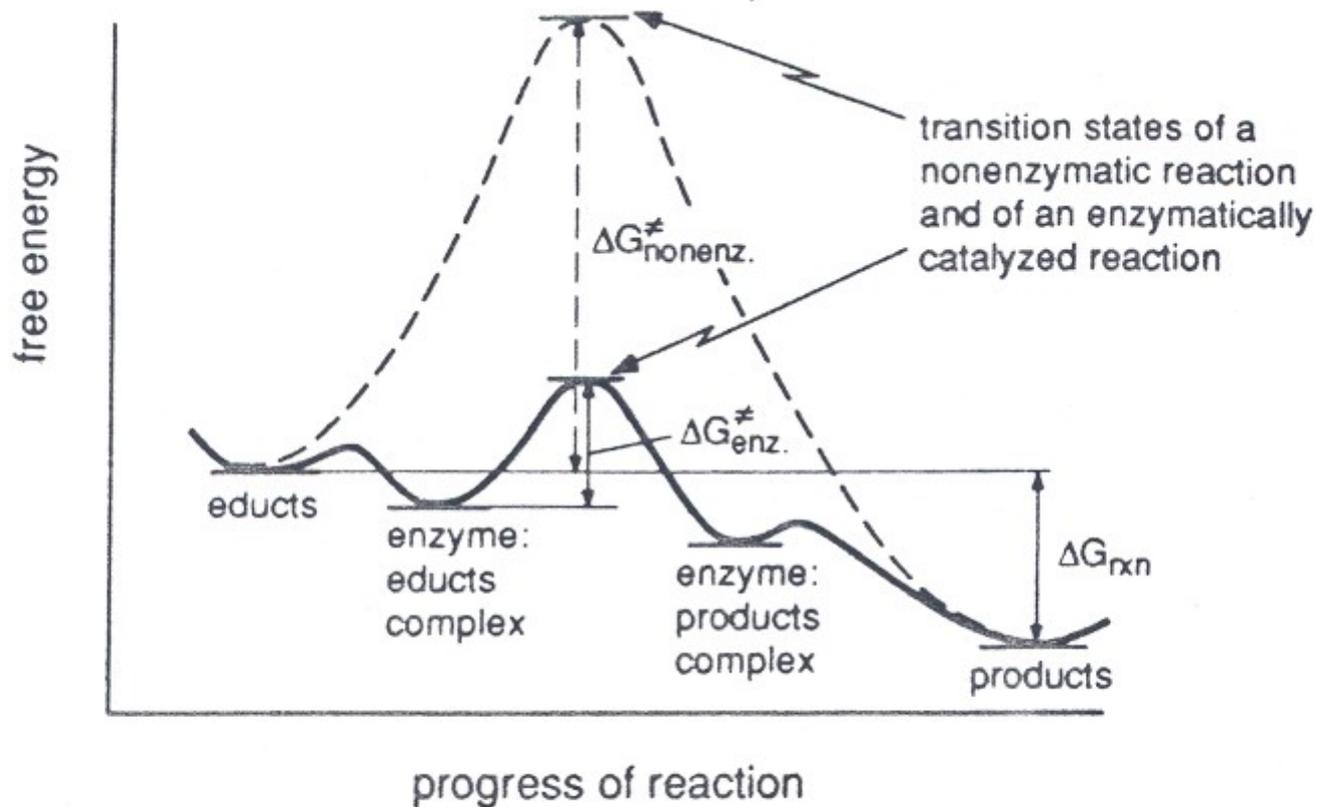


Figure 14.1 Schematic representation of the change in activation energy barriers for an enzymatically mediated reaction as compared to the analogous noncatalyzed chemical reaction.

Mechanisms of biotransformation of the xenobiotics in the living organisms

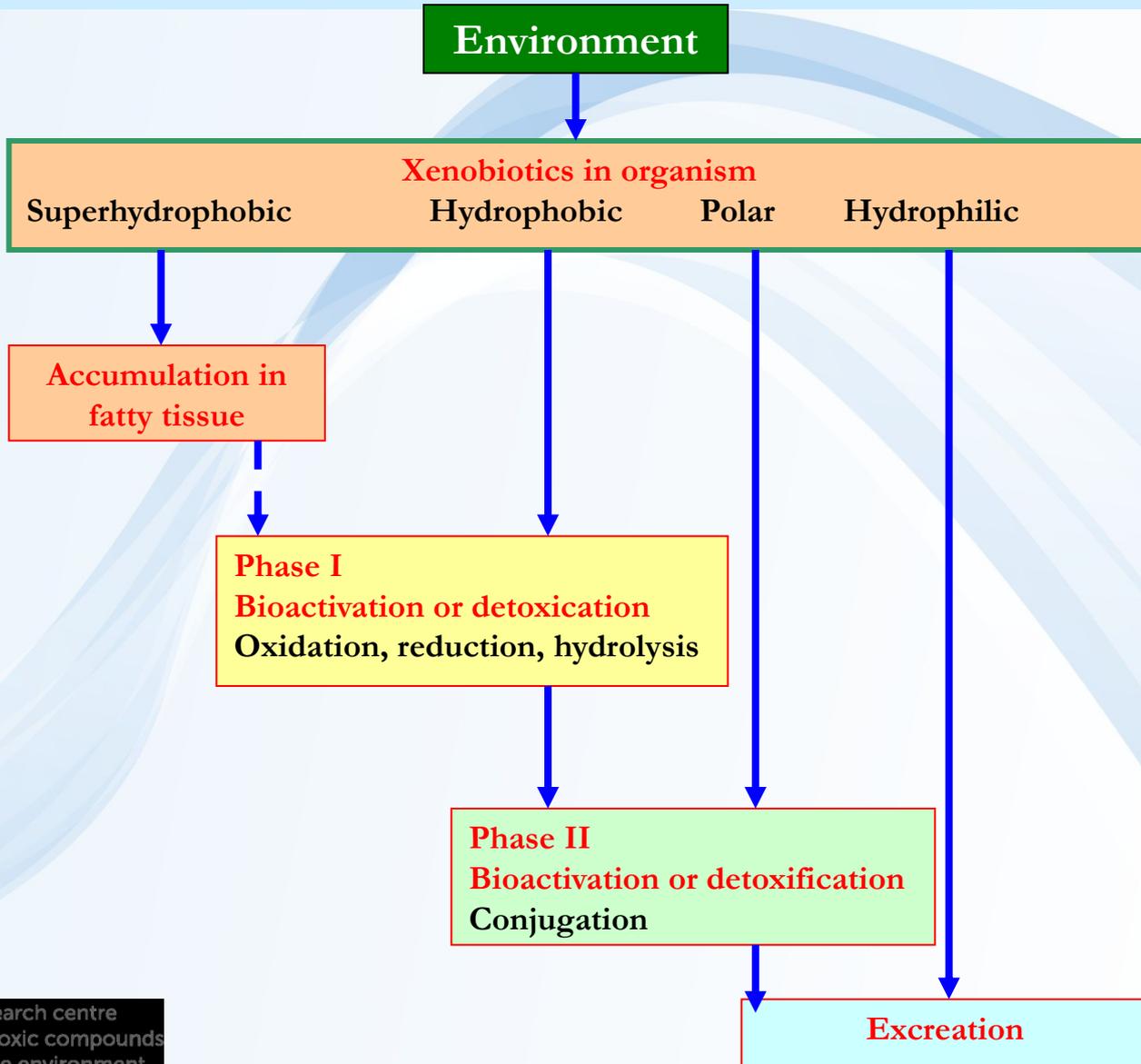
Types of biotransformation reactions

Two types:

Phase I – non-synthetic reactions – hydrolysis, oxidation, reduction – molecules of compound are changed by introducing of polar group (-OH, -COOH, -NH₂) – products are reactive compounds easily conjugated in the phase II

Phase II – synthetic reactions – conjugation – production of conjugates such are glucuronides, sulphates, acetyl and glutathion conjugates – results is conjugated product which can be eliminated by excrements

Mechanisms of biotransformation of the xenobiotics in the living organisms



Biotransformations

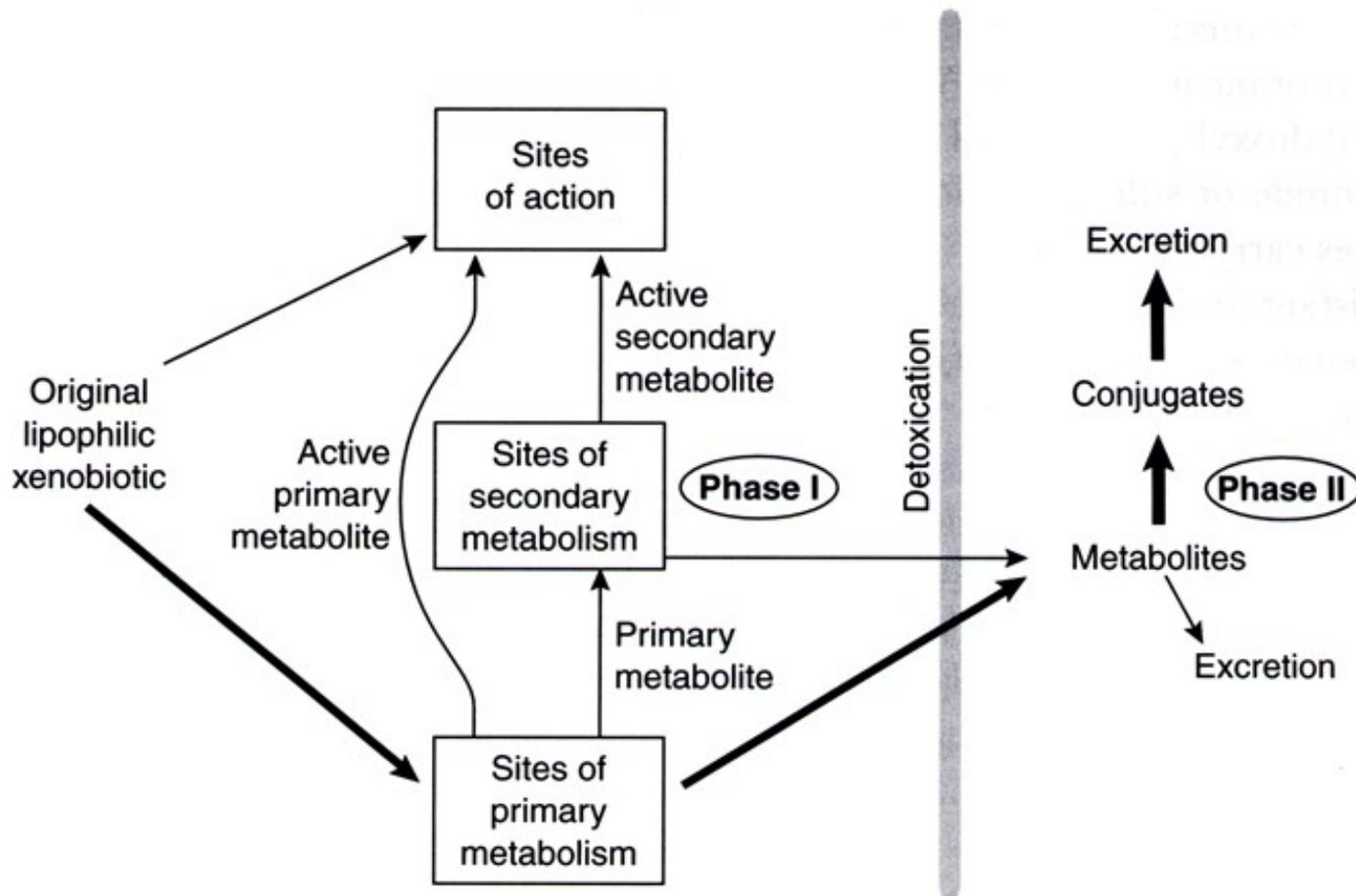


FIGURE 2.2 *Metabolism and toxicity.*

Biotransformations

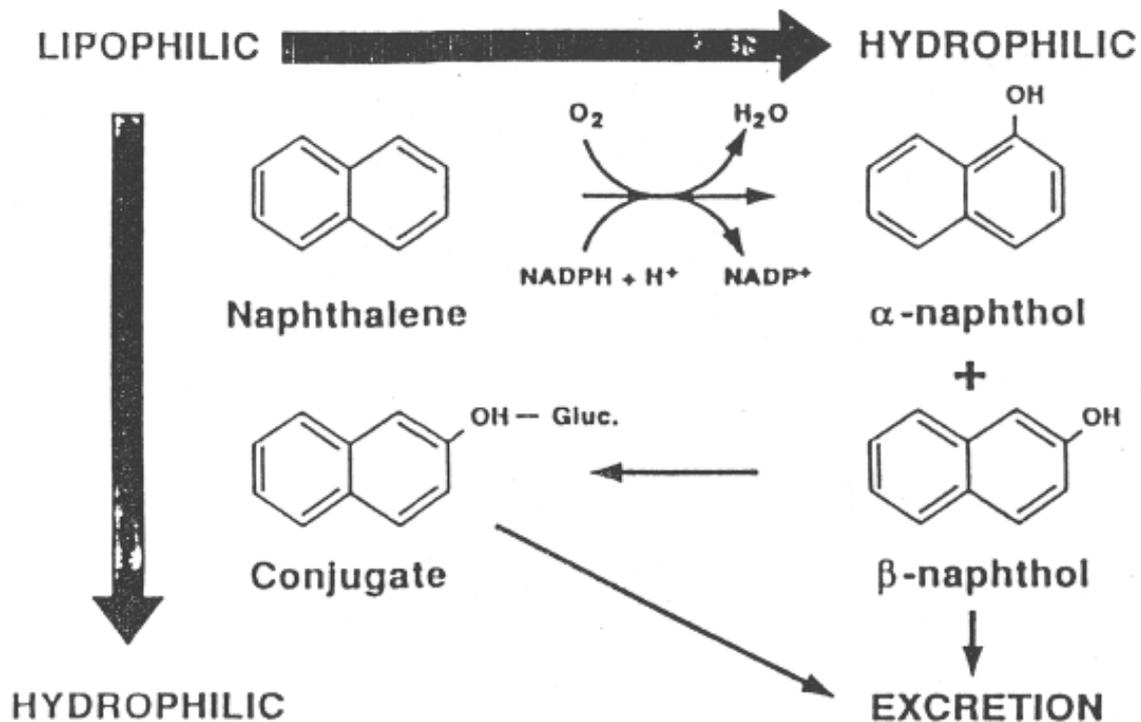


Figure 1. The cytochrome P-450 mixed function oxidase system facilitates excretion of lipophilic organic substrates in terrestrial and aquatic animals by producing metabolites that are more water soluble than the parent compound. Common metabolites of naphthalene are shown (after 2).