Fate of toxic compounds in the environment

Ivan Holoubek

STOCKHOLM
CONVENTION

RECETOX, Masaryk University, Brno, CR
holoubek@recetox.muni.cz; http://recetox.muni.cz

RECETOX - EU Centre of Excellence - http://recetox.muni.cz/

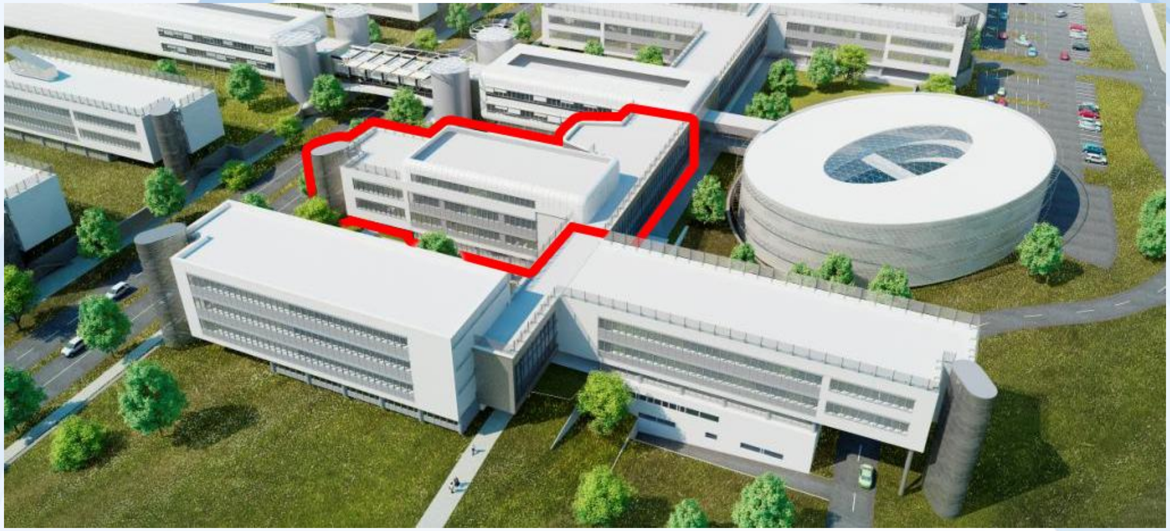
STOCKHOLM CONVENTION

SC Regional POPs Centre for Central and Eastern Europe

Research centre
for toxic compounds
in the environment

cetocoen

Research centre for toxic compounds in the environment



EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND
INVESTING IN YOUR FUTURE

2007–13
OP Research and Development for Innovations

RECETOX research team

15 teachers and professors

20 Ph.D. researchers

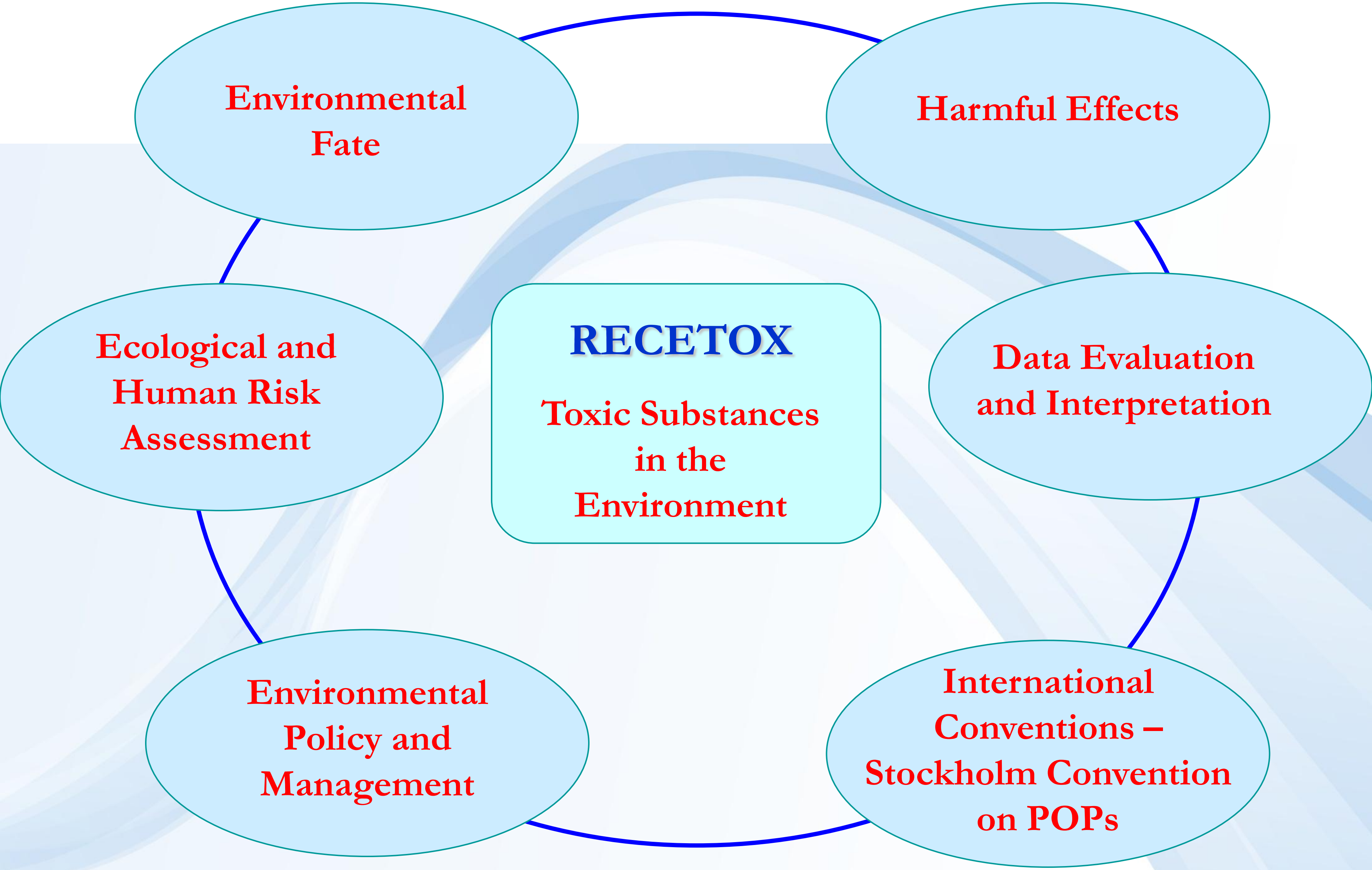
50 Ph.D. students

10 senior researchers and post-docs

6 technical and administrative stuff

http://recetox.muni.cz

Research centre
for toxic compounds
in the environment



RECETOX

Toxic Substances in the Environment

Environmental Fate

Harmful Effects

Data Evaluation and Interpretation

International Conventions – Stockholm Convention on POPs

Environmental Policy and Management

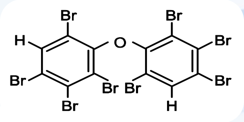
Ecological and Human Risk Assessment

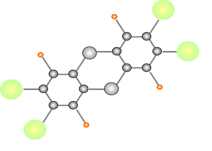
Research centre for toxic compounds in the environment

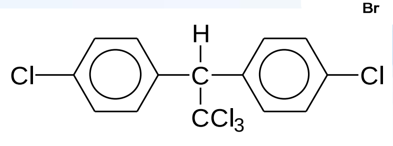
Study of the fate and harmful effects of environmental toxic compounds

Persistent organic pollutants

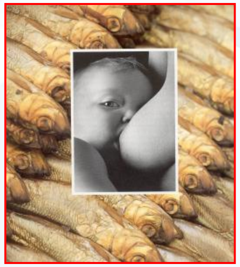
- Persistent

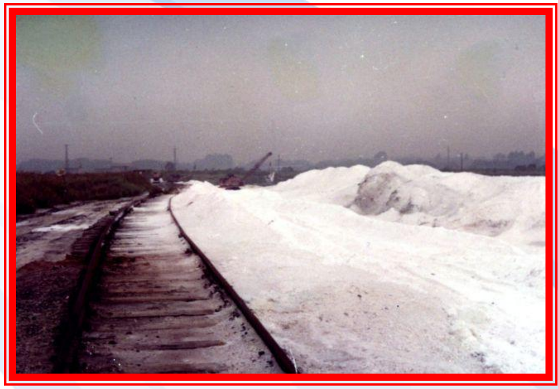




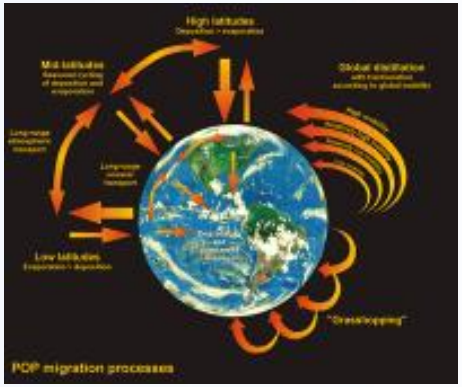


- Bioaccumulation



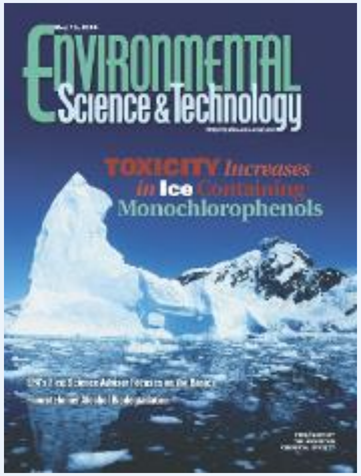


- Toxicity



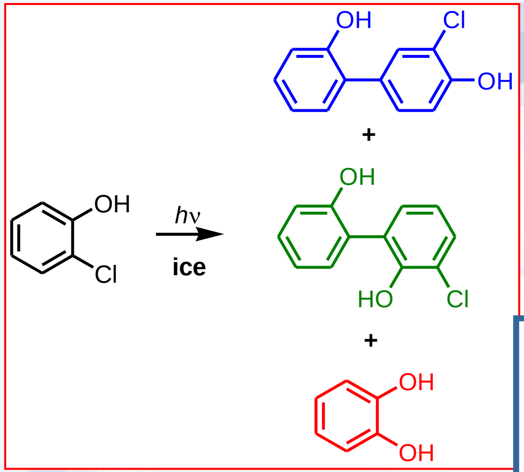
- Long-range transport

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

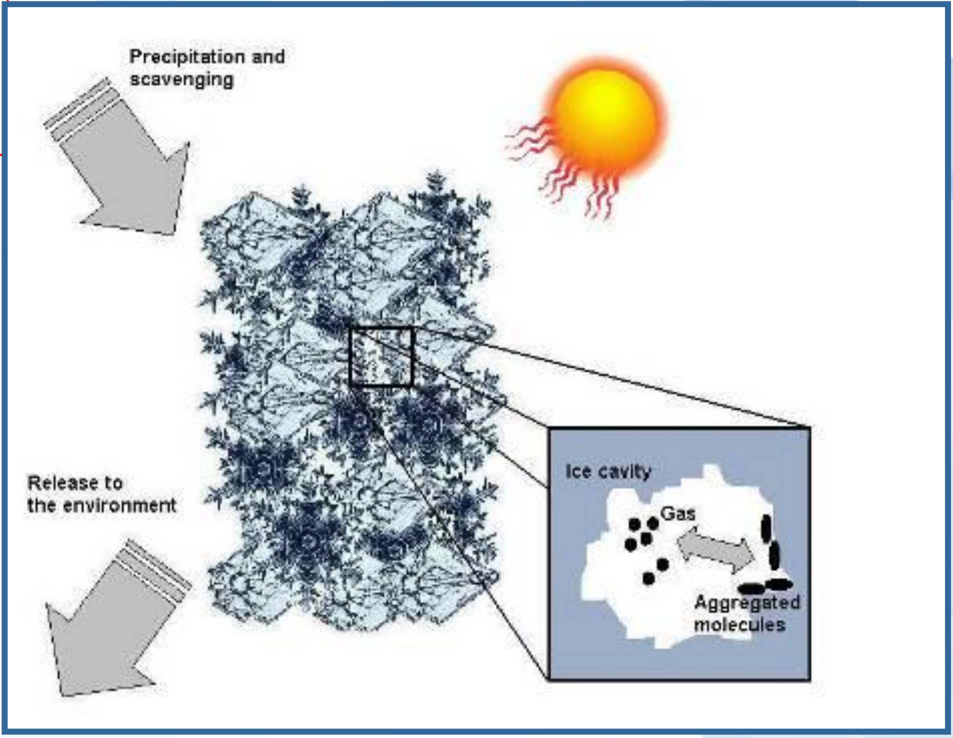


Environmental Science & Technology

TOXICITY Increases in Ice Containing Monochlorophenols



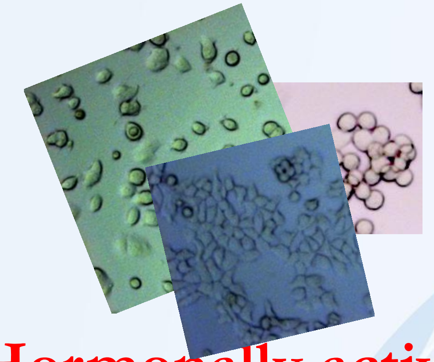
Photochemistry and fate of POPs polar areas



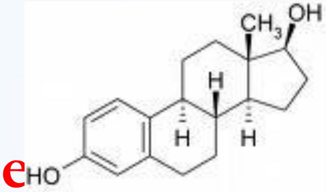
Research centre
for toxic compounds
in the environment

Ecotoxicology and harmull effects of pollutants

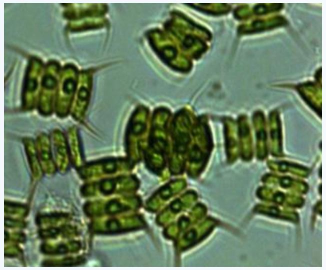
Bioassays for acute and chronic toxicity – air, water,soil



Hormonally active xenobiotics in waste waters



Blue-green algal (cyanobacte

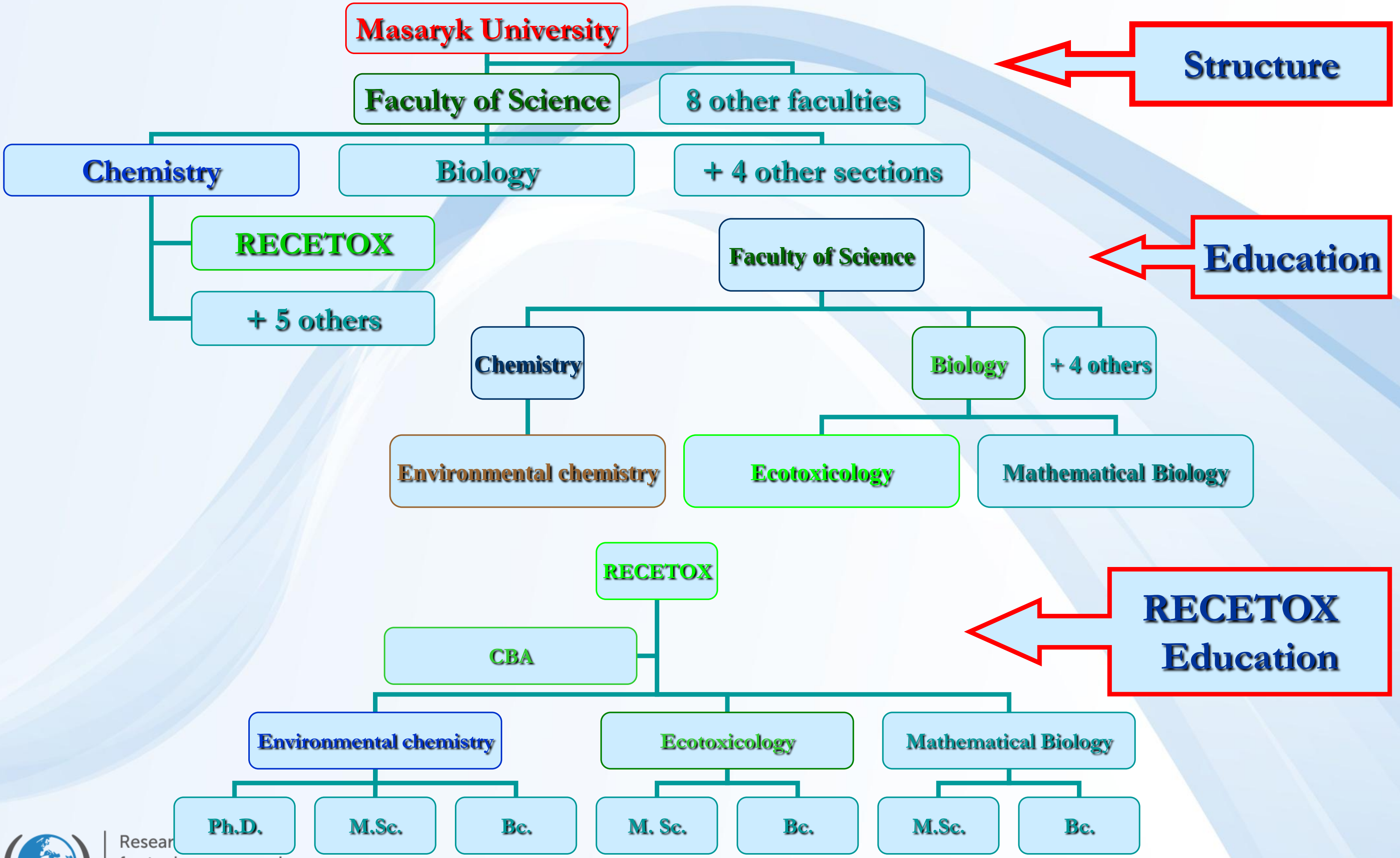


RECETOX activities

Persistent, bioacummulative 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



Masaryk University

Faculty of Science

8 other faculties

Chemistry

Biology

+ 4 other sections

RECETOX

+ 5 others

Structure

Faculty of Science

Chemistry

Biology

+ 4 others

Environmental chemistry

Ecotoxicology

Mathematical Biology

Education

RECETOX

CBA

Environmental chemistry

Ecotoxicology

Mathematical Biology

Ph.D.

M.Sc.

Bc.

M. Sc.

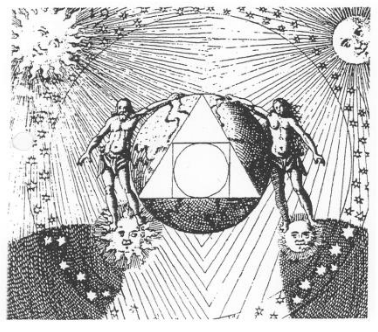
Bc.

M.Sc.

Bc.

RECETOX Education

RECETOX Conceptual approaches



Ecological risk assessment

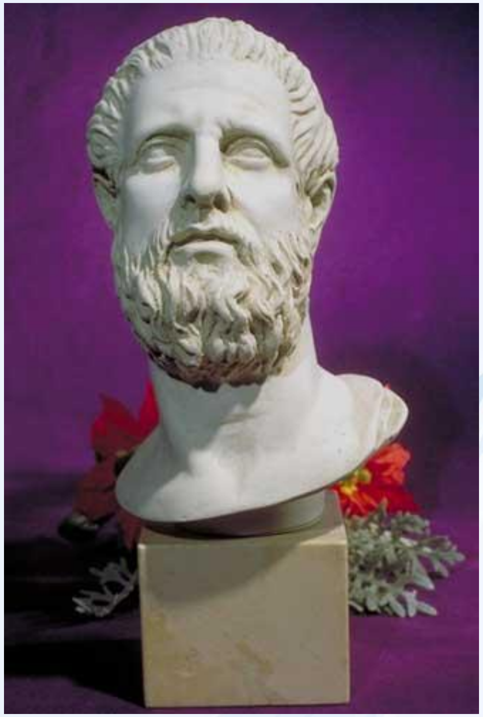
Environmental chemistry

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

Research centre
for toxic compounds
in the 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

Human care products

(cosmetics, perfumes (~300), chemicals for hair bleaching and permanents, UV-filters)

(n=???)

Industrial chemicals

(~ 80000 registered by EPA,
~ 4000 neurotoxins)

Pharmaceuticals

antibiotics, betablockers, anti-epileptics, analgetics)

~ 50000 producs,

~ 2900 effective substances

Metabolites

Tensides, detergents

(~ 800 substances)

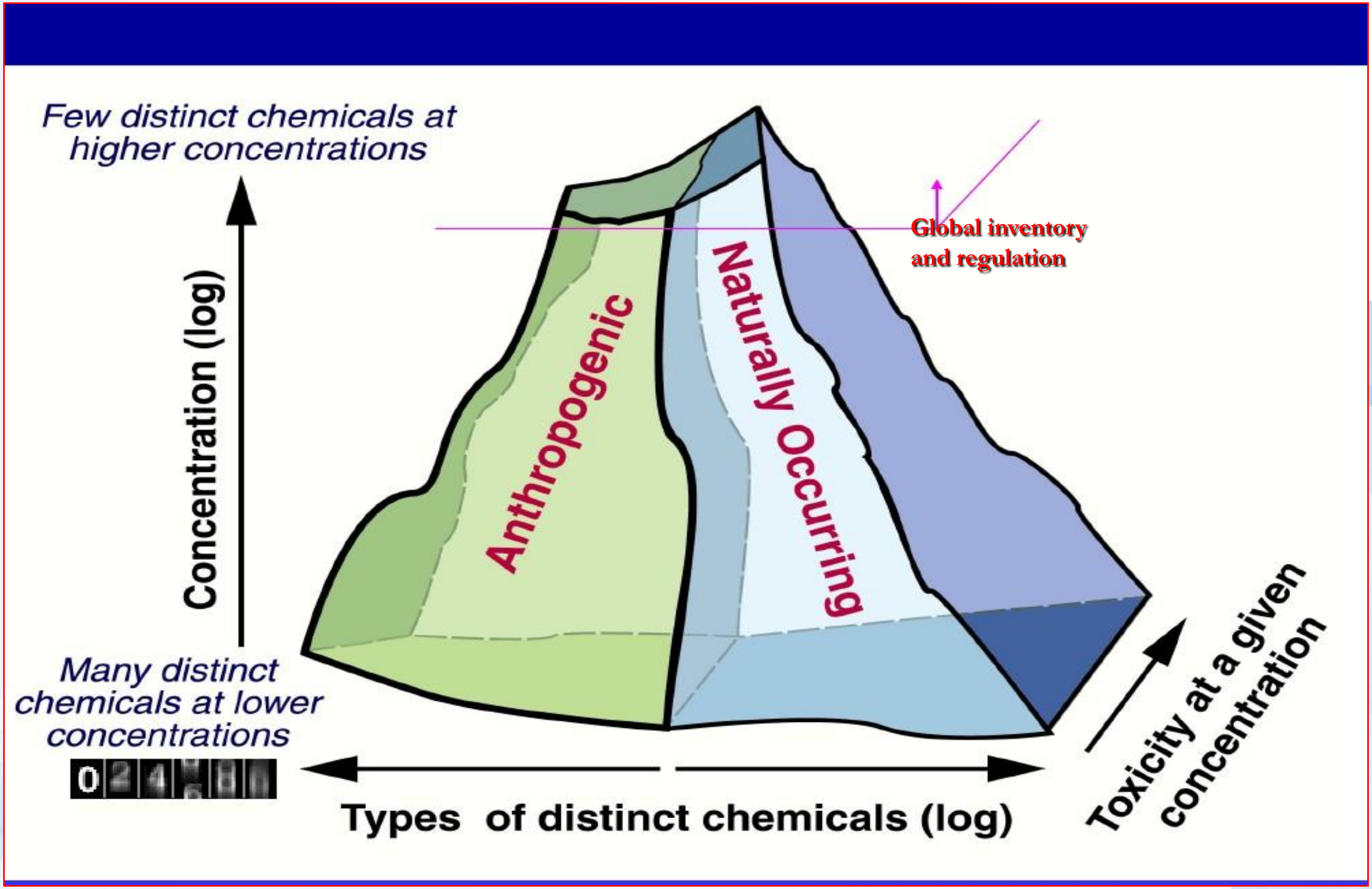
Pesticides

(herbicides, insecticides,fungicides…)

~ 1004 effective substances registered)

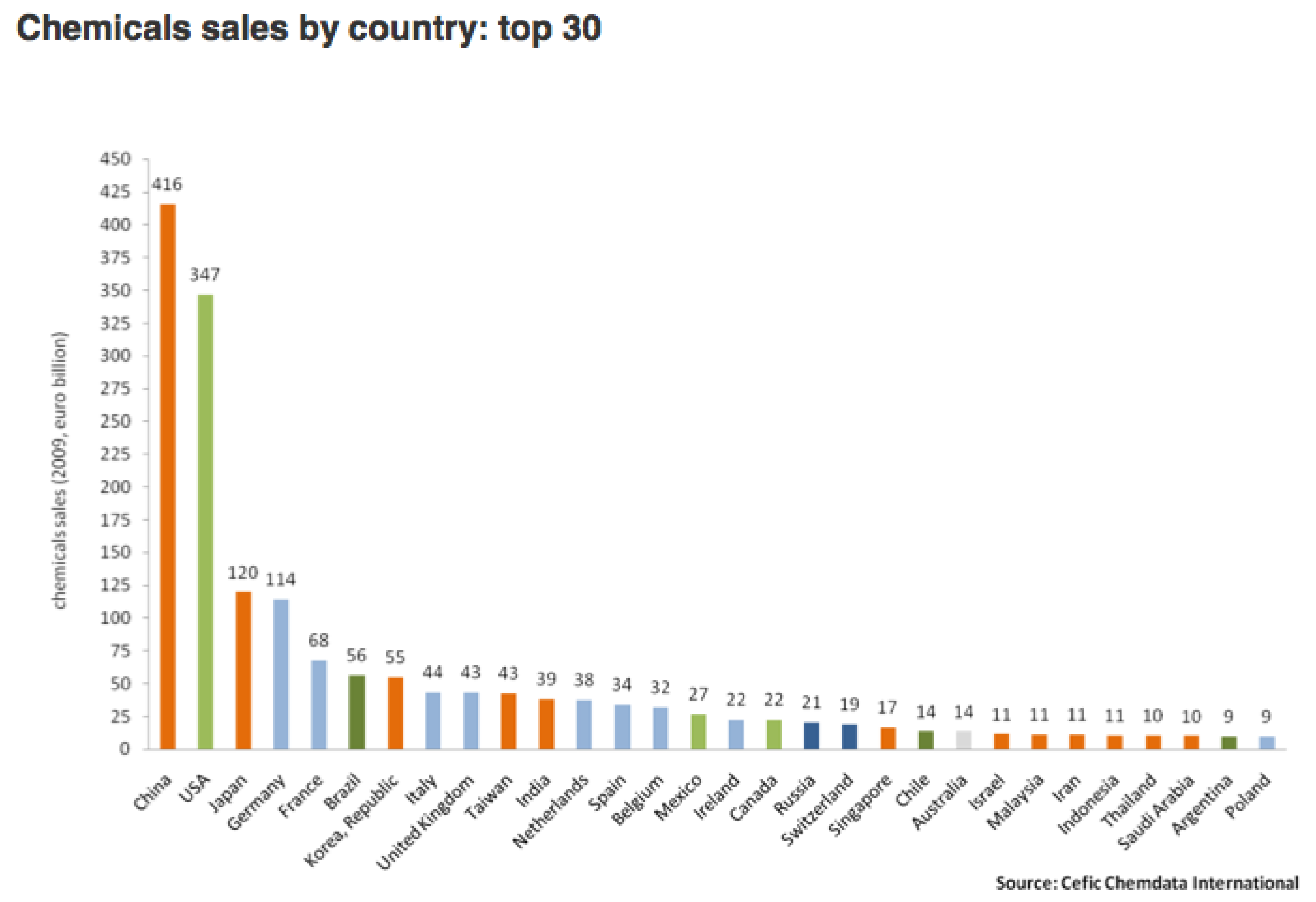
R. Triebskorn

Environmental pollution (> 56 000 000)



Global inventory and regulation

Chemical sales by country – top 30


Chemicals sales by country: top 30

Source: Cefic Chemdata International

Human exposure to chemicals

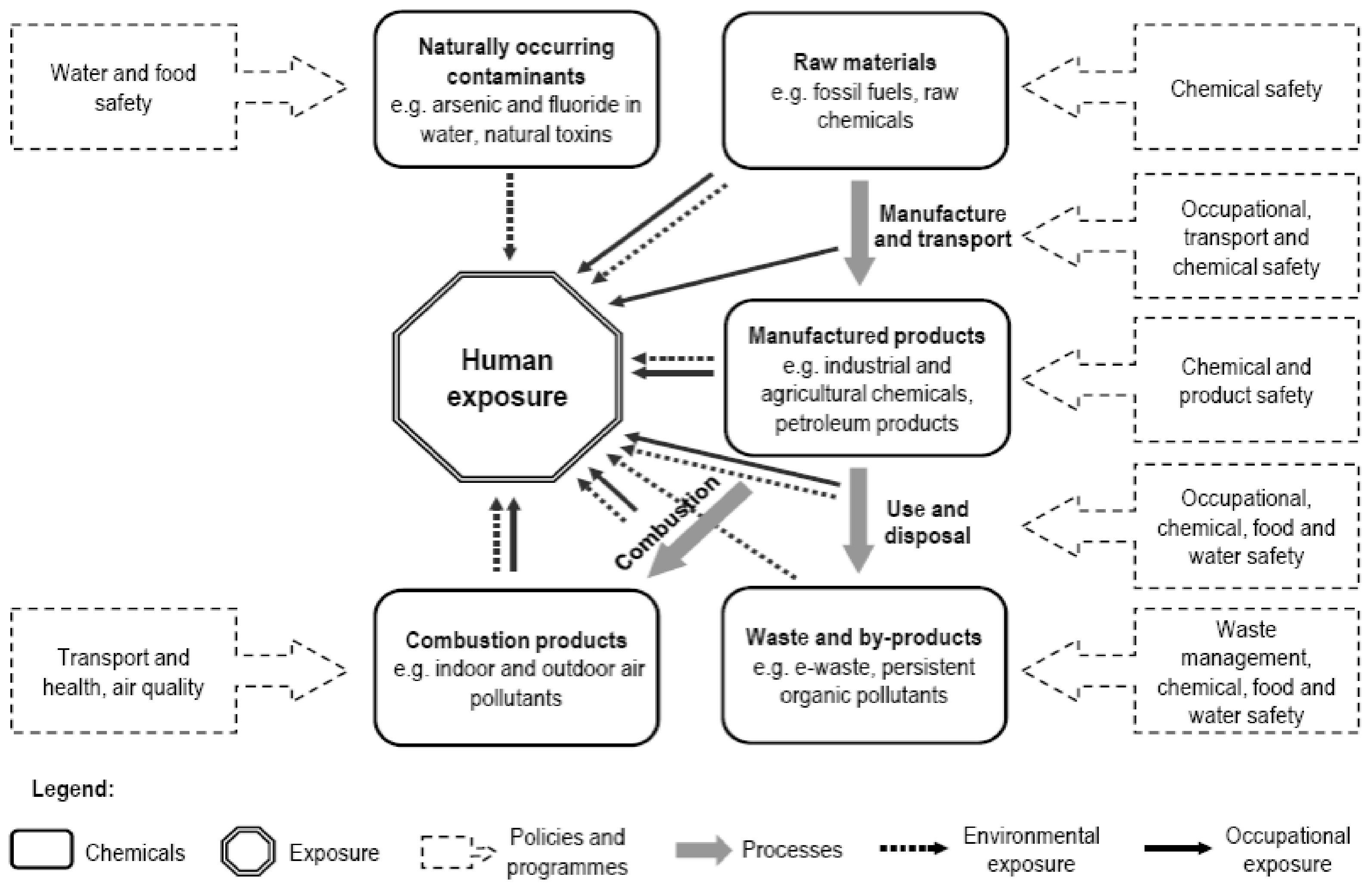


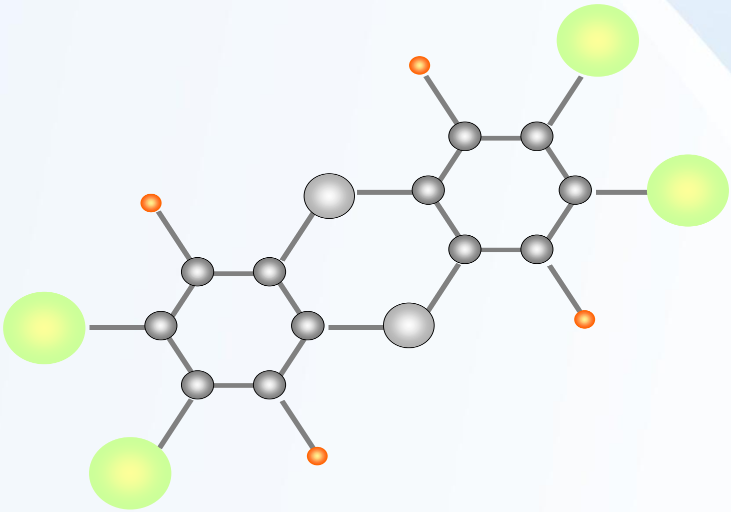
Figure 1 Human exposure to chemicals throughout their life-cycle and selected programmes relevant to their prevention.

Subject of interest

PTS= Persistent toxic substances

PBTs = Persistent, bioaccumulative and toxic substances

POPs = Persistent organic polutants



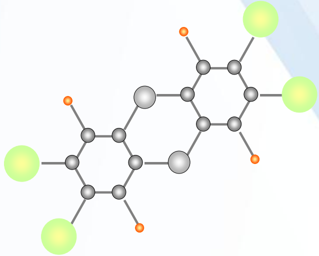
Research centre
for toxic compounds
in the environment

POPs (Persistent organic polutants)

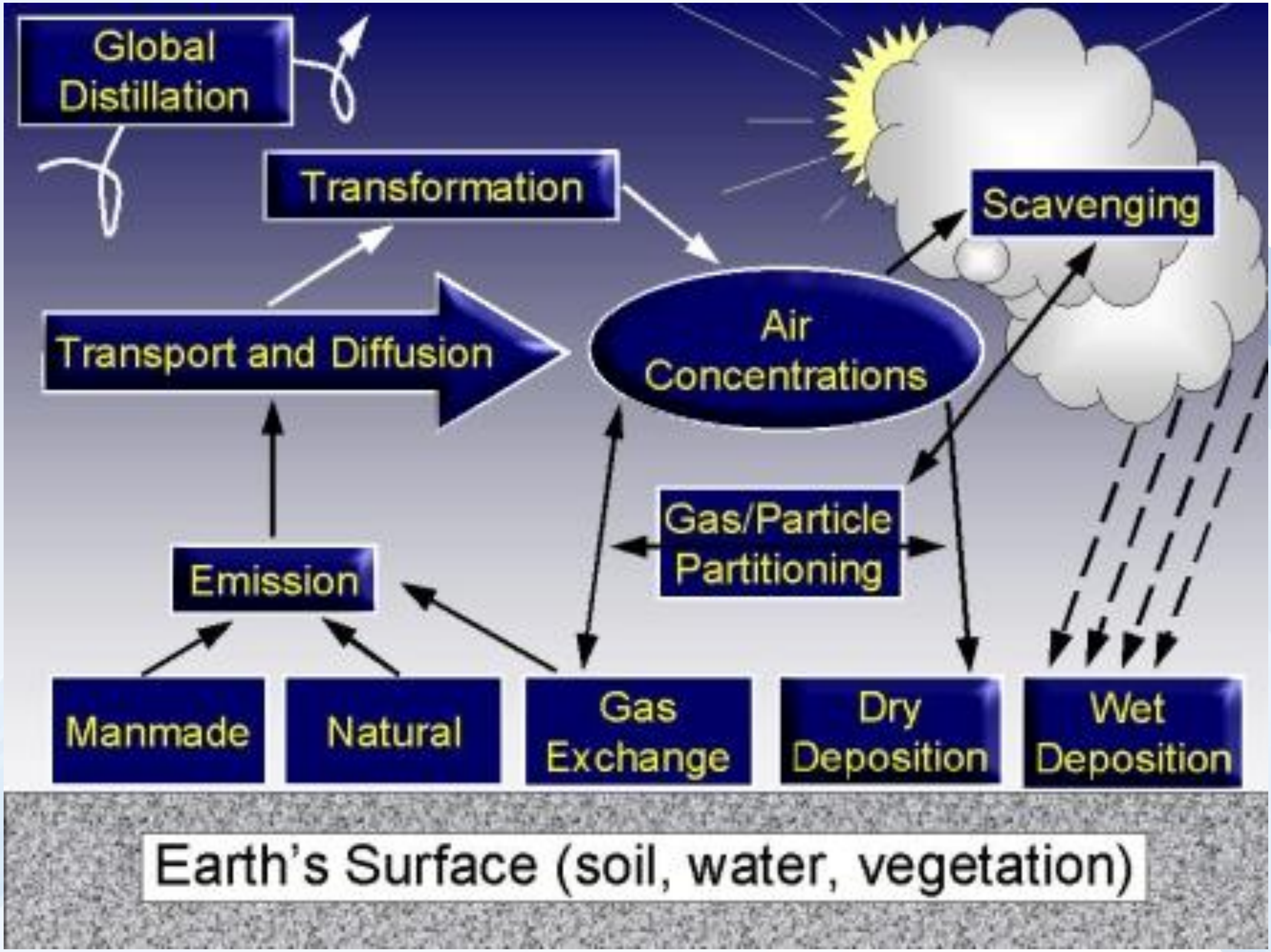
☺ The group of most fascinating pollutants (Kevin C. Jones)

☹ 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

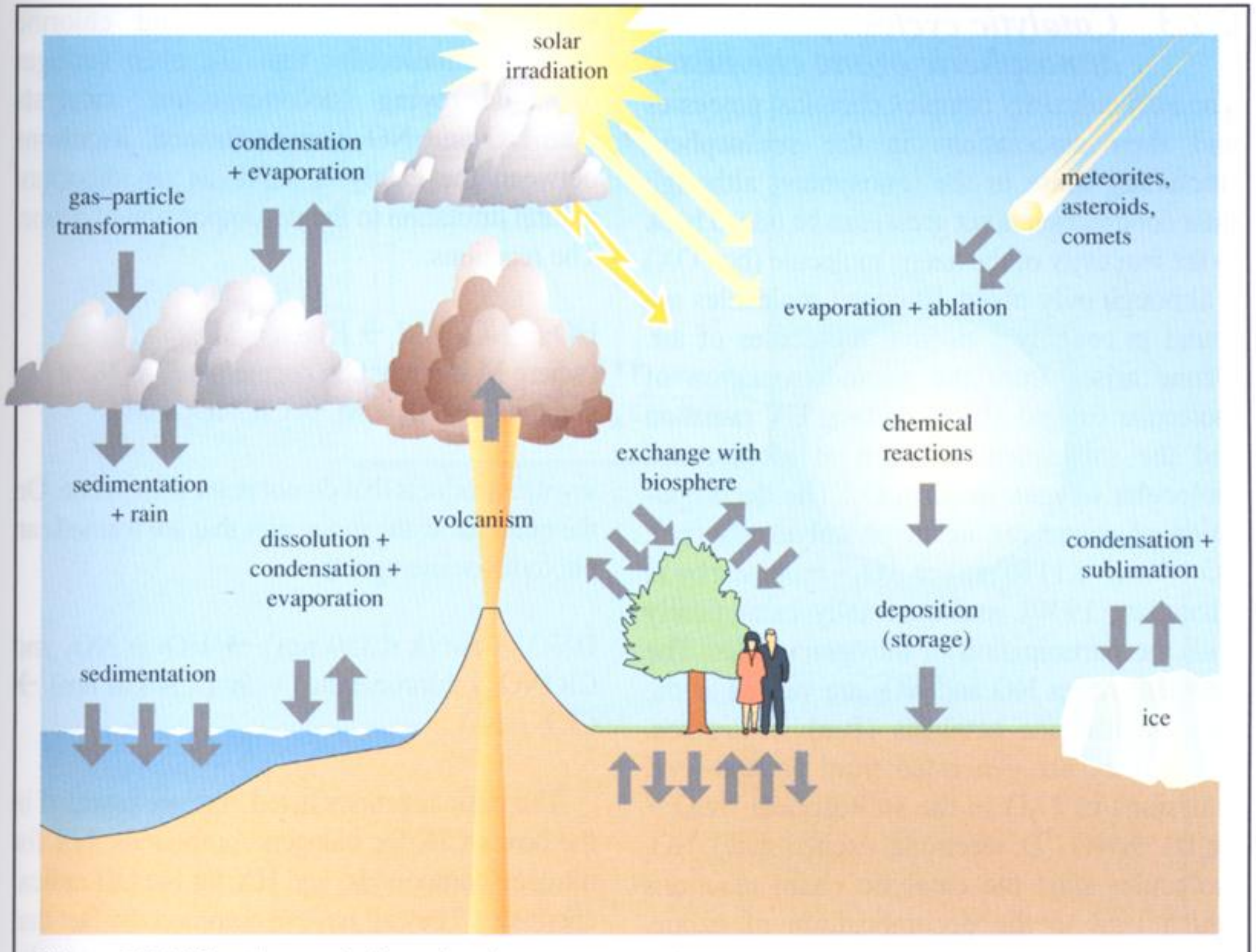


Figure 2.2.1 Chemistry and photochemistry

Environmental interface

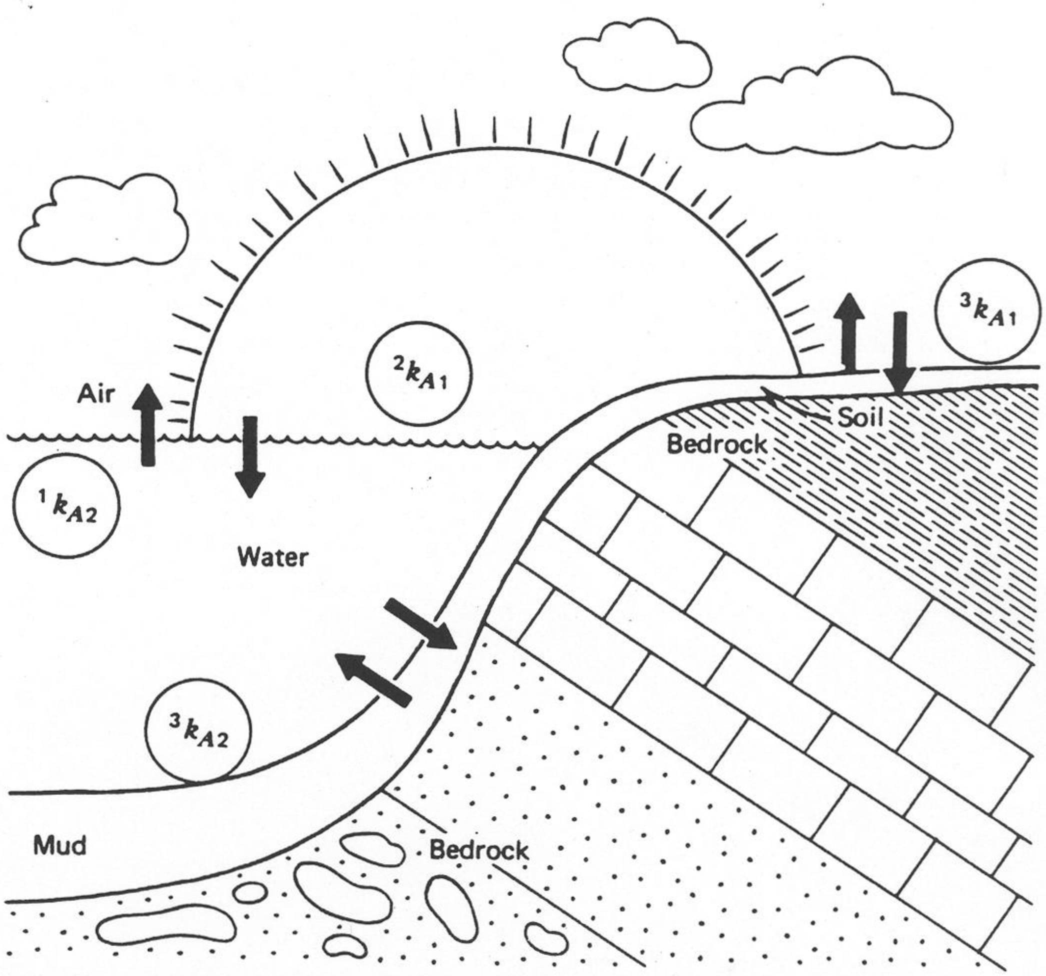
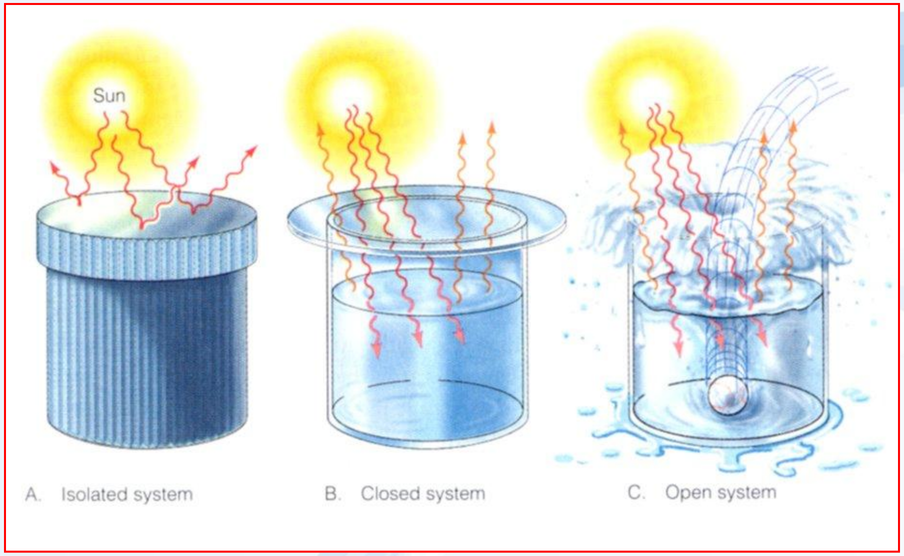


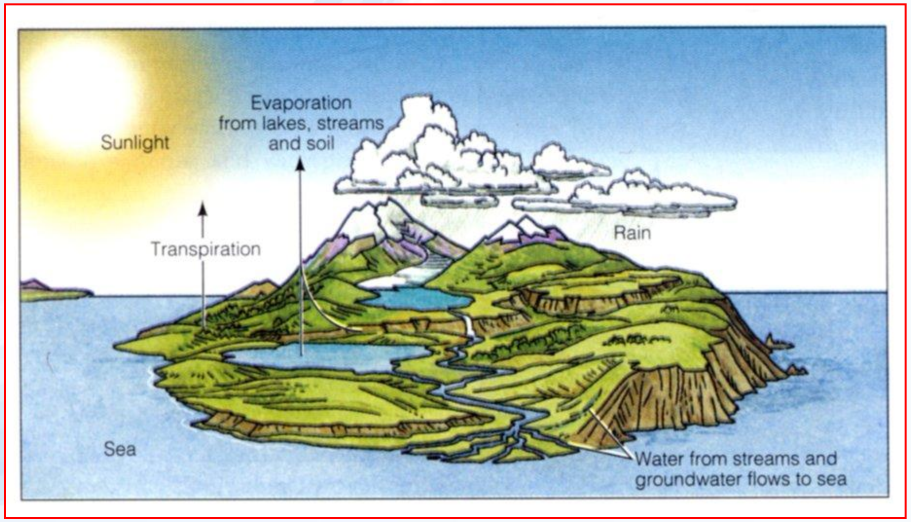
Figure 3.0-1. Interfaces in the geospheres.

Research centre
for toxic compounds
in the environment

Systems, environmental system



- **Isolated**
- **Closed**
- **Opened**



- **Opened**

Research centre
for toxic compounds
in the environment

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

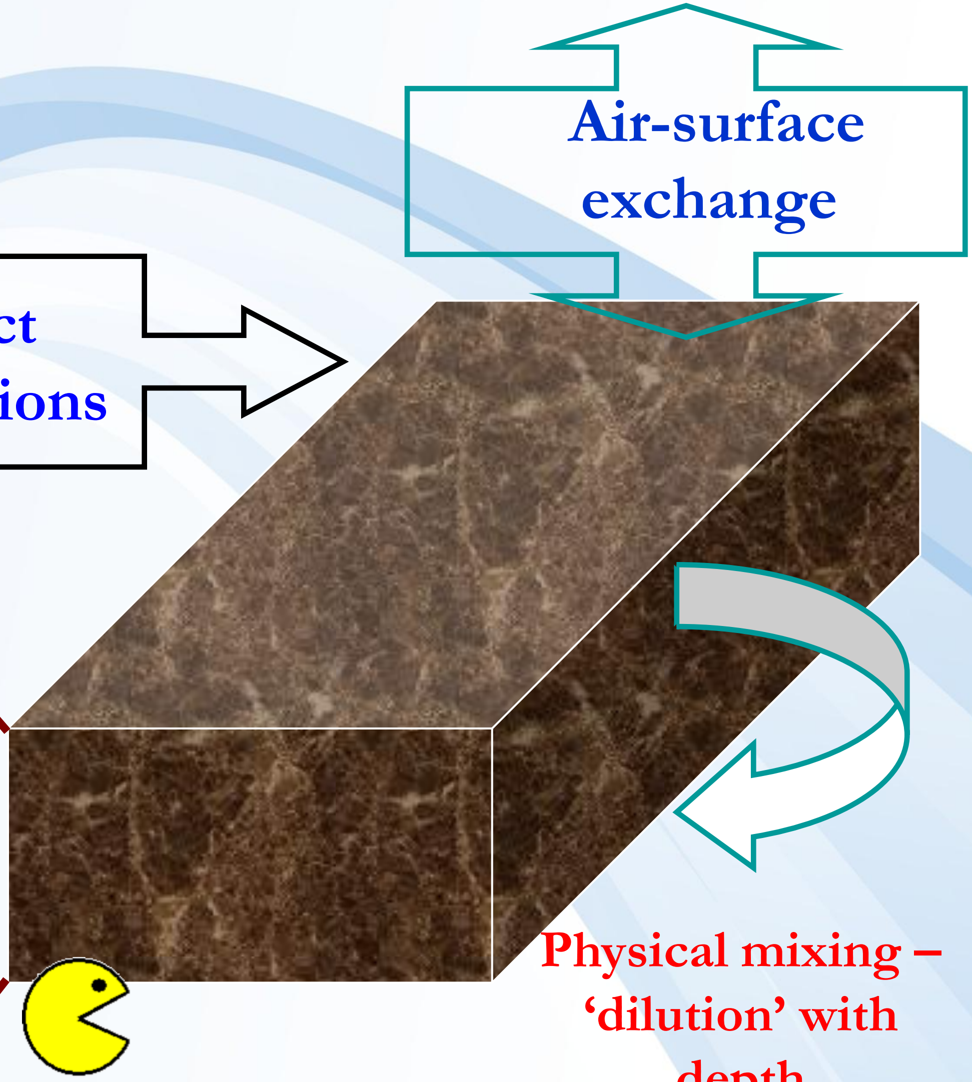
Fate of POPs – environmental transport and transformations

Study of environmental processes:

- Laboratory experiments
- Field experiments
- Monitoring
- Modelling

Research centre
for toxic compounds
in the environment

Soil can be a source or sink of POPs



Direct applications

Air-surface exchange

‘Occlusion’

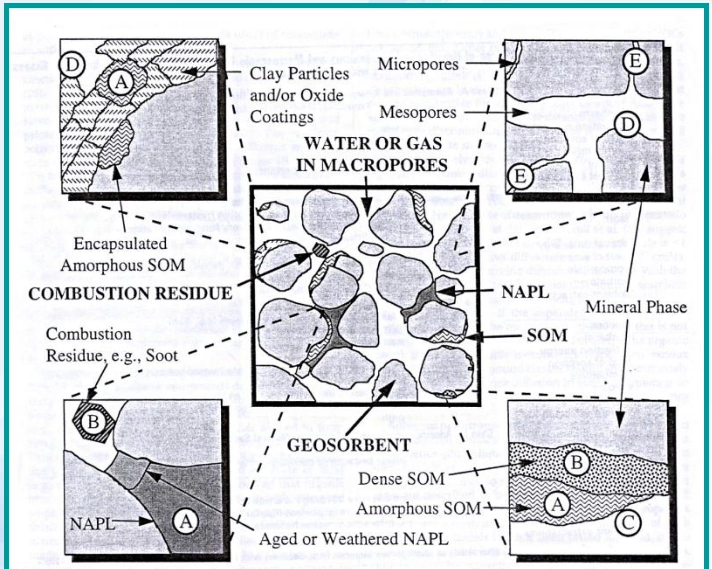


FIGURE 1. Conceptual model of geosorbent domains. The circled letters refer to representations of the sorption mechanisms described in Table 1. The geosorbent domains include different forms of sorbent organic matter (SOM), combustion residue particulate carbon such as soot, and anthropogenic carbon including nonaqueous-phase liquids (NAPLs).

Physical mixing – ‘dilution’ with depth

Biodegradation

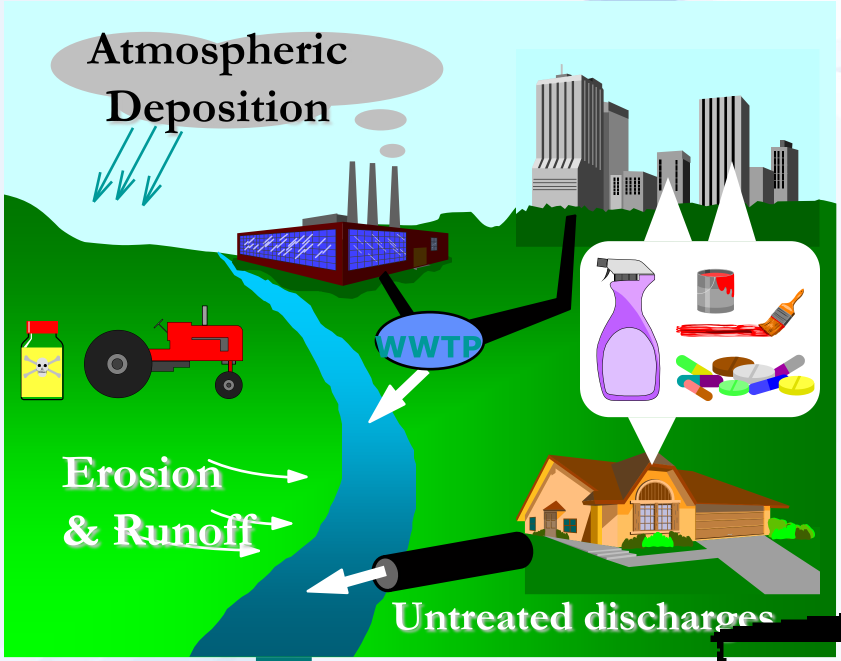
K. C. Jones

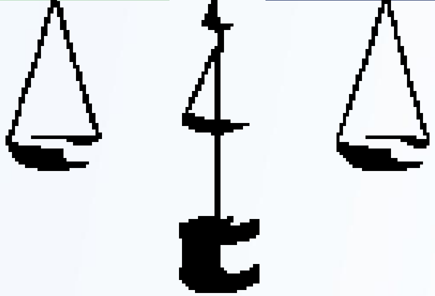
Risk assessment

Exposure

Effects

EUSES European Union System for the Evaluation of Substances





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 = const., then:

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

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

Research centre
for toxic compounds
in the environment

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.

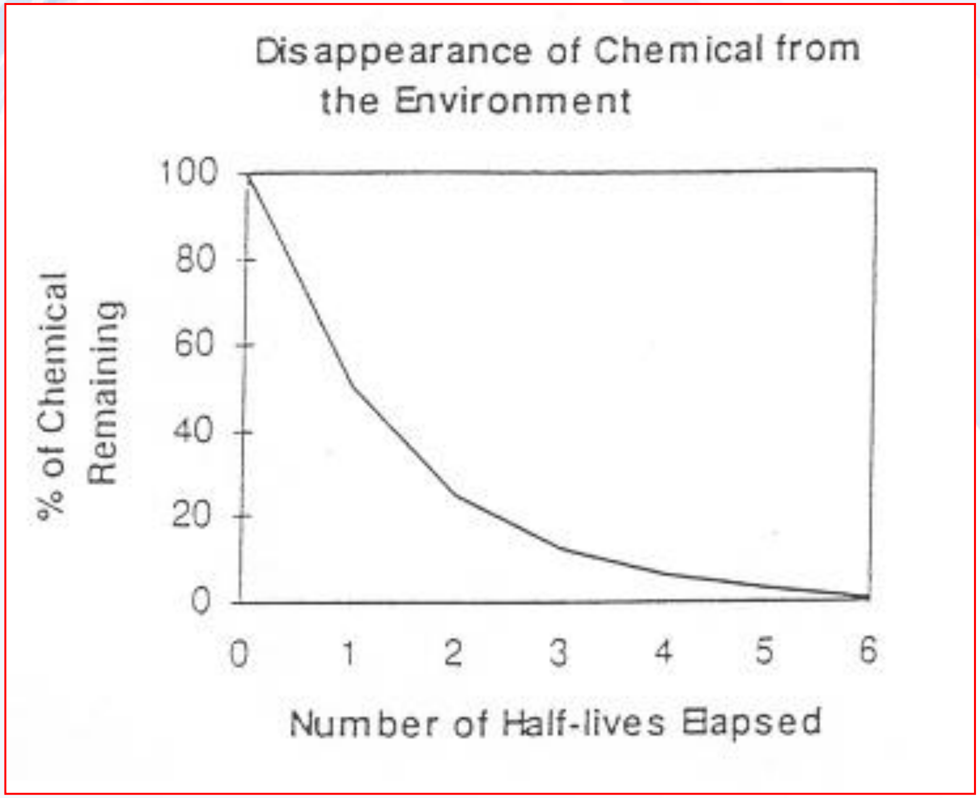
Furthermore, a long half-life in a medium may be relatively inconsequential if the substance is not emitted to that medium or is likely to transfer to it.

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-live ($t_{1/2}$), 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



Research centre
for toxic compounds
in the environment

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 [mol.l^{-1}.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

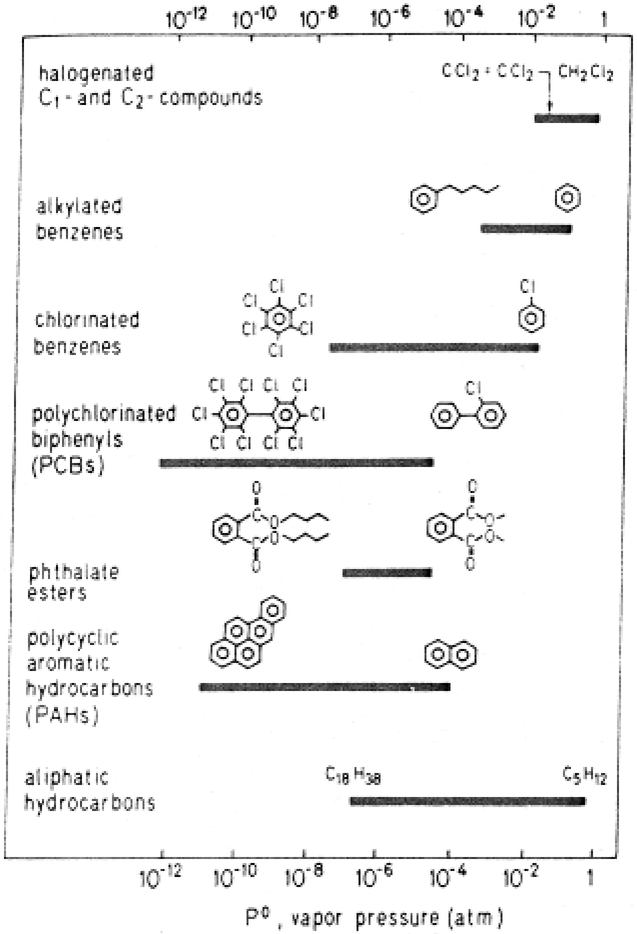
$$H = p/C_W$$

P = partial pressure, Pa
C_W = water concentration, mol/m^3

$K_{AW} = C_A/C_W =$ 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°) values for some important
s of organic compounds.

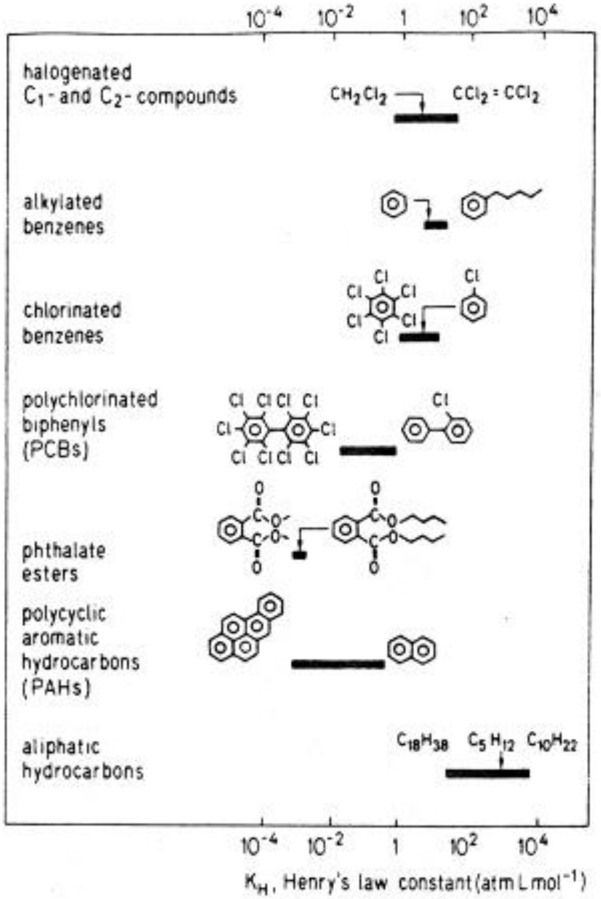


Figure 6.2 Ranges in Henry's Law constants (K_H) for some important classes of organic compounds.

Water solubility (WS, S)

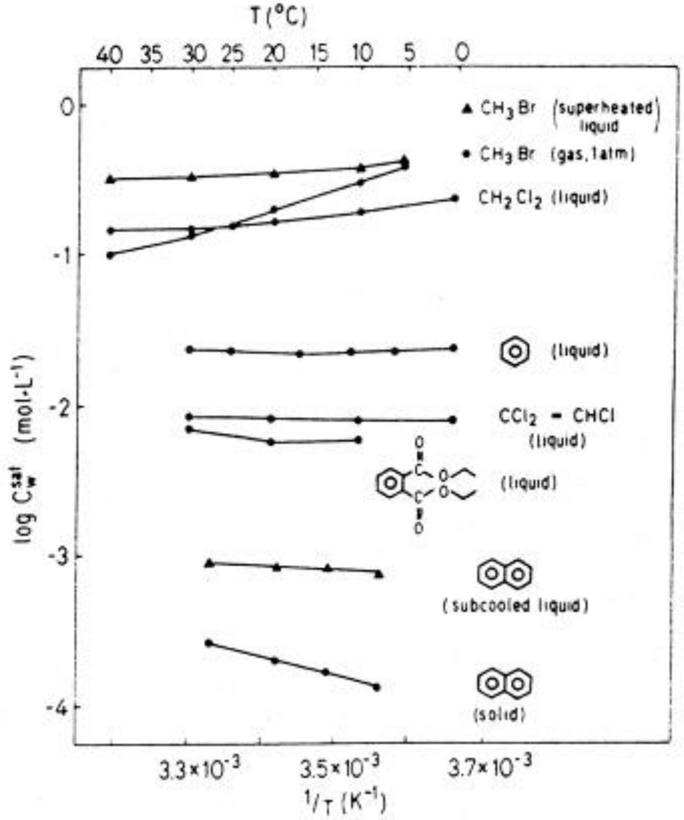


Figure 5.6 Solubility in water as a function of temperature for various compounds.

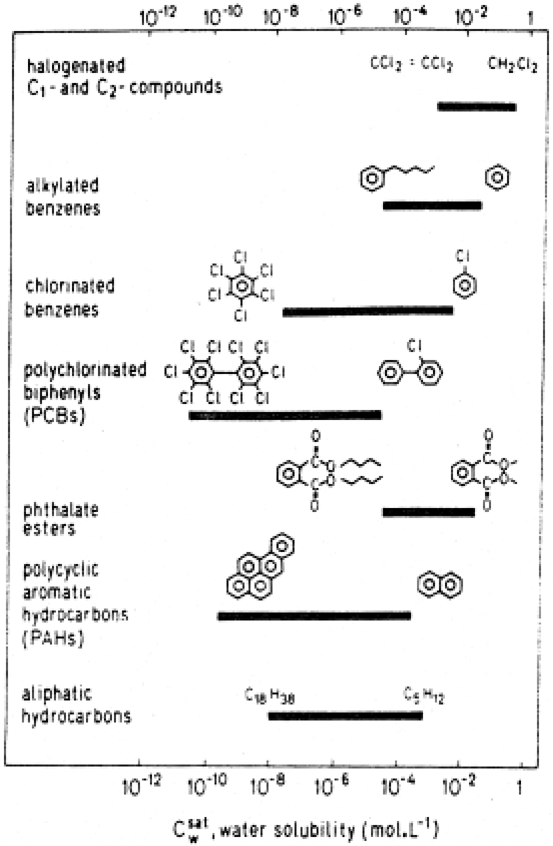


Figure 5.1 Ranges in water solubilities (C_w^{sat}) of some important classes of organic compounds.

Research centre
for toxic compounds
in the environment

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)

$K_{ow} = (X)_{octanol} / (X)_{water}$

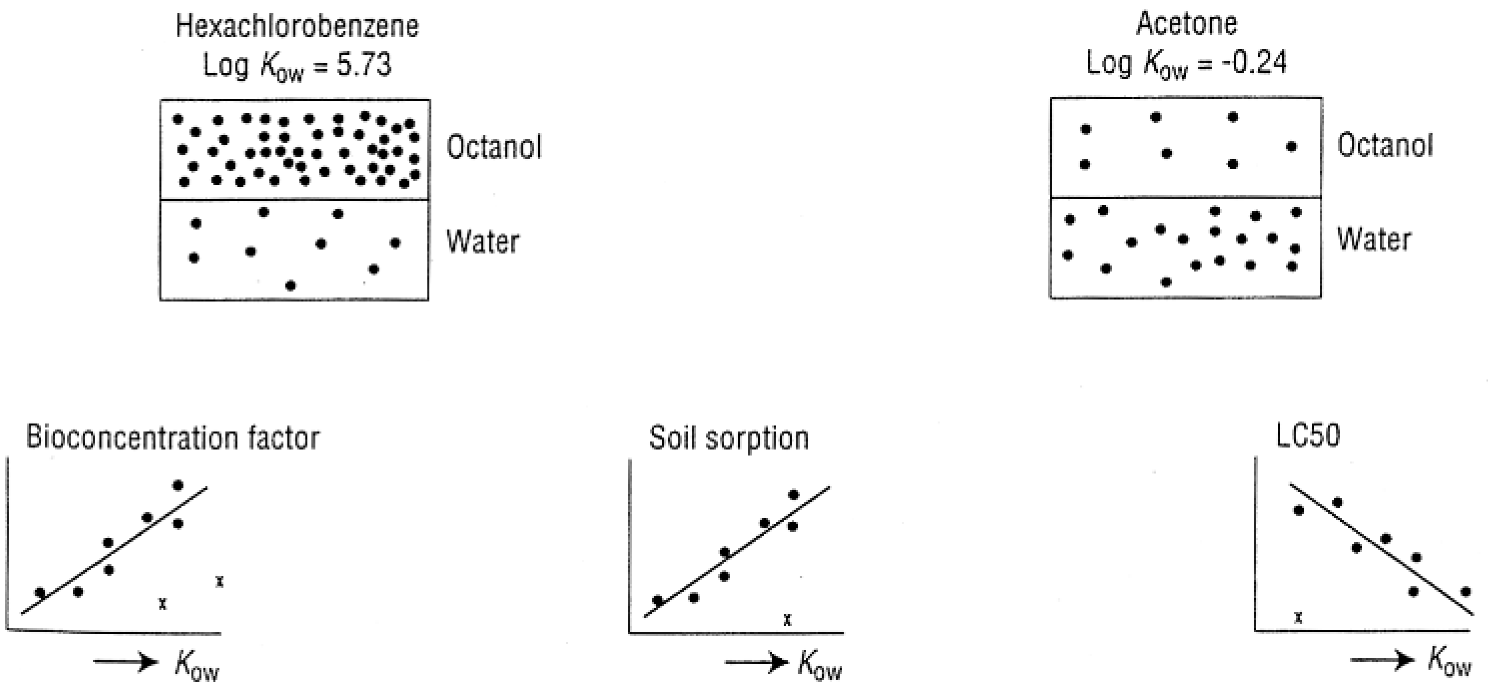


Figure 7.6. The octanol-water partition coefficient (K_{ow}) is defined as the ratio of the concentrations of a chemical in octanol and in the aqueous phase at steady-state. It can be measured, for example, by the shake-flask procedure. K_{ow} is often used for the estimation of bioconcentration, sorption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

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

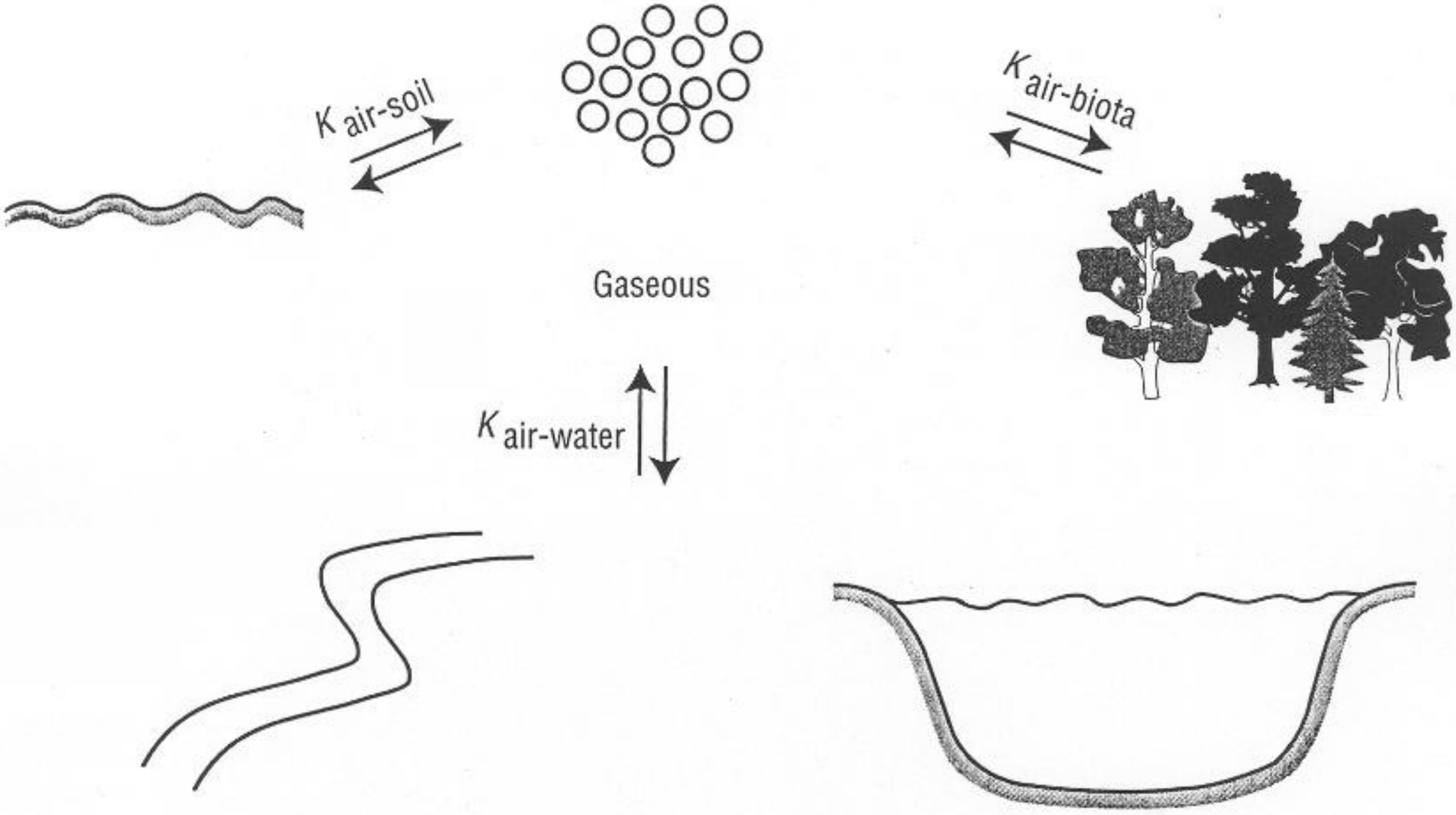
Transfer of compound cross the interface octanol – air can be described by Whitman two-resistance coefficient of mass transfer (MTC), which used the conception of two resistance – in boundary layers of octanol and air.

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

Overall mass transfer coefficient derived from particular MTC:

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

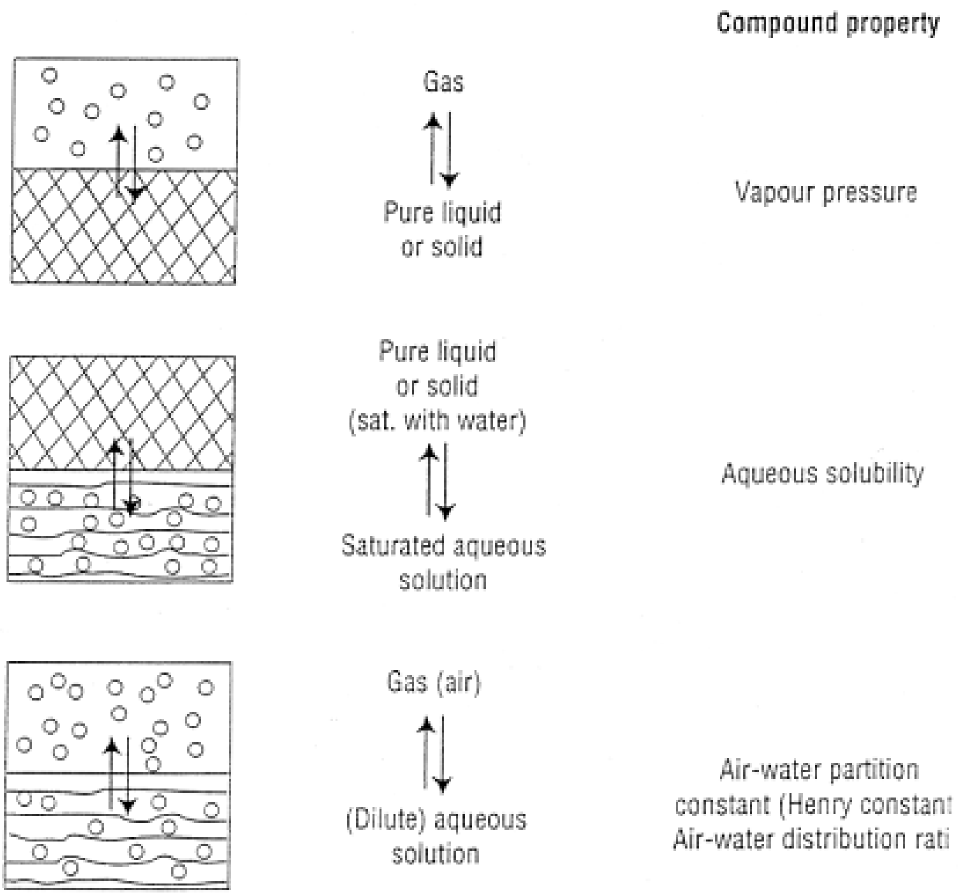
Environmental equilibria



as exchange between the atmosphere and the earth's surface. From Schwarzenbach [13]. With permission.

Research centre
for toxic compounds
in the environment

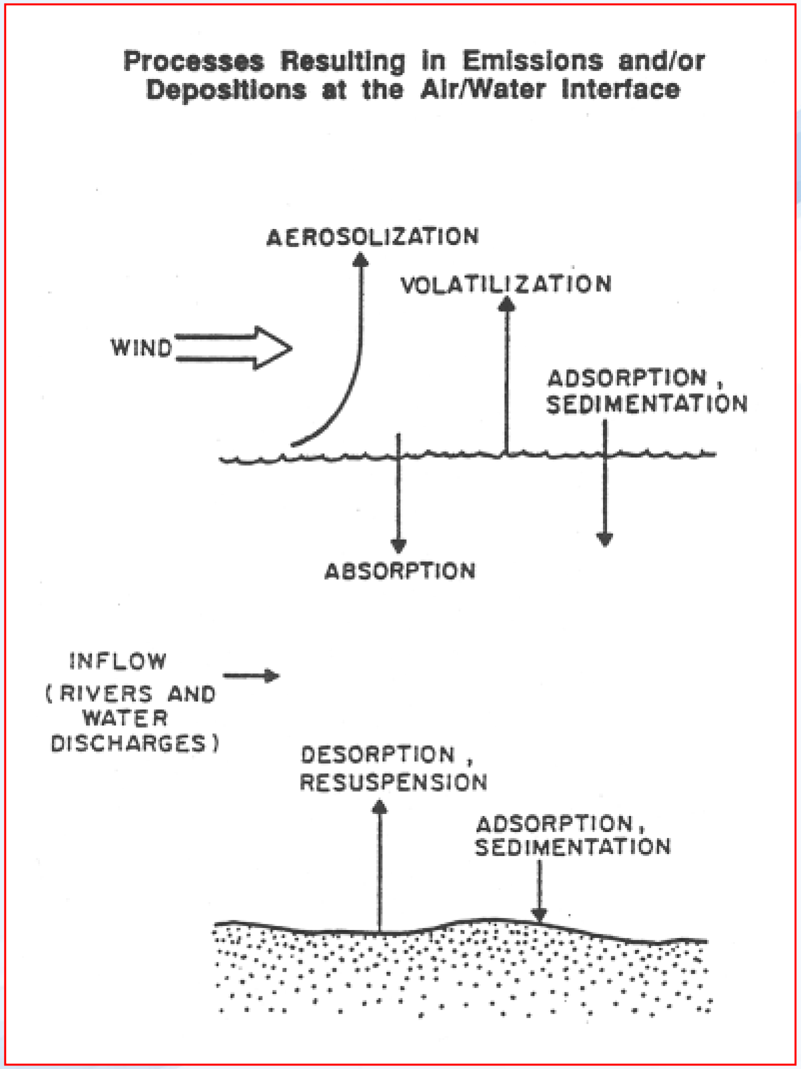
Environmental equilibria



Important compound properties showing the equilibrium partitioning between two phases.

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

Equilibrium air - water



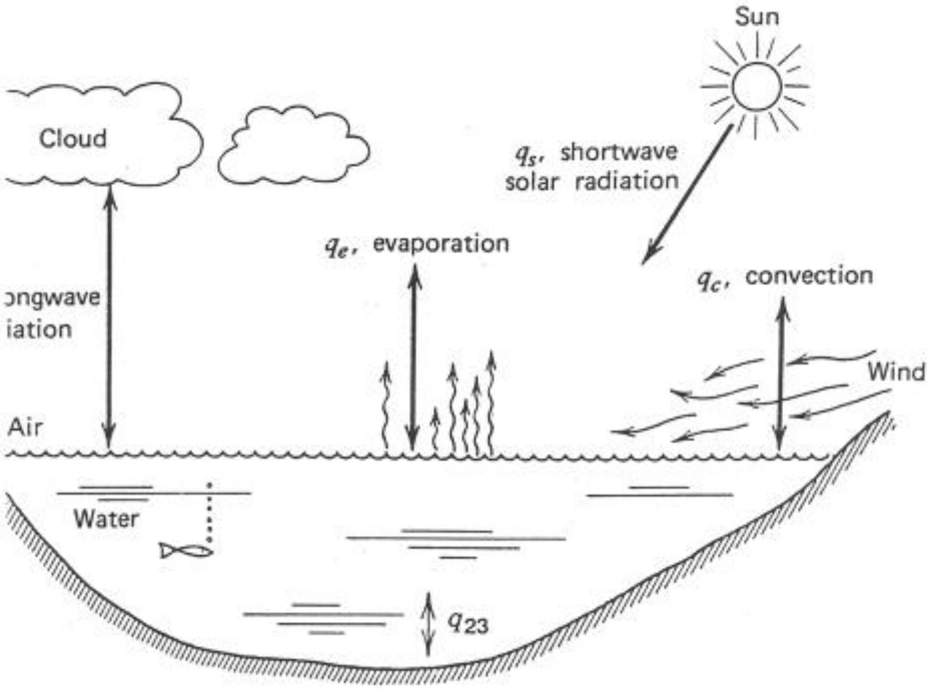


Figure 4.3-1. Heat and energy transfers at the air–water interface.

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 m^2/g)
- Little experimental evidence on magnitude and kinetics of partitioning

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

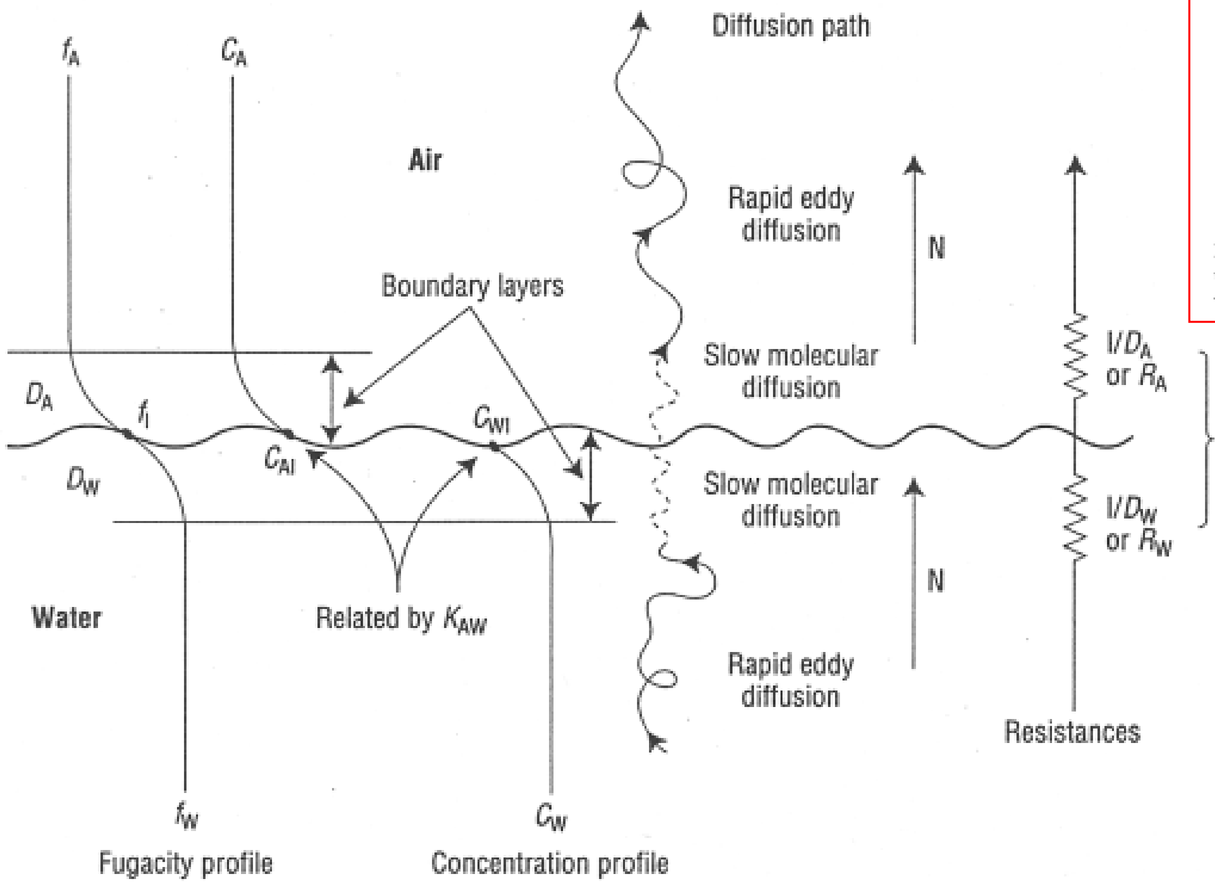


Figure 3.12. Mass transfer of a chemical between two phases, air and water, according to the two resistances concept described l Mackay [1]. Reprinted by permission of Lewis Publishers, an imprint of CRC Press, Boca Raton, Florida.

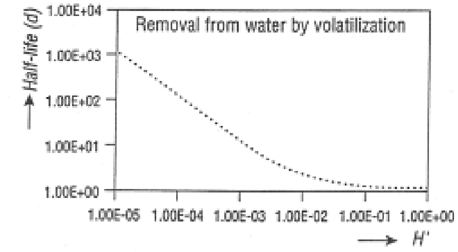
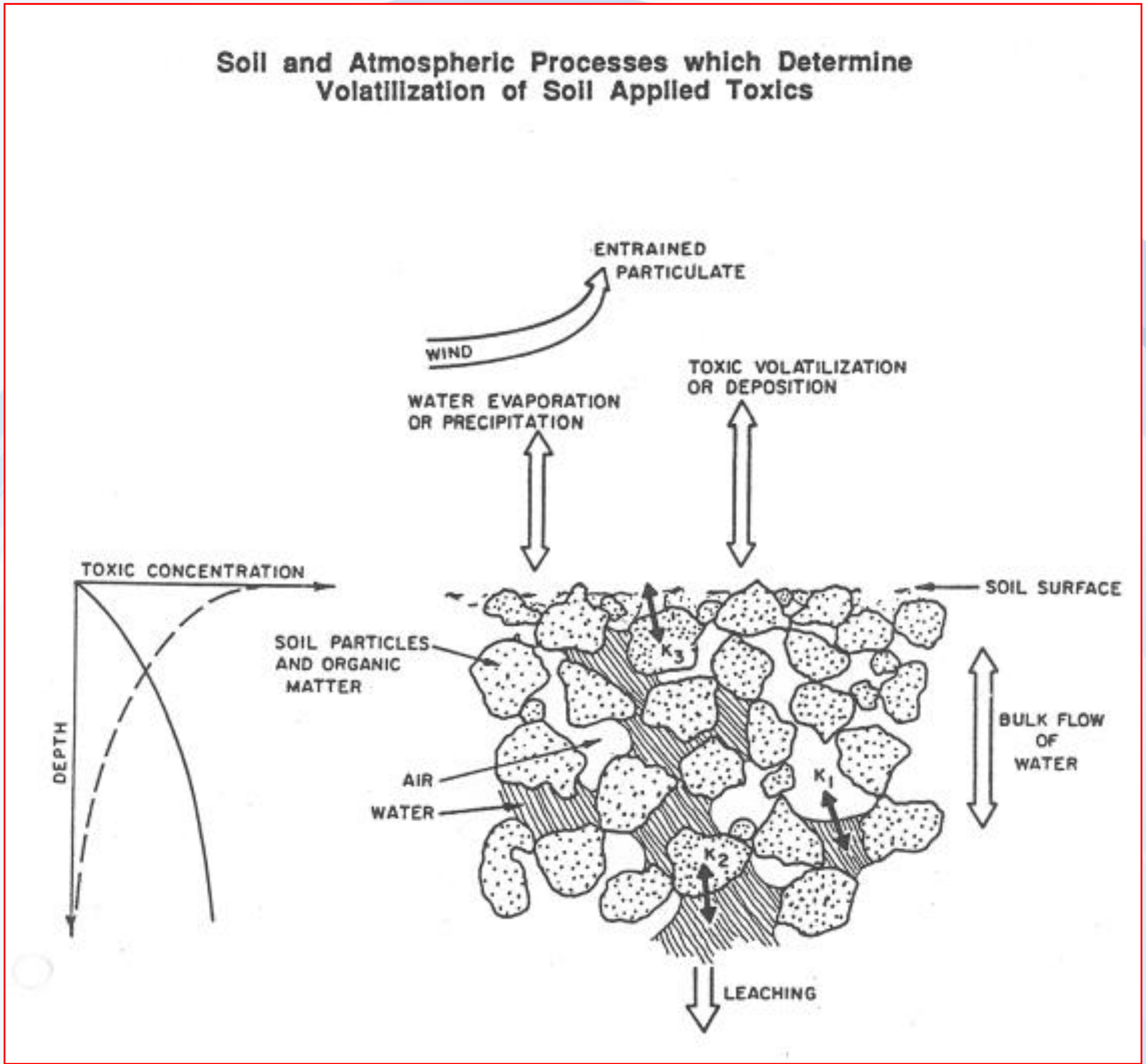


Figure 3.13. Half-lives for the removal of a substance by volatilization from a body of water (depth 2 m), plotted for different values of the dimensionless Henry's law constant.

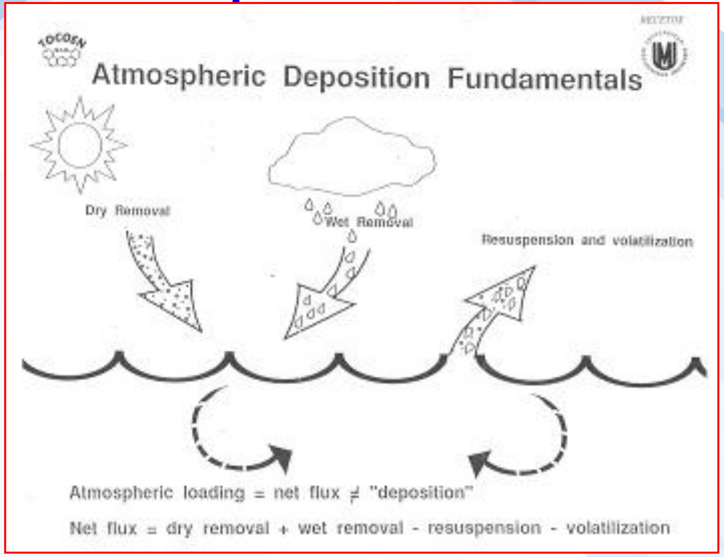
Soil and atmospheric processes which determine volatilization of soil applied chemicals



Research centre for toxic compounds in the environment

Dry and wet atmospheric deposition

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



Atmospheric Deposition Fundamentals

Atmospheric loading = net flux ≠ "deposition"

Net flux = dry removal + wet removal - resuspension - volatilization

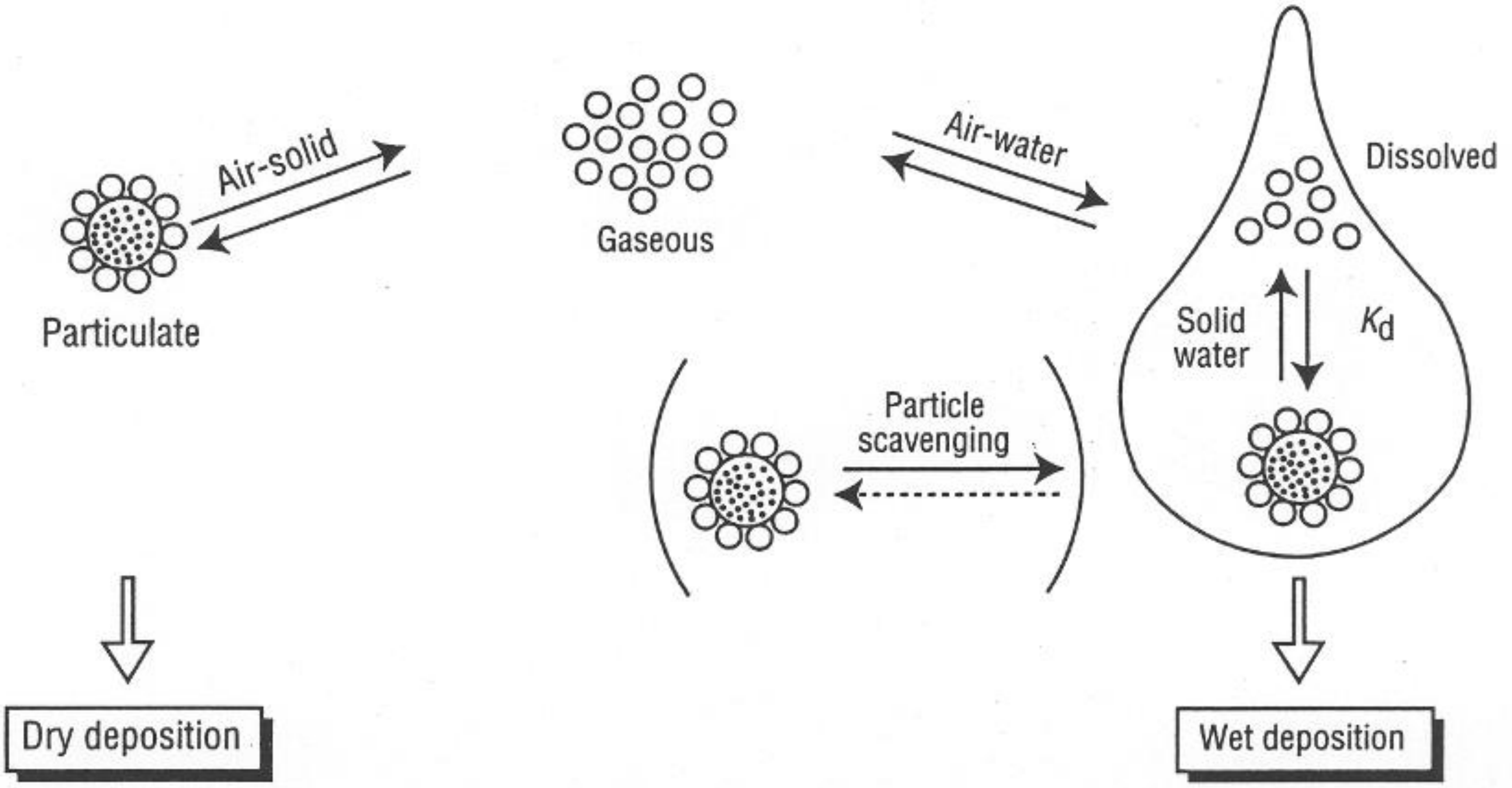
Atmospheric deposition:

- 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.

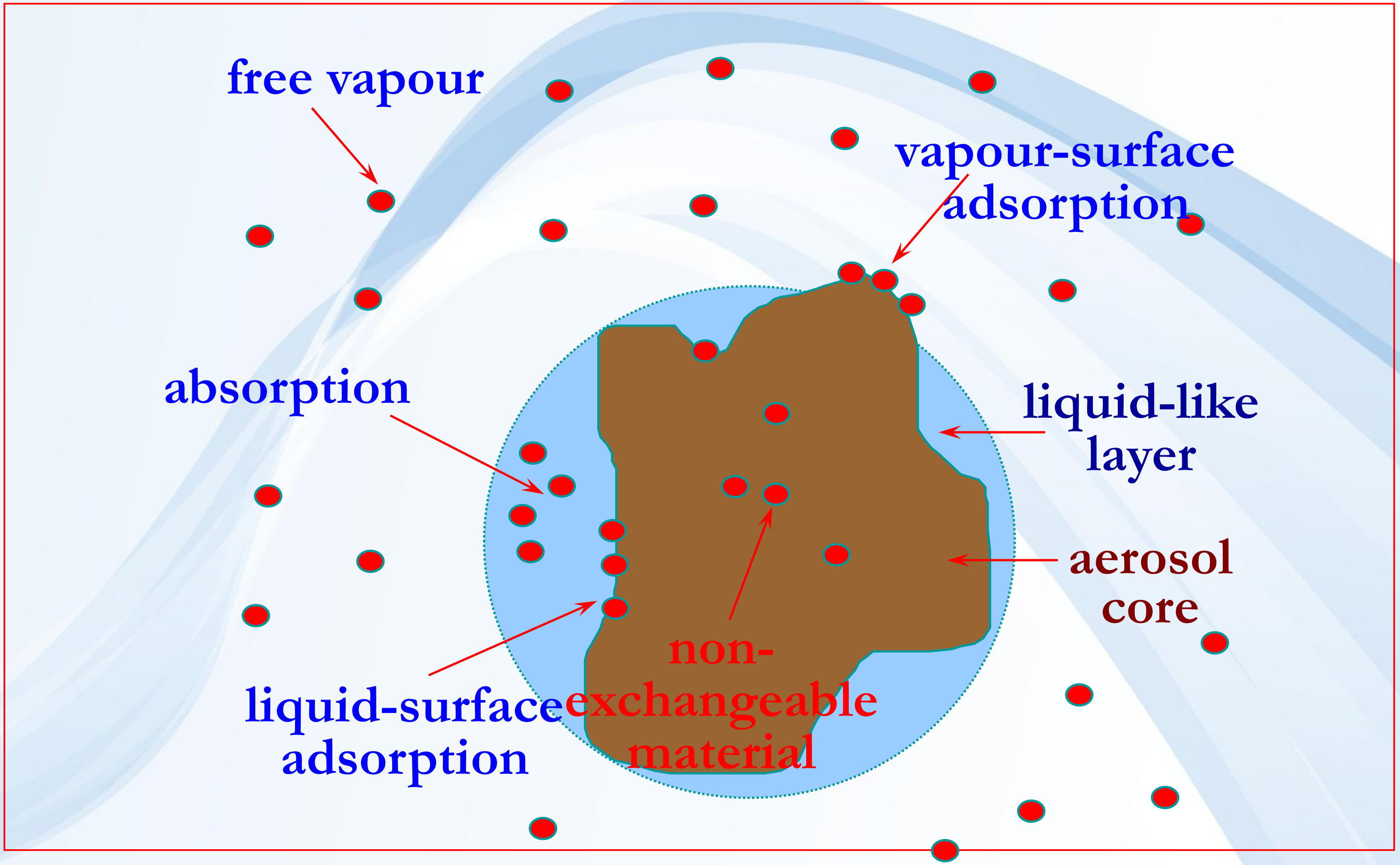
Dry and wet atmospheric deposition



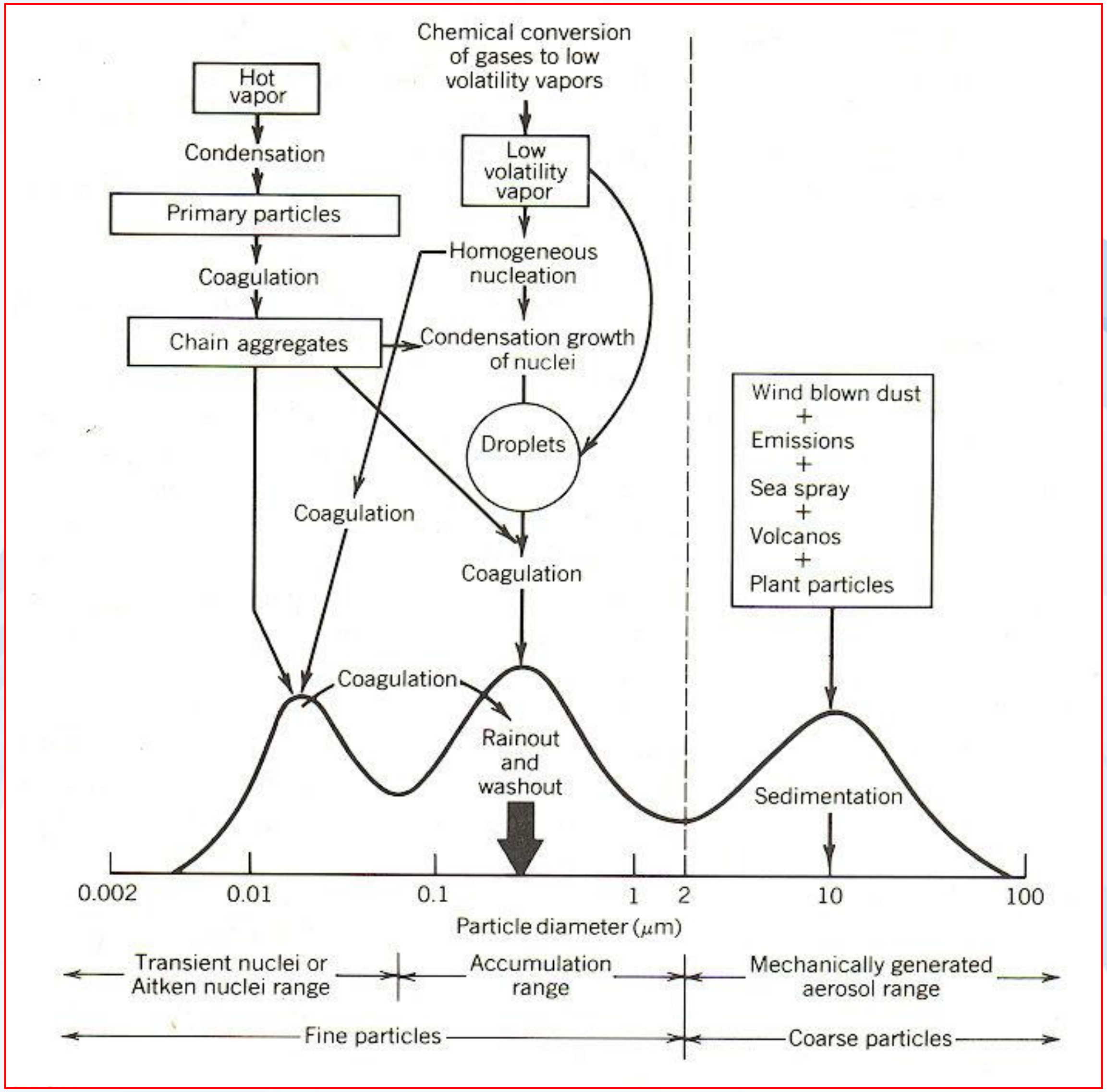
Mechanisms of atmospheric deposition. From Schwarzenbach [13]. With permission.

Research centre
for toxic compounds
in the environment

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.

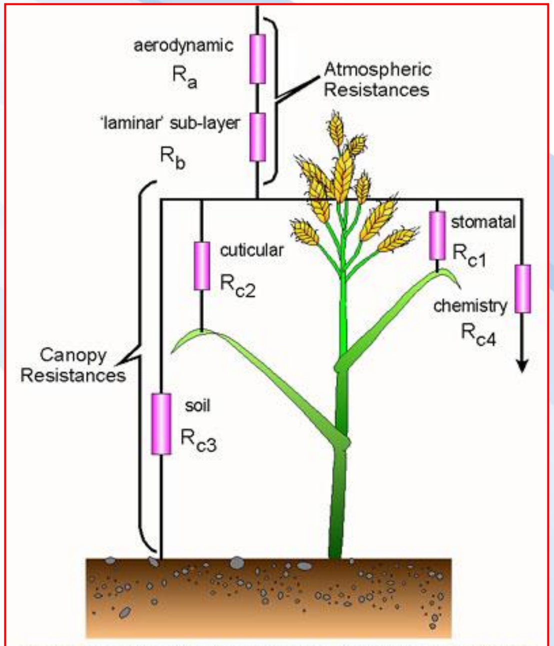
If the fugacity in water or soil is higher, the result is a opposite – the volatilization is coming.

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:

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



Resistance analogy for the deposition of atmospheric pollutants

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.

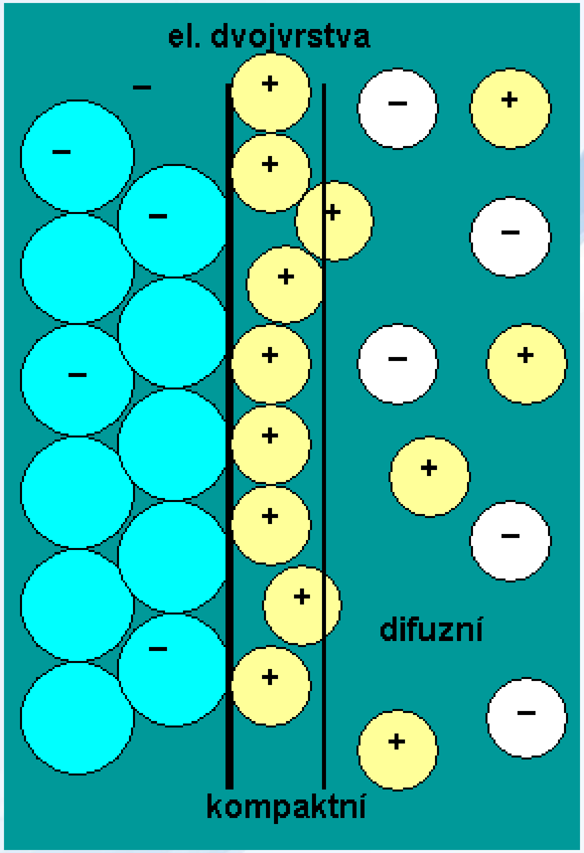
If based on the effect of these powers, the concentration of one component increased in the comparison with the concentrations inside the phase – this cummulation is described as a sorption.

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

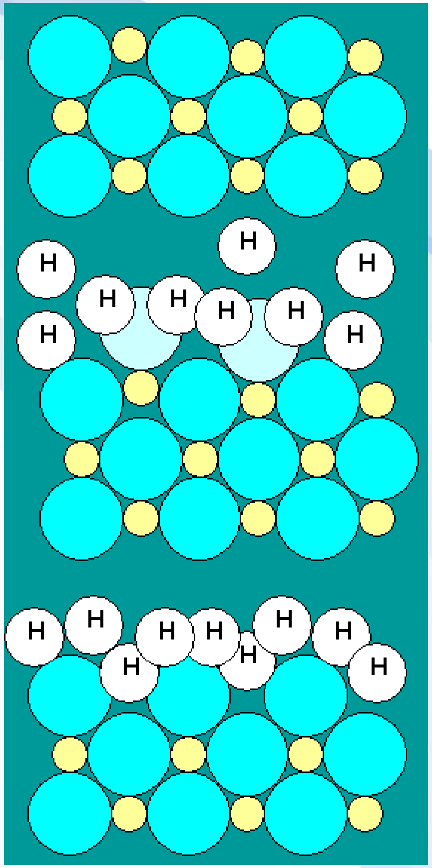
Adsorbent – adsorbate.

Surfaces

Electric double-layer



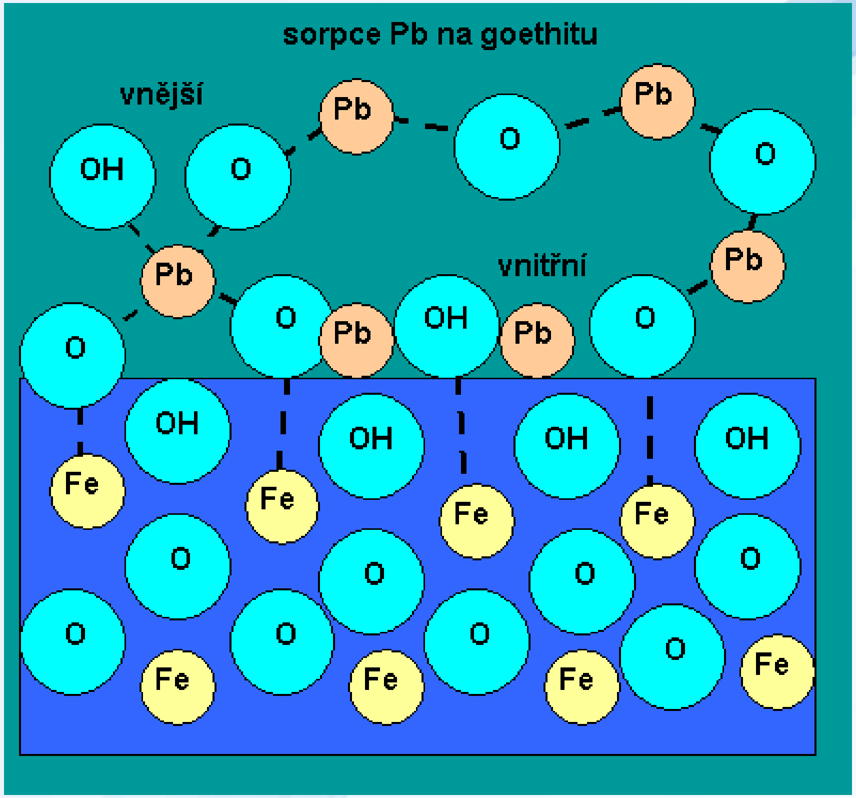
Iont exchange



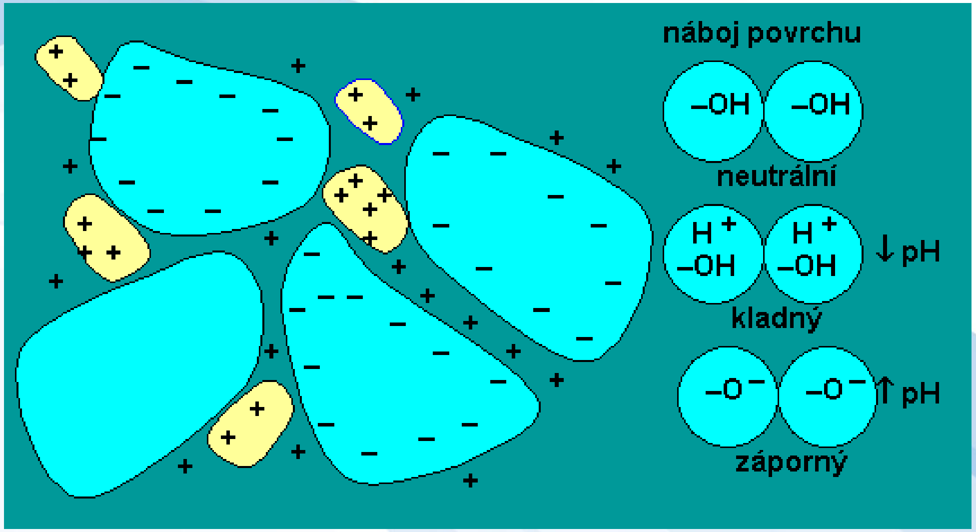
Research centre
for toxic compounds
in the environment

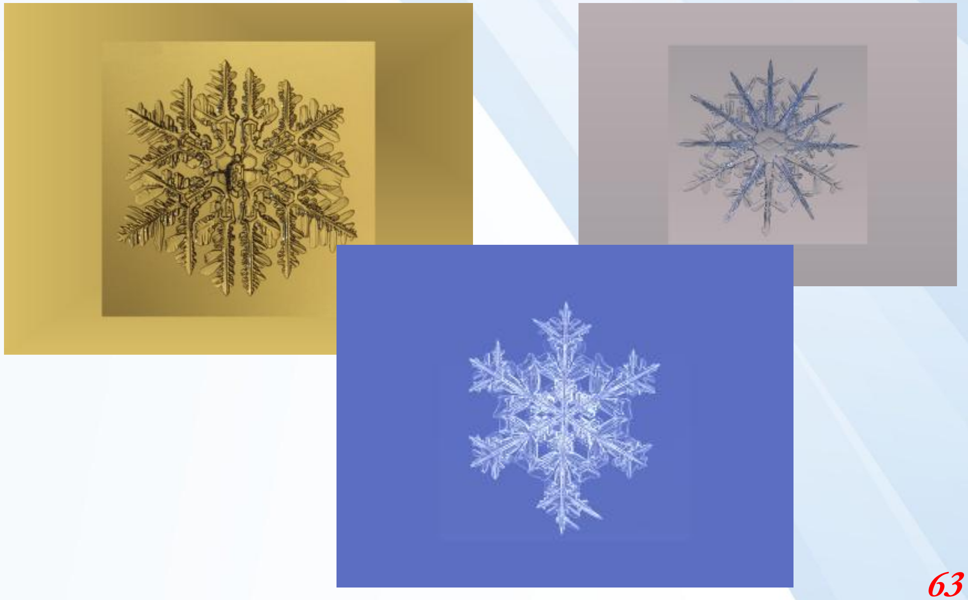
Surfaces

Sorption



Colloids





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 kJ.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 kJ.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:

$$\log C_S = \log K_d + n * \log C_W$$

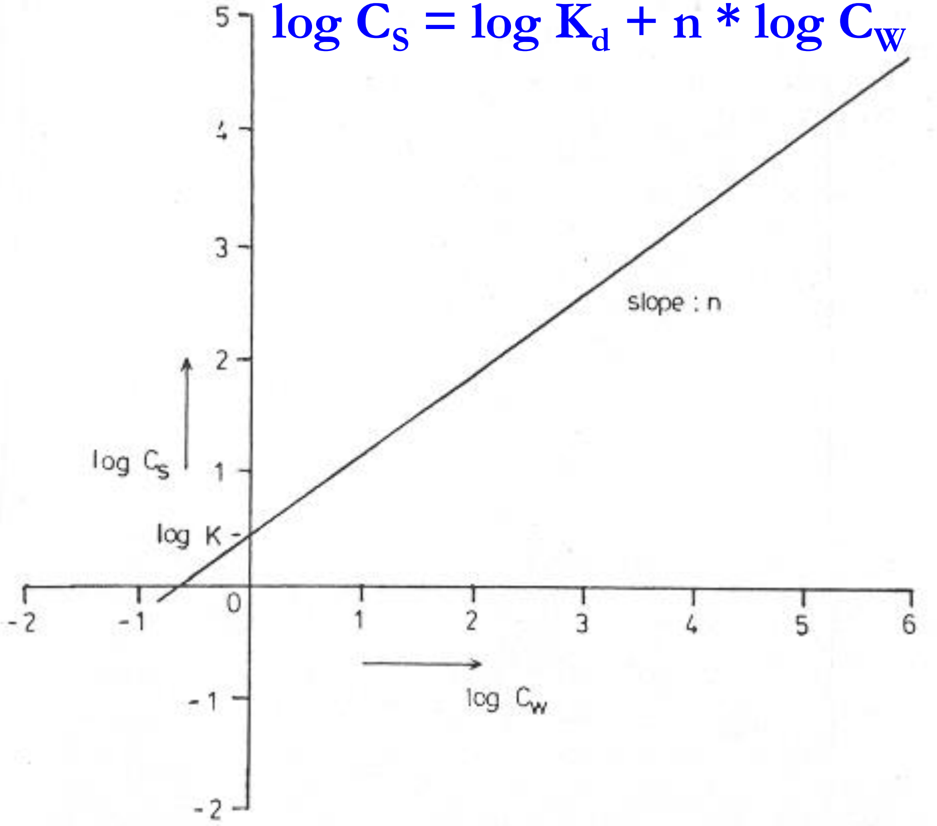


Figure 8. Typical Freundlich adsorption isotherm C_s = concentration on the adsorbent; C_w = concentration in the water; $0 < n \leqslant 1$. $C_s = K C_w^n$ or $\log C_s = n \log C_w + \log K$.

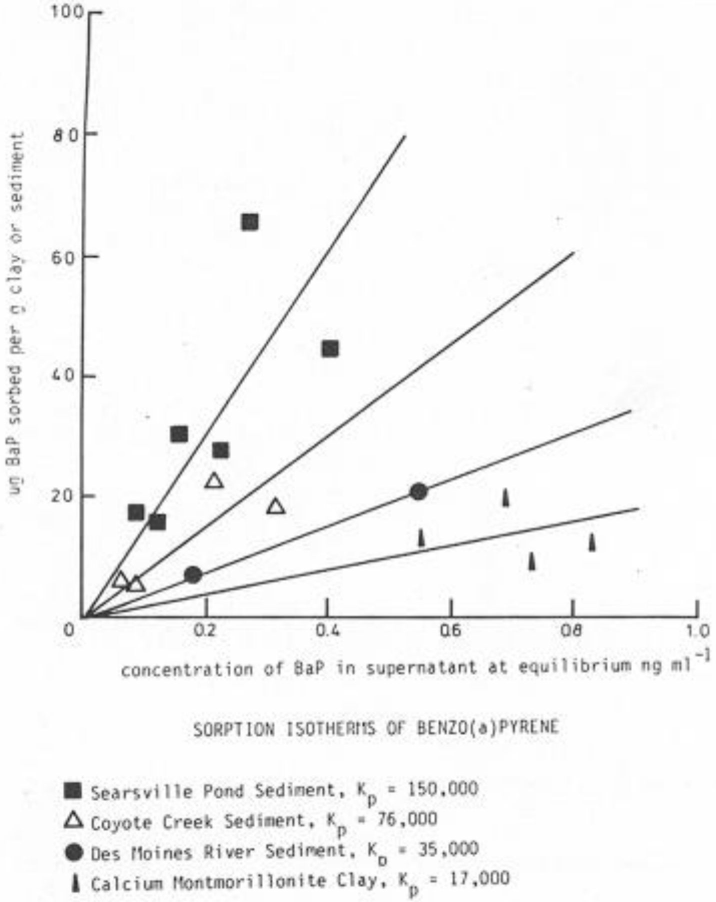
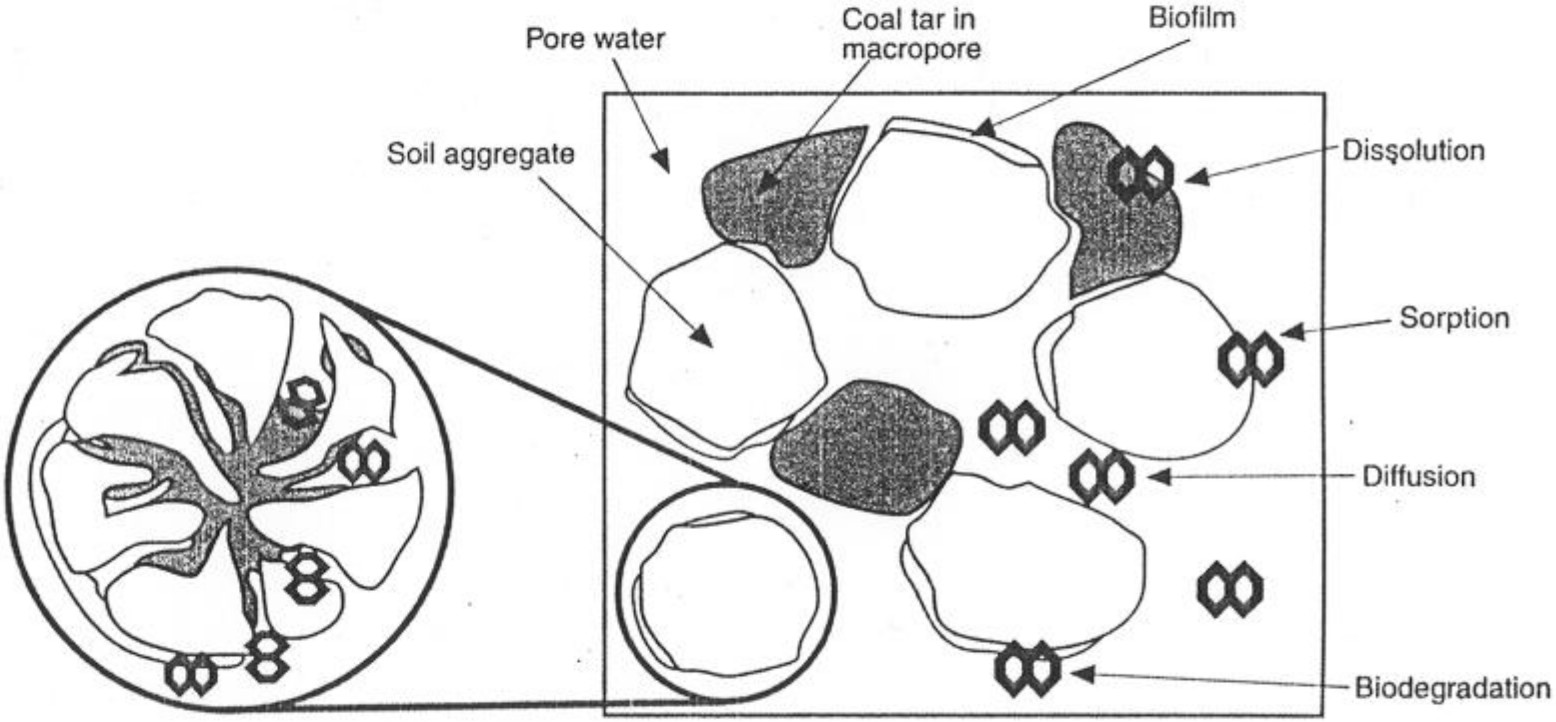


Figure 9. Sorption isotherms of benzo[a]pyrene [45].

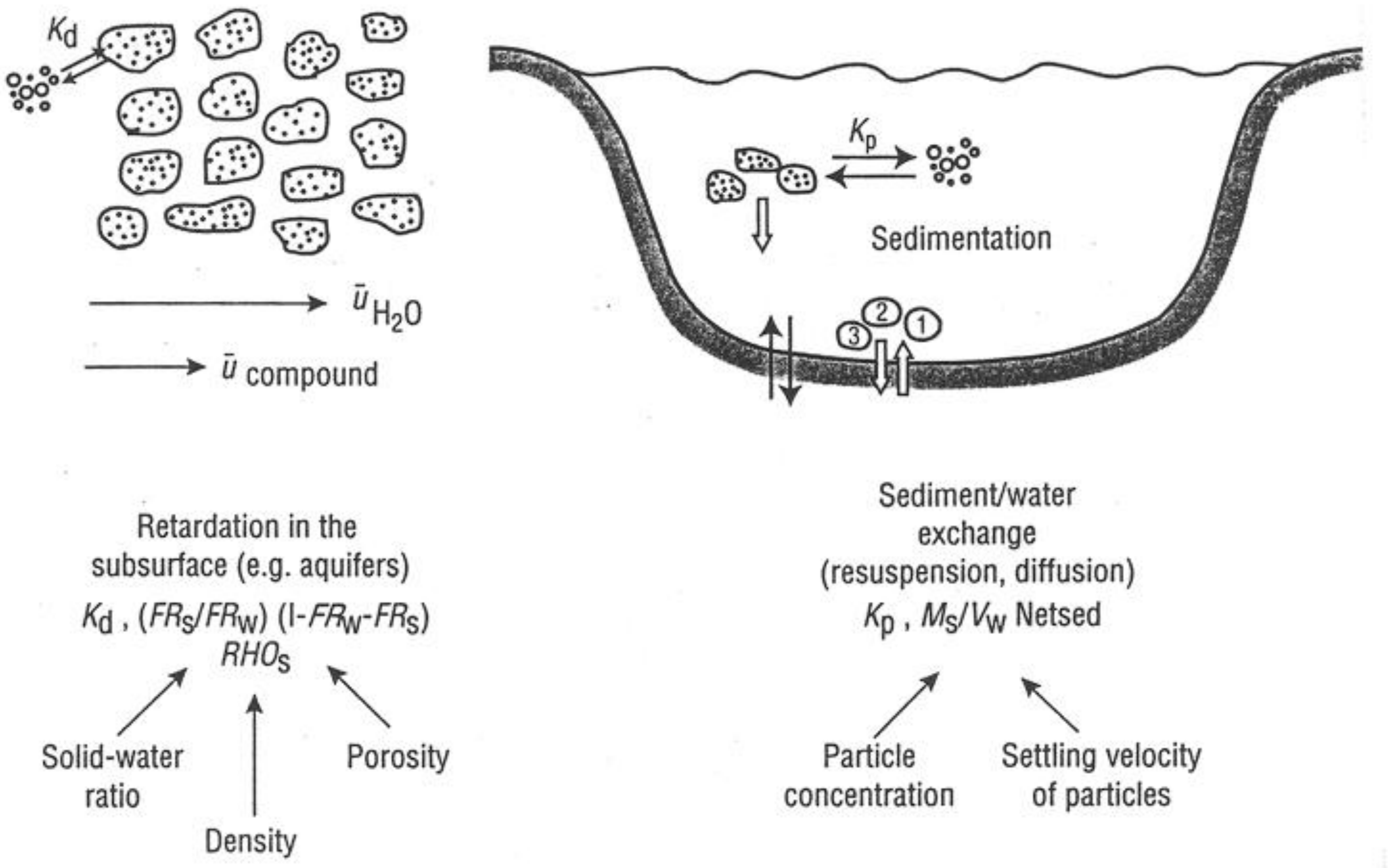
Sorption

FIGURE 2

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



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



Solids-water exchange in natural waters. See text for the explanation of abbreviations. From Schwarzenbach

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)

AMAP
Arctic Monitoring and Assessment Programme

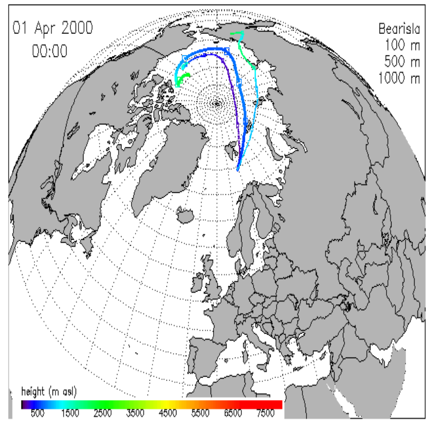
Principles and consequences of long-range transport

- **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**

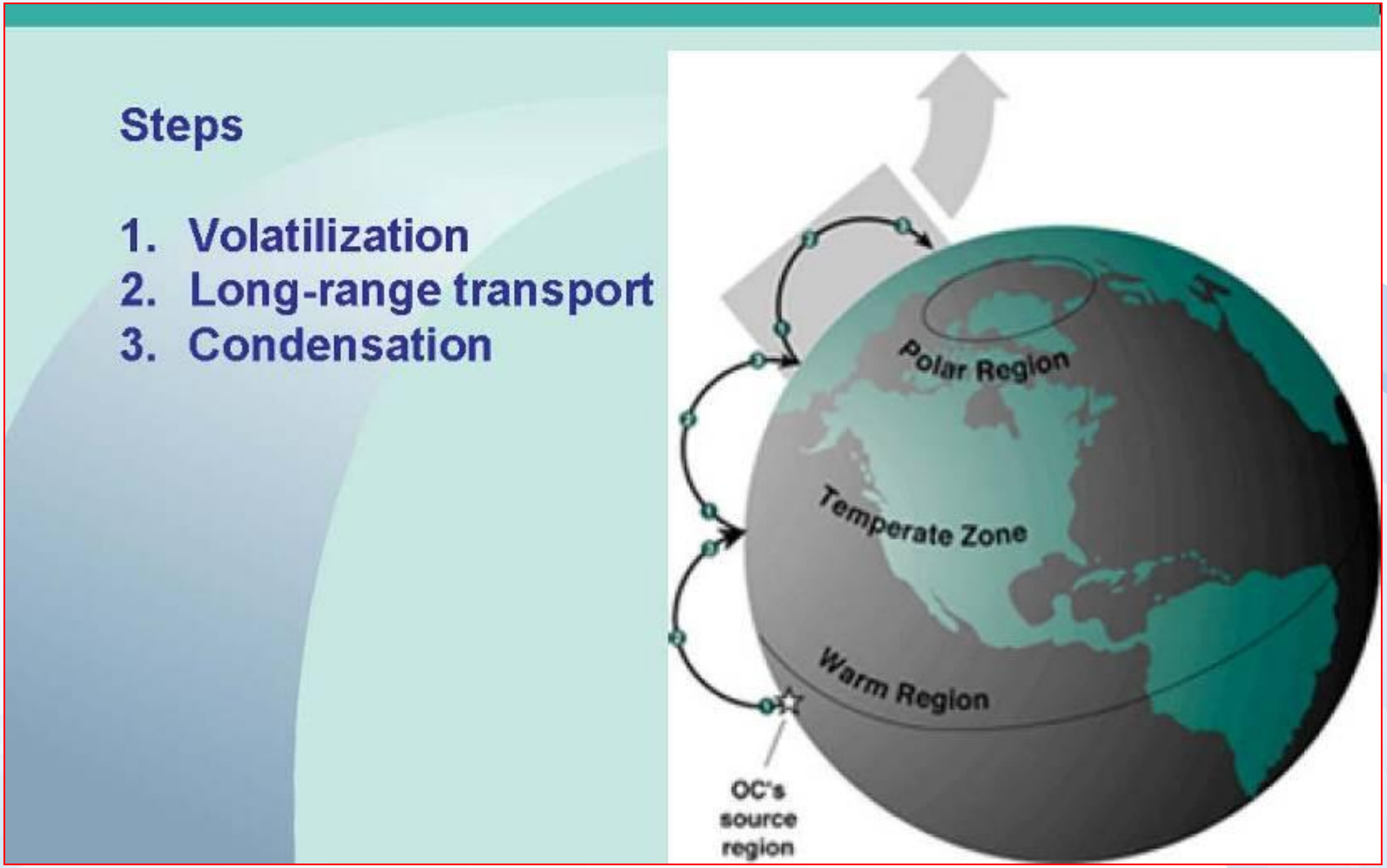
Long-range transport elucidation

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 type
- Transport and fate modeling



The „Grasshopper Effect“

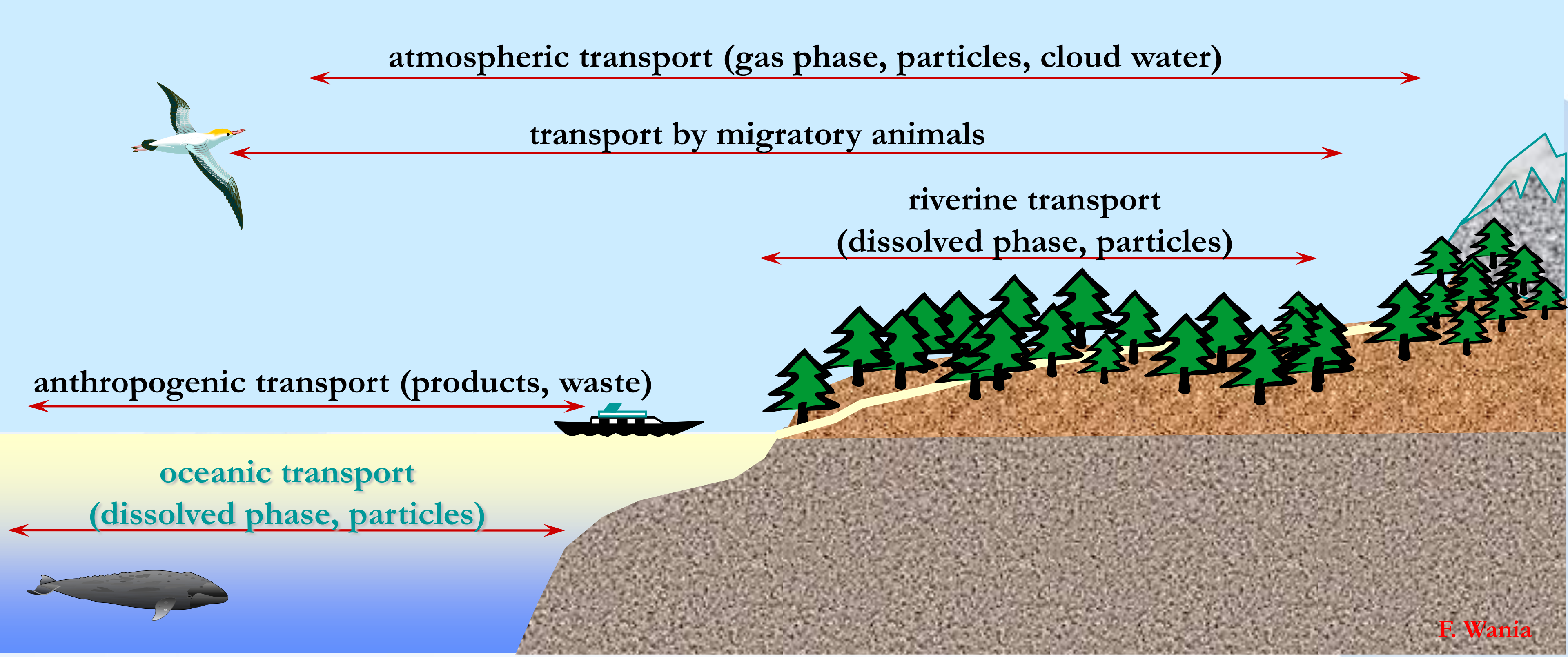


Steps

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)

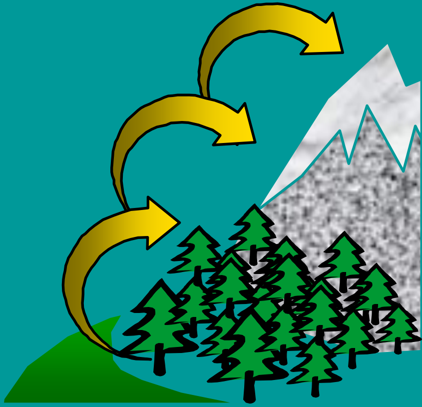


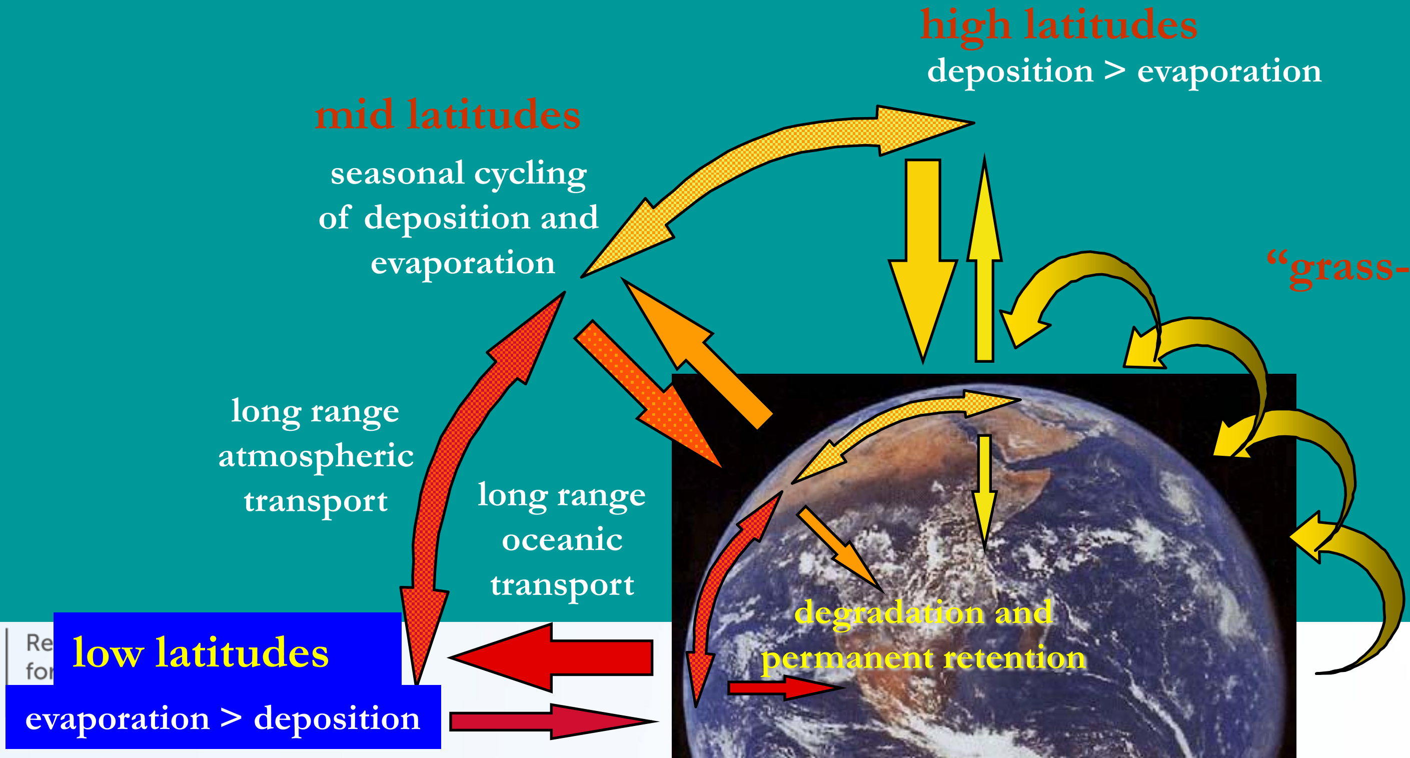
Research centre
for toxic compounds
in the environment

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





high latitudes

deposition > evaporation

mid latitudes

seasonal cycling of deposition and evaporation

"grass-hopping"

long range atmospheric transport

long range oceanic transport

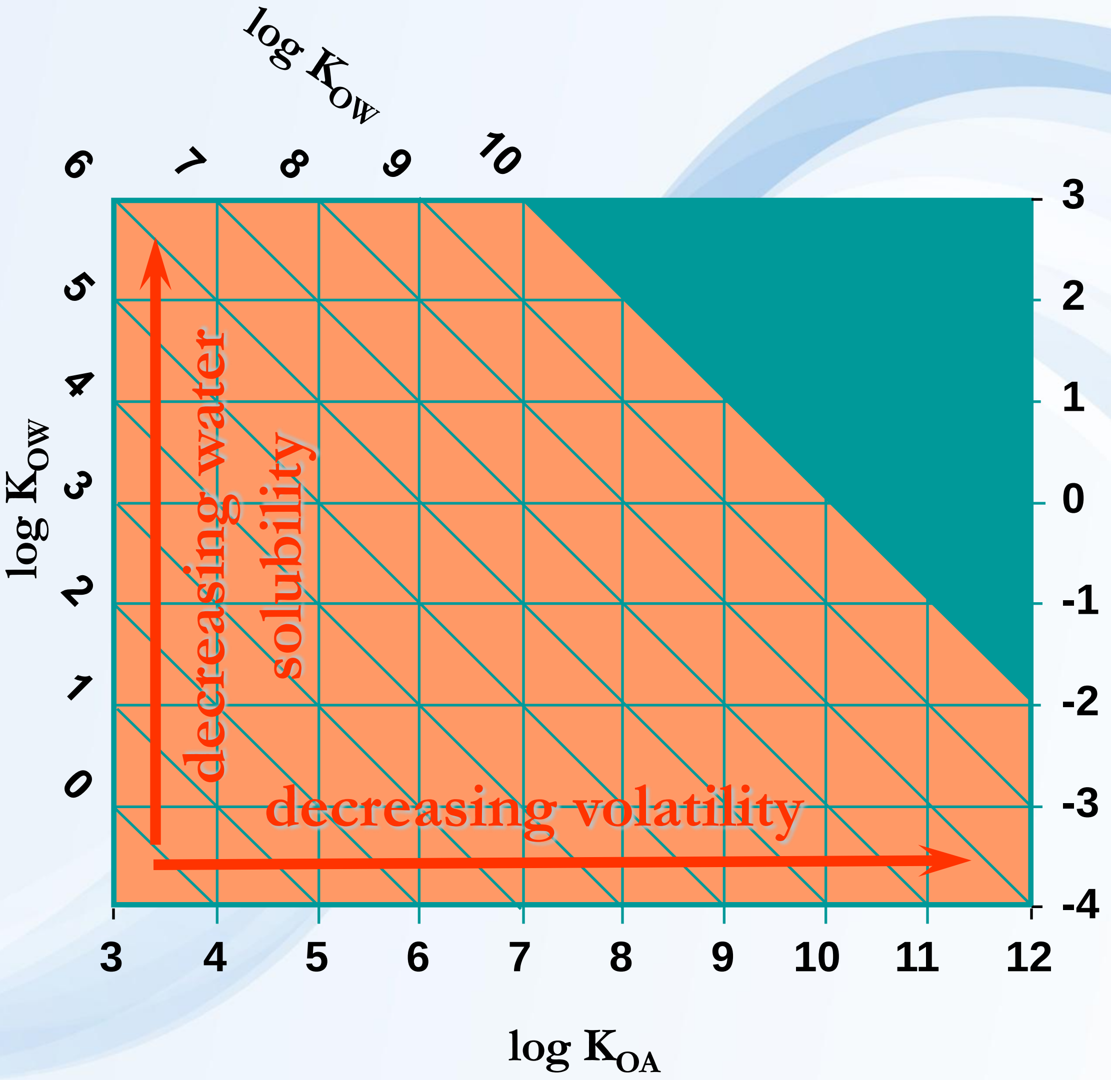
degradation and permanent retention

low latitudes

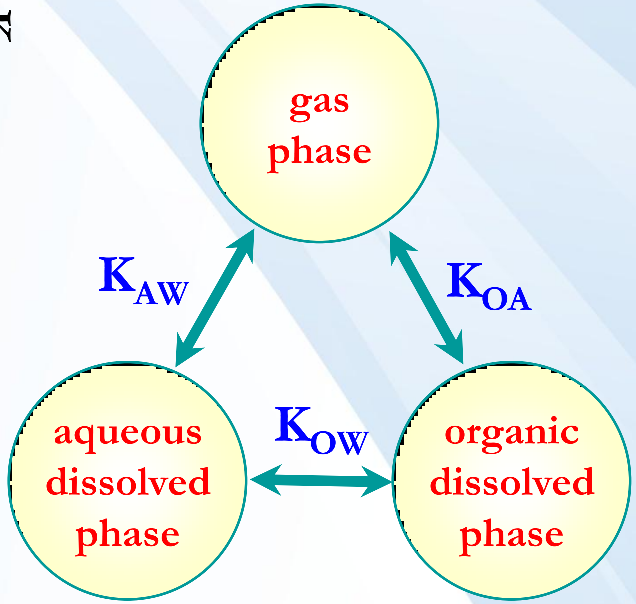
evaporation > deposition

F. Wania

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

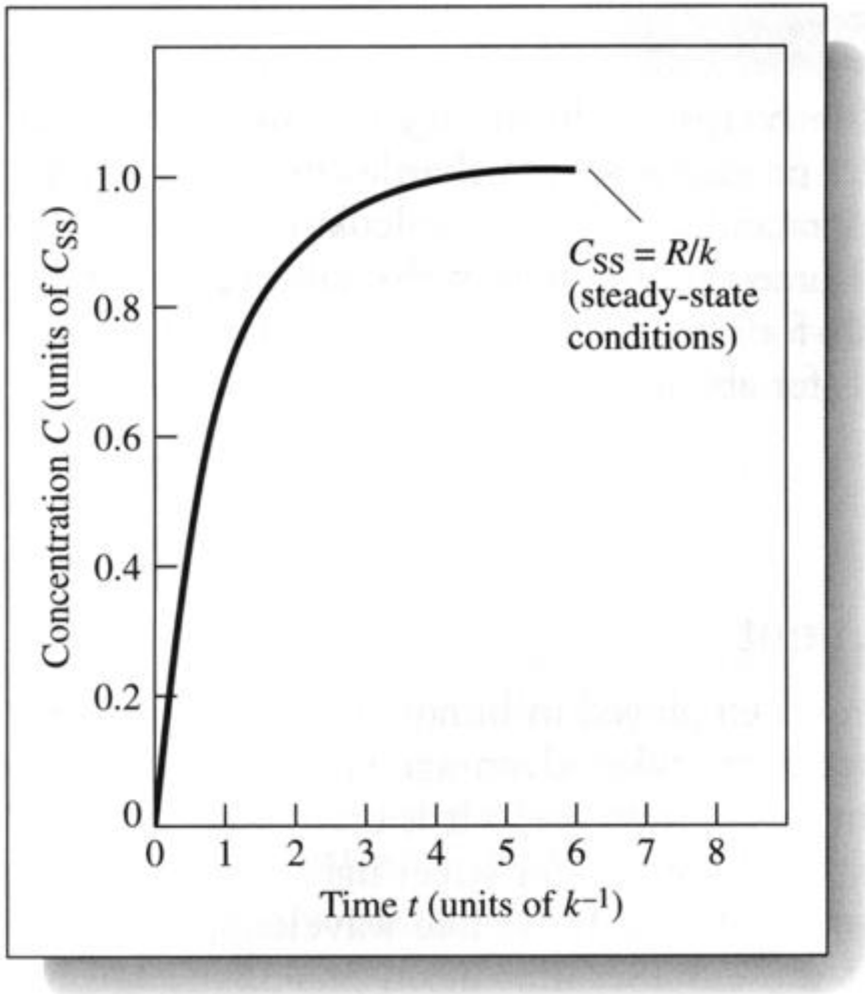


Figure 7-1
Increase in metal concentration with time to reach the steady-state value, C_{ss}.

Bioconcentration – basic definitions

The process in which the chemical concentration in an (aquatic) organism exceeds that in water (soil) as a results 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

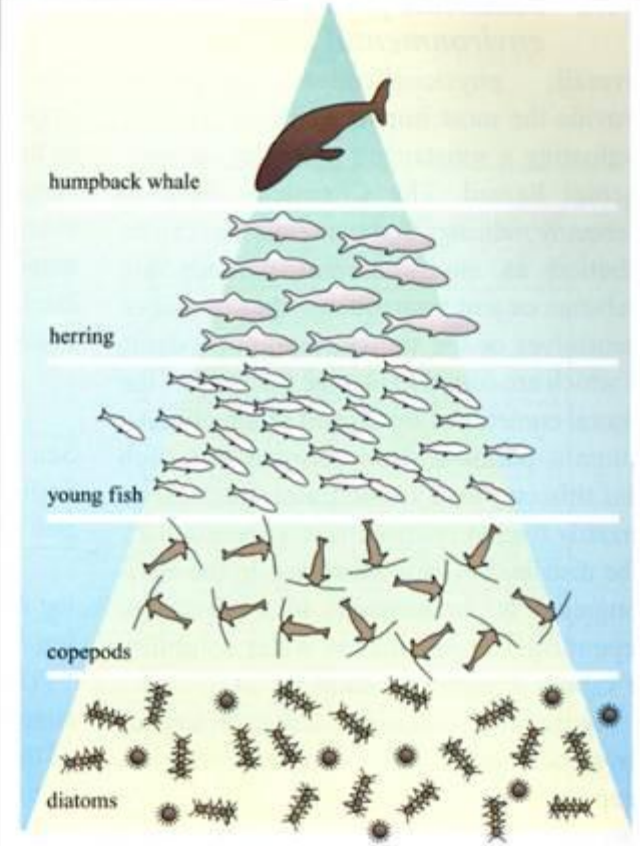


Figure 5.1.4 Food pyramid

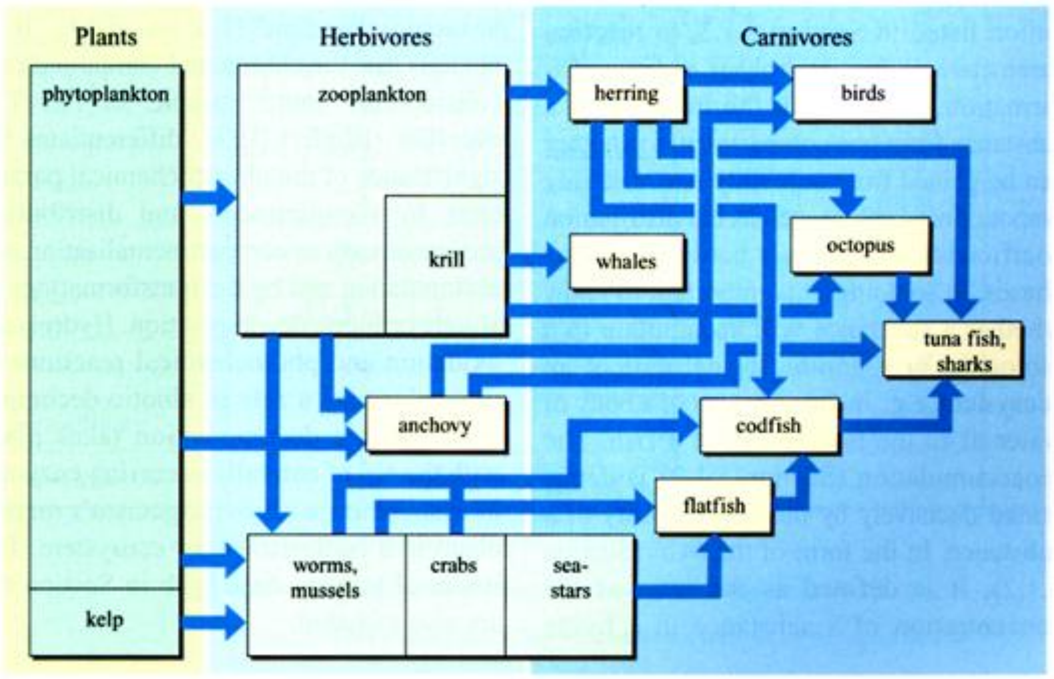


Figure 5.1.5 Food chain network

Bioaccumulation

Bioaccumulation

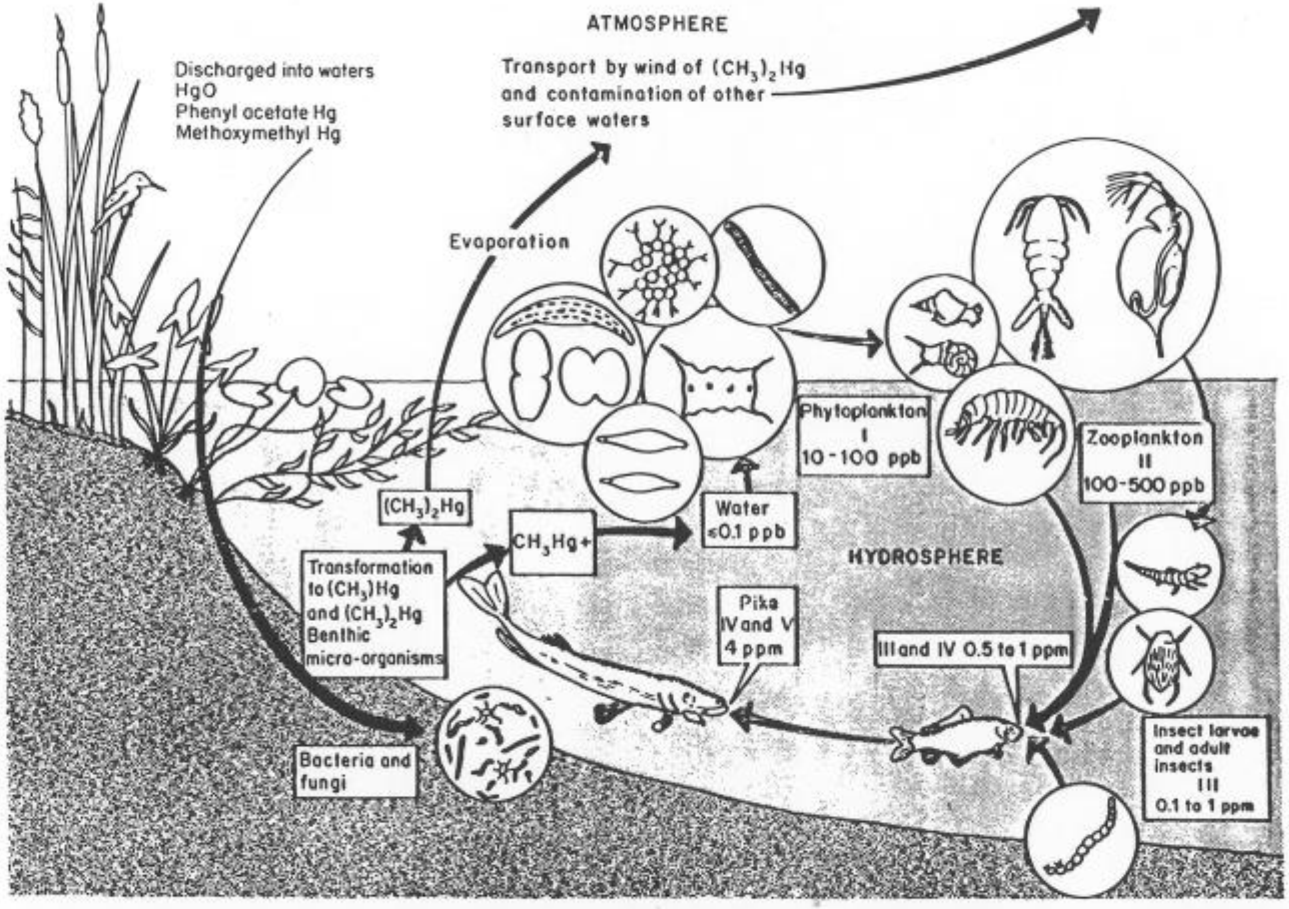


Fig. 3.24 Contamination of the food chain of the pike in Sweden (this diagram has been based on one by Duvigneaud (1974) and on analytical data on mercury contamination from various Swedish researchers). (*In* Ramade, 1982. *Reproduced by permission of McGraw-Hill*)

Bioaccumulation, biomagnification

Elimination process

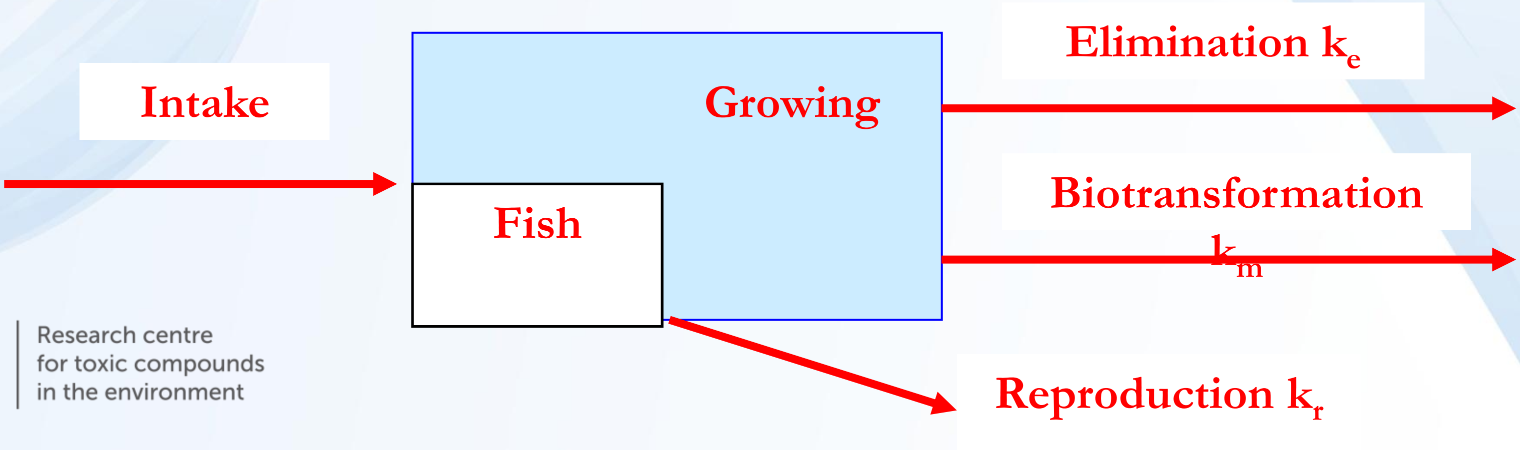
Analogically of the process of intake also the process of elimination can be directed mainly by passive diffusion and active transport.

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 mote hydrophilic compounds is other possible proces of elimination of compound from organism.



Intake

Growing

Fish

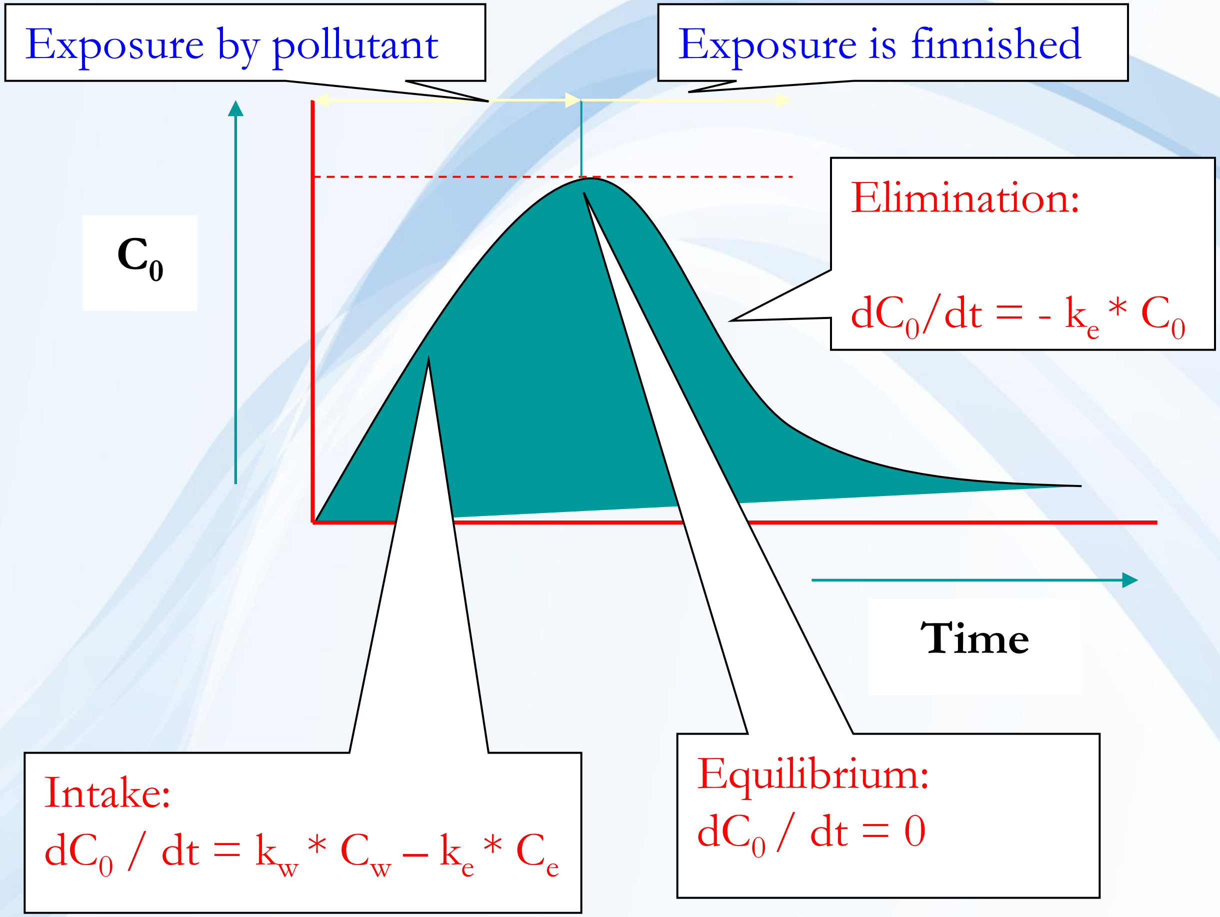
Elimination k_e

Biotransformation k_m

Reproduction k_r

Bioaccumulation, biomagnification

Intake and elimination of compounds by aquatic organism:



Exposure by pollutant

Exposure is finnished

Elimination:

$dC_0/dt = - k_e * C_0$

Intake:

$dC_0 / dt = k_w * C_w – k_e * C_e$

Equilibrium:

$dC_0 / dt = 0$

Bioaccumulation

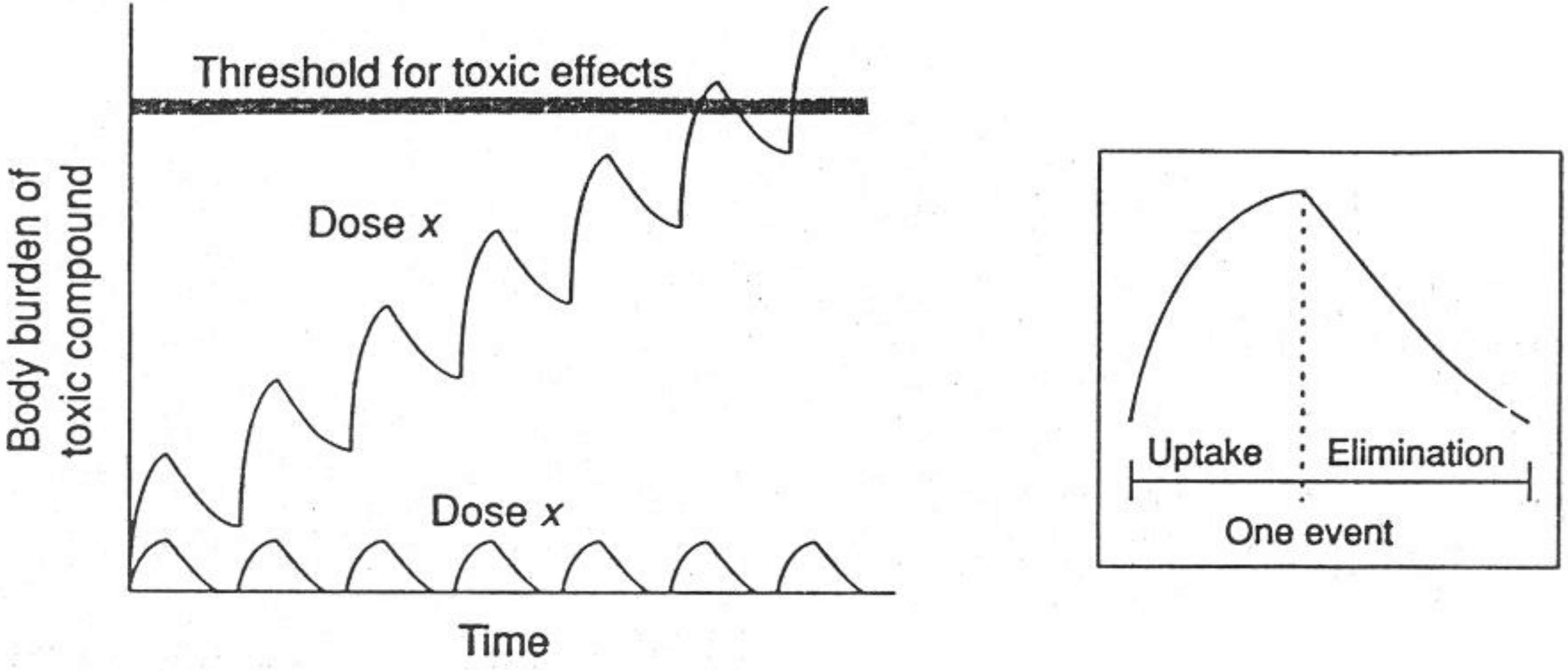


FIGURE 5-5

Effect of dose fractionalization on accumulation of a toxic compound.

Research centre
for toxic compounds
in the environment

Bioaccumulation factor

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

$$BAF = C_B / C_W$$

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}):

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

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 (BCF) is the ratio of the chemical concentration in an organism (C_B) to the concentration in the organism´s diet (C_W):

$$BMF = C_B / C_D$$

Relationship between BCF and log K_{OW}

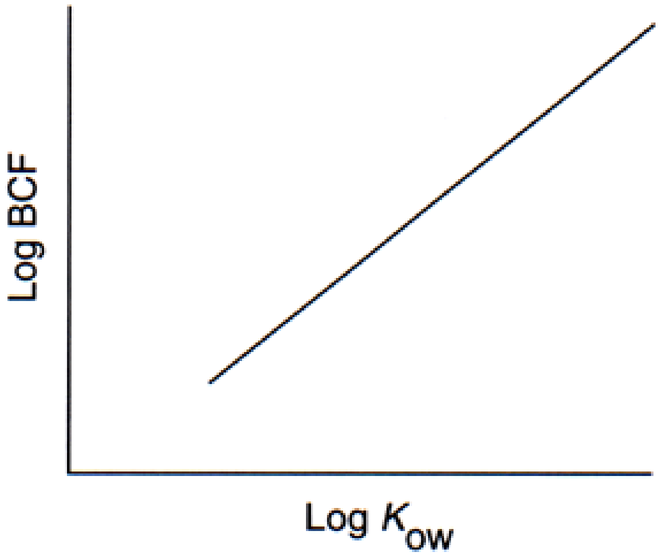
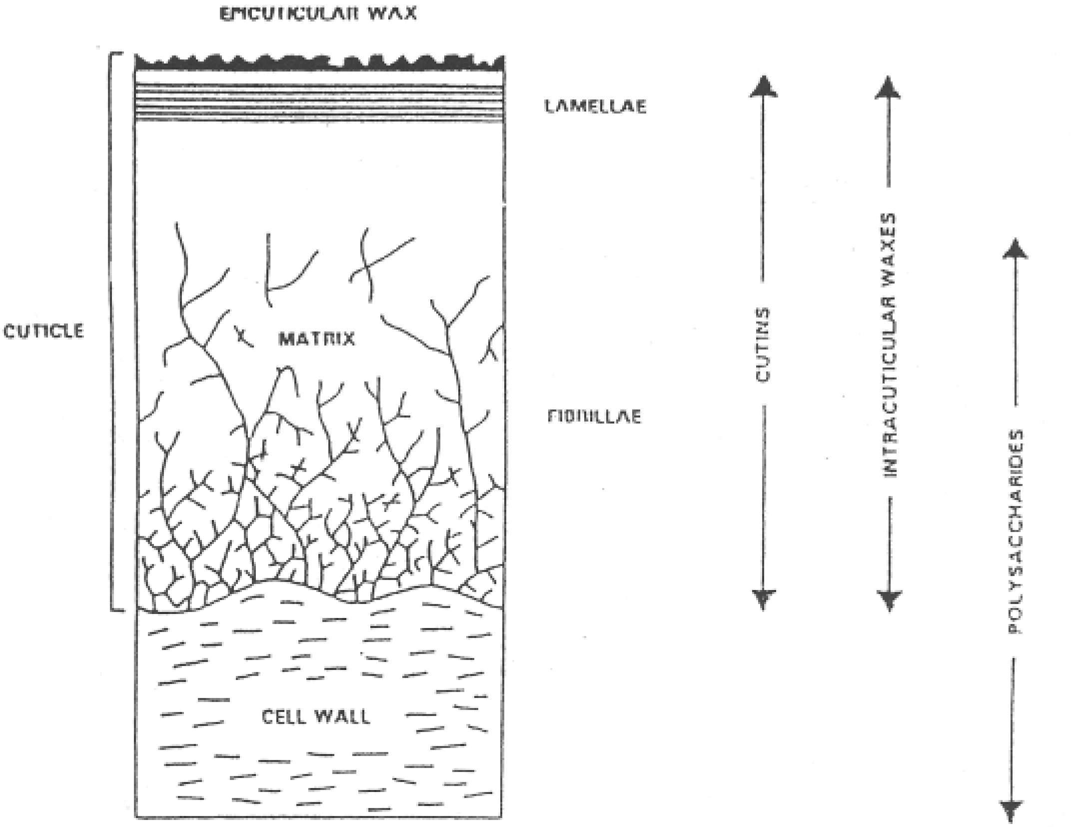


FIGURE 4.1 *Relationship of BCF to log* K_{ow}.

Bioaccumulation in terrestric vegetation



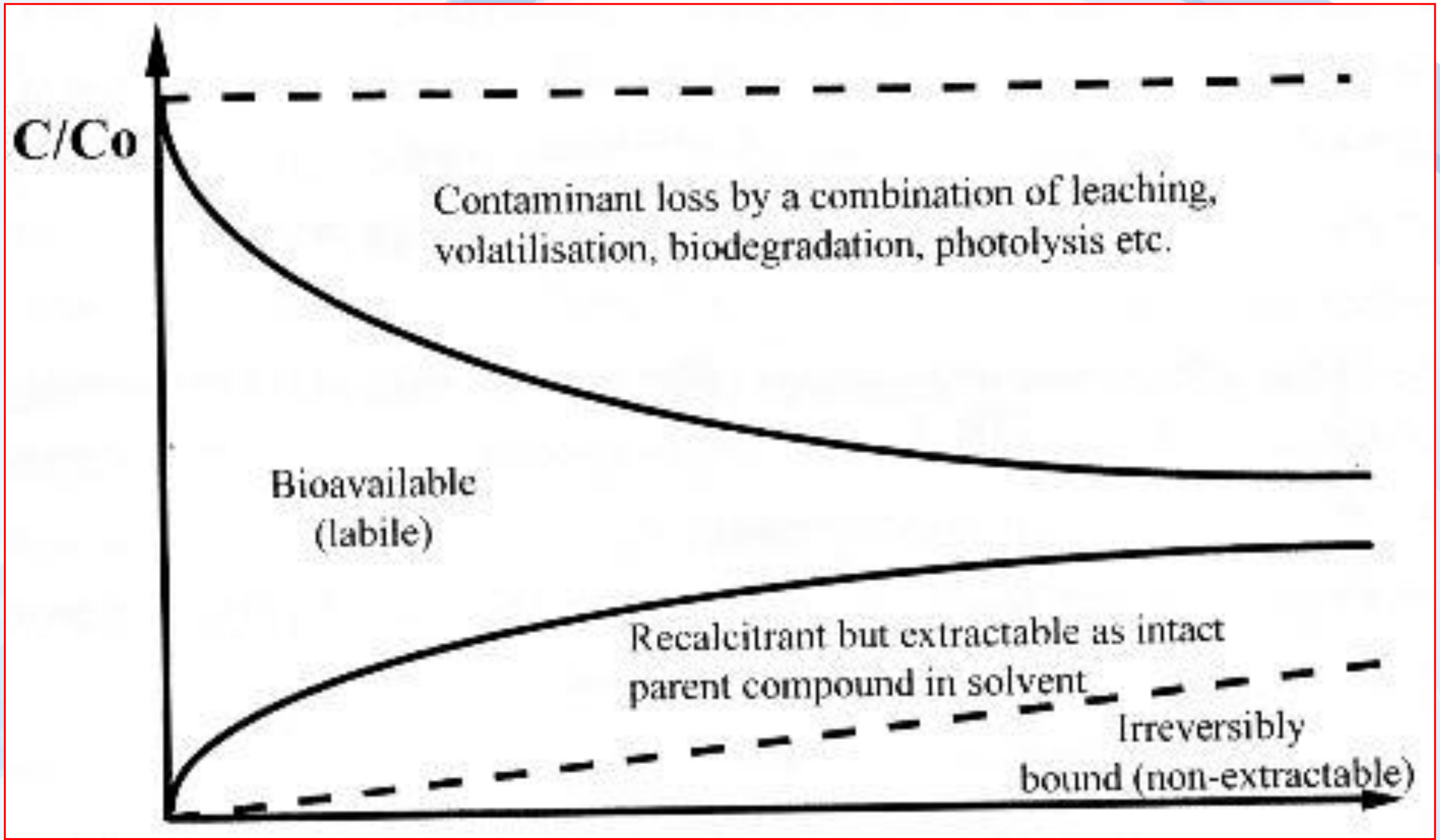
Summary of the main internal ultrastructural and chemical features of plant cuticles (from Holloway, 1993)

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

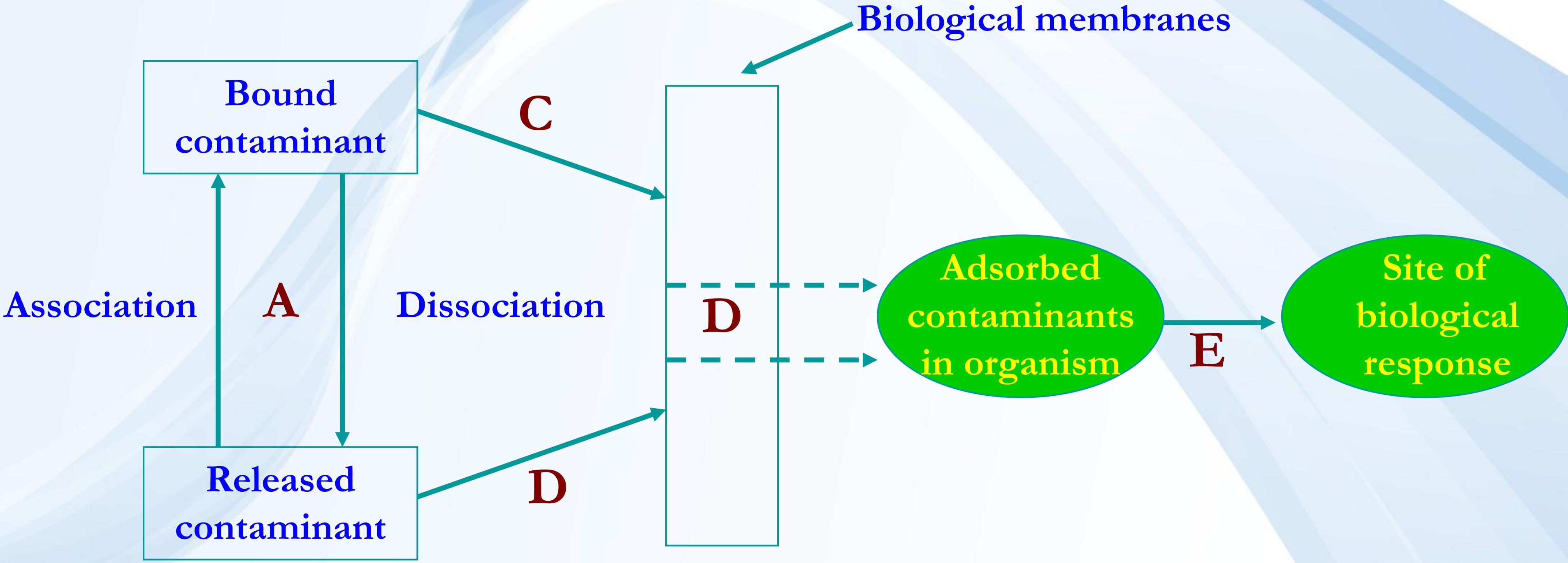
Bioavailability processes can be defined as the individual physical, chemical and biological interactions that determine the exposure of organisms to chemicals associated with soils and sediments.



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)



Biological membranes

Bound contaminant

C

Association

A

Dissociation

D

Released contaminant

D

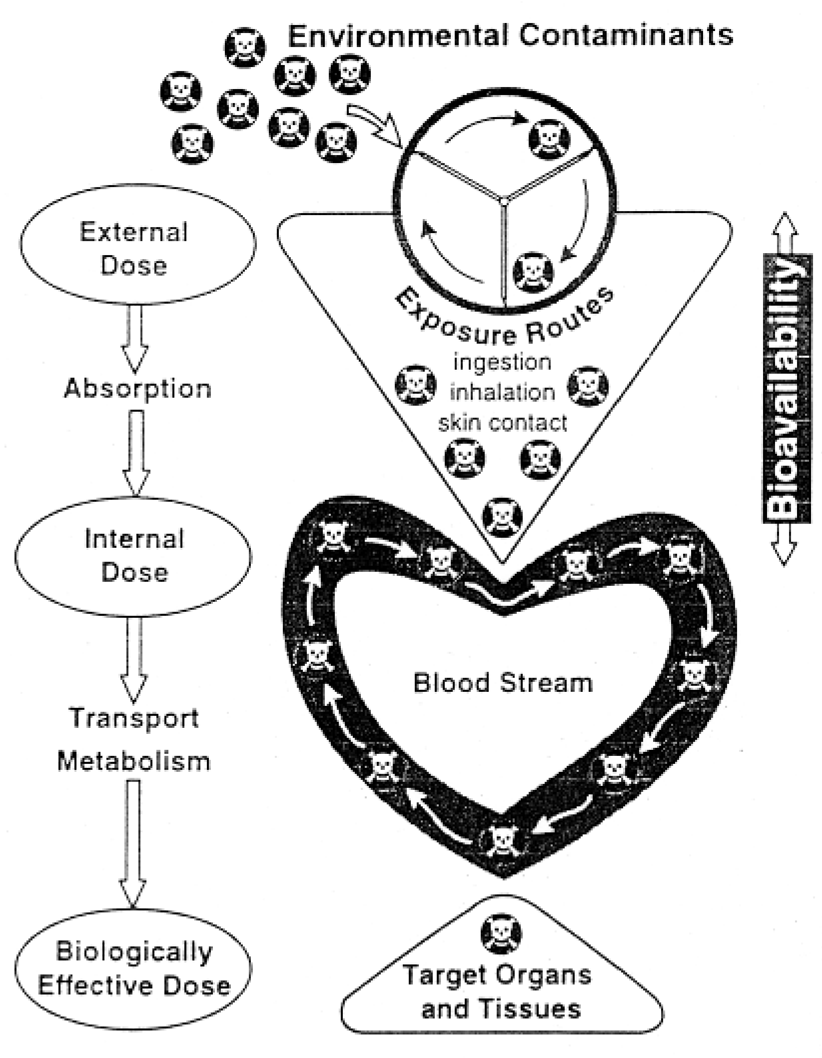
Adsorbed contaminants in organism

E

Site of biological response

Ehlers and Luthy, 2003

Chemicals in the living organisms



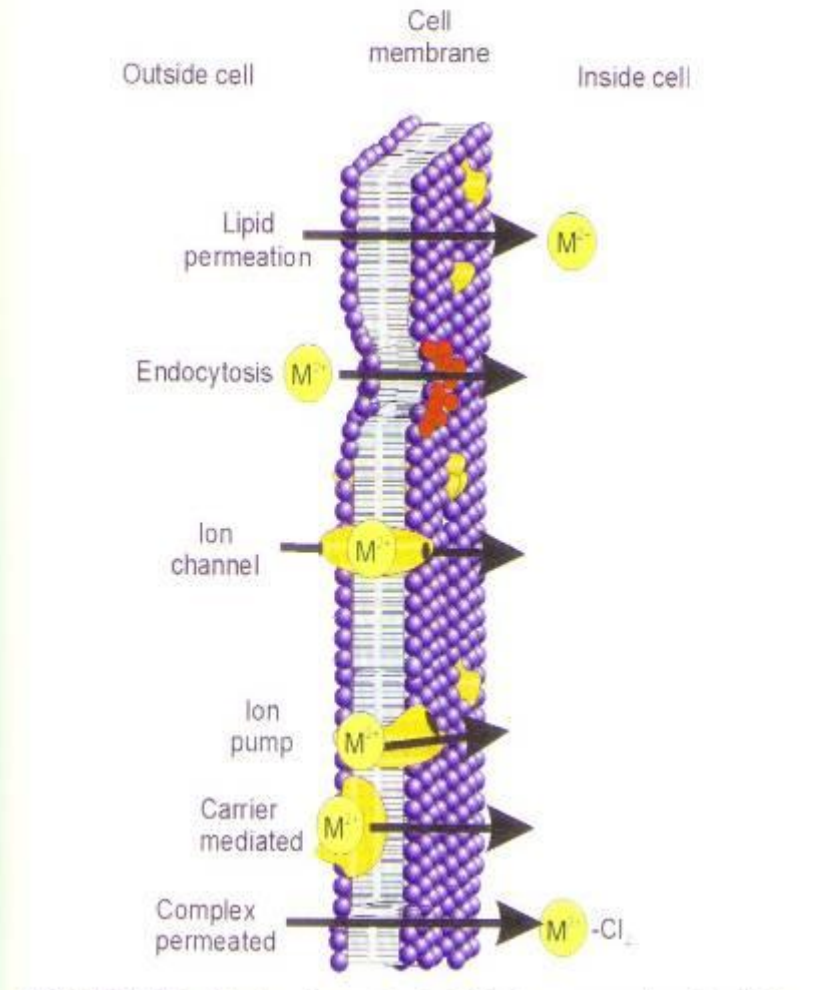
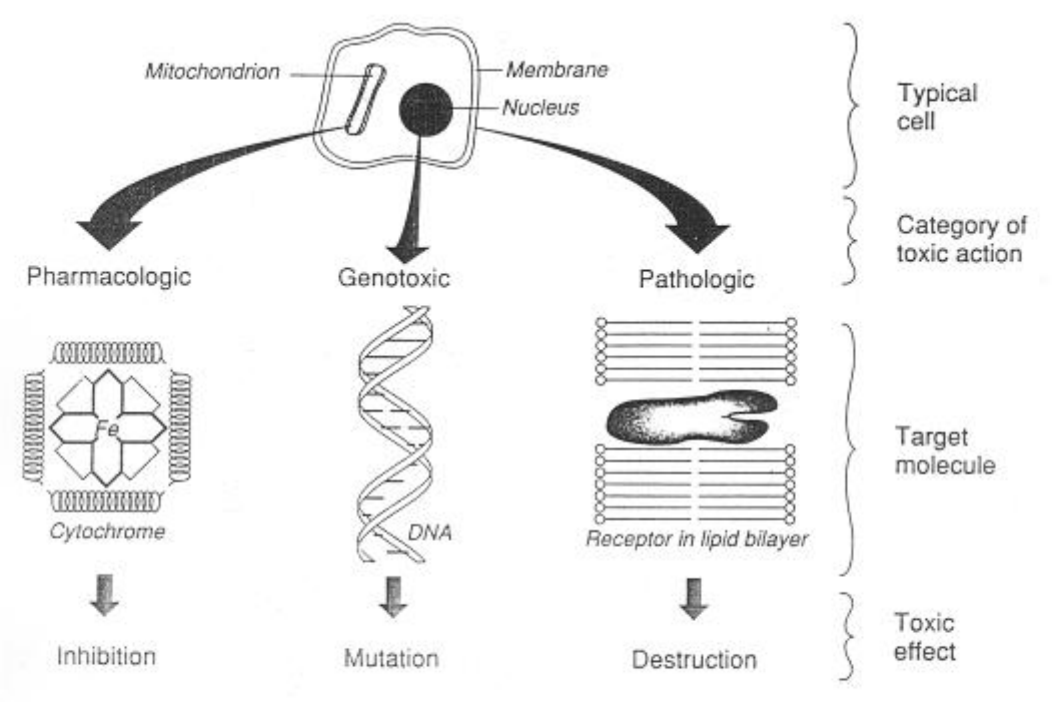


FIGURE 17.4 Mechanisms of metal (M) flux across the microbial cell membrane. (Adapted from Simkiss and Taylor, 1989.)

Toxic effects of chemical compounds



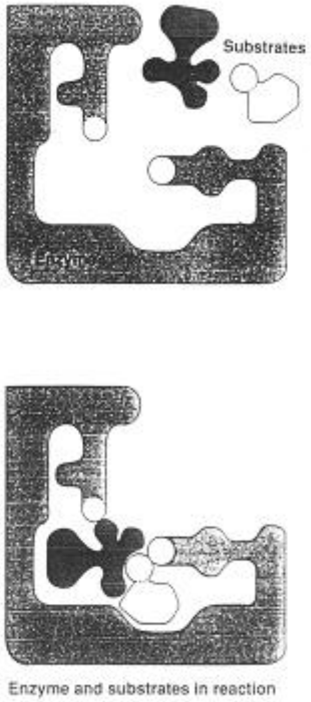
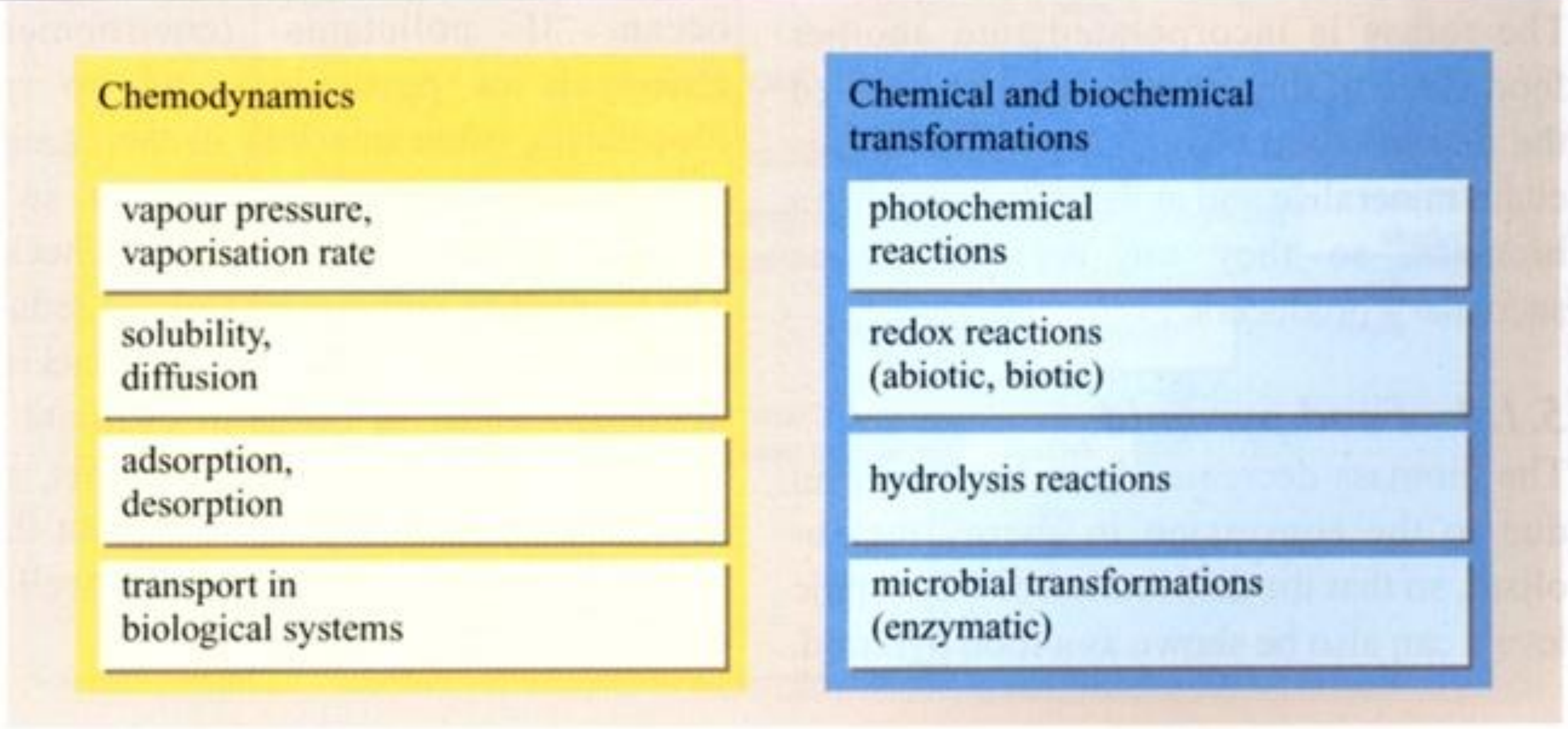


FIGURE 5-8
Lock-and-key model for toxic action.[29]

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.**

Chemical transformation processes

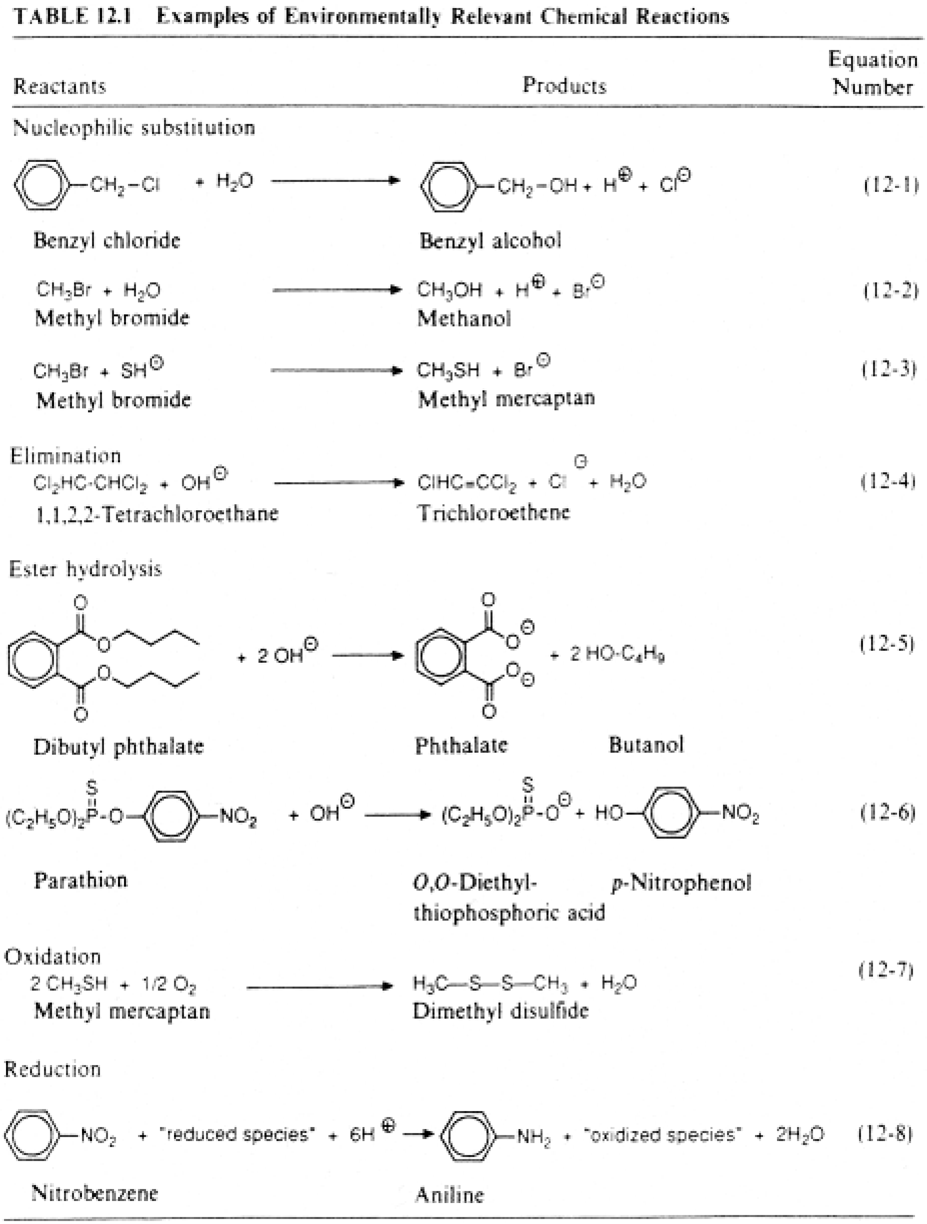


TABLE 12.1 Examples of Environmentally Relevant Chemical Reactions

Reactants	Products	Equation Number
Nucleophilic substitution		
—CH_2-Cl + H_2O Benzyl chloride	—CH_2-OH + $H^{\oplus}$ + $Cl^{\ominus}$ Benzyl alcohol	(12-1)
$CH_3Br + H_2O$ Methyl bromide	$CH_3OH + H^{\oplus} + Br^{\ominus}$ Methanol	(12-2)
$CH_3Br + SH^{\ominus}$ Methyl bromide	$CH_3SH + Br^{\ominus}$ Methyl mercaptan	(12-3)
Elimination		
$Cl_2HC\text{-}CHCl_2 + OH^{\ominus}$ 1,1,2,2-Tetrachloroethane	$ClHC{=}CCl_2 + Cl^{\ominus} + H_2O$ Trichloroethene	(12-4)
Ester hydrolysis		
+ 2 $OH^{\ominus}$ Dibutyl phthalate	+ 2 HO-C_4H_9 Phthalate Butanol	(12-5)
$(C_2H_5O)_2\overset{S}{\overset{\parallel}{P}}\text{-}O$—$NO_2$ + $OH^{\ominus}$ Parathion	$(C_2H_5O)_2\overset{S}{\overset{\parallel}{P}}\text{-}O^{\ominus}$ + HO—NO_2 *O,O*-Diethyl- thiophosphoric acid *p*-Nitrophenol	(12-6)
Oxidation		
$2\ CH_3SH + 1/2\ O_2$ Methyl mercaptan	$H_3C-S-S-CH_3 + H_2O$ Dimethyl disulfide	(12-7)
Reduction		
—NO_2 + "reduced species" + $6H^{\oplus}$ Nitrobenzene	—NH_2 + "oxidized species" + $2H_2O$ Aniline	(12-8)

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

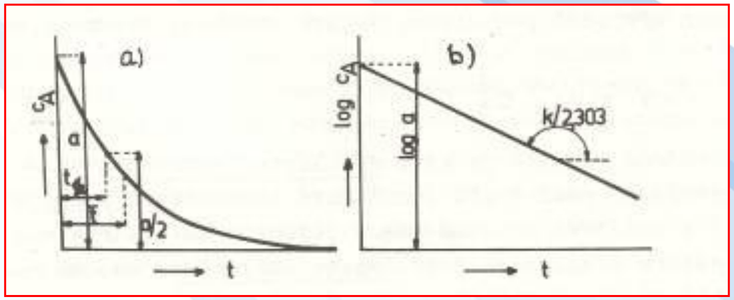
Reaction of the first order:

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

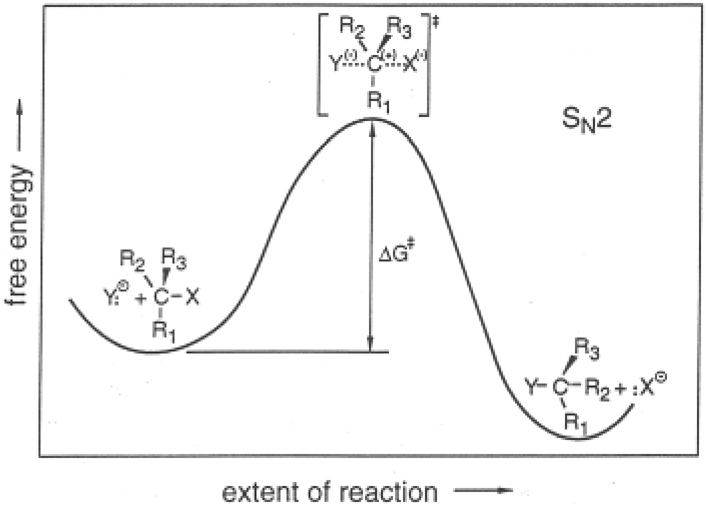


Figure 12.3 Two-dimensional portrayal of relative free energies exhibited by the educts, activated complex, and products of an S_N2 reaction.

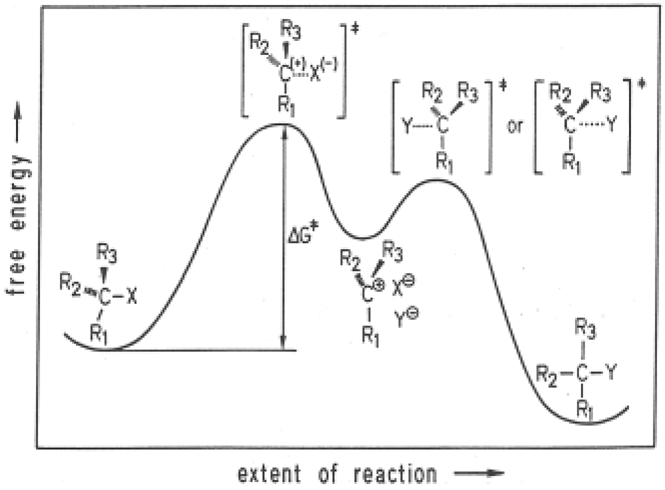


Figure 12.4 Two-dimensional portrayal of the relative free energies exhibited by educt, activated complexes, an intermediate, and product of an S_N1 reaction.

Oxidation

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

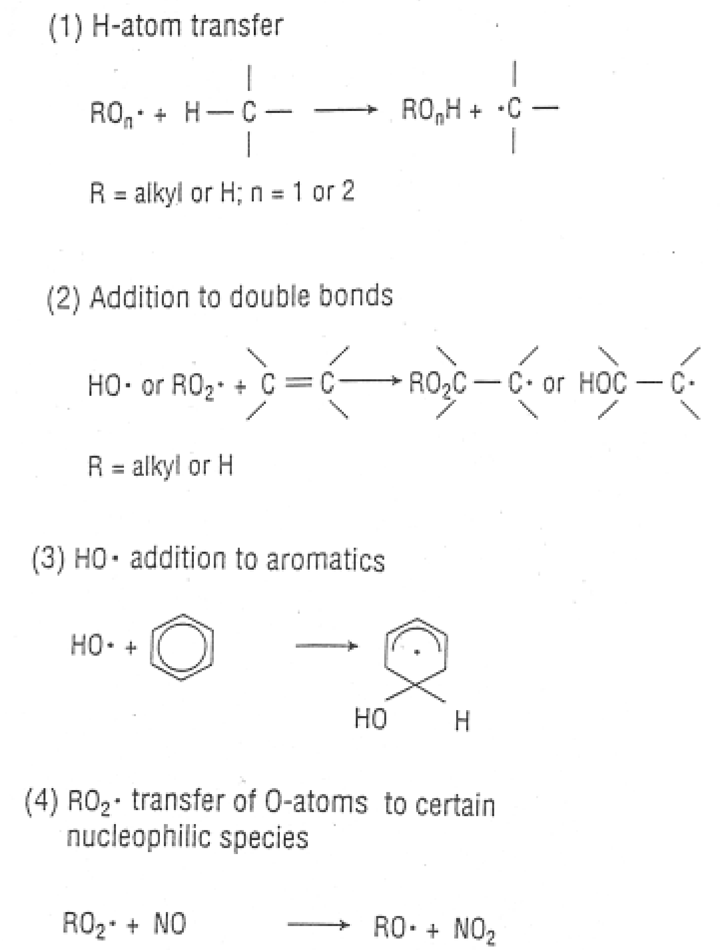
Examples of oxidants present under environmental conditions in sufficient high concentrations and react quickly with organic substances:

- alkoxy radicals (RO•)
- peroxy radicals (ROO•)
- hydroxyl radicals (OH•)
- singlet oxygen ($^1O_2$)
- 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 troposhere and surface waters.

Oxidation



(1) H-atom transfer

$RO_n\cdot + H-\overset{|}{\underset{|}{C}}- \longrightarrow RO_nH + \cdot\overset{|}{\underset{|}{C}}-$

R = alkyl or H; n = 1 or 2

(2) Addition to double bonds

$HO\cdot \text{ or } RO_2\cdot + \rangle C=C\langle \longrightarrow RO_2\rangle C-C\langle\cdot \text{ or } HO\rangle C-C\langle\cdot$

R = alkyl or H

(3) HO· addition to aromatics

$HO\cdot +$

(4) $RO_2\cdot$ transfer of O-atoms to certain nucleophilic species

$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2$

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

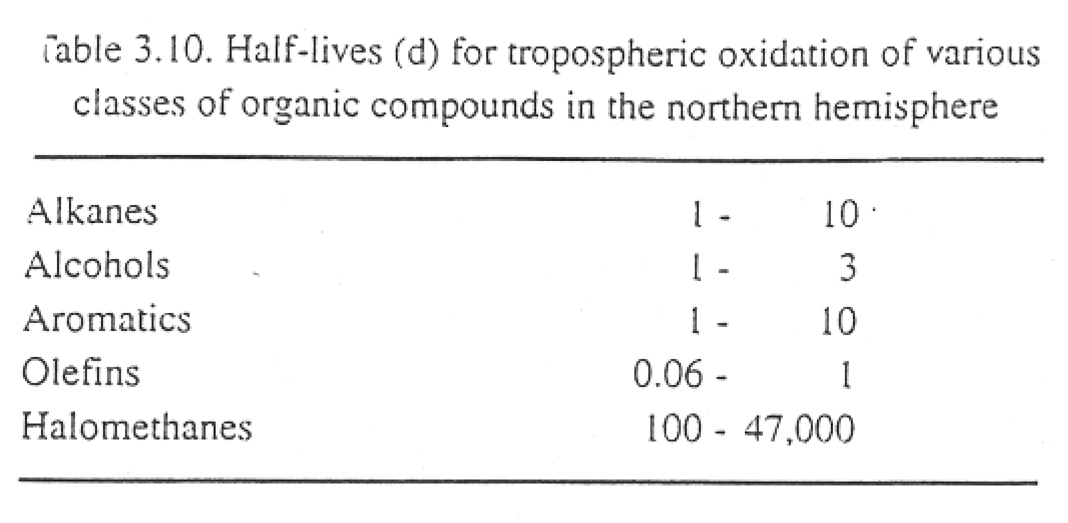
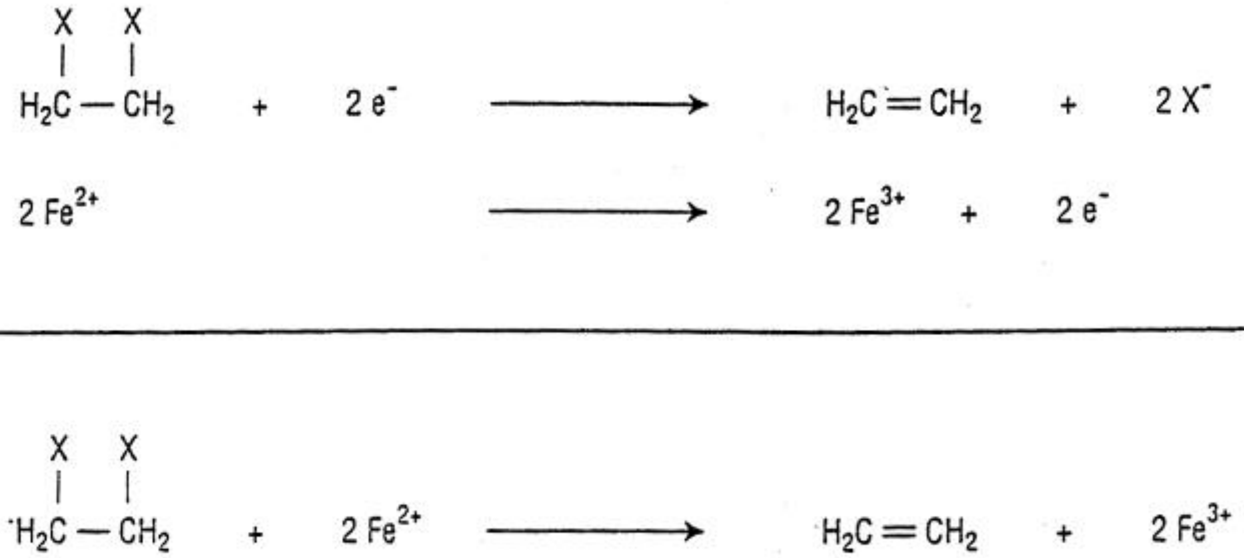


Table 3.10. Half-lives (d) for tropospheric oxidation of various classes of organic compounds in the northern hemisphere

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

Reduction



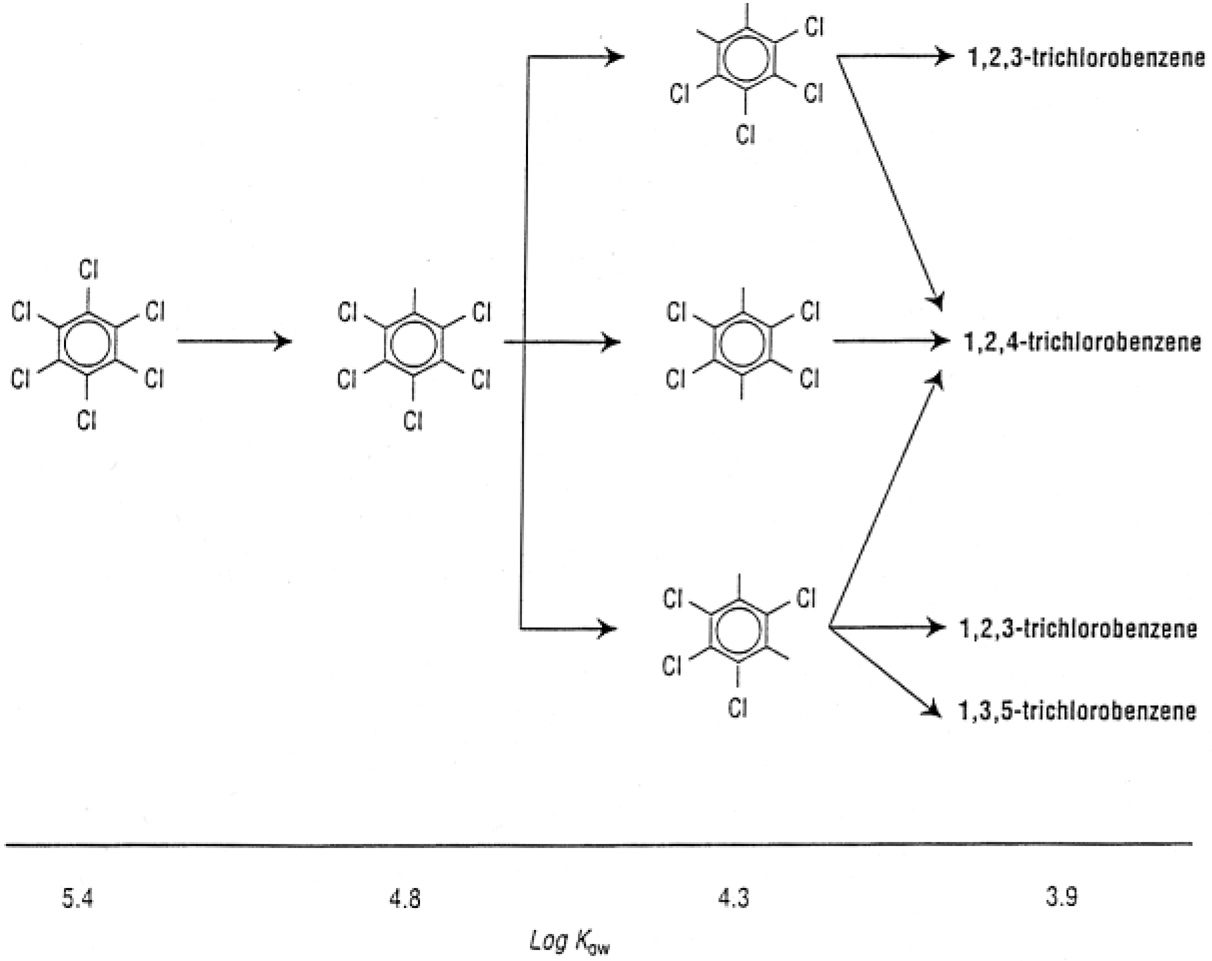
$$\mathrm{XH_2C{-}CH_2X} + 2\,e^- \longrightarrow \mathrm{H_2C{=}CH_2} + 2\,X^-$$

$$2\,Fe^{2+} \longrightarrow 2\,Fe^{3+} + 2\,e^-$$

$$\mathrm{XH_2C{-}CH_2X} + 2\,Fe^{2+} \longrightarrow \mathrm{H_2C{=}CH_2} + 2\,Fe^{3+}$$

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



Products formed by reductive dehalogenation of hexachlorobenzene and the corresponding values of log K_{ow}.

Photochemical transformation processes

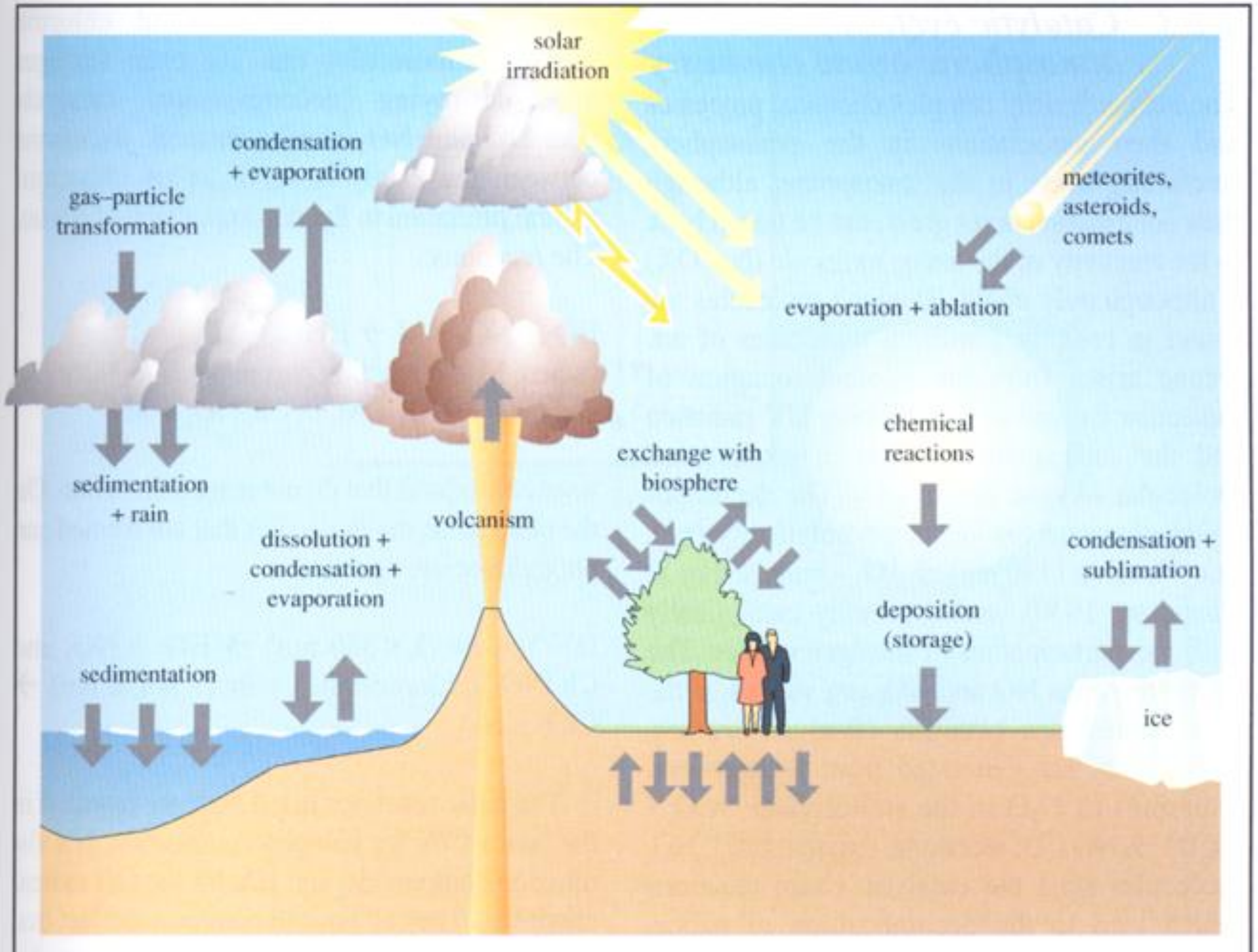
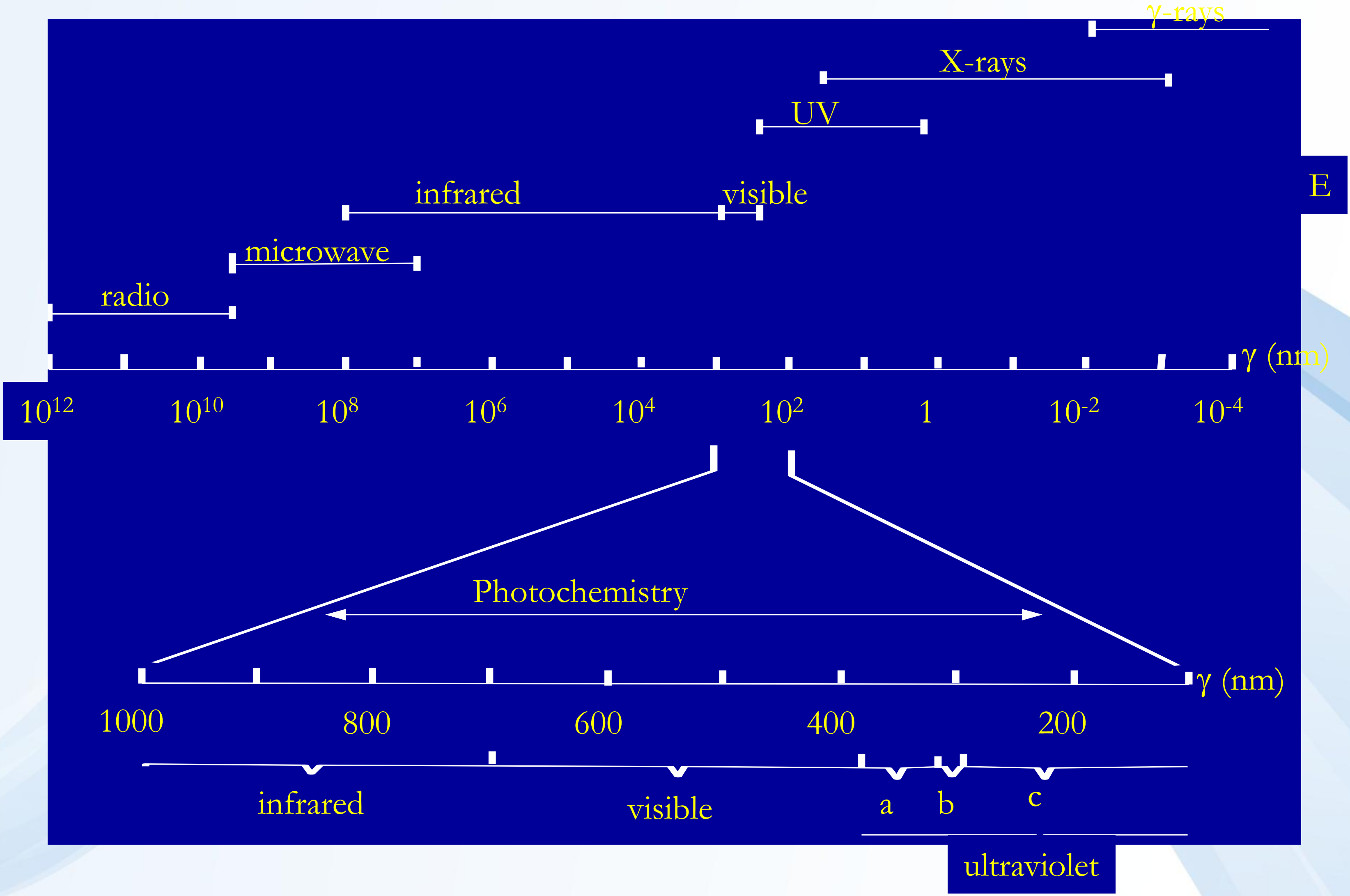


Figure 2.2.1 Chemistry and photochemistry

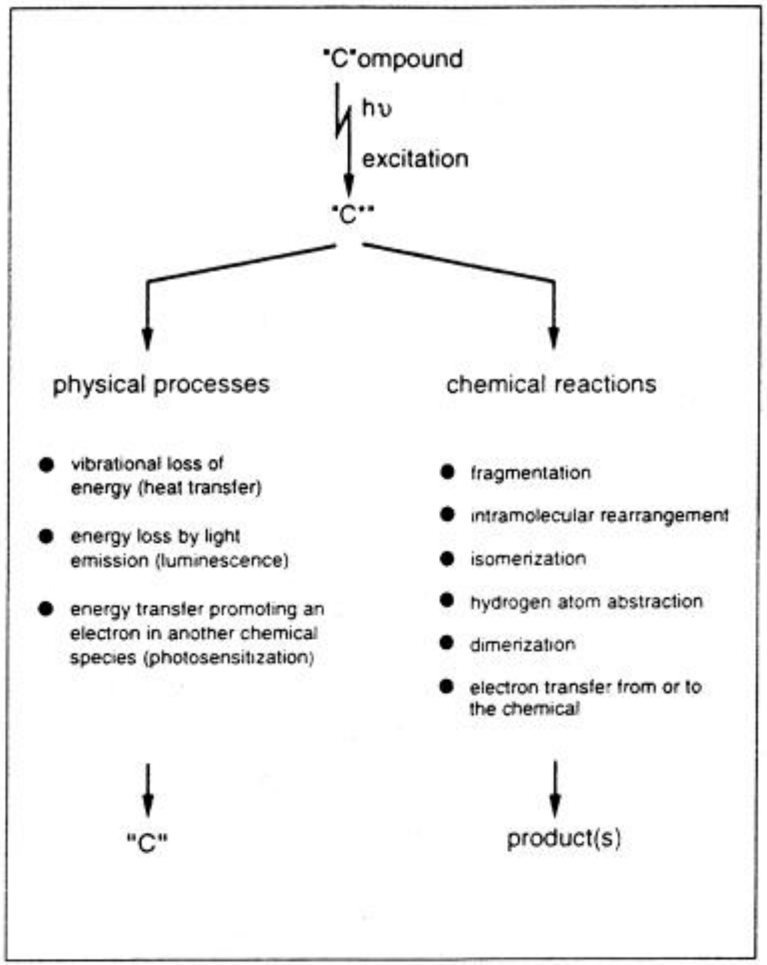
Research centre
for toxic compounds
in the environment

Photochemical transformation processes



Research centre
for toxic compounds
in the environment

Photochemical transformation processes



"C"ompound

$h\nu$

excitation

"C"*

physical processes

- vibrational loss of energy (heat transfer)
- energy loss by light emission (luminescence)
- energy transfer promoting an electron in another chemical species (photosensitization)

"C"

chemical reactions

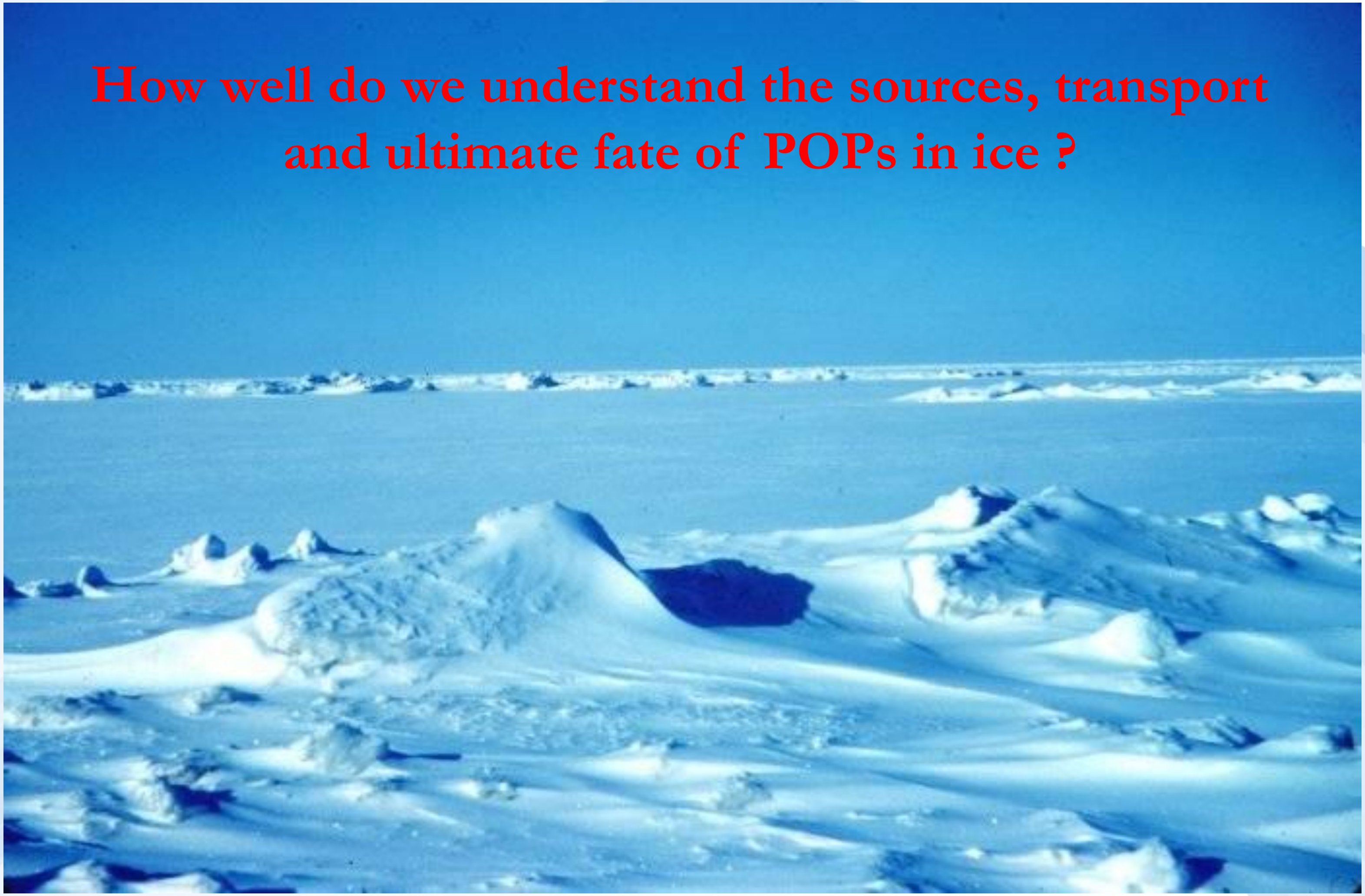
- fragmentation
- intramolecular rearrangement
- isomerization
- hydrogen atom abstraction
- dimerization
- electron transfer from or to the chemical

product(s)

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

Research centre
for toxic compounds
in the environment

Photochemistry of organic pollutants in solid matrices

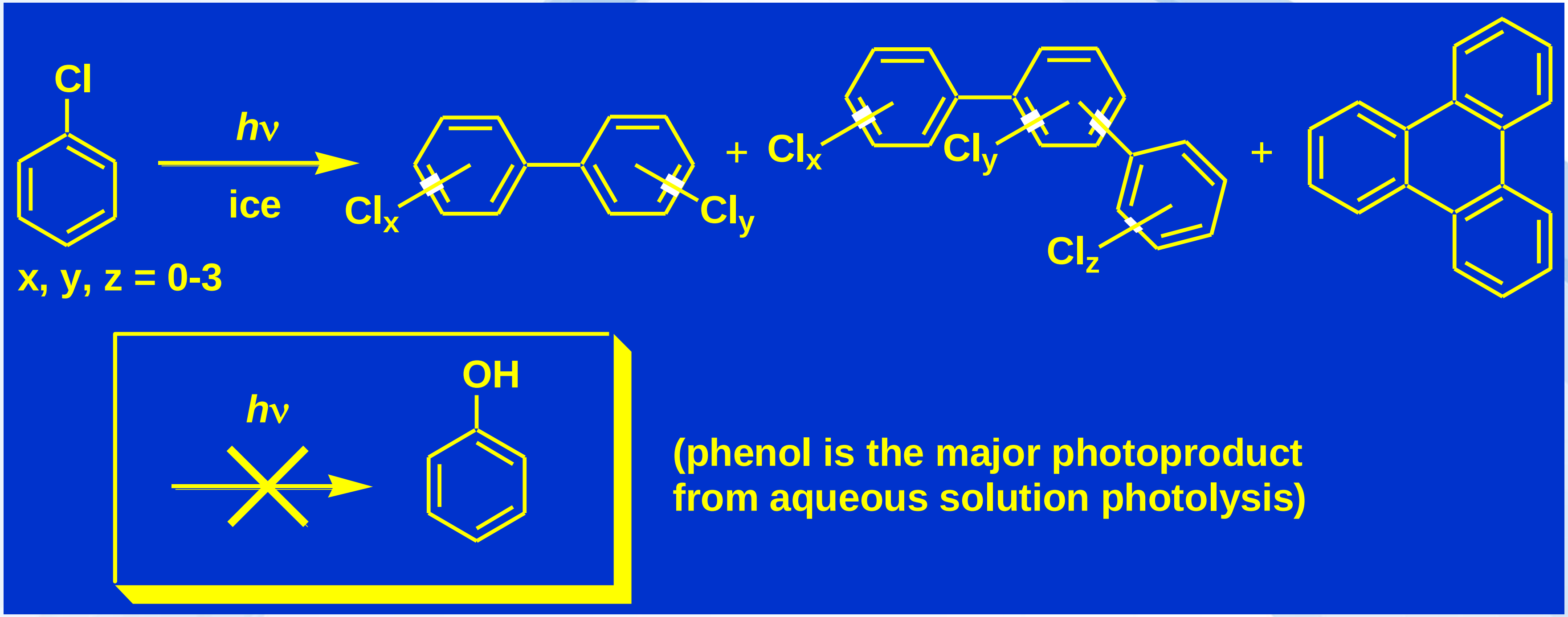


How well do we understand the sources, transport and ultimate fate of POPs in ice ?

Research centre
for toxic compounds
in the environment

Ice Photochemistry of organic pollutants

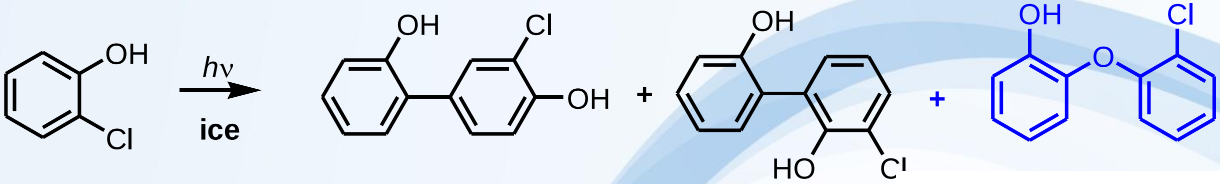
Chlorobenzene - unique transformation pathways in ice matrix



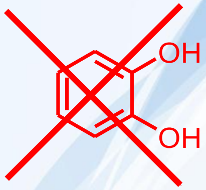
(phenol is the major photoproduct from aqueous solution photolysis)

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

Toxicity increases in ice upon photolysis



no photosolvolysis:

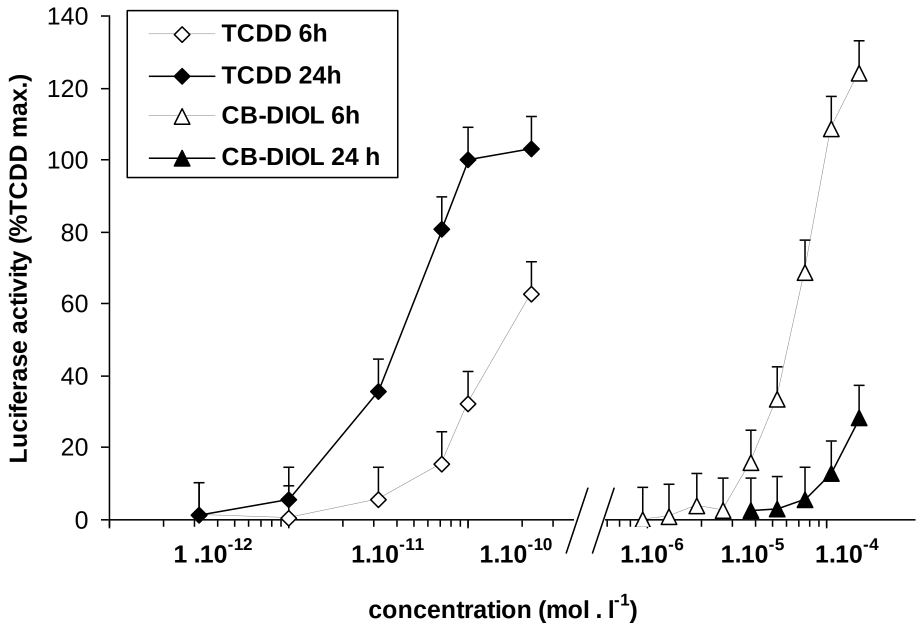



Environmental Science & Technology

TOXICITY Increases in Ice Containing Monochlorophenols

EPA's First Science Advisor Focuses on the Basics

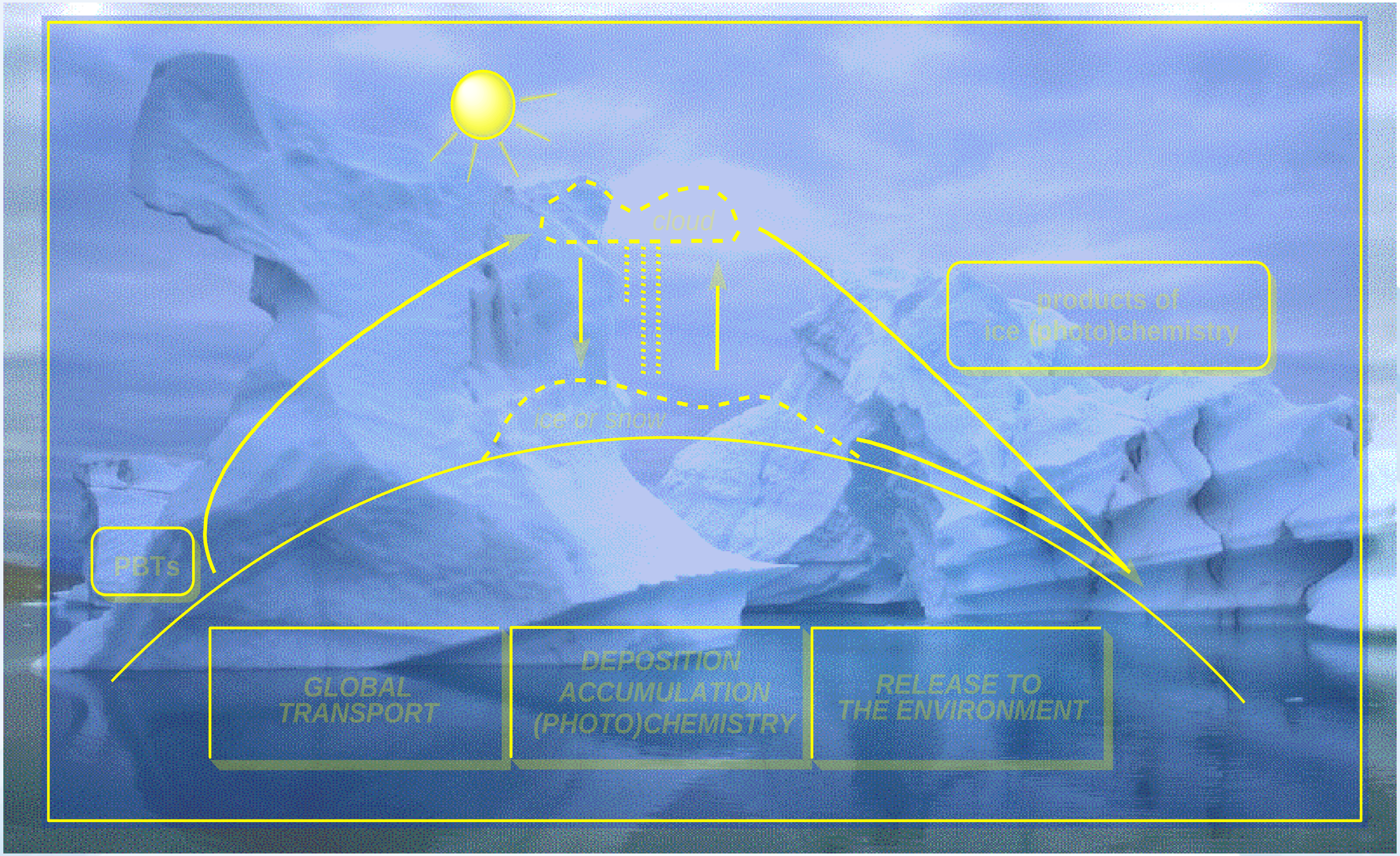
Fluorotelomer Alcohol Biodegradation



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



cloud

products of
ice (photo)chemistry

ice or snow

PBTs

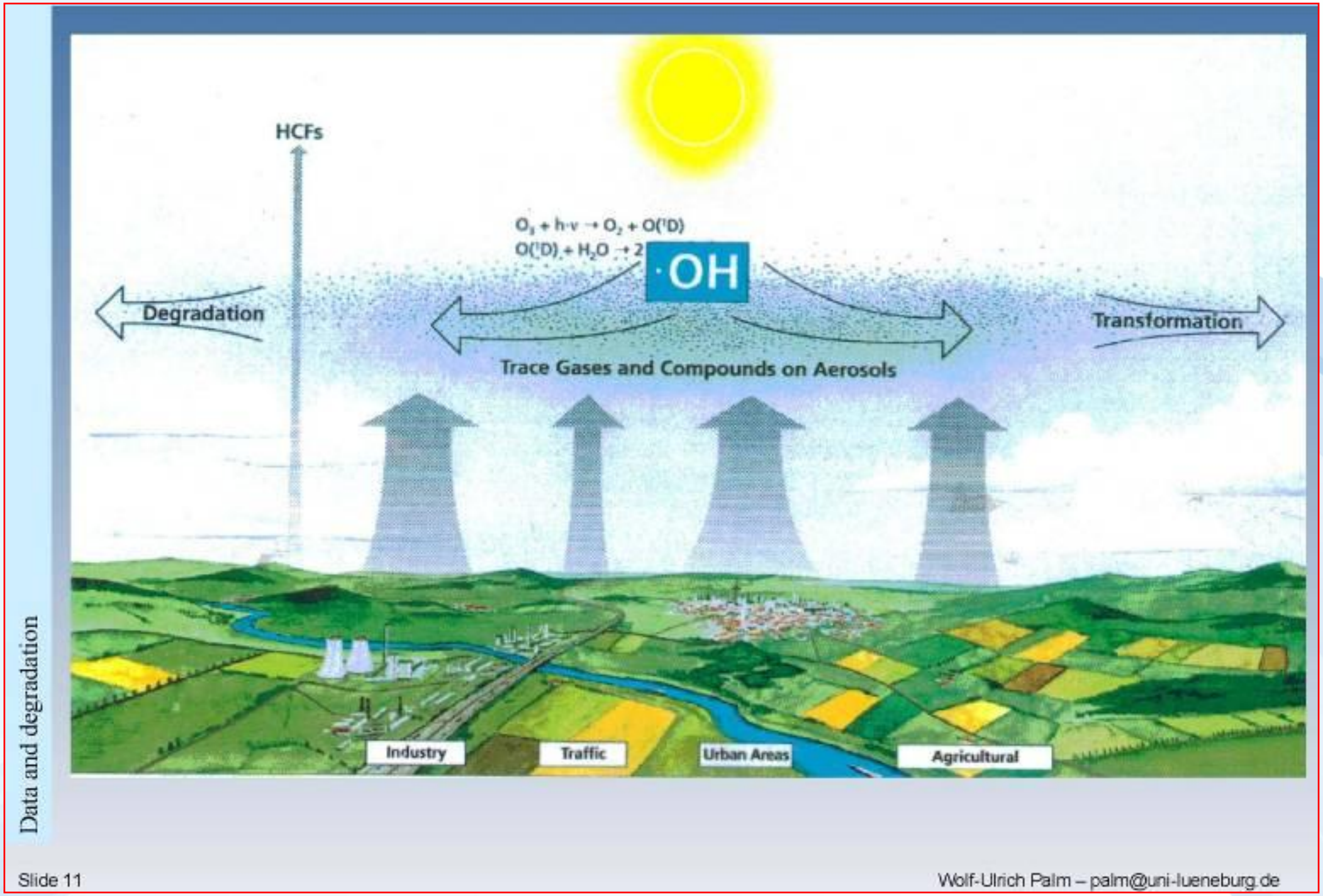
GLOBAL
TRANSPORT

DEPOSITION
ACCUMULATION
(PHOTO)CHEMISTRY

RELEASE TO
THE ENVIRONMENT

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

OH radicals in the atmosphere



Data and degradation

Slide 11

Wolf-Ulrich Palm – palm@uni-lueneburg.de

W.-U. Palm

Research centre
for toxic compounds
in the environment

Biodegradation

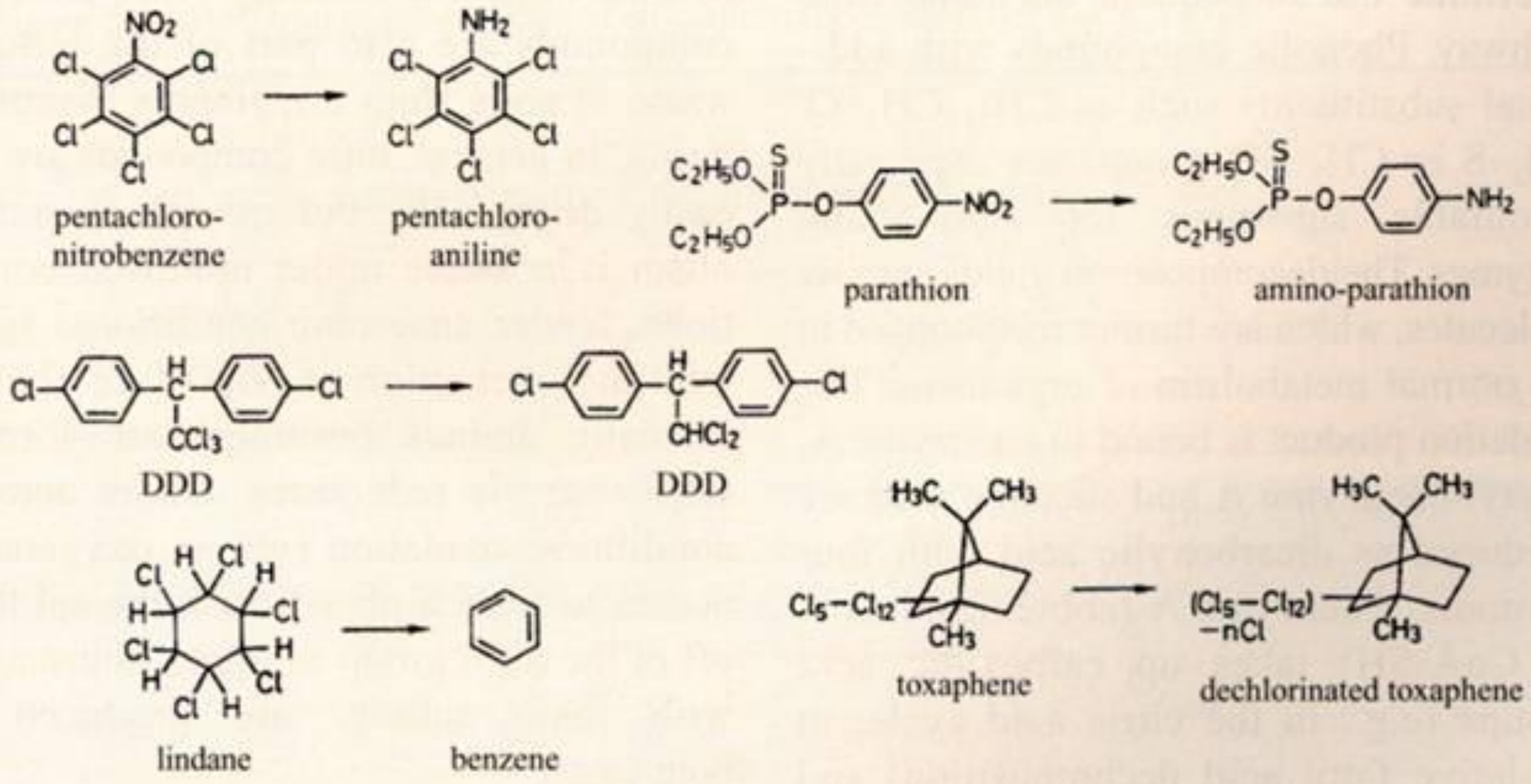


Figure 5.2.2 Reductive (anaerobic) reactions of xenobiotics

Biodegradation

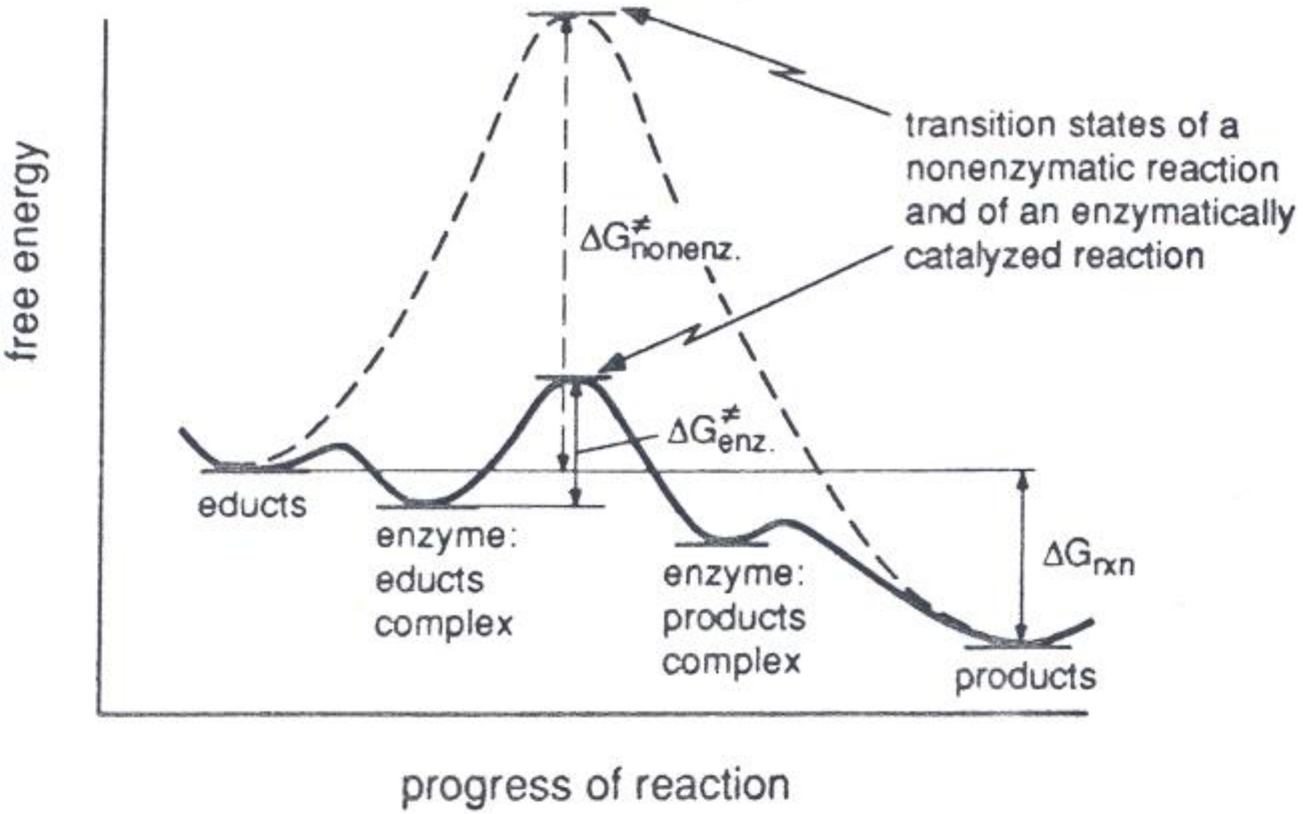


Figure 14.1 Schematic representation of the change in activation energy barriers for an enzymatically mediated reaction as compared to the analogous noncatalyzed chemical reaction.

Mechanisms of biotransformation of the xenobiotics in the living organisms

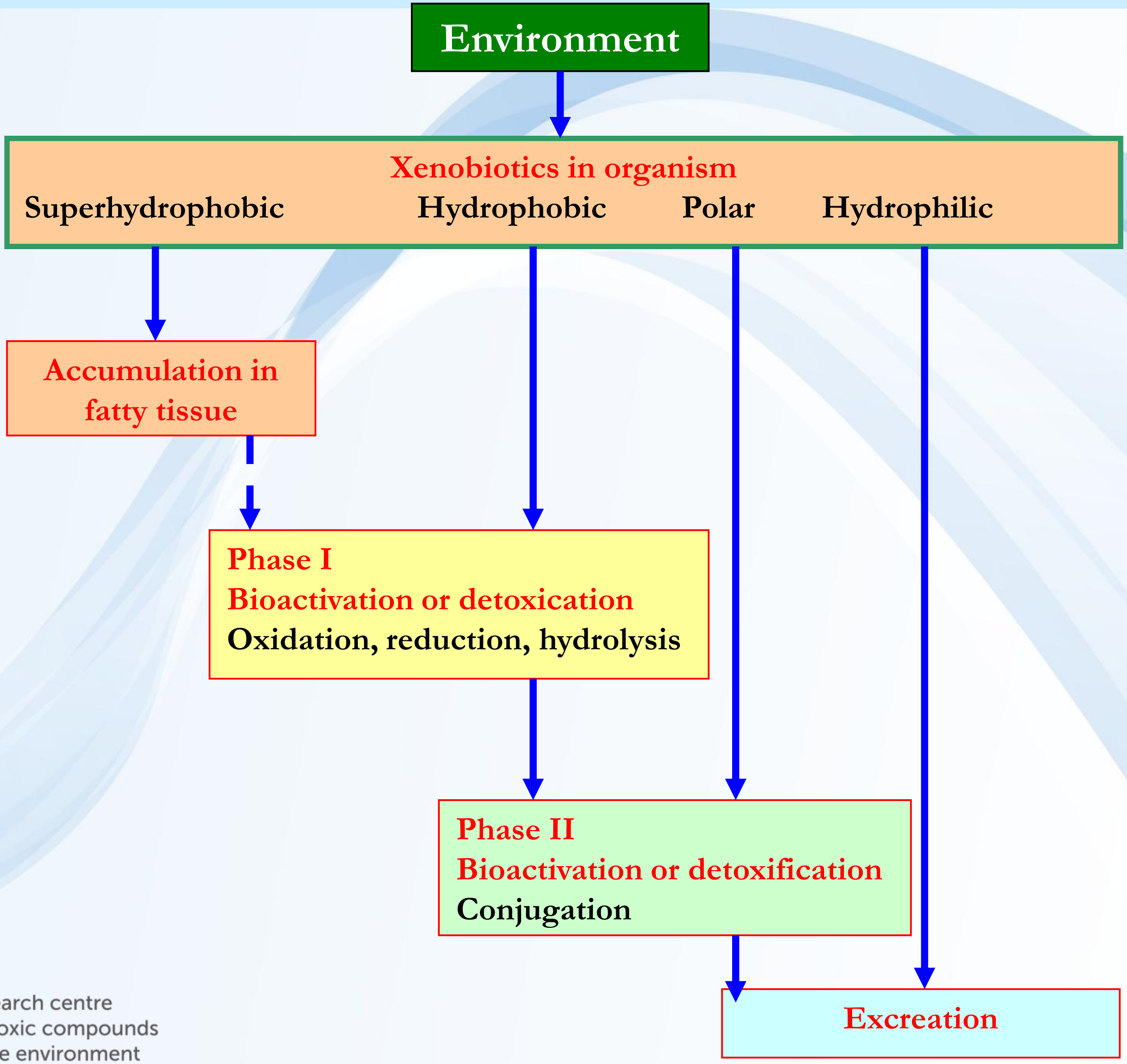
Types of biotransformation reactions

Two types:

Phase I – non-synthetic reactions – hydrolysis, oxidation, reduction – molecules of compound are changed by introducing of polar group (-OH, -COOH, -NH_2) – 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



Environment

Xenobiotics in organism

Superhydrophobic Hydrophobic Polar Hydrophilic

Accumulation in fatty tissue

Phase I
Bioactivation or detoxication
Oxidation, reduction, hydrolysis

Phase II
Bioactivation or detoxification
Conjugation

Excreation

Biotransformations

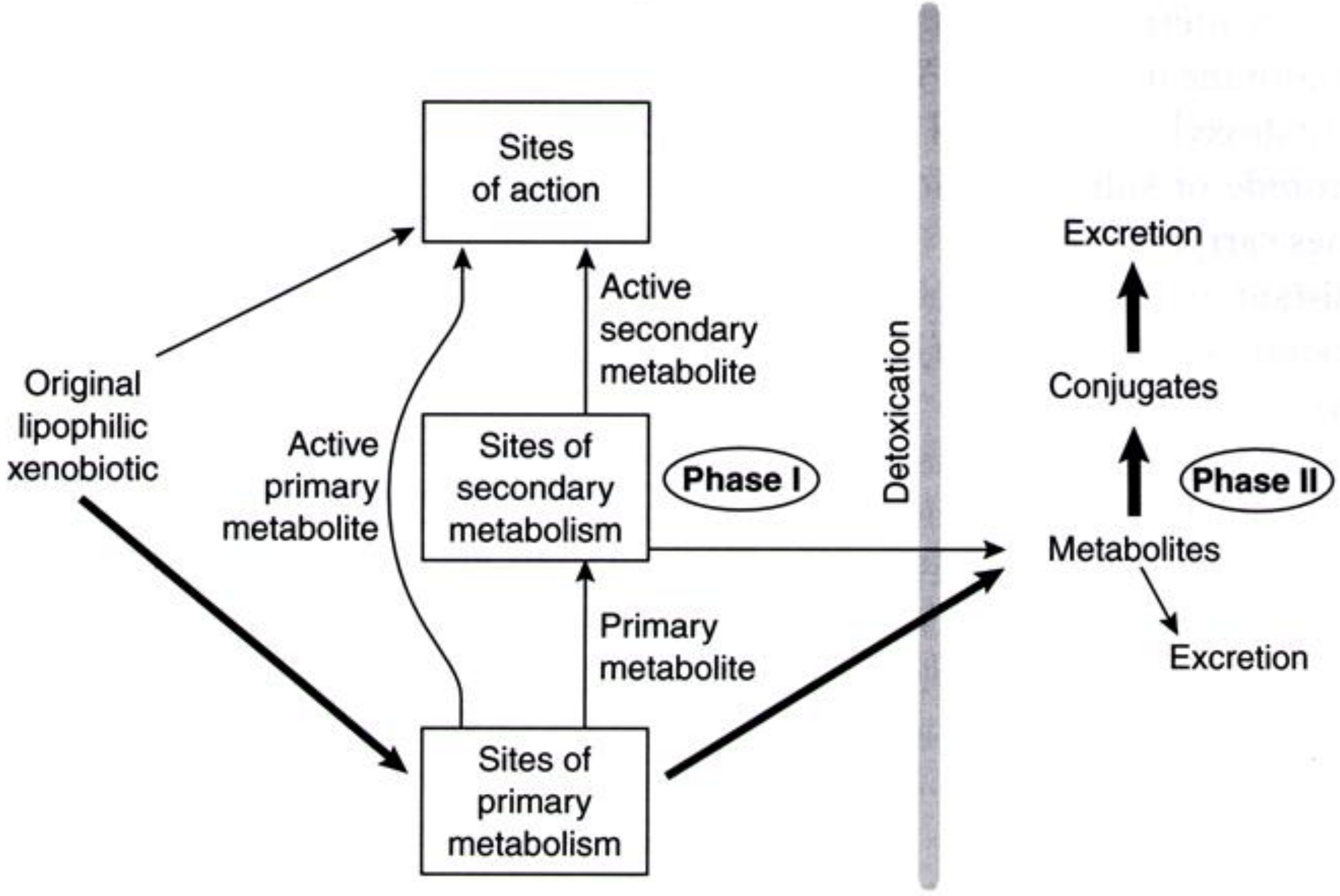


FIGURE 2.2 *Metabolism and toxicity.*

Biotransformations

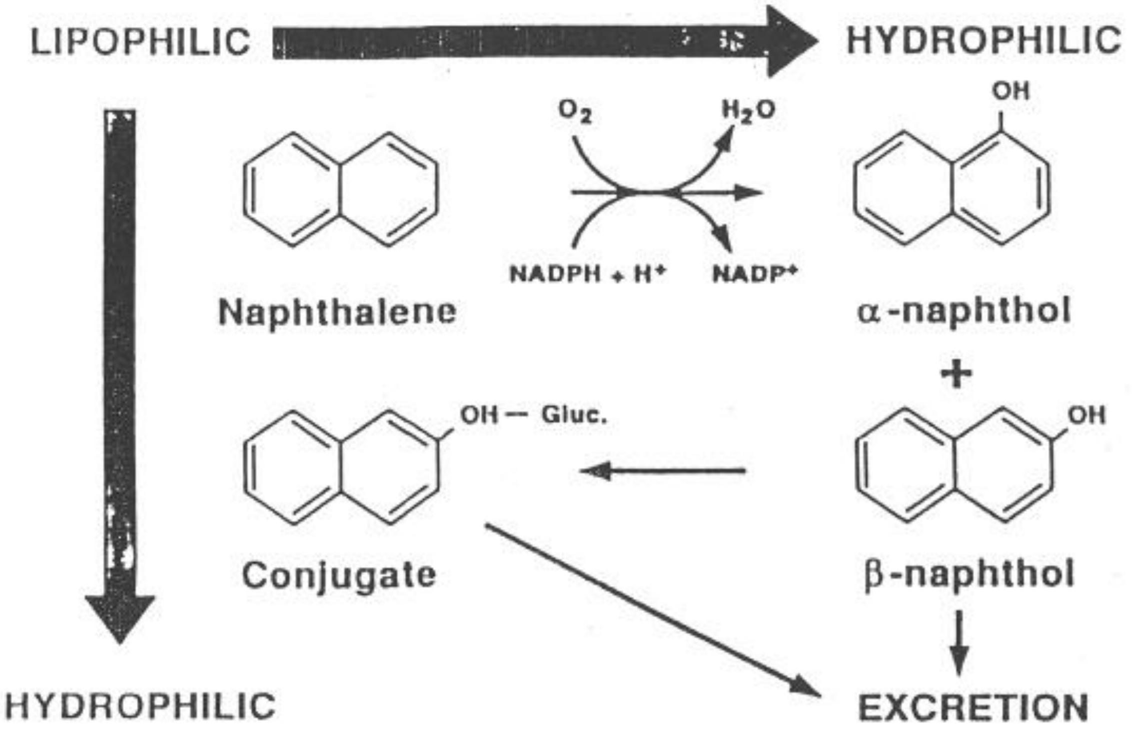


Figure 1. The cytochrome P-450 mixed function oxidase system facilitates excretion of lipophilic organic substrates in terrestrial and aquatic animals by producing metabolites that are more water soluble than the parent compound. Common metabolites of naphthalene are shown (after 2).