Persistent Organic Pollutants (POPs) – Physical-chemical properties and partition among environmental compartments

Ivan Holoubek

RECETOX, Masaryk University, Brno, CR

holoubek@recetox.muni.cz; http://recetox.muni.cz

Contents

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- Introduction of the RECETOX
- What are the persistent organic pollutants (POPs), Stockholm Convention
- Fate of POPs
- Environmental problems connected with the POPs
- Main groups of POPs
- Monitoring of POPs – sampling, analysis, monitoring programmes

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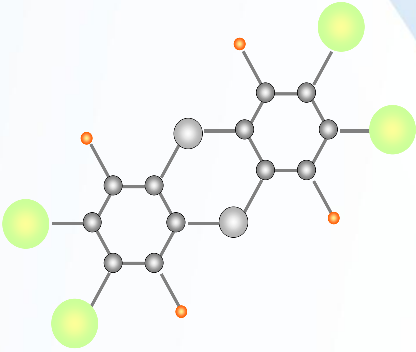
Persistent Organic Pollutants (POPs)

POPs:

☺ The group of most fascinating
(Prof. K. C. Jones - scientific approach)

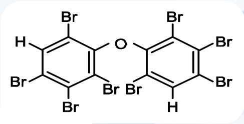
☹ Ghost of the past, devilish rest of human activities
(Terry Bidlemann - public feelling)

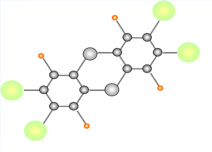
God creates 90 elements, man round 17, but Devil only one – chlorine – Otto Hutzinger

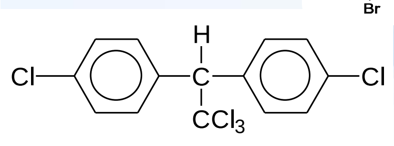


Persistent organic pollutants

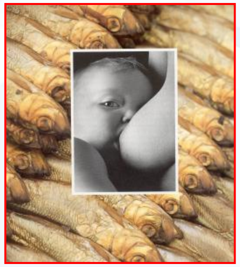
- Persistent

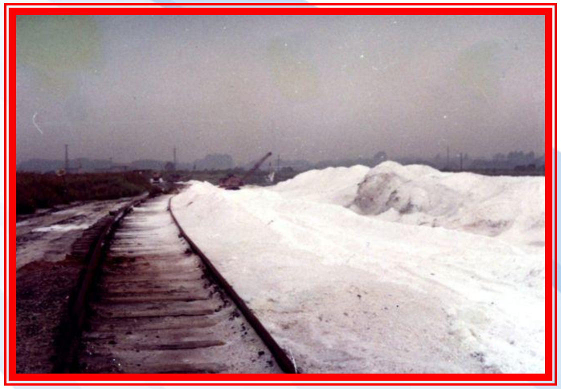




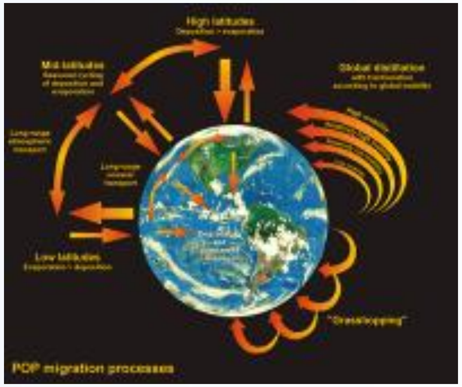


- Bioaccumulation





- Toxicity



- Long-range transport

The objective of SC

The objective of the Stockholm Convention is to protect human health and the environment from persistent organic pollutants. It differentiates between three categories of POPs:

- Intentionally produced POPs that are slated for elimination;
- Intentionally produced POPs are to be reduced and ultimately eliminated, except where there is a specified "acceptable purpose," such as disease vector control, or exempted usage, in which case the production and/or use of the substance is restricted; and
- POPs that are unintentionally produced as the result of human activity and which are slated for continued minimization and, where feasible, ultimate elimination of total releases derived from anthropogenic sources.

www.pops.int

12 Stockholm Old POPs

	Pesticide	Industrial Chemical	By-product
Aldrin	+		
Chlordane	+		
DDT	+		
Dieldrin	+		
Endrin	+		
Heptachlor	+		
Mirex	+		
Toxaphene	+		
Hexachlorobenzene	+	+	+
PCB		+	+
PCDD			+
PCDF			+

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10 Stockholm New POPs

	Pesticide	Industrial Chemical	By-product
Chlordecone	+		
HBB		+	
α-HCH	+		+
β-HCH	+		+
γ-HCH	+	+	+
PeDBE		+	+
OCBDE		+	+
PFOS		+	
PeCBz	+	+	+
Endosulfan	+		

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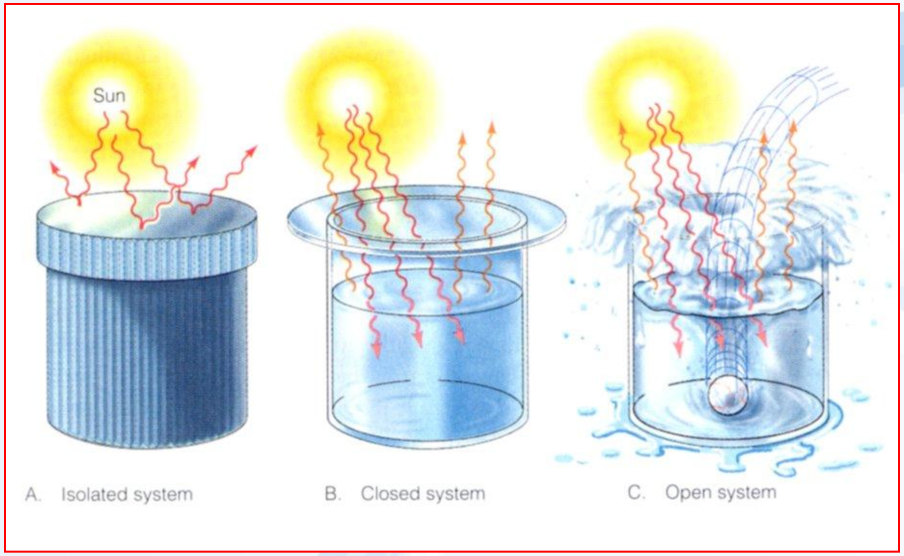
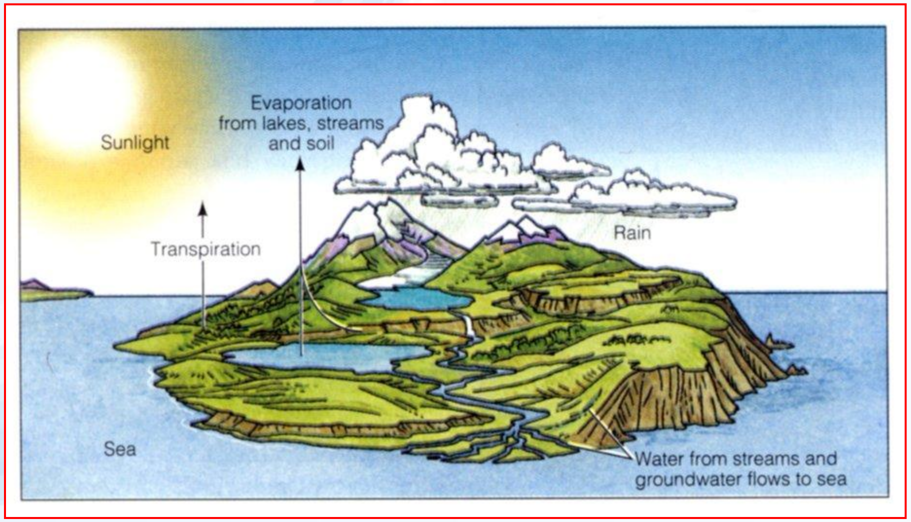
Systems, environmental system

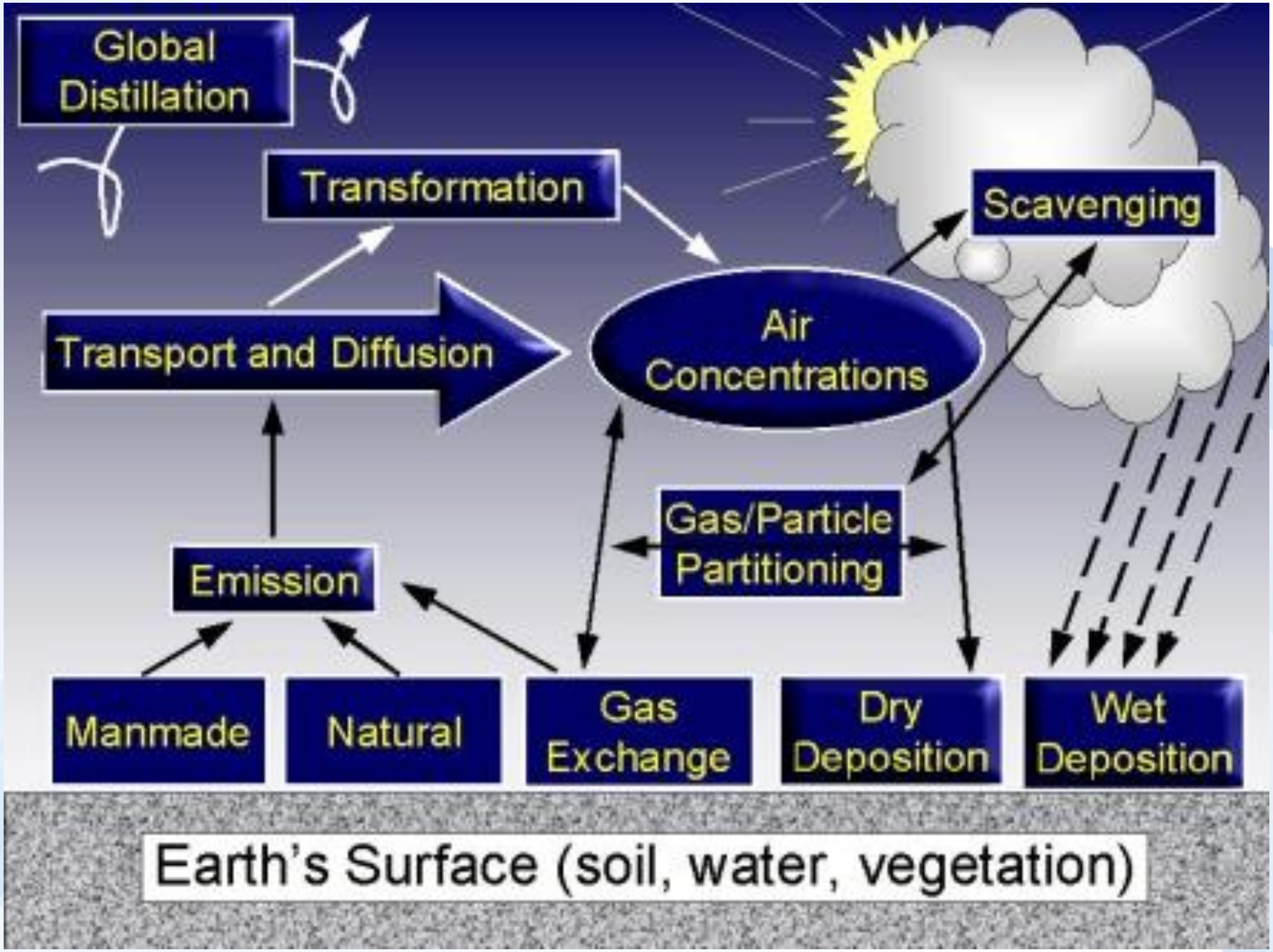


- Isolated
- Closed
- Opened



- Opened

Environmental fate of chemicals



Environmental chemistry and photochemistry

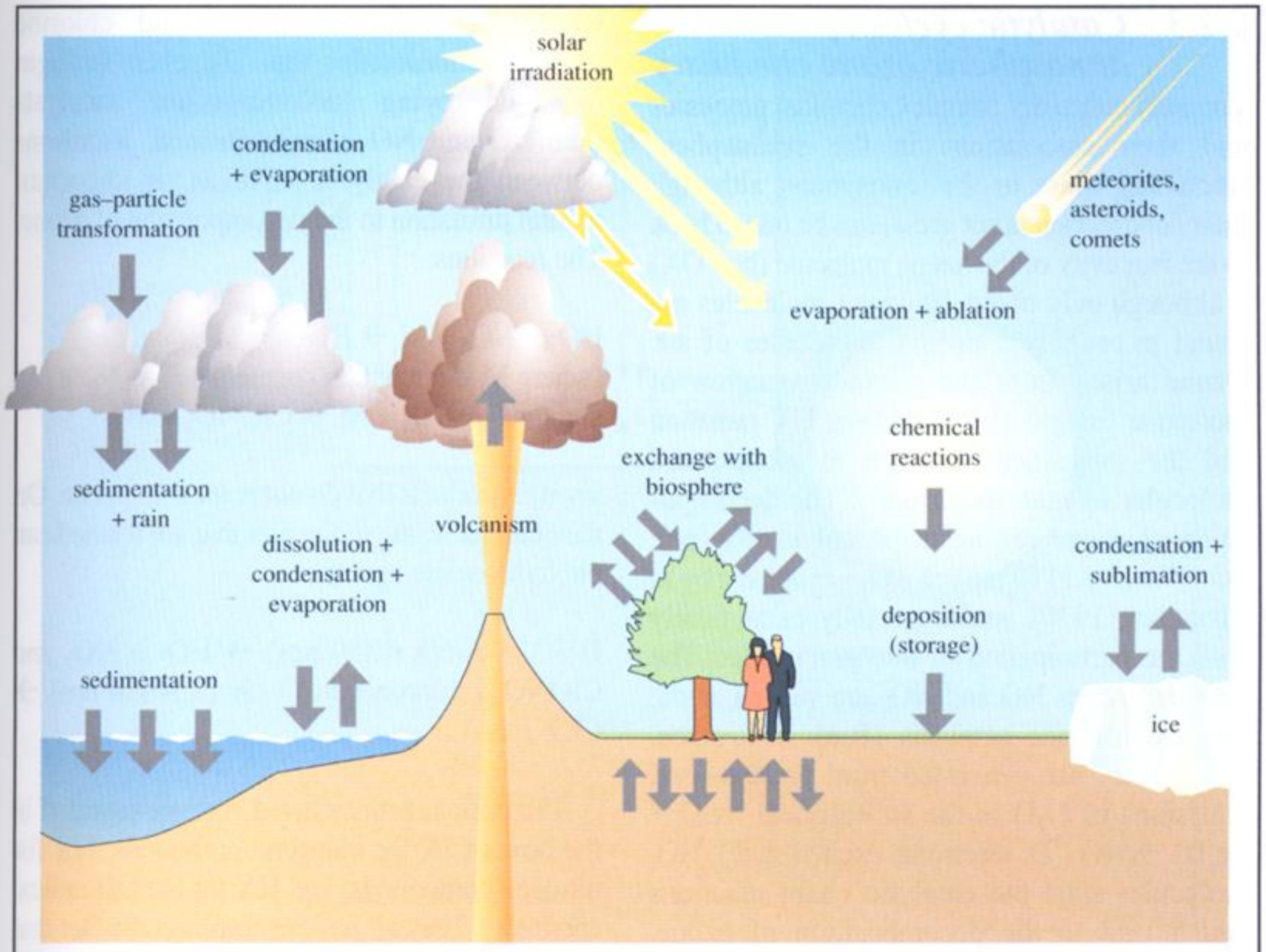


Figure 2.2.1 Chemistry and photochemistry

Environmental interface

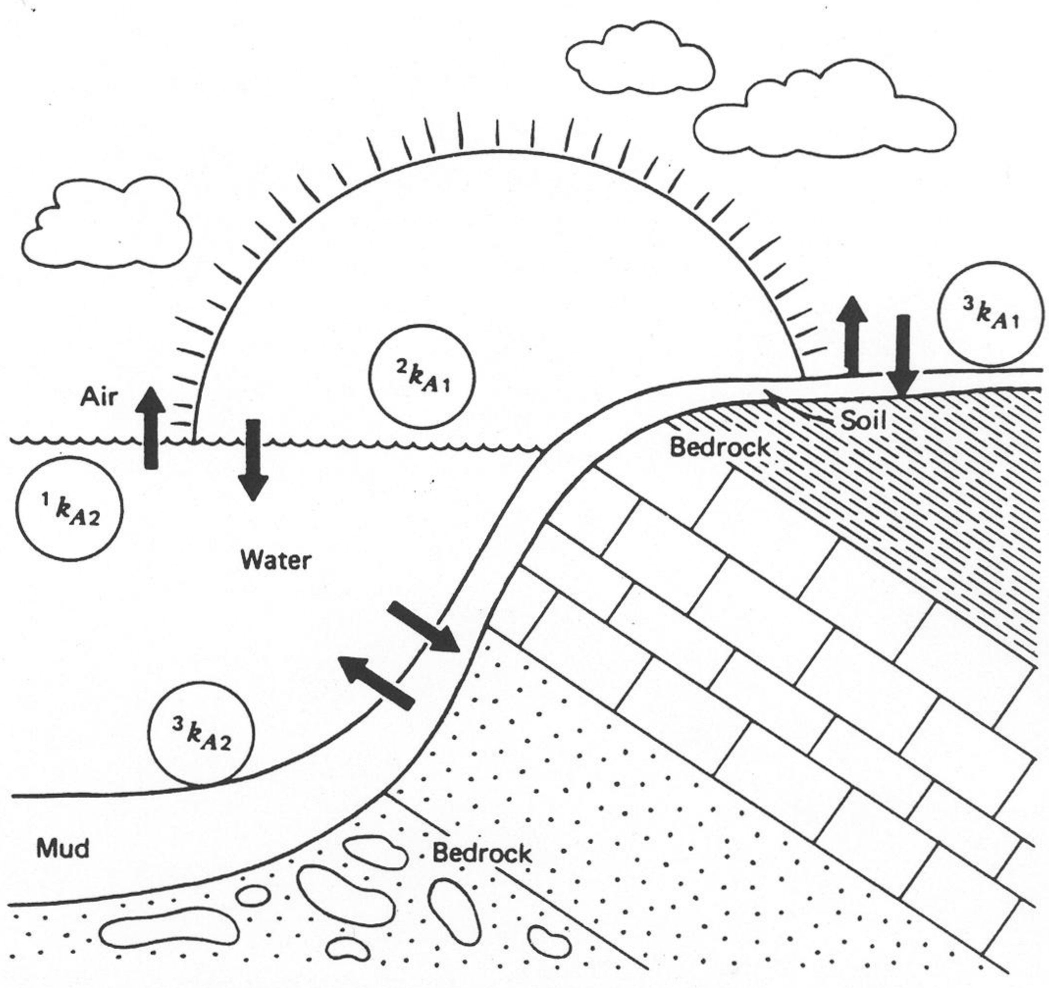


Figure 3.0-1. Interfaces in the geospheres.

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Environmental fate of POPs

How well do we understand the fate of POPs ?

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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

Air-surface exchange

Direct applications

'Occlusion'

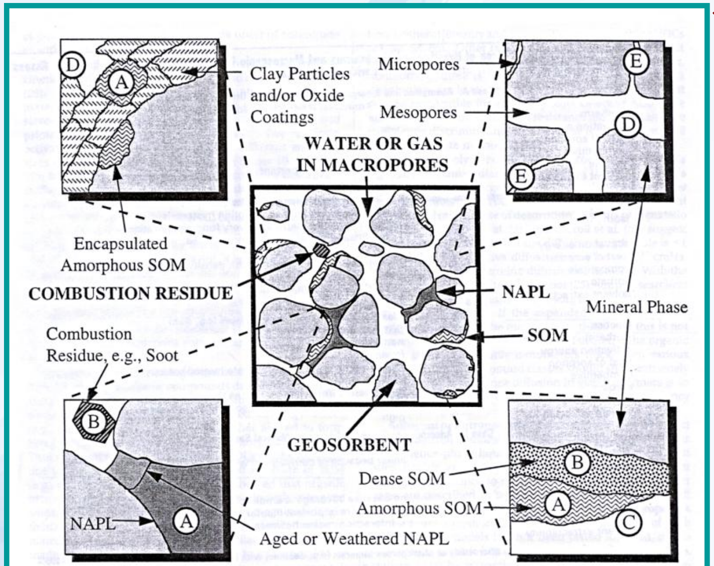
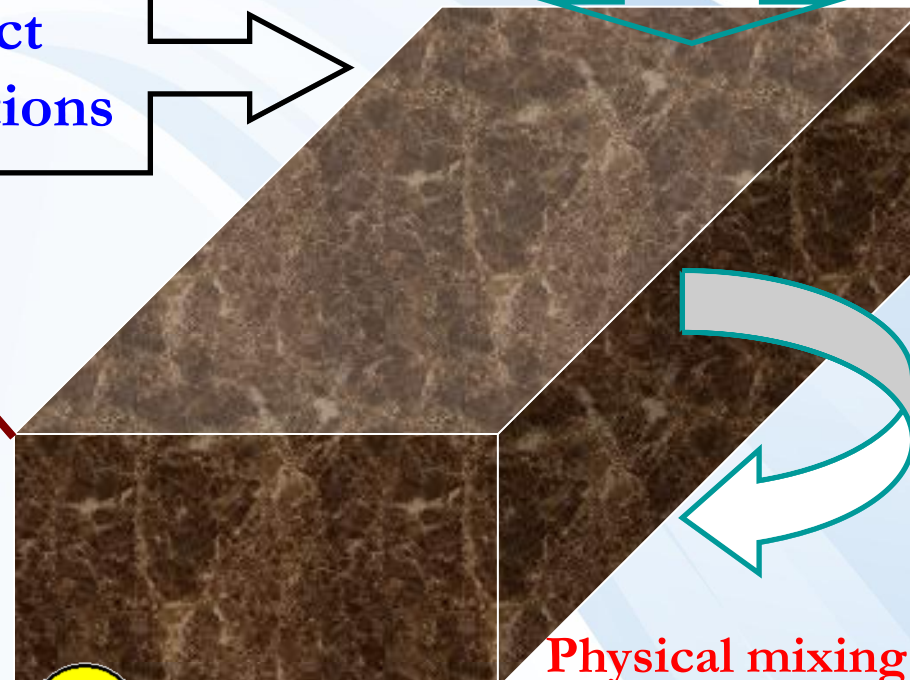


FIGURE 1. Conceptual model of geosorbent domains. The circled letters refer to representations of the sorption mechanisms described in Table 1. The geosorbent domains include different forms of sorbent organic matter (SOM), combustion residue particulate carbon such as soot, and anthropogenic carbon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



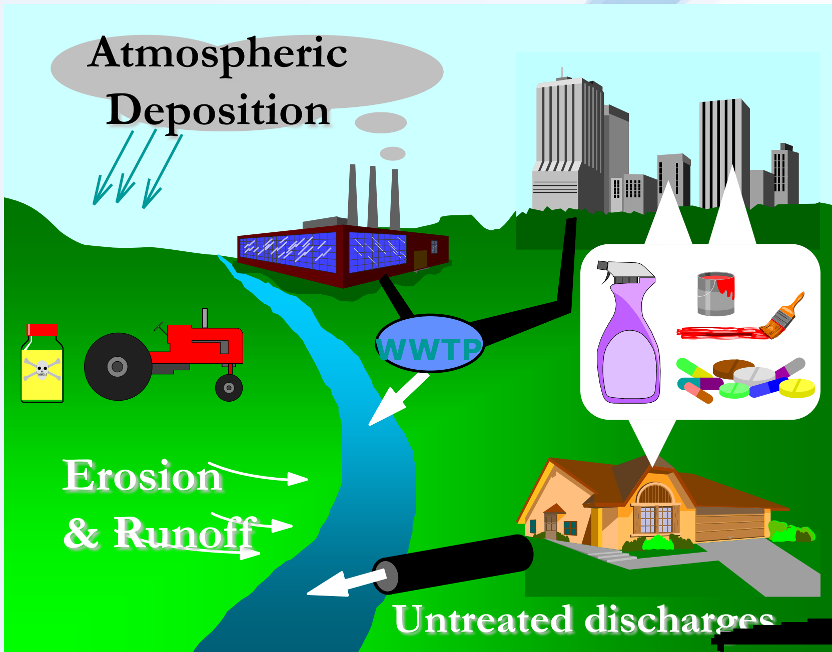
Biodegradation

Physical mixing – 'dilution' with depth

K. C. Jones

Risk assessment

Exposure



Predicted Exposure Concentration (PEC)

Effects

EUSES European Union System for the Evaluation of Substances

Predicted No Effect Concentration (PNEC)

Environmental re-cycling

The basic trends of usage and emissions to the environment - four steps (Jones, de Voogt, 1999):

(1) synthesis and development for use earlier in this century (1930s)

(2) increasingly widespread use in Europe and North America and other industrialized regions through the 1950s and 1960s

(3) concern over environmental persistence and food chain accumulation in the 1960s/early 1970s, resulting in restrictions in usage in Europe and North America, and

(4) reductions in emissions in Europe, North America and other industrialized regions arising from the bans/controls in the 1970s through the 1980s and 1990s

Environmental re-cycling

This general pattern may be unrepresentative of the global emission profile - when the chemical is used extensively outside of Europe and North America - a global shift in the place of manufacture.

Trends in emissions with maximum in 1950s and 1960s - fundamental implications for concentration trends in air, soil, water and sediments and direction of fluxes between these compartments for PCB capable of dynamic, multimedia exchange.

Control/reduction of air concentration based on reduction of primary sources - volatilization ("outgassing") of recyclable PCBs from the terrestrial and aquatic compartments.

Environmental re-cycling

This process depends on a number of factors:

- size of reservoir of compound in the soil/sediment/water compartments
- persistence in the soil/sediment compartments
- physical-chemical properties of compounds
- free exchange of the compound which has been deposited in the past

➲ compounds primarily associated with particulates - outgassing will be limited and concentrations/burden of soil or water will tend to remain high/increase

➲ compounds readily enter the gas phase, outgassing will result in the soil/water body concentration/burden declining.

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The global distribution and contamination

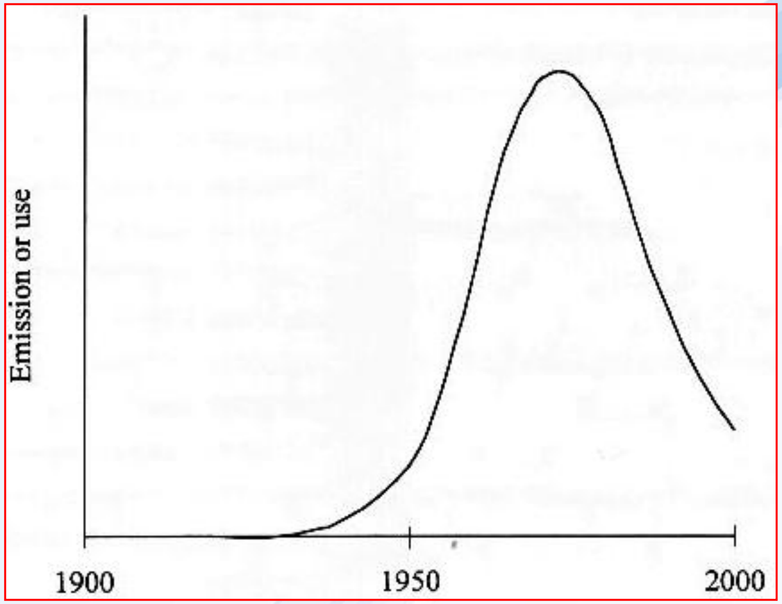
Present trends - declining of environmental levels

Several ways of POPs for example PCBs enter the environment:

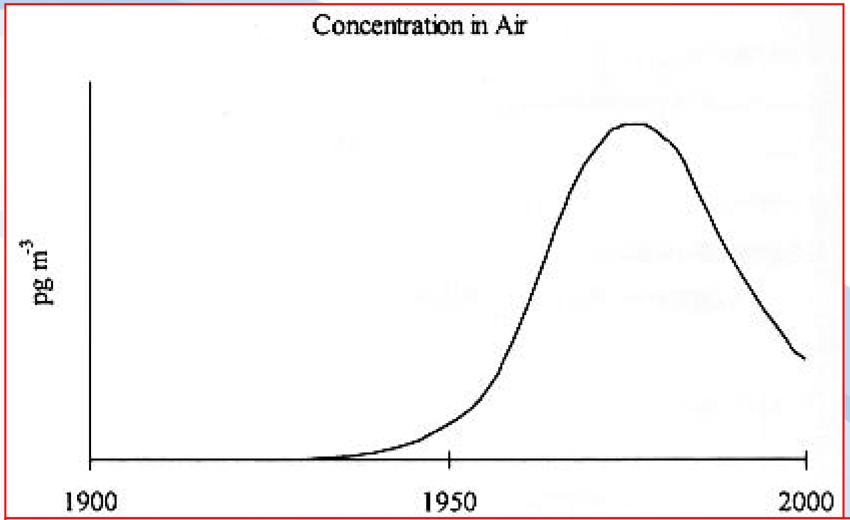
- direct waste discharges from manufacturing facilities and industry which employed large amounts of PCBs
- today - hot spots occur at locations where types of operations where centered (Balkan)
- these “old loads” - secondary sources of contamination - direct emissions from historical sites - the large reservoirs of PCBs - soil and sediments of lakes and rivers near these historical storage - hazardous landfills, place of operation, etc.

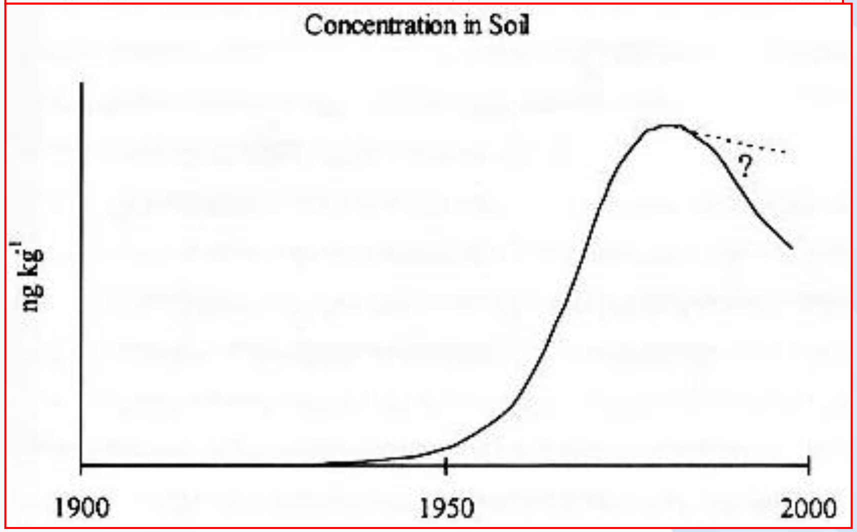
Changes in the temporal trends

Typical POPs time trend



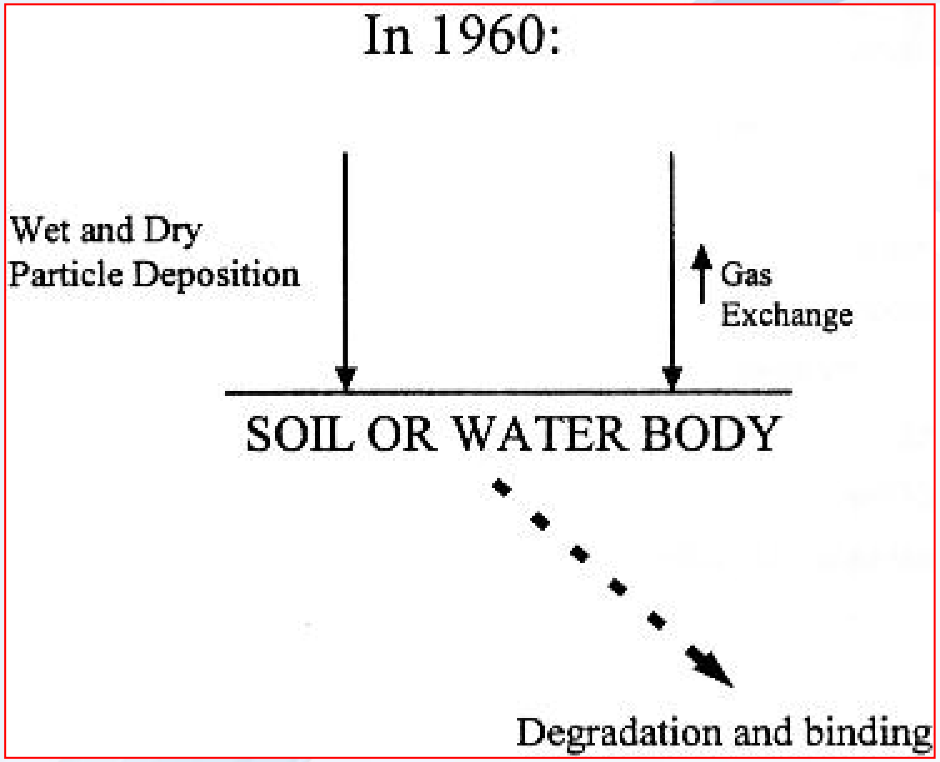
Typical POPs air and soil residues

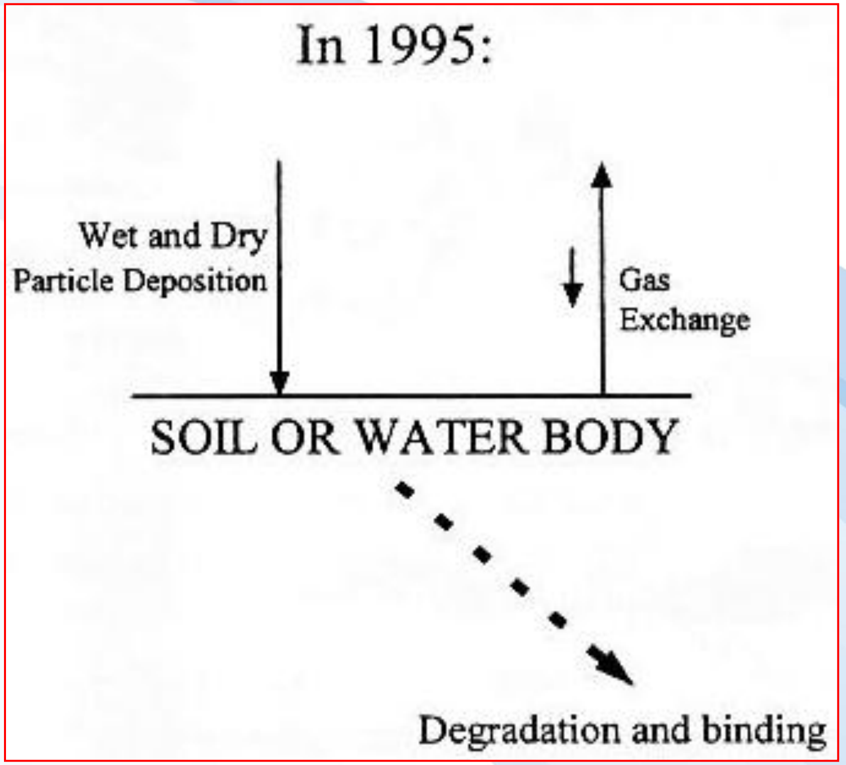




Changes in the temporal trends

Air – soil exchange processes





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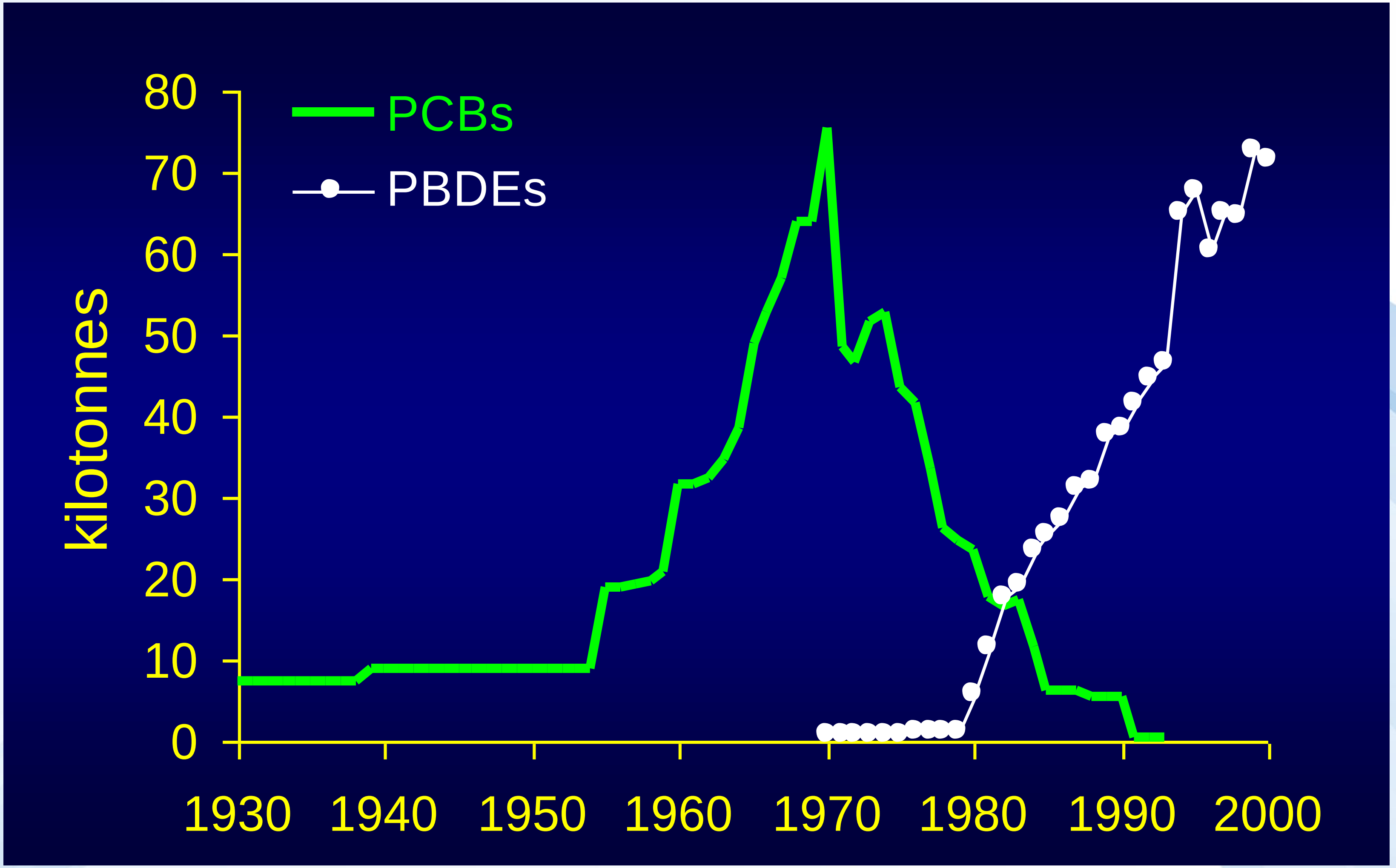
Changes in time trends



PBDEs: Anna Palm (Pers. Comm.) PCBs: Breivik et al (2002)

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Contents

Persistent Toxic Substances (PTS)

Persistent

- Resists degradation in the environment
- Other chemicals, even though degrading faster in the environment, are persistent due to continuous release

Properties of persistent organic pollutants (POPs)

Persistency:

Half time in water	> 2 months
Half time in soil	> 6 months
Half time in sediments	> 6 months
Air - half time	> 2 days

Bioacumulation:

Biological concentration factor for water biotop > 5000

Log Kow > 5

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Effects of POPs

Bio-accumulative

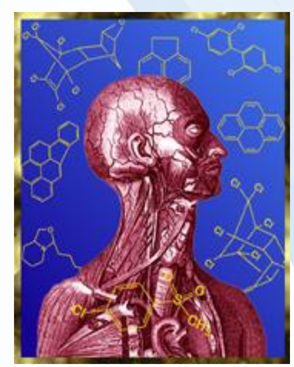
- Concentrates in fatty tissue (lipophilic)
- Bio-accummulation factor in animals dependent on the Log K_{ow} – a measure of the affinity of chemicals to lipids
- Chemicals to be included – Log K_{ow} > 3 but molecular weight < 1 000 Daltons
- Chemical accummulates up the food chain

Effects of POPs

Toxicity

- **Chemicals show chronic toxicity properties including : developmental, reproductive, carcinogenic, immunotoxic and neurotoxic activities in humans and wildlife**
- **ADI values are compared to NOEL/LOEL values to establish risk from exposure**
- **Substances with acute toxicity and with continuous release/exposure to be considered**





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Effects of POPs

The most important effects:

- **Induction of AHH receptors**
- **Neurotoxicity**
- **Imunotoxicity**
- **Endocrinne disruption:**

  - estrogens/antiestrogens
  - antiandrogens
  - thyroid hormones

Effects of POPs - chloracne

The Seveso accident

Effects of POPs - chloracne

Viktor Yushchenko (Before and After)

Persistent Toxic Substances

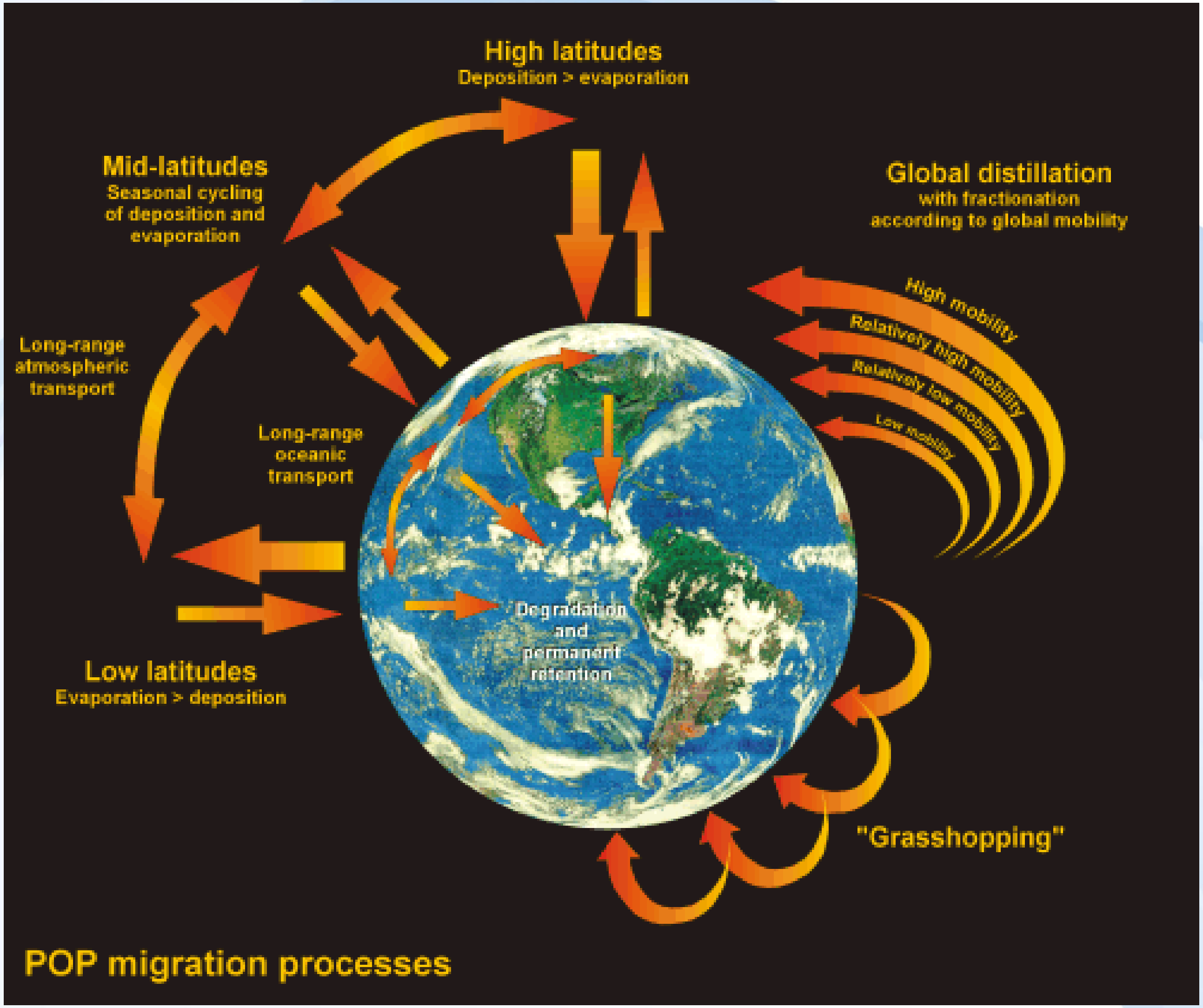
Transboundary Movement

- Chemicals transported through erosion, flood plains, water, biota etc.
- Chemicals are semi-volatile
- Evaporate over warmer regions and condense in colder atmospheres

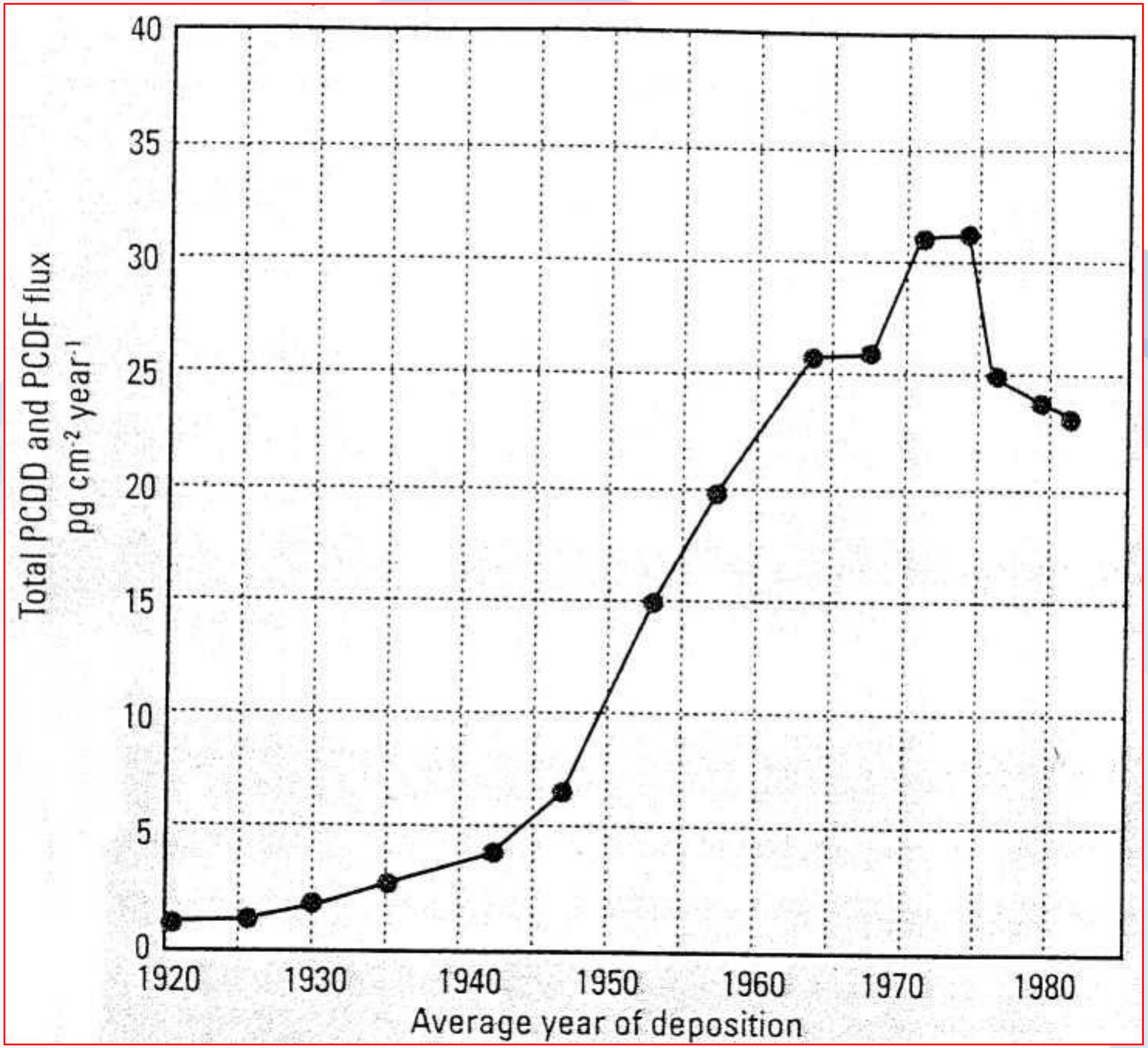
- Can affect regions where use is non-existent

Persistent Toxic Substances

Transboundary Movement



Historical trends of environmnetal levels of PCDDs/Fs



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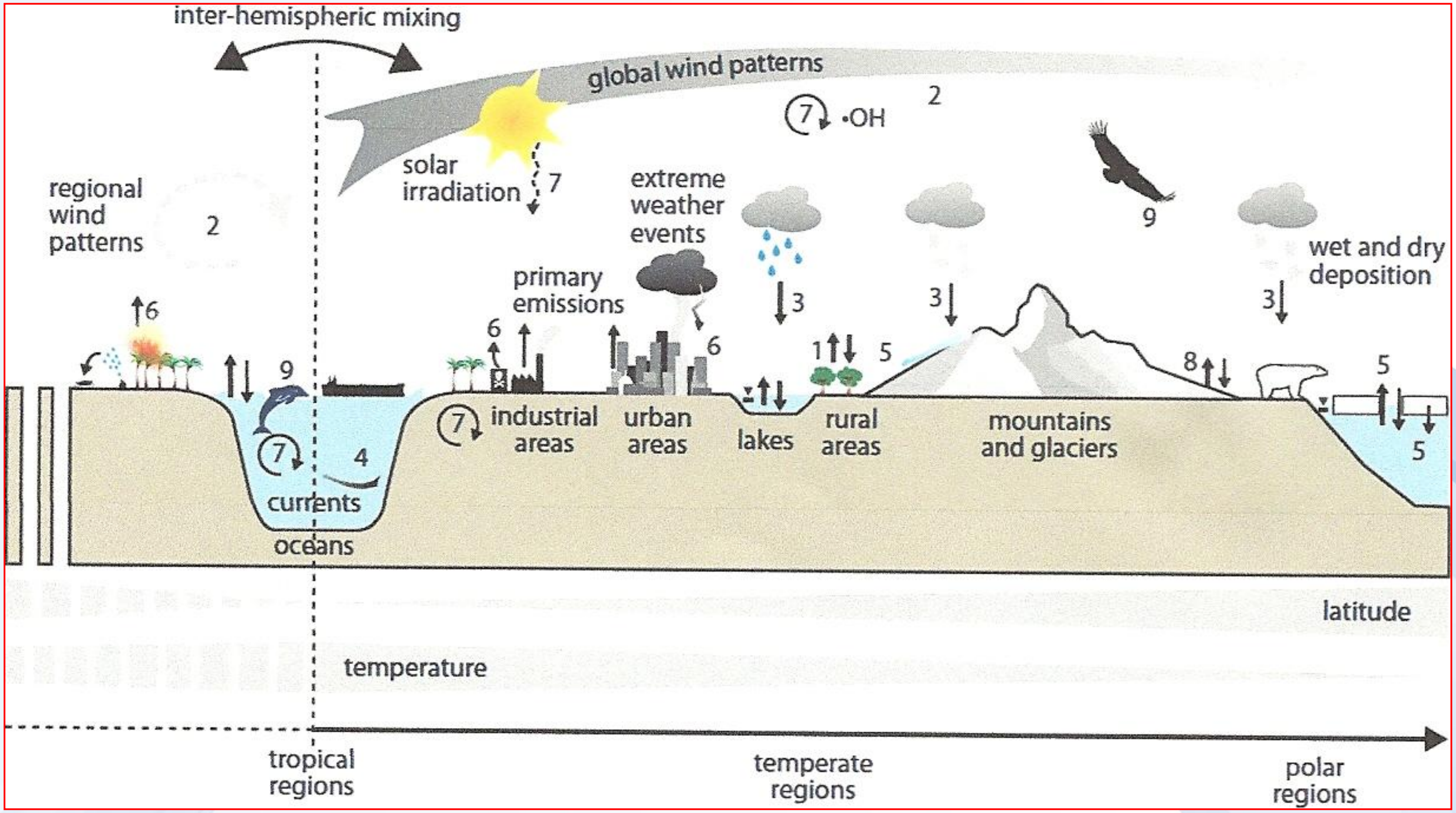
Local problems





Climate change and POPs – Predicting the impacts



Conceptual representation of key factors influencing the environmental fate and transport of POPs under a climate change scenario. Numbers in the Figure correspond to enumerated items in the text, including climate-change-induced modifications in (1) strength of secondary re-volatilization sources, (2) wind fields and wind speed, (3) precipitation, (4) ocean currents, (5) melting of polar ice caps and mountain glaciers, (6) frequency of extreme events, (7) degradation and transformation of chemicals, (8) environmental partitioning of chemicals, and (9) biotic transport of chemicals. Note that the processes depicted for the Northern hemisphere are the same in the Southern hemisphere.

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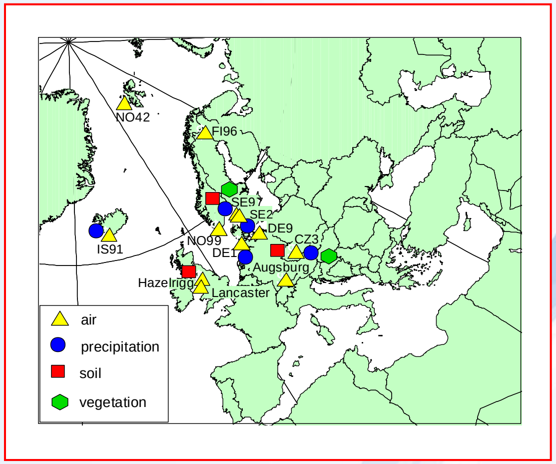
Concept of superstation - observatory Košetice, ČR

EMEP POPs Network



Integrated POPs monitoring - observatory Košetice

Comparison of existing programmes (EMEP, GAPS, MONET) and approaches (active vs. passive sampling)

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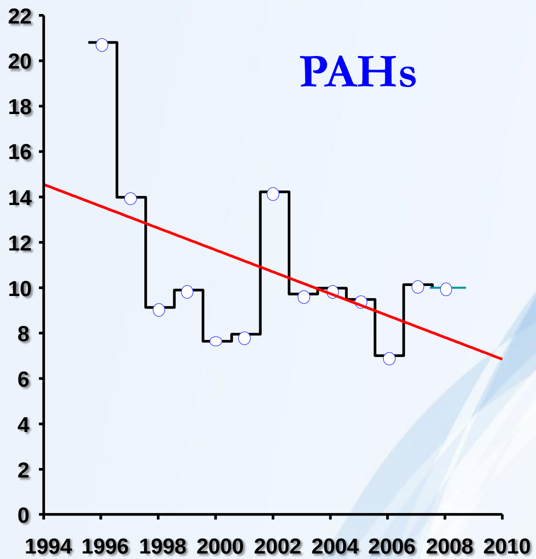
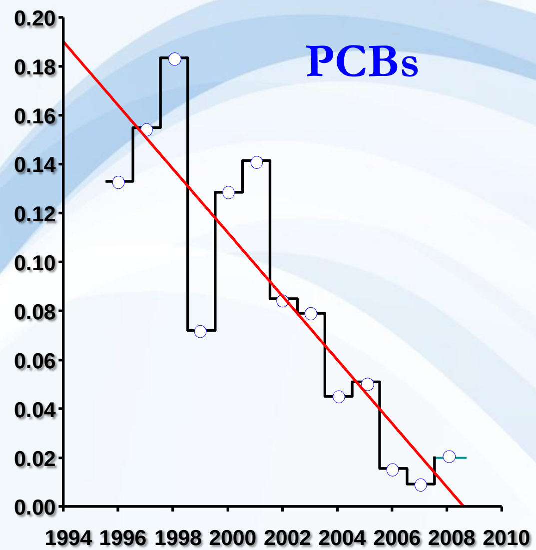
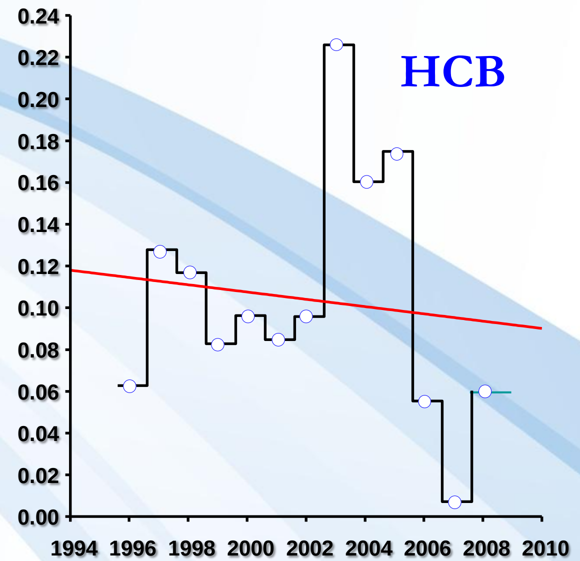
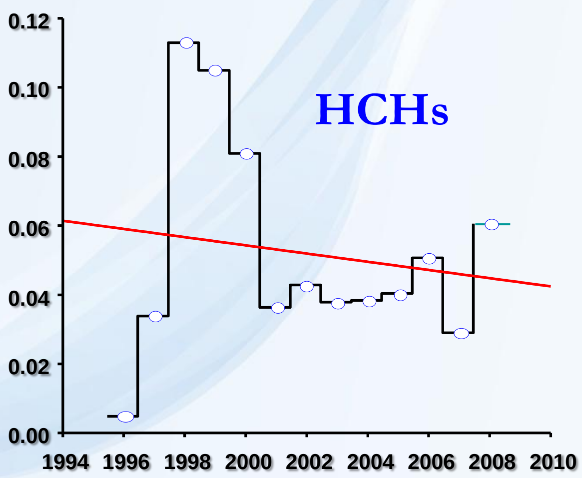
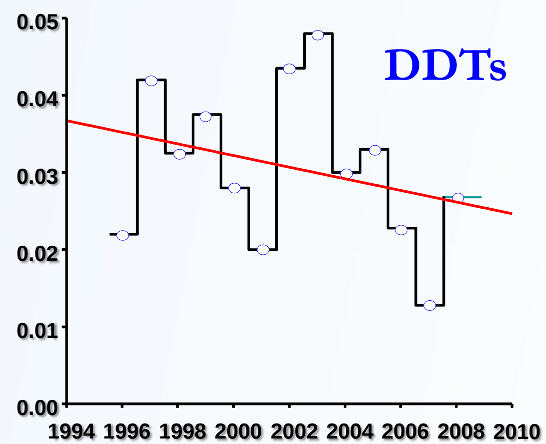
Long-term temporal trends of POPs in ambient air – observatory Košetice – 1996-2008 [$ng.m^{-3}$]











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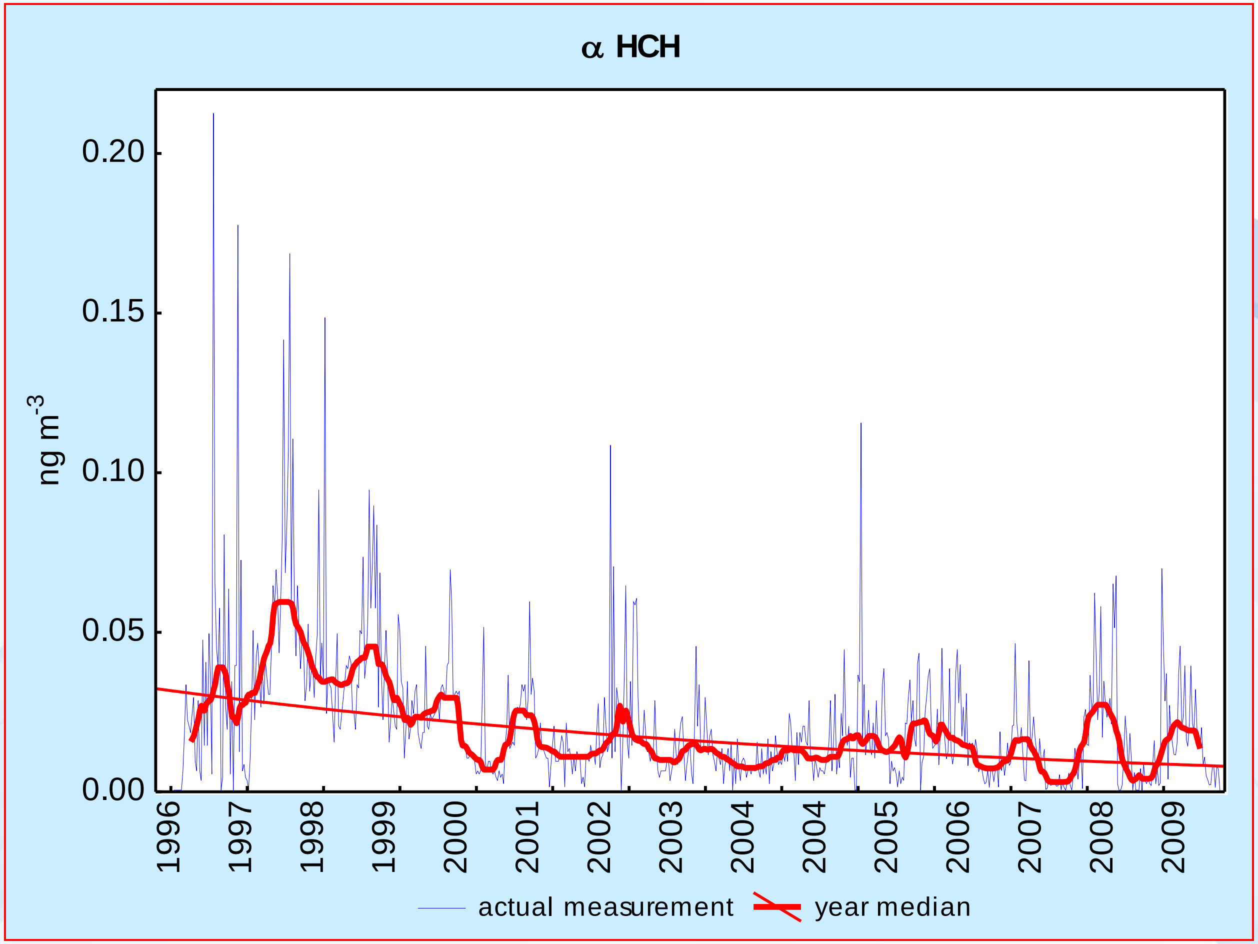
Long-term monitoring of POPs in ambient air, EMEP observatory Košetice – α-HCH, 1996-2009 [ng.m^{-3}]



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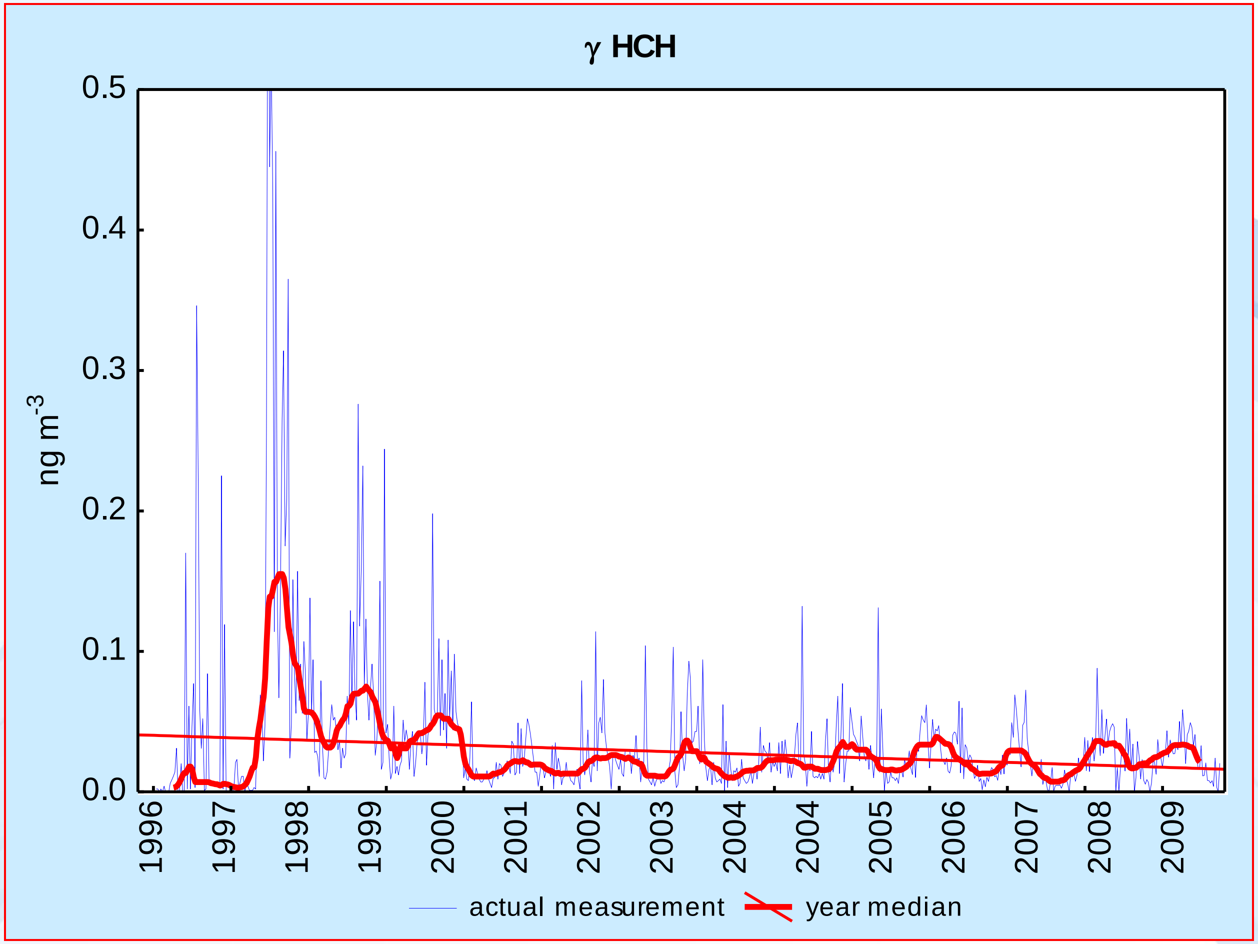
Long-term monitoring of POPs in ambient air, EMEP observatory Košetice – γ-HCH, 1996-2009 [$ng.m^{-3}$]



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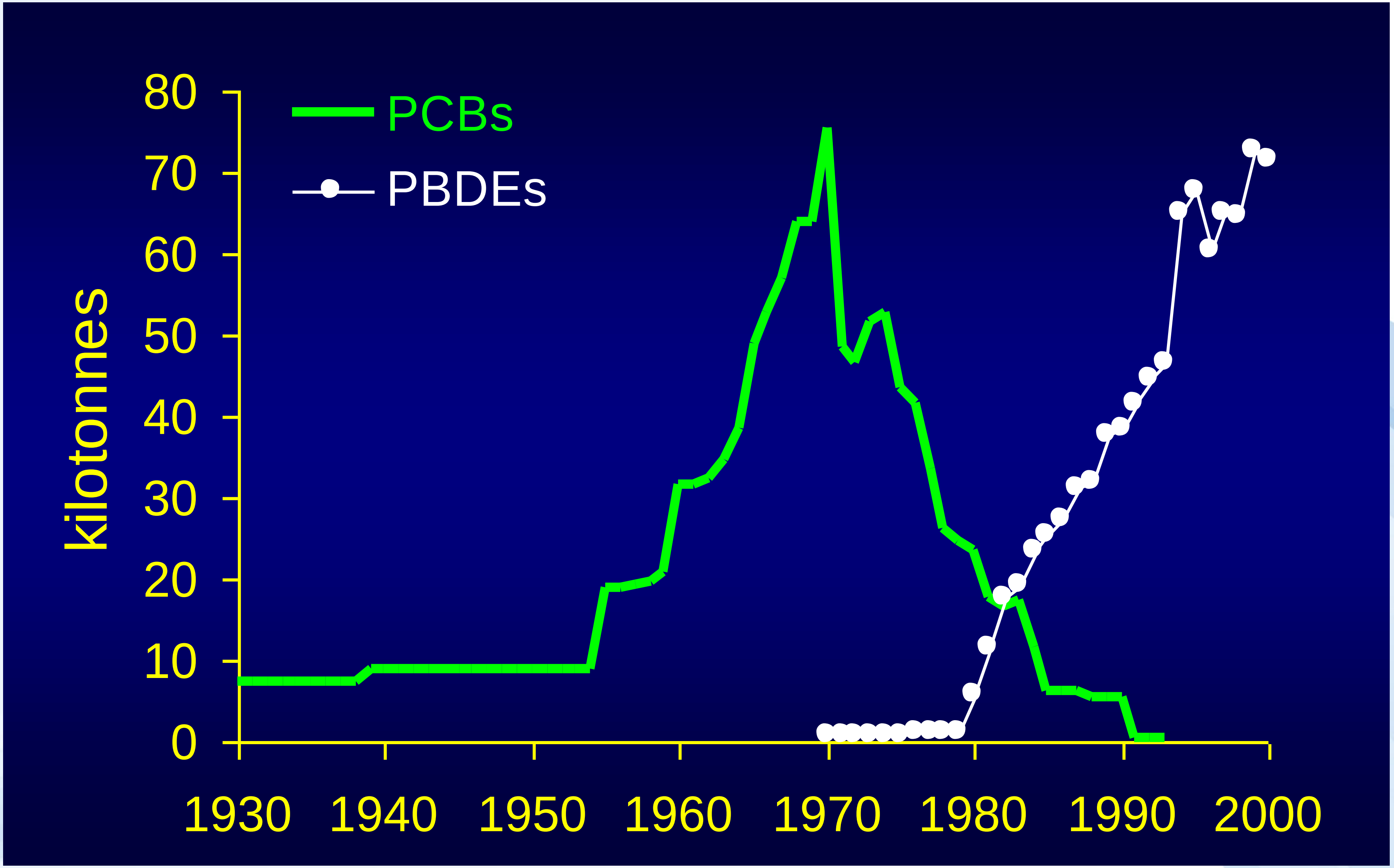
Changes in temporal trends



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PBDEs: Anna Palm (*Pers. Comm.*) PCBs: Breivik et al (2002)

HBM can be used to :

Reinforce regulatory actions by providing actual data about which chemicals get into people and at what levels.

Improve exposure assessment.

Establish baselines or reference ranges.

Facilitate people's right to know what chemicals are in their bodies.

Establish priorities for tackling environmental health-related problems.

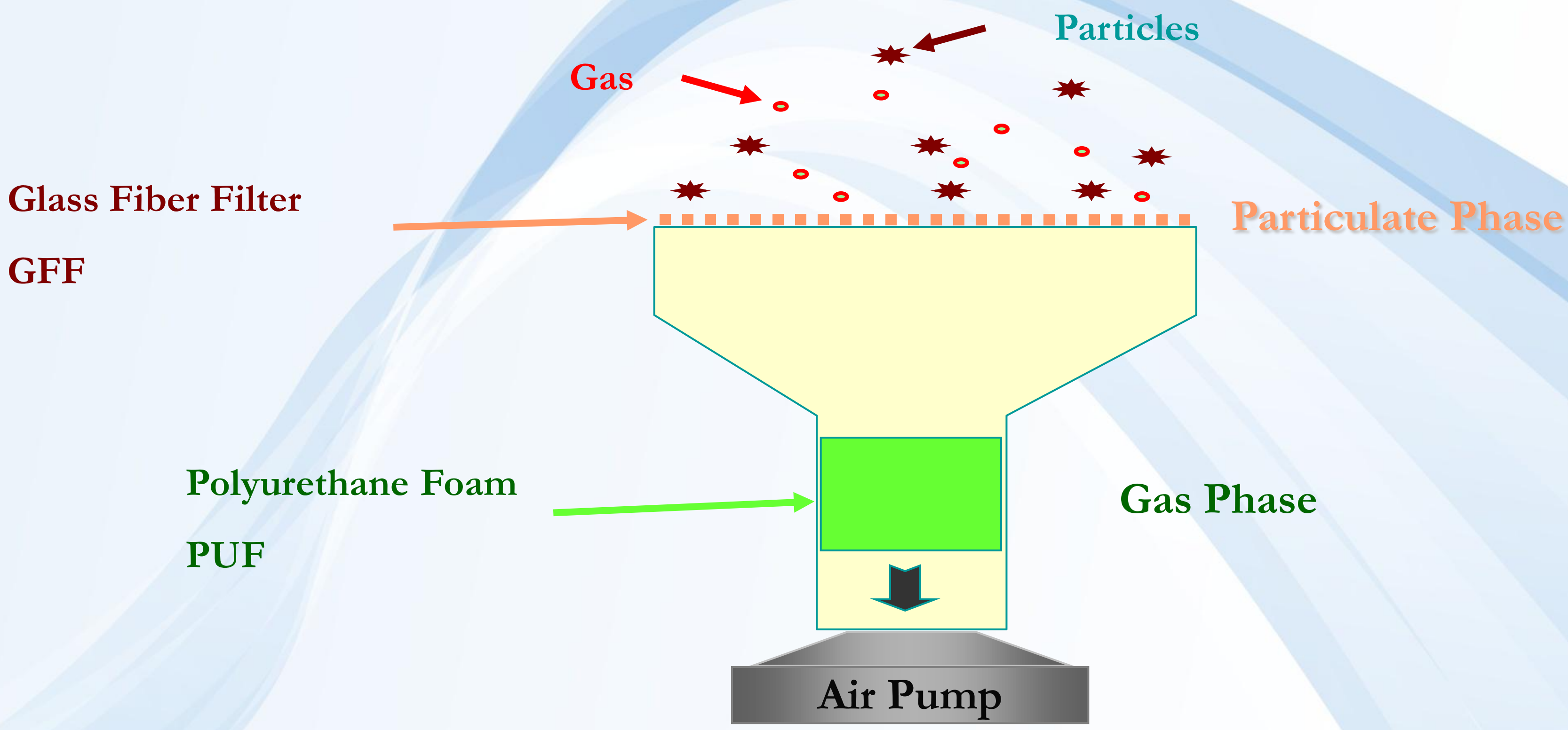
Active sampling

- Active sampling – cost, training, power, supporting meteo data
- Establish regional 'super stations'?

High volume samplers for active POPs sampling

Active sampling techniques

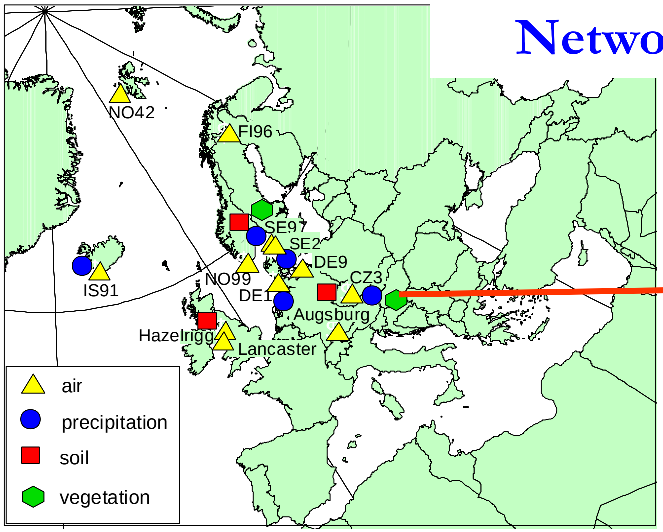
✓ <u>AEROSOLS</u>

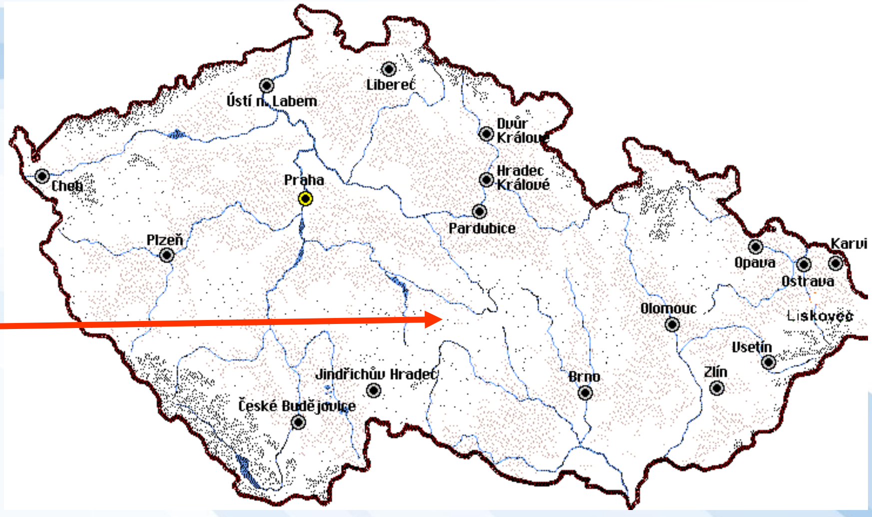


High-Volume sampler

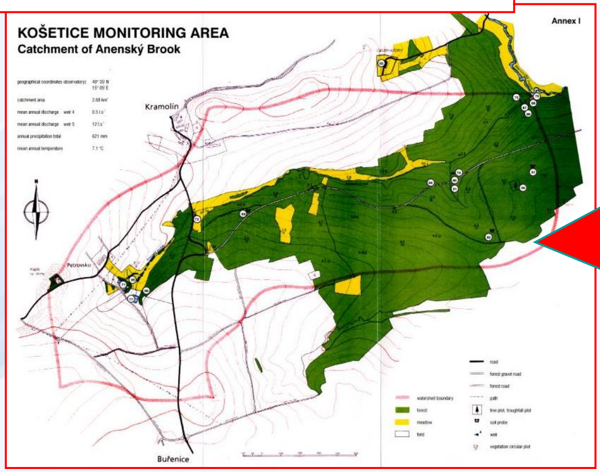
Regional monitoring of POPs

EMEP POPs Network

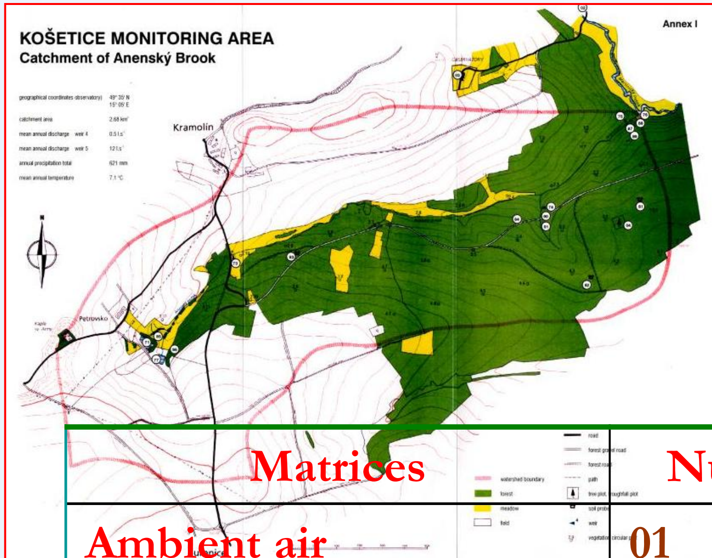


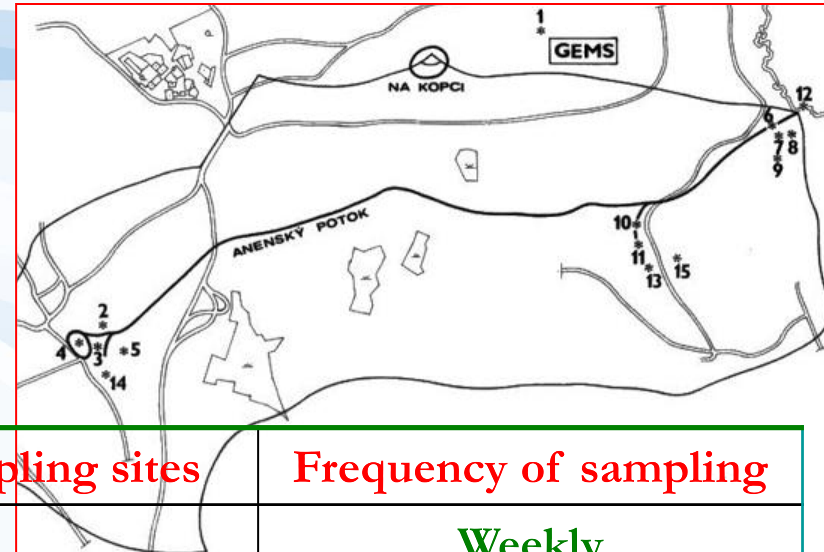


Observatory Košetice



Integrated monitoring of POPs – sampling sites and sampling frequency – Observatory Košetice – from 1988





Matrices	Number of sampling sites	Frequency of sampling
Ambient air	01	Weekly
Wet deposition	01	Evently
Surface waters	02, 04, 10, 12a, 12b, 14	Yearly
Sediments	02, 04, 10, 12a, 12b, 14	Yearly
Soils	01, 03, 05, 07, 08, 09, 11, 13, 15	Yearly
Litter	09	Yearly
Spruce and pine needles	05, 07, 08, 09, 13, 15, 16	Yearly
Mosses	05, 07, 08, 09, 13, 15, 16	Yearly

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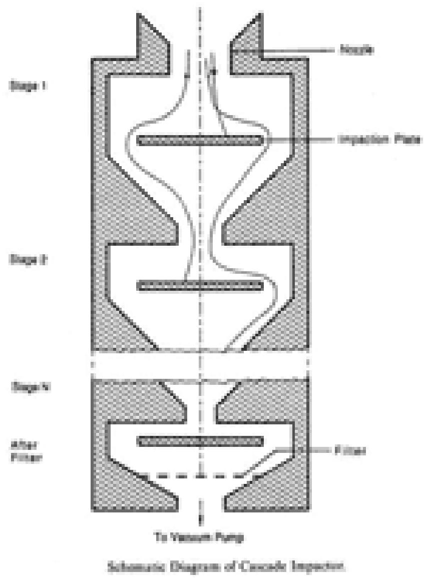
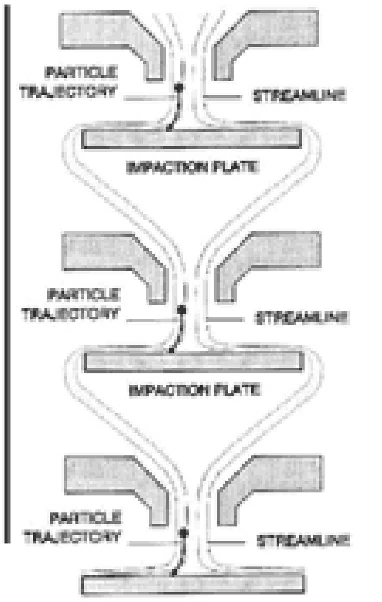
Fractionation of particulate matter (PM)





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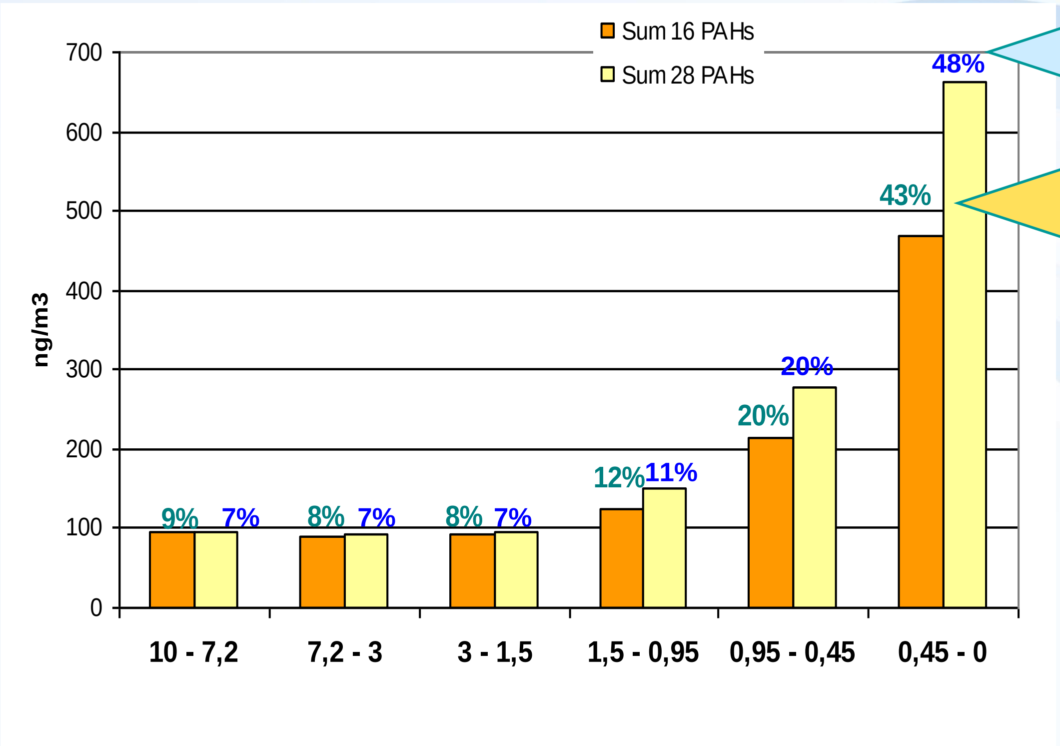
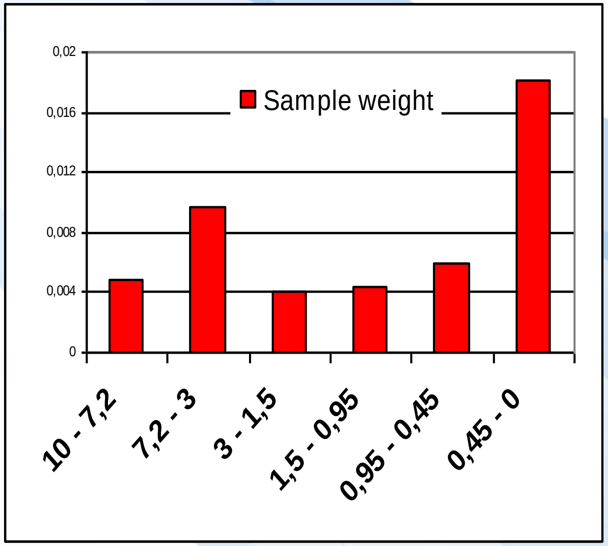


% of TOTAL SUM

ng/m^3 in fraction



A comparison between the umu assay based B[a]P equivalencies and equivalences determined using chemical analysis showed that in the particle phase only 10% of chemicals were identified and less than 1% in the gas phase (Bartkow et al., 2008).

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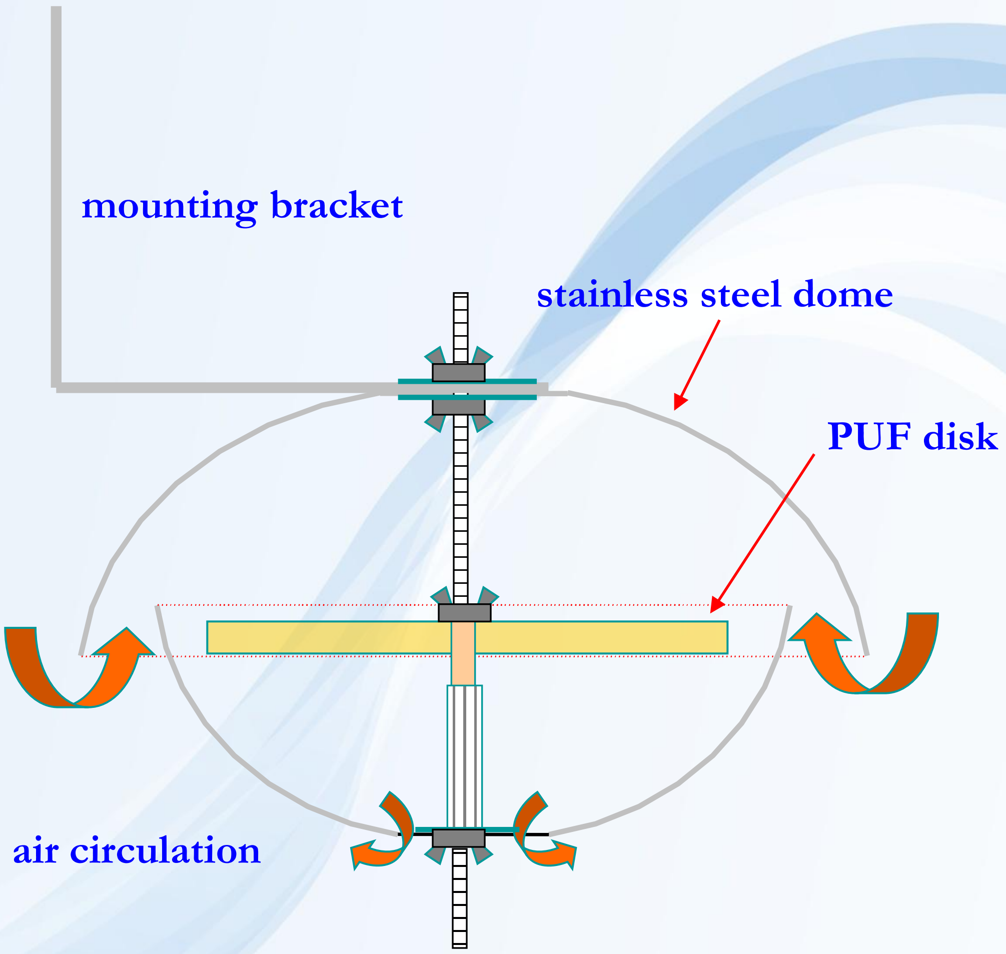
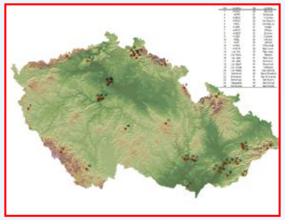
PUF passive samplers for POPs sampling



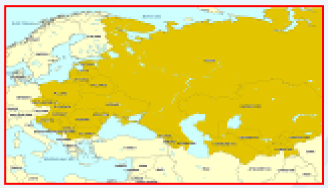
RECETOX Monitoring Network

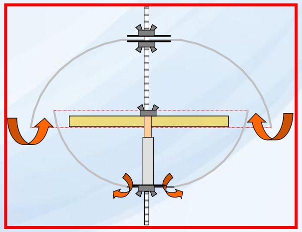
MONET = MOnitoring NETwork



MONET-CZ = Czech Republic	MONET-PIs = Pacific islands - Fiji
MONET-CEECs = 20 CEE countries + 2 CA countries	MONET-Africa = 17 African countries

MONET-EUROPE – 55 sampling sites round whole Europe





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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

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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.

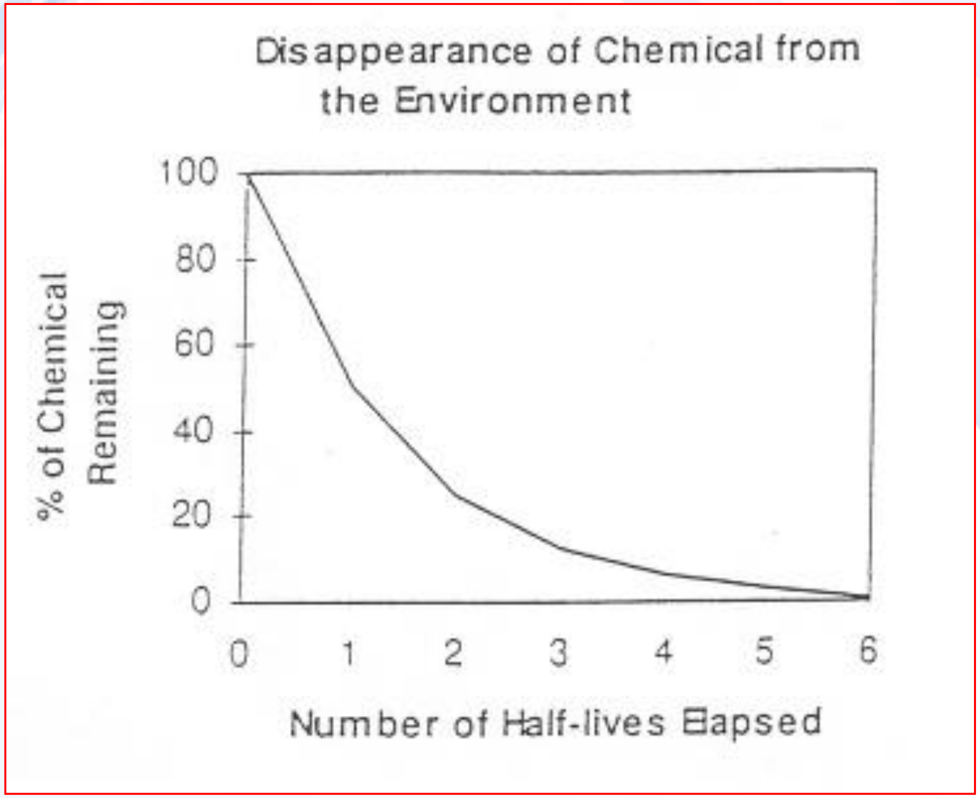
Furthermore, a long half-life in a medium may be relatively inconsequential if the substance is not emitted to that medium or is likely to transfer to it.

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



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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

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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

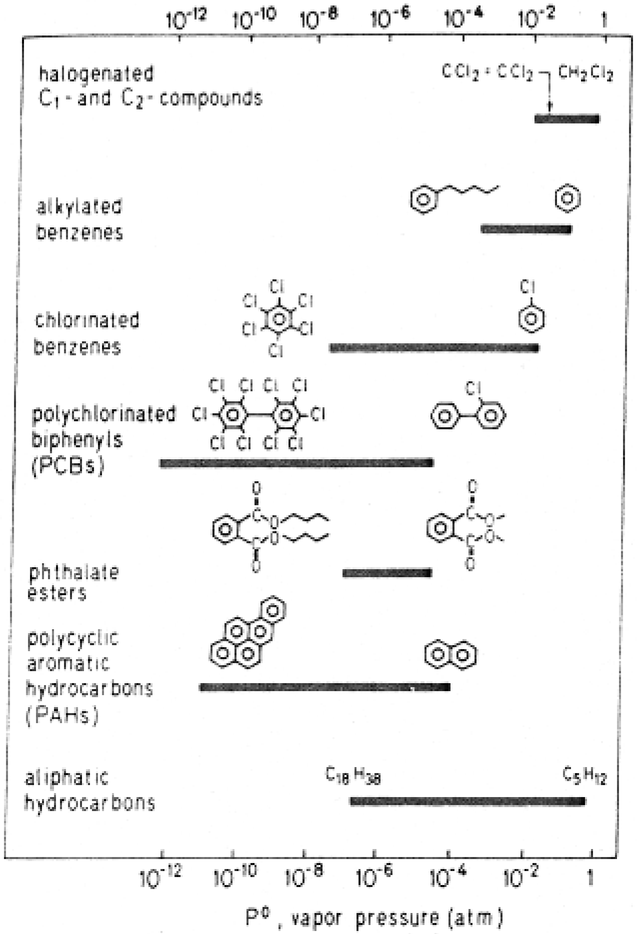
$$H = p/C_W$$

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

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

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 s of organic compounds.

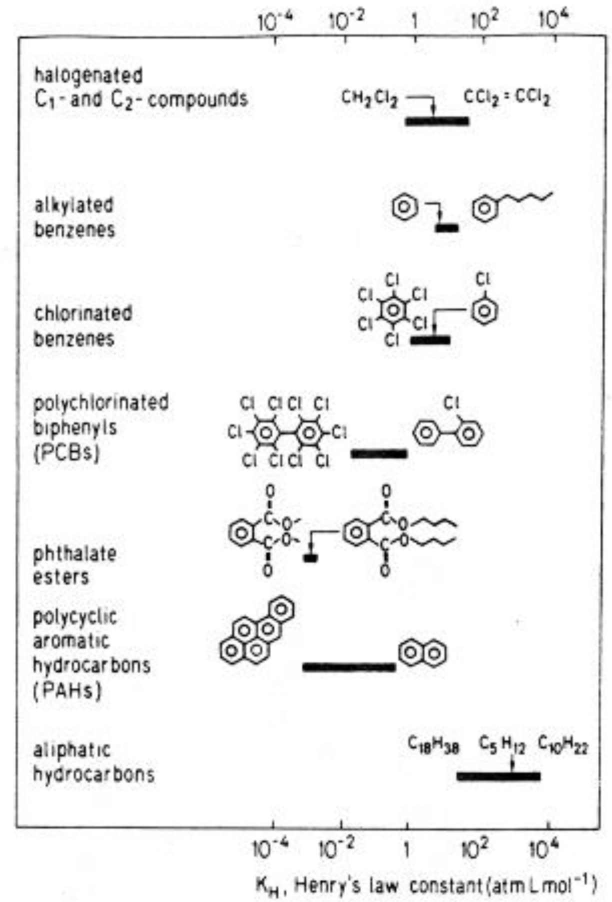


Figure 6.2 Ranges in Henry's Law constants (K_H) for some important classes of organic compounds.

Water solubility (WS, S)

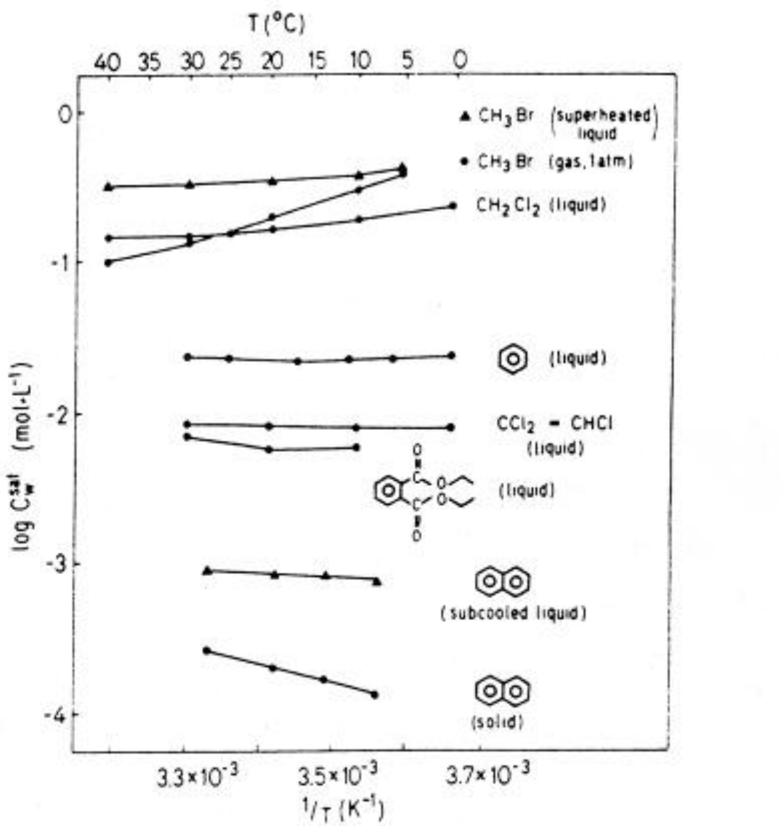


Figure 5.6 Solubility in water as a function of temperature for various compounds.

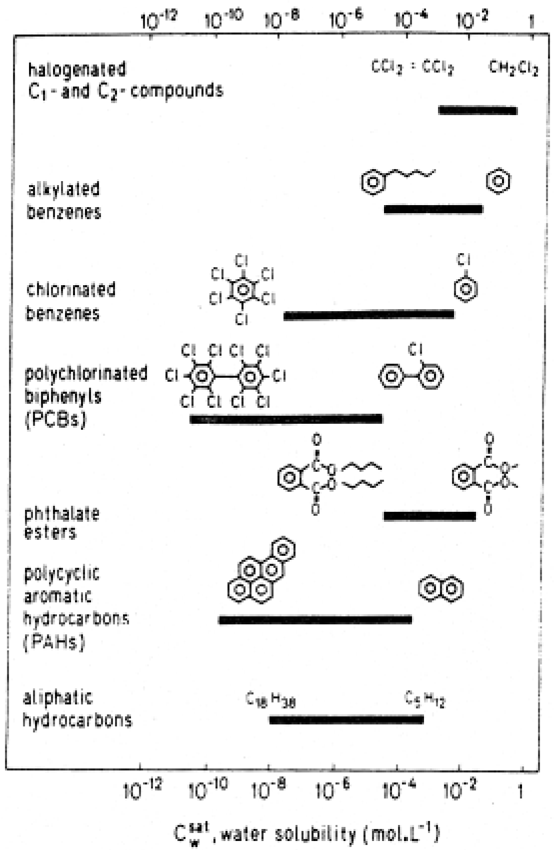


Figure 5.1 Ranges in water solubilities (C_w^{sat}) of some important classes of organic compounds.

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)

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

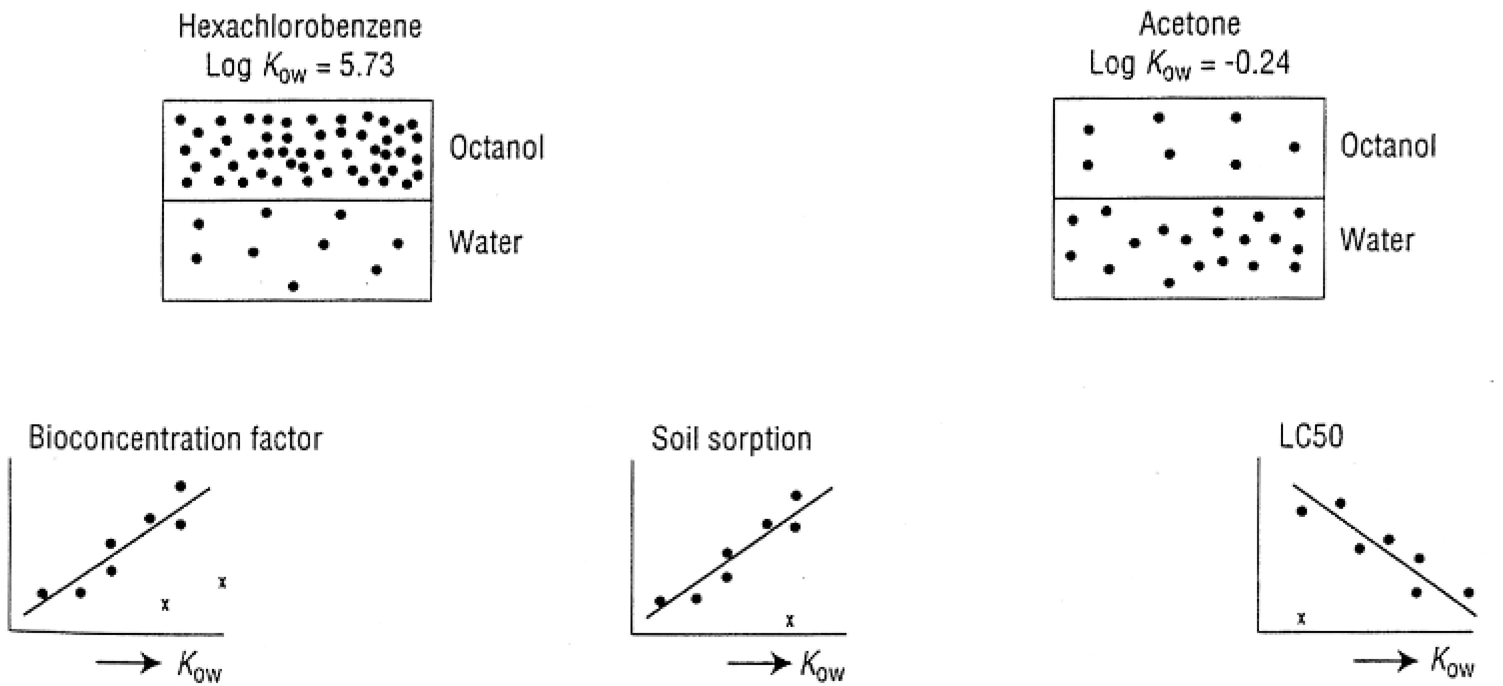


Figure 7.6. The octanol-water partition coefficient (K_{ow}) is defined as the ratio of the concentrations of a chemical in octanol and in the aqueous phase at steady-state. It can be measured, for example, by the shake-flask procedure. K_{ow} is often used for the estimation of bioconcentration, sorption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

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

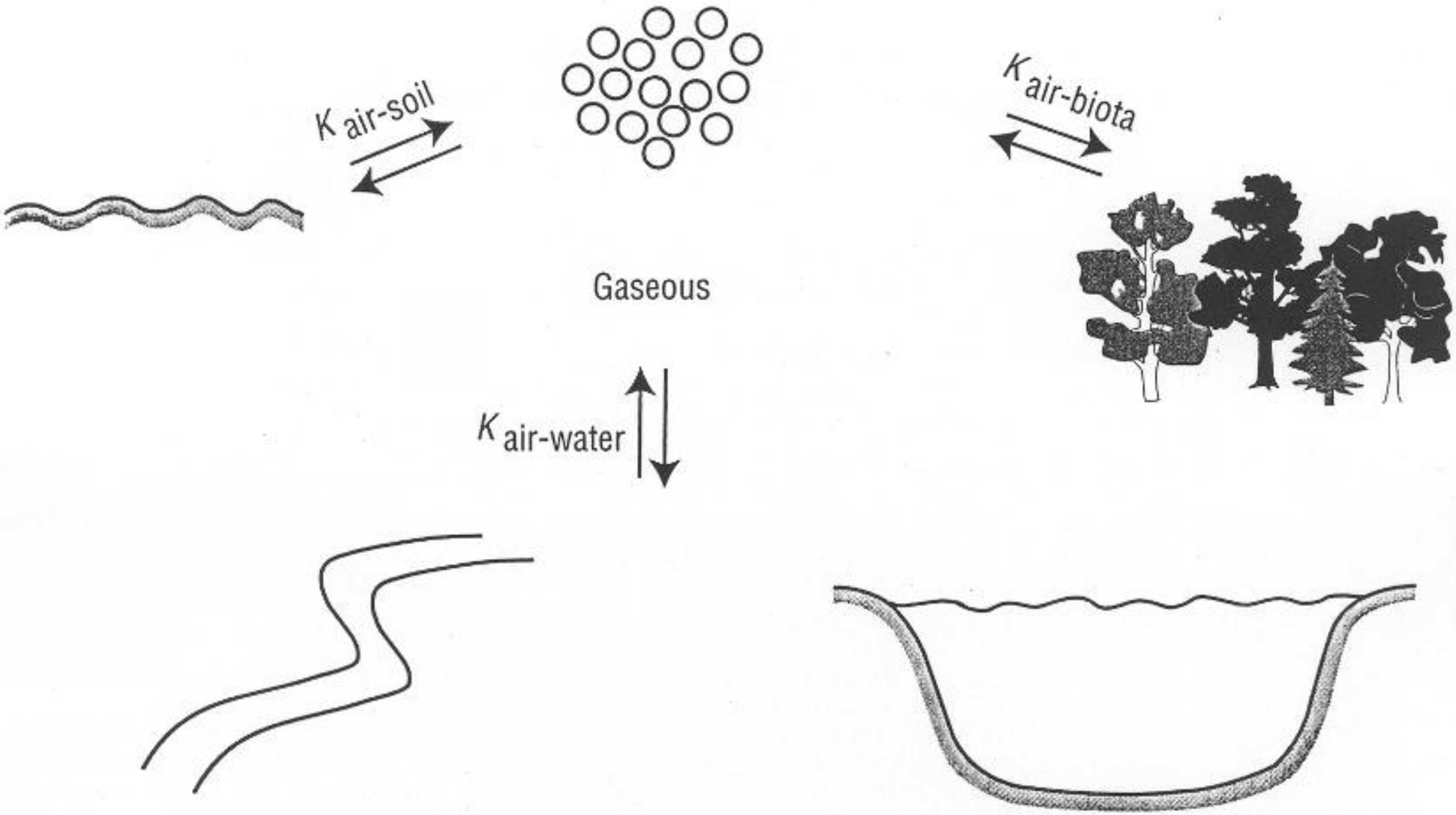
Transfer of compound cross the interface octanol – air can be described by Whitman two-resistance coefficient of mass transfer (MTC), which used the conception of two resistance – in boundary layers of octanol and air.

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.

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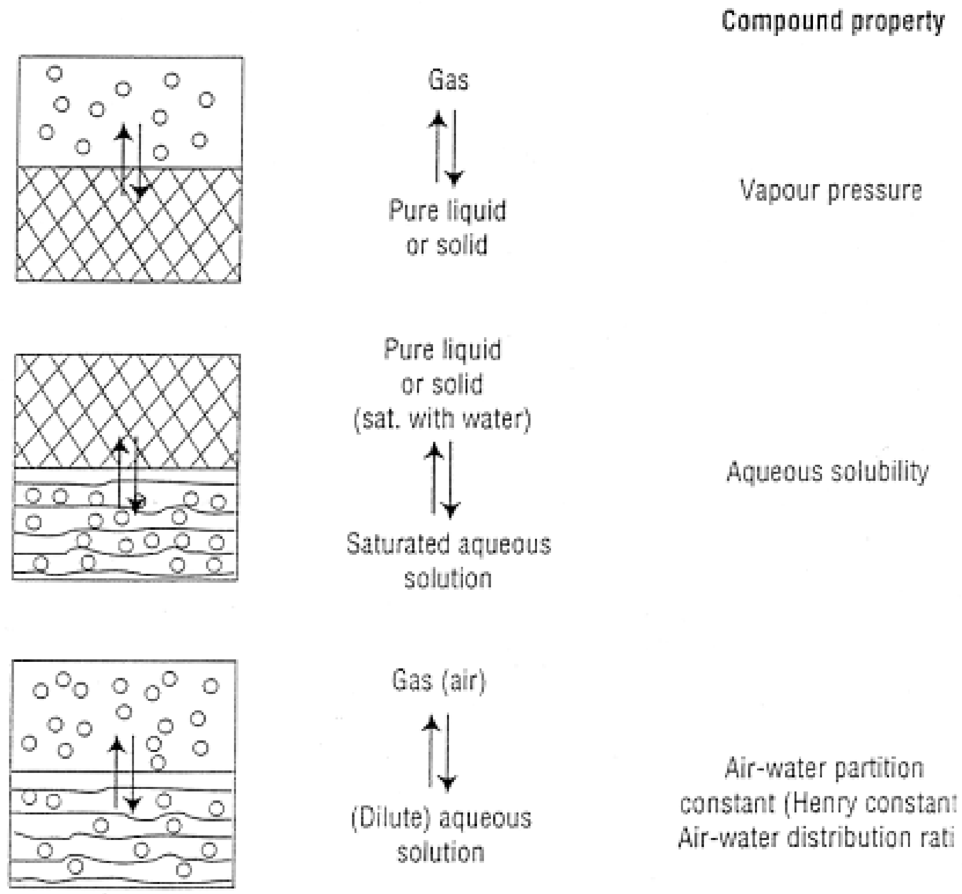
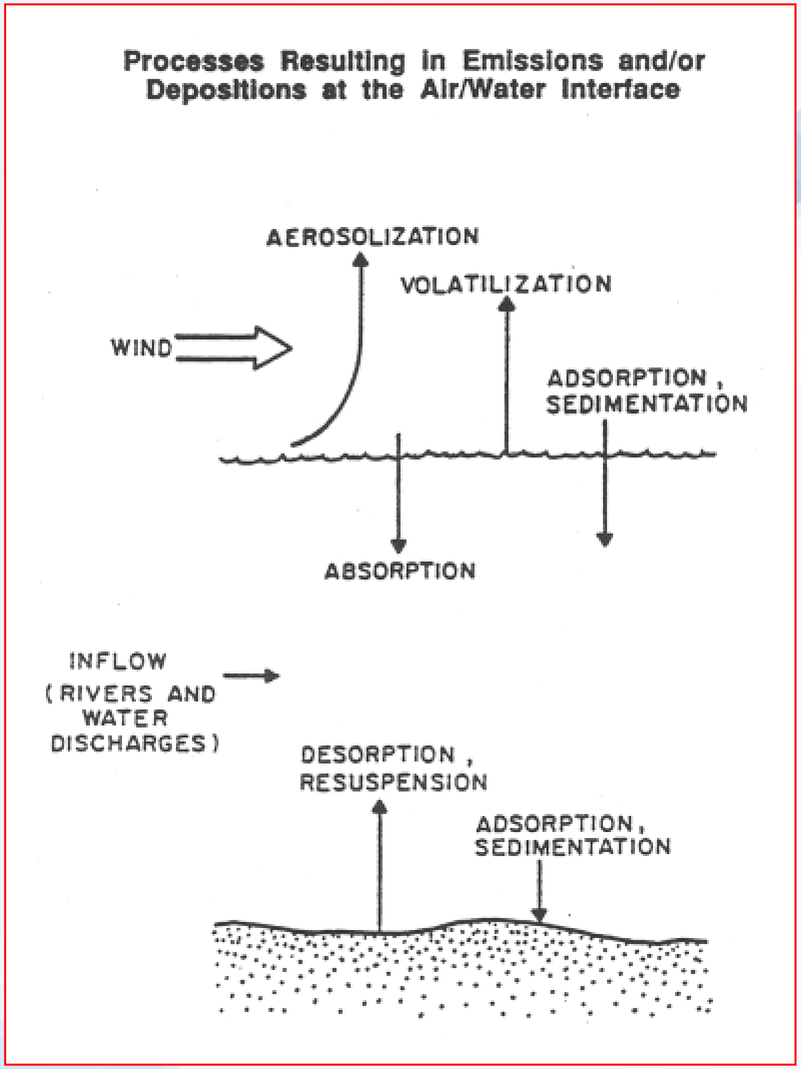
Environmental equilibria



Important compound properties showing the equilibrium partitioning between two phases.

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

Equilibrium air - water



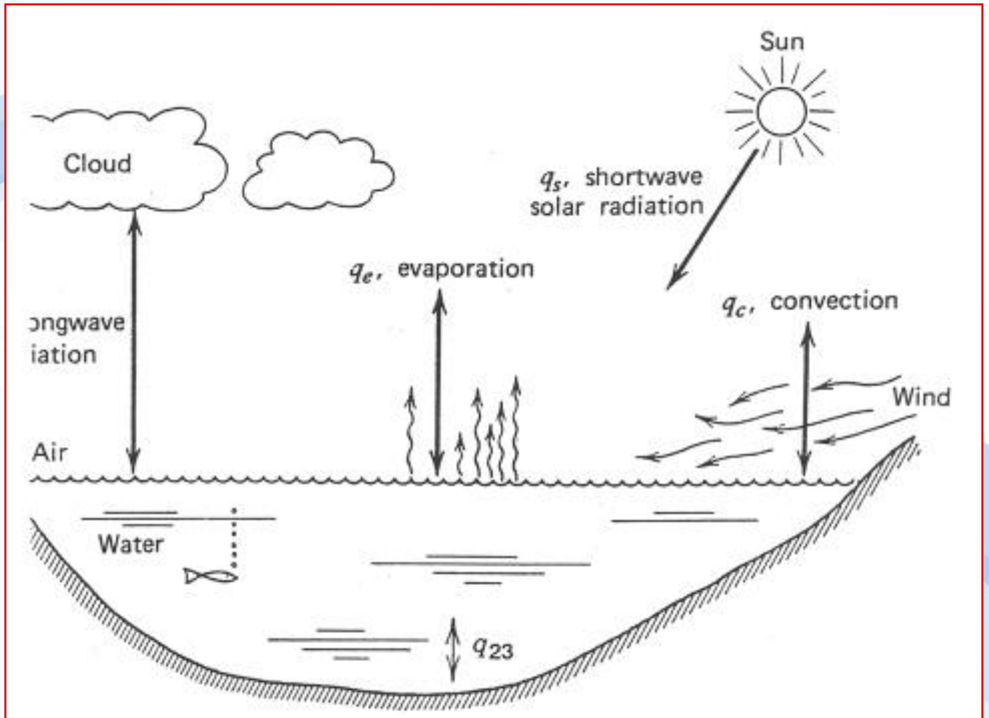


Figure 4.3-1. Heat and energy transfers at the air–water interface.

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**

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

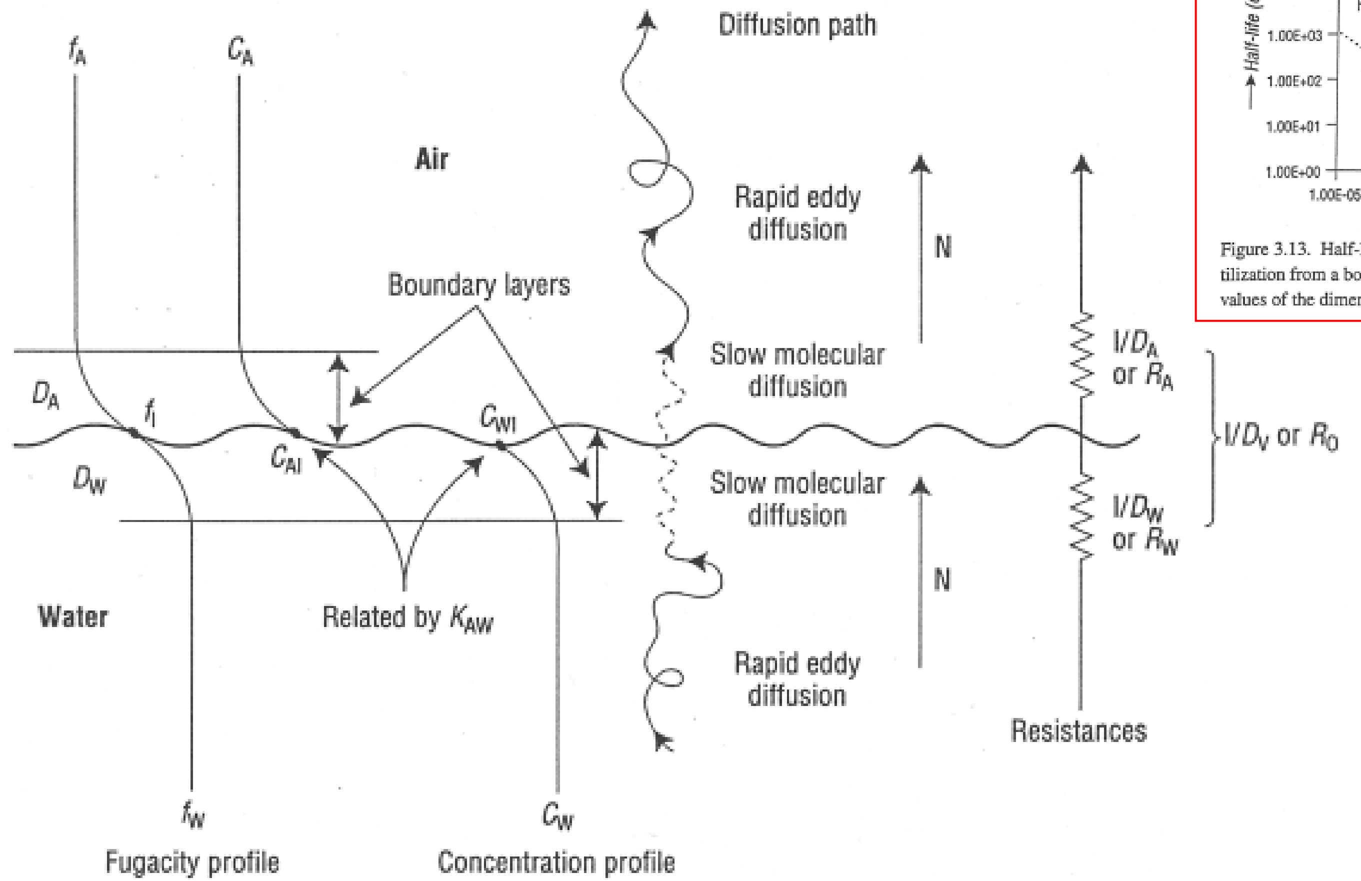


Figure 3.12. Mass transfer of a chemical between two phases, air and water, according to the two resistances concept described l Mackay [1]. Reprinted by permission of Lewis Publishers, an imprint of CRC Press, Boca Raton, Florida.

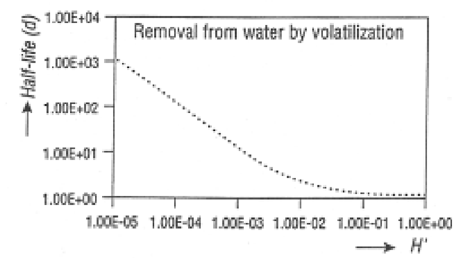
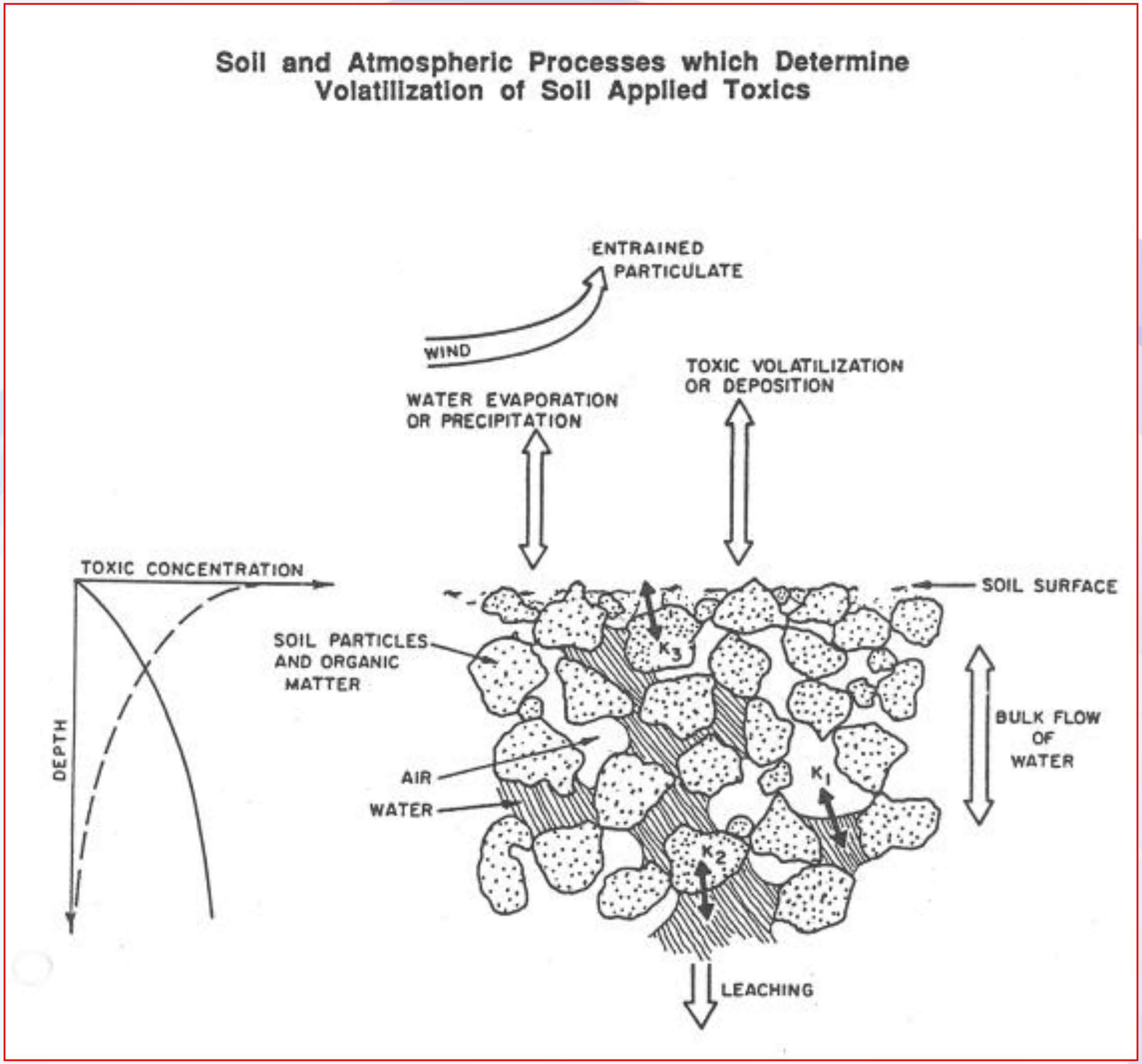


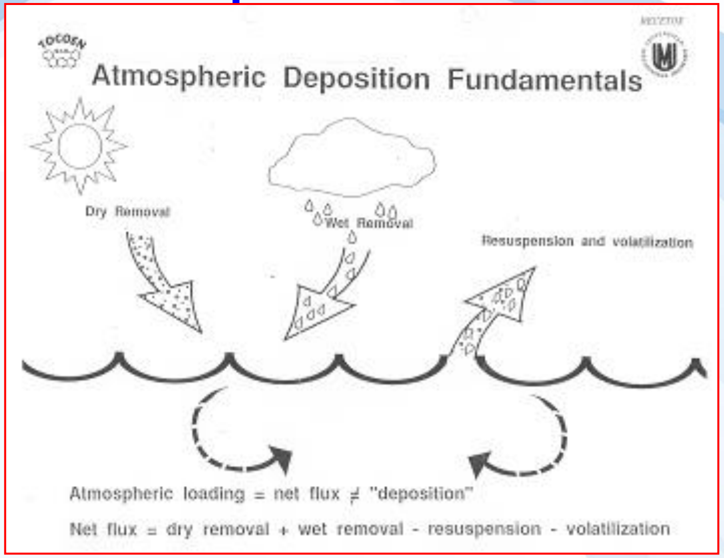
Figure 3.13. Half-lives for the removal of a substance by volatilization from a body of water (depth 2 m), plotted for different values of the dimensionless Henry's law constant.

Soil and atmospheric processes which determine volatilization of soil applied chemicals



Dry and wet atmospheric deposition

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



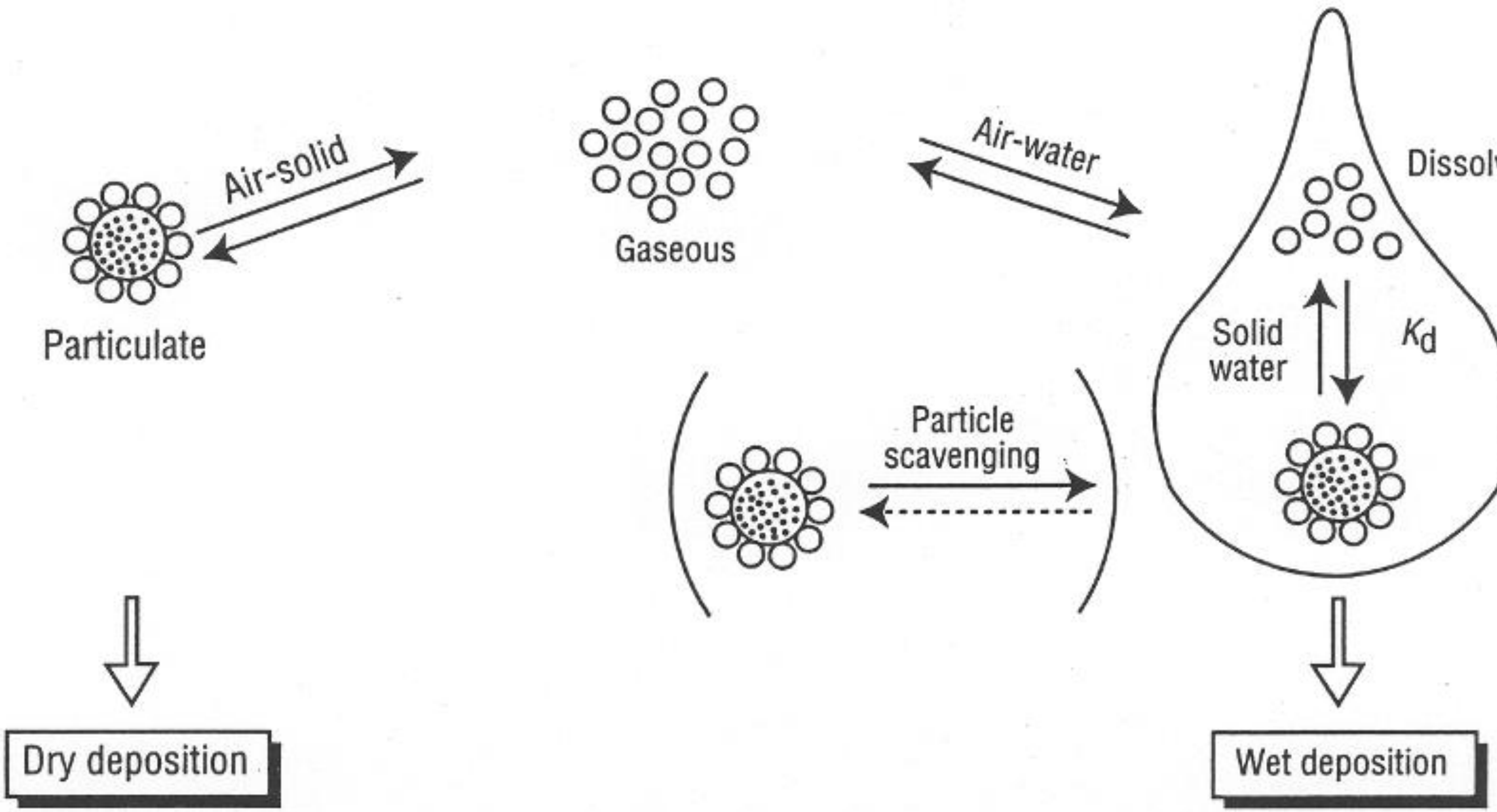
Atmospheric deposition:

- wet
- dry

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

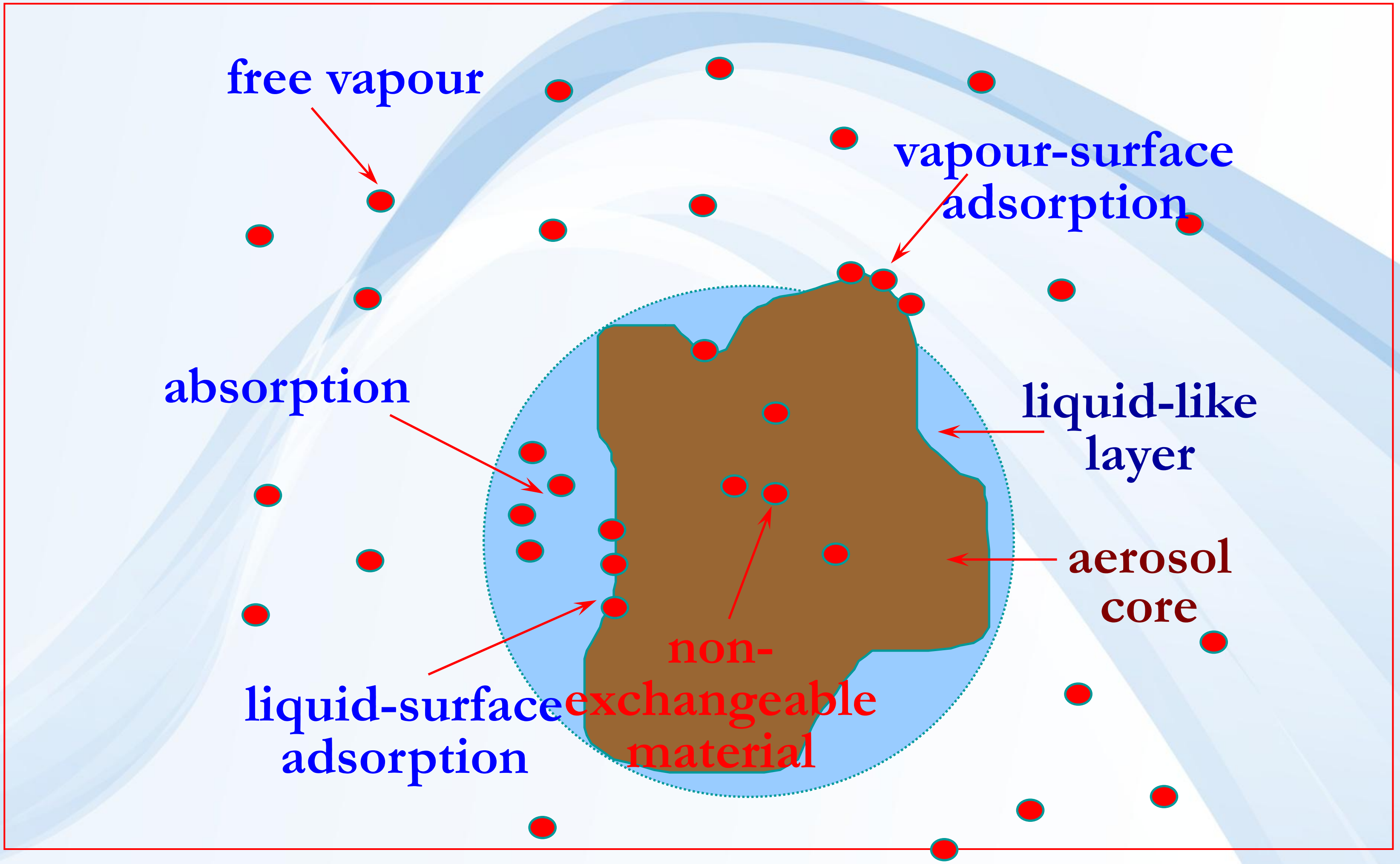
Dry atmospheric deposition – sum of aerosol deposition and gas absorption.

Dry and wet atmospheric deposition

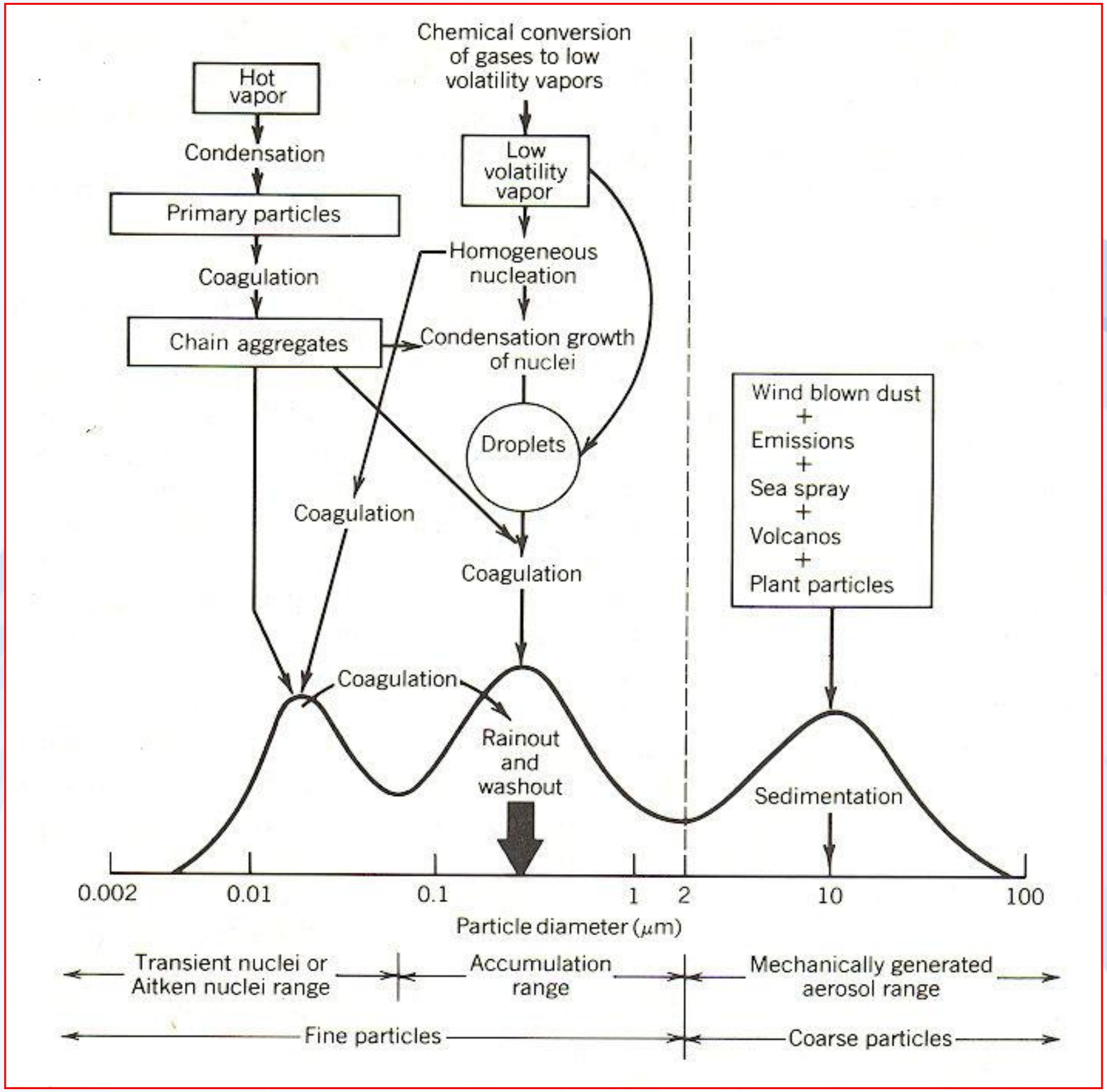


Mechanisms of atmospheric deposition. From Schwarzenbach [13].With permission.

Particle - gas interactions



Particles in the Atmosphere



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

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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.

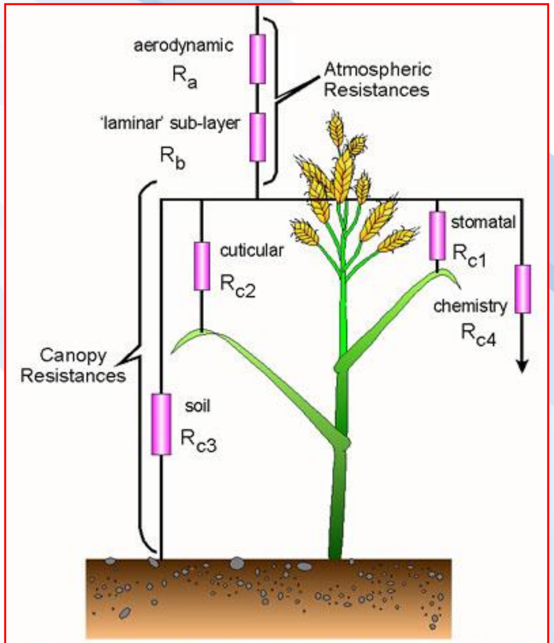
If the fugacity in water or soil is higher, the result is a opposite – the volatilization is coming.

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.

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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.

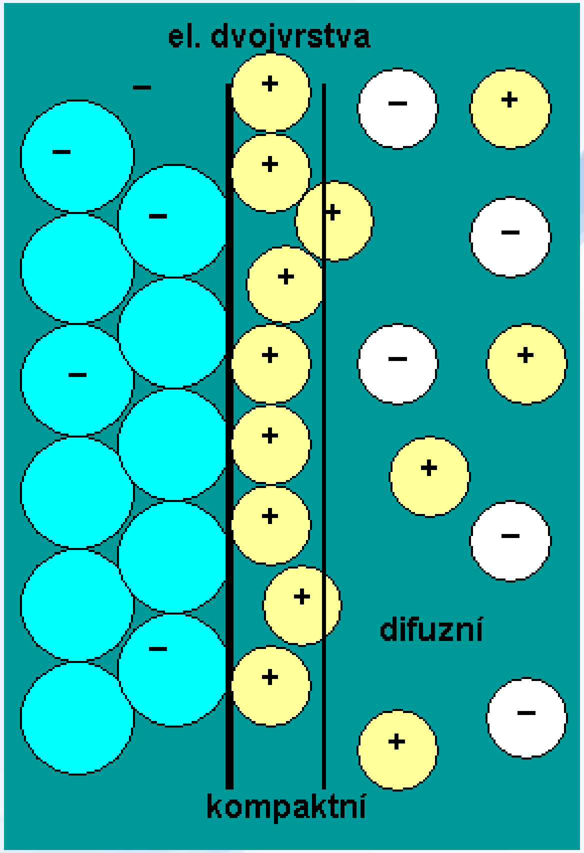
If based on the effect of these powers, the concentration of one component increased in the comparison with the concentrations inside the phase – this cummulation is described as a sorption.

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

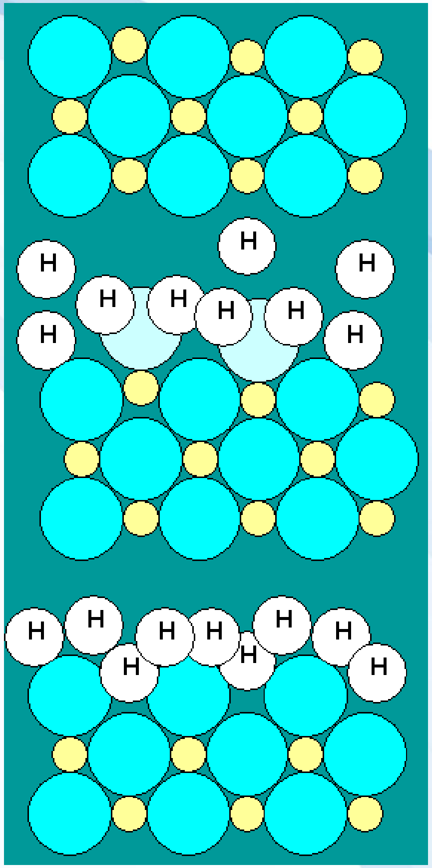
Adsorbent – adsorbate.

Surfaces

Electric double-layer

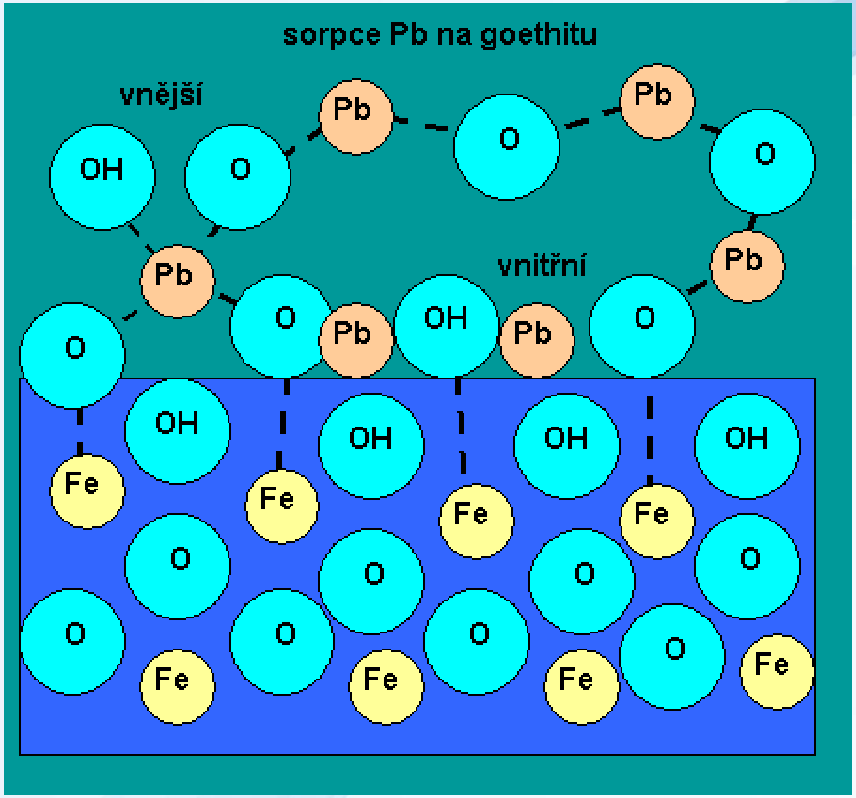


Iont exchange

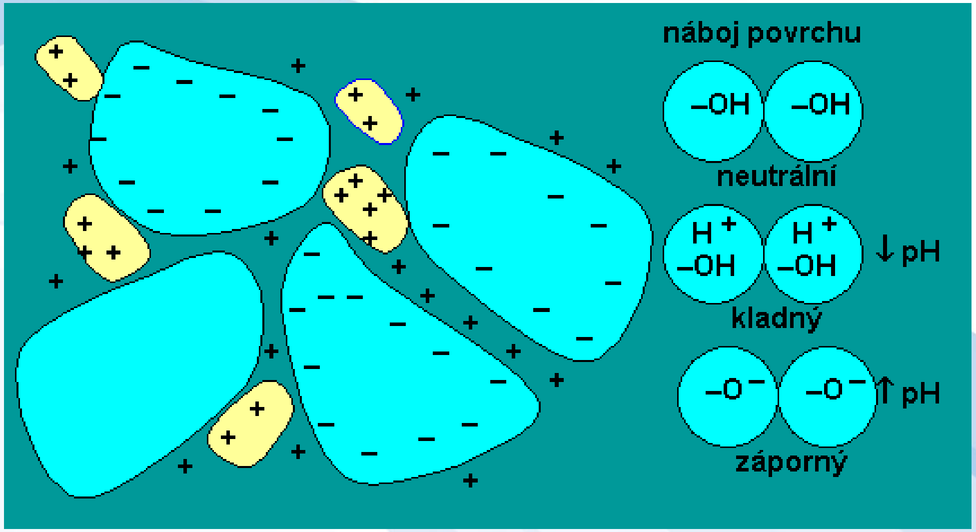


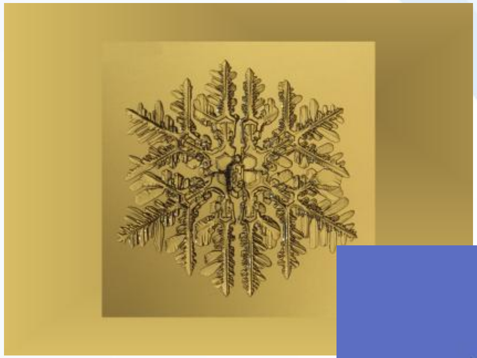
Surfaces

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:

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

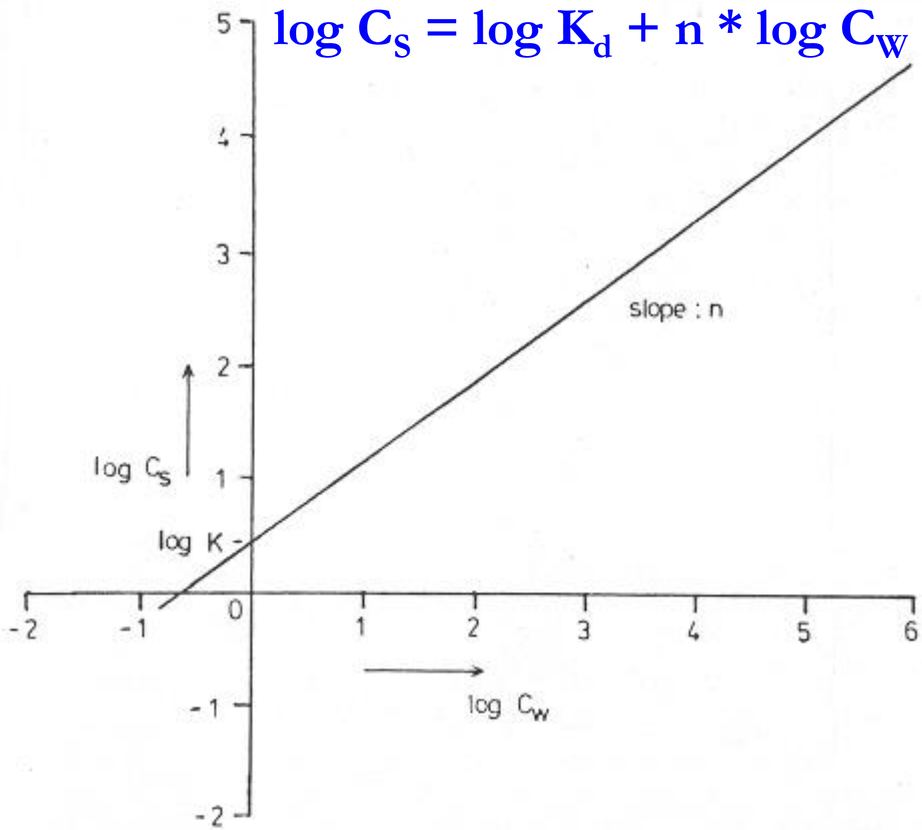


Figure 8. Typical Freundlich adsorption isotherm C_s = concentration on the adsorbent; C_w = concentration in the water; $0 < n \leqslant 1$. $C_s = K C_w^n$ or $\log C_s = n \log C_w + \log K$.

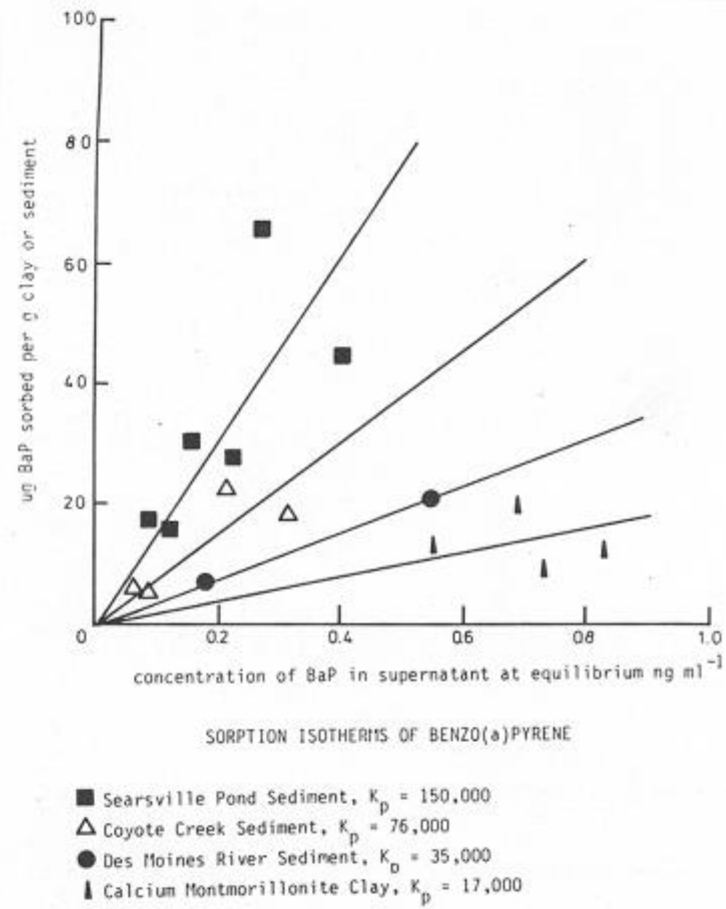


Figure 9. Sorption isotherms of benzo[a]pyrene [45].

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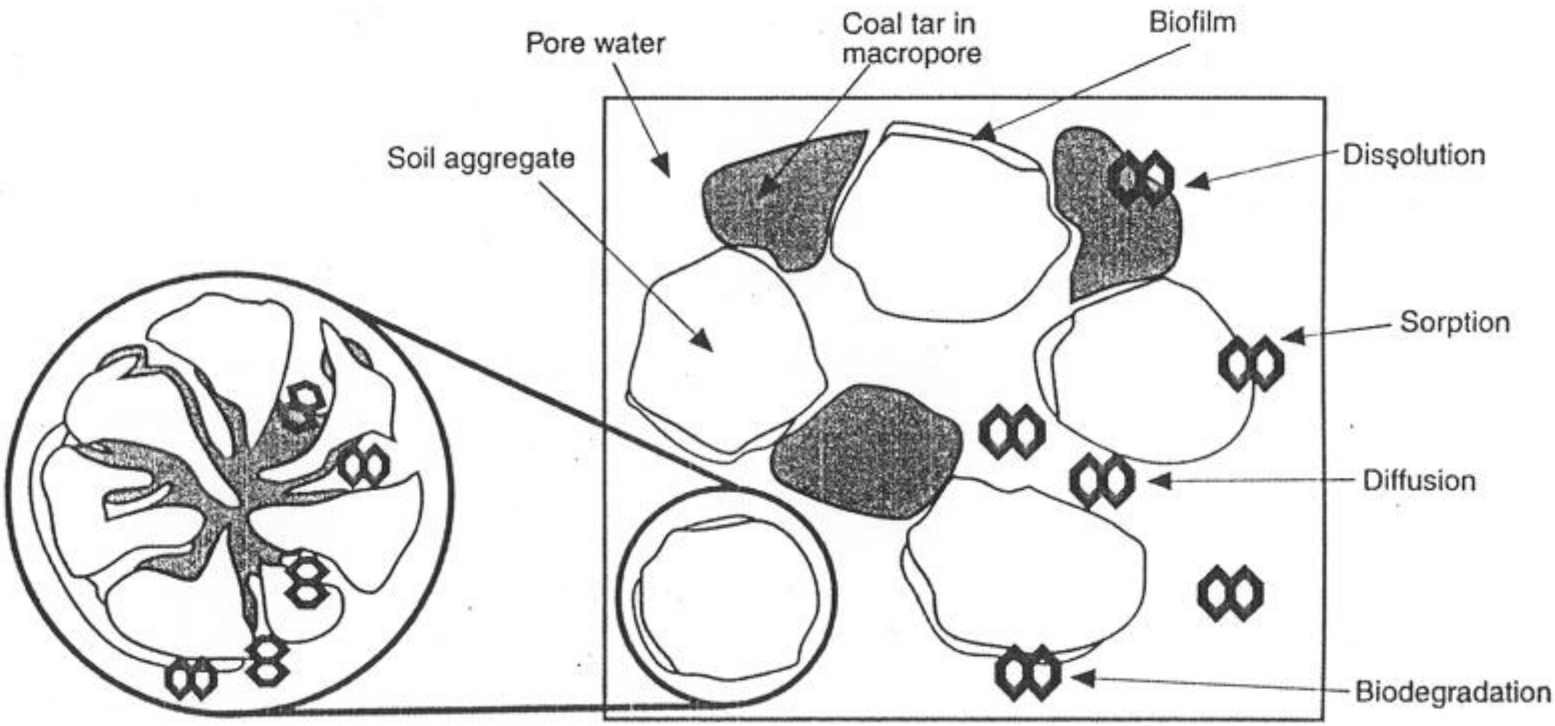
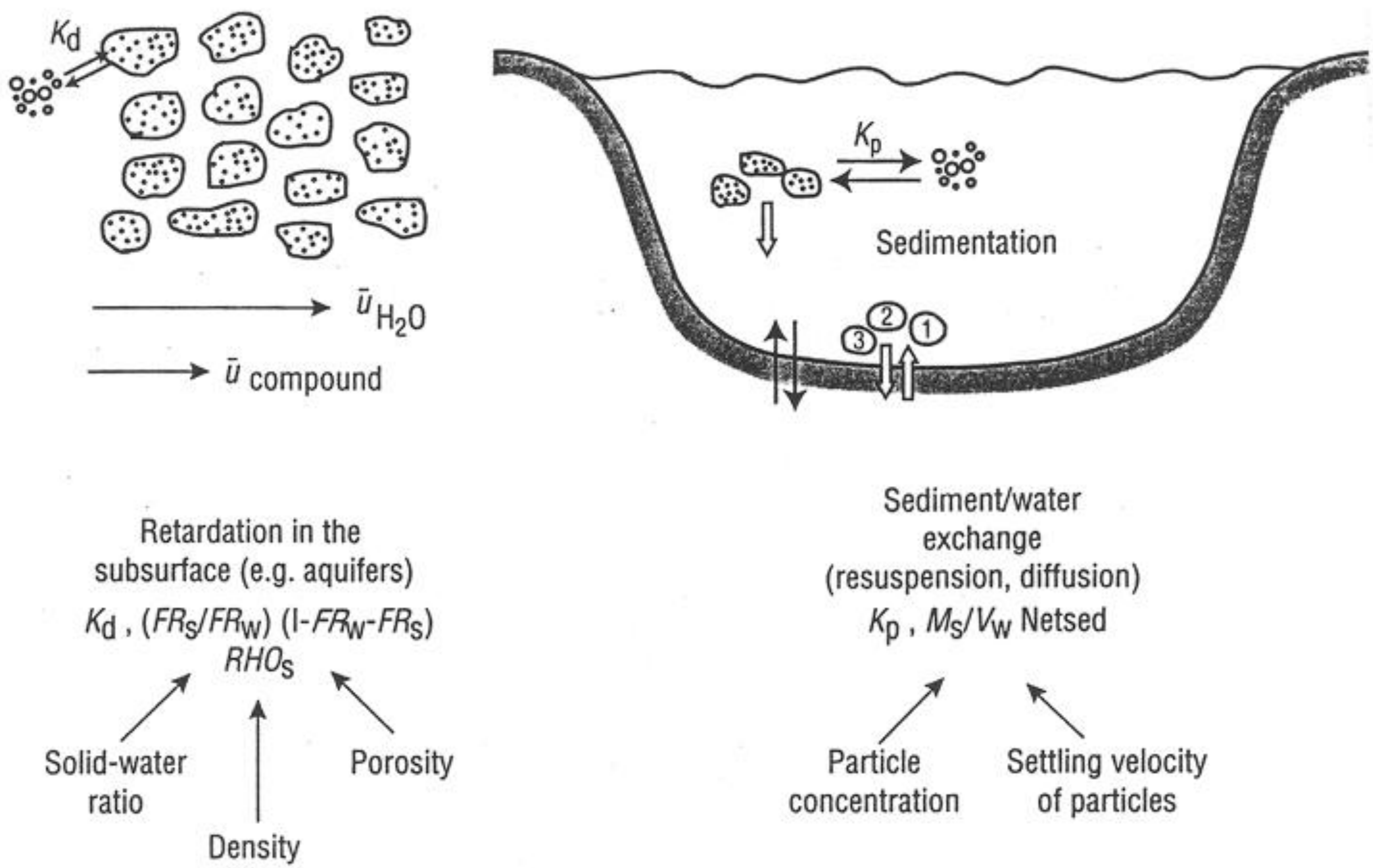
Sorption

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

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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

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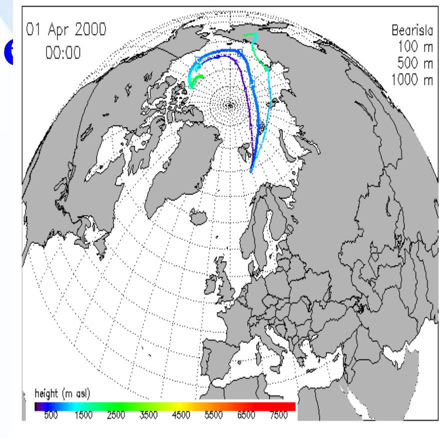
Principles and consequences of long-range transport

- 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

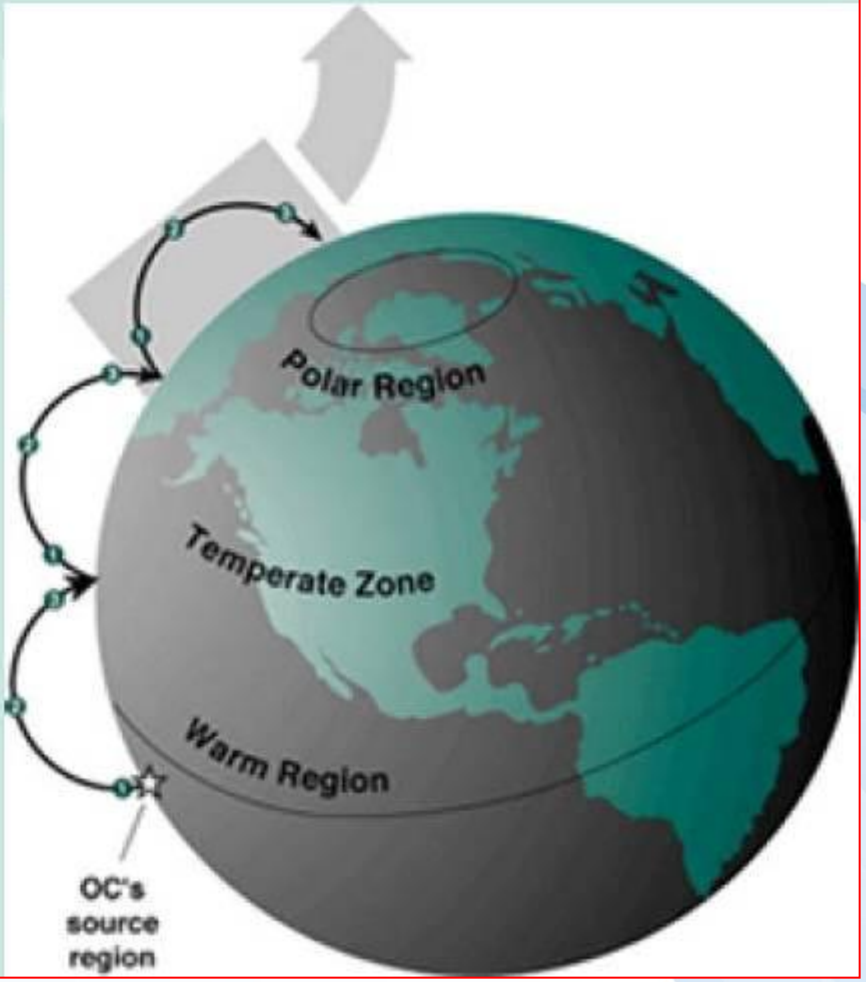
- Estimation of meteorological, hydrological, oceanographic conditions during the transport event (e.g, air mass back trajectories)
- Physico-chemical properties and characterisation
- Compound pattern elucidation
- Assessment of concentration levels including ratio evaluation between different contaminant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



The „Grasshopper Effect“

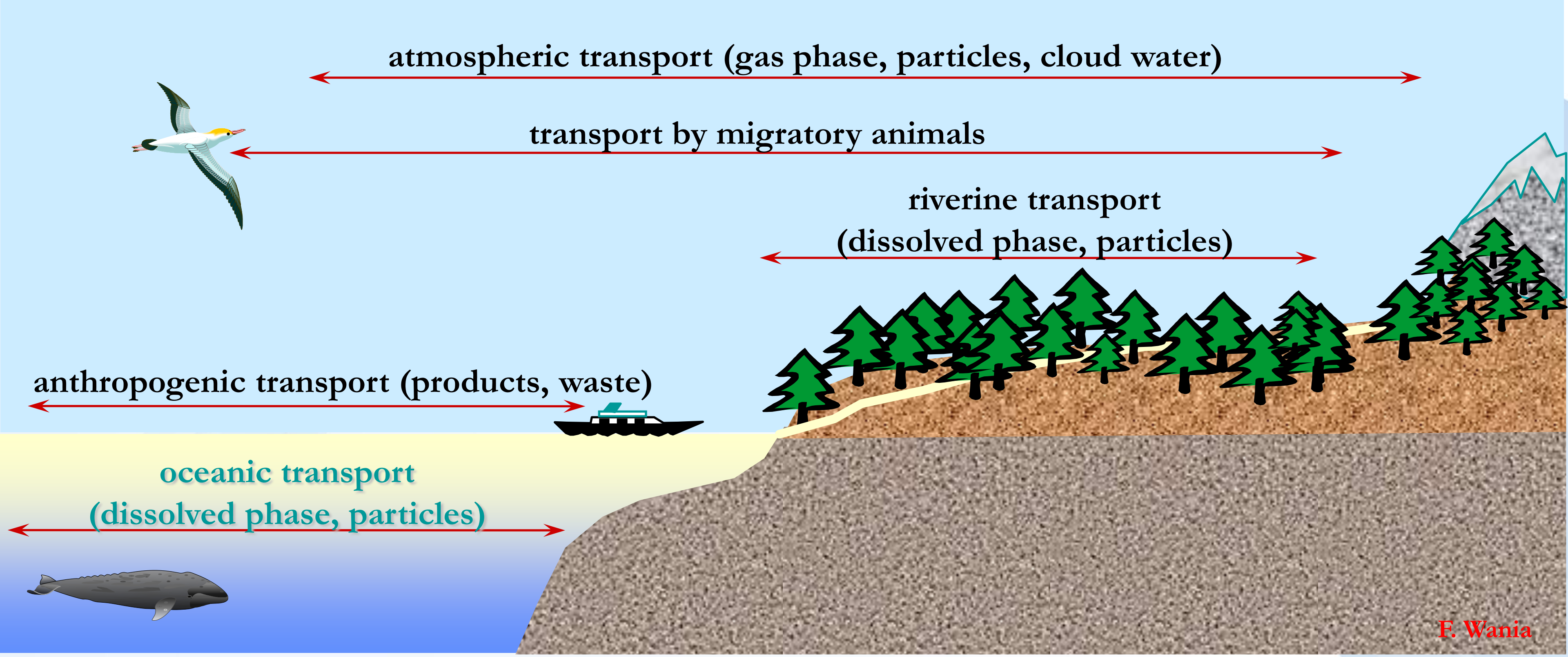
Steps

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



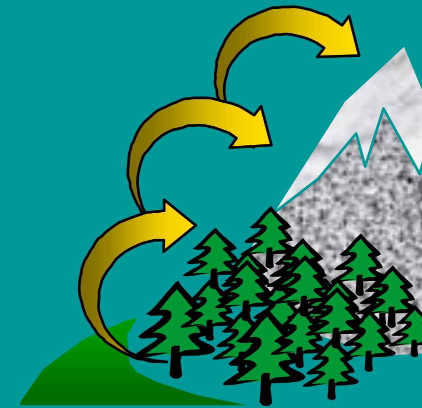
PTS Transport Pathways

- 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)

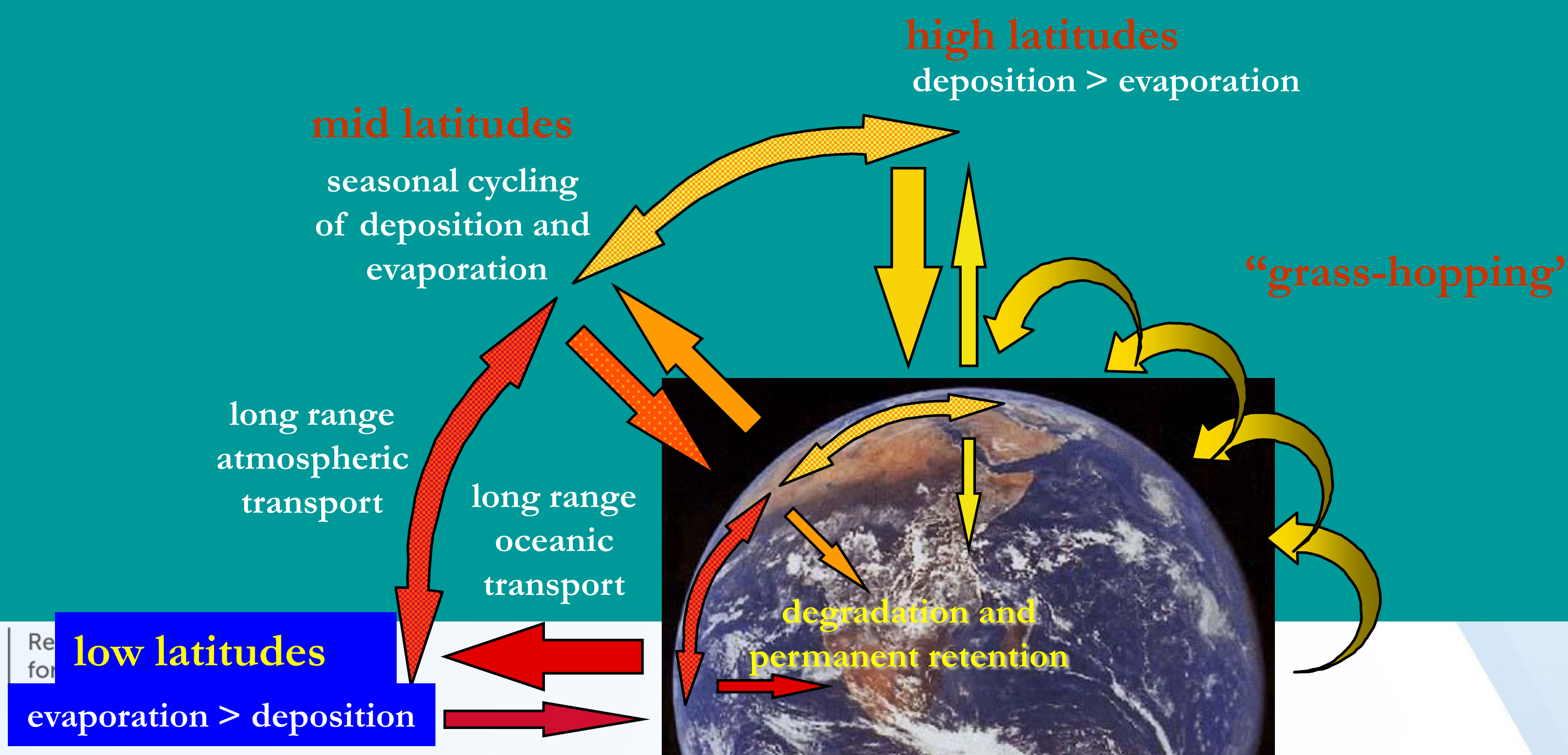


Long-range transport of PTS, e.g. HCB

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



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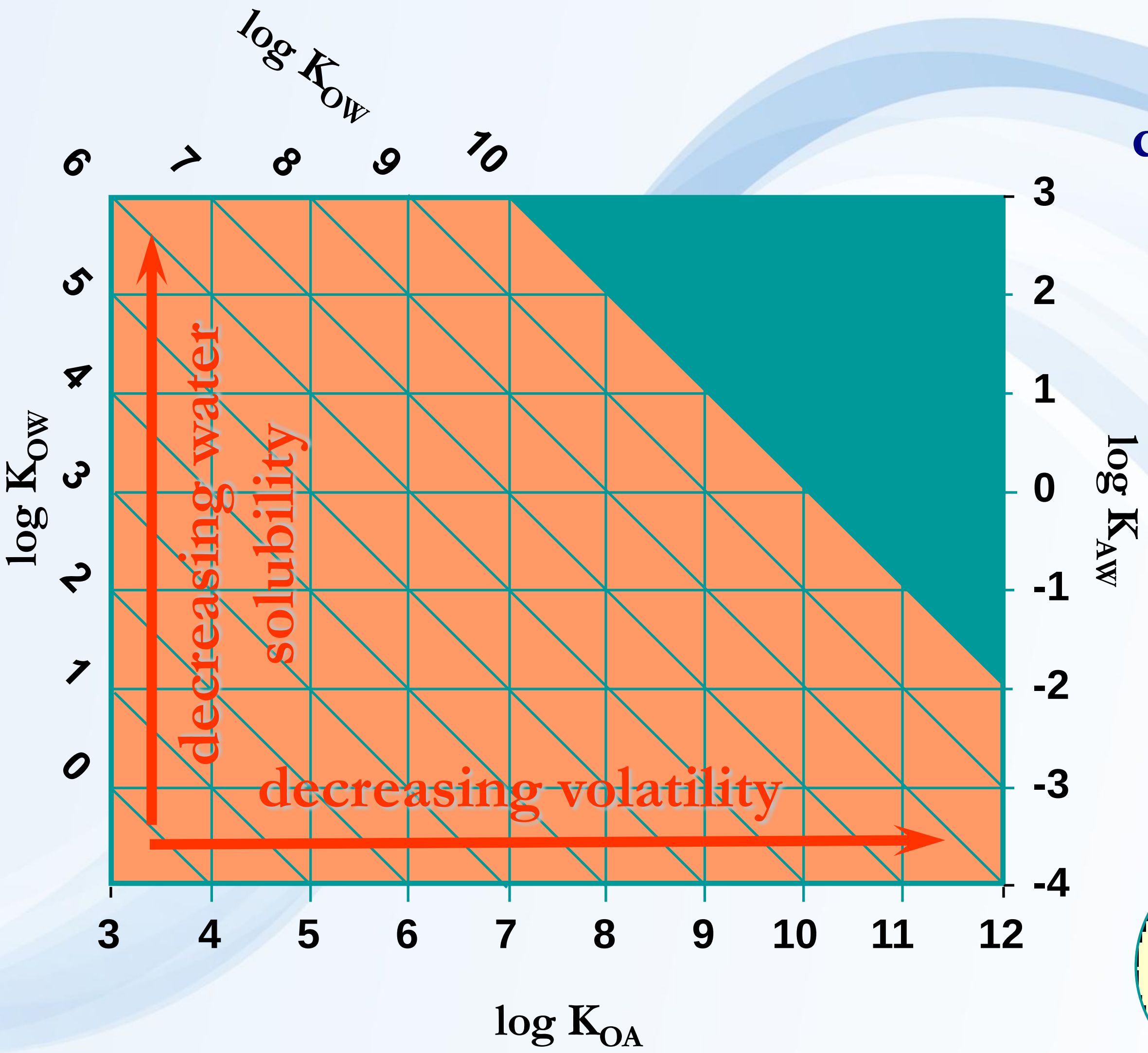
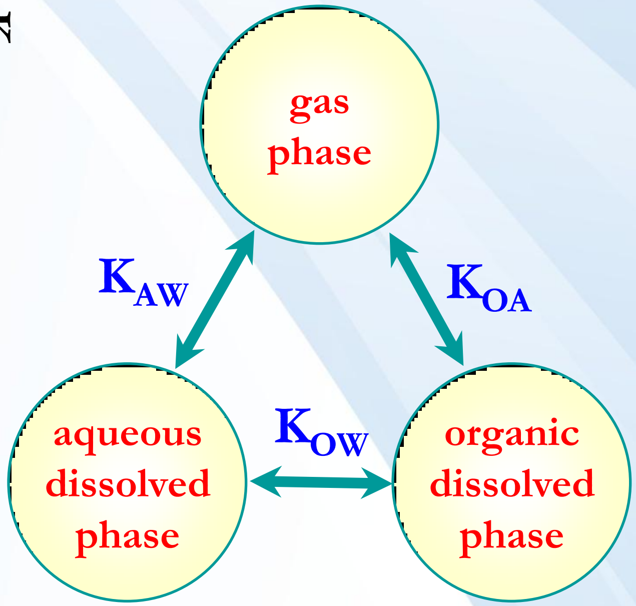
The Chemical Partitioning Space



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

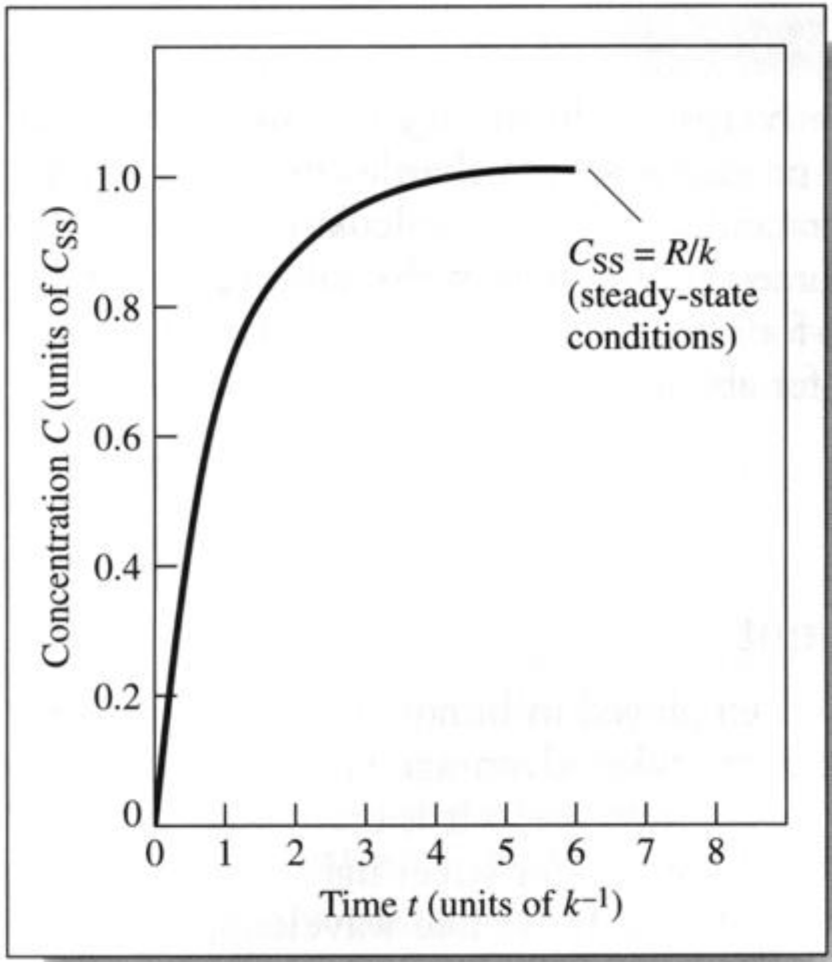


Figure 7-1
Increase in metal concentration with time to reach the steady-state value, C_{ss}.

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

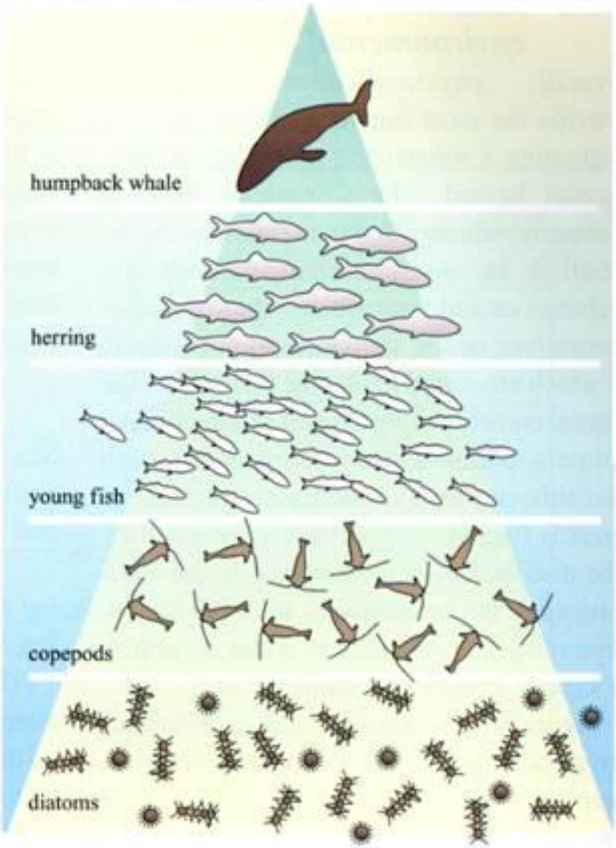


Figure 5.1.4 Food pyramid

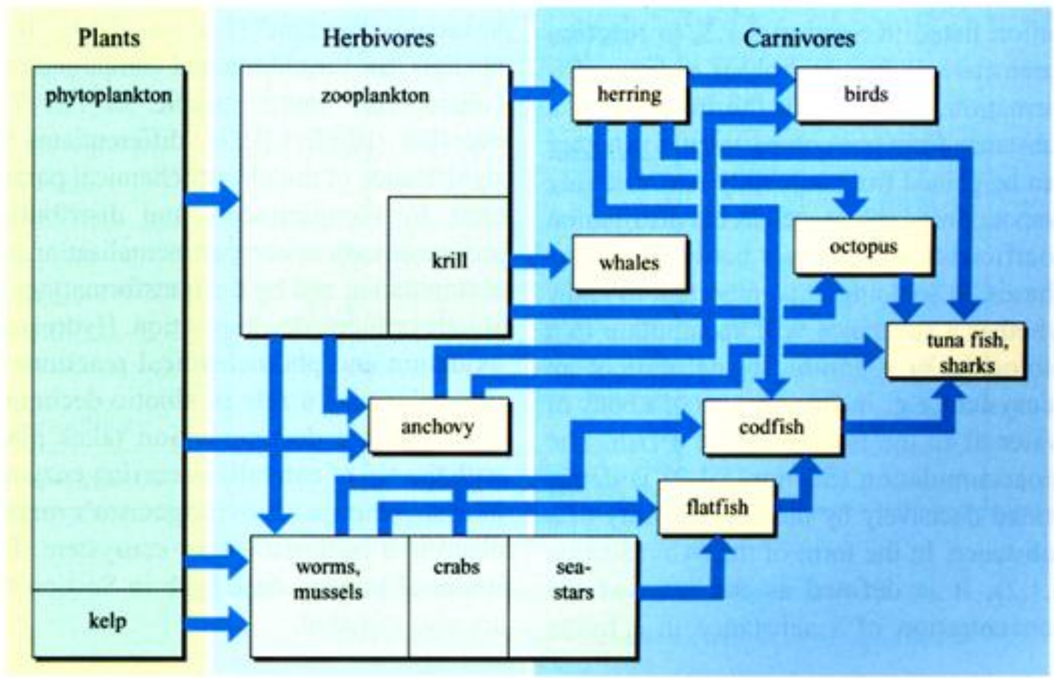


Figure 5.1.5 Food chain network

Bioaccumulation

Bioaccumulation

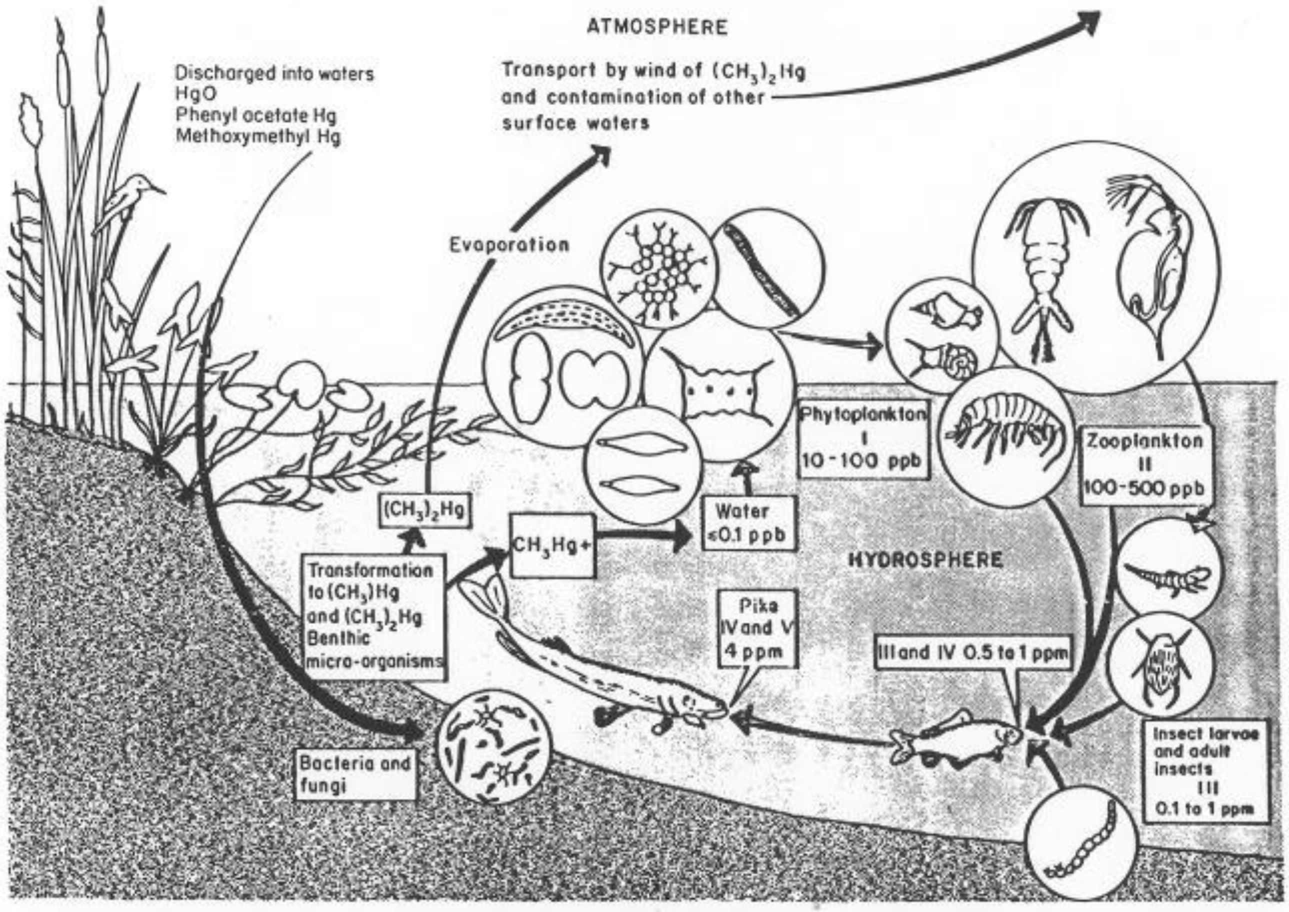


Fig. 3.24 Contamination of the food chain of the pike in Sweden (this diagram has been based on one by Duvigneaud (1974) and on analytical data on mercury contamination from various Swedish researchers). (*In* Ramade, 1982. *Reproduced by permission of McGraw-Hill*)

Bioaccumulation, biomagnification

Elimination process

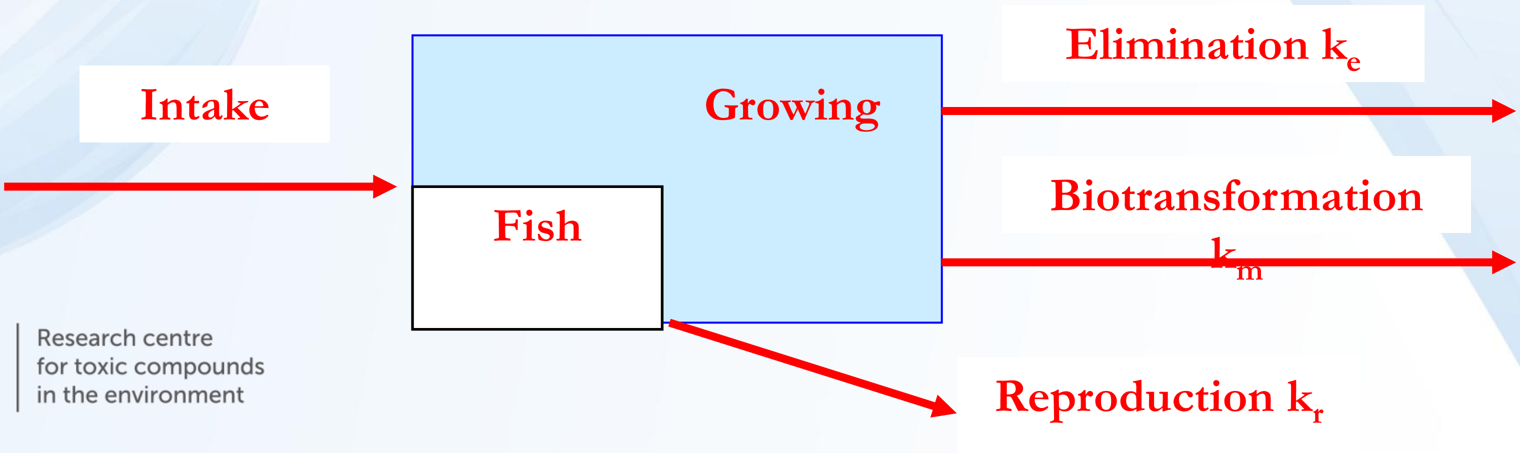
Analogically of the process of intake also the process of elimination can be directed mainly by passive diffusion and active transport.

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.

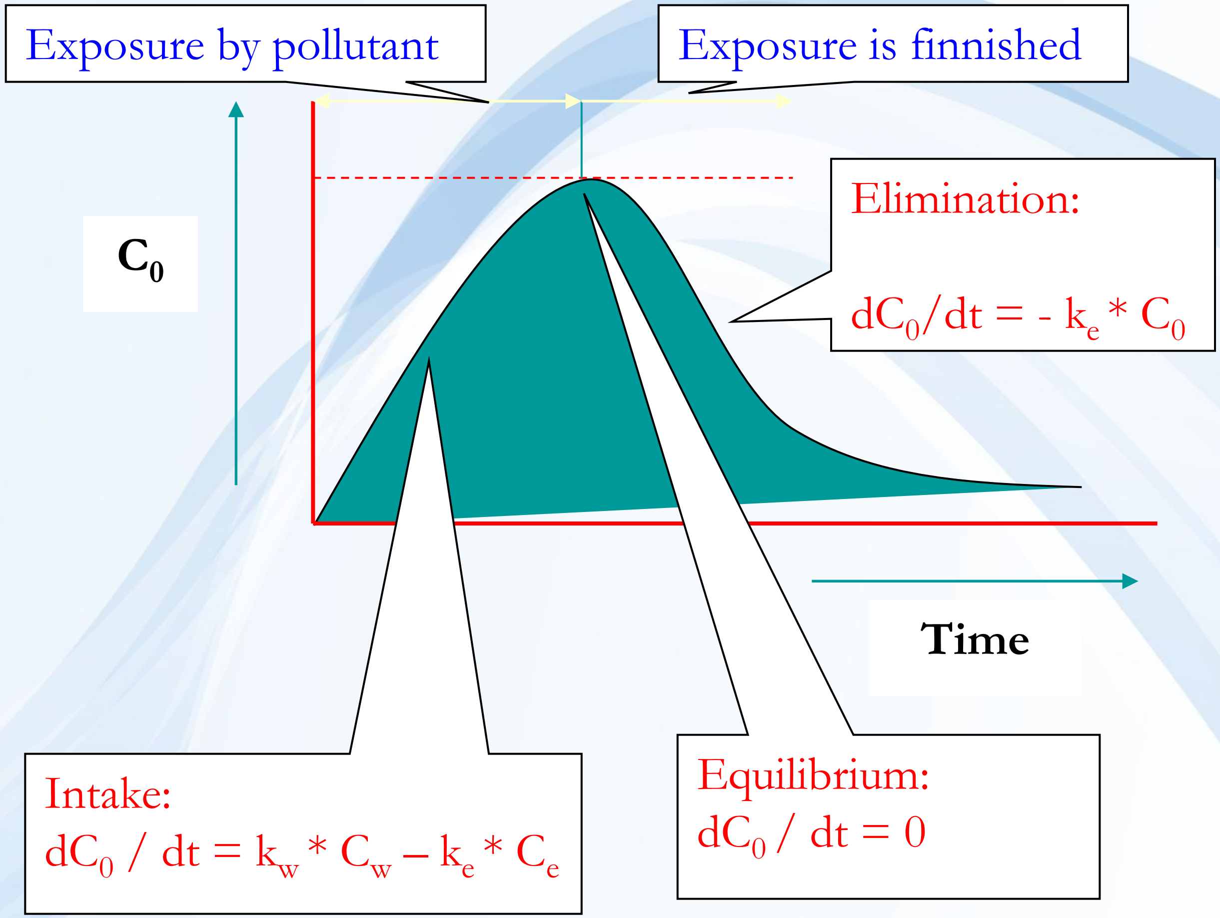
Other possible elimination process is breathing or transfer of chemicals to the eggs.

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



Bioaccumulation, biomagnification

Intake and elimination of compounds by aquatic organism:



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Bioaccumulation

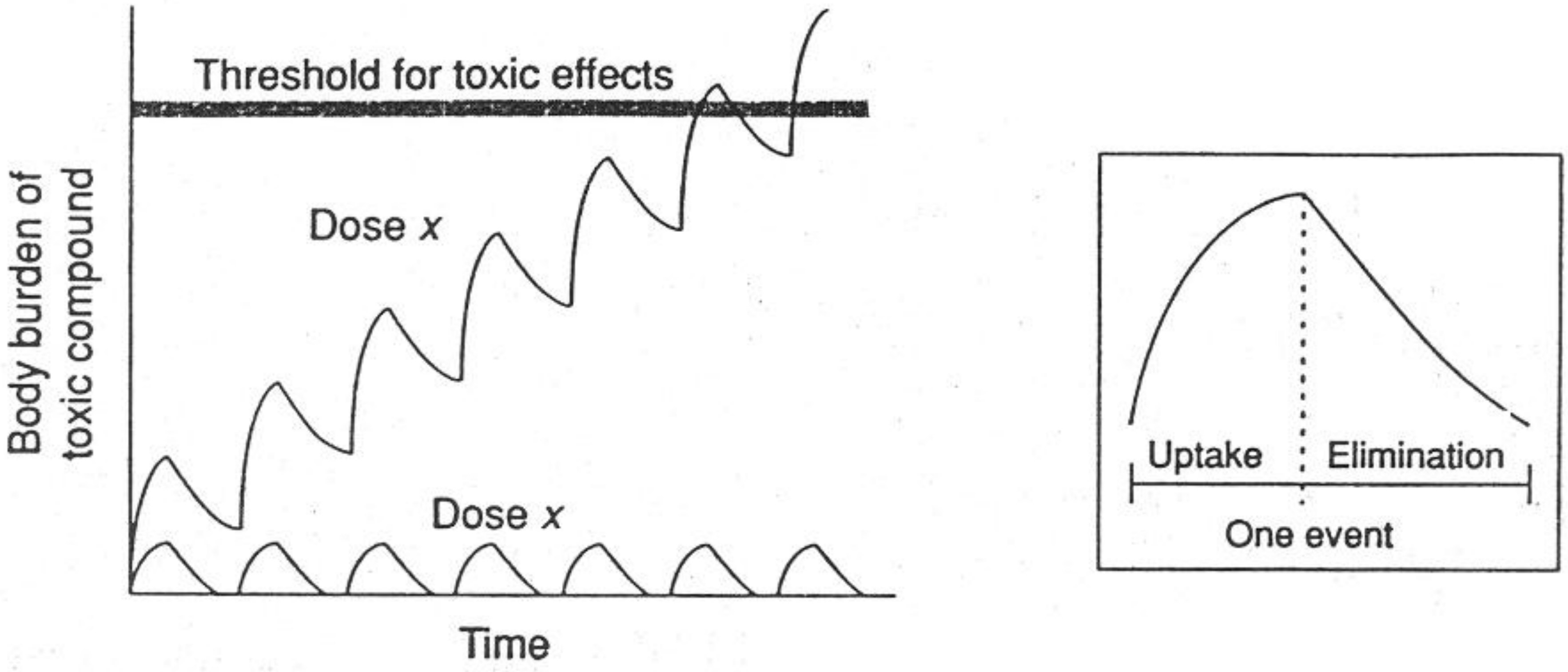

FIGURE 5-5

Effect of dose fractionalization on accumulation of a toxic compound.

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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}

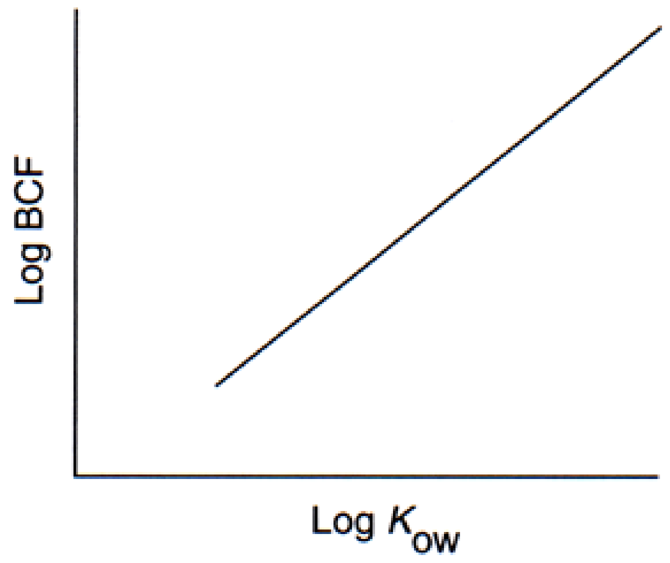
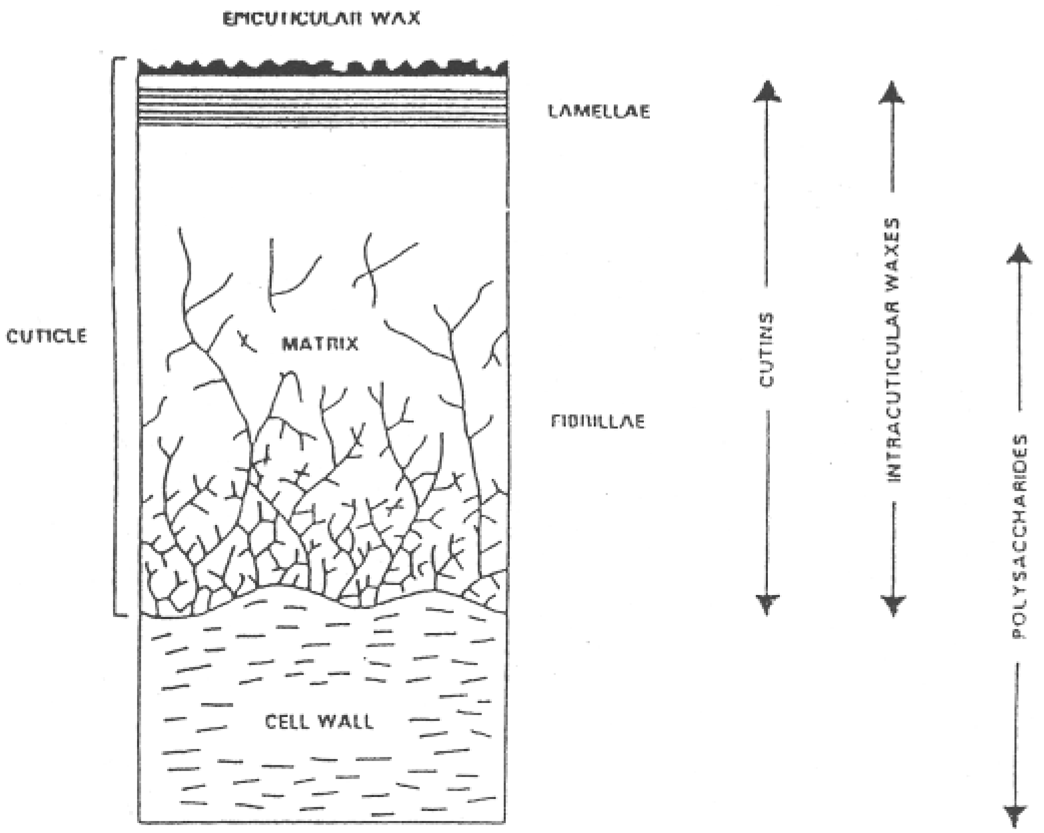


FIGURE 4.1 *Relationship of BCF to log* K_{ow}.

Bioaccumulation in terrestric vegetation



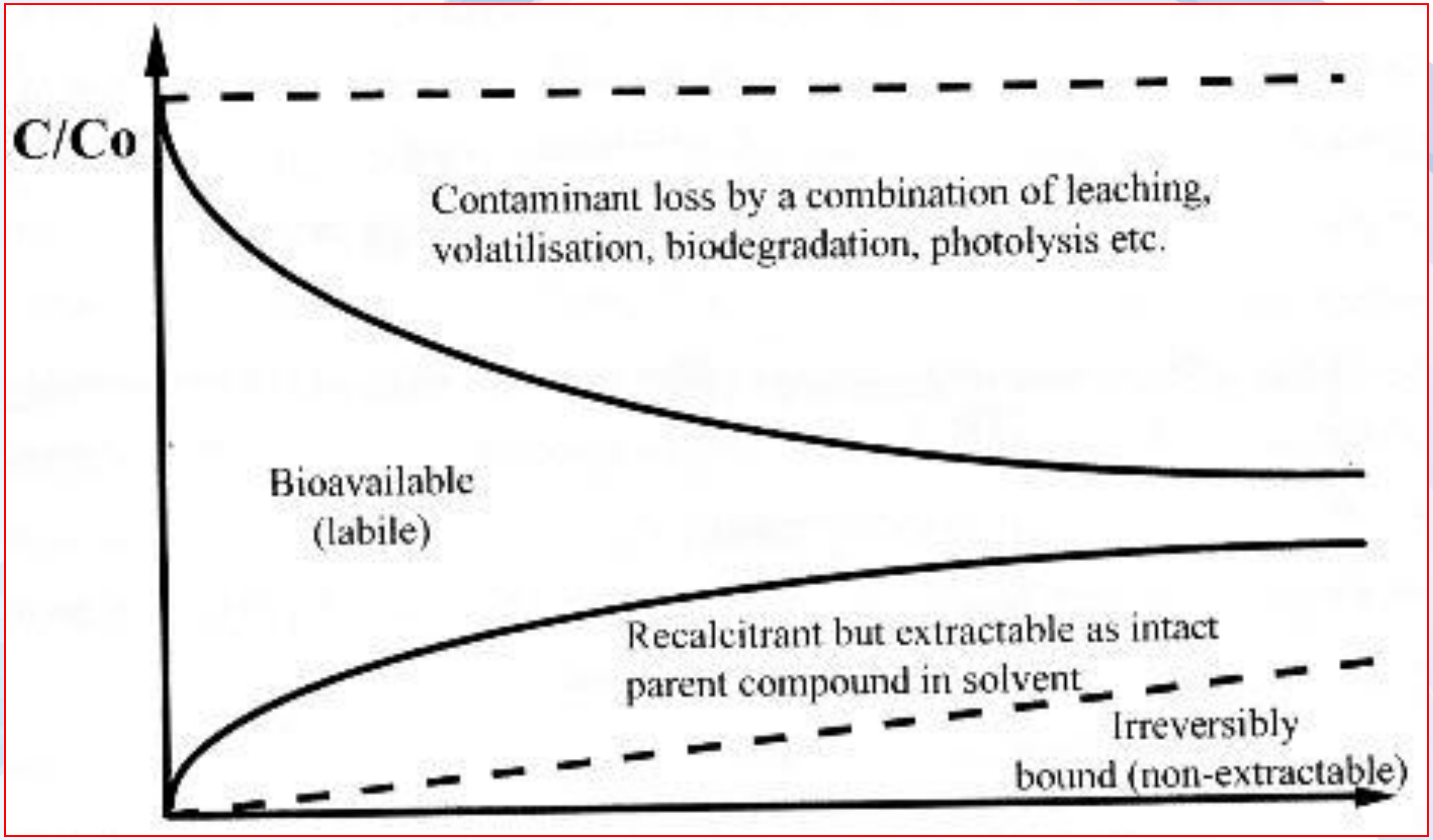
Summary of the main internal ultrastructural and chemical features of plant cuticles (from Holloway, 1993)

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

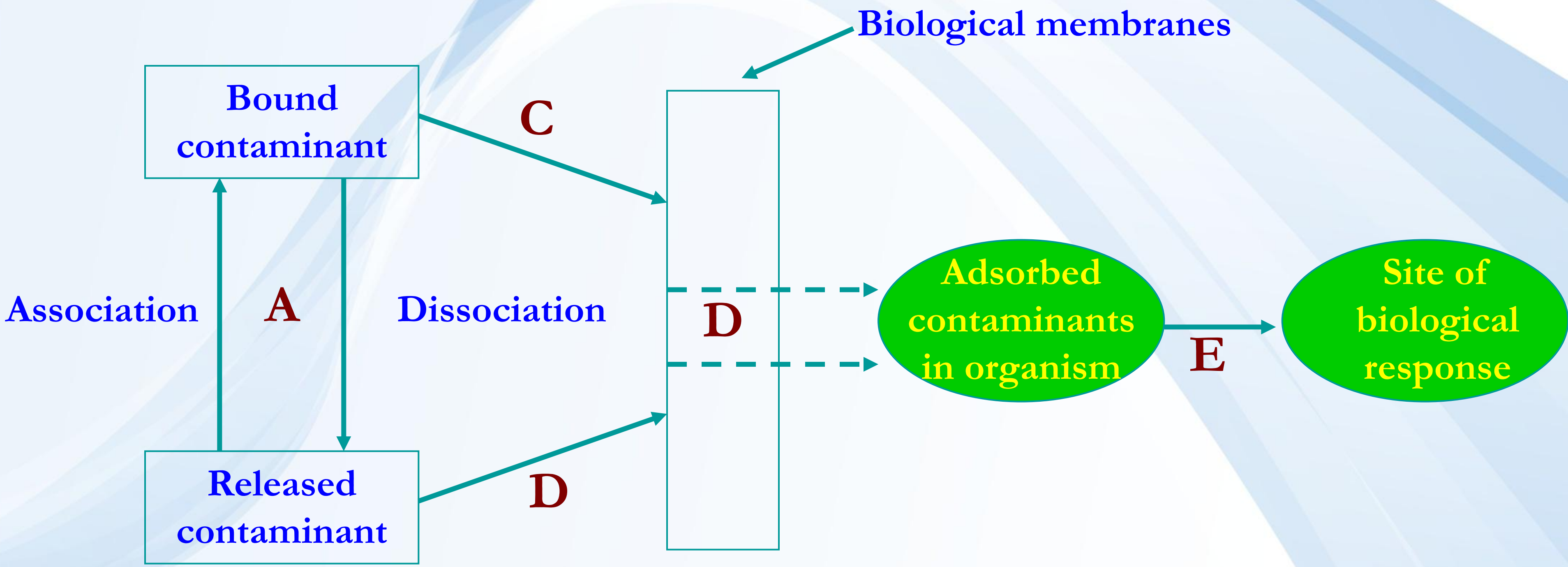
Bioavailability processes can be defined as the individual physical, chemical and biological interactions that determine the exposure of organisms to chemicals associated with soils and sediments.



K. Semple

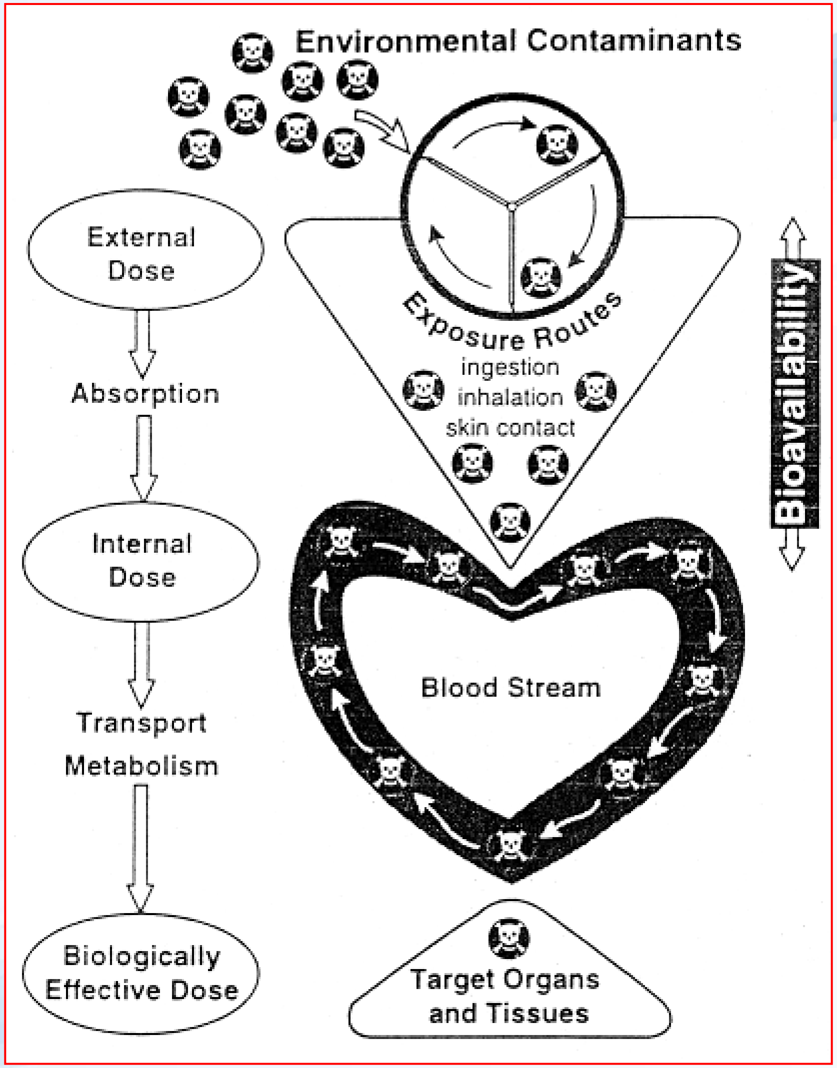
Bioavailability

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)



Ehlers and Luthy, 2003

Chemicals in the living organisms



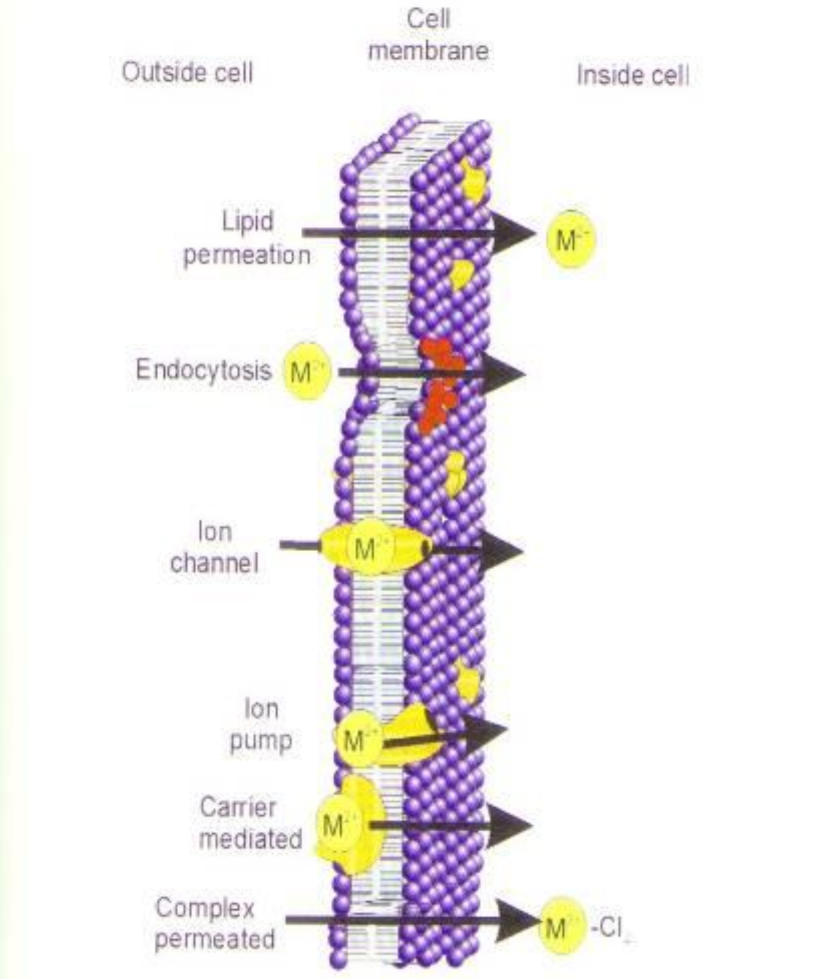
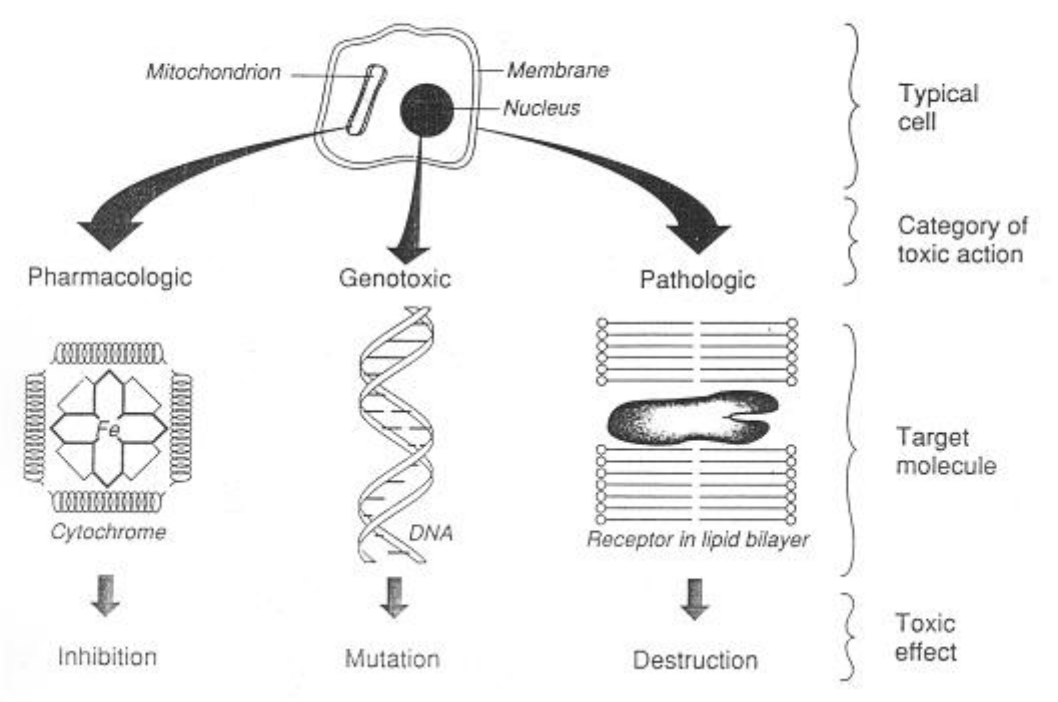


FIGURE 17.4 Mechanisms of metal (M) flux across the microbial cell membrane. (Adapted from Simkiss and Taylor, 1989.)

Toxic effects of chemical compounds



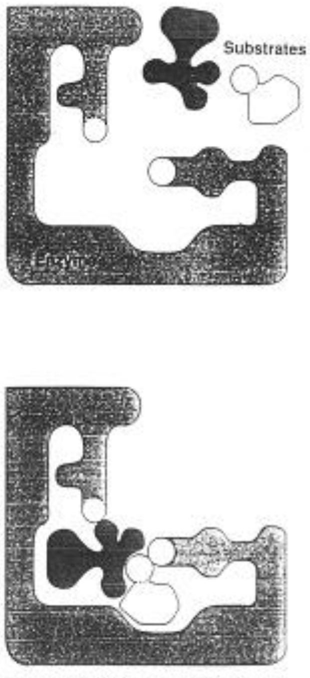


FIGURE 5-8
Lock-and-key model for toxic action.[29]

Environmental transport and transformation processes

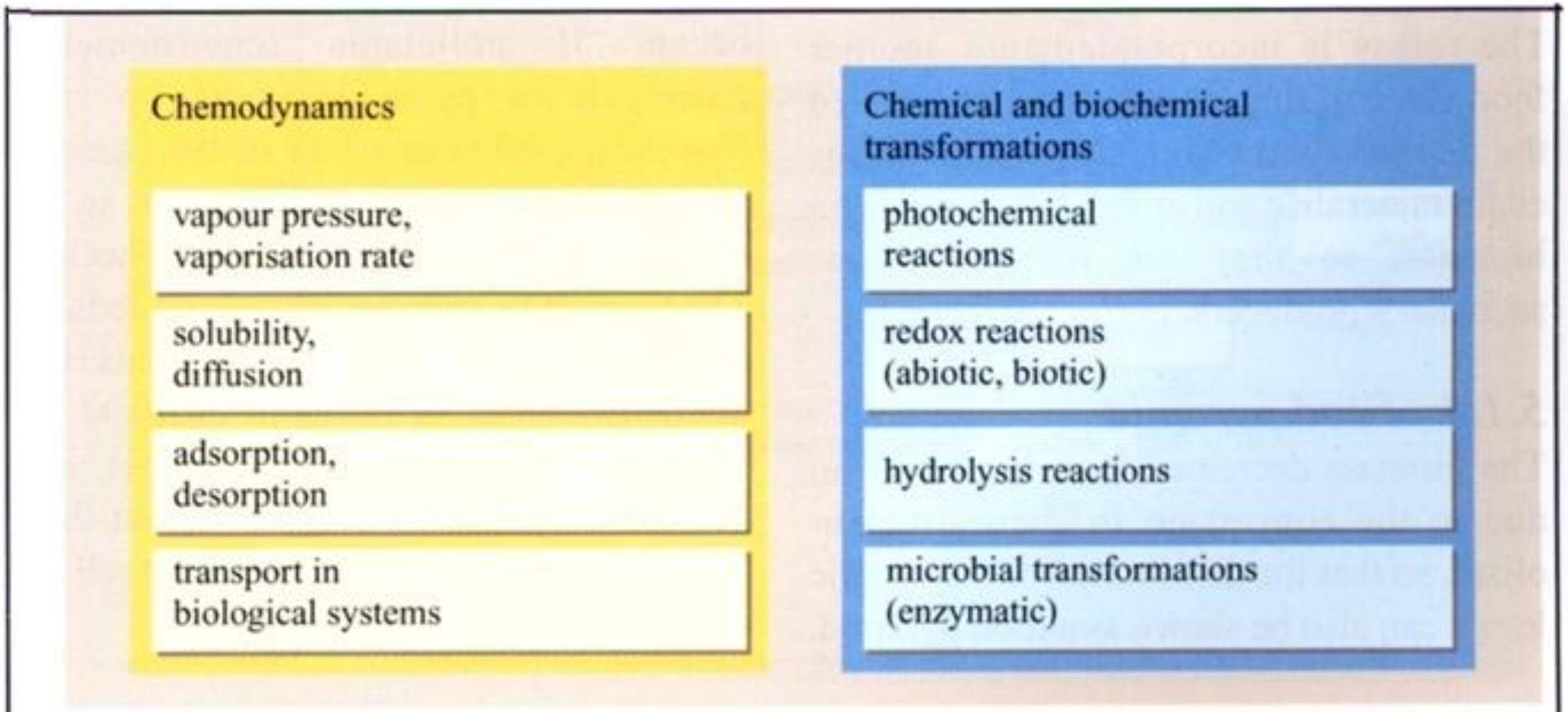


Figure 5.1.2 Basic principles of pollutant distribution and transformation

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.

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Chemical transformation processes

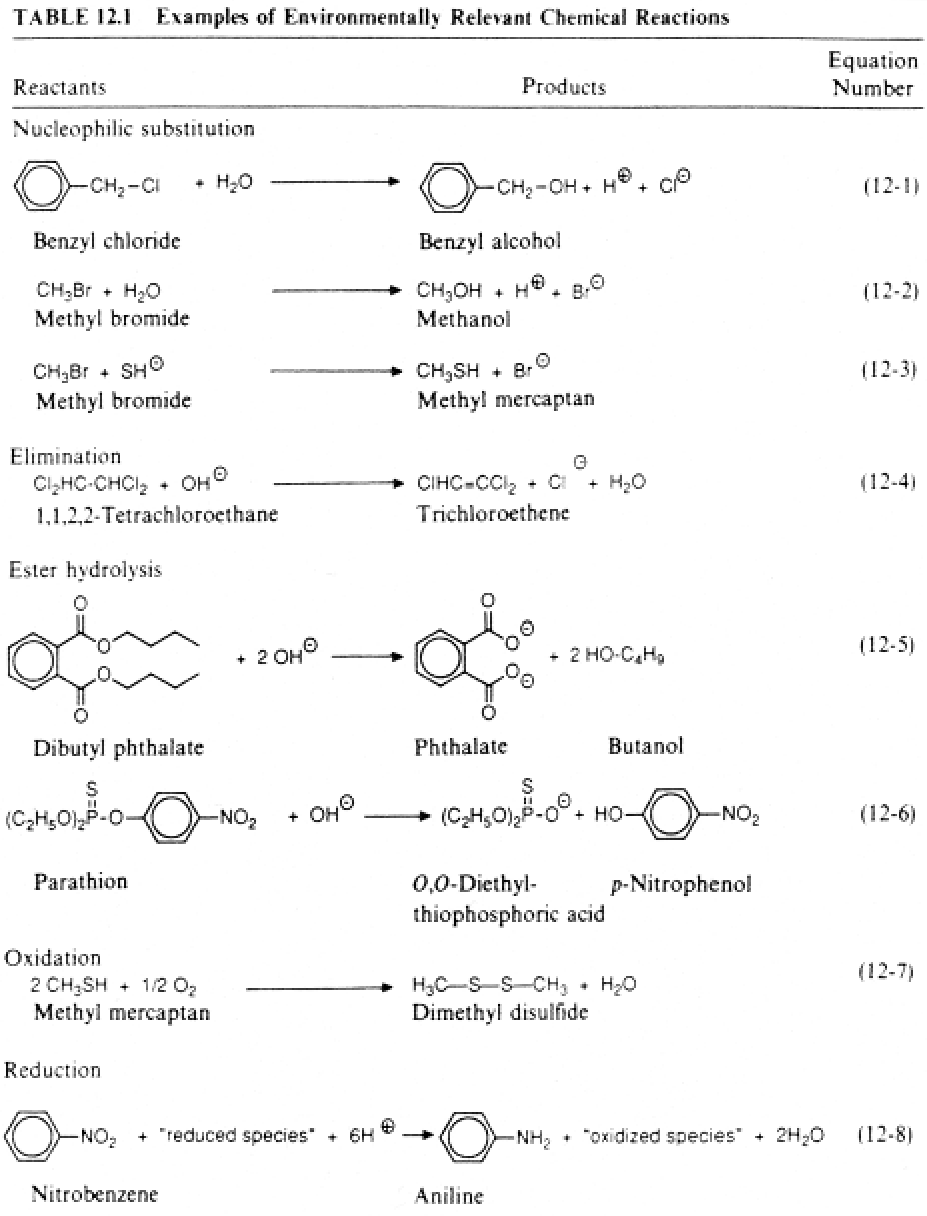


TABLE 12.1 Examples of Environmentally Relevant Chemical Reactions

Reactants	Products	Equation Number
Nucleophilic substitution		
$C_6H_5-CH_2-Cl + H_2O$ →	$C_6H_5-CH_2-OH + H^{\oplus} + Cl^{\ominus}$	(12-1)
Benzyl chloride	Benzyl alcohol	
$CH_3Br + H_2O$ →	$CH_3OH + H^{\oplus} + Br^{\ominus}$	(12-2)
Methyl bromide	Methanol	
$CH_3Br + SH^{\ominus}$ →	$CH_3SH + Br^{\ominus}$	(12-3)
Methyl bromide	Methyl mercaptan	
Elimination		
$Cl_2HC\text{-}CHCl_2 + OH^{\ominus}$ →	$ClHC{=}CCl_2 + Cl^{\ominus} + H_2O$	(12-4)
1,1,2,2-Tetrachloroethane	Trichloroethene	
Ester hydrolysis		
Dibutyl phthalate $+ 2\,OH^{\ominus}$ →	Phthalate $+ 2\,HO\text{-}C_4H_9$	(12-5)
Dibutyl phthalate	Phthalate; Butanol	
$(C_2H_5O)_2P(S)\text{-}O\text{-}C_6H_4\text{-}NO_2 + OH^{\ominus}$ →	$(C_2H_5O)_2P(S)\text{-}O^{\ominus} + HO\text{-}C_6H_4\text{-}NO_2$	(12-6)
Parathion	*O,O*-Diethyl-thiophosphoric acid; *p*-Nitrophenol	
Oxidation		
$2\,CH_3SH + 1/2\,O_2$ →	$H_3C-S-S-CH_3 + H_2O$	(12-7)
Methyl mercaptan	Dimethyl disulfide	
Reduction		
$C_6H_5-NO_2$ + "reduced species" $+ 6H^{\oplus}$ →	$C_6H_5-NH_2$ + "oxidized species" $+ 2H_2O$	(12-8)
Nitrobenzene	Aniline	

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

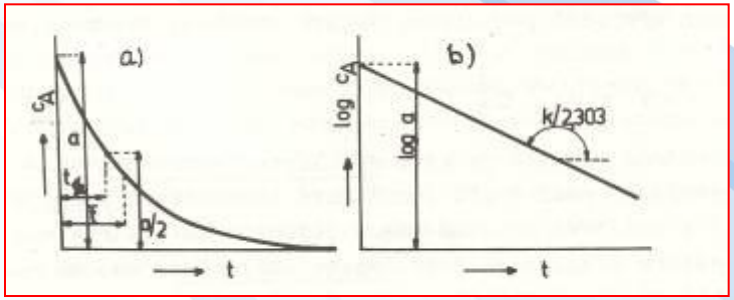
Reaction of the first order:

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 $A = \ln 2 / k'[B]$

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Hydrolysis

Nucleophilic substitution of halogens on the saturated C atom

S_N2 mechanism

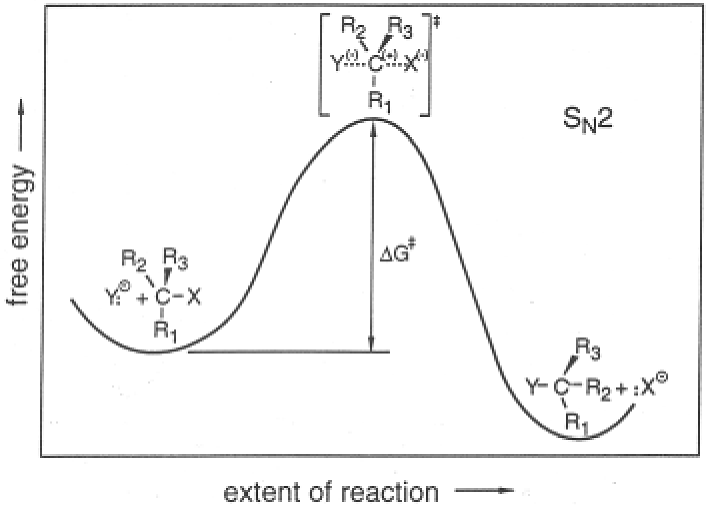


Figure 12.3 Two-dimensional portrayal of relative free energies exhibited by the educts, activated complex, and products of an S_N2 reaction.

S_N1 mechanism

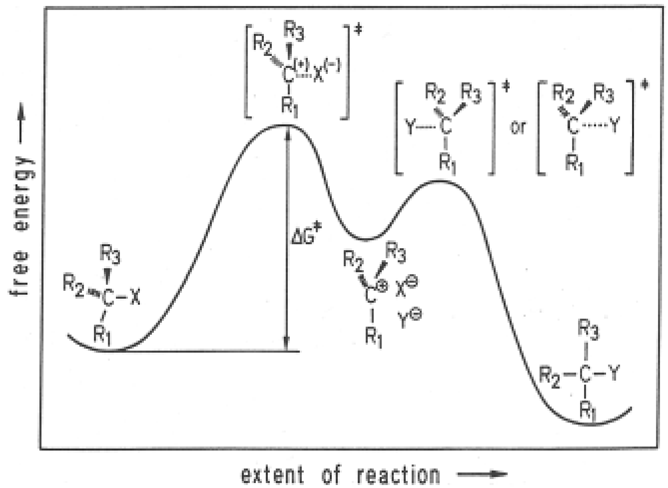


Figure 12.4 Two-dimensional portrayal of the relative free energies exhibited by educt, activated complexes, an intermediate, and product of an S_N1 reaction.

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:

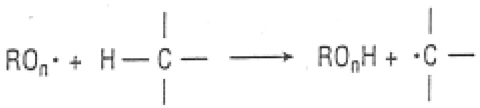
- alkoxy radicals (RO•)
- peroxy radicals (ROO•)
- hydroxyl radicals (OH•)
- singlet oxygen ($^1O_2$)
- ozone (O_3)

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.

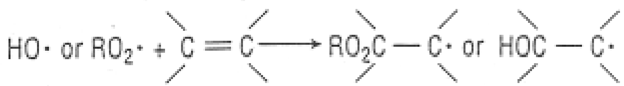
Oxidation

(1) H-atom transfer



R = alkyl or H; n = 1 or 2

(2) Addition to double bonds



R = alkyl or H

(3) HO· addition to aromatics

(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

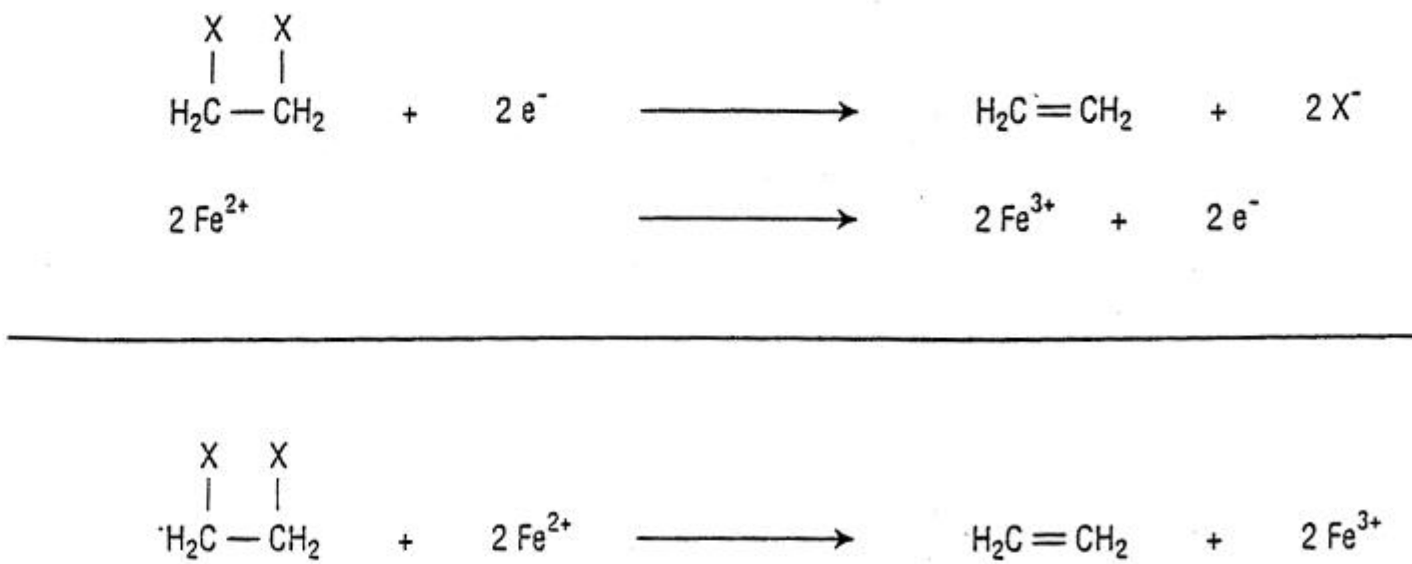
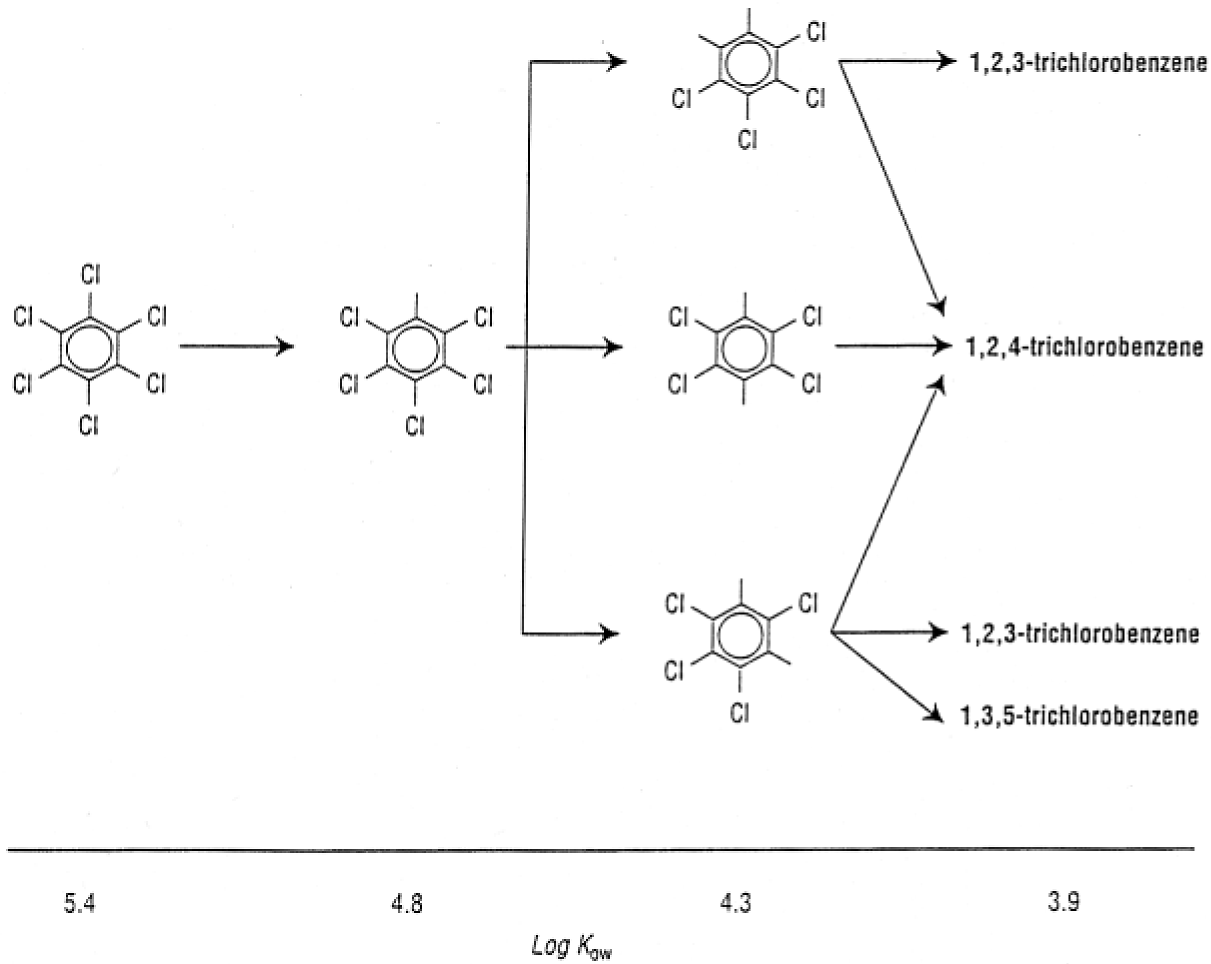


Figure 3.32. Example of a reductive transformation: electron transfer from Fe^{2+} to 1,2-dihalogen substituted ethane (X denotes a halogen atom).

Reduction



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

Photochemical transformation processes

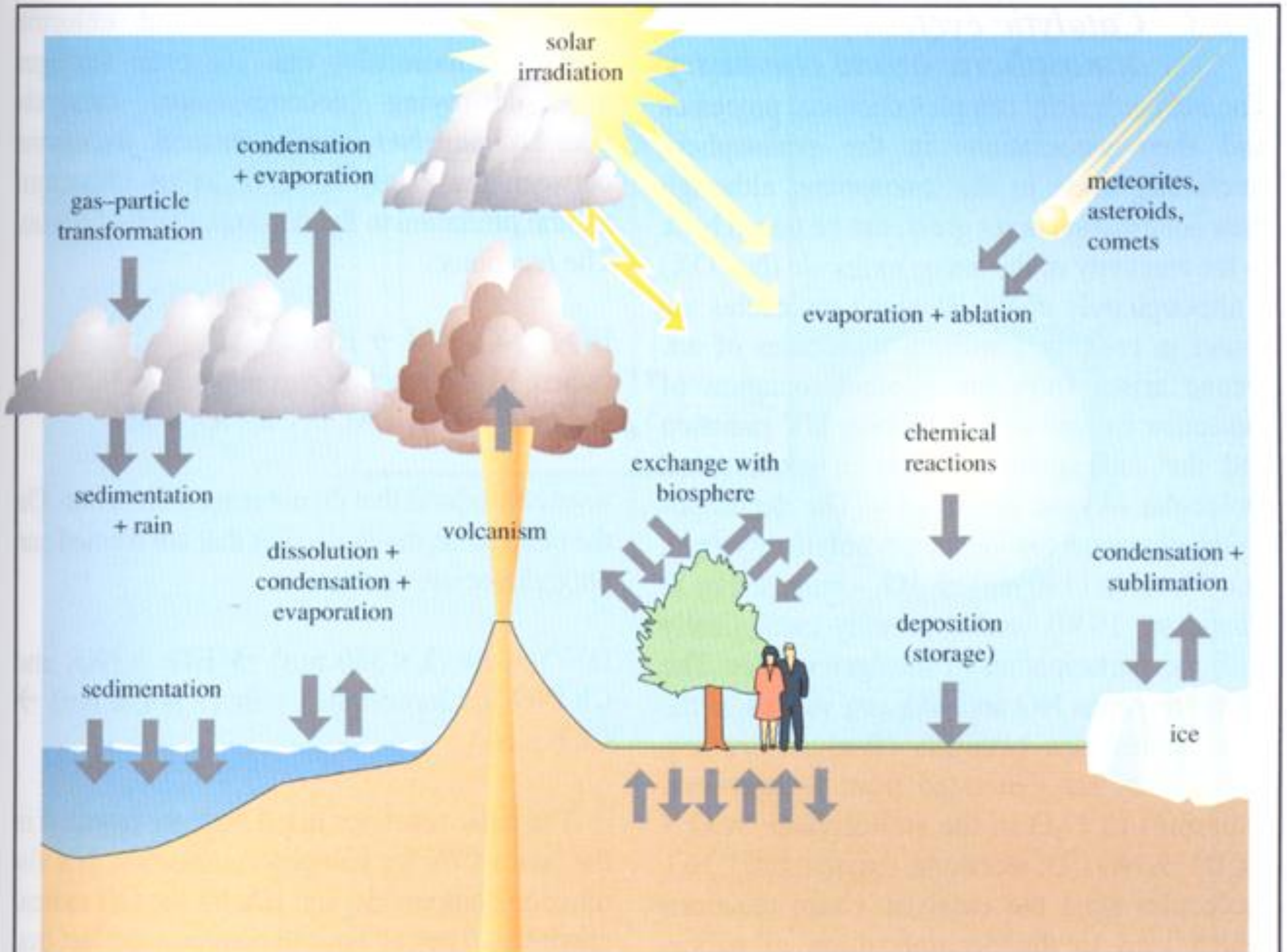
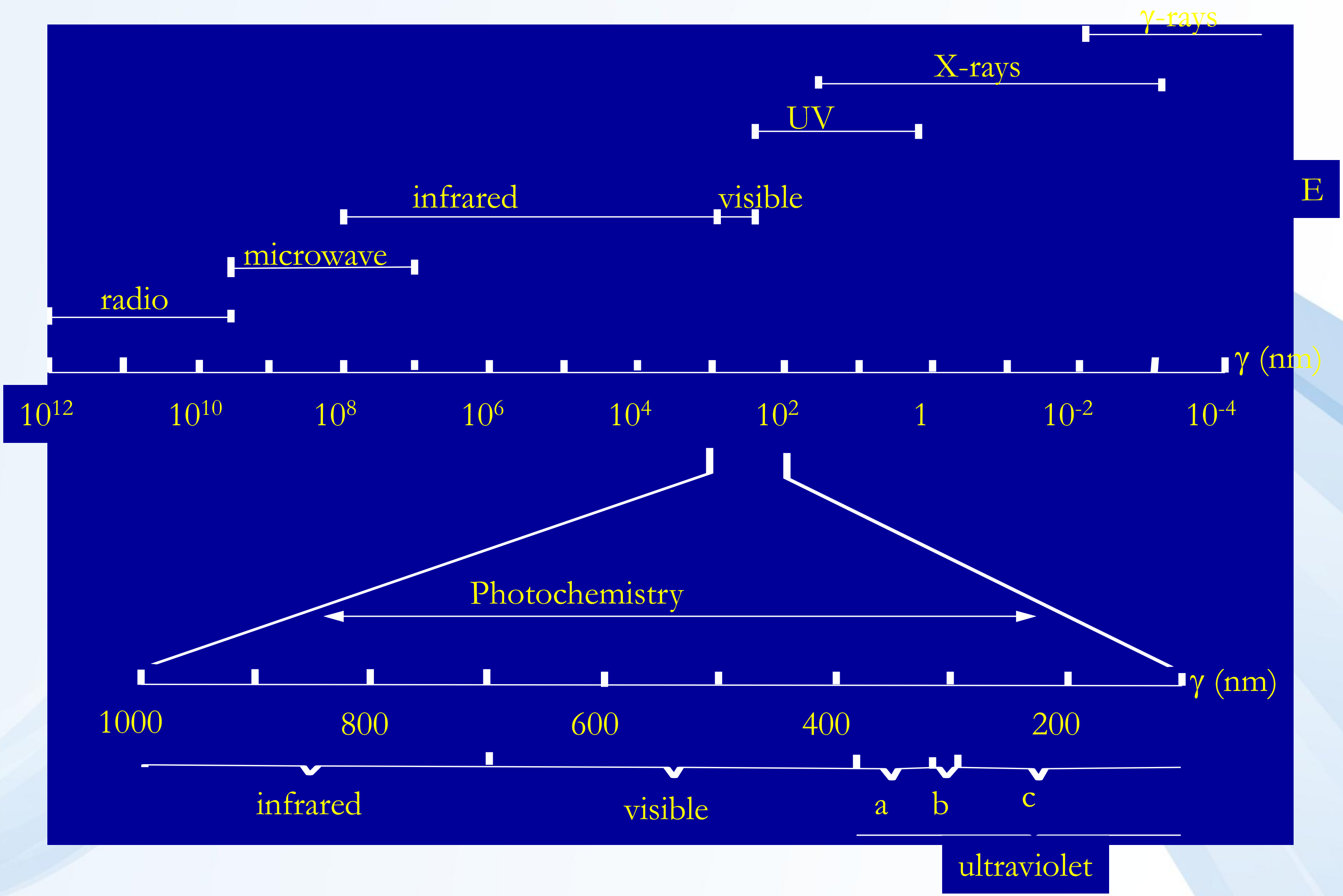


Figure 2.2.1 Chemistry and photochemistry

Photochemical transformation processes



Photochemical transformation processes

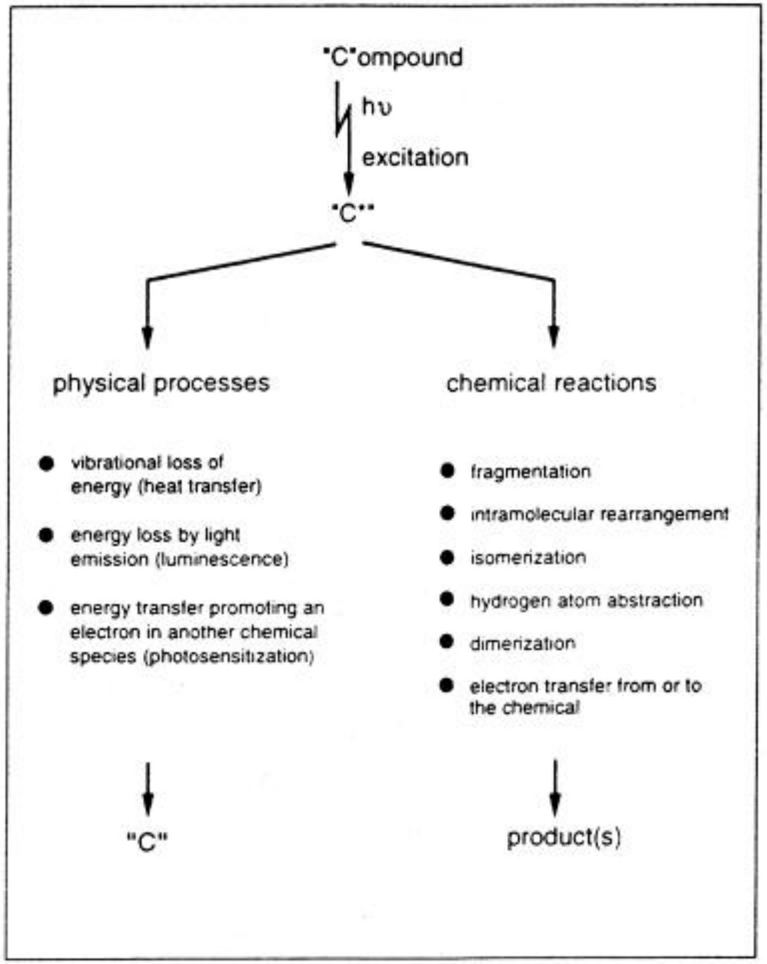


Figure 13.6 Physical processes and chemical reactions of a photochemically excited organic species.

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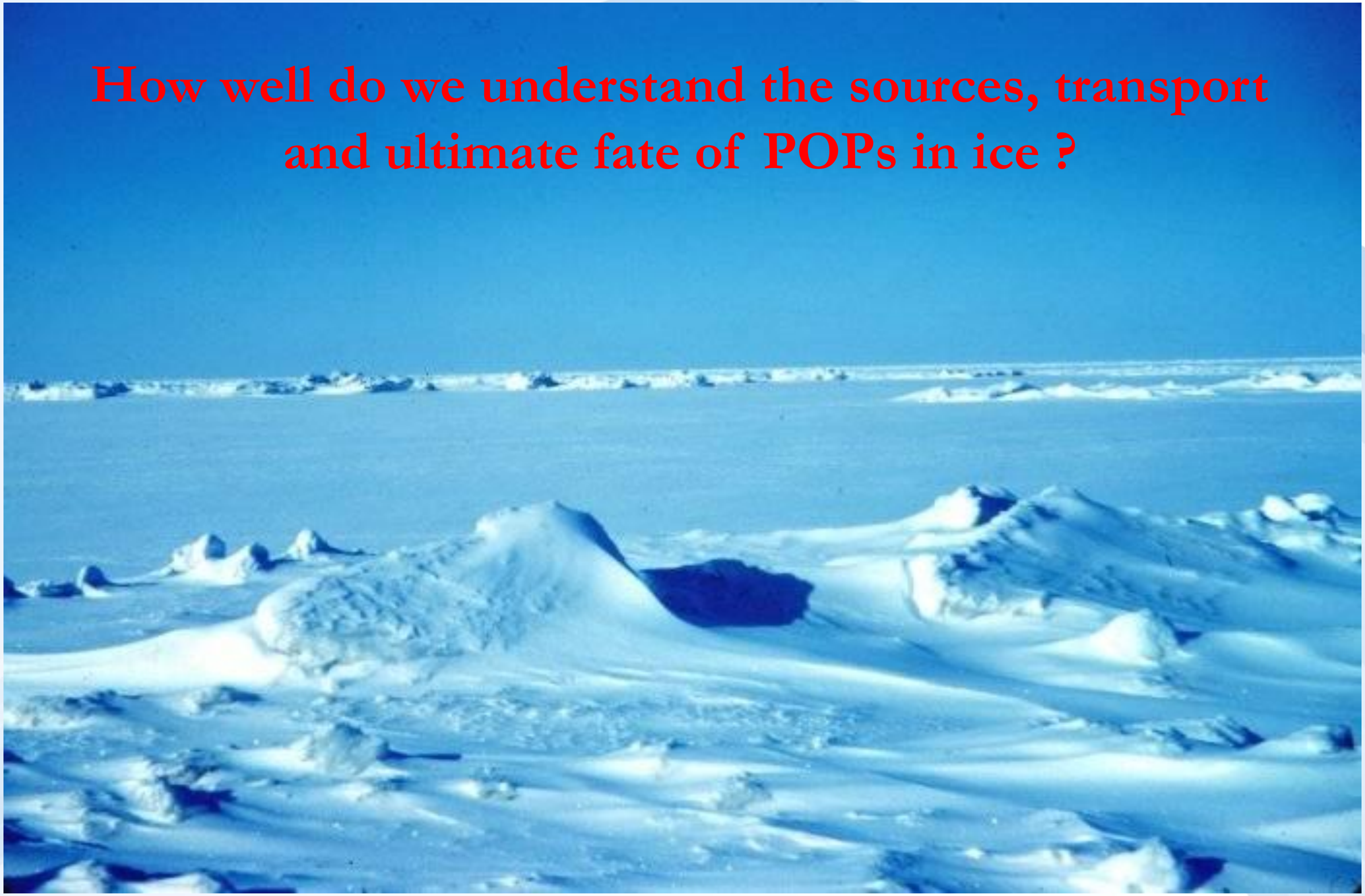
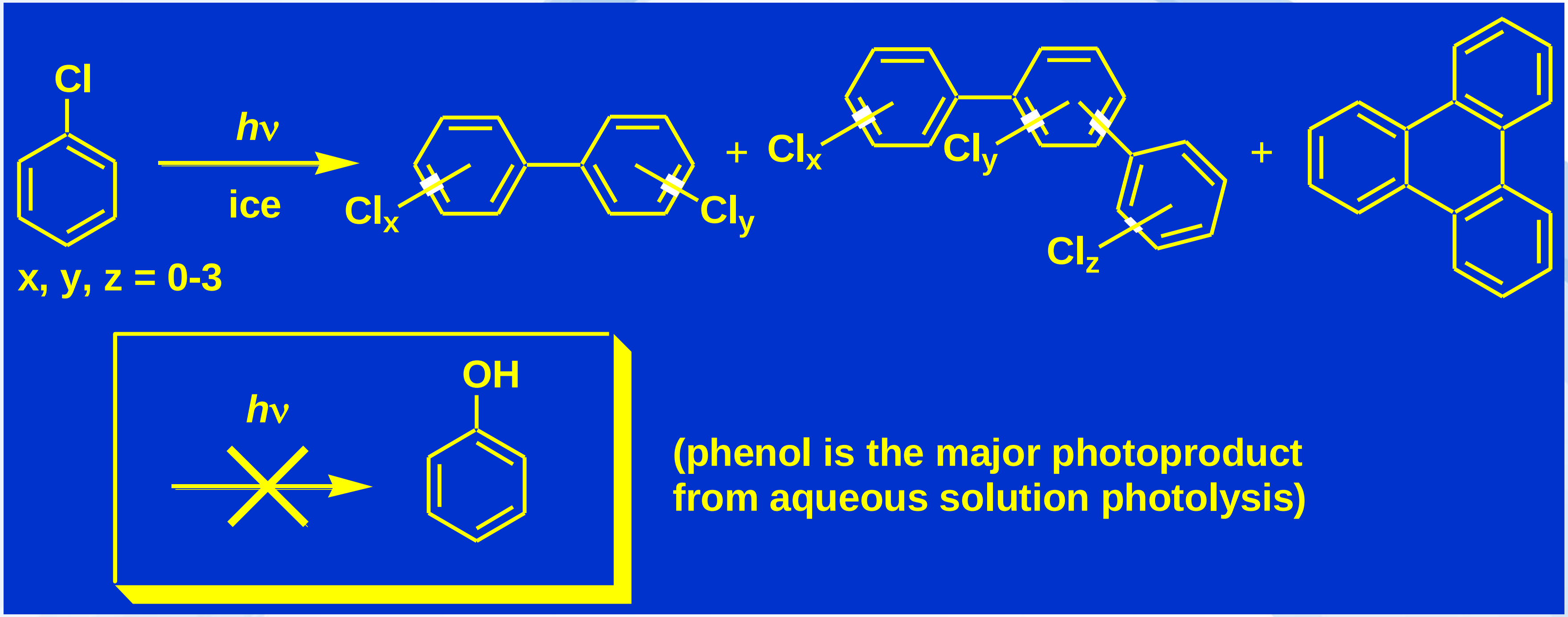
Photochemistry of organic pollutants in solid matrices



Chlorobenzene - unique transformation pathways in ice matrix



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

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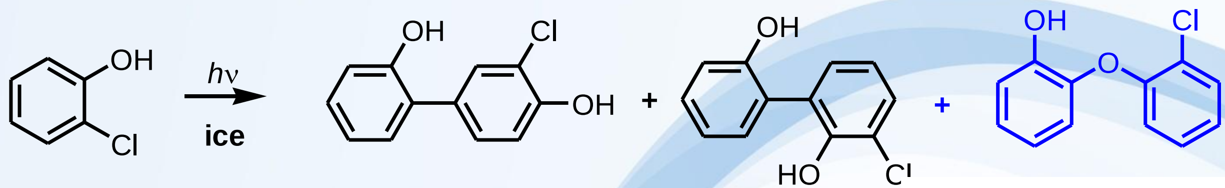
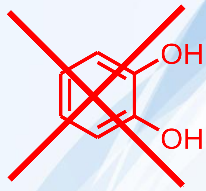
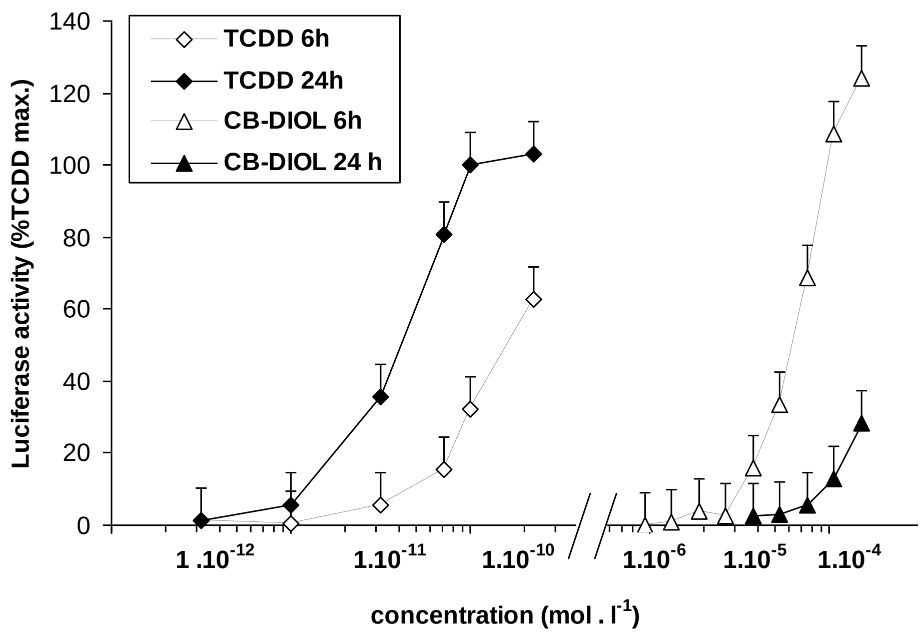
Toxicity increases in ice upon photolysis



no photosolvolysis:





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

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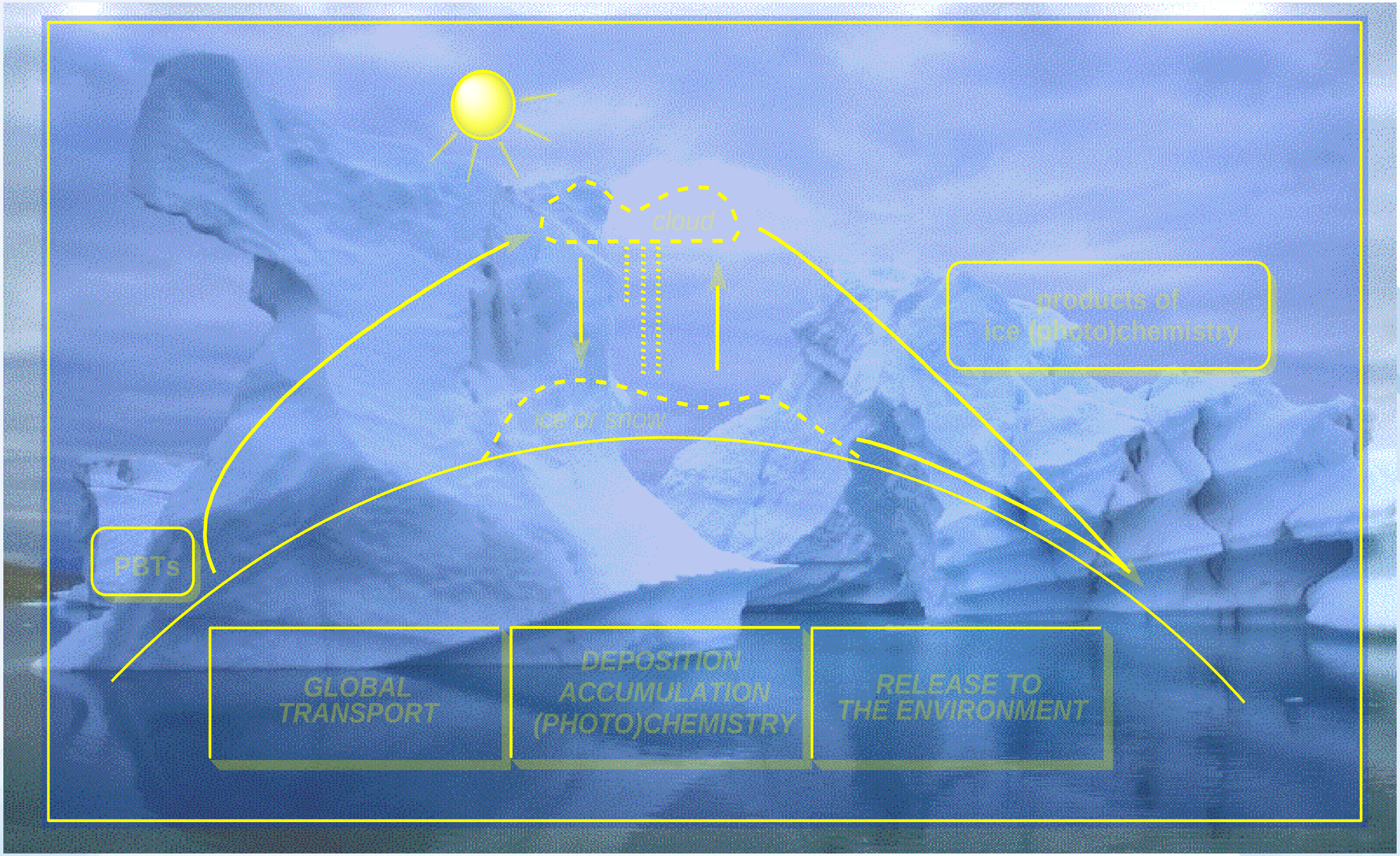
Environmental consequences



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

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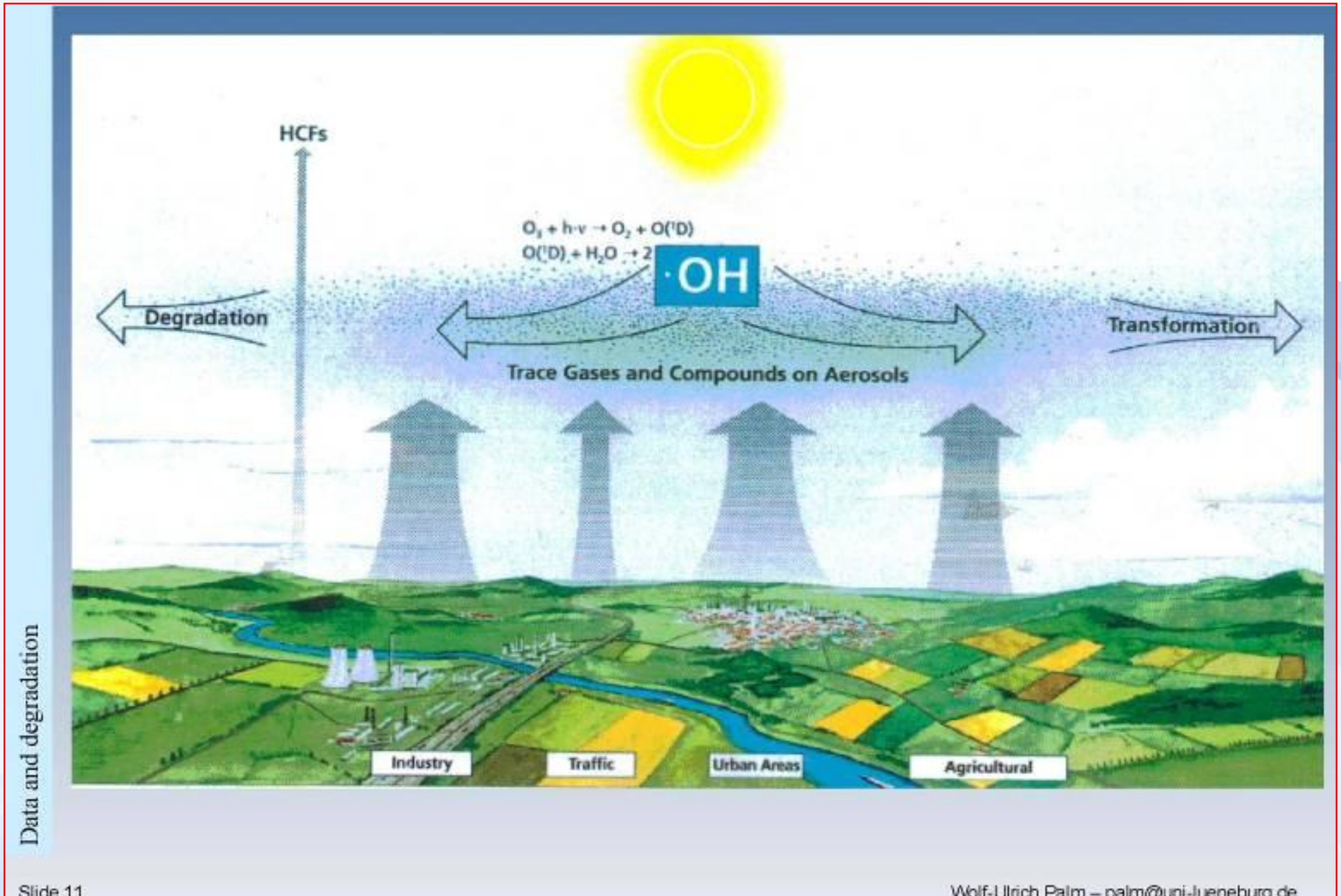
OH radicals in the atmosphere



W.-U. Palm

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Biodegradation

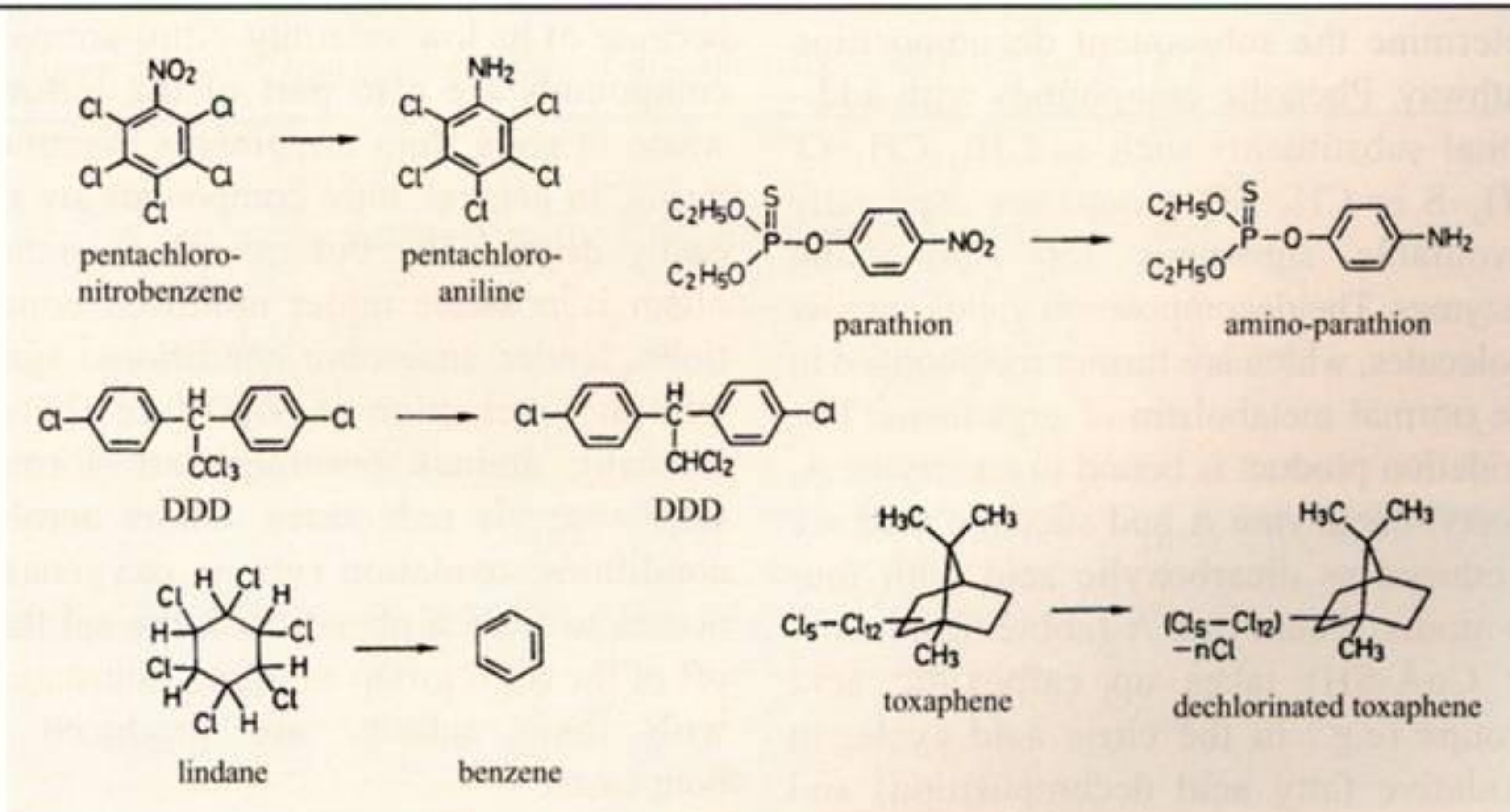


Figure 5.2.2 Reductive (anaerobic) reactions of xenobiotics

Biodegradation

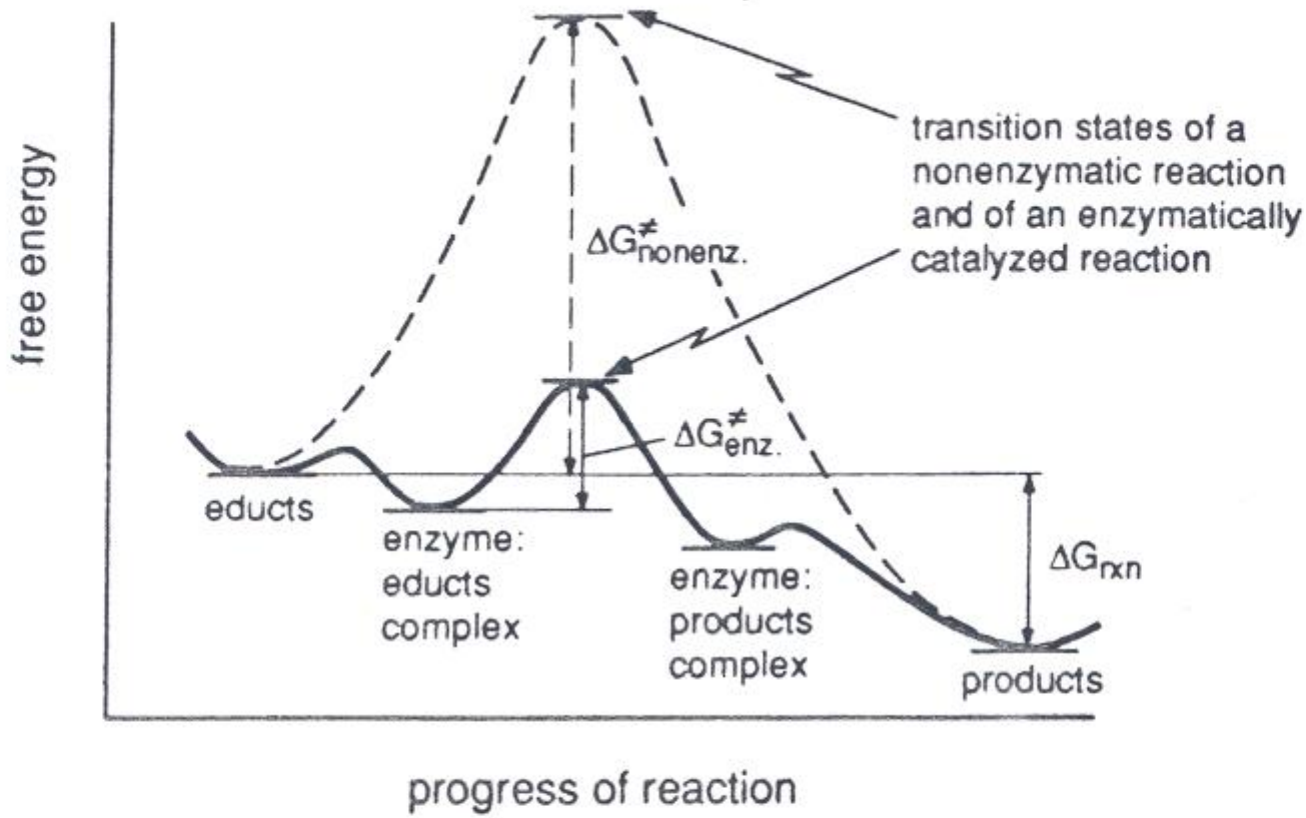


Figure 14.1 Schematic representation of the change in activation energy barriers for an enzymatically mediated reaction as compared to the analogous noncatalyzed chemical reaction.

Mechanisms of biotransformation of the xenobiotics in the living organisms

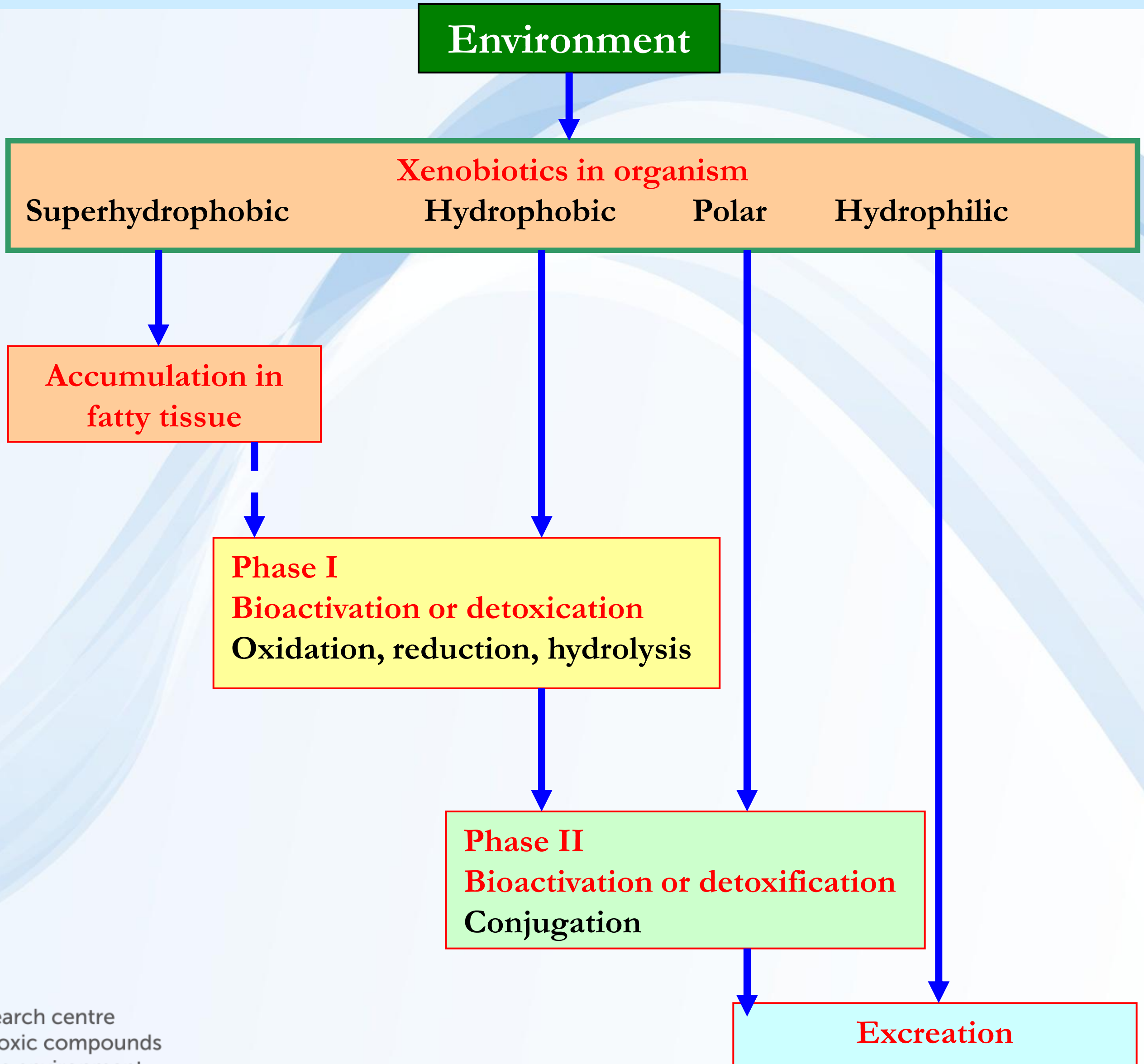
Types of biotransformation reactions

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



Biotransformations

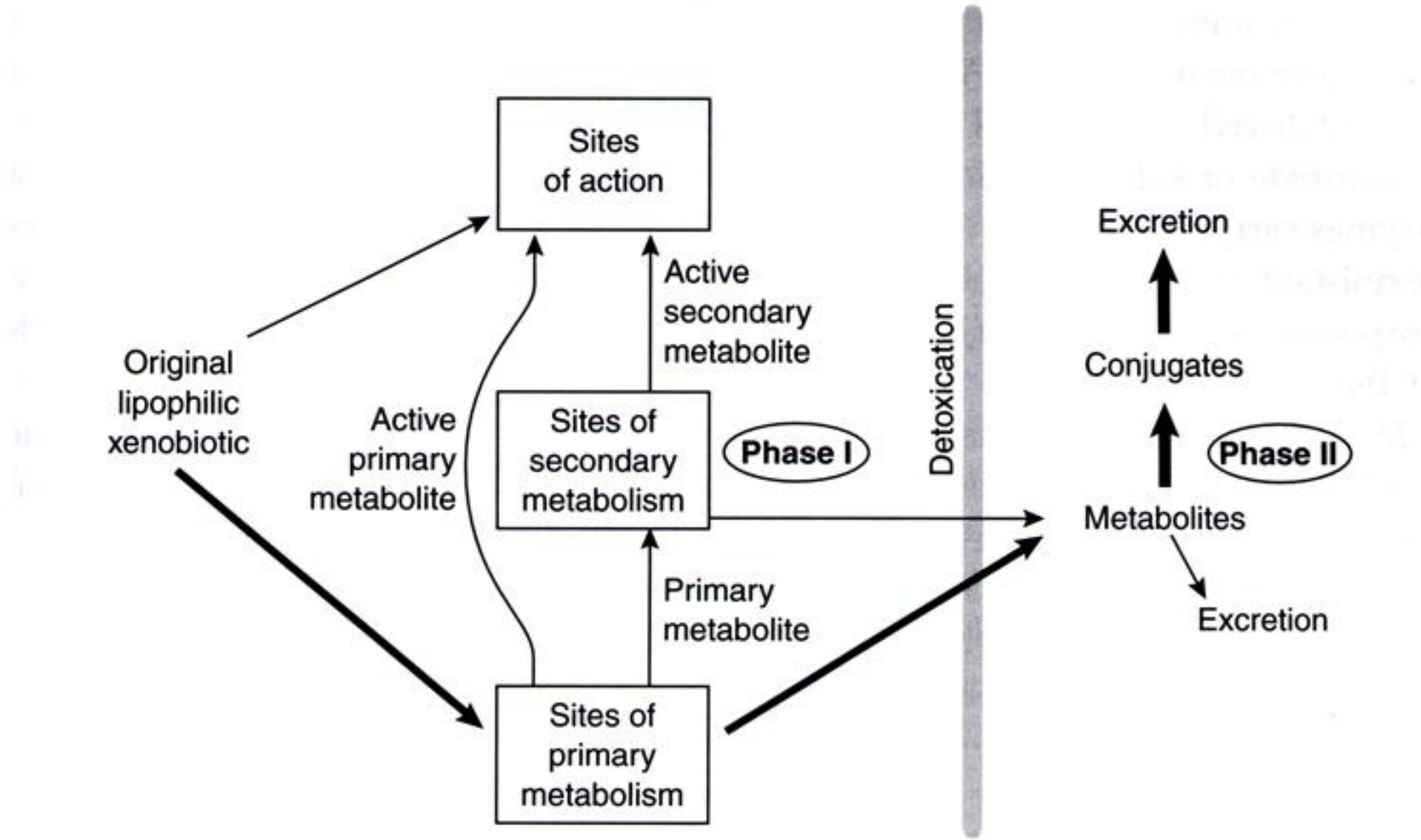


FIGURE 2.2 *Metabolism and toxicity.*

Biotransformations

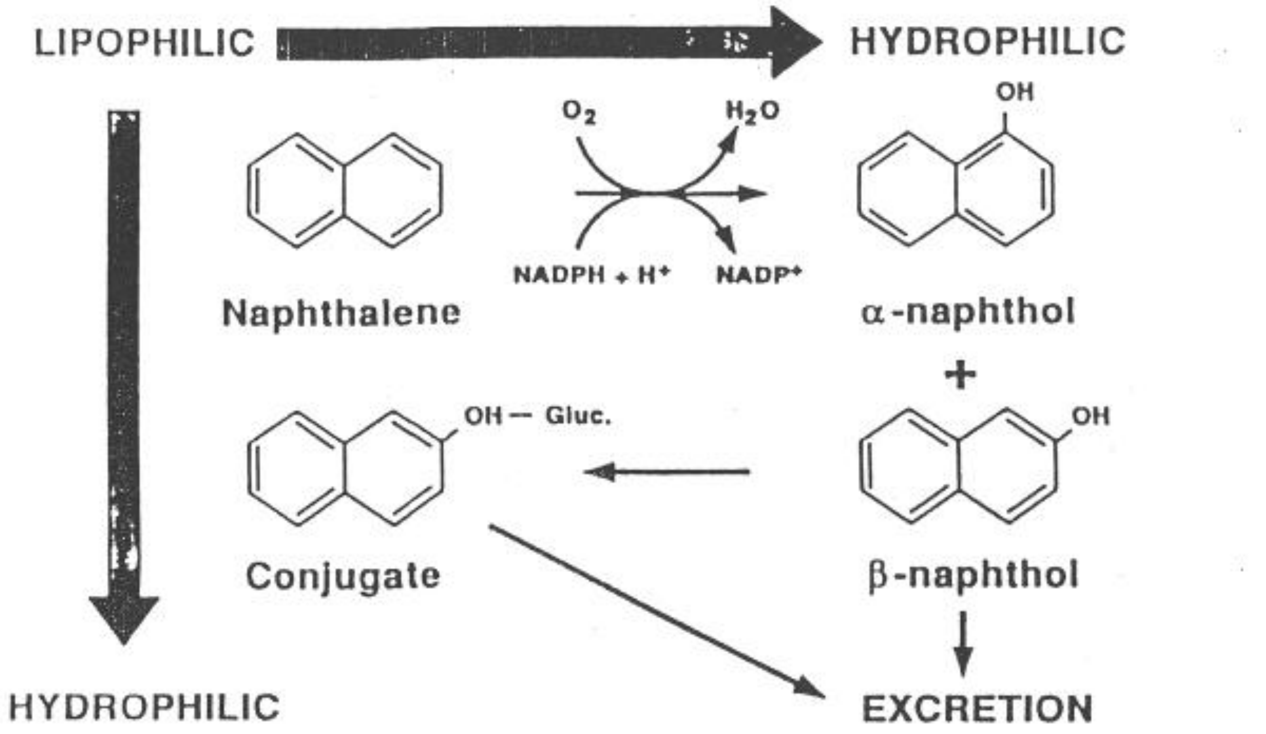
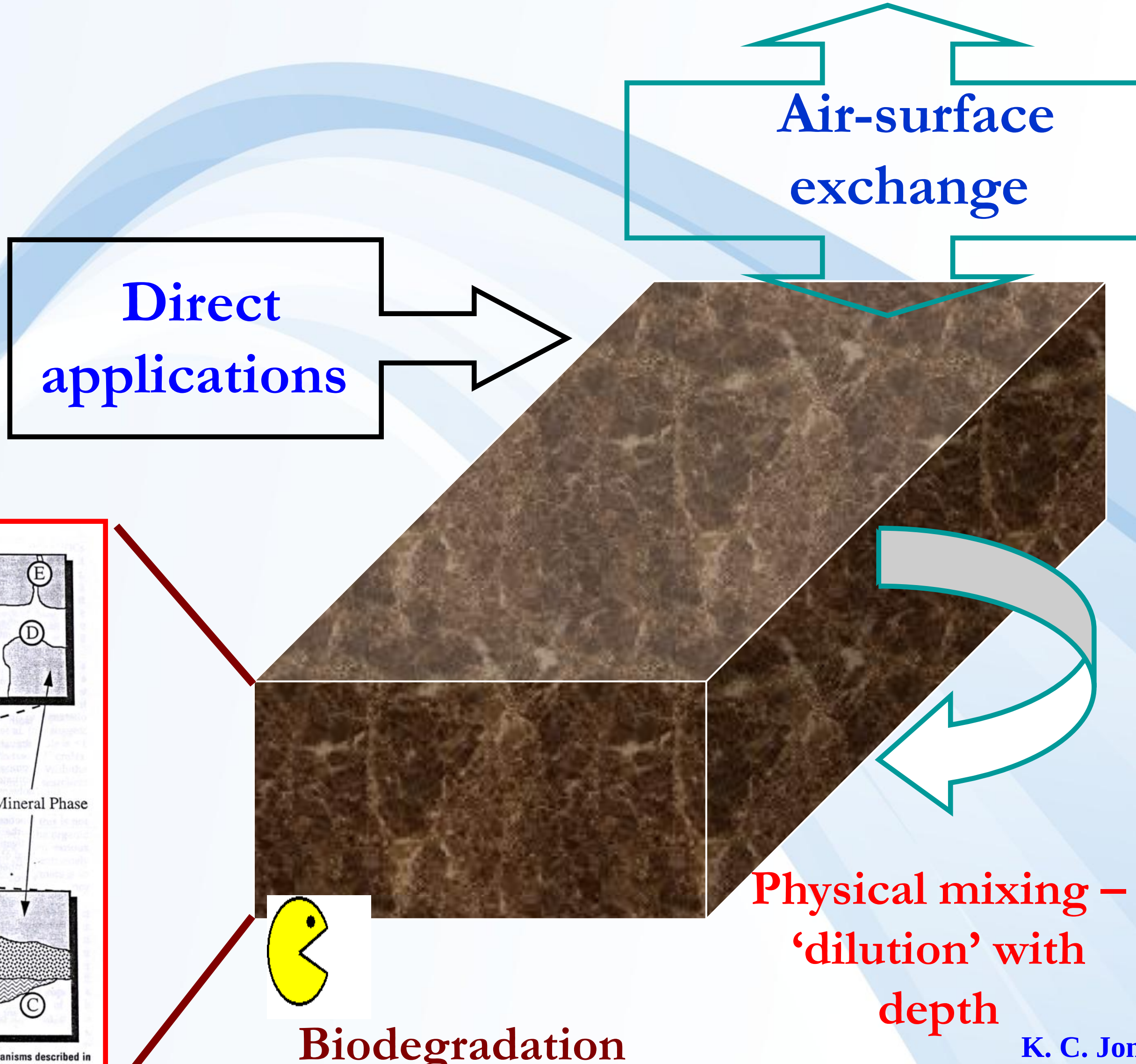


Figure 1. The cytochrome P-450 mixed function oxidase system facilitates excretion of lipophilic organic substrates in terrestrial and aquatic animals by producing metabolites that are more water soluble than the parent compound. Common metabolites of naphthalene are shown (after 2).

Soil can be a source or sink of POPs



'Occlusion'

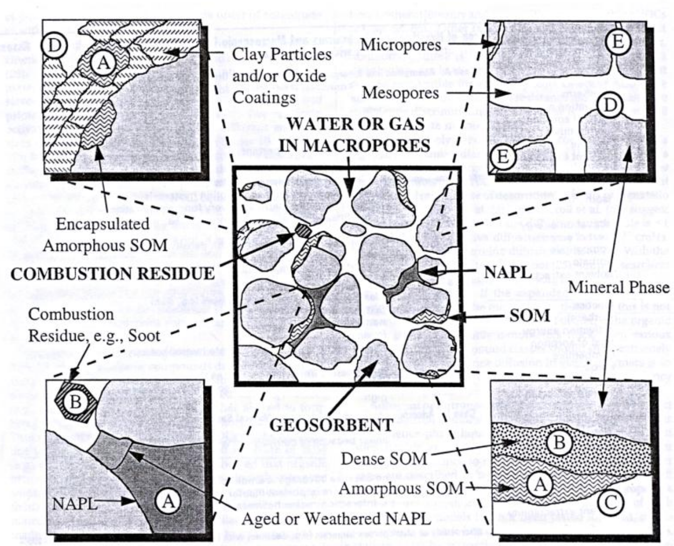


FIGURE 1. Conceptual model of geosorbent domains. The circled letters refer to representations of the sorption mechanisms described in Table 1. The geosorbent domains include different forms of sorbent organic matter (SOM), combustion residue particulate carbon such as soot, and anthropogenic carbon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

K. C. Jones

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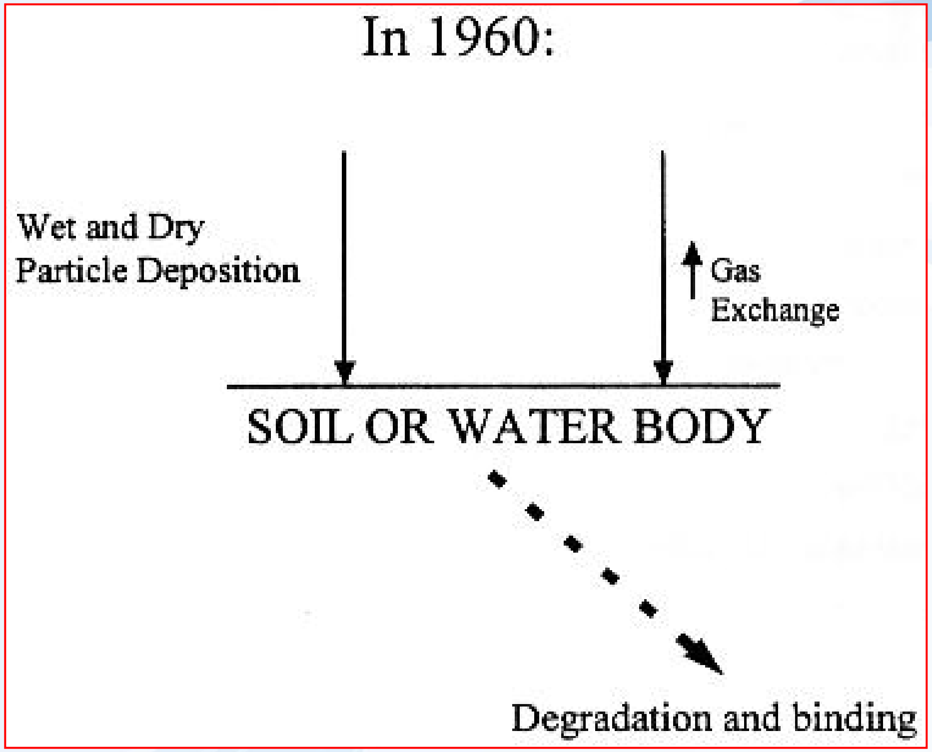
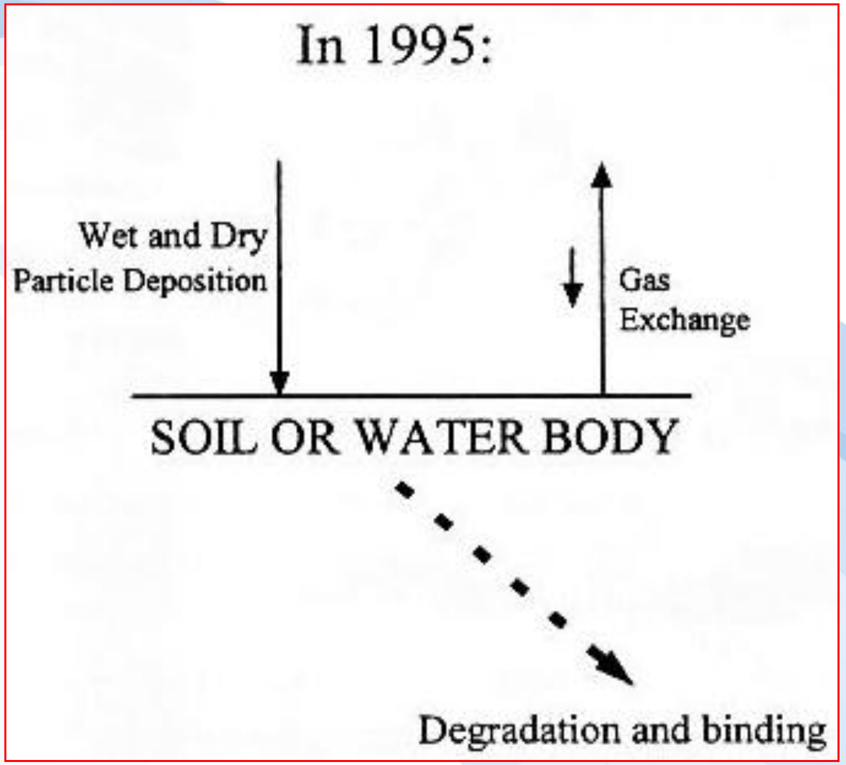
Exchange processes air – soils, temporal trends





Jones and de Voogt, 1999

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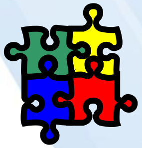
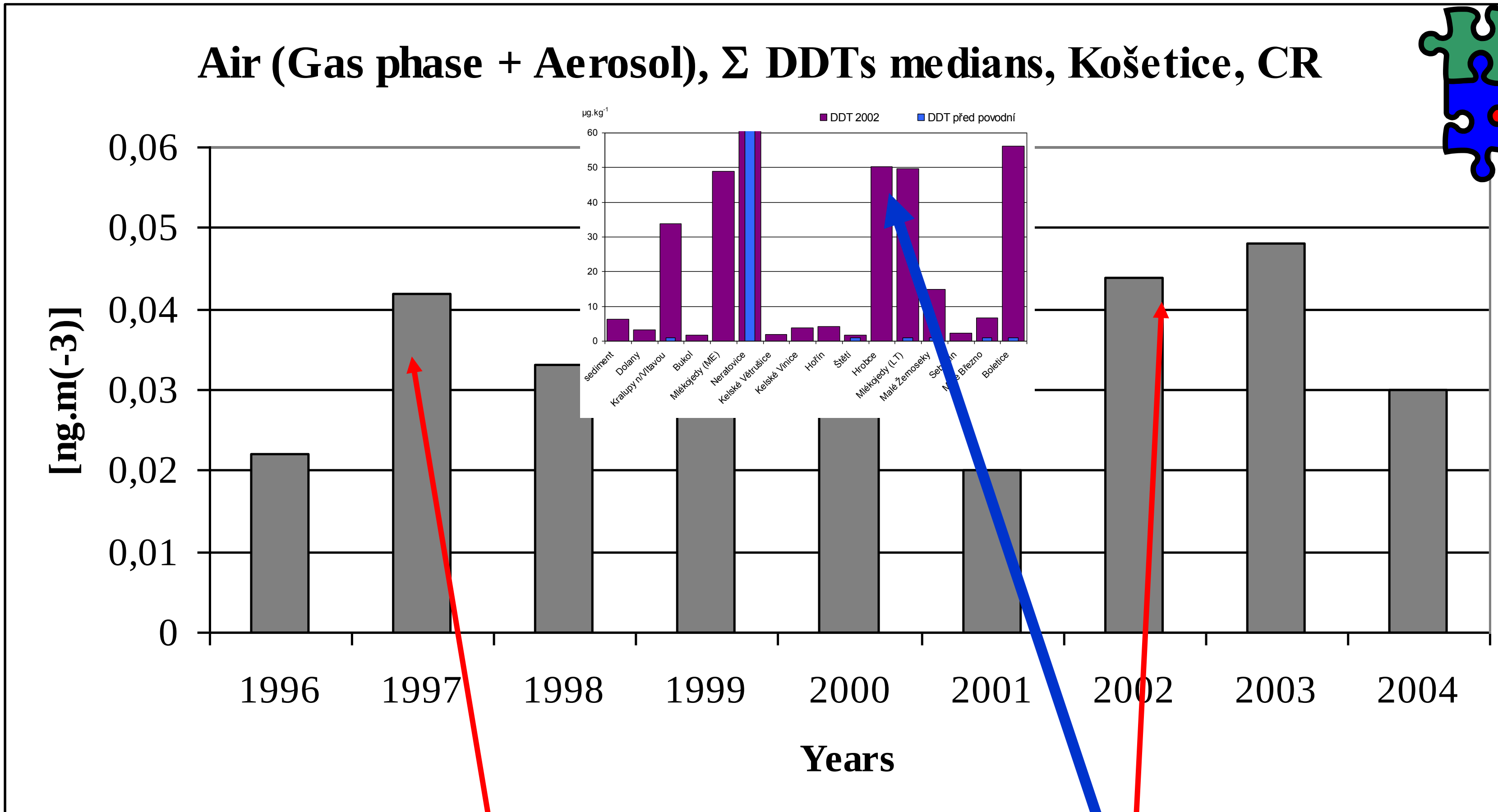
Case of the CR

Working hypothesis

- Summarised the levels of POPs (PAHs, OCPs, PCBs, PCDDs/Fs) in soils of the Czech Republic for the reference year 2001 and evaluated them;
- Calculation of the POPs soil burden in the CR;
- To measure laboratory volatilisation of basic POPs from various types of soils as a base from the estimation of POPs emission fluxes;
- Based on the knowledge of real soil POPs burden and using of experimental soil emission factors to calculate the contribution of POPs volatilisation from soils in the CR to the actual levels of these substances in ambient air;
- Estimation of risk potentials for human and wildlife of contaminated soils in the CR.
- Fate and behaviour of the POPs in the high-mountains area



Σ 3 DDTs in air, observatory Košetice, time trends, medians, sampling every week, 1996 - 2004 [$ng.m^{-3}$]



Effects of floods in Moravian region at 1997 and in South and Central Bohemia at 2002

Holoubek et al., 2007

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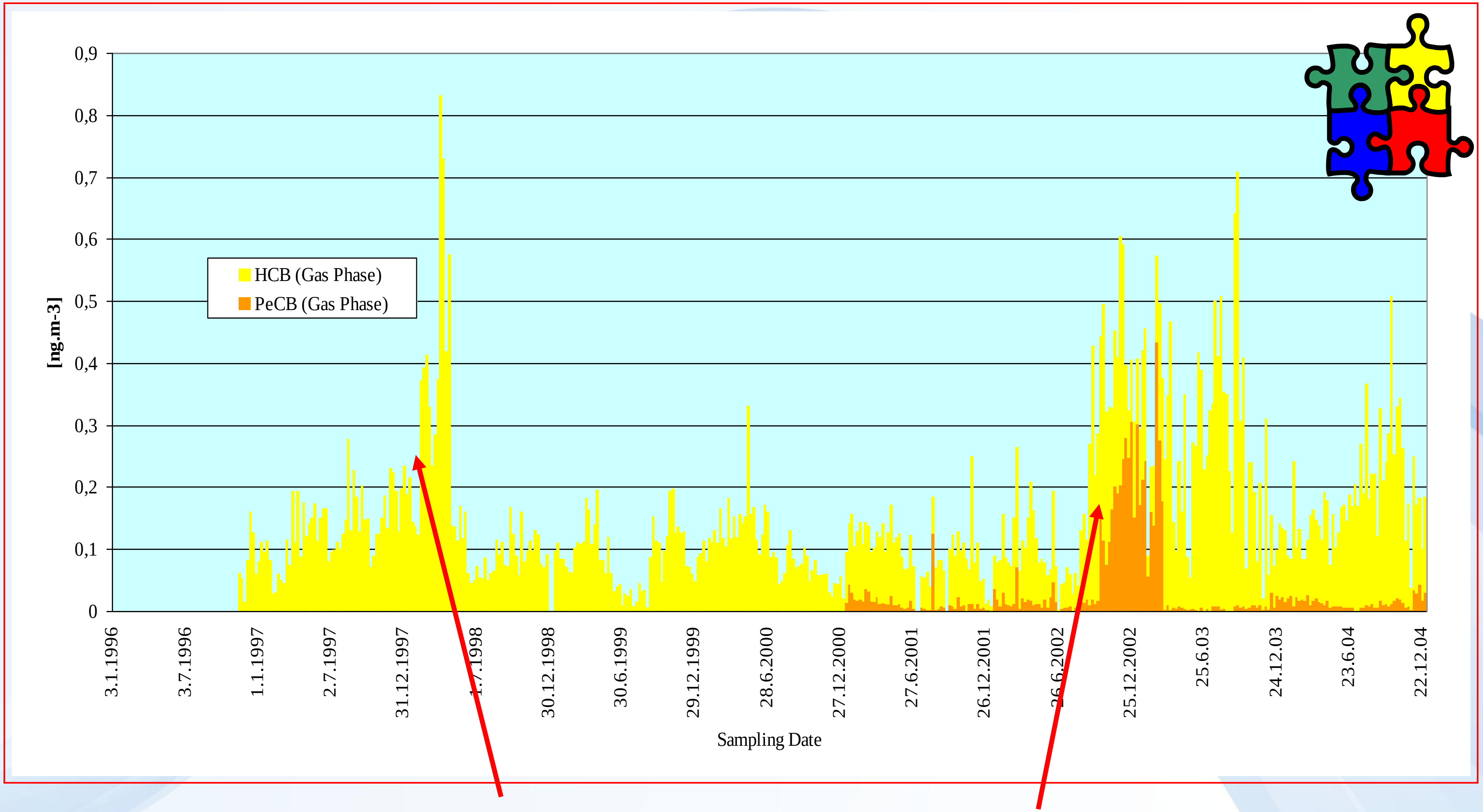
HCB and PeCBz in ambient air, observatory Košetice, temporal trends, medians, weekley sampled, 1996 - 2004 [$ng.m^{-3}$]



Effects of floods, Moravia, 1997 and in South and Central Bohemia, 2002

Holoubek et al., 2007

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Medians of PAHs, PCBs ($\mu g.kg^{-1}$) and PCDDs/Fs ($ng.kg^{-1}$) in the Czech soils, 2001

Σ PAHs	Σ PCBs	Σ 2378-PCDDs/Fs	Σ homologous PCDFs	TEQ Σ 2378-PCDDs/Fs
Arable soils (n = 46/38)				
700.90	3.78	48.22	73.25	1.24
Grassland soils (n = 34/28)				
445.30	5.82	48.87	113.36	1.51
Forest soils (n = 23/18)				
704.40	10.78	365.79	988.86	16.63
Mountains soils (n = 9)				
3 713	22.64	1 041	2 133	46.09

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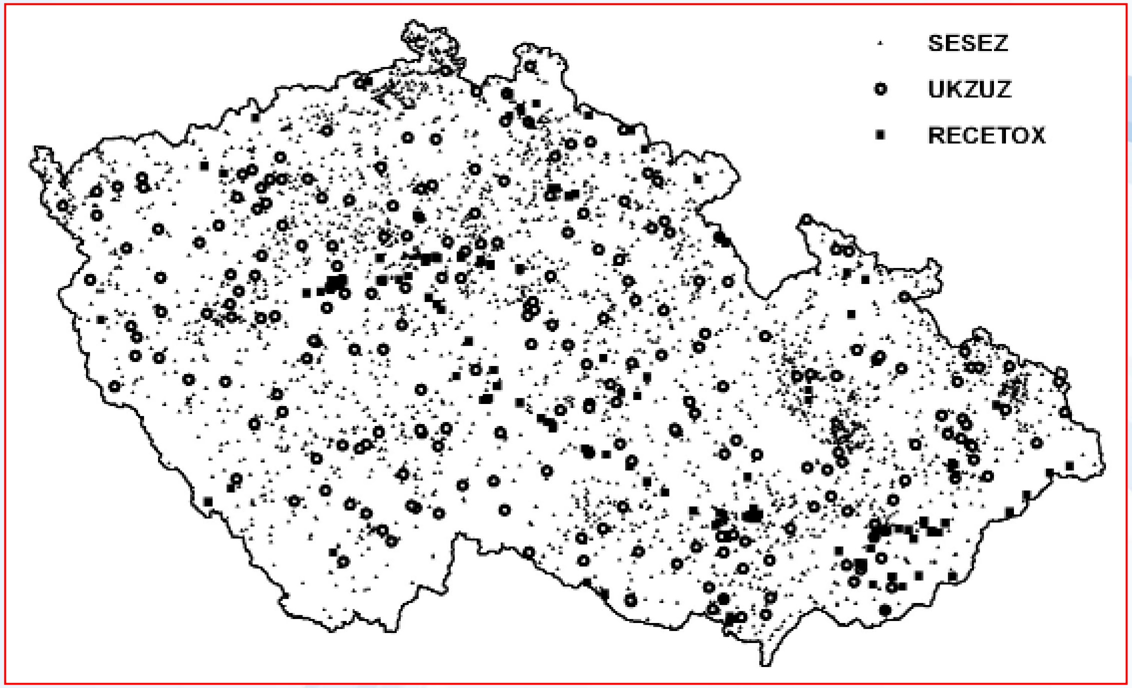
SoilRISK – POPs Stockpile



soil samples database	soil type		
	Forrest	Agriculture	Other
RECETOX	63	180	-
Bazal monitoring	-	237	-
SESEZ	547	2386	128

The number of sampled localities in agricultural, forest and other areas (e.g. cities, mines, etc.)

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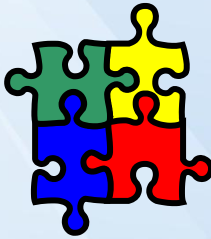
POPs Stockpile

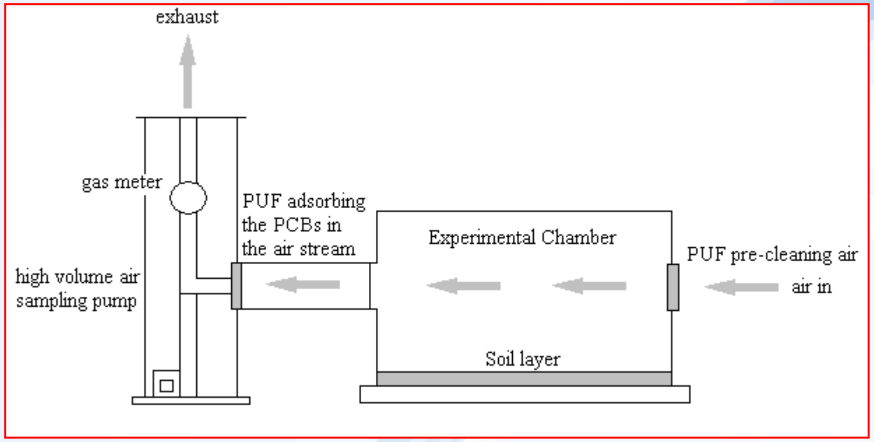
Stockpiles of POPs in the soil [t] - area of the Czech Republic

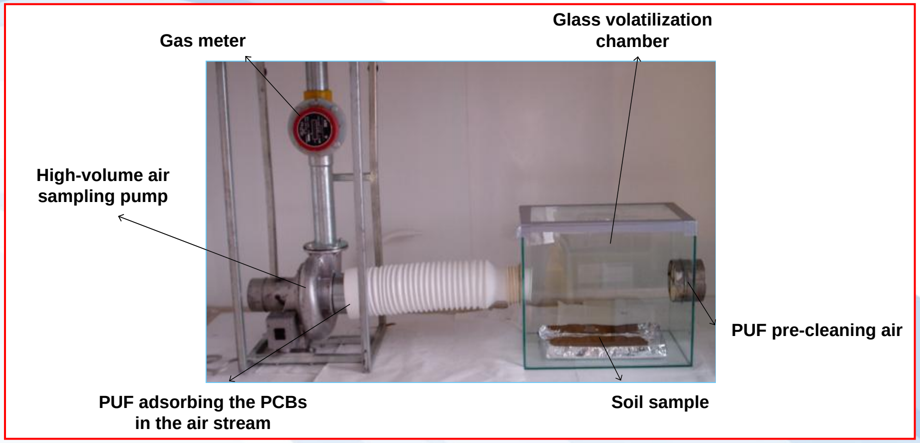
pp´-DDT	897.18
pp´-DDD	51.43
pp´-DDE	529.64
op´-DDT	149.32
op´-DDD	19.22
op´-DDE	22.32
DDTs	1 669.11
α-HCH	71.85
β-HCH	88.33
γ-HCH	118.89
δ-HCH	24.16
HCHs	303.23

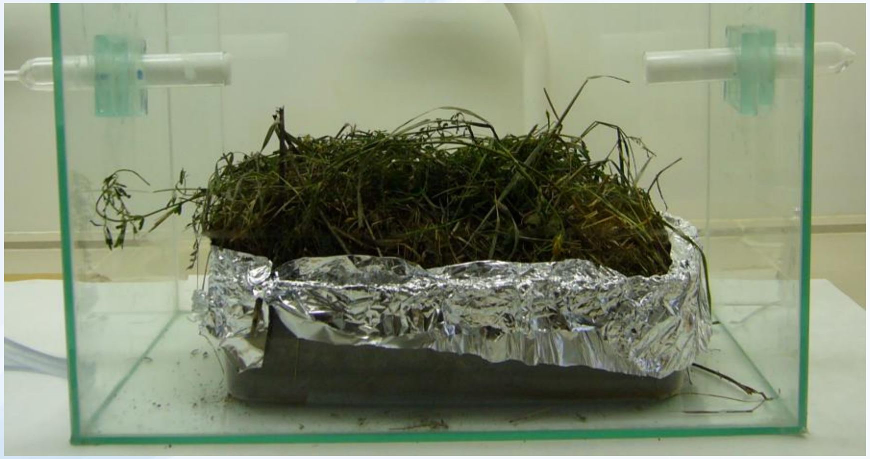
HCB	120.96
PCB118	19.06
PCB101	25.48
PCB52	15.52
PCB28	13.57
PCB180	63.25
PCB153	61.39
PCB138	82.44
PCBs	280.70



Measuring volatilization fluxes of SVOC from soils
Passive samplers for POPs sampling







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Preliminary estimation of soil fluxes in the CR

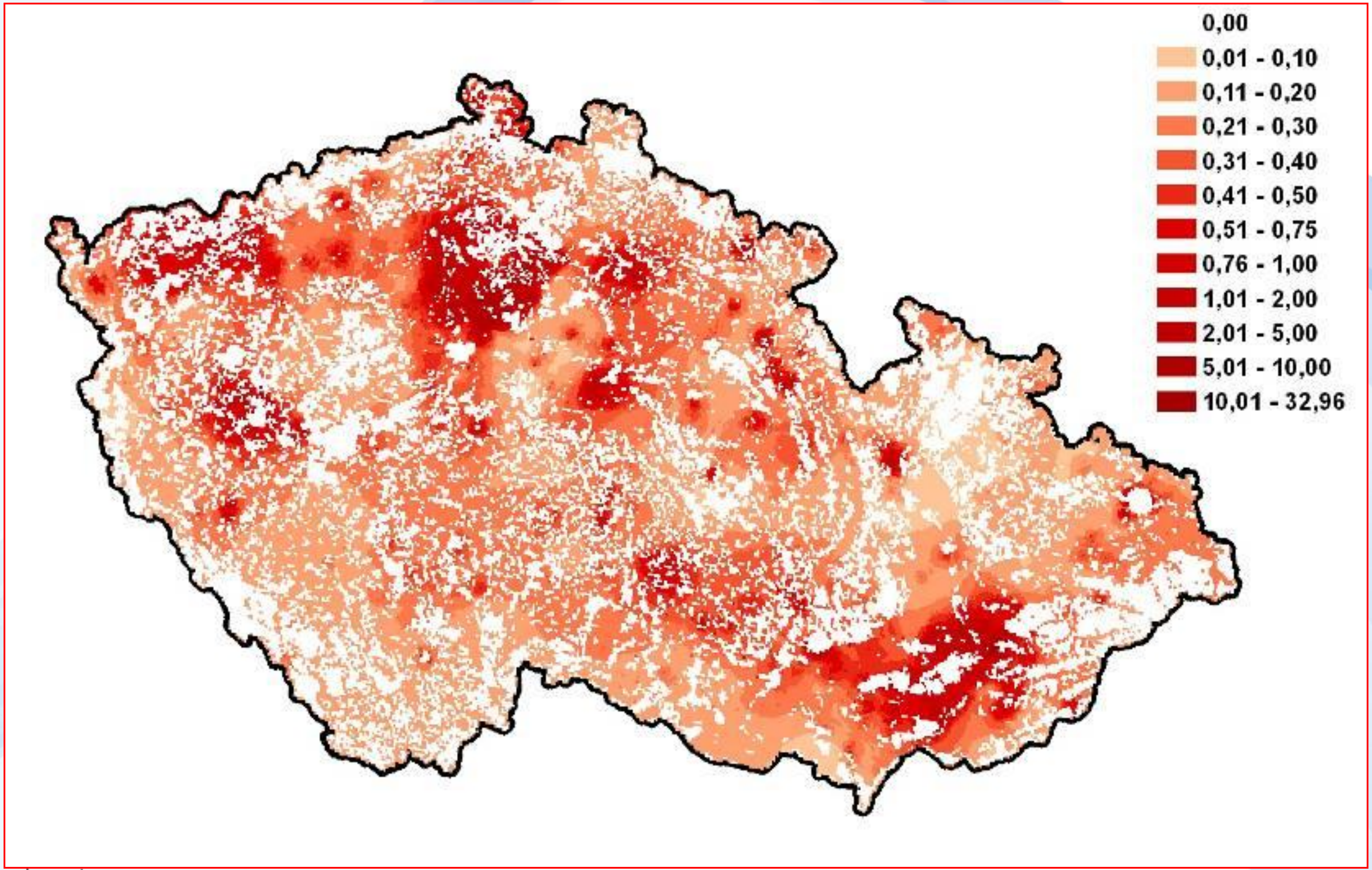
- PCB 153: 62.39 tonnes
- DDE: 529.64 tonnes

- Evaporation flux from the soils in the CR

- 22 kg/y for PCB 153 / 0°C
- 65 kg/y for PCB 153 / 20°C

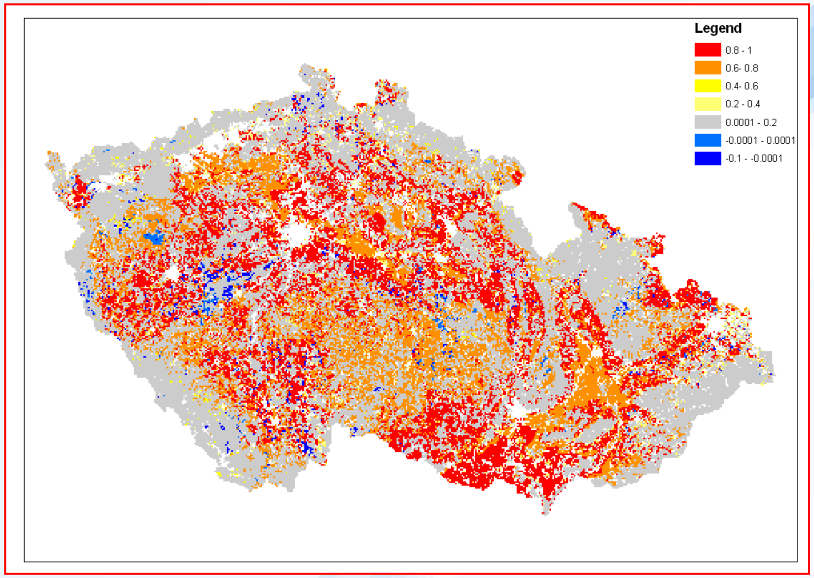
Reported amounts of Σ PCBs from the industrial sources: 48 kg/y

Filled 1x1 km grids maps of risk from POPs exposure via soil (selected PCBs and OCPs) were produced by IDW interpolation

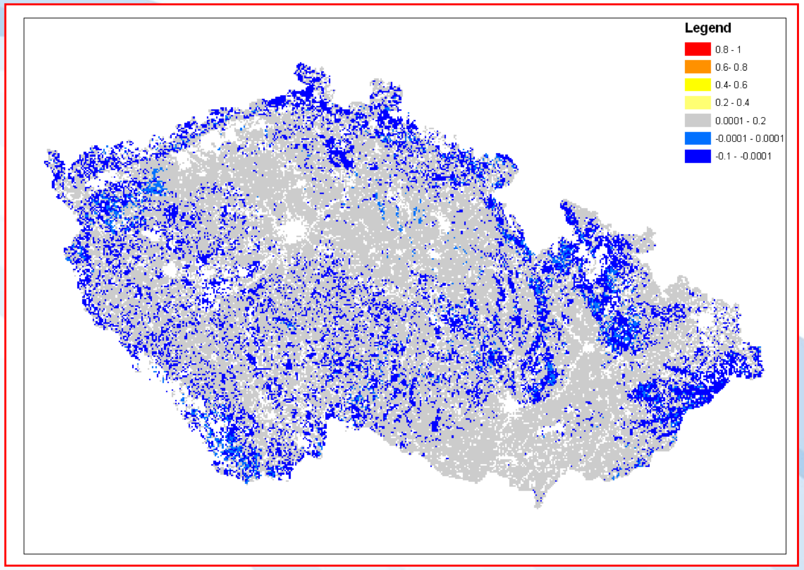


Predicted volatilisation fluxes (HCB)

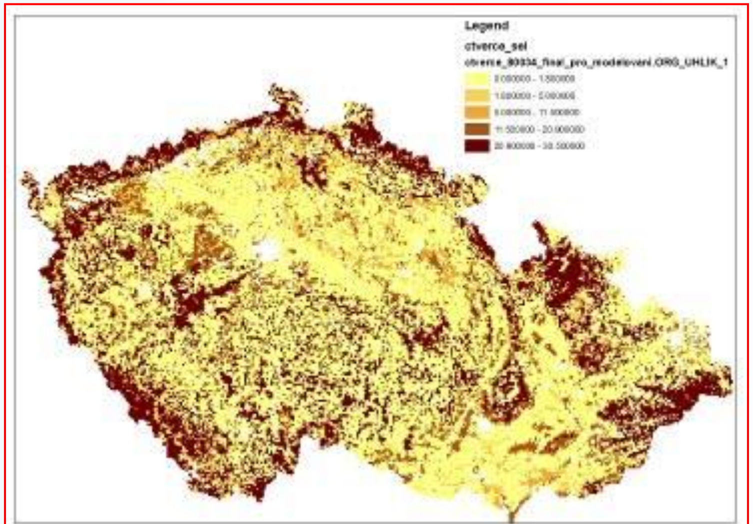
July



January



TOC in soils



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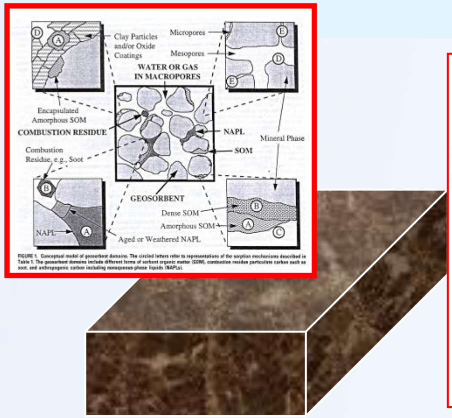
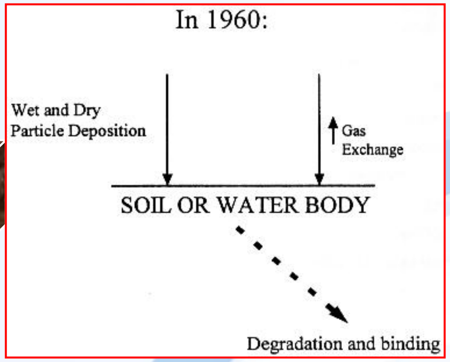
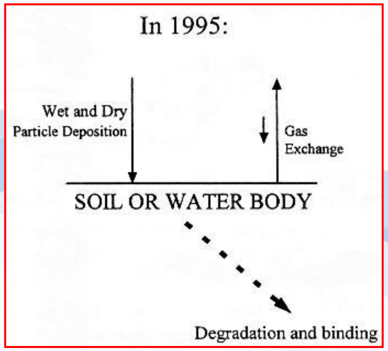
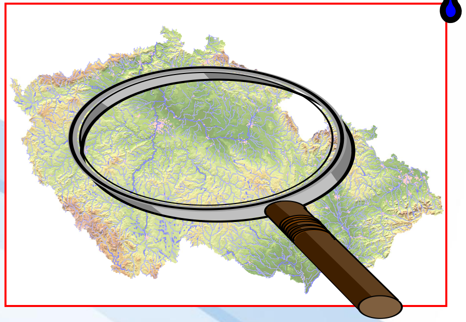
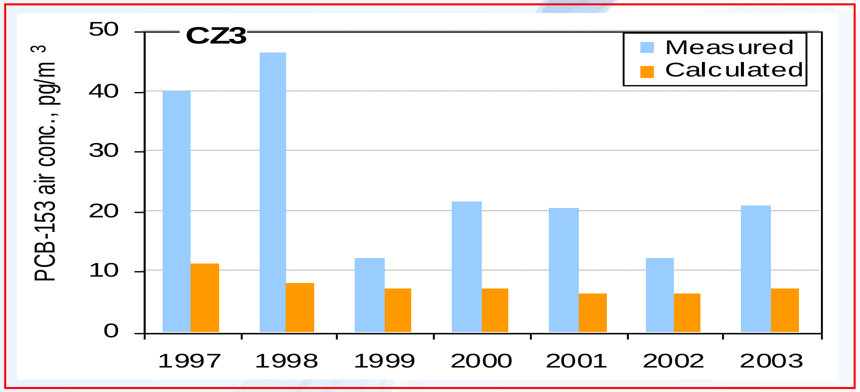
POPs Stockpiles

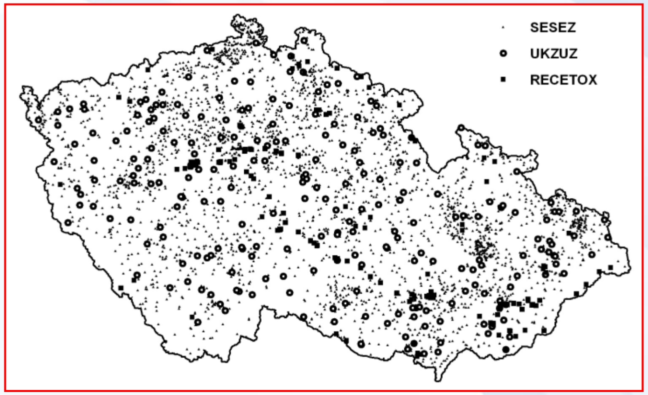


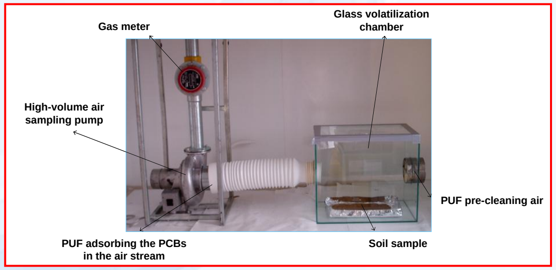


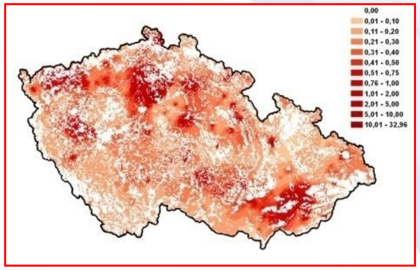












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