



Centrum pro výzkum  
toxických látek  
v prostředí

# Chemical compounds in ecosystems – introduction –

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Tento projekt je spolufinancován Evropským sociálním fondem a státním rozpočtem České republiky.



INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

## Take home messages of this lecture:

- Know the names, chemical properties (basic structural character) and sources of the main groups of pollutants
- Explain what environmental factors (i.e. external) and what properties of chemicals (inherited) influence the **behavior** of compounds in the environment ( $\log K_{ow}$ , H, persistence)...
- ... and thus condition the extent of **bioavailability** of compounds in the environment and **exposure** of organisms



# Important terms

**Definitions are ambiguous...** however, it is desired to understand the meaning of individual terms

TOXICANTS / TOXINS / ECOTOXICANTS

## → TOXICANTS

= compounds toxic in relatively low concentrations, introduced into the environment by human activities

## → TOXINS

= natural tox. compounds – produced by plants, bacteria, animals

→ Note - some examples of [environmentally significant natural toxins](#), which are at the same time ecotoxicants: cyanobacterial toxins – environmentally relevant due to anthropogenic activities - eutrophication



# Ecotoxicants

- Compounds selected from a wide range of chemical substances (petroleum and its products – organic compounds, pharmaceuticals, pesticides), which **can be released into the environment and can cause specific effects/interactions in ecosystems**
- **Each human activity is accompanied by introduction of (toxic) compounds into the environment**
  - products and side products of industry
  - household waste (*detergents, plastics ....*)
  - products used in agriculture
  - wastes from transport
  - veterinary and human pharmaceuticals
  - other ...



# Ecotoxicants vs. Contaminants ?

- **Contaminants**
- Compounds polluting the environment  
(*Not necessarily directly toxic, but harmful at the end*)
  - **! nutrients (NO<sub>x</sub> and PO<sub>x</sub>)**
    - are not ecotoxicants BUT do have many secondary effects  
→ eutrophication
  - **! organic communal waste**
    - not directly toxic BUT increases the content of organic carbon
    - → decomposition processes → reduction of oxygen content → toxic to aquatic organisms
  - **! toxic metals, polycyclic aromatic hydrocarbons (PAHs)**
    - natural occurrence in the nature BUT in “background” concentrations
  - **! simple soaps**
    - released in high concentrations BUT rapidly hydrolyzed to nontoxic products



# What numbers of CHEMICALS ?

www.cas.org

The screenshot shows the top portion of the CAS Registry website. On the left is the CAS logo with the text "A Division of the American Chemical Society". To its right is a navigation menu with "SOLUTIONS", "RESOURCES", "CAS DATA", and "ABOUT". Further right are icons for "CONTACT", "TRAINING", and "SEARCH", along with a "LOGIN" button. The main content area has a dark blue background with a pattern of white hexagons. The text "CAS REGISTRY®" is prominently displayed in yellow. Below it, a paragraph describes the registry as the premier source for chemical information. A yellow "CONTACT US" button is visible on the right side.

CAS  
A Division of the  
American Chemical Society

SOLUTIONS ▾ RESOURCES ▾ CAS DATA ▾ ABOUT ▾

CONTACT TRAINING SEARCH LOGIN


## CAS REGISTRY®


CAS REGISTRY®, the CAS substance collection, is the premier source relied upon by scientists, manufacturers, regulators, and data scientists worldwide for accurate information on chemical substances.


CONTACT US

The screenshot shows the "FEATURES" section of the CAS Registry website. It has a dark blue background with three vertical columns, each containing an icon and a text block. A red arrow points from the top left towards the first column.

## FEATURES

- 

Authoritative source for accurate chemical names, structures, and CAS Registry Numbers®.
- 

188 million organic and inorganic substances, including alloys, coordination compounds, minerals, mixtures, polymers, and salts disclosed in publications since the early 1800s.
- 

~70 million protein and nucleic acid sequences



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# What numbers of CHEMICALS ?

<https://echa.europa.eu/information-on-chemicals/ec-inventory>

Cc  
**22,000**  
are used  
by industry

**ECHA**  
EUROPEAN CHEMICALS AGENCY

About Us Contact Search the ECHA Website

LEGISLATION PUBLIC CONSULTATIONS INFORMATION ON CHEMICALS SUPPORT

ECHA > Information on Chemicals > Registered substances

## Registered substances

The data comes from registration dossiers submitted to ECHA by the date indicated as last update. The Total Tonnage Band is compiled from all the dossiers with two exceptions; any tonnages claimed confidential and any quantity used as an intermediate to produce a different chemical. The Total Tonnage band published does not necessarily reflect the registered tonnage band(s).

Please note that some of the information on registered substances may belong to third parties. The use of such information may therefore require the prior permission of the third party owners. Please consult the *Legal Notice* for further information.

Please note that information on chemical properties of registered substances is directly accessible via *eChemPortal*.

[Chemical Property Data Search](#)

### FURTHER INFORMATION

- Registered substances information
- How to determine what will be published (Data Submission Manual 15)
- Understanding REACH Regulation
- Q&A on registered substances
- What is an Infocard? [PDF]
- What is a Registered substance Factsheet? [PDF]
- eChemPortal
- REACH study results download

See a problem or have feedback?

Last updated 03 October 2019. Database contains 22422 unique substances and contains information from 96356 dossiers.

Substance identity

Substance name:  CAS number:

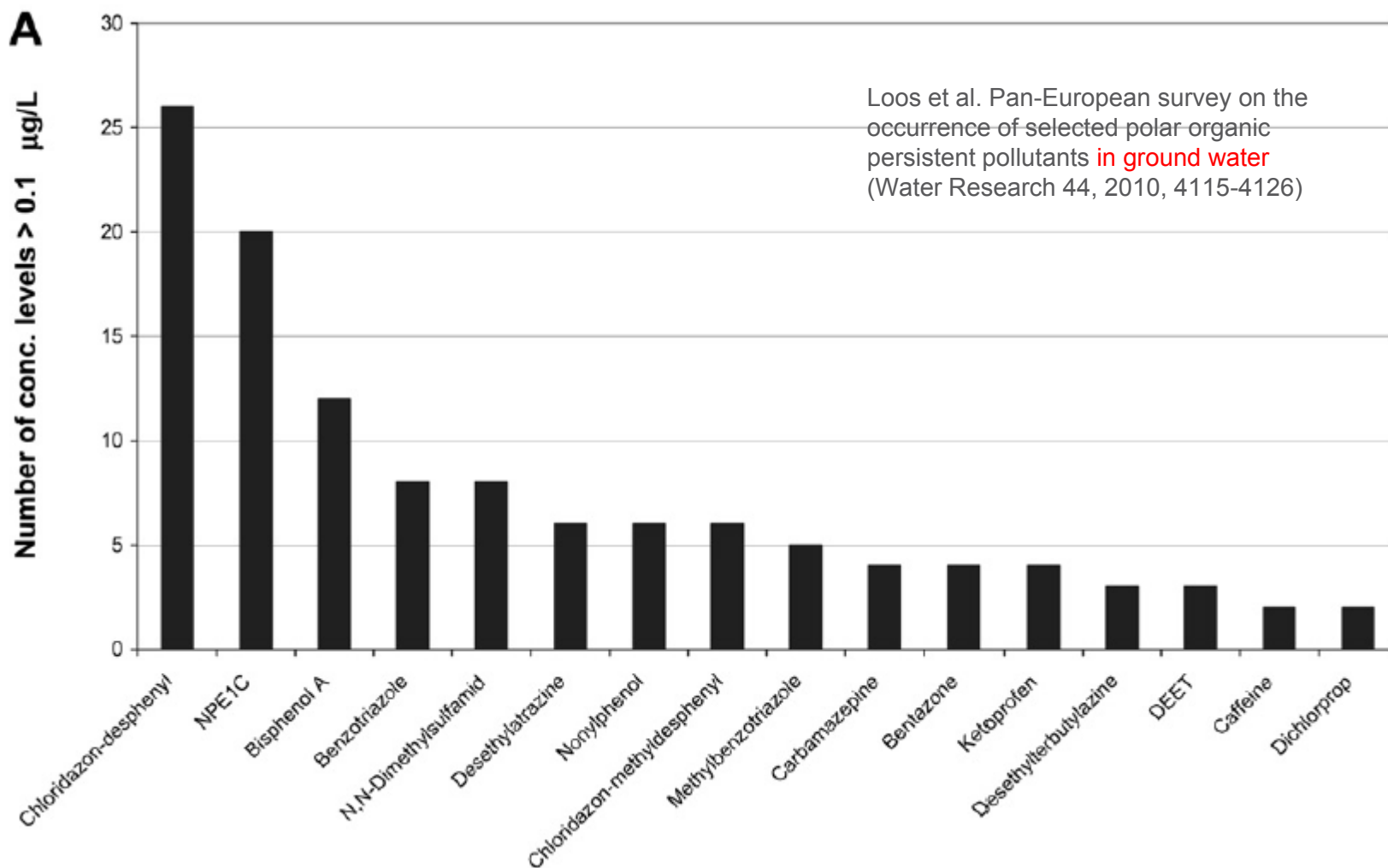
EC / List number:  Other Numerical Identifiers:







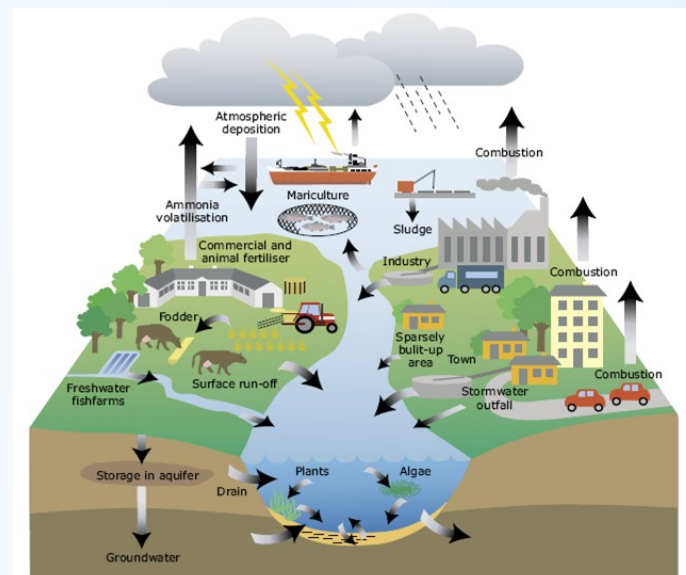
# What chemicals for example?... In EU groundwaters?



# Sources... and examples of representative contaminants

## • Overview of contamination sources

- *a student should have a general overview and be able to name representative examples*
- POINT SOURCES (easier to control and penalize)
  - communal wastewaters
  - industrial wastewaters
  - solid urban- and industrial wastes – dumps / combustion
- DIFFUSE SOURCES (difficult to control)
  - industry, engine emissions, energy production
  - surface run-offs (roads, roofs, coatings...)
  - agricultural activities
- LINE SOURCES (difficult to control)
  - (highways) traffic



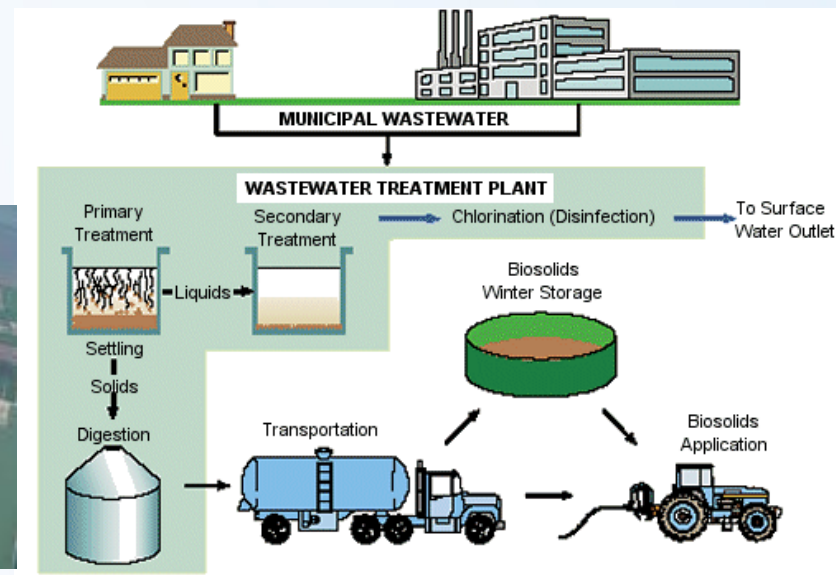
# Communal wastewaters

- **Effect on environmental components**

- Primary **effect on water** ... secondary also on soil and further influence on food chain (irrigation, WWT sludges)

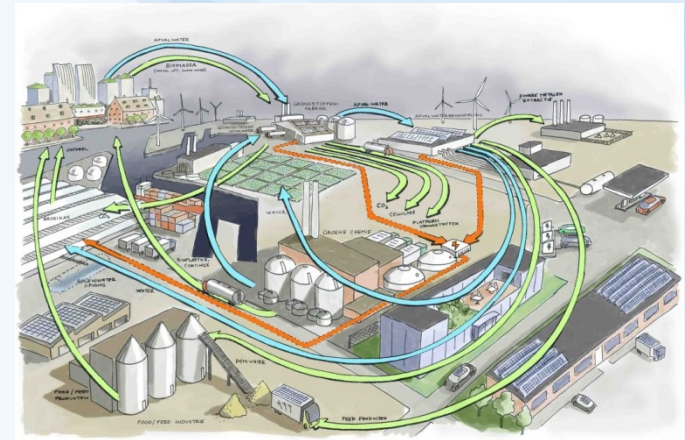
- **Significant contaminants**

- Nontoxic organic compounds (fecal pollution)
- **PPCP** (Pharmaceuticals and Personal Care Products)
  - Pharmaceuticals
  - Household chemicals (detergents, softeners, fragrances/musks)
- Polycyclic aromatic hydrocarbons (PAHs)
- Chlorinated compounds
- Toxic metals



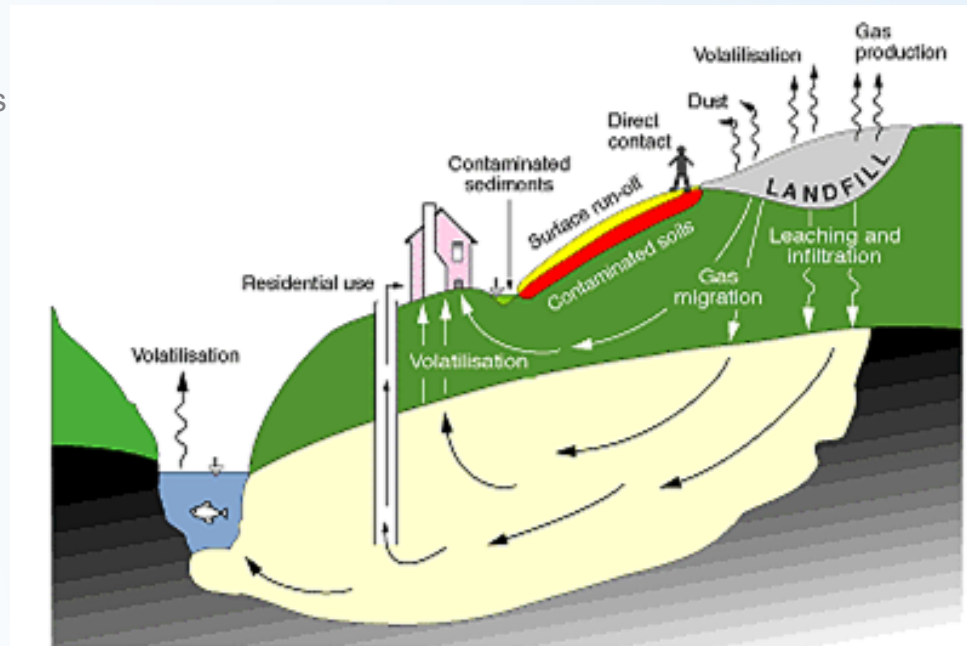
# Industrial wastewaters

- **Effect on environmental components**
  - Primary **effect on water** ...
- **Significant contaminants**
  - Specific products regarding the industrial type, examples:
    - Food industry – organic pollution, phytoestrogens
    - Pulp and paper industry – chlorine, organochlorine compounds
    - Metal processing – cooling and metalworking-fluids (chlorinated alkanes / paraffins)
    - etc.
  - Toxic metals
  - Acids, solvents (incl. halogenated)
  - Contaminants with global importance
    - Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)
    - Polychlorinated biphenyls (PCBs)
    - Polycyclic aromatic hydrocarbons (PAHs)



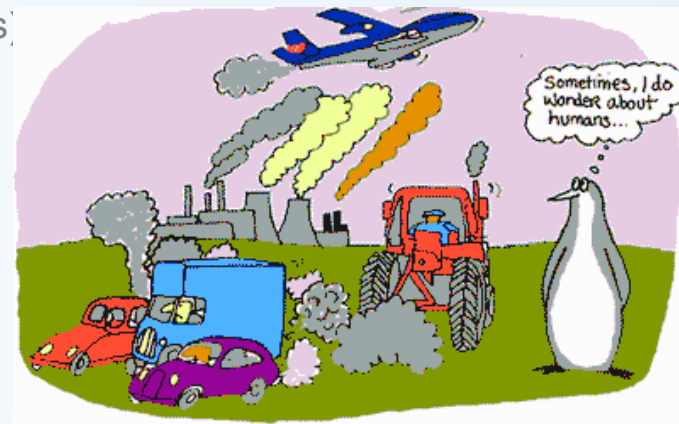
## Landfills & Industrial zones (brownfields)

- **Effect on environmental components**
  - Primary effect on **ground water** (GW)
- **Significant contaminants**
  - Specific products regarding the industrial type and landfilling, frequent GW contaminants
    - BTEX – benzene, toluene, ethylbenzene, and xylenes
    - Low molecular weight halogenated solvents– e.g. ethylenes (TCE, DCE)
  - Toxic metals
  - Contaminants with global importance
    - Polychlorinated dibenzo-p-dioxins and furans
    - Polychlorinated biphenyls (PCBs)
    - Organochlorine pesticides (OCPs)



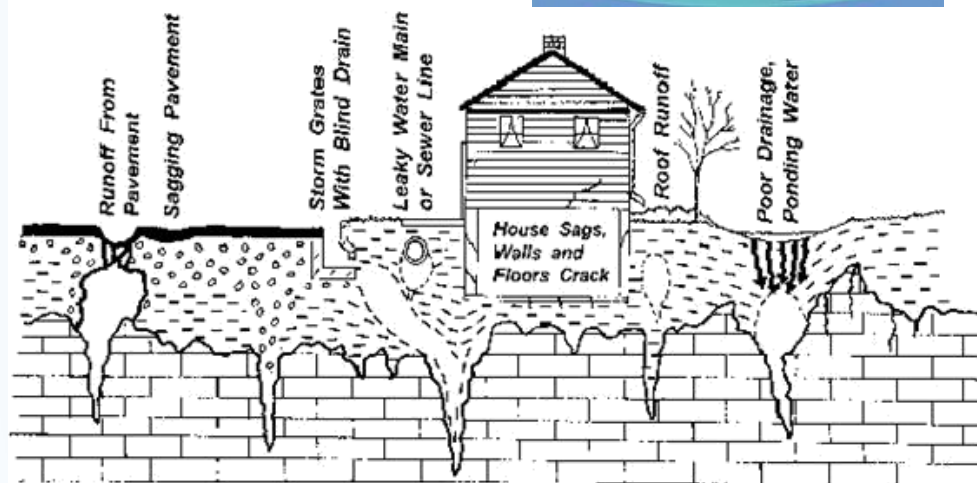
# Industry, internal combustion engines, energy production

- **Effect on environmental components**
  - Diffuse pollution
  - Primary **effect on atmosphere** + on all ecosystems
- **Significant contaminants**
  - Toxic metals (e.g. Pb, Cd etc.)
  - CO, CO<sub>2</sub>
  - Polycyclic aromatic hydrocarbons (PAHs)
  - SO<sub>x</sub>, NO<sub>x</sub>
  - Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)
- **Specific organic compounds used by industry**
  - Regarding the type of the industry
  - Global importance e.g. Polychlorinated biphenyls (PCBs)



# Surface run off

- **Effect on environmental components**
  - Diffuse pollution
  - Primary **effect on water** (surface and ground)...
- **Significant contaminants**
  - Construction chemicals
  - Chlorinated compounds
  - Toxic metals
  - Contaminants with global importance
    - Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)
    - Polychlorinated biphenyls (PCBs)
    - Polycyclic aromatic hydrocarbons (PAHs)



# Agriculture

- **Effect on environmental components**
  - Diffuse pollution
  - Primary **effect on soil...** but indirectly also on all other env. components
- **Significant contaminants**
  - Plant protection treatments (pesticides)
  - Fertilizers (N-, P-) and contaminants therein (often e.g. Cd)
  - Veterinary pharmaceuticals (→ application of manure)

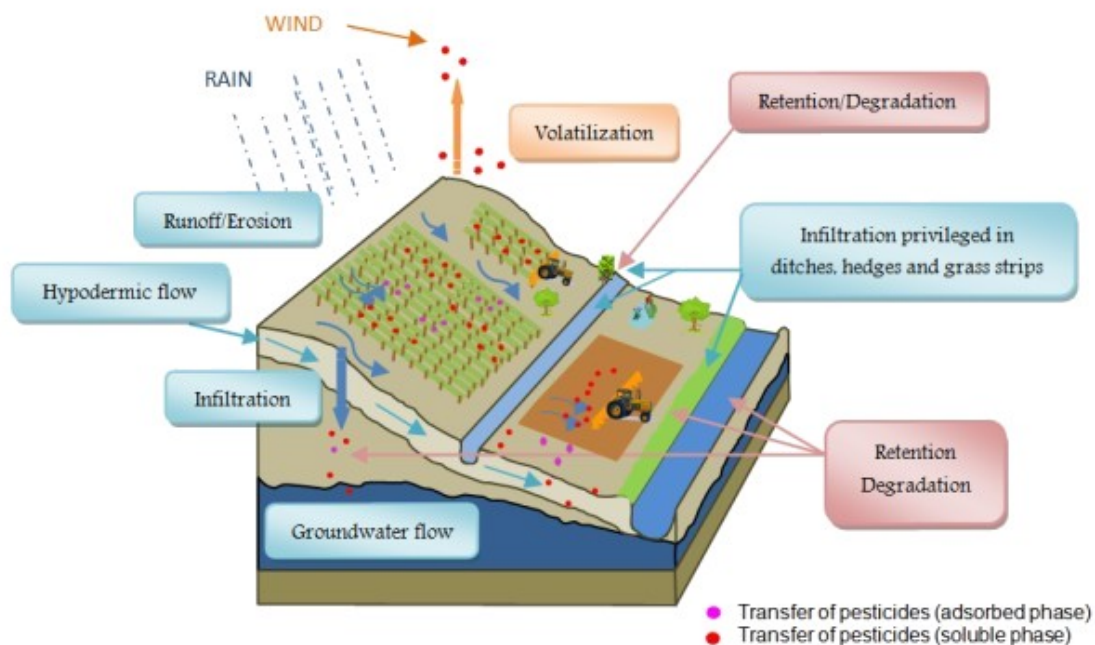


Figure 1: Main pesticides transfers at the catchment area scale





# Main groups of pollutants

## Important terms, abbreviations... and structures



## Compounds grouped by effect

Pesticides ( <i>Plant Protection Products: primarily agriculture use</i> )	Toxic for pests	DDT, parathion, atrazine glyphosate (RoundUp)
Biocides ( <i>For household use</i> )	Toxic to biota, including also anti-bacterial agents	Chlorine (bleach), Triclosan (antibacterial soaps)
Insecticides	Toxic for insect/arthropods	DDT, parathion
Herbicides	Toxic for plants	2,4-D, glyphosate, atrazine
Fungicides	Toxic for fungi/moulds	Pesticides containing toxic metals (Hg, Cu)
Rodenticides	Toxic for rodents	Cyanide
Carcinogens	Induce cancer	Benzo[a]pyrene
Reprotoxins	Effect on reproduction	Ethinylestradiol
Endocrine disruptors	Effects on hormone systems	Ethinylestradiol, tributyltin

# Compounds grouped by physico-chemical properties

Lipophilic (hydrophobic)	Soluble in fat / low solubility in water	DDT
Hydrophilic	Soluble in water	Phenol, modern insecticides
Neutral organic compounds	Uncharged compounds (do not ionize)	DDT, PCB
Radioactive compounds	Unstable, decay and emit radiation	Radon
Surfactants, detergents	Compounds lowering surface tension between two phases	Nonylphenol, alkylbenzene sulfonates
Persistent compounds	Very long half-life in the environment (do not degrade)	DDT, PCB
Volatile organic compounds	Volatile organic compounds ( <b>VOCs</b> )	Acetone, Benzene, Formaldehyde, Xylene, Perchloroethylene, Toluene etc.



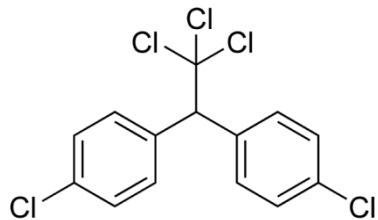
# Significant compounds grouped by their structure

Chlorinated hydrocarbons, organochlorine compounds		DDT, PCB, PCDD/Fs
<b>PCBs</b>	Polychlorinated biphenyls	PCB153
<b>PAHs</b>	Polycyclic aromatic hydrocarbons	Benzo[a]pyrene
<b>PCDD/Fs</b>	Polychlorinated dibenzo-p-dioxins and -furans	2,3,7,8-TCDD
Toxic metals, heavy metals		Hg, Pb, Cd (+ others)
Organometallics		Alkyl tins, Methyl-mercury
<b>OPs</b>	Organophosphates	Compounds (insecticides) – e.g. parathion
<b>BTEX</b>	Benzene and its derivatives – contamination of ground water and air (volatiles)	Benzene, Toluene, Ethylbenzene, Xylenes

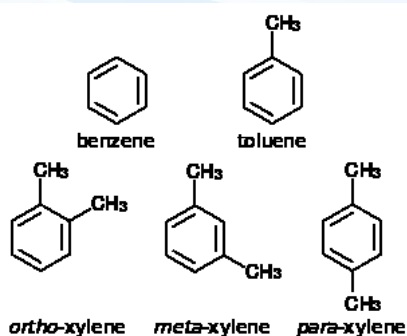


# Student should be aware of the most important structures

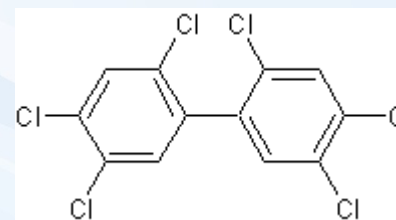
DDT



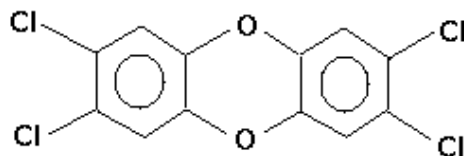
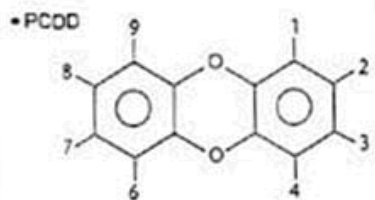
BTEX



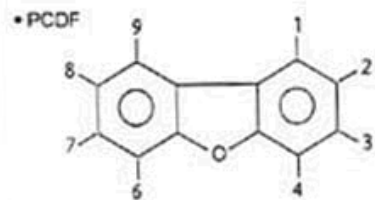
PCB153 (very abundant)



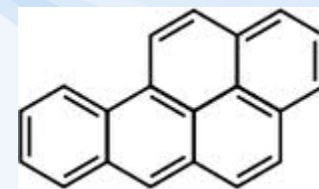
Polychlorinated dioxines and furans (PCDD/Fs)



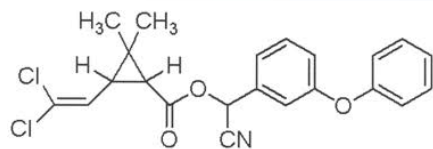
2, 3, 7, 8 - p - TCDD



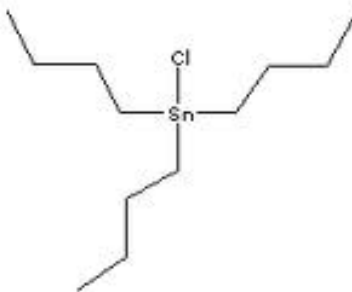
Benzo[a]pyrene – example of PAHs



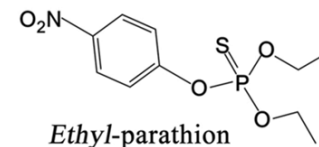
Cypermethrin



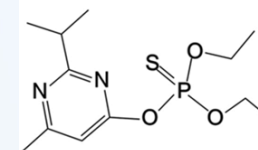
Tributyltin chloride (Organometal)



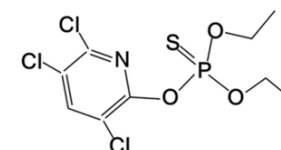
Organophosphates



Ethyl-parathion



Diazinon



Chlorpyrifos



## Further common terms/abbreviations – groups of compounds

- **HPVC** - High-production volume chemicals (from the REACH legislation)
- **CMR** - Carcinogenic, mutagenic or reprotoxic (from the REACH legislation)
- **EDC** - Endocrine disruptive compounds
- **POPs** – Persistent organic pollutants (as defined in the Stockholm Convention)
- **OCPs** – Organochlorine pesticides (e.g. DDT, lindane etc.)
- **PBT** – Persistent bioaccumulative and toxic compounds
  - very dangerous - specific legislation
- **PPCP** - Pharmaceuticals and personal care products
- **PPP** - Plant protection products
  - (generally „pesticides“)
- **HCs** - Halogenated compounds (usually at ground water contamination)
- **Emerging contaminants** – generally polar compounds, which are not well studied, yet (previously most attention to persistent compounds!)



# Environmental processes



# Risk of compound presence to the environment – which parameters are determining?

Chart summarizes terms explained in the next part of the lecture

## RISK

(e.g. % decline in population of salmonid fish in CZ)

*This presentation*

### Properties of the substance HAZARD

Is **hazardous/toxic** to fish?  
What is the mode of action/toxicity type?

At what concentrations?



### Situation in the environment EXPOSURE

Is the compound in the water? (**fate**)  
Is the compound in a form available to fish?  
(**bioavailability**)  
Does it enter the fish? (**bioconcentration**)  
Can **bioaccumulate**?, Concentrates in the food chain (**biomagnification**)?

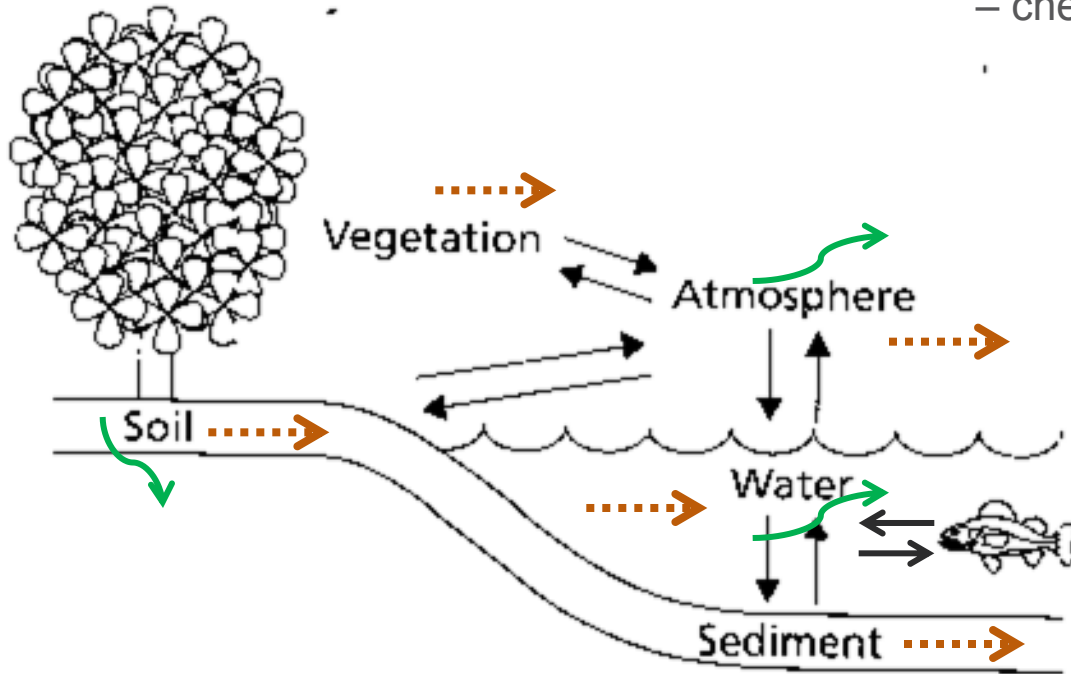
What is the bioavailable concentration?



# Environmental FATE of the compound determines the EXPOSURE

## ENVIRONMENTAL FATE describes

- ? In which environmental compartments is the compound present
- ? How it migrates within the compartments
- ? How it transforms within the compartments



**DISTRIBUTION** between compartments

**TRANSPORT** – e.g. by air

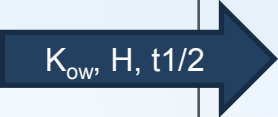
**TRANSFORMATION**  
– chemical and biological

## EXPOSURE

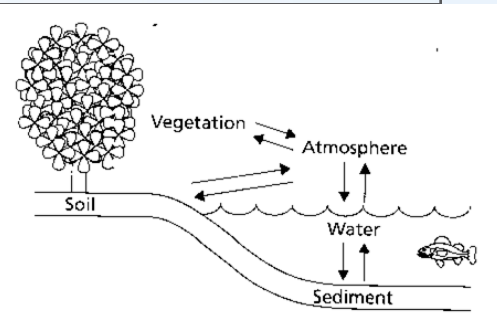
Extent of exposure of an organism to a compound (in a specific concentration, for a specific time etc. = *Exposure scenarios*)

# What parameters determine the fate of a chemical compound?

	DISTRIBUTION	TRANSPORT	TRANSFORMATION
<b>Compound properties</b>	Polarity vs hydrophobicity ( <b>K<sub>ow</sub></b> , water solubility) Volatility, boiling point, evaporation ( <b>H</b> , boiling point) Reactivity vs stability and persistence ( <b>t<sub>1/2</sub></b> )		
<b>Environmental properties</b>	Drift (pace, direction, type ...) Temperature Light (and its parameters) Chemical composition		
Water	pH (free H <sup>+</sup> )		
Sediments	Redox potential (... presence of O <sub>2</sub> )		
Soil	Presence of inorganic ions / cation-exchange capacity (e.g. clay)		
Atmosphere	Particles – type, size, amount Organic matter – type, amount (humic acids etc.)		
<b>Biota properties</b> vegetation, consumers...	Number / Motion / Size (surface) / Fat content (%) / Food chain level etc. etc.		



The fate and resulting exposure of organisms is defined by a combination of listed parameters



Which parameters are especially crucial regarding the risk of **ECOTOXICITY**?

- **1) Tendency to enter the organism**
  - higher **hydrophobicity** (fat in organisms)
  - partition coefficient octanol/water ( $K_{ow}$ ,  $\log P$ )
- **2) Stability (persistence, low degradability)**
  - long-term functionality in the environment
  - half-life ( $t_{1/2}$ )
- **3) Toxic effects in organisms**

*... information on each parameter is needed*

1+2 – in this part of the course  
3 – other lectures

Entry of compound into the biota (transport from the environment into the organism)

- **Compound distribution between environmental compartments**

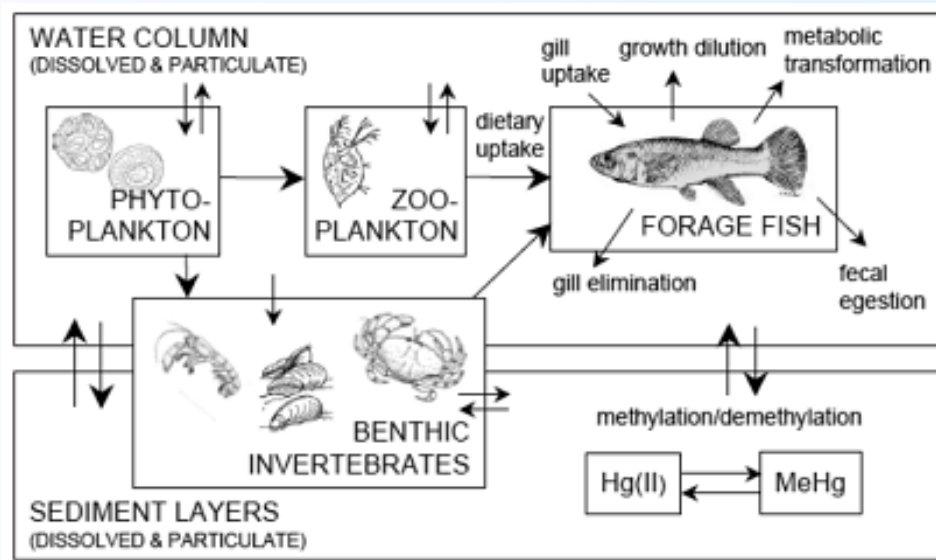
- Partition processes between environmental compartments (compartments/matrices/phases)

- biota/atmosphere
- sediment (soil) / water
- soil/atmosphere
- water/atmosphere

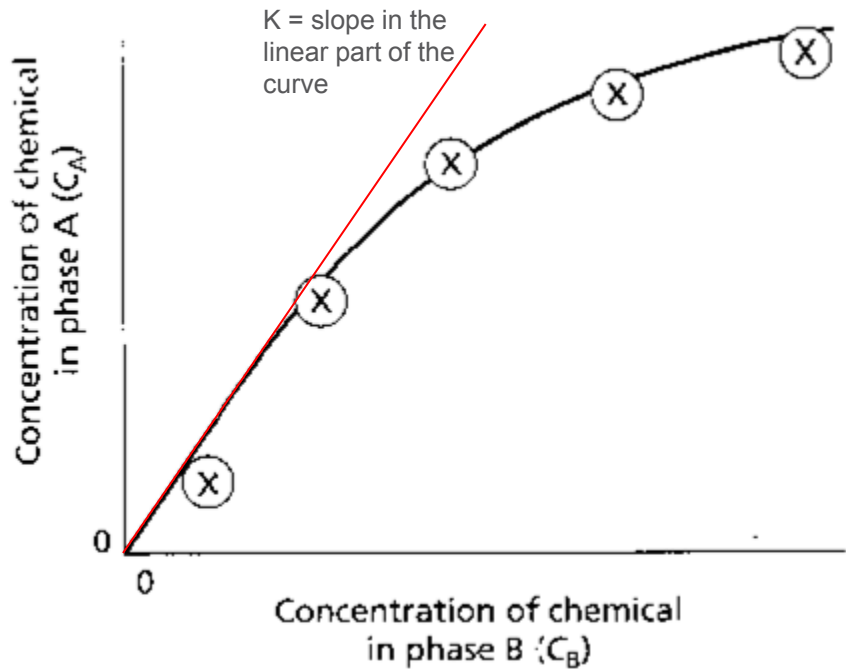
- **BIOTA as one of the compartments**

- important are partition processes “environment  $\leftrightarrow$  biota”

- Atmosphere / biota
- Water / biota
- Sediment / biota
- Soil / biota
- Biota(food) / Biota (predator)



Partition processes between two phases  
in EQUILIBRIUM are consistent with the first order kinetics – defined by the *Freundlich equation*



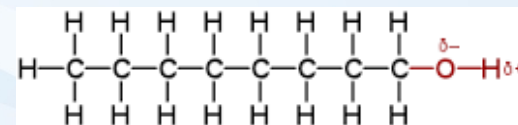
- **$C_a = K \cdot C_b^{1/n}$**   
C – concentration in phases A ( $C_a$ ) and B ( $C_b$ )  
K – partition constant  
n – nonlinearity constant
- In case of a linear relationship ( $n=1$ )  **$K = C_a / C_b$**   
= “partition coefficient”
  - The size of K determines the tendency of the compound to transfer from phase B into phase A
- From a practical experiment (*compound partitioning between two phases*) respective constants can be determined

$$\log C_a = 1/n \cdot \log C_b + \log K$$

# “Biota-Water” partition model

- **BIOTA / Water partition coefficient**

- difficult to determine  
(*standard procedure – bioconcentration determination: see further*)
- Alternatively – model with **n-octanol**



- **N-octanol**

- Immiscible with water, similar properties to fats or phospholipids of biological membranes

- **n-octanol/water partitioning**

- **K<sub>ow</sub>** – partition coefficient
- Characterizes **HYDROPHOBICITY** (resp. **LIPOPHILICITY**)
- Often expressed as logK<sub>ow</sub> (resp. logP)

## Experimental K<sub>ow</sub> determination

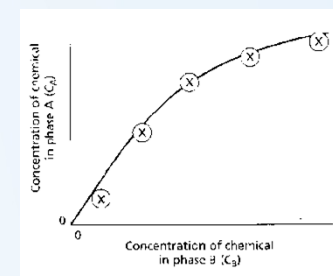
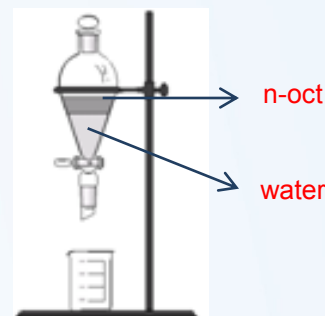
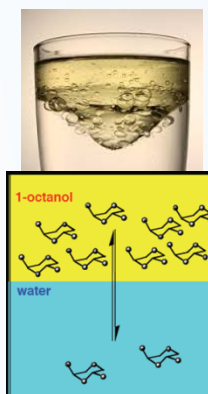
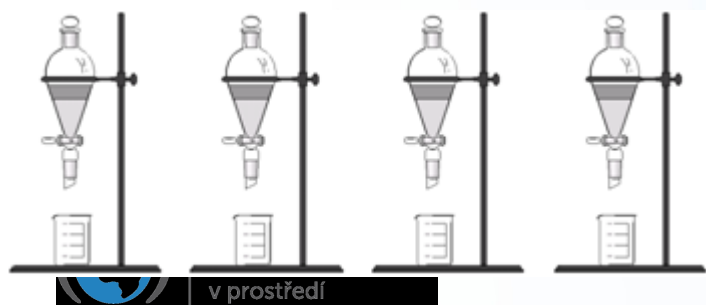
System  
n-octanol/water + compound insertion

Shaking until equilibrium  
is established

Chemical analysis of  
concentrations

K<sub>ow</sub> calculation

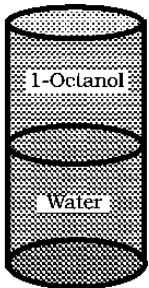
4 different initial concentrations



# $K_{ow}$ – examples

Compound	$K_{ow}$	$\log K_{ow}$ (logP)	$K_{\text{bioaccumulation}}$ (experimental)
Lindane	5 250	3.72	470
DDT	2 290 000	6.35	1 100 000
Arochlor 1242 (PCB)	199 600	5.30	3 200
Naphthalene	3 900	3.59	430
Benzene	135	2.13	13

## Hydrophobicity



Measured as Water/Octanol  
Partition Coefficient (P)

$$\log P_A = \log \frac{[A]_{1\text{-octanol}}}{[A]_{\text{water}}}$$

$\log P > 0$  lipid phase  
 $\log P < 0$  water phase

$$\log BCF = \log Kow - 1.32$$

# Bioaccumulation, Bioconcentration, Biomagnification

## Bioconcentration

The extent of compound uptake into the organism (fish) from water

**BCF** – Bioconcentration factor

$$BCF = \frac{Concentration_{Biota}}{Concentration_{Water}}$$

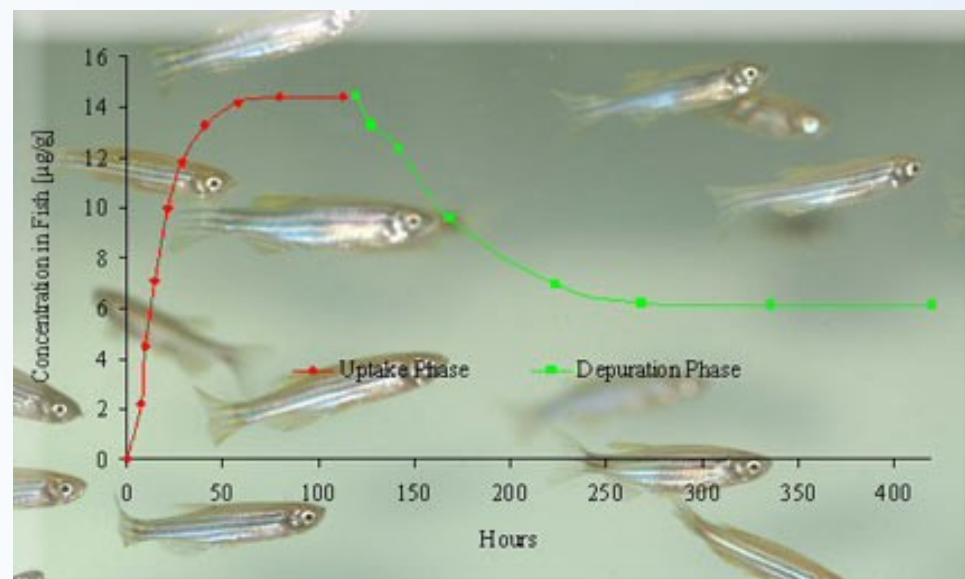
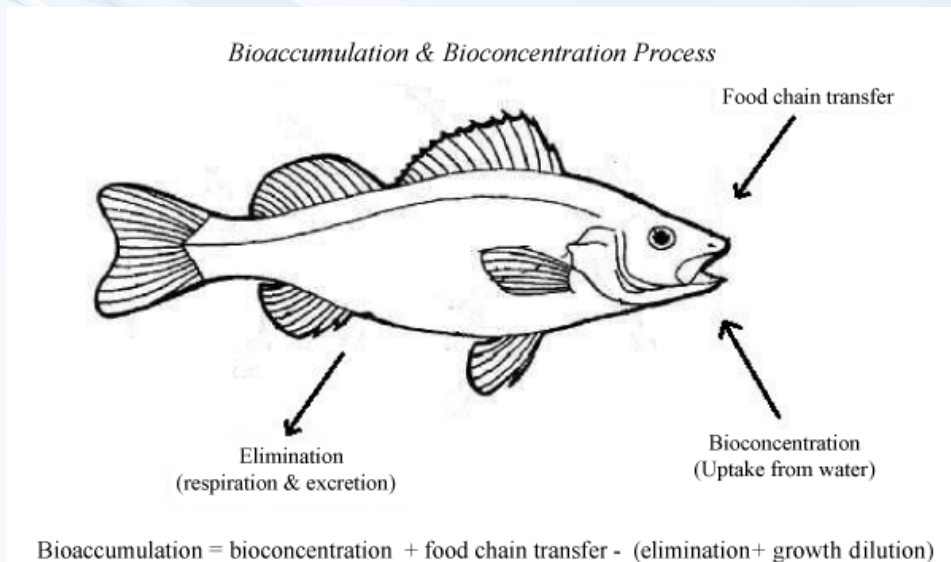
## Experimental determination

Tests with fish (standard OECD 305)

Time consuming, demanding tests, tests with fish *in vivo*

It is possible to predict BCF from

$$K_{ow} \quad \log BCF = \log Kow - 1.32$$





# Bioaccumulation, Bioconcentration, Biomagnification

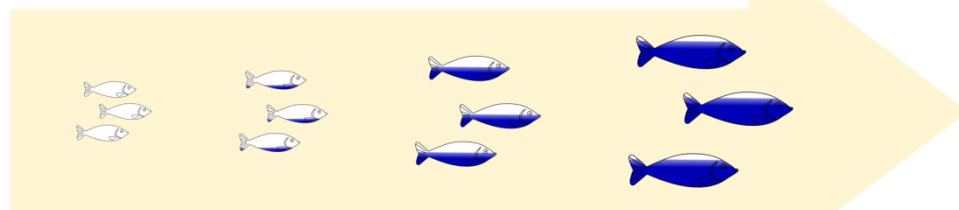
## Bioaccumulation

Compound accumulation (all routes of exposure)

**BAF** – Bioaccumulation factor

$$\text{BAF} = \frac{\text{Concentration of HM in dry fish tissue (mg Kg}^{-1}\text{)}}{\text{Concentration of HM in rivulet water (mg L}^{-1}\text{)}}$$

## Bioaccumulation



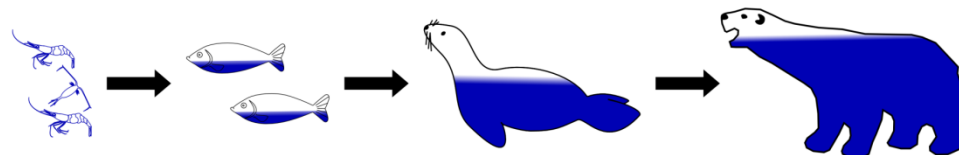
● Contaminant Levels

T I M E

## Biomagnification

Increasing concentration of compounds in organisms via food chain

**BMF** – Biomagnification factor ( $C_{\text{predator}}/C_{\text{food}}$ )

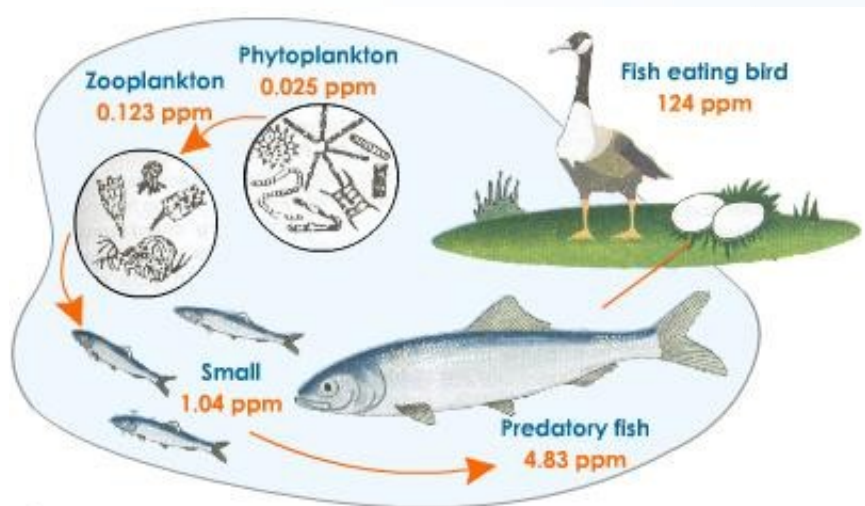


● Contaminant Levels

**Biomagnification**



# Biomagnification






Process of Biological Magnification;  
DDT concentrations increase in organisms along the food chain






Centrum pro výzkum  
toxických látek  
v prostředí



(a) Freshwater Lakes in Southern Sweden

			
	<b>phytoplankton</b>	<b>zooplankton</b>	<b>juvenile fish</b>
PCB 153 (7.1)	60 (25 - 170)	48 (25 - 125)	180 (90 - 500)

(b) Fjord in Northern Norway

			
	<b>sandeel (whole fish)</b>	<b>cod (liver)</b>	<b>seal (blubber)</b>
$\Sigma$ DDT (7.6 - 7.9)	60 (30 - 130)	200 (100 - 470)	2000 (600 - 7800)
PCB 153 (7.1)	25 (10 - 60)	95 (45 - 300)	1200 (550 - 2800)
HCB (5.1)	4 (2 - 8)	60 (40 - 70)	95 (90 - 100)
$\Sigma$ HCH (3.8)	40 (25 - 60)	30 (20 - 40)	65 (5 - 200)

(c) Bobio River in Chile

		
	<b>various fish</b>	<b>various water birds</b>
$\Sigma$ DDT (7.6 - 7.9)	890 (480 - 1340)	1570 (970 - 2350)
PCB 153 (7.1)	80 (50 - 130)	550 (400 - 700)
HCB (5.1)	25 (10 - 35)	50 (25 - 75)
$\Sigma$ HCH (3.8)	150 (80 - 360)	45 (24 - 94)

Average values of lipid-normalized concentrations (ranges in parentheses) of some organochlorine compounds: PCB153,  $\Sigma$ DDT = *o,p*-DDT + *p,p*-DDT = *o,p*-DDE + *p,p*-DDE,  $\Sigma$ HCHs =  $\alpha$ - +  $\beta$ - +  $\delta$ -hexachlorohexane, and HCB = hexachlorobenzene in organisms belonging to some food chains ( $\log K_{ow}$  values are given in parentheses after the compound names). All concentrations are expressed in  $\mu\text{g}/\text{kg}^{-1}$  lip. (a) Planktonic food webs in 19 lakes in Southern Sweden (Berglund et al., 2000). The average lipid contents were 5.4, 8.8, and 6.6% for the phytoplankton, zooplankton, and fish. (b) Local marine food chain in a fjord in Northern Norway (Ruus et al., 1999) (c) Fish and fish-eating water birds from the Santa Barbara location, Bobio River, Chile (Focardi et al., 1996)

# ATMOSPHERE / WATER partitioning



# ATMOSPHERE / WATER partitioning

- ionized compounds do not evaporate into the atmosphere
- significant partitioning (again) at **organic neutral compounds**
- partitioning between water- and liquid phase is described by the **Henry's law**:

$$p = H \cdot C_w$$

$p$  – partial pressure of a compound (Pa)

$H$  – Henry's law constant ( $\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ ) – *characteristic for a specific compound*

$C_w$  – concentration in water ( $\text{mol} \cdot \text{m}^{-3}$ )

*Note: boiling point of a specific compound is a measure of volatility*

H ( $\text{Pa} \cdot \text{mol}^{-1} \cdot \text{m}^{-3}$ )	Description
> 100	Very fast released from water Example: halogenated aliphatic hydrocarbons ( <b>dichloroethane</b> and such)
25-100	Volatilization slower Example: <b>chlorinated benzenes</b>
1-25	Sow volatilization Example: <b>most of the PCBs</b>
< 1	Insignificant volatilization Example: <b>high chlorinated PCDDs</b>



# Environmental transformation / Persistence



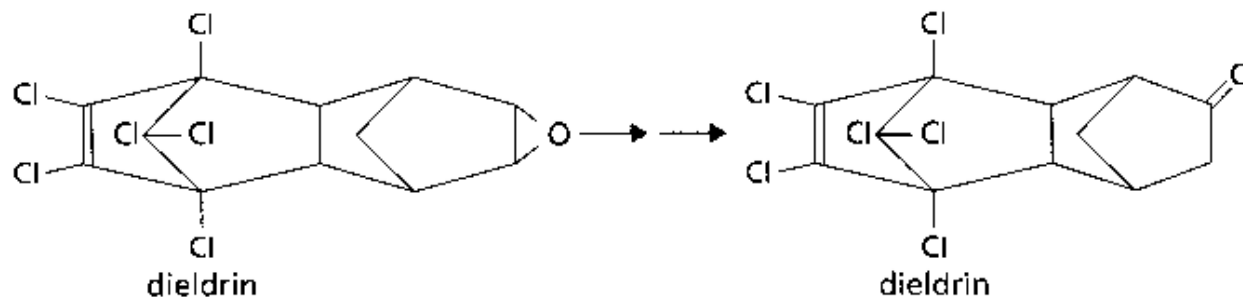
# Environmental transformation – (bio)transformation

- **Types of transformation of organic compounds:**
  - partial structural change (e.g. introduction of OH into neutral fatty acids)
  - degradation into smaller organic molecules
  - total degradation of the org. compound (CO<sub>2</sub>, H<sub>2</sub>O)
- **Main processes**
  - **Chemical** – regarding the type of the environment
    - atmosphere – photochemical reactions, reactions with oxygen (!)
    - water – hydrolysis, oxidations
    - anoxic environment (sediments, ground water) – reductions
  - **Biotic (enzymatic)**
    - **Ready biodegradability**
      - compound serves as a carbon source to microorganisms → CO<sub>2</sub> production
    - **Cometabolism**
      - microorganisms require other (main) C source (compound transformation as a part of „ancillary/other“ processes)
- **Result of transformation**
  - nontoxic products
  - production of even more toxic products (! e.g. Hg → methyl-Hg)
- **Biodegradability vs Persistence**
  - Polar and reactive compounds – mostly short half-life
  - Halogenated, neutral compounds – persistent in the environment

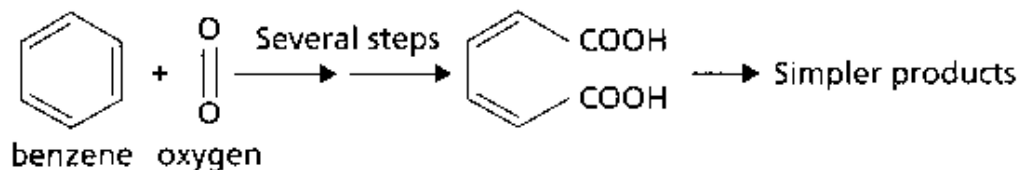


# Simple transformation processes (with oxygen supply)

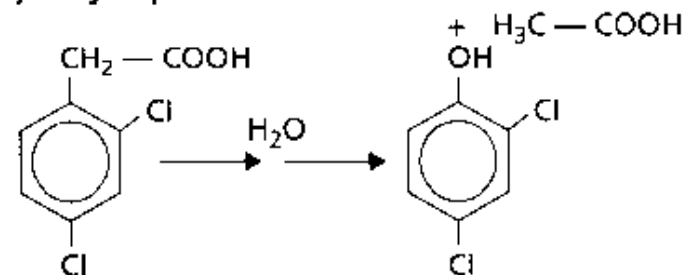
## Transforming process



## Transforming process



## Hydrolysis process



2, 4-dichlorophenyl  
acetic acid

**Fig. 3.6** Some transformation and degradation patterns for chemicals discharged to the environment.



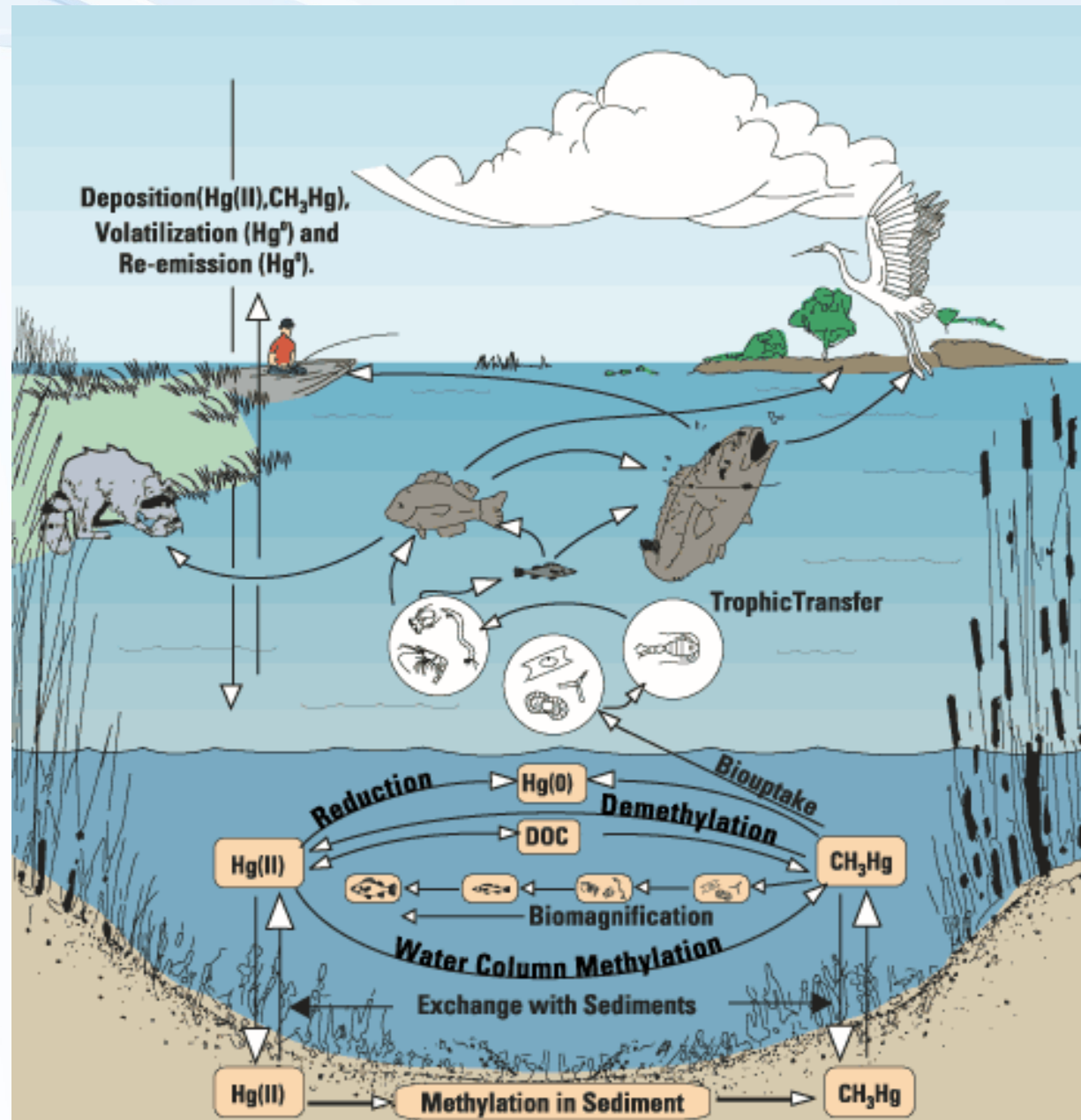
# ANAEROBIC (no oxygen) biotransformation – example methylmercury

## Me-Hg

- Bioaccumulation
- High toxicity

## Look on web for

- MINAMATA disease
- CONVENTION





# Persistence characterisation – half-life

- Transformation kinetics – first order kinetics

- $C_t = C_0 \cdot e^{-kt}$

- $C_t$  – concentration in time  $t$

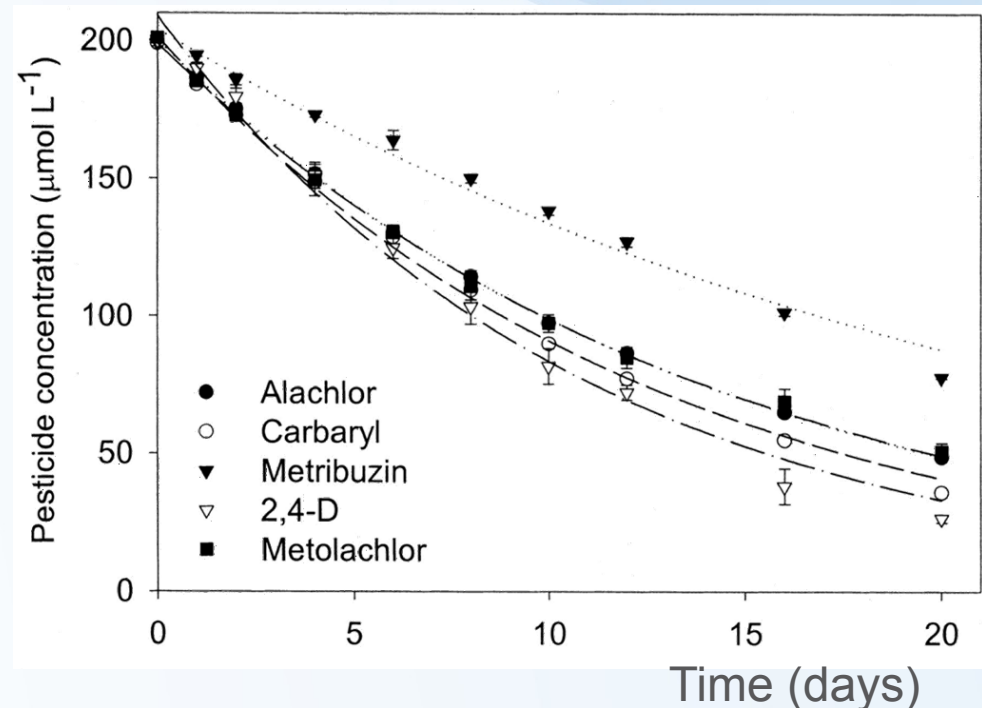
- $C_0$  – initial concentration

- $k$  – constant (degradation speed)

- $t$  – time

- After derivation (half-life)

- $t_{1/2} = \ln 2 / k = 0.693 / k$



## Half-life of selected pesticides in soil - examples

Compound	Half-life in soil (years) <i>(t<sub>1/2</sub> or DT50 – disappearance time 50%)</i>
<b>Chlorinated compounds</b>	
DDT	3-10
Dieldrin	1-7
Toxaphene	10
<b>Organophosphate – chlorfenos</b>	0,2
<b>Carbamate – carbofuran</b>	0,05 – 1

# Degradation assessment in praxis (standards) OECD recommendation – guideline 307

- Aerobic and Anaerobic Transformation in Soil
  - Introduction of examined compound (can be radioactively labelled)
  - Incubation in time
    - soil extraction (volatile fraction)
    - assessment of decrease in concentration of compound and transformation products for  
→ Chemical methods (GC, LC etc.)

## Example of standardized OECD guideline

Anaerobic Biodegradation Experiment see YOUTUBE  
[http://www.youtube.com/watch?v=Y\\_zFPkbrwSY](http://www.youtube.com/watch?v=Y_zFPkbrwSY)



Fate (processes) in the environment → Exposure  
→ BIOAVAILABILITY



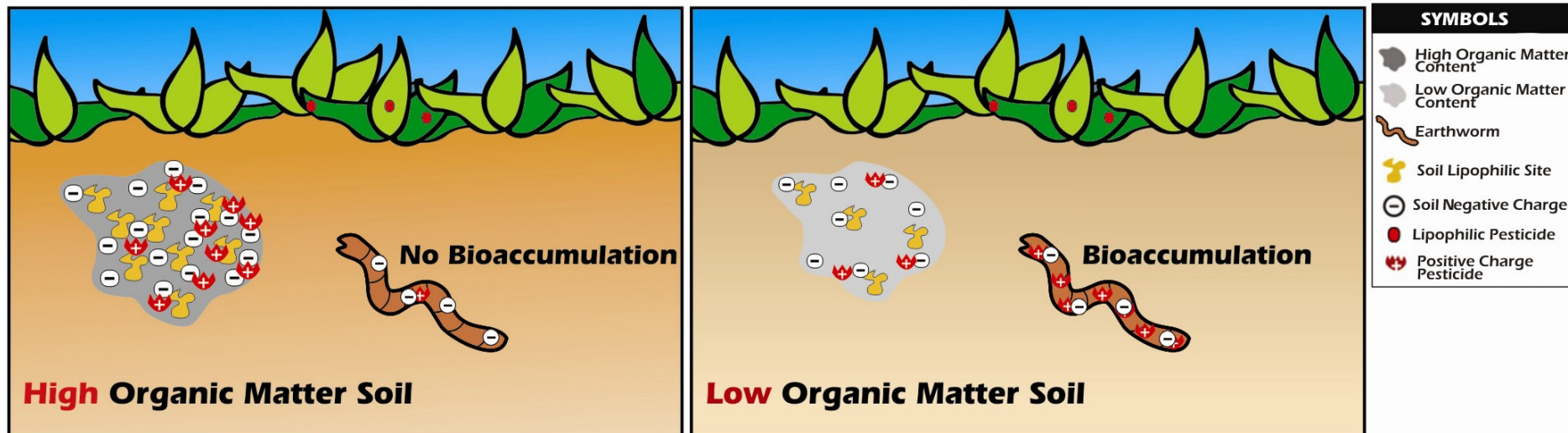
# BIOAVAILABILITY

- **The term comes from pharmacology**
  - compound fraction that is effective in the body
- **In environmental sciences**
  - compound fraction, that can enter the organism = compound is in available form (it is not bound in the environment – e.g. to organic carbon etc.)
- **Bioavailability describes processes (relations) between**
  - Compounds present in the environment
  - Entry (accumulation) of compounds into the organisms
  - Environmental properties

## Example - Soil

two distinct soils (high and low organic carbon content)

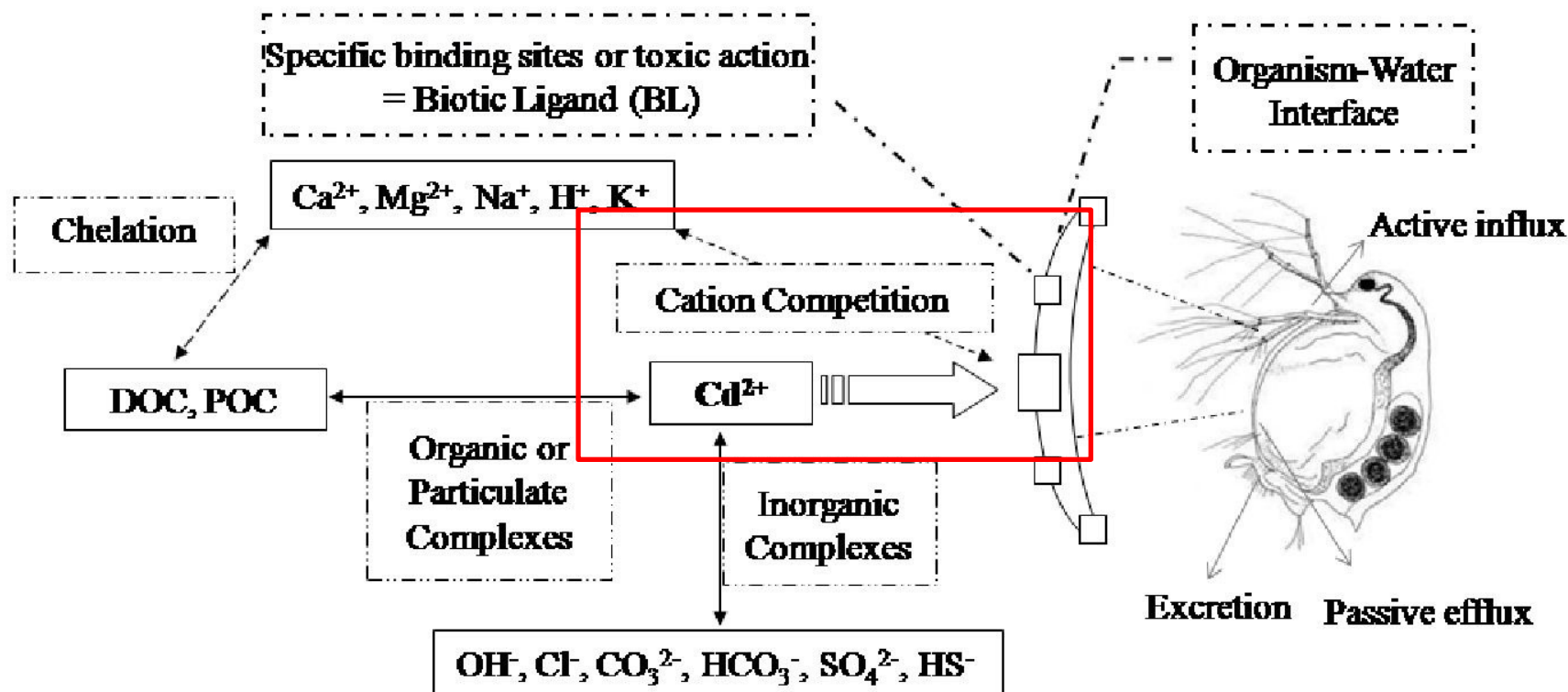
bioavailability (and thus bioaccumulation as well) is higher in the case of “low”



# Bioavailability - examples

## Toxic metals in waters vs. water hardness

-> **higher water hardness (more Ca / Mg) – lower bioavailability / lower metal toxicity**  
(competition with toxic metals for binding sites in biota)

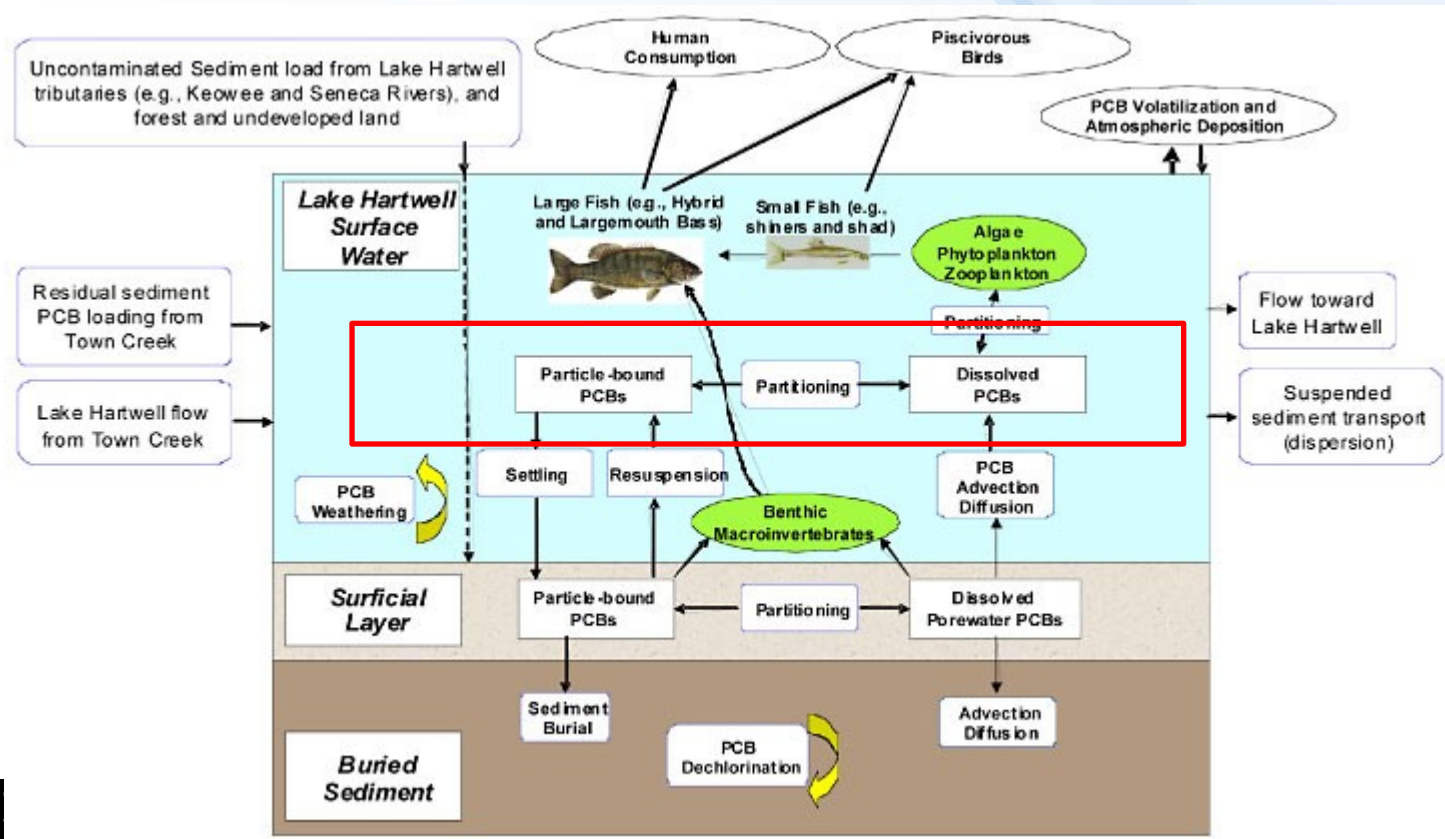


# Bioavailability - examples

## Hydrophobicity – organic compounds vs. organic carbon (humins)

-> hydrophobic compounds – tendency to accumulate in fat / in biota  
(at the same time also in dead organic matter - OC)

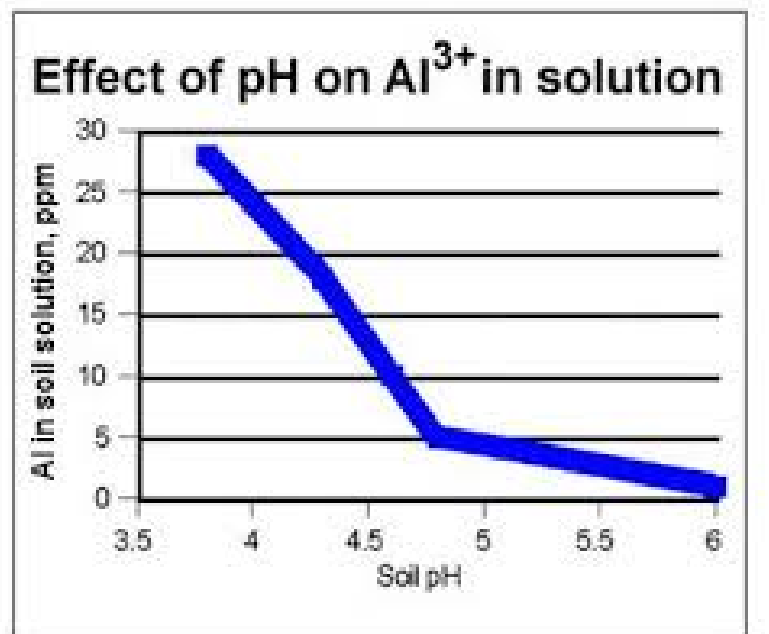
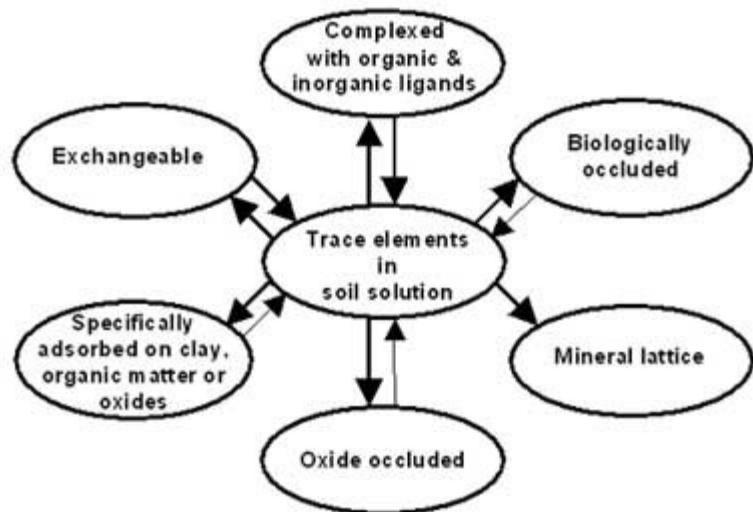
-> **high OC content in the environment (in water): lower bioavailability of compounds**



# Bioavailability - examples

## Toxic metals in water vs. pH / water composition

- > higher pH: metals present in insoluble hydroxides (lower bioavailability)
- > **lower (acidic) pH – higher solubility and higher toxicity of metals**





Where can the information on environmental properties be found?  
( $K_{ow}$ ,  $t_{1/2}$  etc.)



- **CAS – Chemical Abstract Services**
  - Provided/Operated by American Chemical Society (ACS)
  - CAS Number – unique identifier
- **eChemPortal.org**



Print

English ▾

The Global Portal to Information on Chemical Substances



eChemPortal ▾

› Home

› Substance Search

› Property Search

› What's new?

› General Information

› Participating Databases

› Roles & Responsibilities

## Substance Search

Substance Search

Search Result Step 1

Search Result Step 2

### *Search history*

- You searched for  
Name: limonen\*



Centrum pro výzkum  
toxických látek  
v prostředí

## SUMMARY – questions 1/3

Describe what are toxicants, ecotoxicants, toxins, and give examples.  
What are the main sources of toxic compounds in the environment? Provide an overview.

Which human activity releases into the environment the most polychlorinated biphenyls, polychlorinated dioxins, polycyclic aromatic hydrocarbons?

What is the main source of household chemistry (soaps, perfumes), pharmaceuticals for the environment?

What compounds are released into the environment from areal pollution sources?

Give examples – source:compounds

What compounds enter the environment from point pollution sources? Give examples – source:compounds

What are pesticides? insecticides? herbicides? fungicides? rodenticides?  
carcinogens? reprotoxins? endocrine disruptors? organophosphates? pyrethroids?  
toxic metals?

Give example for each of the listed groups and describe the main features of the chemical structure (aromatic/aliphatic?, neutral/ionized?, halogenated?, hydrophilic or hydrophobic?, persistent or degradable?)

## SUMMARY – questions 2/3

What key properties make a compound dangerous (hazardous) for the environment?

What does the term “environmental fate of compounds” define/describe?

Describe the main processes a compound can undergo in the environment and name the compound's properties (features) key for these processes.

What properties play a key role in entering of a chemical compound into the organism?

What is bioconcentration? What compound's property does it depend on?

What is  $K_{ow}$ ? How can it be determined experimentally?

Which compound has higher  $K_{ow}$  - hexane OR hexanol?

Which compound has higher Henry's law constant - dichloromethane or dichlorobenzene?

What is biomagnification? Give an example of a compound that can be biomagnified and what levels does its BMF reach?

What is bioavailability? Give examples of different scenarios, when the bioavailability of a selected compound would be very high and very low.

The DDT concentrations in a river were determined as follows: (1) DDT bound to suspended particles 1 milligram/L water, (2) DDT dissolved in water 1 microgram/L water. What fraction (%) of DDT is approximately directly bioavailable for transfer through fish gills?

## SUMMARY – questions 3/3

Which element plays a crucial role in chemical transformations of compounds in soil environment?

What major transformation processes do compounds undergo in different environmental matrices (air, soil, water, sediments)?

Define the half-life of a compound. Give examples of compounds with short and long half-life. How long are half-lives of these compounds?

How is the biodegradability of a chemical compound determined in practice?

How would the half-lives of benzo[a]pyrene (BaP) differ in the following scenarios? BaP bound to aerosol particles in the air, BaP bound to sediment on the bottom of a water reservoir/pond.

The concentration of triazine in soil is 120 mg/kg and the DT50 is 180 days. When can we expect the decrease of triazine to 10 mg/kg?

