MUNI | RECETOX

Chemical compounds in ecosystems
– introduction –

Luděk Bláha, SCI MUNI

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) are the most important and affect the **behavior** of compounds in the environment ($\log K_{ow}$, H, persistence)…
- … and thus affect the **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

- Different classes of compounds, a wide range of chemical substances (petroleum and its products – organic compounds, pharmaceuticals, pesticides, metals etc.), 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 …

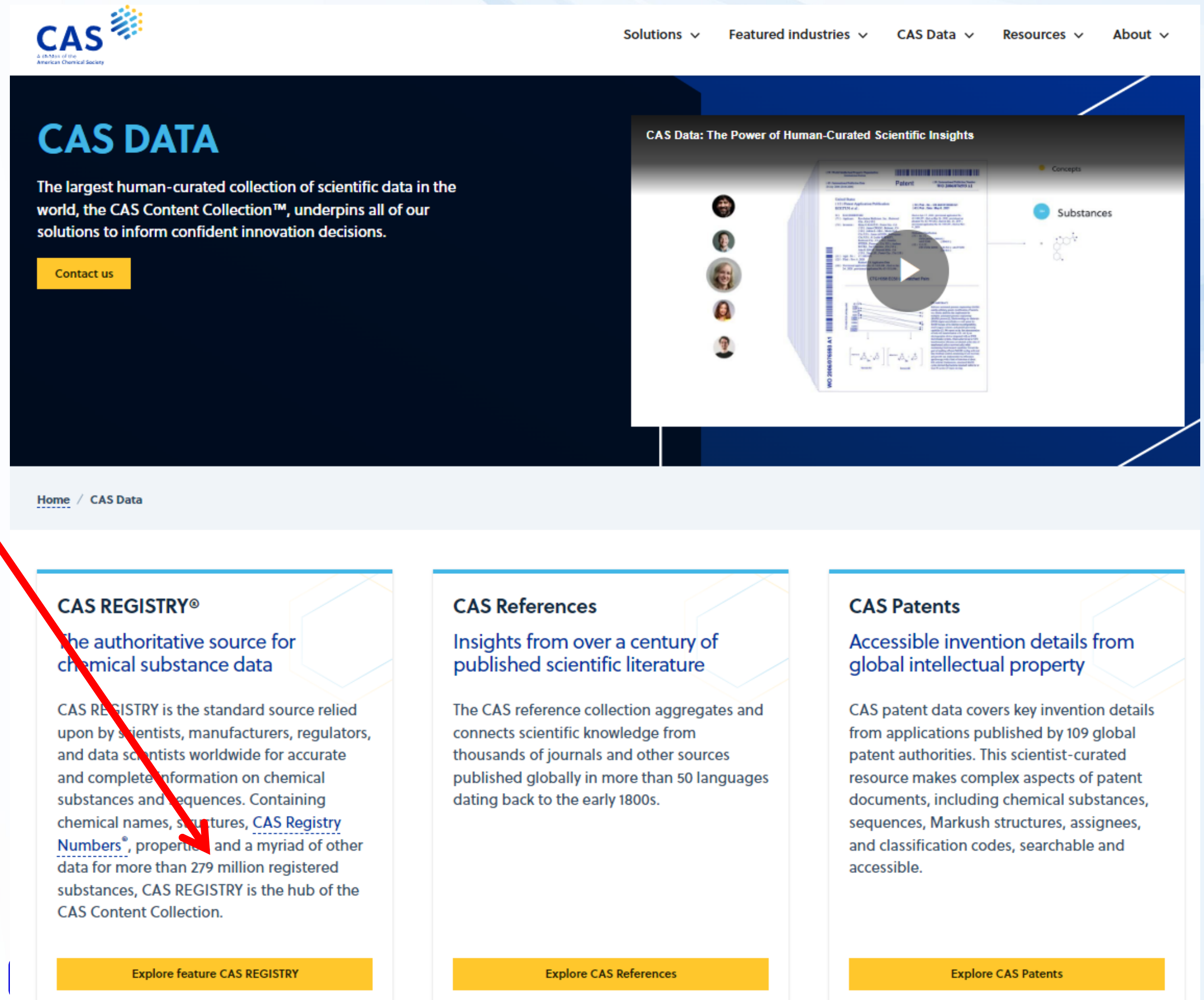
Ecotoxicants vs. Contaminants ?

- **Contaminants**
- Compounds polluting the environment
  (Not necessarily directly toxic … but may be harmful at the end)

  - ! nutrients (NOx and POx)
    - are not ecotoxicants BUT do have many secondary effects
      → eutrophication
  - ! organic municipal 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 do we know?

https://www.cas.org/cas-data/cas-registry

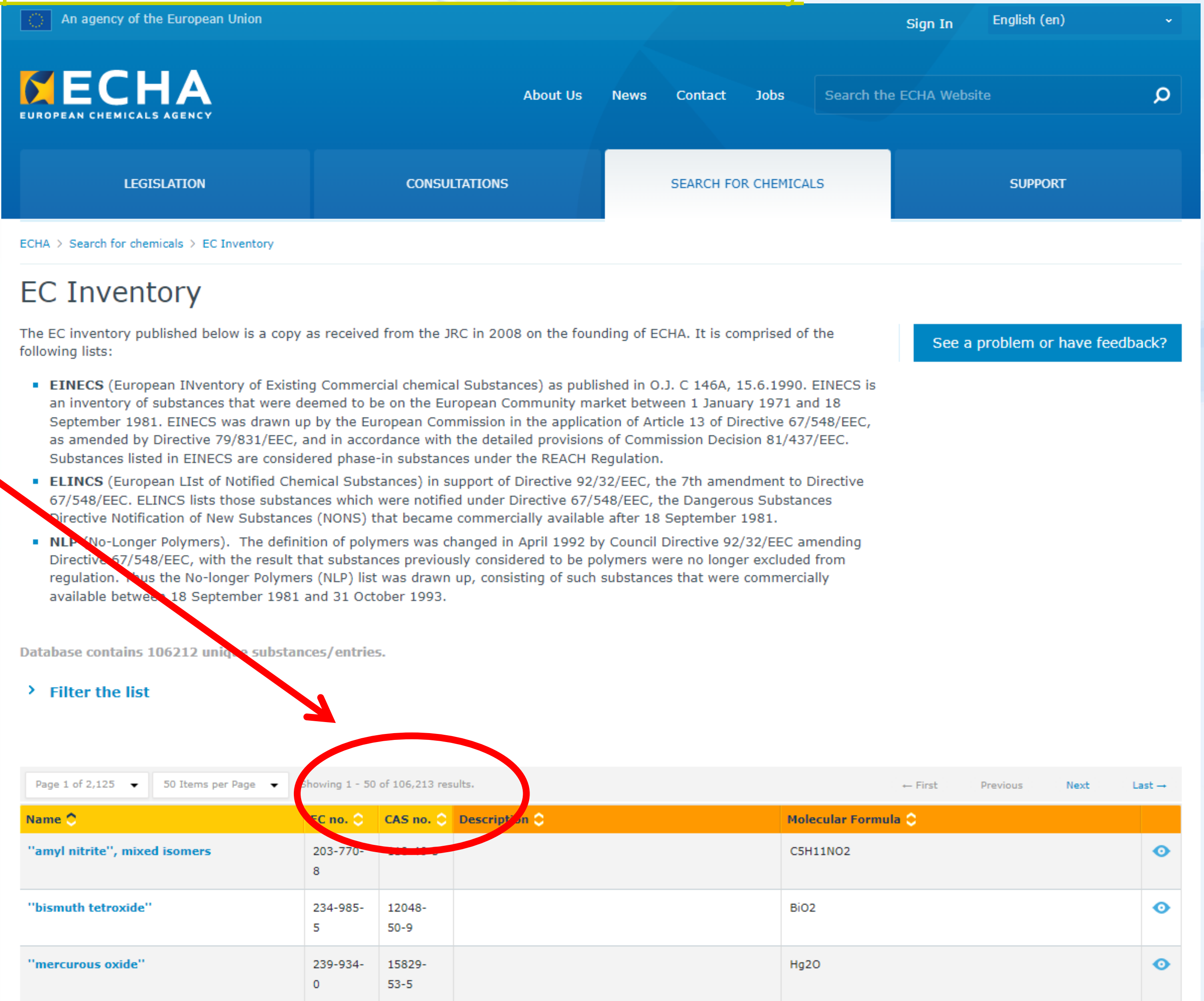


CAS
A division of the American Chemical Society

What numbers of CHEMICALS ?

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

Ca 0,03%, i.e. „only“ **100 000** are used in practice



An agency of the European Union

Sign In English (en)

ECHA EUROPEAN CHEMICALS AGENCY

About Us News Contact Jobs

Search the ECHA Website

LEGISLATION CONSULTATIONS SEARCH FOR CHEMICALS SUPPORT

ECHA > Search for chemicals > EC Inventory

EC Inventory

The EC inventory published below is a copy as received from the JRC in 2008 on the founding of ECHA. It is comprised of the following lists:

See a problem or have feedback?

- **EINECS** (European INventory of Existing Commercial chemical Substances) as published in O.J. C 146A, 15.6.1990. EINECS is an inventory of substances that were deemed to be on the European Community market between 1 January 1971 and 18 September 1981. EINECS was drawn up by the European Commission in the application of Article 13 of Directive 67/548/EEC, as amended by Directive 79/831/EEC, and in accordance with the detailed provisions of Commission Decision 81/437/EEC. Substances listed in EINECS are considered phase-in substances under the REACH Regulation.
- **ELINCS** (European LIst of Notified Chemical Substances) in support of Directive 92/32/EEC, the 7th amendment to Directive 67/548/EEC. ELINCS lists those substances which were notified under Directive 67/548/EEC, the Dangerous Substances Directive Notification of New Substances (NONS) that became commercially available after 18 September 1981.
- **NLP** (No-Longer Polymers). The definition of polymers was changed in April 1992 by Council Directive 92/32/EEC amending Directive 67/548/EEC, with the result that substances previously considered to be polymers were no longer excluded from regulation. Thus the No-longer Polymers (NLP) list was drawn up, consisting of such substances that were commercially available between 18 September 1981 and 31 October 1993.

Database contains 106212 unique substances/entries.

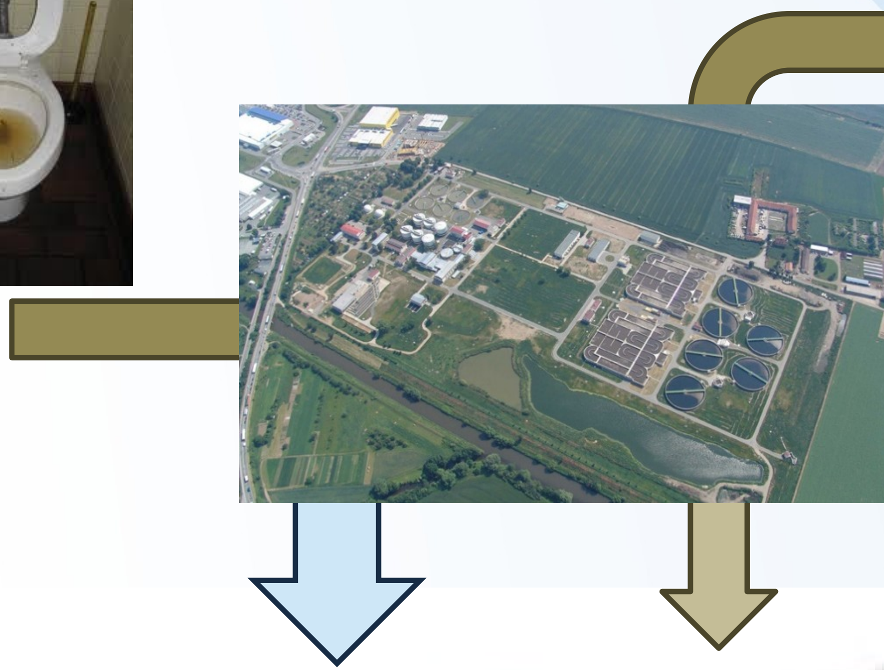
> Filter the list

Page 1 of 2,125 | 50 Items per Page | Showing 1 - 50 of 106,213 results. | ← First | Previous | Next | Last →

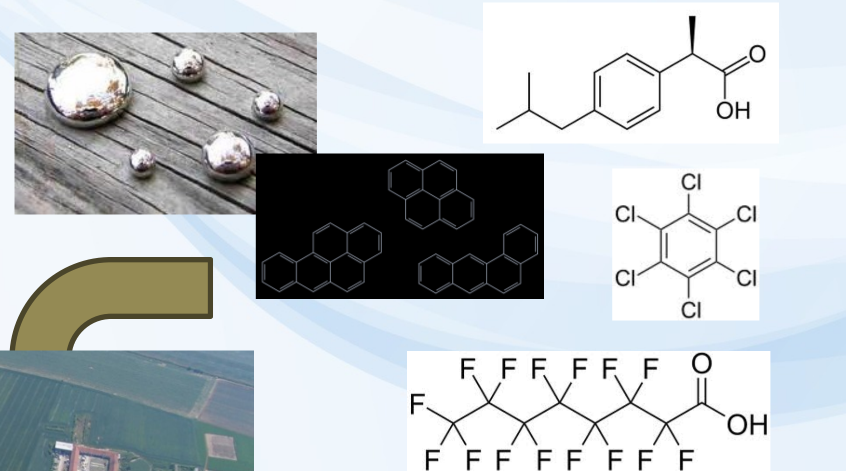
Name	EC no.	CAS no.	Description	Molecular Formula
"amyl nitrite", mixed isomers	203-770-8	[illegible]		C5H11NO2
"bismuth tetroxide"	234-985-5	12048-50-9		BiO2
"mercurous oxide"	239-934-0	15829-53-5		Hg2O

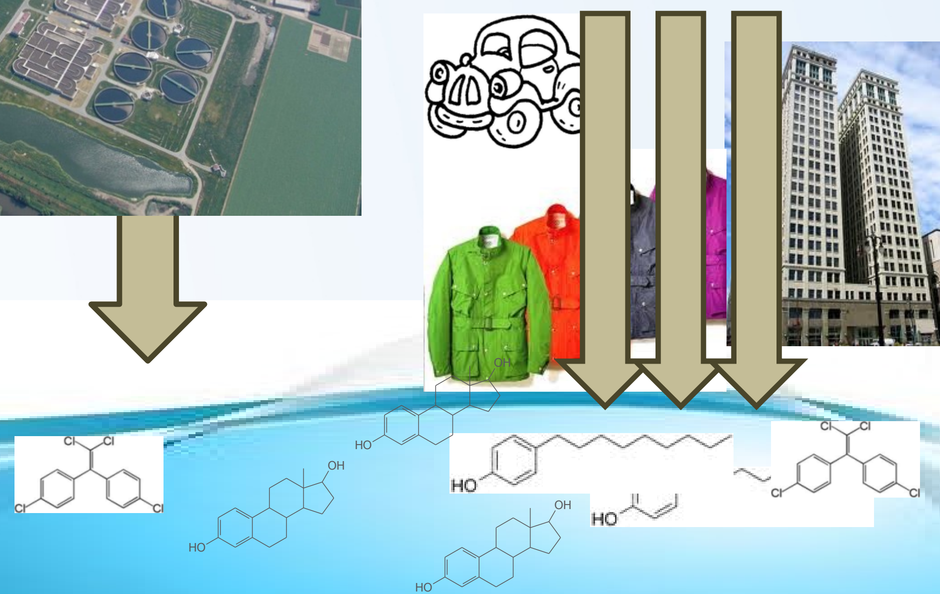
Contamination of water – what different chemicals ?

Degradable „nontoxic“
organic material
+ nutrients / fertilizers (N/P)

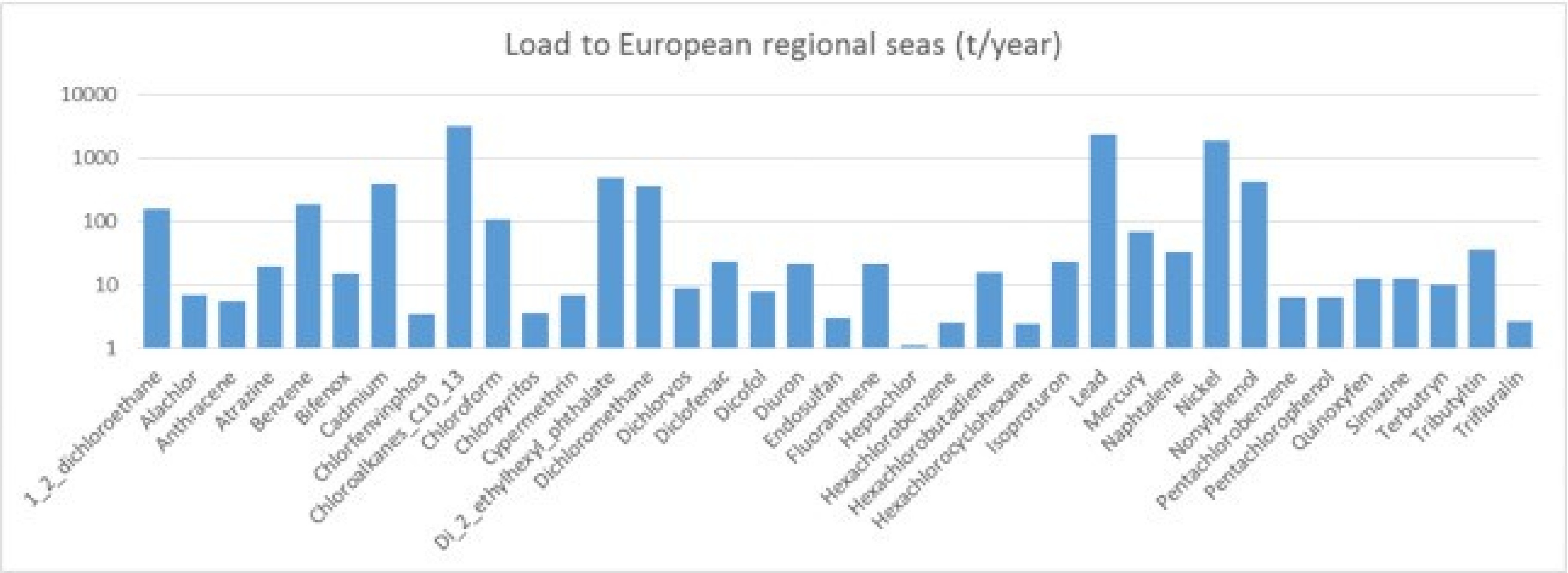


„Other“ chemicals





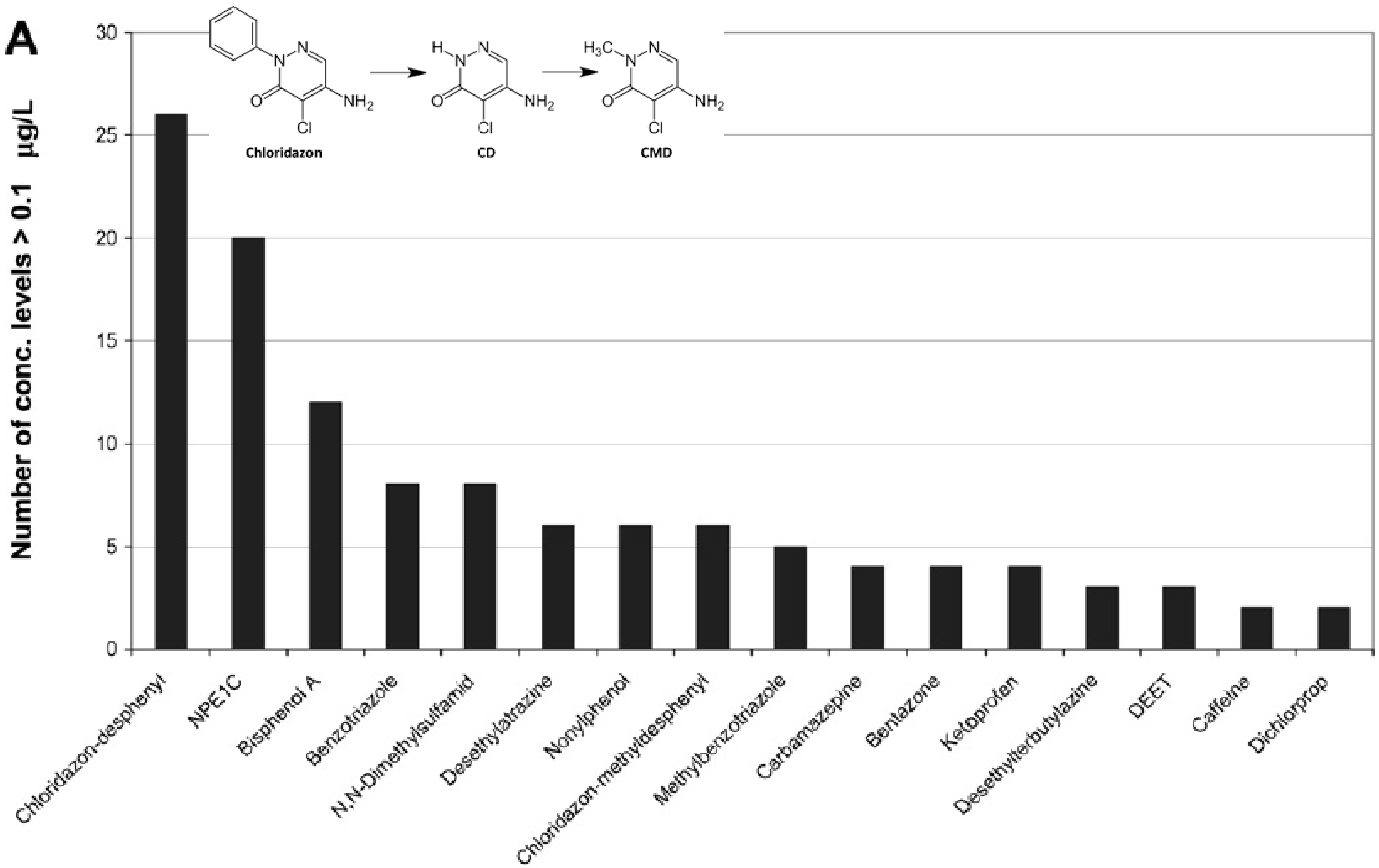
What chemicals for example? - PRIORITIZATION



EU Water Framework Directive – **36 priority** substances

https://www.sciencedirect.com/science/article/pii/S0048969718352471

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

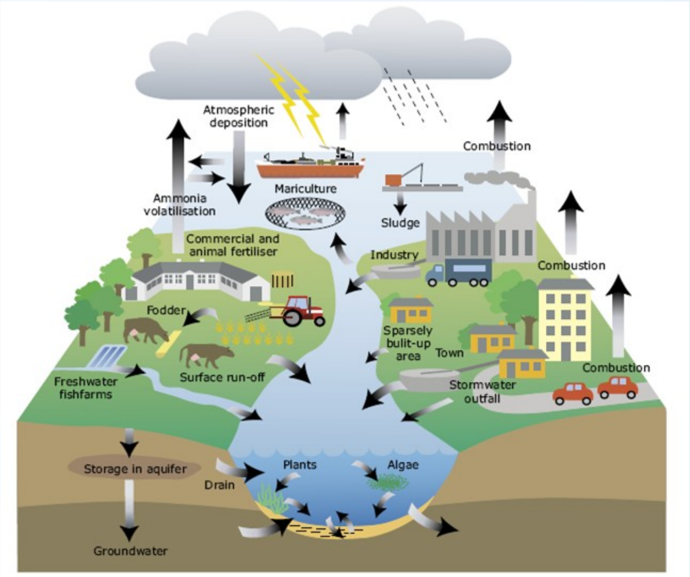


Loos et al. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water (Water Research 44, 2010, 4115-4126)

MUNI | RECETOX

Sources... and examples of representative contaminants

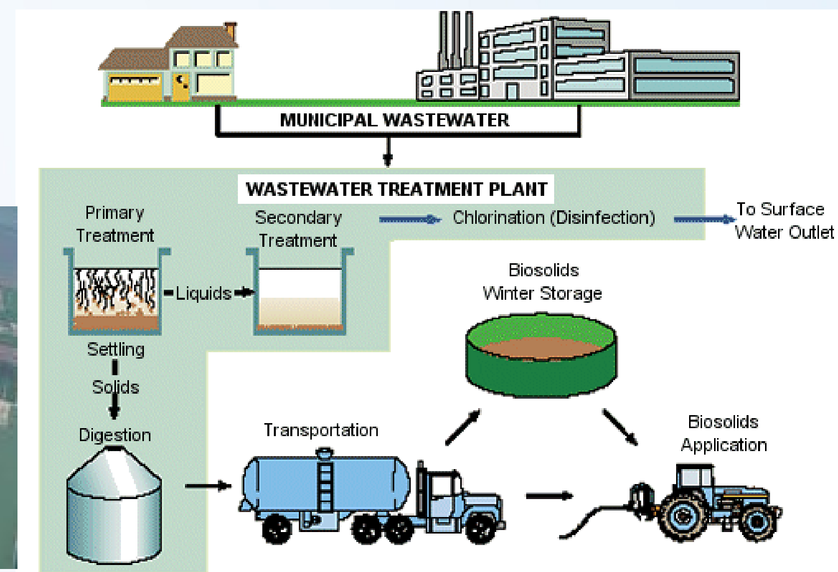
- **Overview of contamination sources**
  - *a student should have a general overview and be able to name representative examples*
  - POINT SOURCES (easier to control and penalize)
    - municipal (communal) wastewaters
    - industrial wastewaters
    - solid urban- and industrial wastes – damps / 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



Municipal (communal) wastewaters

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

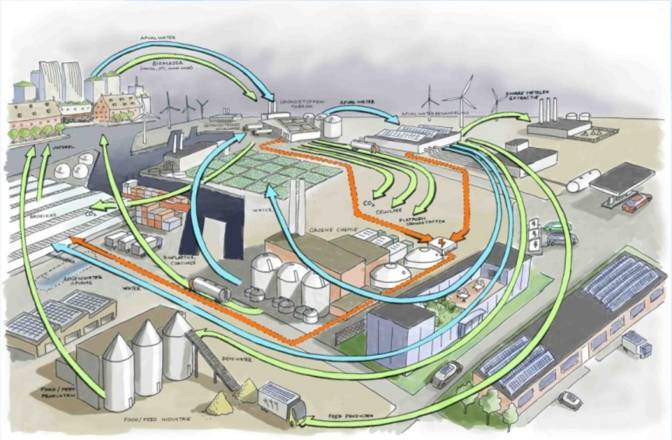
- **Significant contaminants**
  - Nontoxic organic compounds (fecal pollution)
  - **PPCP** (Pharmaceuticals and Personal Care Products)
    - Pharmaceuticals
    - Household chemicals (detergents, softeners, fragrances/musks)
  - Polycyclic aromatic hydrocarbons (PAHs)
  - Chlorinated compounds
  -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



Industrial wastewaters

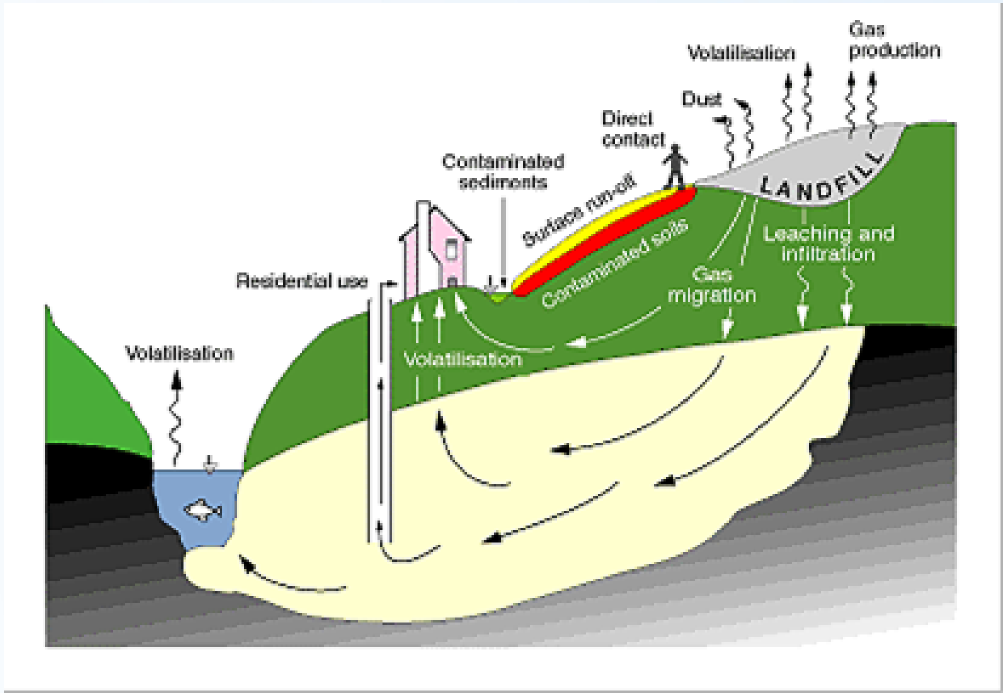
- **Effect on environmental components**
  - Primary **effect on water** ...

- **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)

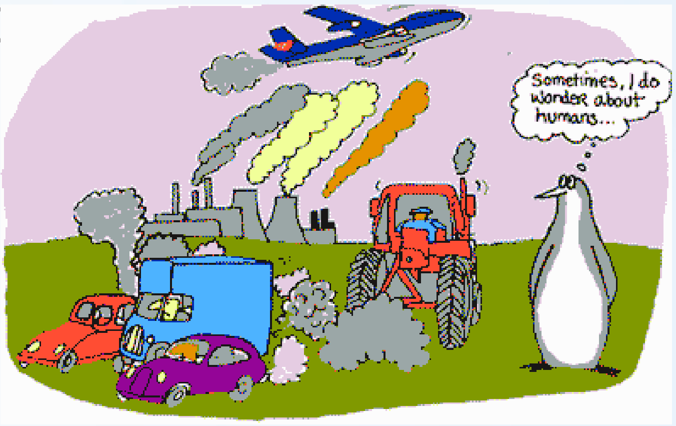


Industry, combustion engines, energy production

- **Effect on environmental components**
  - Diffuse pollution
  - Primary **effect on atmosphere** + on all ecosystems

- **Significant contaminants**
  - Toxic metals (e.g. Pb, Cd etc.)
  - CO, CO2
  - Polycyclic aromatic hydrocarbons (PAHs)
  - SOx, NOx
  - 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)

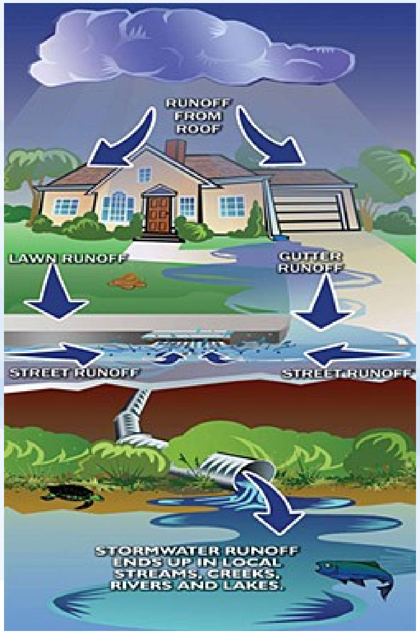


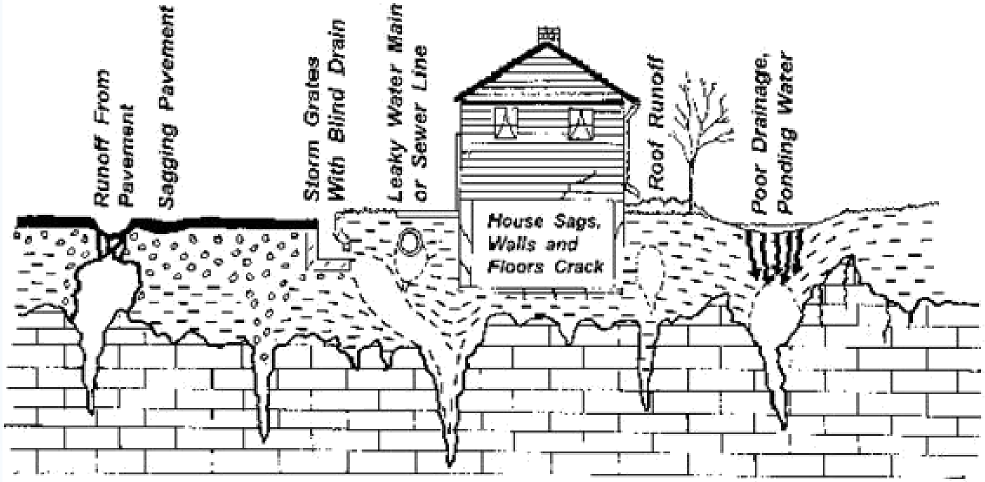
Surface run off

- **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)

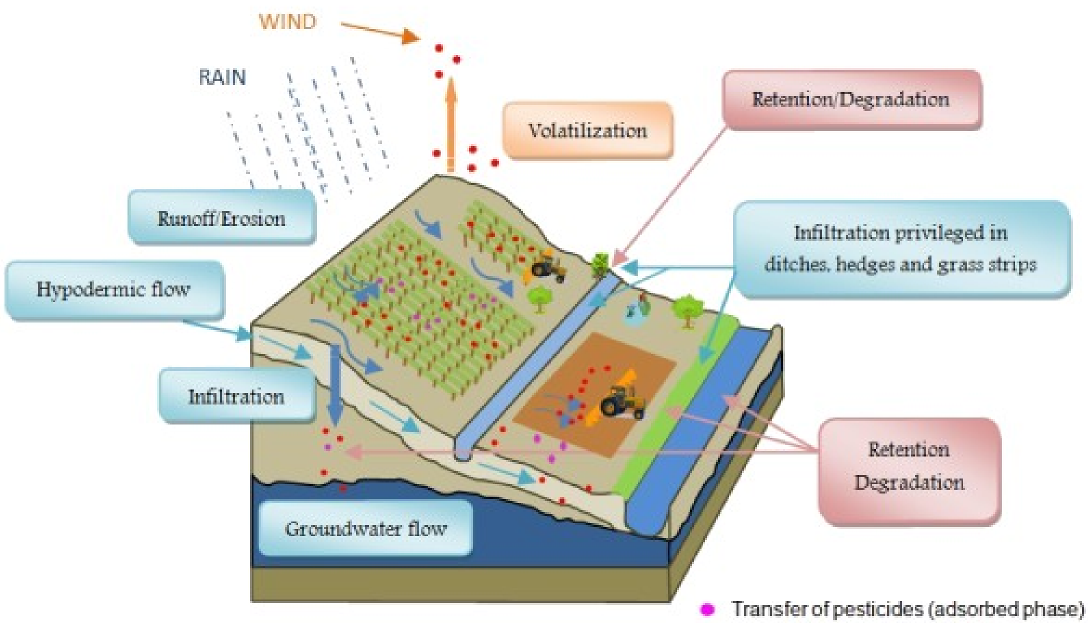




Agriculture

- **Effect on environmental components**
  - Diffuse pollution
  - Primary **effect on soil**... but indirectly also on all other env. components

- **Significant contaminants**
  - Pant Protection Products = PPPs (pesticides)
  - Fertilizers (N-, P-) and contaminants therein (often e.g. Cd)
  - Veterinary pharmaceuticals (→ application of manure)



Transfer of pesticides (adsorbed phase)
Transfer of pesticides (soluble phase)

Figure 1: Main pesticides transfers at the catchment area scale

MUNI | RECETOX

Main groups of pollutants
Important terms, abbreviations... and structures

Compounds grouped by effect

Pesticides *(Plant Protection Products: primarily agriculture use)*	Toxic for pests	DDT, parathion,atrazine glyphosate (RoundUp)
Biocides *(For household use)*	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

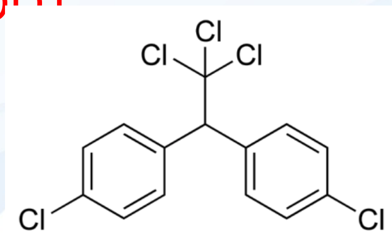
Lipophilic (hydrophobic)	Soluble in fat / low solubility in water	DDT
Hydrophilic	Soluble in water	Phenol, modern insecticides
Neutral organic compounds	Uncharged compounds (do not ionize)	DDT, PCB
Radioactive compounds	Unstable, decay and emit radiation	Radon
Surfactants, detergents	Compounds lowering 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 (**VOCs**)	Acetone, Benzene, Formaldehyde, Xylene Perchloroethylene, Toluene etc.

Significant compounds grouped by their structure

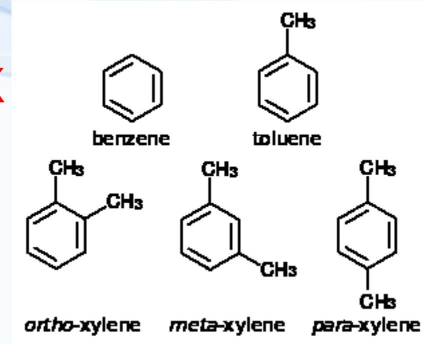
Chlorinated hydrocarbons, organochlorine compounds		DDT, PCB, PCDD/Fs
PCBs	Polychlorinated biphenyls	PCB153
PAHs	Polycyclic aromatic hydrocarbons	Benzo[a]pyrene
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and -furans	2,3,7,8-TCDD
Toxic metals, heavy metals		Hg, Pb, Cd (+ others)
Organometallics		Alkyl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

Student should be aware of the most important structural domains

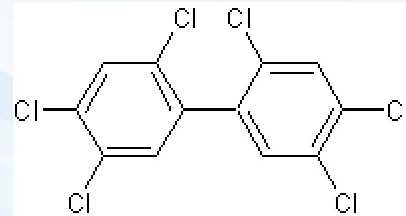
DDT



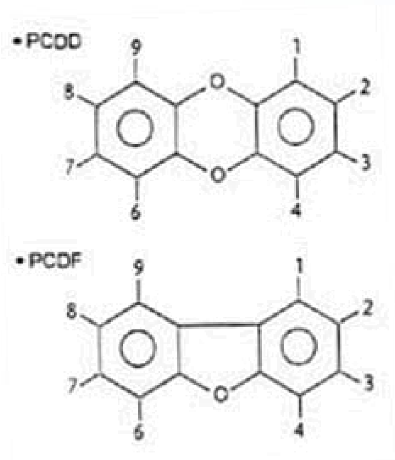
BTEX

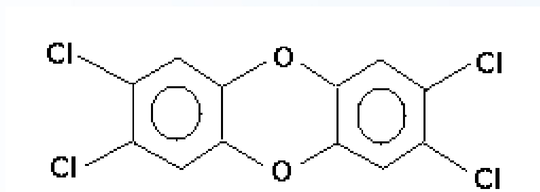


PCB153 (very abundant)



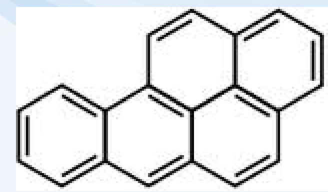
Polychlorinated dioxines and furans (PCDD/Fs)



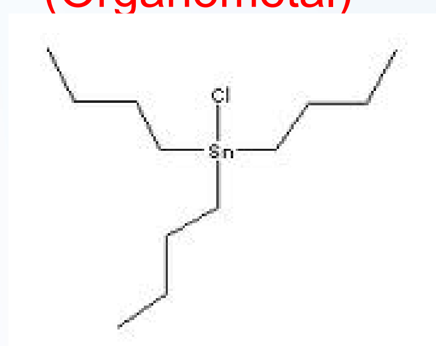


2, 3, 7, 8 - p - TCDD

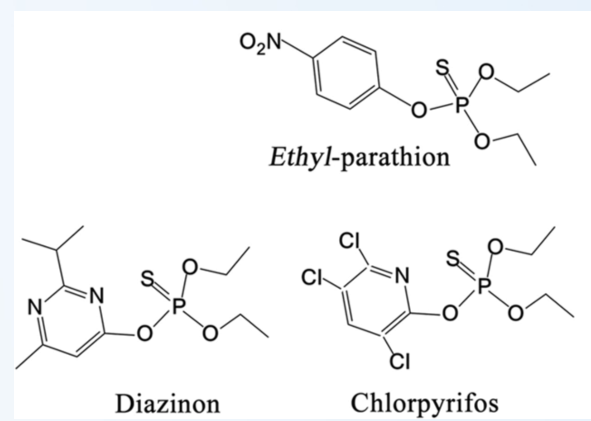
Benzo[a]pyrene – example of PAHs



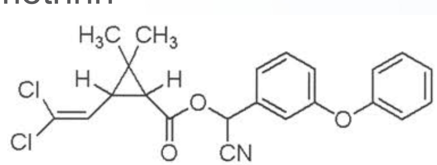
Tributyltin chloride (Organometal)



Organophosphates



Cypermethrin

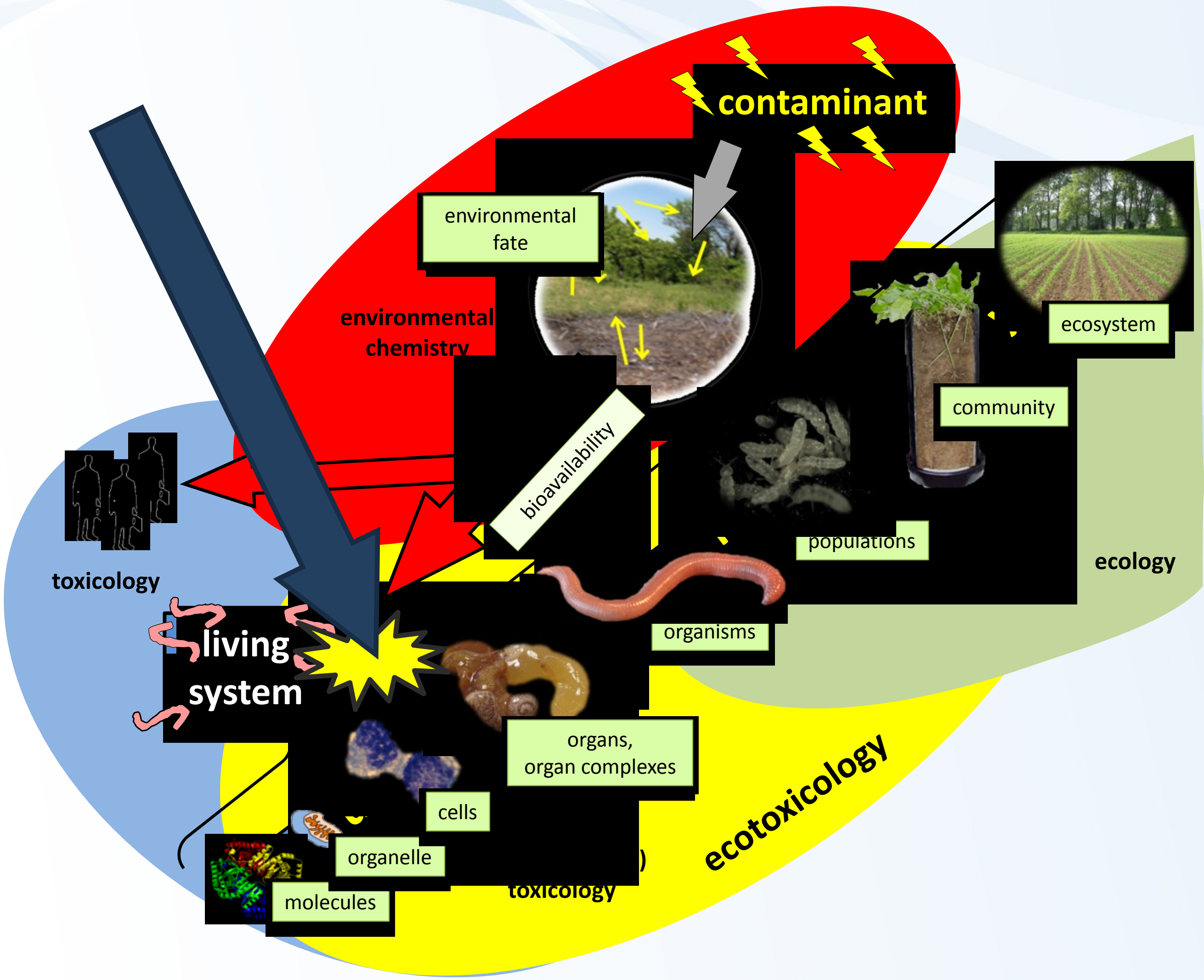


Further commont terms/abbreviations – groups of compounds

- **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
Exposure

Exposure



contaminant
environmental fate
environmental chemistry
bioavailability
ecosystem
community
populations
ecology
organisms
toxicology
living system
organs, organ complexes
cells
organelle
molecules
ecotoxicology
toxicology

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?

+

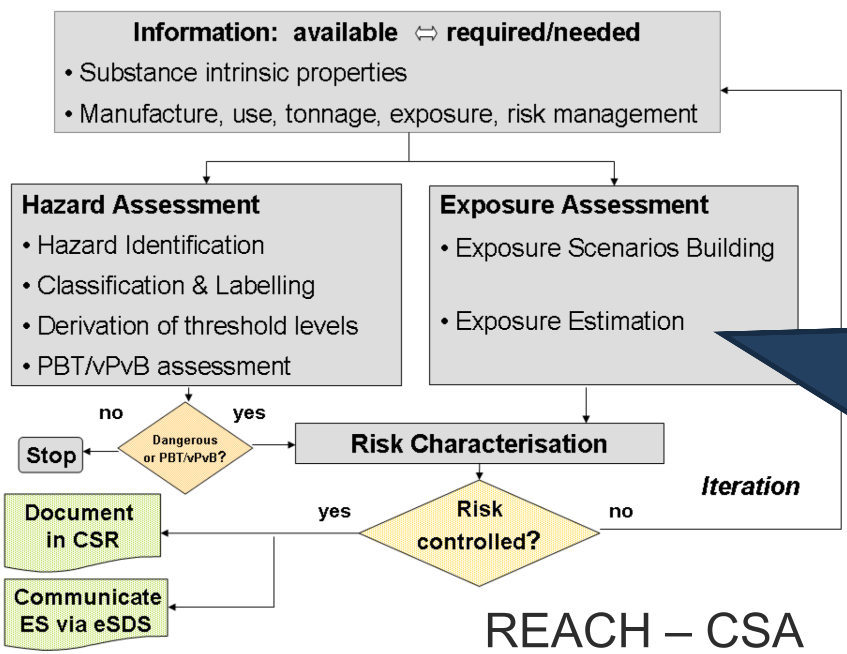
Situation in the environment
EXPOSURE

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)?

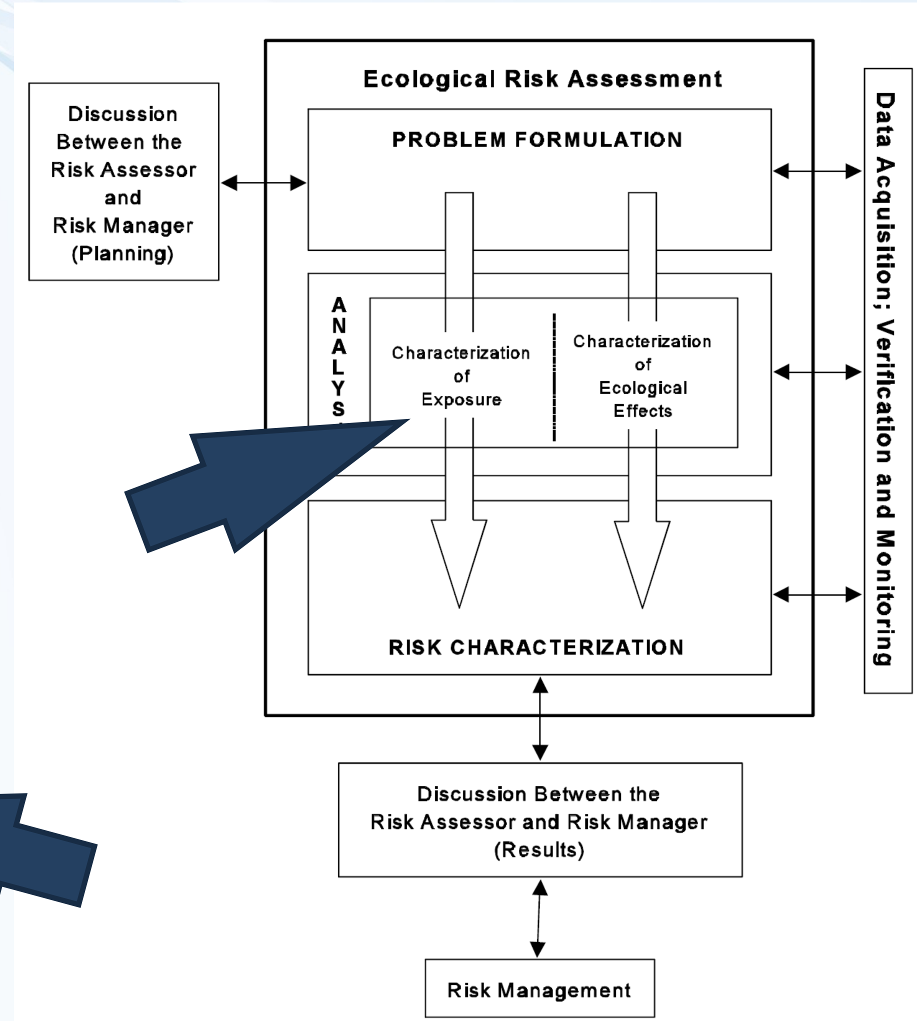
What is the bioavailable concentration?

Exposure characterization as a part of Risk Assessment

- **EcoRA** – ecological risk assessment
- **CSA** - chemical safety assessment (REACH)
- **ERA** – environmental risk assessment
- **HHRA** – human health risk assessment



REACH – CSA

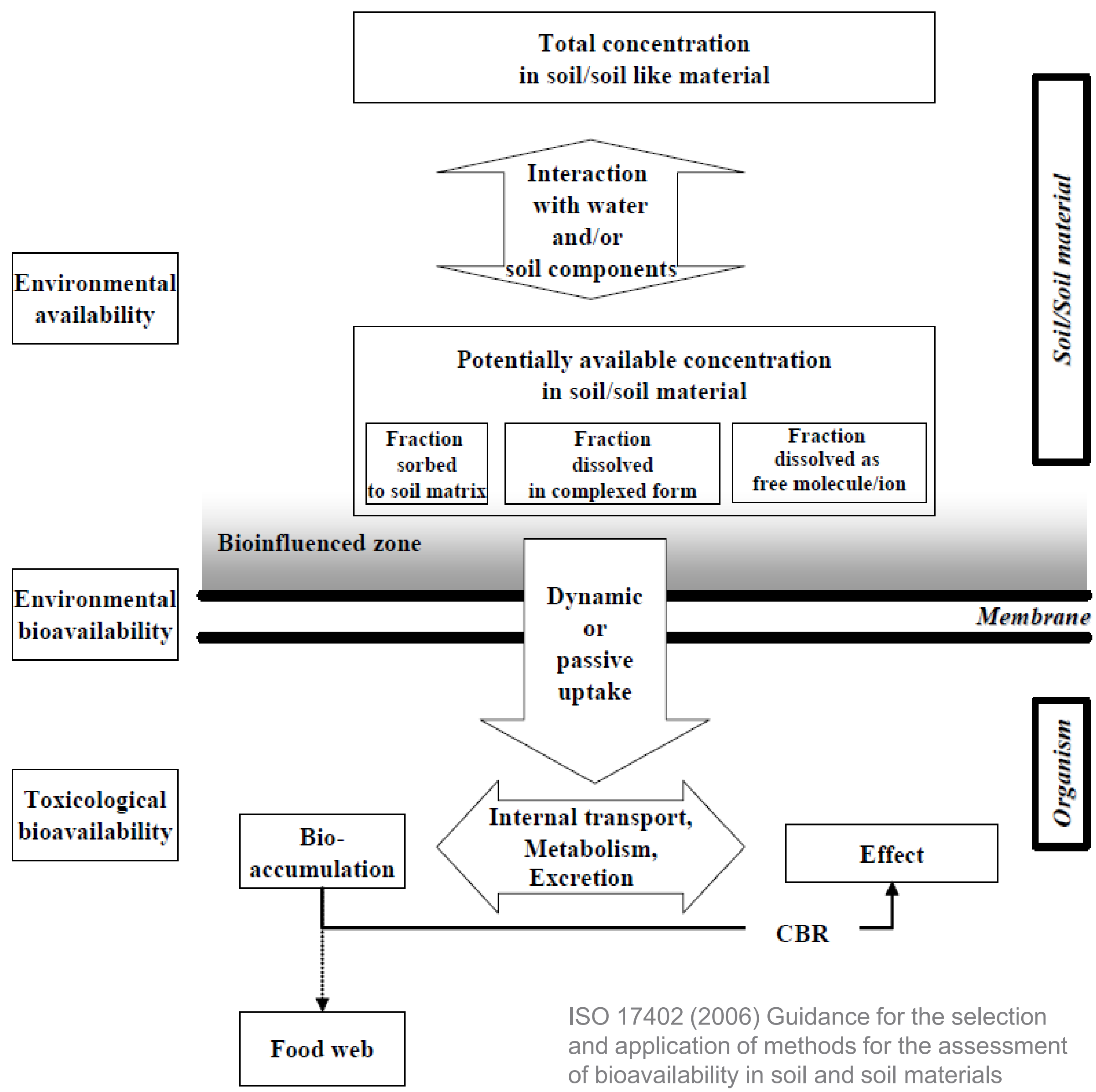


US EPA (1999) Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments

Exposure in ecotoxicology

- overlap with **environmental chemistry**
- exposure results from the **fate of the contaminant in the environment**, which cannot be ignored by ecotoxicology:
  - The fate affects general presence in the environment
    - change in total environmental concentration
    - change in distribution in different parts of the environment
    - change in the forms of occurrence of the substance (e.g. metals - speciation) and transformation
    - depends mainly on the properties of the substance and properties of the environment ([*Q to students – do you know some?*])
  - … and also specific bioavailability and bioaccessibility
    - binding to environmental compartments
    - limitation of uptake by organisms
    - depends on the properties of the substance, the environment but also on the properties of the organisms
      ([*Q to students – which organismal properties might be important?*])

Exposure in ecotoxicology



ISO 17402 (2006) Guidance for the selection and application of methods for the assessment of bioavailability in soil and soil materials

Environmental FATE of the compound determines the EXPOSURE

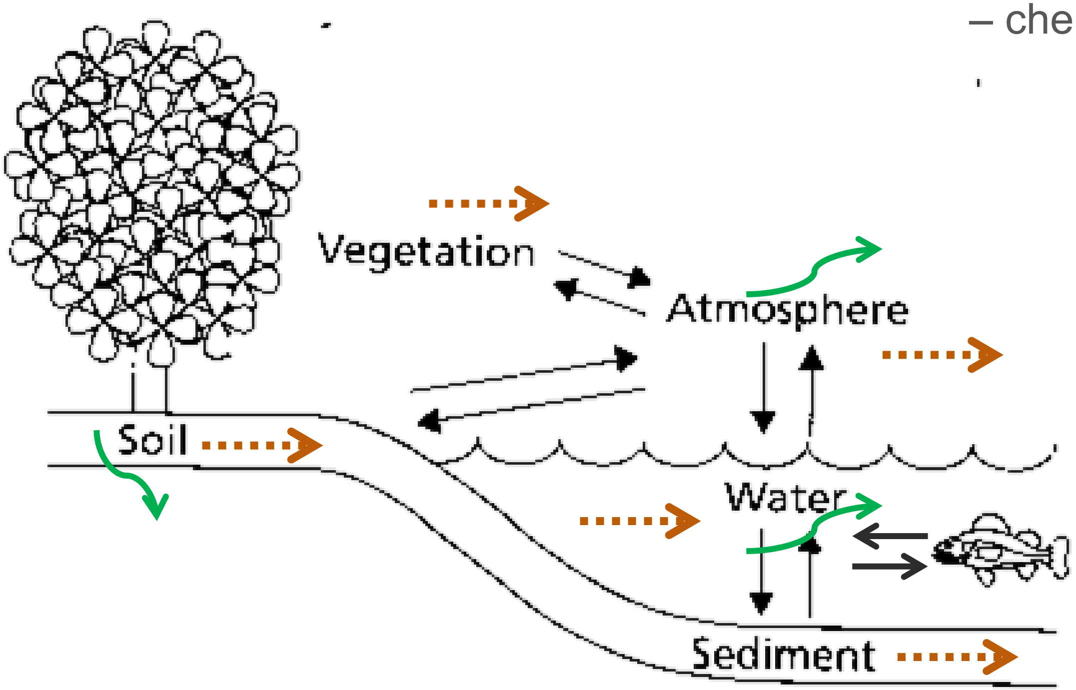
ENVIRONMENTAL FATE describes

? 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

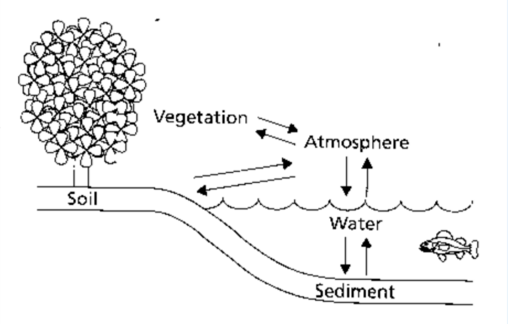
Extent of exposure of an organism to a compound (in a specific concentration, for a specific time etc. = *Exposure scenarios*)

What parameters determine the fate of a chemical compound?

	DISTRIBUTION	TRANSPORT	TRANSFORMATION
Compound properties	Polarity vs hydrophobicity (**K_{ow}, water solubility**) Volatility, boiling point, evaporation (**H, boiling point**) Reactivity vs stability and persistence (**t1/2**)		
Environmental properties Water Sediments Soil Atmosphere	**Drift (pace, direction, type ...)** **Temperature** **Light** (and its parameters) **Chemical composition** pH (free H+) Redox potential (... presence of O_2) Presence of inorganic ions / cation-exchange capacity (e.g. clay) Particles – type, size, amount Organic matter – type, amount (humic acids etc.)		
Biota properties vegetation, consumers...	Number / Motion / Size (surface) / Fat content (%) / Food chain level etc. etc.		

K_{ow}, H, t1/2

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}**, logP)*

- **2) Stability (persistence, low degradability)**
  - long-term functionality in the environment
  *- half-life (**t1/2**)*

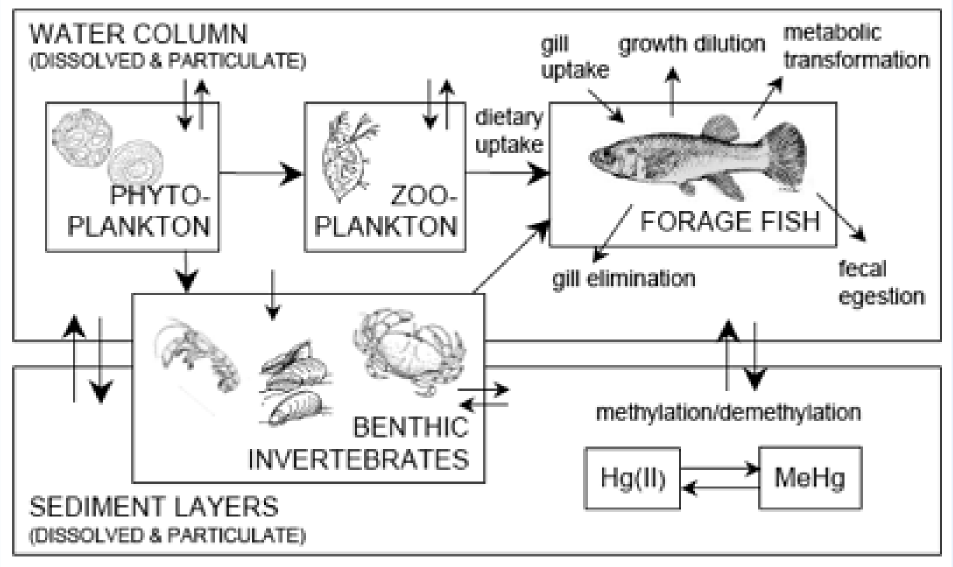
- **3) Toxic effects in organisms**

… information on each parameter is needed

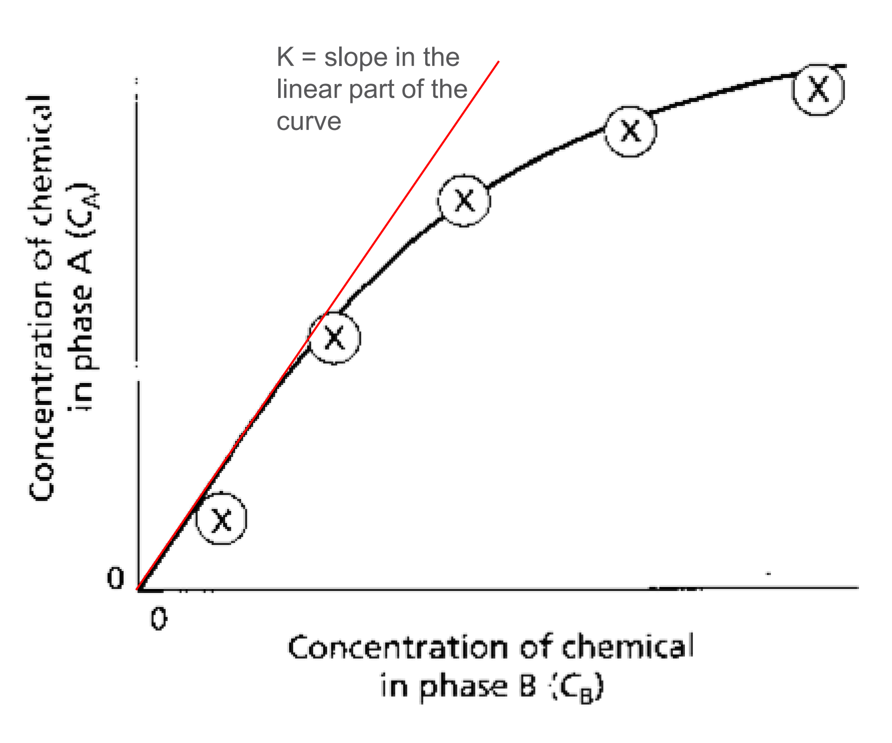
1+2 – in this part of the course
3 – other lectures

- **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 ← → 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*

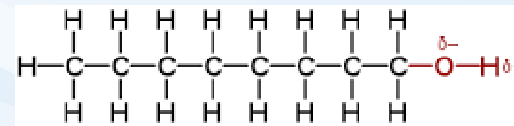


- **Ca = K. Cb** $^{1/n}$
  C – concentration in phases A (Ca) and B (Cb)
  K – partition constant
  n – nonlinearity constant
- In case of a linear relationship (n=1) **K = Ca / Cb**
  = "partition coefficient"
  - The size of K determines the tendency of the compound to transfer from phase B into phase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

  log Ca = 1/n . log Cb + **log K**

“Biota-Water” partition model

- **BIOTA / Water partition coefficient**
  - difficult to determine
    (standard procedure –bioconcentration determination: see further)
  - → Alternatively – model with **n-octanol**



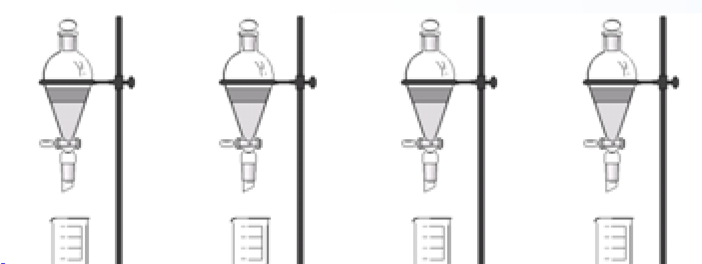
- **N-octanol**
  - Immiscible with water, similar properties to fats or phospholipids of biological membranes

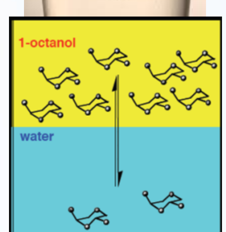
- **n-octanol/water partitioning**
  - K_{ow} – partition coefficient
  - Characterizes HYDROPHOBICITY (resp. LIPOPHILICITY)
  - Often expressed as logK_{ow} (resp. logP)

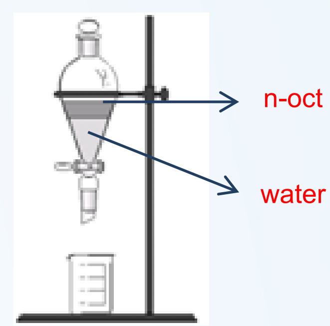
Experimental K_{ow} determination

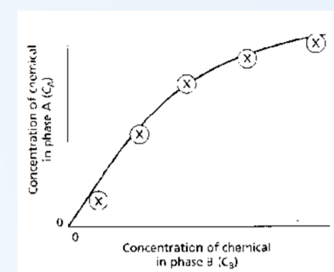
System n-octanol/water + compound insertion → Shaking until equilibrium is established → Chemical analysis of concentrations → K_{ow} calculation

4 different initial concentrations



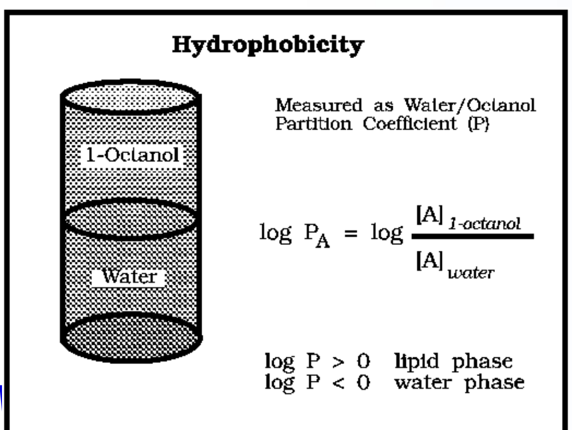






K_{ow} – examples

Compound	K_{ow}	$logK_{ow}$ (logP)	K_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



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

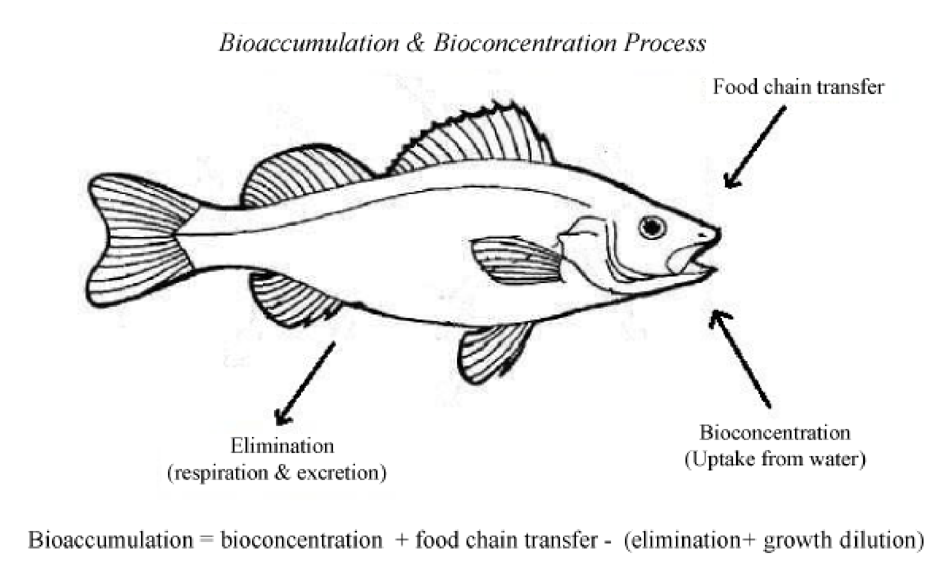
Bioaccumulation, Bioconcentration, Biomagnification

Bioconcentration

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

BCF – Bioconcentration factor

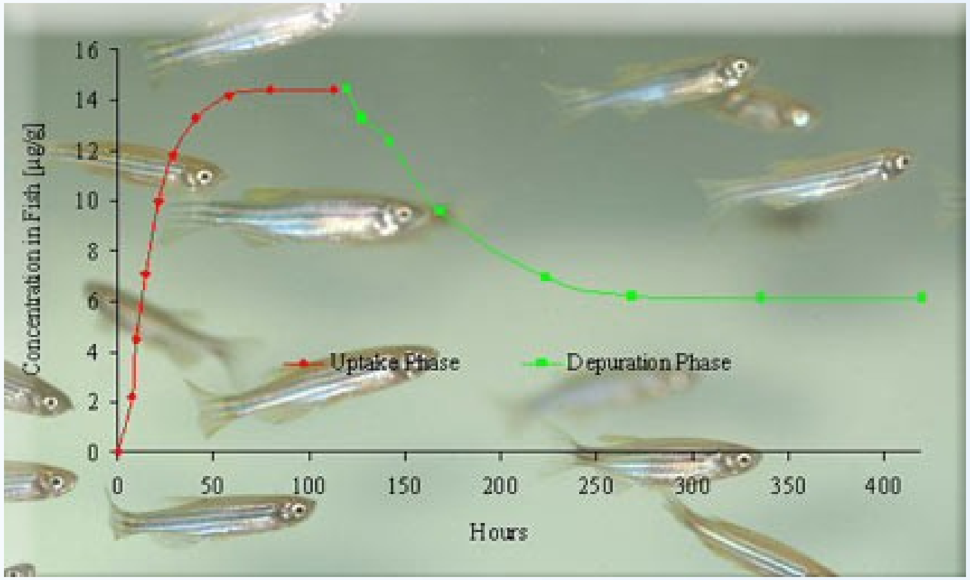
$$BCF = \frac{Concentration_{Biota}}{Concentration_{Water}}$$



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}

$$log BCF = log Kow - 1.32$$

MUNI | RECETOX

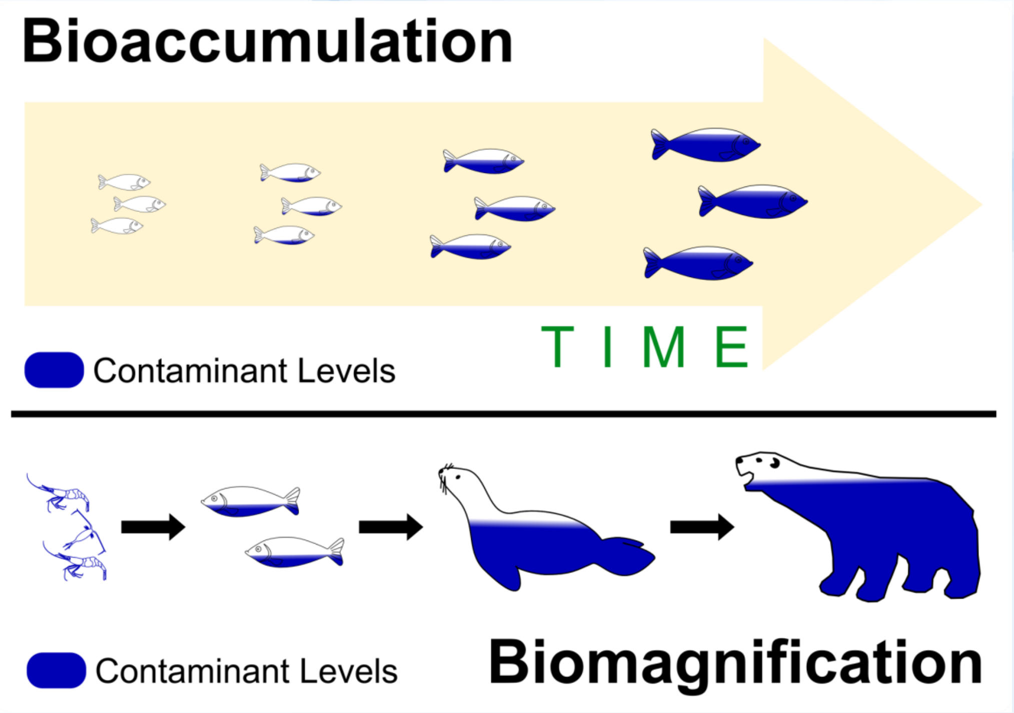
Bioaccumulation, Bioconcentration, Biomagnification

Bioaccumulation

Compound accumulation (all routes of exposure)

BAF – Bioaccumulation factor

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

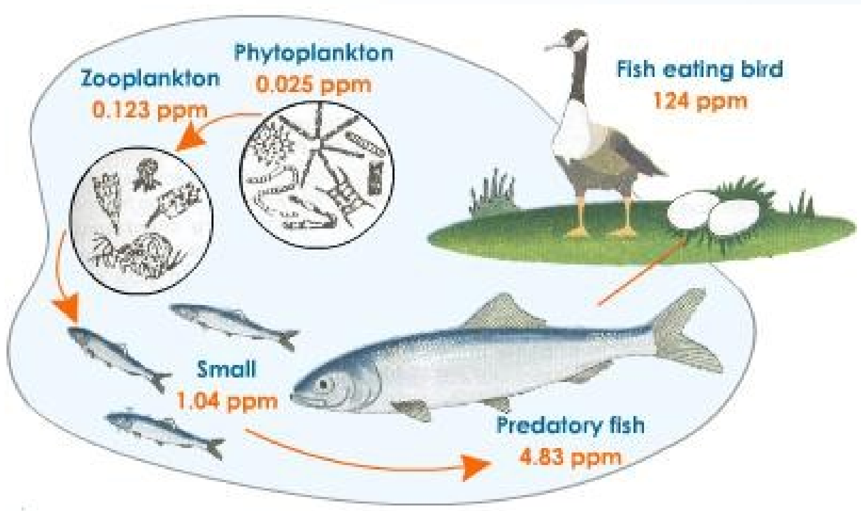


Biomagnification

Increasing concentration of compounds in organisms via food chain

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

Biomagnification



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

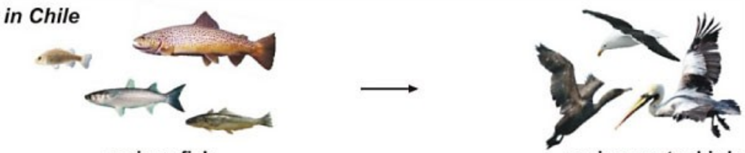
(a) Freshwater Lakes in Southern Sweden

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

(b) Fjord in Northern Norway

	sandeel (whole fish)	cod (liver)	seal (blubber)
ΣDDT (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)
ΣHCH (3.8)	40 (25 - 60)	30 (20 - 40)	65 (5 - 200)

(c) Bobio River in Chile



	various fish	various water birds
ΣDDT (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)
ΣHCH (3.8)	150 (80 - 360)	45 (24 - 94)

Average values of lipid-normalized concentrations (ranges in parentheses) of some organochlorine compounds: PCB153, ΣDDT = *o.p*-DDT + *p.p*-DDT = *o.p*-DDE = *p.p*-DDE, ΣHCHs = α- + β- + δ-hexochlorohexane, and HCB = hexachlorobenzene in organisms belonging to some food chains (logK_{ow} values are given in parentheses after the compound names). All concentrations are expressed in μg/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 ($Pa.m^3.mol^{-1}$) – *characteristic for a specific compound*

C_W – concentration in water ($mol \cdot m^3$)

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

H (Pa . mol-1 . m-3)	Description
> 100	Very fast released from water Example: halogenated aliphatic hydrocarbons (**dichloroethane** and such)
25-100	Volatilization slower Example: **chlorinated benzenes**
1-25	Sow volatilization Example: **most of the PCBs**
< 1	Insignificant volatilization Example: **high chlorinated PCDDs**

Environmental transformation / Persistence

Environmental transformation – (bio)transformation

- **Types of transformation of organic compounds:**
  - partial structural change (e.g. introduction od OH into neutral fatty acids)
  - degradation into smaller organic molecules
  - total degradation of the org. compound (CO_2, H2O)

- **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_2 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)

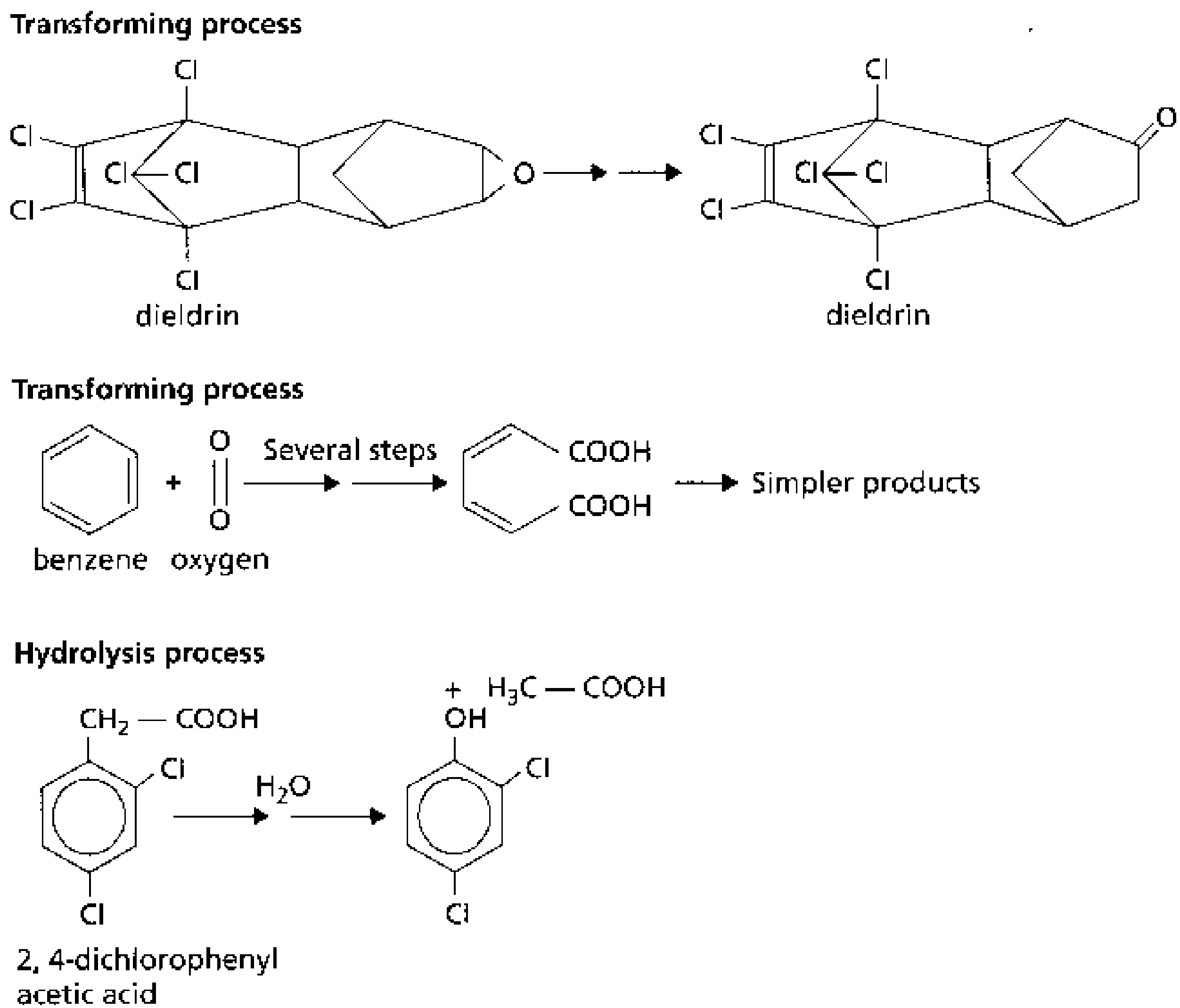


Fig. 3.6 Some transformation and degradation patterns for chemicals discharged to the environment.

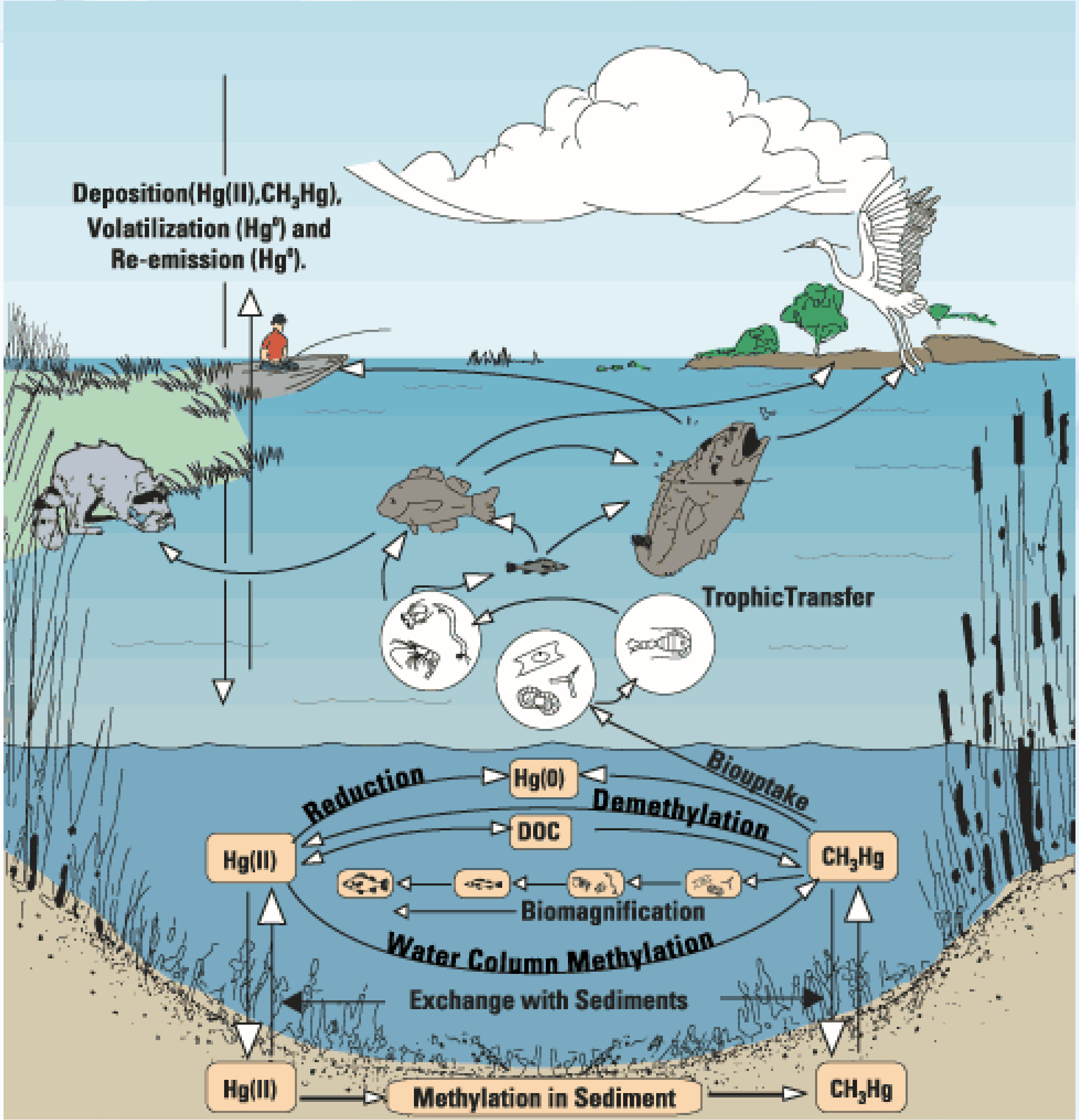
ANAEROBIC (no oxygen) biotransformation – example methylmercury

Me-Hg

- Bioaccumulation
- High toxicity

<u>**Look on web for**</u>

- MINAMATA disease
- CONVENTION

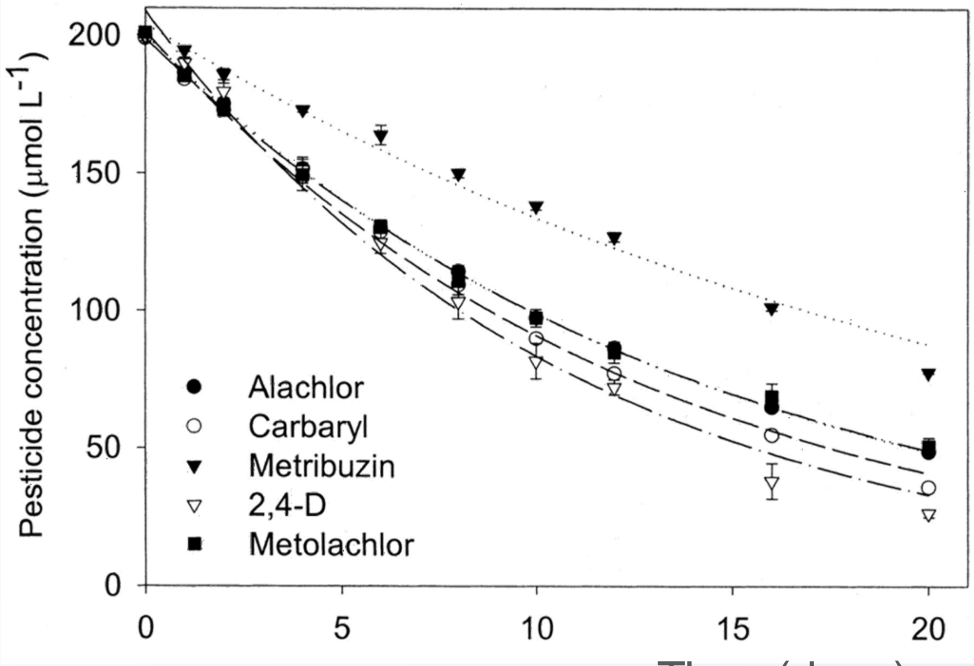


Persistence characterisation – half-life

- Transformation kinetics – first order kinetics
  - $C_t = C_0 \, . \, e^{-kt}$

    C_t – concentration in time t
    C_0 – initial concentration
    k – constant (degradation speed)
    t – time
- After derivation (half-life)

  $t_{1/2}$ = **ln2 / k** = 0.693 / k



Half-life of selected pesticides in soil - examples

Compound	Half-life in soil (years) *($t_{1/2}$ or DT50 – disappearance time 50%)*
Chlorinated compounds	
DDT	3-10
Dieldrin	1-7
Toxaphene	10
Organophosphate – chlorfenos	0,2
Carbamate – carbofuran	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 compound and transformation products f
      - → Chemical methods (GC, LC etc.)

Example of standardized OECD guideline

Anaerobic Biodegradation Experiment see YOUTUBE
http://www.youtube.com/watch?v=Y_zFPkbrwSY

Fate (processes) in the environment → Exposure → BIOAVAILABILITY

BIOAVAILABILITY

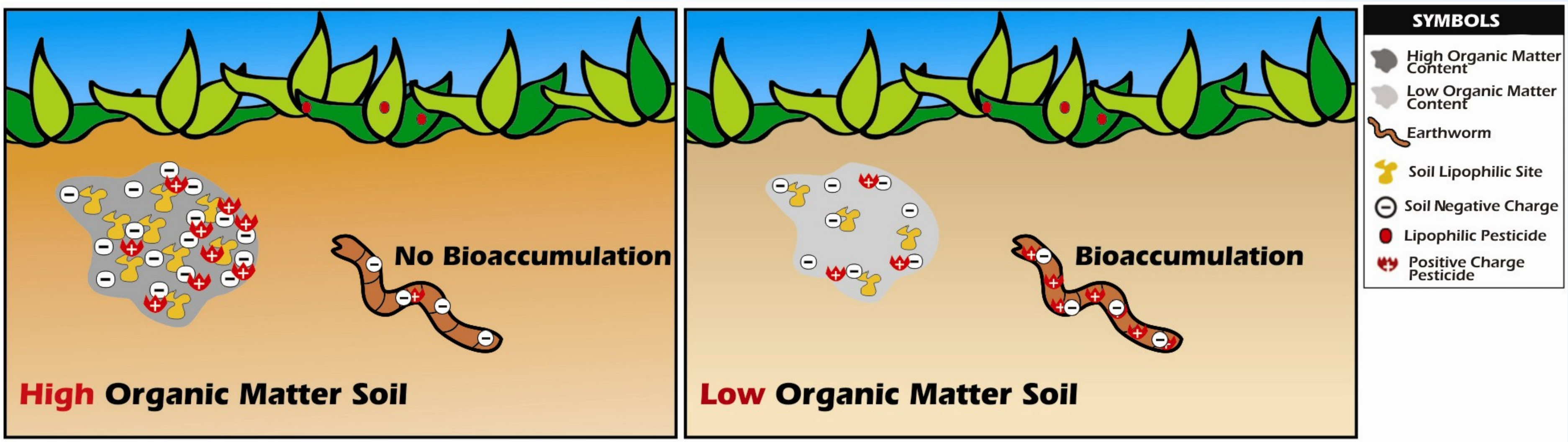
- **The term comes from pharmacology**
  - compound fraction that is effective in the body
- **In environmental sciences**
  - compound fraction, that can enter the organism = compound is in available form (it is not bound in the environment – e.g. to organic carbon etc.)

- **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”

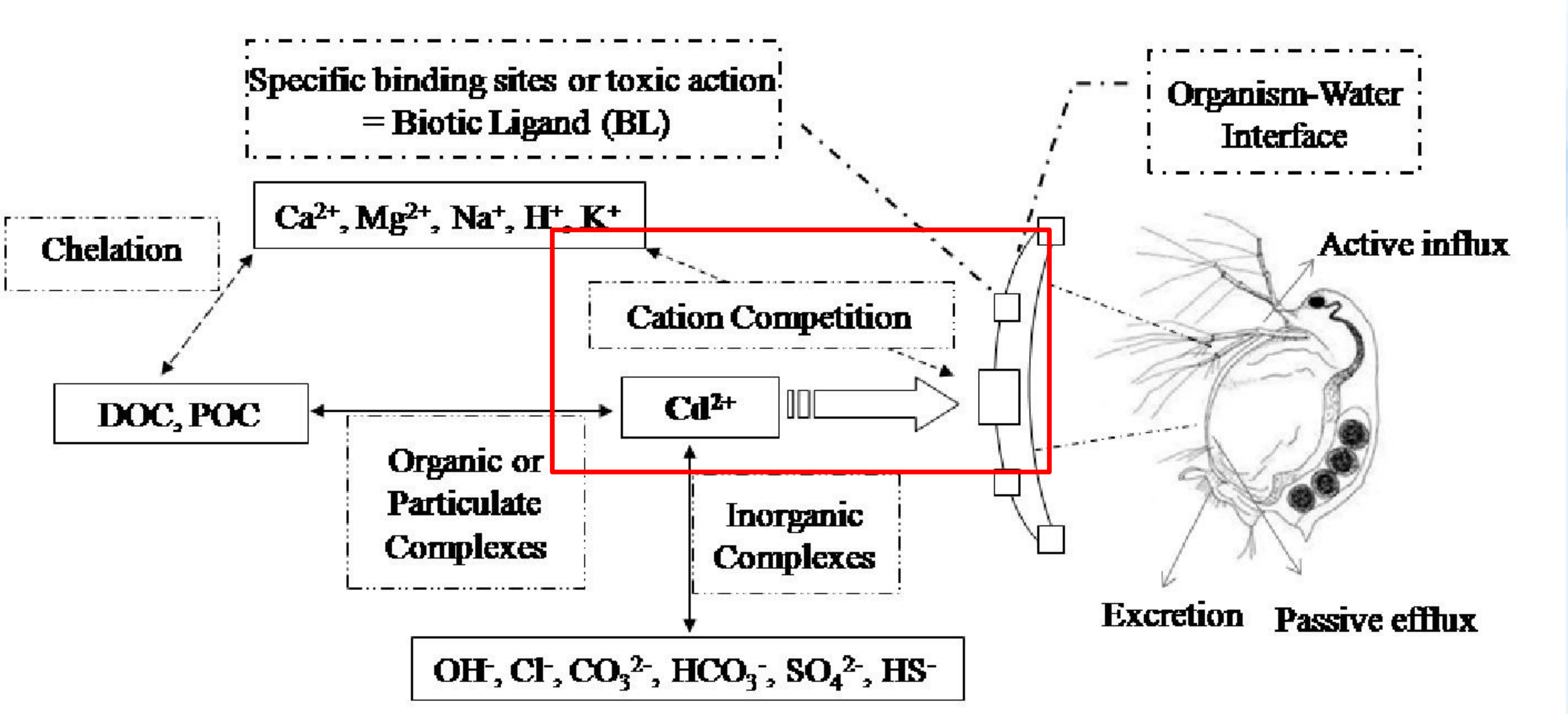


Bioavailability - examples

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)



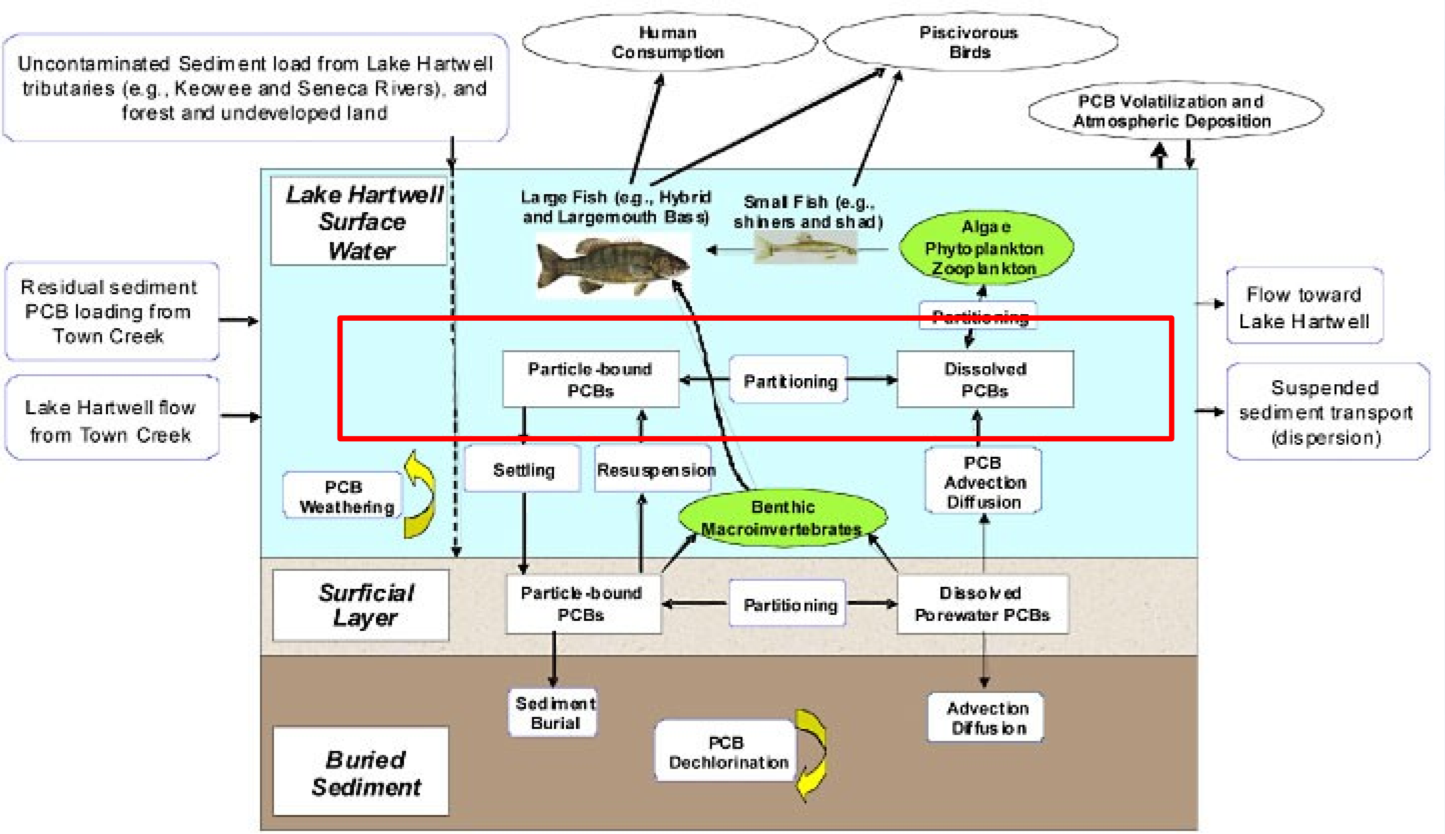
Bioavailability - examples

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**

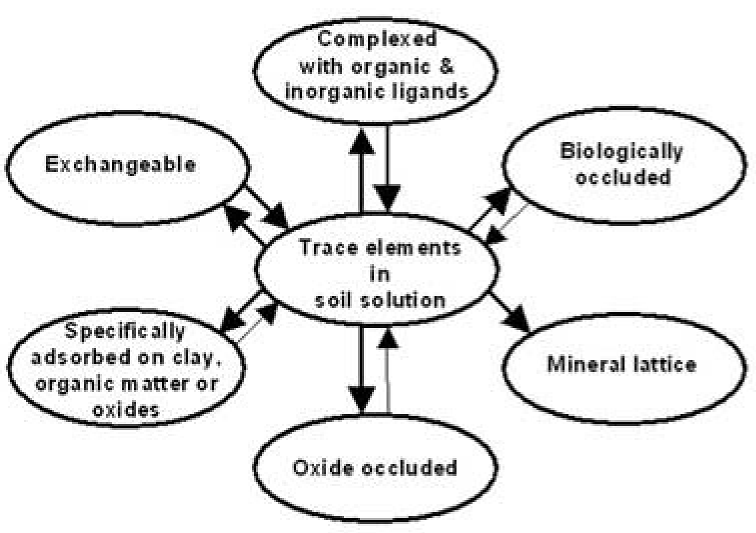


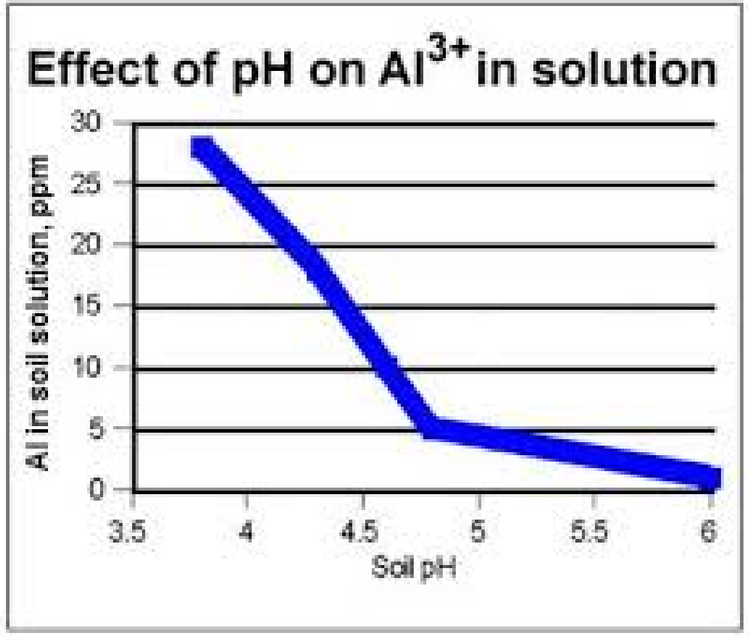
Bioavailability - examples

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**

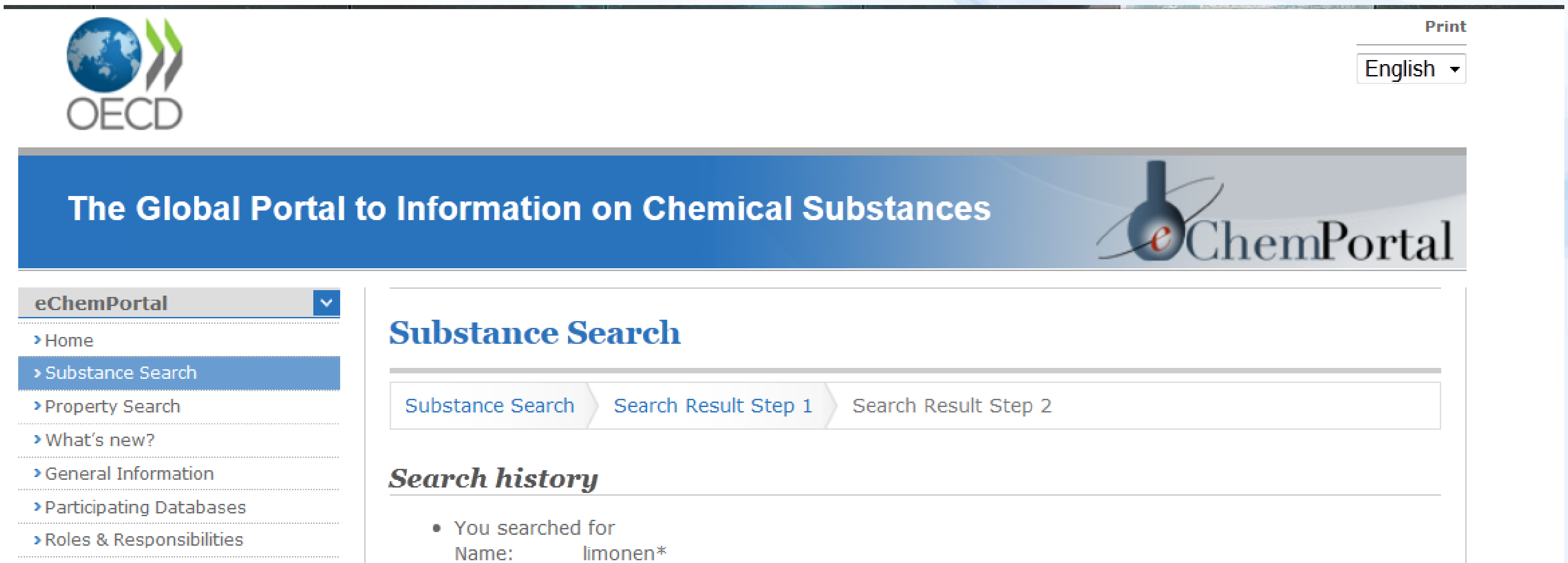




Where can the information on environmental properties be found? (K_{ow}, t1/2 etc.)

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

- **eChemPortal.org**



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?