

# SOIL CONTAMINATION



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# SOIL CONTAMINATION (POLLUTION)

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- Increased content of dangerous or xenobiotic substances in soils
- **Occurrence of contaminants in soil above a certain level causing deterioration or loss of one or more soil functions**, which can be in the form of point pollution or diffuse pollution. Soil pollutants can consist of various forms, such as organic and inorganic or particulate pollutants (EJP SOIL: SERENA)

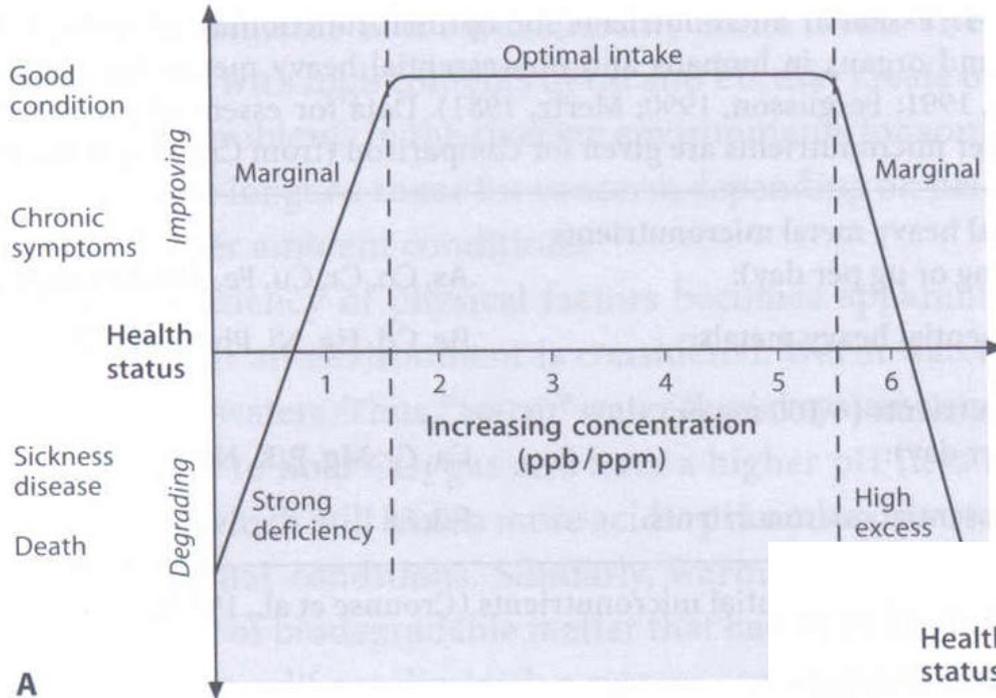
# SOIL POLLUTANTS (1)

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## Potentially toxic elements (PTE):

- alternative terms:
  - trace elements, risk elements, metals and metalloids (heavy metals)
- include:
  - As, Cd, Hg, Pb, Mn, Ni, Tl...
  - some essential elements (B, Cu, Cr, Zn, Mo, Se)
  - radionuclides
- both natural and anthropogenic origin
- cannot be decomposed

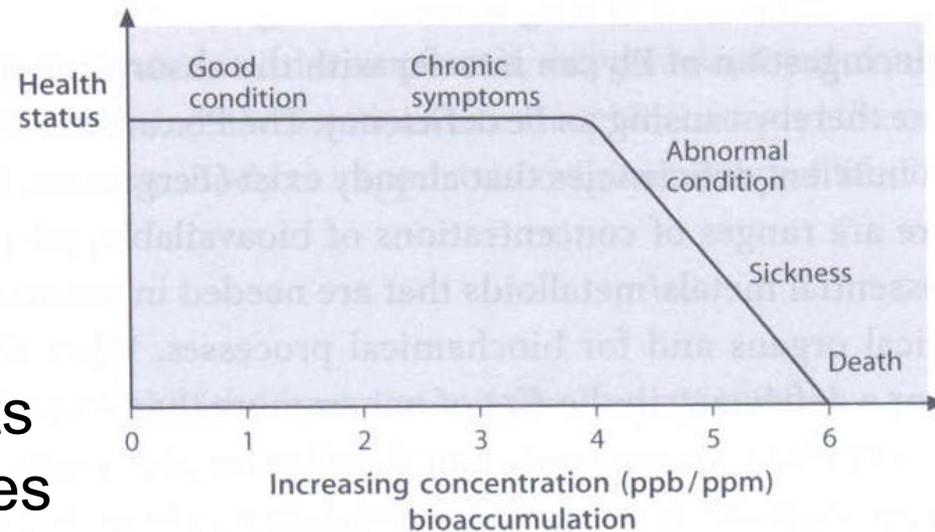
# Essenciality and toxicity



Nutrients,  
essential elements

A

Toxic elements  
and substances



B

# SOIL POLLUTANTS (2)

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## Organic pollutants (organic xenobiotic substances):

- include:
  - petroleum-derived substances
  - polycyclic aromatic hydrocarbons (PAHs)
  - organochlorine compounds (OCPs)
  - dioxins,
  - polychlorinated biphenyls (PCBs)
  - plant protection products (pesticides)
  - volatile organic compounds (VOC) - trichloroethylene, tetrachloroethylene, 1,1,1- trichloroethane, vinyl chloride
- mainly anthropogenic origin
- possible decomposition (microorganisms)

# SOIL POLLUTANTS (3)

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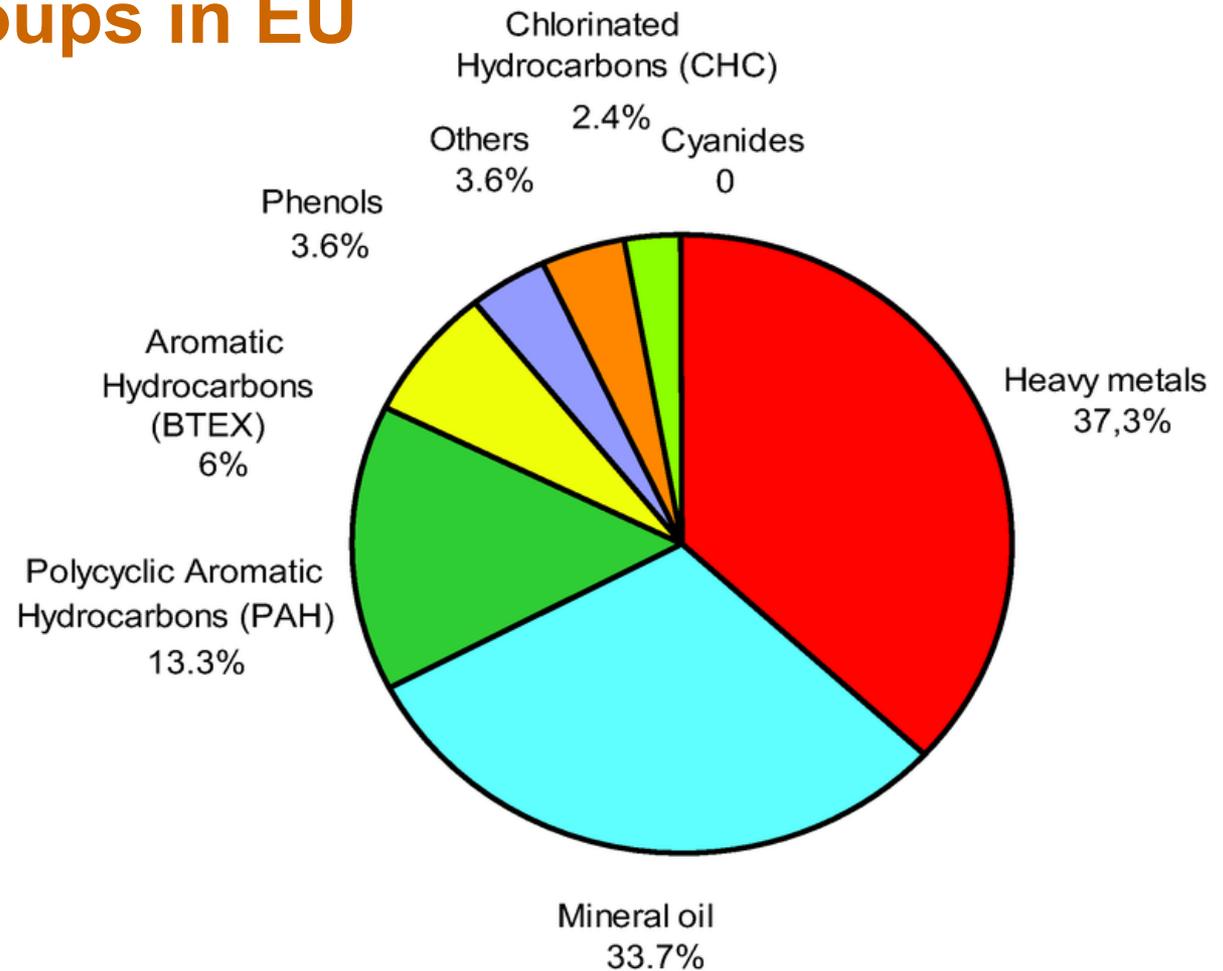
## Emerging pollutants:

- include:
  - polyfluoroalkyl substances (PFAS),
  - pharmaceuticals (veterinary drug residues and antibiotics)
  - phthalates and other plasticizers (e.g. bisphenol A)
  - disinfectant residues
  - artificial nanomaterials
  - rare earth elements (as new PTE)
  - flame retardants (brominated)
  - plastics (microplastics) and synthetic polymers

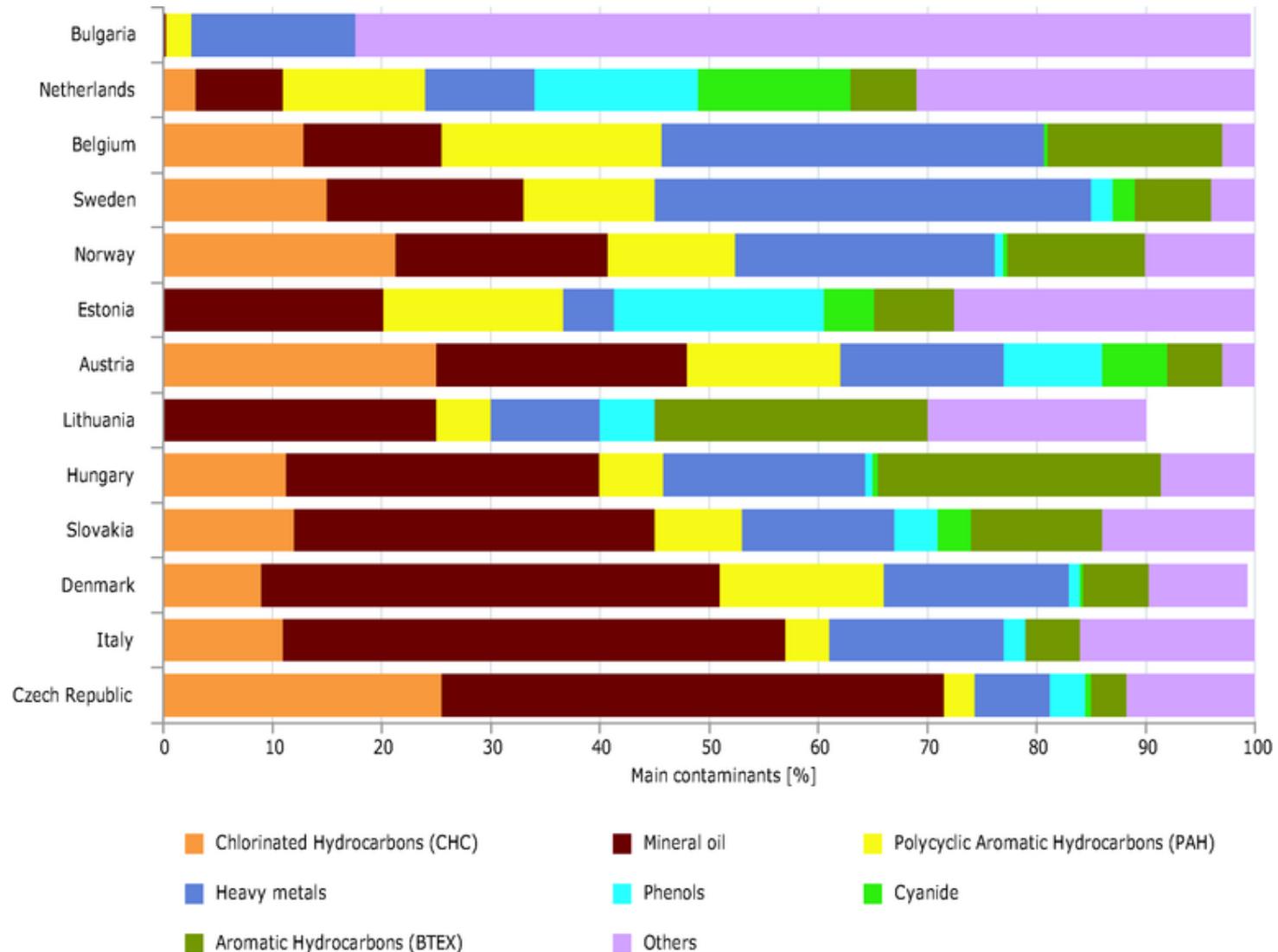
# SOIL POLLUTION

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## Relative importance of various soil and water pollutant groups in EU



# Relative importance of various soil pollutant groups in EU countries



# SOIL POLLUTION

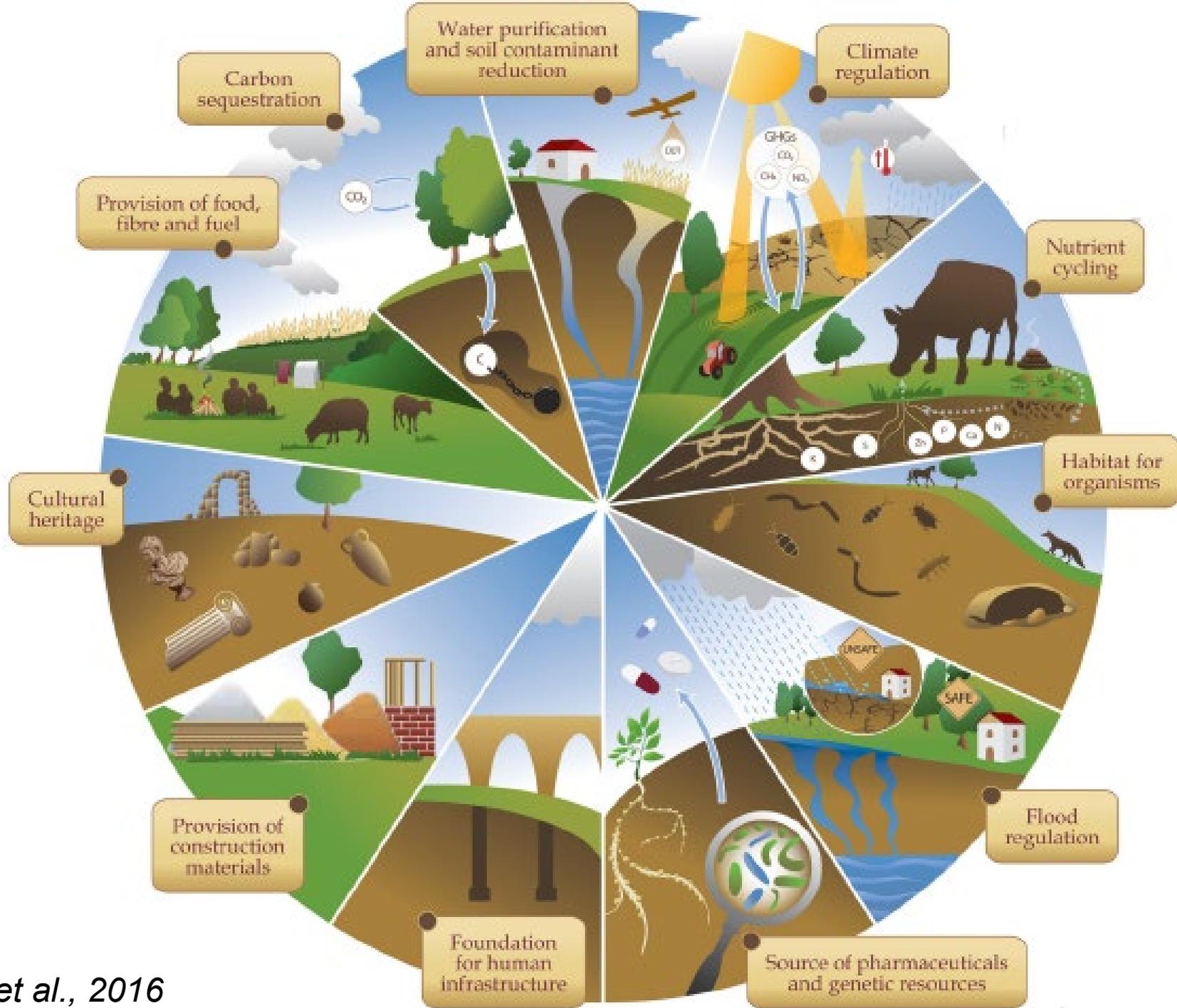
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## Why a problem:

- Toxicity of pollutants
  - Entering the food chain
    - through plants...
    - human and animal health effects
  - Leaching to ground- and surface waters
  - Effect on ecosystem health and behaviour
    - soil biological activity
    - plant growth
    - lower production (yields)
- Impact on soil functions and ecosystem services



# Soil functions

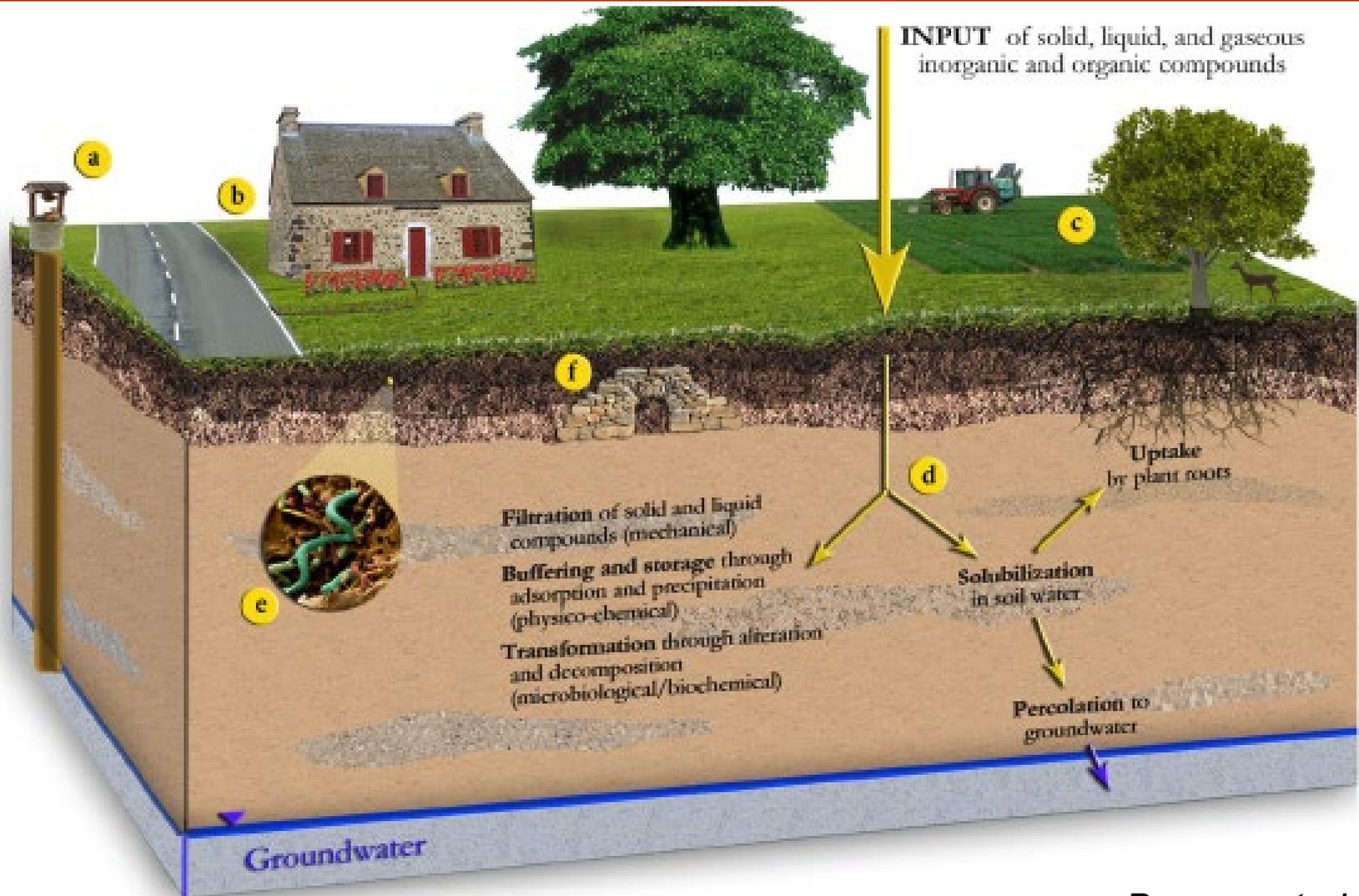


# Impact of contamination on soil functions and ecosystem services

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- food supply
  - soil productivity
  - quality of food produced
- carbon sequestration
- water quality protection
- nutrient cycling
- habitat for soil organisms, biodiversity
  - decrease of the number and activity of soil organisms
  - changes in the soil community structure
  - alteration of biochemical cycles
- secondary source of water contamination

# Soil functions related to pollution



# Indication/determination of soil contamination with PTE

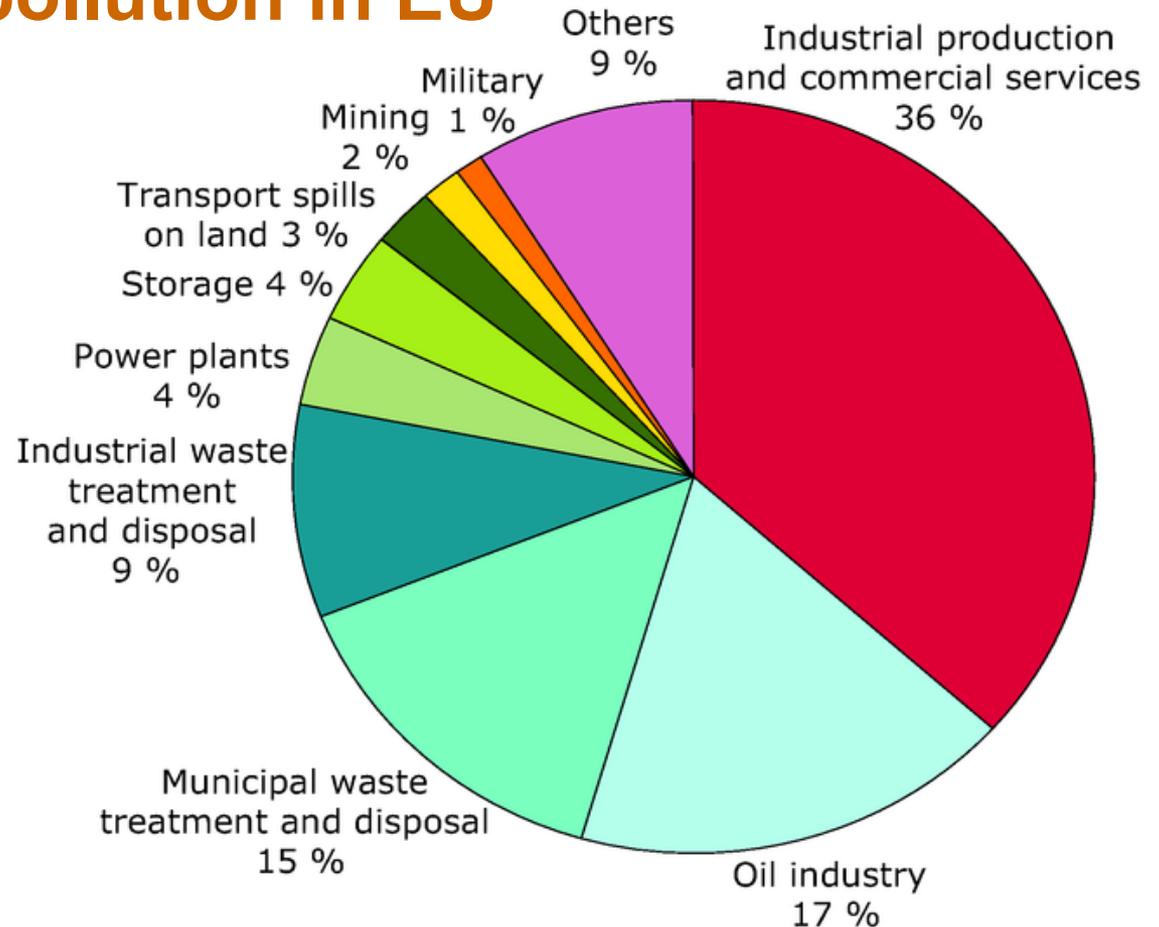
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- Microbial / enzymatic activity
  - Plant indicators
  - Magnetometry
    - magnetic susceptibility
  - **Chemical analysis**
    - X-ray fluorescence spectrometry (XRFS)
    - PTE extraction
    - Total sample decomposition
- } Non-specific
- } Measurement on  
AAS, ICP-OES...

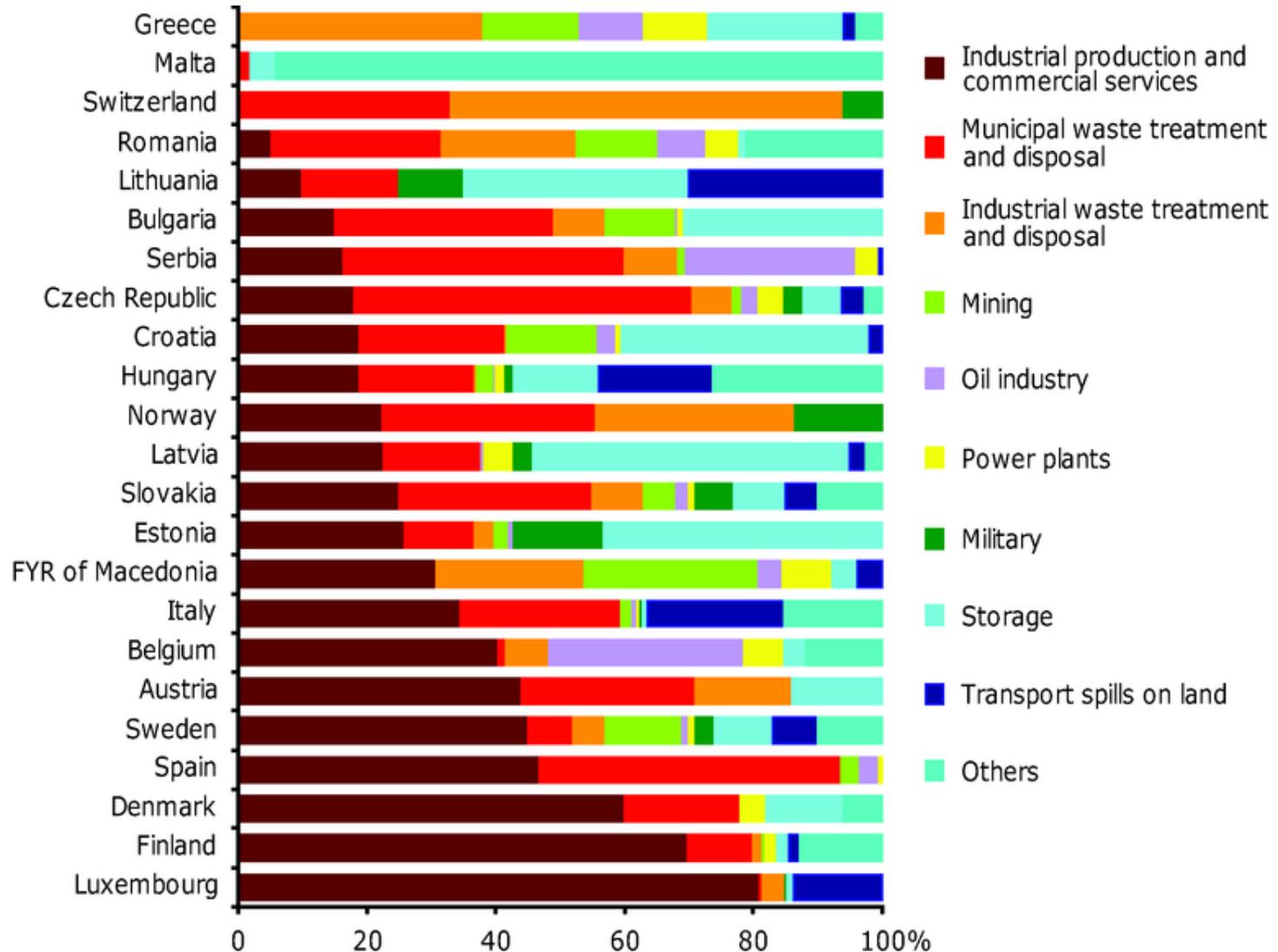
# SOIL POLLUTION

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## Relative importance of anthropogenic activities causing soil pollution in EU



# Relative importance of various soil pollution sources in EU countries



# Types of soil contamination

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## Point (local) pollution

- ❑ intensive industrial activities, power stations
- ❑ inadequate waste disposal
- ❑ mining and smelting
- ❑ military activities
- ❑ accidents

## Diffuse (non-point) pollution

- ❑ atmospheric deposition
- ❑ long-term use of low-quality fertilizers
- ❑ uncontrolled use of sewage sludge
- ❑ intensive use of pesticides and manure

In Europe ~2.8 million sites are potentially contaminated

# POTENTIALLY TOXIC ELEMENTS

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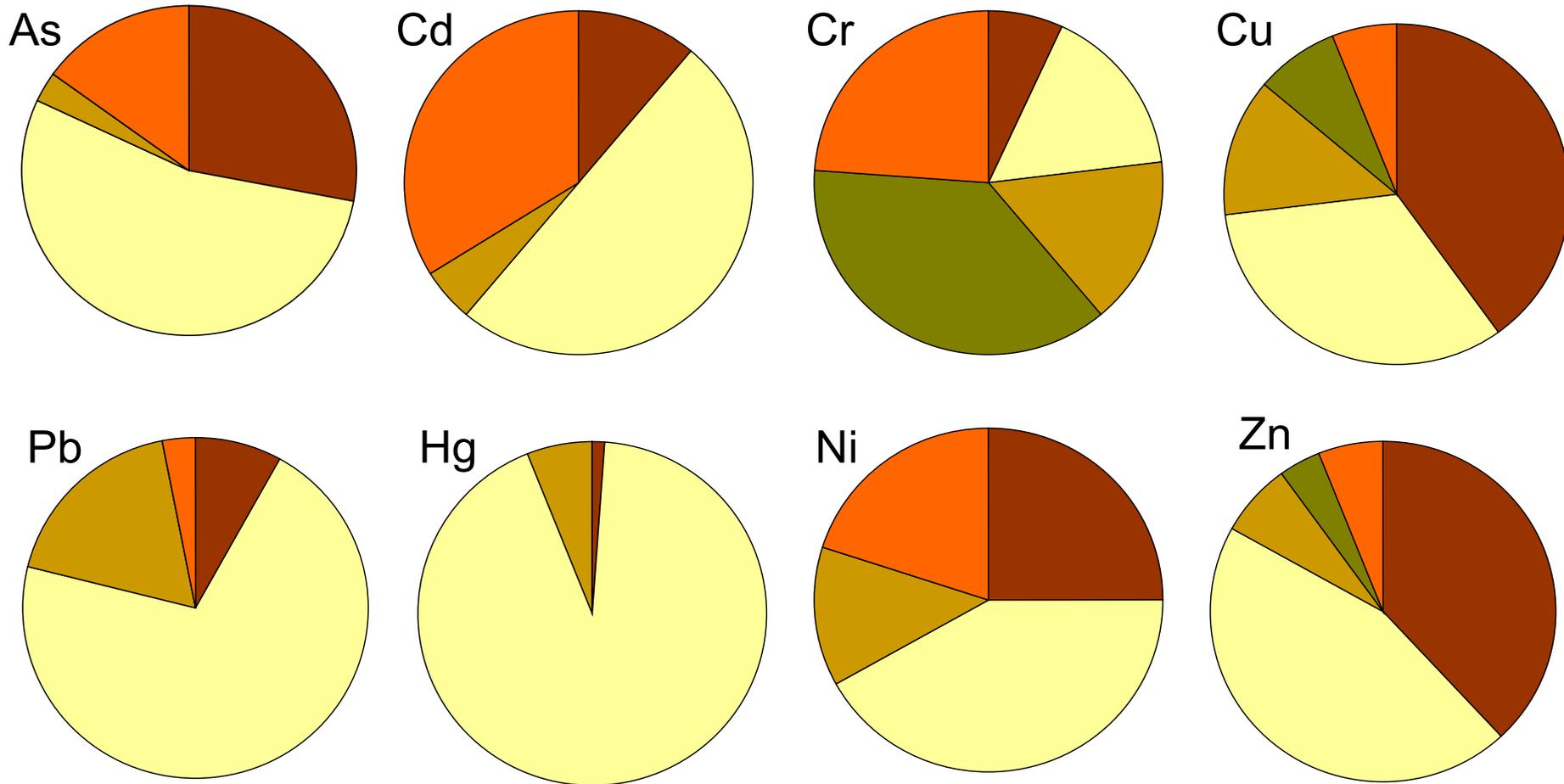
## Origin in soil:

- lithogenic (geogenic)
  - natural background
- anthropogenic
  - from human activities
- (pedogenic)

# PTE content in materials introduced to soils (mg.kg<sup>-1</sup> dry wt.; *Kabata-Pendias a Pendias, 1992*)

Elem.	S.sludge	P-fert.	Liming	N-fert.	Manure	Pesticid.
As	2-26	2- <b>1200</b>	0.1-24	2.2-120	3-25	22-60
Cd	2- <b>1500</b>	0.1- <b>170</b>	0.04-0.1	0.05-8.5	0.3-0.8	-
Co	2-260	1-12	0.4-3.0	5.4-12	0.3-24	-
Cr	20- <b>40600</b>	66-245	10-15	3.2-19	5.2-55	-
Cu	50- <b>3300</b>	1-300	2-125	<1-15	2-60	12- <b>50</b>
Hg	0,1-55	0.01-1.2	0.05	0.3-2.9	0.09-0.2	0.8- <b>42</b>
Mo	1-40	0.1-60	0.1-15	1-7	0.05-3	-
Ni	16- <b>5300</b>	7-38	10-20	7-34	7.8-30	-
Pb	50- <b>3000</b>	7-225	20- <b>1250</b>	2-27	6.6-15	60
Se	2-9	0.5-25	0.08-0.1	-	2.4	-
Zn	700- <b>49000</b>	50-1450	10-450	1-42	15-250	1.3-25

# Relative proportion of anthropogenic sources of potentially toxic elements in agricultural soils in the UK (*Adriano, 2001*)



Manure    Atm. deposition    Sludges    Industrial by-products    Fertilizers

# Mean values and common ranges of PTE concentrations in world soils (mg.kg<sup>-1</sup>; *Bowen, 1979*)

Element	Median	Range	Element	Median	Range
As	6	0.1-40	Ag	0.05	0.01-8
Cd	0.35	0.01-2.0	Ba	500	100-3,000
Co	8	0.05-65	Be	0.3	0.01-40
Cr	70	5-1,500	Cs	4	0.3-20
Cu	30	2-250	<i>Ga</i>	30	0.4-300
Hg	0.06	0.01-0.5	<i>Rb</i>	100	20-600
Mo	1.2	0.1-40	Sn	4	1-200
Ni	50	2-750	Sr	250	4-2,000
Pb	35	2-300	Ti	5,000	150-25,000
Se	0.4	0.01-12	<i>U</i>	1	0.9-9
Zn	90	1-900	V	90	3-500

# Processes affecting PTE behavior in soils

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- Adsorption/desorption
- Dissolution/precipitation
- Binding by organic substances
- Forming inorganic and organic complexes
- Occlusion, diffusion to minerals
- Uptake by organisms
- Volatilisation (Hg, methylated metals)
- Transport

## Retention rate in soils:

Pb > Sb > Cu > Cr > Zn > Ni > Co > Cd

# Soil pollution

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## Forms of potentially toxic elements in soils:

- ❑ water-soluble
- ❑ exchangeable
- ❑ organically bound
  - bound on stable humic substances
  - complexed with dissolved organic matter
- ❑ bound on iron and manganese oxides
- ❑ in defined compounds (carbonates, sulfides, phosphates...)
- ❑ bound in silicates (residual fraction)

Concentration of bioavailable forms is more important than the total content in soil

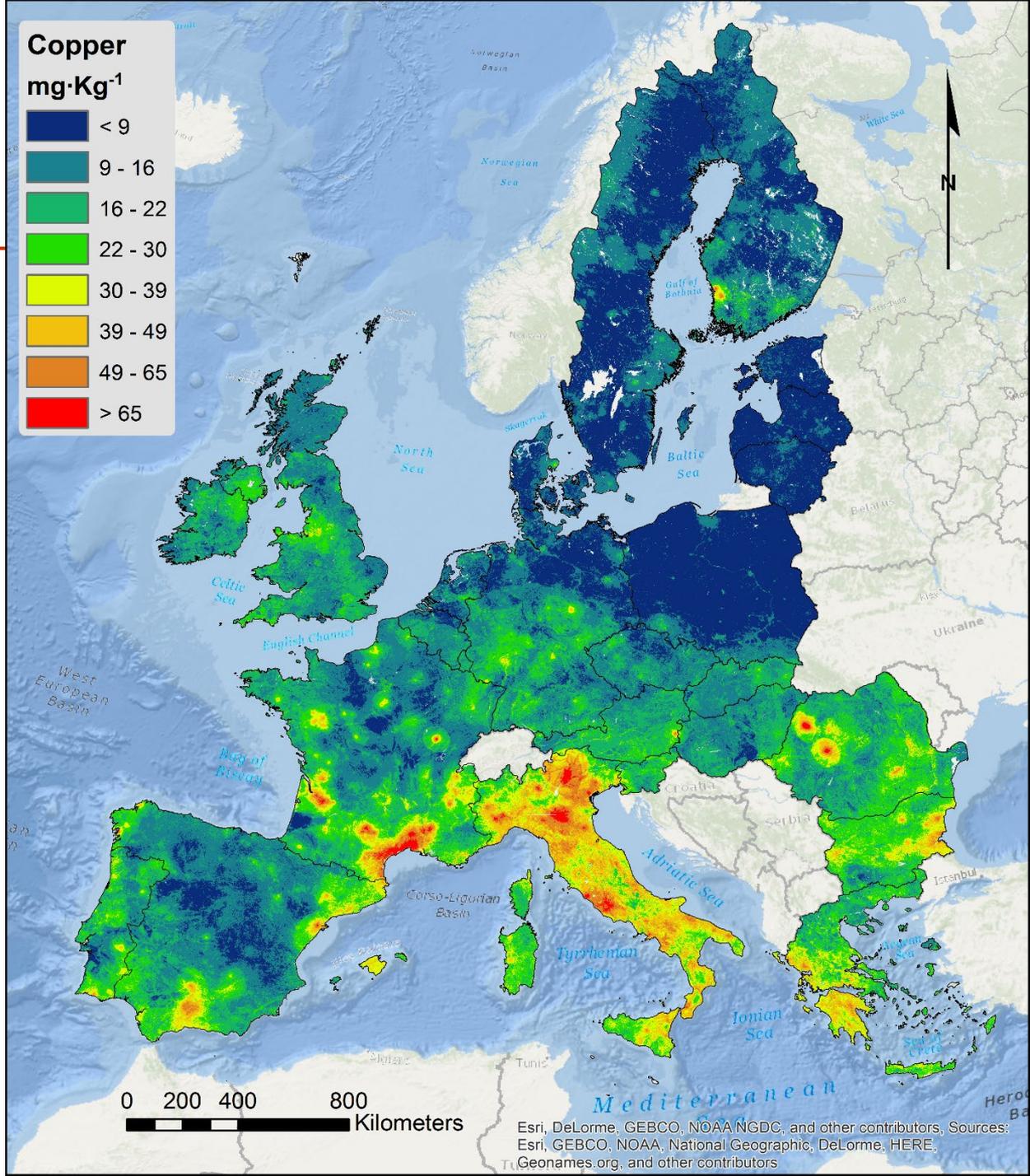
# Prevailing PTE forms in soil solution and the most toxic species *(Adriano, 2001)*

Elem.	Acid soils	Alkaline soils	Tox. spec.
Ag(I)	$\text{Ag}^+$ , $\text{AgCl}^0$	$\text{Ag}^+$	$\text{Ag}^+$
As(III)	$\text{As}(\text{OH})_3$	$\text{AsO}_3^{3-}$	$\text{AsO}_4^{3-}$
As(V)	$\text{H}_2\text{AsO}_4^-$	$\text{HAsO}_4^{2-}$	
B(III)	$\text{B}(\text{OH})_3$	$\text{B}(\text{OH})_4^-$	$\text{B}(\text{OH})_3$
Be(II)	$\text{Be}^{2+}$	$\text{Be}(\text{OH})_3^-$ , $\text{Be}(\text{OH})_4^{2-}$	$\text{Be}^{2+}$
Cd(II)	$\text{Cd}^{2+}$ , $\text{CdSO}_4^0$ , $\text{CdCl}^-$	$\text{Cd}^{2+}$ , $\text{CdCl}^-$ , $\text{CdSO}_4^0$ , $\text{CdHCO}_3^+$	$\text{Cd}^{2+}$
Co(II)	$\text{Co}^{2+}$ , $\text{CoSO}_4^0$	$\text{Co}(\text{OH})_2^0$ ,	$\text{Co}^{2+}$
Cr(III)	$\text{Cr}(\text{OH})^{2+}$	$\text{Cr}(\text{OH})_4^-$	$\text{Cr}^{6+}$
Cr(VI)	$\text{CrO}_4^{2-}$	$\text{CrO}_4^{2-}$	
Cu(II)	$\text{Cu}^{2+}$ , $\text{CuCl}^-$ , fulvates	$\text{CuCO}_3^0$ , $\text{CuHCO}_3^+$	$\text{Cu}^{2+}$
Hg(II)	$\text{Hg}^{2+}$ , $\text{HgCl}_2^0$ , $\text{CH}_3\text{Hg}^+$	$\text{Hg}(\text{OH})_2^0$	$\text{CH}_3\text{Hg}^+$
Mn(II)	$\text{Mn}^{2+}$ , $\text{MnSO}_4^0$	$\text{Mn}^{2+}$ , $\text{MnSO}_4^0$ , $\text{MnCO}_3^0$ , $\text{MnHCO}_3^+$	$\text{Mn}^{2+}$
Mo(V)	$\text{H}_2\text{MoO}_4^0$ , $\text{HMoO}_4^-$	$\text{HMoO}_4^-$ , $\text{MoO}_4^{2-}$	$\text{MoO}_4^{2-}$

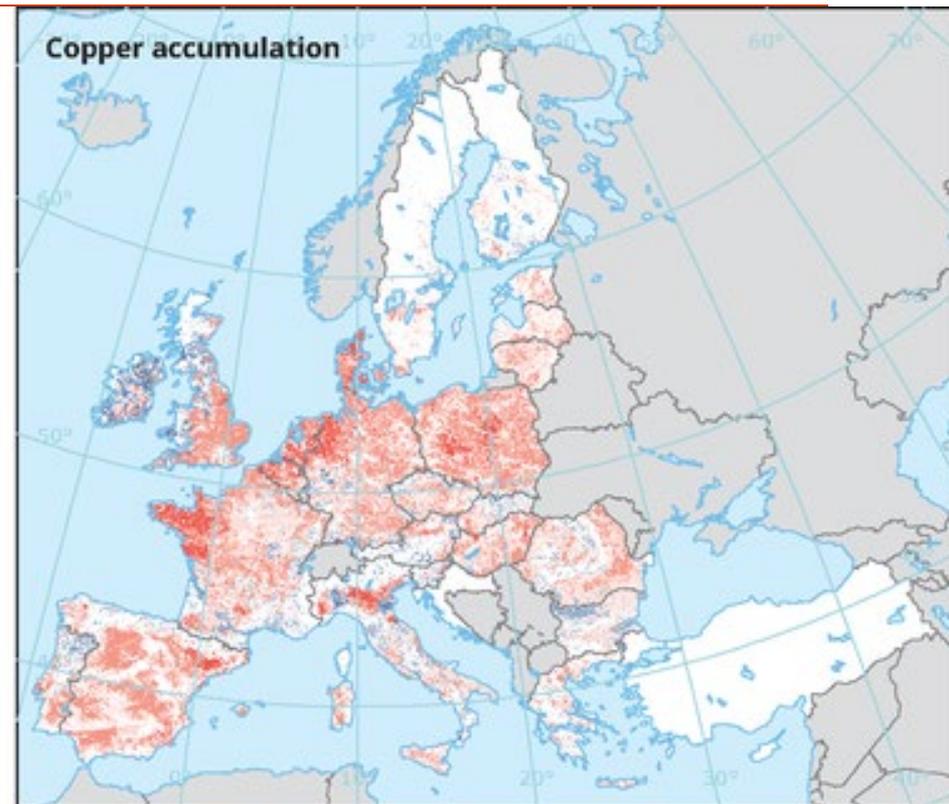
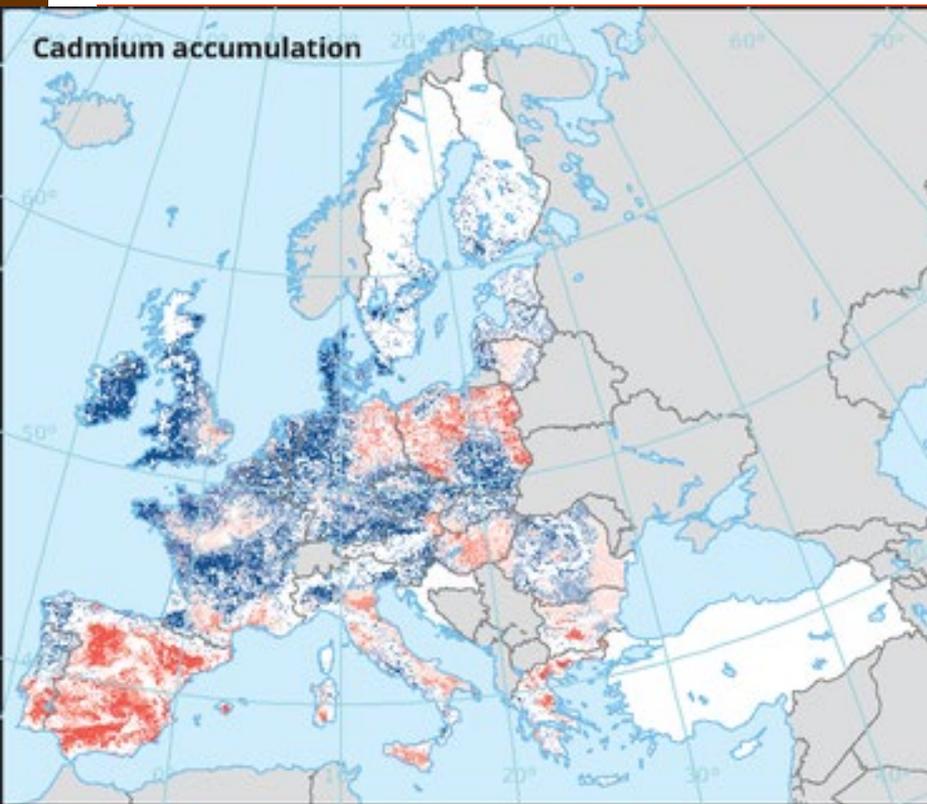
# Prevailing forms of PTE in soils and their effect on plants and animals

Element	Forms	Effect
As	$\text{AsO}_4^{3-}$	toxic for plants and animals
Be	$\text{Be}^{2+}$	toxic for plants and animals
Cd	$\text{Cd}^{2+}$	toxic for animals
Co	$\text{Co}^{2+}$	toxic for plants and animals
Cr	$\text{Cr}^{3+}$ , $\text{CrO}_4^{2-}$	essential for animals, $\text{Cr}^{6+}$ carcinogenic
Cu	$\text{Cu}^{2+}$	essential/toxic for plants and animals
Hg	$\text{Hg}^{2+}$ , $(\text{CH}_3)_2\text{Hg}$	toxic for animals
Mo	$\text{MoO}_4^{2-}$	essential/toxic for plants and animals
Ni	$\text{Ni}^{2+}$	essential/toxic for plants and animals
Pb	$\text{Pb}^{2+}$	toxic for plants and animals
Se	$\text{SeO}_4^{2-}$	essential for animals, toxic for plants and anim.
Sn	$\text{Sn}^{4+}$	essential/toxic for animals
Zn	$\text{Zn}^{2+}$	essential/toxic for plants and animals

# Copper concentration in European topsoils ( $\text{mg}\cdot\text{kg}^{-1}$ )

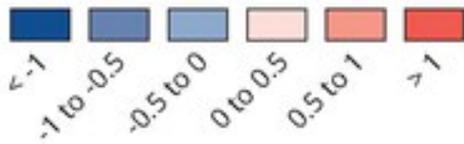


# Accumulation rates of Cd and Cu in European soils (g/ha/yr)



Accumulation rates of Cadmium (left) and Copper (right), 2010

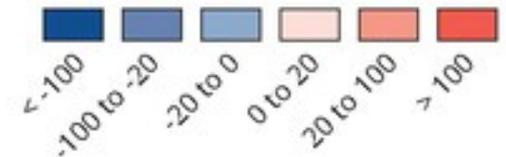
g/ha/yr



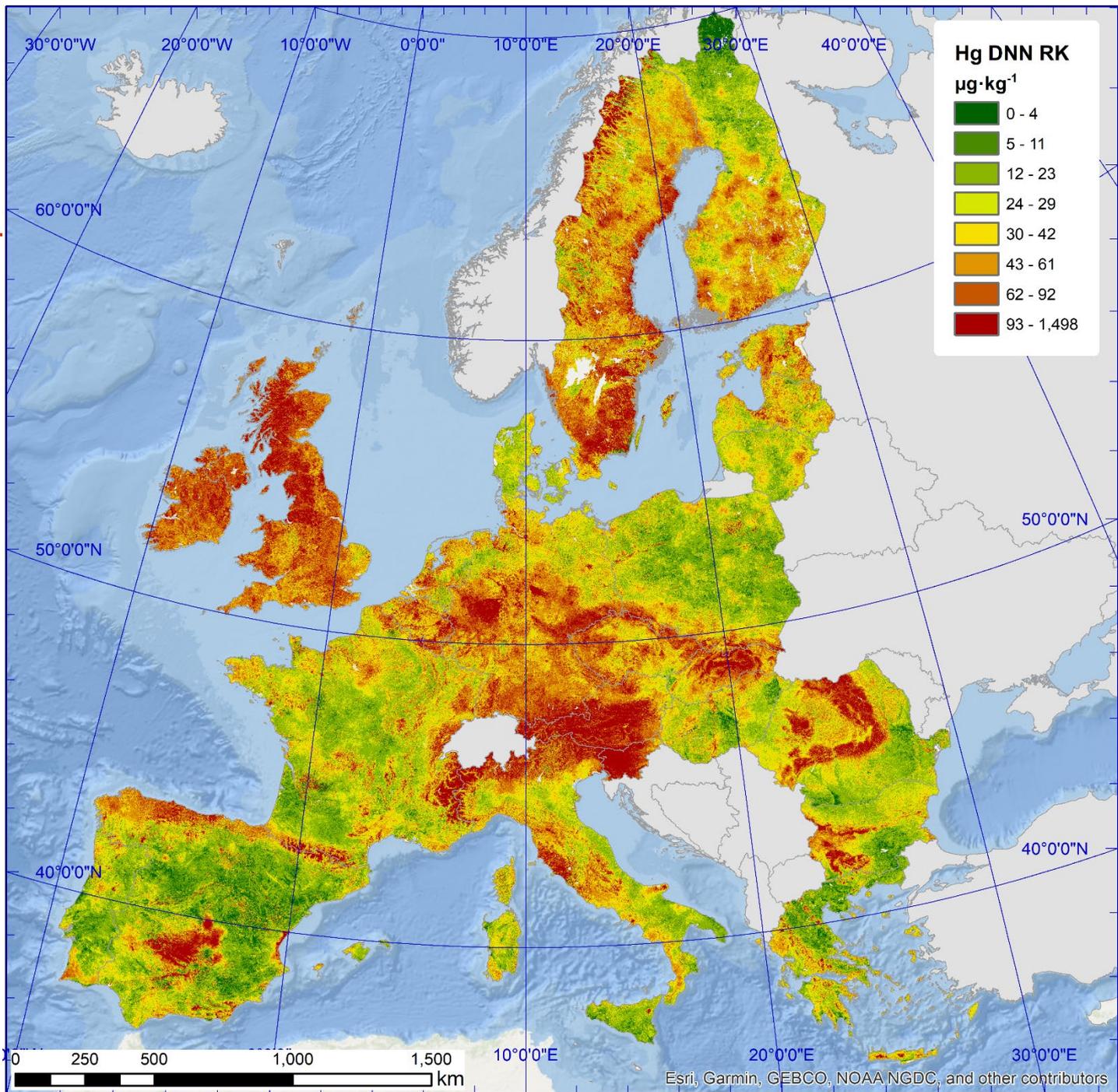
0 500 1 000 1 500 km

No data Outside coverage

g/ha/yr



# Mercury concentration in European topsoils ( $\mu\text{g}\cdot\text{kg}^{-1}$ )



# Radiative isotopes in soil

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- various isotopes of natural or anthropogenic origin
  - Ce, Cs, Kr, Pu, Ra, Rn, Ru, Th, Sr, U etc.
  - I, Co, Fe, Zn
  - Ba, C, H, P, S

## Forms in soil:

- cations, oxyanions, salts...
- organic complexes and compounds

## Behaviour in soil:

- common reactions and processes according to their chemical and physical nature
- **radioactive decay**

# ORGANIC POLLUTANTS IN SOILS

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## Origin – mostly anthropogenic:

- oil processing and petroleum products
- sewage sludge, waste waters and other wastes
- plant protecting products (pesticides)
- solvents, detergents
- atmospheric deposition



# Behaviour of organic pollutants in soil

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## Factors:

### – properties of OP:

- solubility and mobility
- sorptivity
- degradability
- toxicity

### – soil properties:

- texture, clay content
- pH
- SOM content and quality
- sorption characteristics
- biological activity

## Processes:

- accumulation
- sorption/desorption
- uptake by organisms
- degradation
  - chemical
  - biodegradation
  - photolysis
- volatilisation
- leaching
- runoff, erosion

# Biodegradability of organic pollutants in aerobic conditions

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## Easy and rather fast:

- Petroleum hydrocarbons (benzene, toluene, ethylene, xylene, petrol)
- Volatile org. compounds (tri- and perchlorethylene)
- Current pesticides
- Organic solvents

## Difficult and long-term:

- PCB – polychlorinated biphenyles
- PAH - polycyclic aromatic hydrocarbons
- DDT
- Plastics

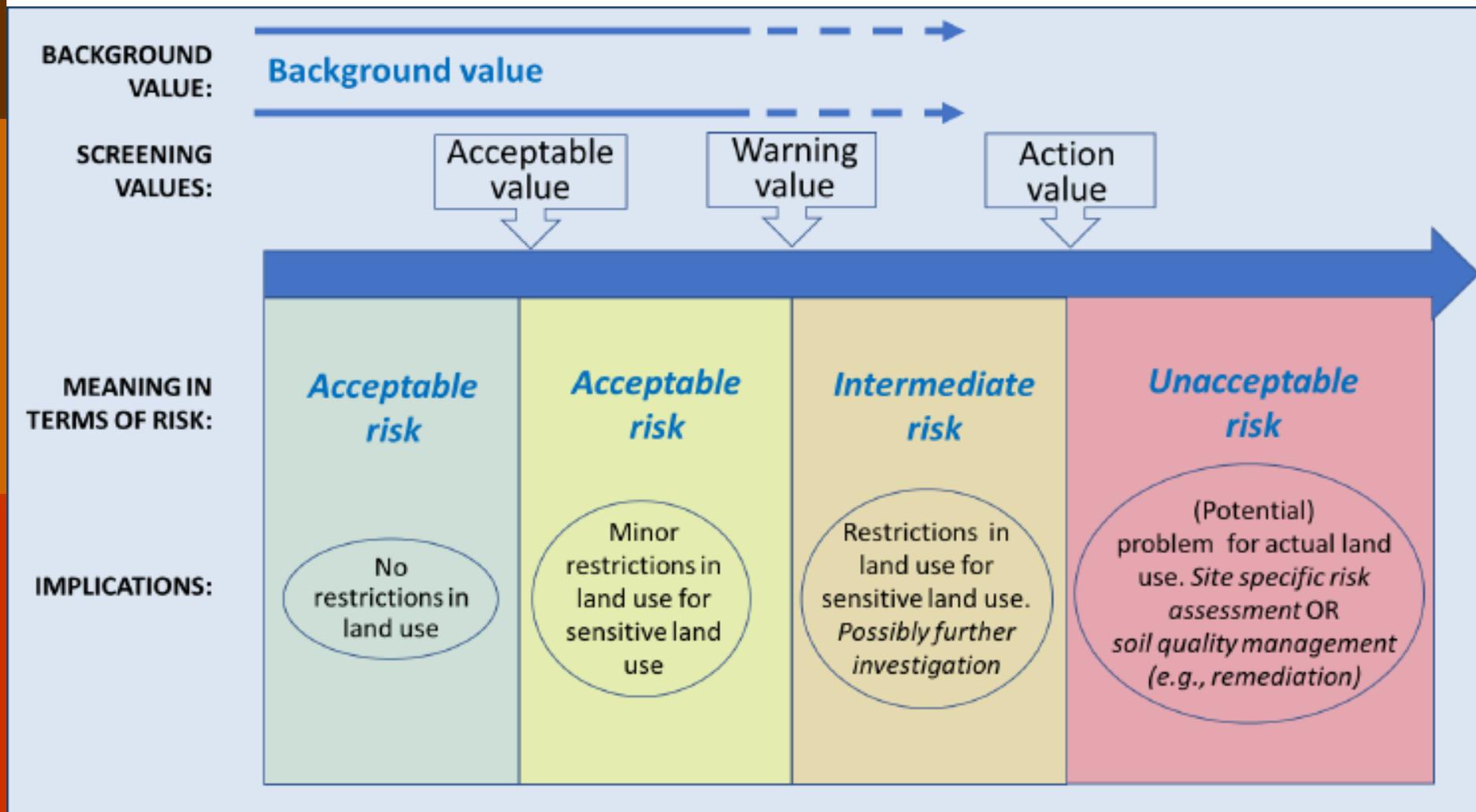
# Criteria for soil pollution assessment

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## Should take into account:

- potential risk
  - phyto-, zoo-, humanotoxicity
  - impact on the ecosystem
- transfer pathway
  - soil – plant – animal – man
  - soil – plant – man
  - soil – water – man
  - soil – man
  - land use (agriculture, forest, playground, water sources...)
- soil properties:
  - soil texture, organic matter
  - pH, sorption characteristics

# Different levels of risk posed by soil contamination



# Criteria for soil pollution assessment

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## A-B-C values:

### Preventive values (A)

- ❑ based on natural background (PTE) and common diffuse contents (OP)

### Indication (warning) values (B)

- ❑ maximum tolerable contents
- ❑ based on ecotoxicology and risk analysis

### Intervention (action, intoxication) values (C)

- ❑ serious risk, action necessary

# QUESTIONS?



# Control questions

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**Most potentially toxic elements like heavy metals (Cd, Zn, Cu, Pb, Ni etc.) are more soluble:**

- a) at alkaline reaction
- b) at low pH
- c) in clayey soils

# Control questions

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**Which elements are present in soil solution mostly in anionic form (as oxyanions)?**

- a) As, Mo
- b) Pb, Zn
- c) Cd, Hg

# Control questions

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**Which of the following forms of PTE is most mobile?**

- a) bound on iron and manganese oxides
- b) bound in defined compounds (sulfides, phosphates...)
- c) exchangeable

# Control questions

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**Unlike PTE, organic pollutants in soil:**

- a) are only of natural origin
- b) can be completely decomposed
- c) can be present as simple cations in soil solution

# Control questions

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**Which transfer pathway of soil pollutants is the most typical for agricultural land?**

- a) soil – plant – man
- b) soil – water – man
- c) soil – man



**Thank you for your attention  
See you after the break!**

# PREVENTING SOIL CONTAMINATION

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## European Green Deal

- by 2050, soil pollution should be reduced to levels no longer considered harmful to human health and natural ecosystems and respect the boundaries our planet can cope with, thus creating a toxic-free environment

# Preventing soil contamination

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- ❑ clean industry
- ❑ sustainable product design
- ❑ improved recycling, waste management and nutrient recovery
- ❑ efficient fertilizer application
- ❑ reduced pesticide use and risk
- ❑ reducing use of antimicrobials and microplastics and the per- and polyfluoroalkyl substances (PFAS)

# Determination of PTE origin in soils

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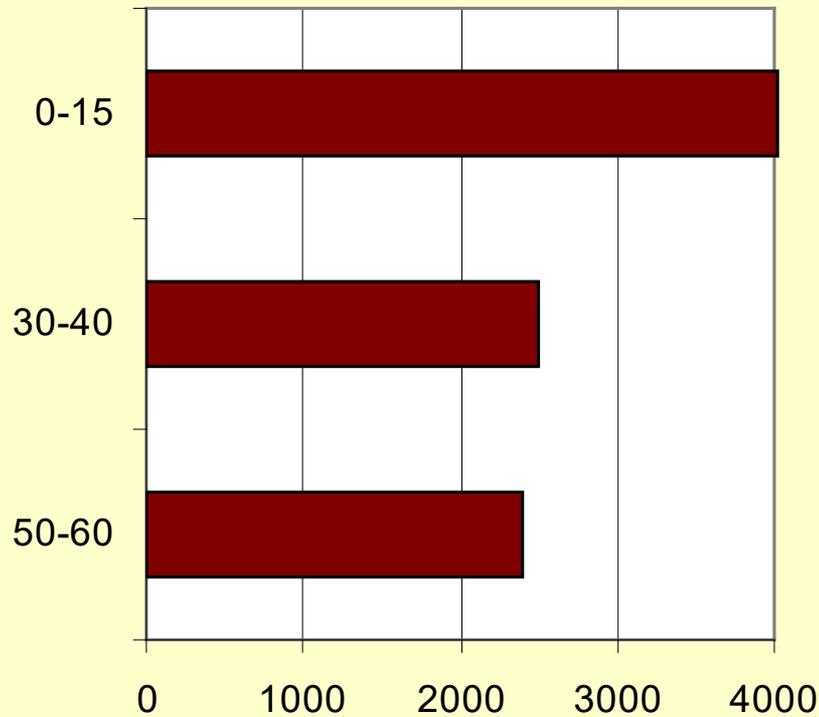
## PTE origin determination:

- distribution in soil profile
  - anthropogenic pollution – higher concentration at the topsoil
- spatial distribution
  - in case of point pollution sources
- proportion of mobile forms
  - recently entering PTE are usually less bound
- isotopic signature
  - supposing we know the potential pollution sources

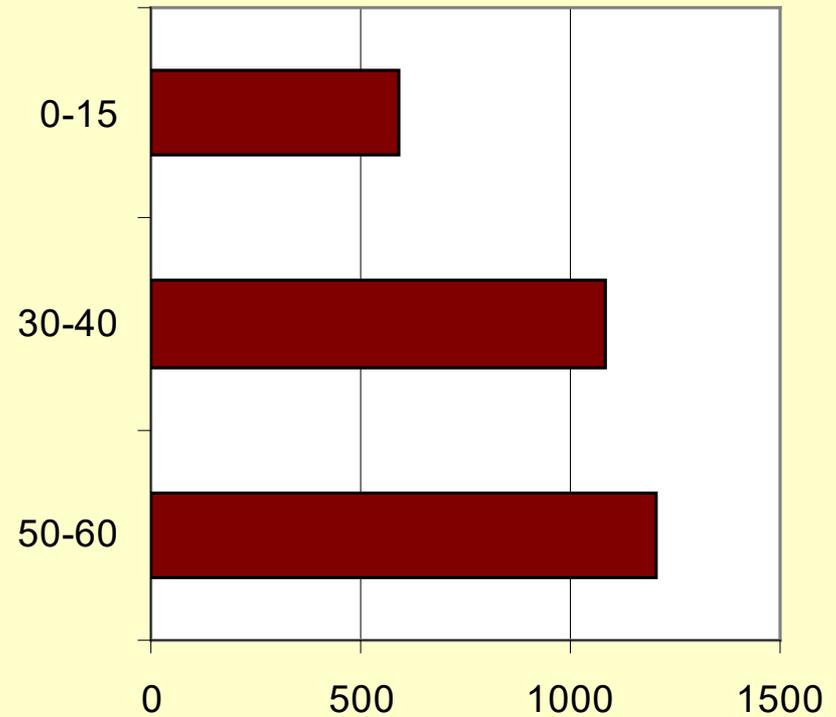
Complete distinction of the PTE origin is almost impossible.

# Pb distribution in soil profile (mg.kg<sup>-1</sup>)

## Anthropogenic enrichment



## Geogenic origin



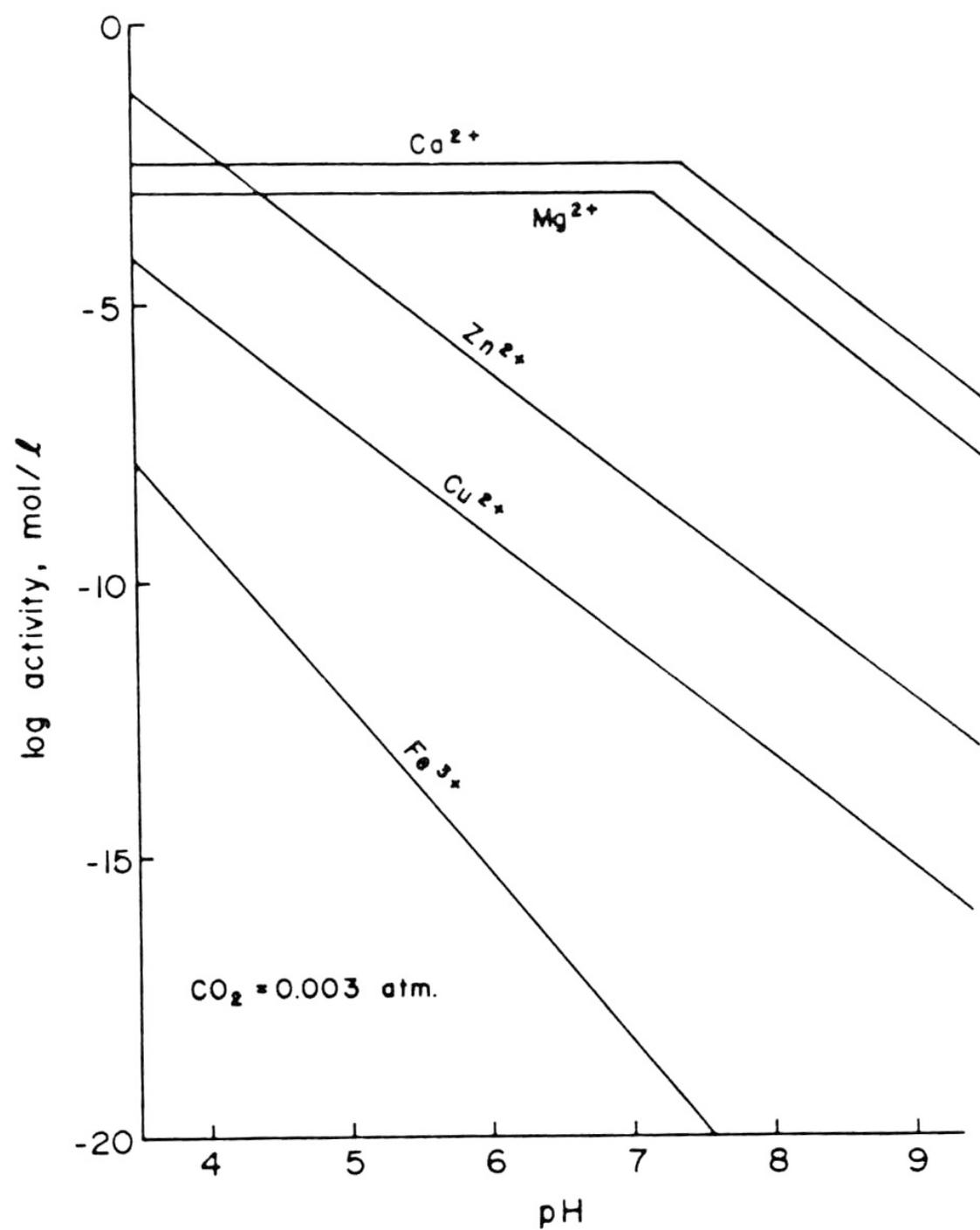
# Factors controlling behaviour and speciation of PTE in soil

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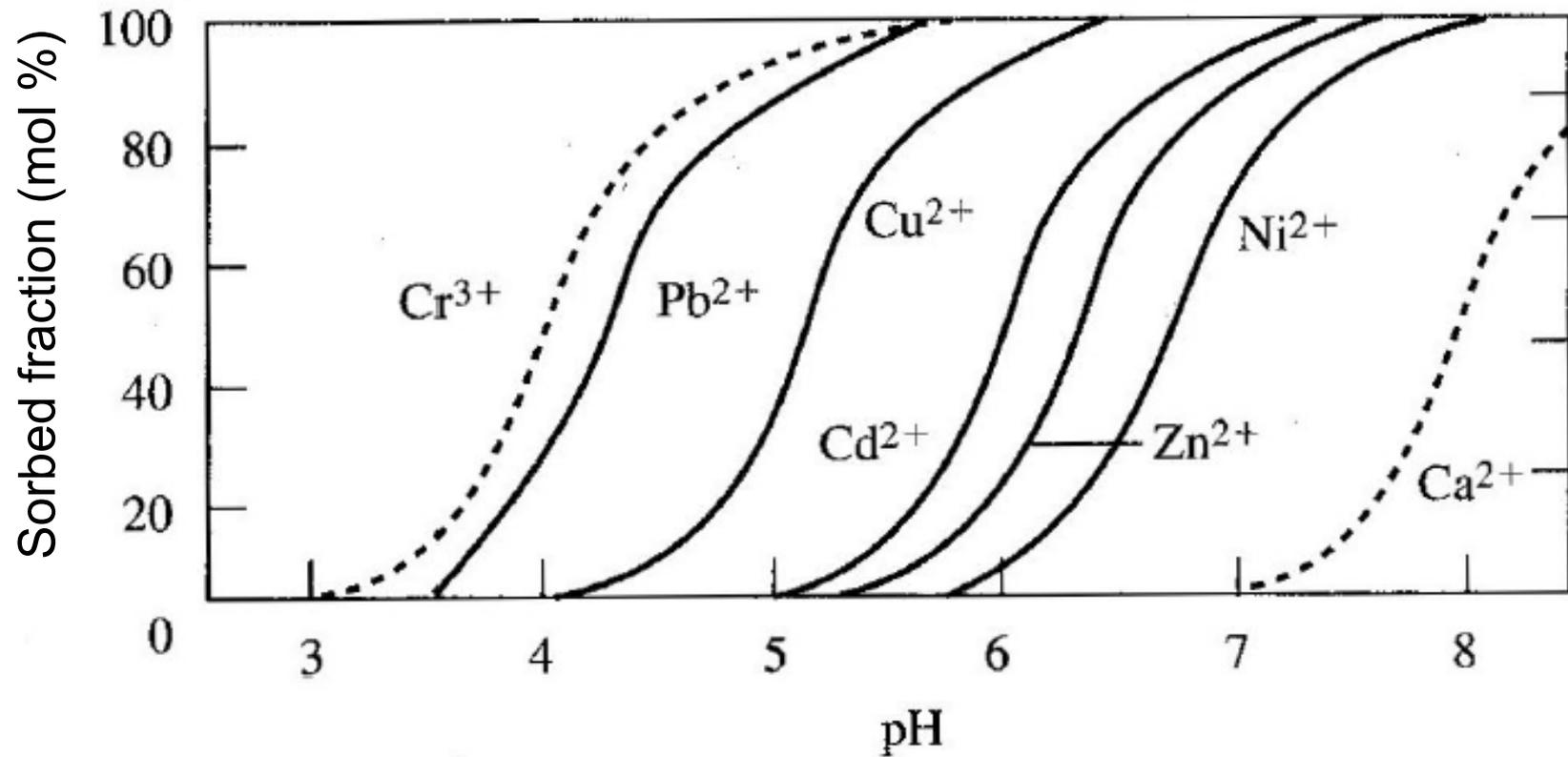
- Element characteristics
- Soil conditions
  - soil pH, redox
  - presence of ions
  - content and quality of soil organic matter
  - mineral composition
  - soil texture
- Biological factors
- Climatic conditions
  - precipitation, evapotranspiration, temperature
- Human activity

# Stability diagram

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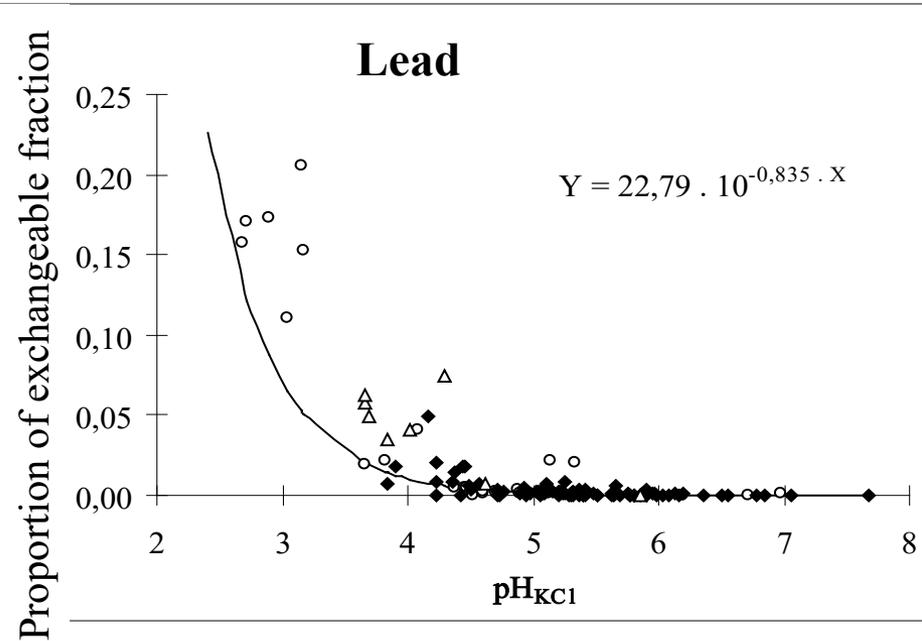
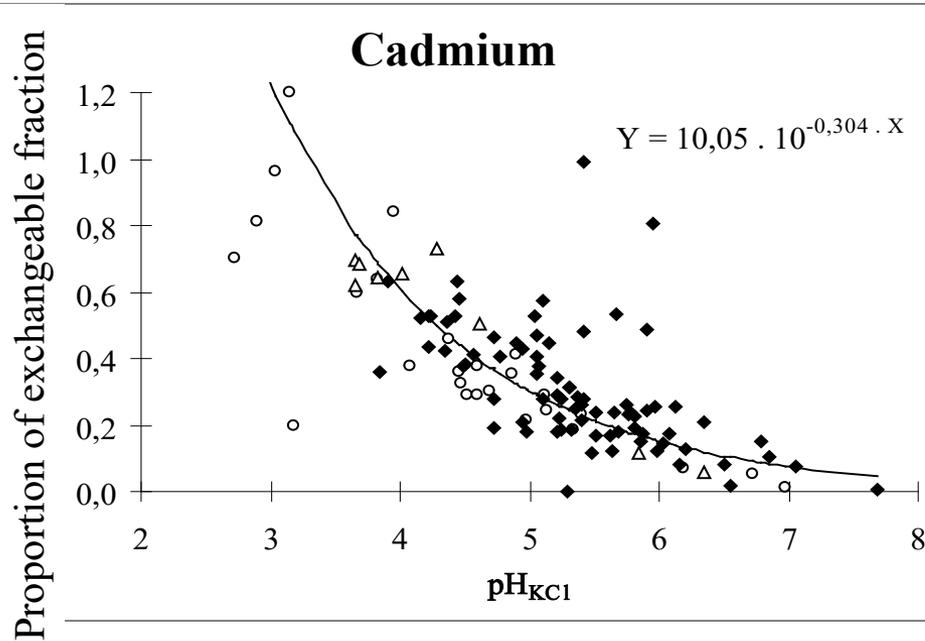
# pH effect on PTE sorption



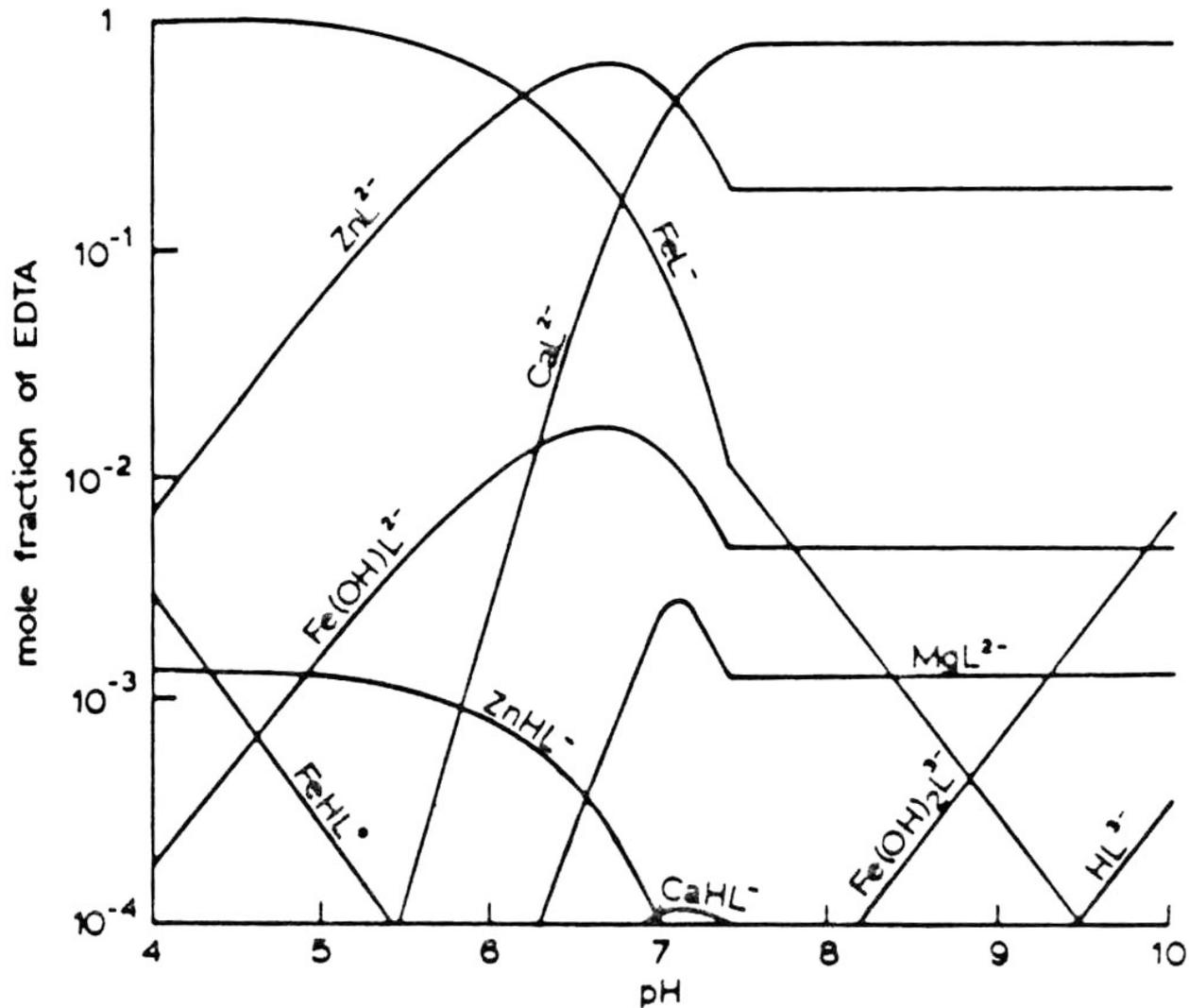
**Relative immobilization of PTE in soils:**

Pb > Sb > Cu > Cr > Zn > Ni > Co > Cd

# pH effect on PTE – case study



# Metal binding on EDTA (complexing agent) as dependent on pH



# Soil vulnerability to pollution

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## Soil vulnerability:

- buffering ability of soil to resist pollution vs. contamination – real loading of soil
- based on:
  - mobility of pollutants
  - pollutant uptake by plants
  - soil properties

# SOIL REMEDIATION

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- A way to reduce or eliminate soil degradation and restore its basic functions
  - elimination of problem sources (prevention)
  - correction of consequences
  
- Engl. *remedy* (accord. to Collins English Dict.)
  - = put right
  - = means of curing, counteracting or relieving disease, trouble
  - correction of current state (esp. pollution)

# Soil remediation

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## Methods for soil remediation:

- in situ x ex situ (on excavated soil)
- gentle x harsh
- stabilization x decontamination

## Methods:

- physical – classification/sorting, vaporization, thermal degradation, melting, vitrification, solidification, isolation, electrokinetic methods...
- chemical – immobilization, extraction, degradation...
- biological – bioremediation, bioaccumulation, phytoextraction, phytostabilization, natural attenuation...

# Factors to be considered (1)

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- ❑ type of pollution
- ❑ pollutant type and amount
- ❑ pollutant form and its properties
- ❑ origin – source and age of pollution
- ❑ importance of pollution
- ❑ the area and its exploitation

# Factors to be considered (2)

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- effectiveness and time
- ease, technical demands of the method
- financial costs
- possible consequences of the method
- local conditions, soil properties and environmental conditions
- ownership, activists ...

# Exploited properties of pollutants

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- volatility
- solubility and polarity
- chemical and thermal (in)stability
- biological degradability, bioavailability
- sorption and precipitation
- electro-magnetic properties
- size, shape, mass density

# Remediation *in situ*

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## □ Natural attenuation

- leaving soil without treatment (only monitoring)
- soil self-cleansing

Processes: decomposition, sorption, precipitation, volatilisation etc.

Problems – pollutant transport, possible toxic products, changes of conditions, long duration

## □ Dilution

- mixing with non-polluted soil

# Remediation *in situ*

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## □ Extraction (leaching, washing, flushing)

- 3 steps:
  - 1) extraction by leaching
  - 2) collection of extract
  - 3) extract treatment
- extractants: water (optionally diluted acids, chelating agents, surfactants ...)
- application: - PTE
  - anions, salts
  - organic pollutants
  - radioactive substances

# Remediation *in situ*

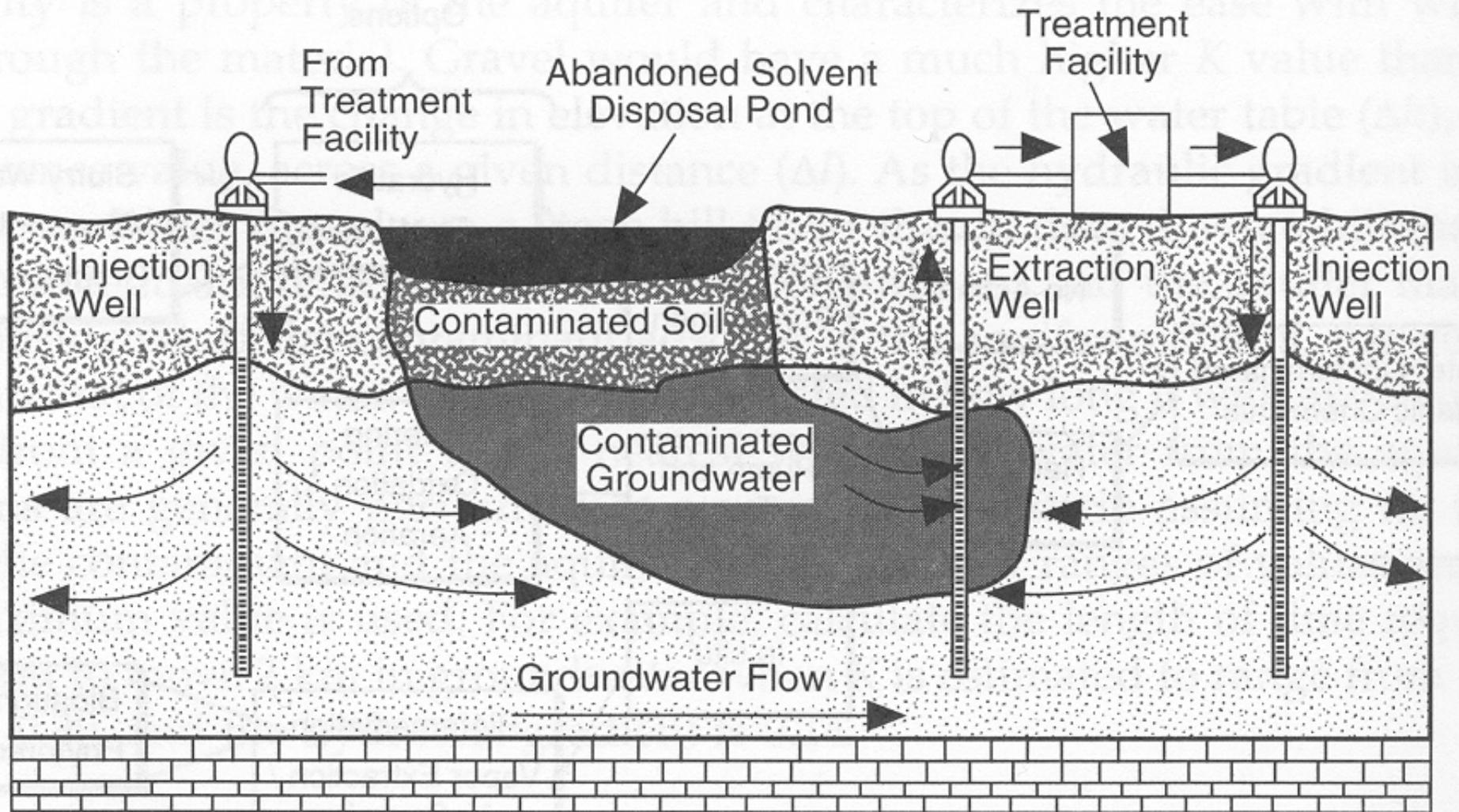
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## □ Extraction (leaching, washing, flushing)

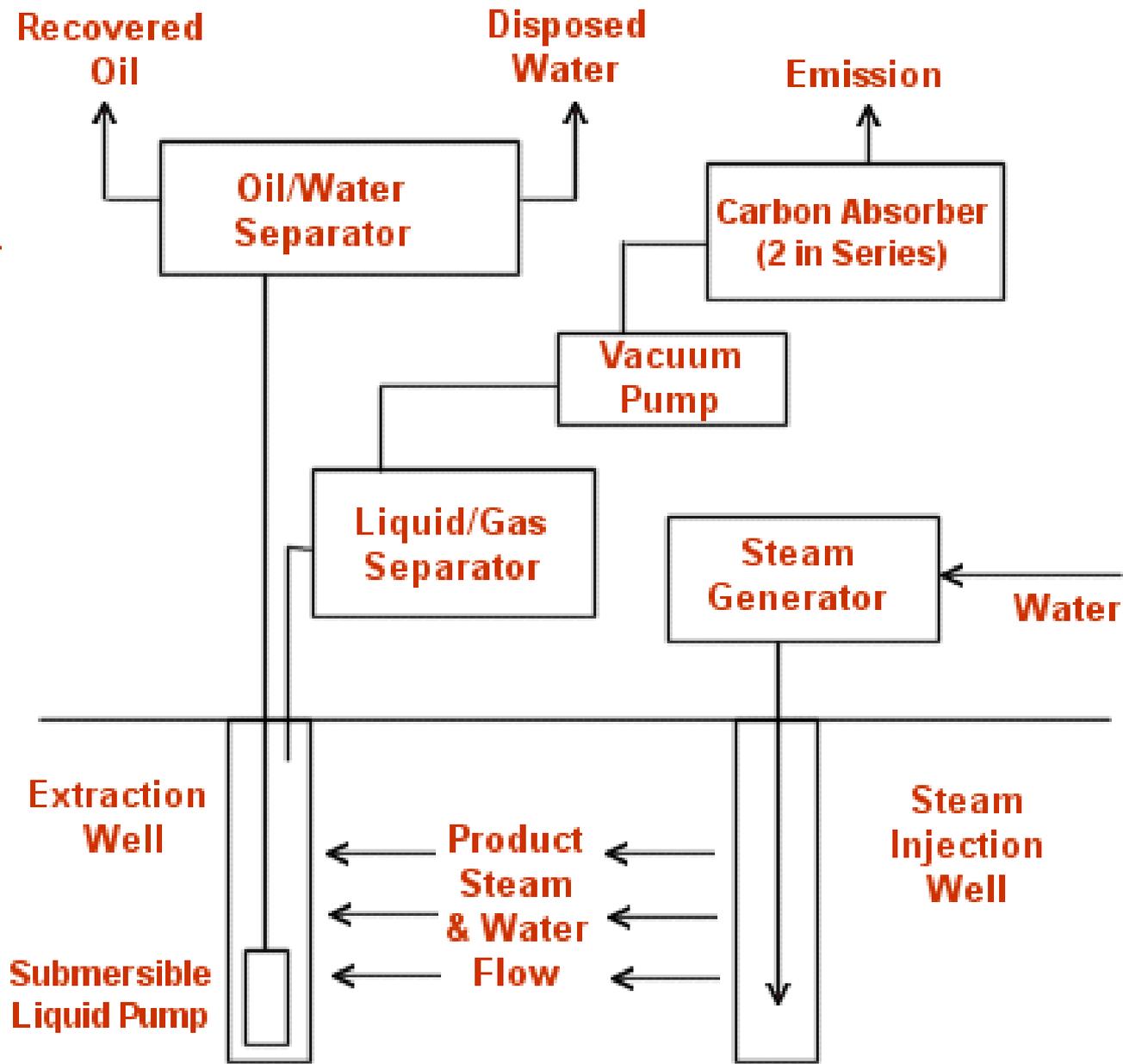
### ■ critical factors:

- pollutant solubility
- hydraulic conductivity of soil
- sorption properties and specific surface of soil
- soil pH and buffering capacity
- content and quality of SOM
- bedrock (subsoil) permeability

→ limitation: sandy soils with impermeable subsoil



**Scheme of a pump-and-treat process for polluted groundwater**



**Scheme of oil-products extraction from soil with steam**

# Remediation *in situ*

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## □ Vapour extraction (vapour stripping)

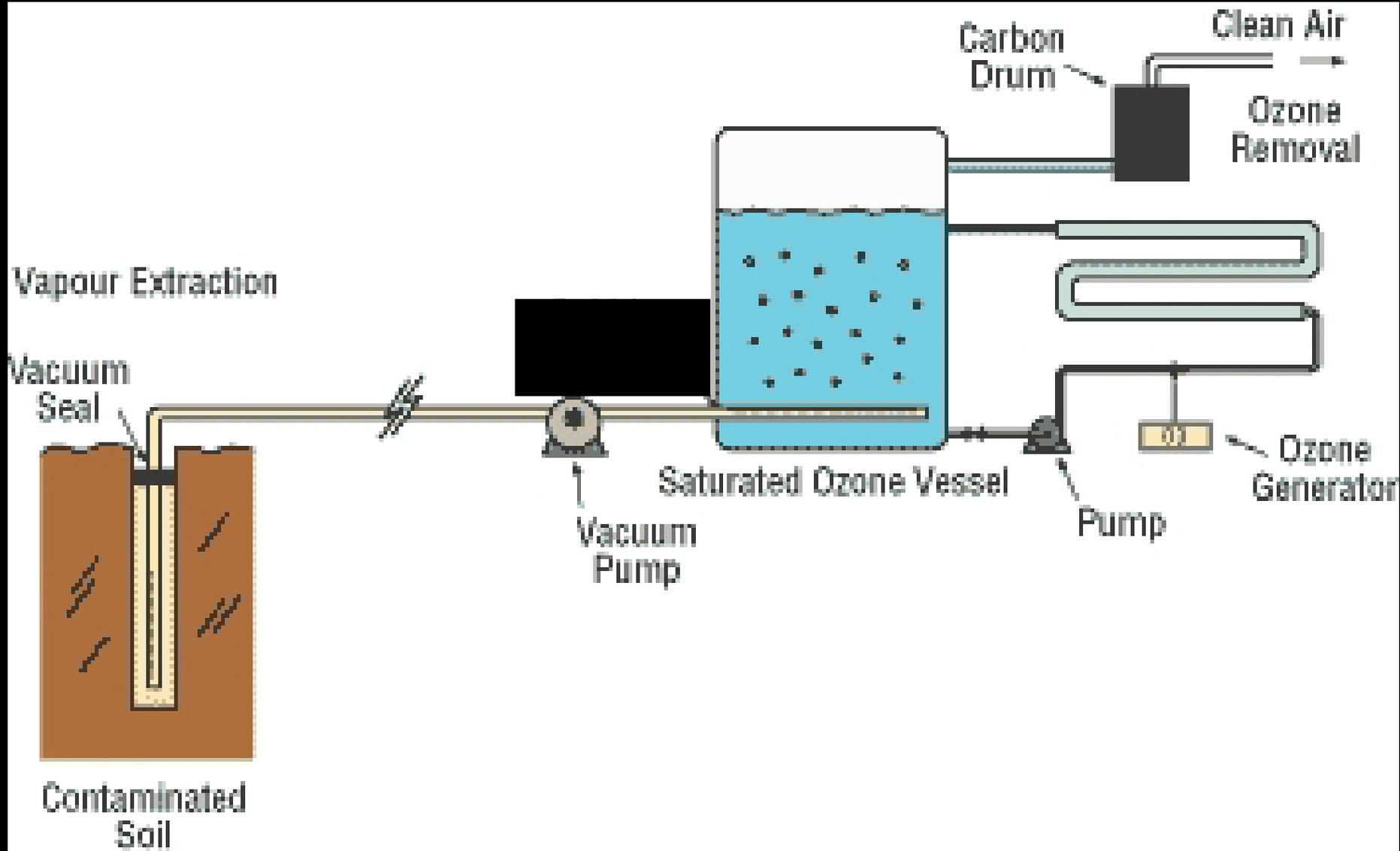
- volatile organic substances – exhaustion

### Pre-requisites:

- pollutant volatility, soil permeability (sandy soils)
- low pollutant solubility or low soil moisture
- pollution above groundwater table

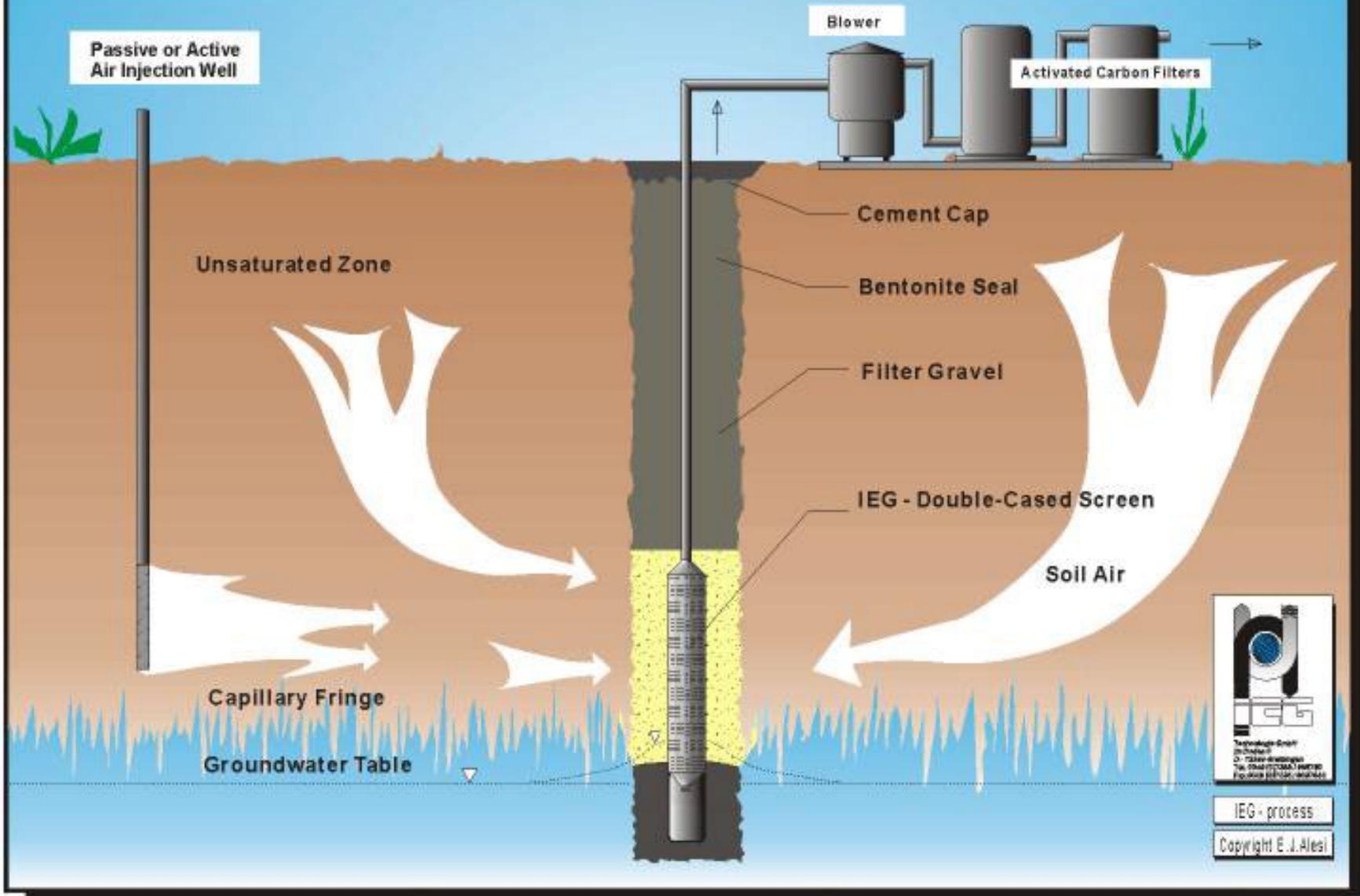
## □ Air sparging

- for saturated soils and groundwater pollution
- volatilization of pollutants by air injected below the water table



**Scheme of soil vapour extraction**

# Soil Air Venting System Using a Double-Cased Screen (DMF)



IEG - process  
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# Remediation *in situ*

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## □ Heating technologies

- can improve vapour extraction
- stimulate biodegradation

### Methods of heating:

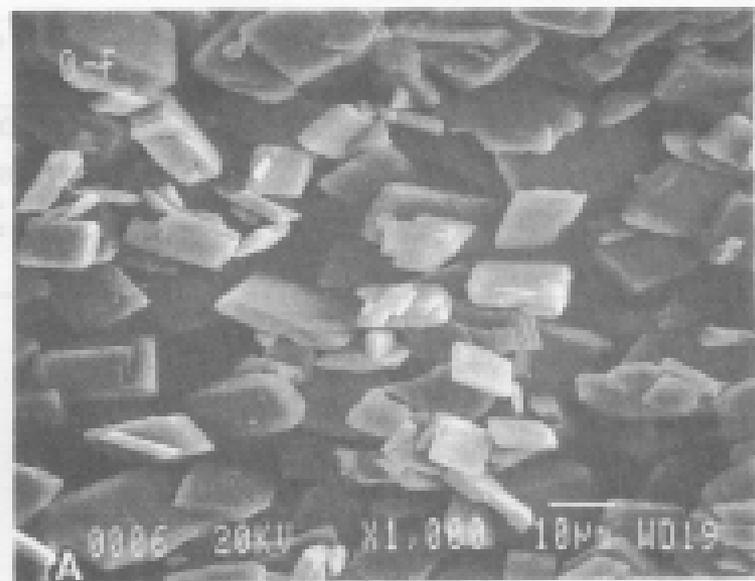
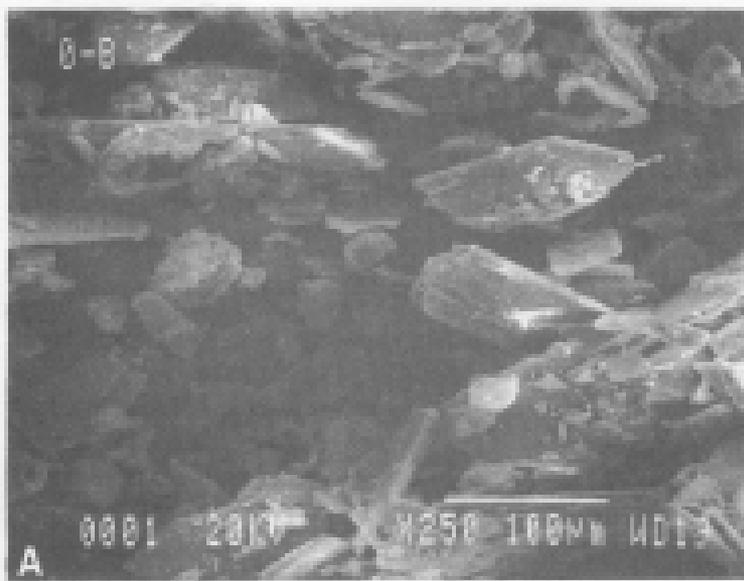
- thermal conduction (x limited radius)
- radio-frequency heating (electromagnetic radiation)
- electrical heating (clays and silts)
- steam flooding

# Remediation *in situ*

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## □ Immobilisation

- **by soil adjustment** (e.g. pH - liming)
- **soil additives:**
  - **simple inorg. compounds** - sulphides, carbonates, phosphates...
  - **inorganic sorbents** – zeolites (natural or synthetic), bentonites, clay minerals, slags, goethite, steel dust, apatites etc.
  - **organic sorbents** – farm manures, composts, straw, sludges, activated carbon, synthetic resins
  - **complexing agents** (tetrene)



**Microphotography of hydroxyapatite (left) and CaHPO<sub>4</sub> (right), separately (top) and after reaction with 500 mg Pb.L<sup>-1</sup> (bottom)**

# Remediation *in situ*

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## □ Chemical degradation

### - oxidation

- injection of peroxide, permanganate or ozone
- for organic chemicals

### - reduction, hydrolysis ...

### Potential problems:

- presence of organic matter
- distribution of applied reagents
- toxic by-products, gas evolution etc.

# Remediation *in situ*

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## □ **Photolysis**

- photochemical transformation
- e.g. UV radiation for PCB, dioxins, PAH, benzene, toluene

## □ **Bioremediation, biodegradation**

## □ **Phytoremediation**

# Remediation *in situ*

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## □ **Electrokinetic processes**

Principle: transport of electrically charged particles in electric field

- *electroosmosis* (solutions, electrolytes)
- *electrophoresis* (colloids)
- *electrolysis* (ions, complexes)

Applications:

- both *in situ* and *ex situ*, no soil disturbance
- even loamy and clayey soils

# Remediation *in situ*

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## □ **Electrokinetic processes**

### Applicable for:

- PTE (Pb, Hg, Cd, Ni, Cu, Zn, Cr)
- radioactive particles ( $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{60}\text{Co}$ , U)
- anions (nitrates, sulphates, cyanides)
- petroleum hydrocarbons
- halogenated hydrocarbons (e.g. PCB)
- polycyclic aromatic hydrocarbons (PAH)
- ...

# Remediation *in situ*

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## □ **Electrokinetic processes**

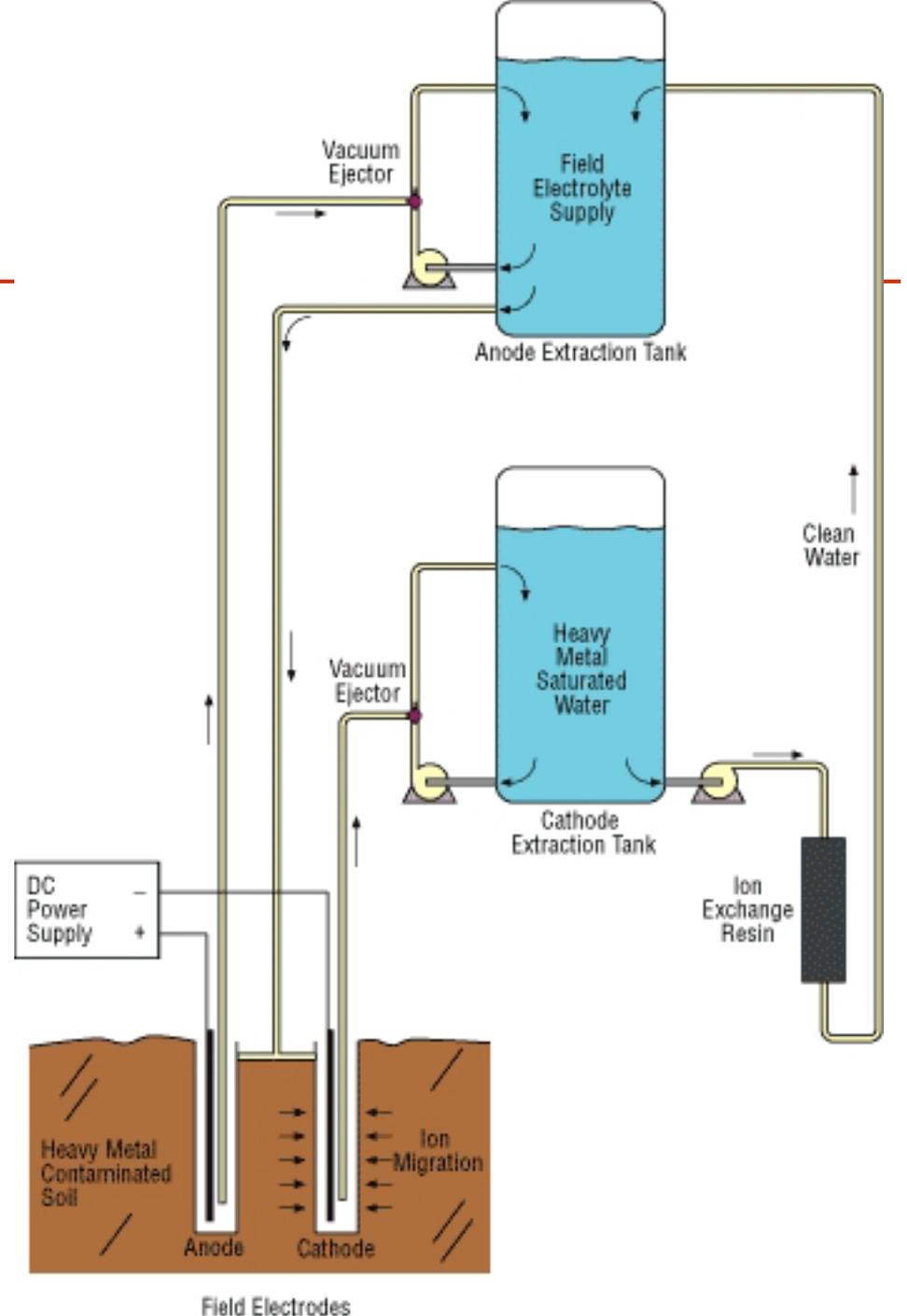
### Possible combinations with:

- bioremediation (electrokin. biorem, bioelectric rem.)
- oxidation and other degradation
- fixation (electrokinetically-deployed fixation)
- extraction (electroheated extraction)
- surfactant amendments ...

### Potential problems:

- pollutant solubility and desorption
- electrode corrosion (esp. in acid conditions)

# Scheme of soil remediation by electrolysis (heavy metal pollution)



# Remediation *in situ*

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## □ Electrokinetic processes

- Example of application for PTE pollution:
  - power consumption  $\sim 500 \text{ kWh/m}^3$
  - distance between electrodes 1-1.5 m
  - average speed of pollutant movement – 2.5 cm/day
  - direct costs  $\sim \$25/\text{m}^3$

# Remediation *in situ*

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## □ Grouting

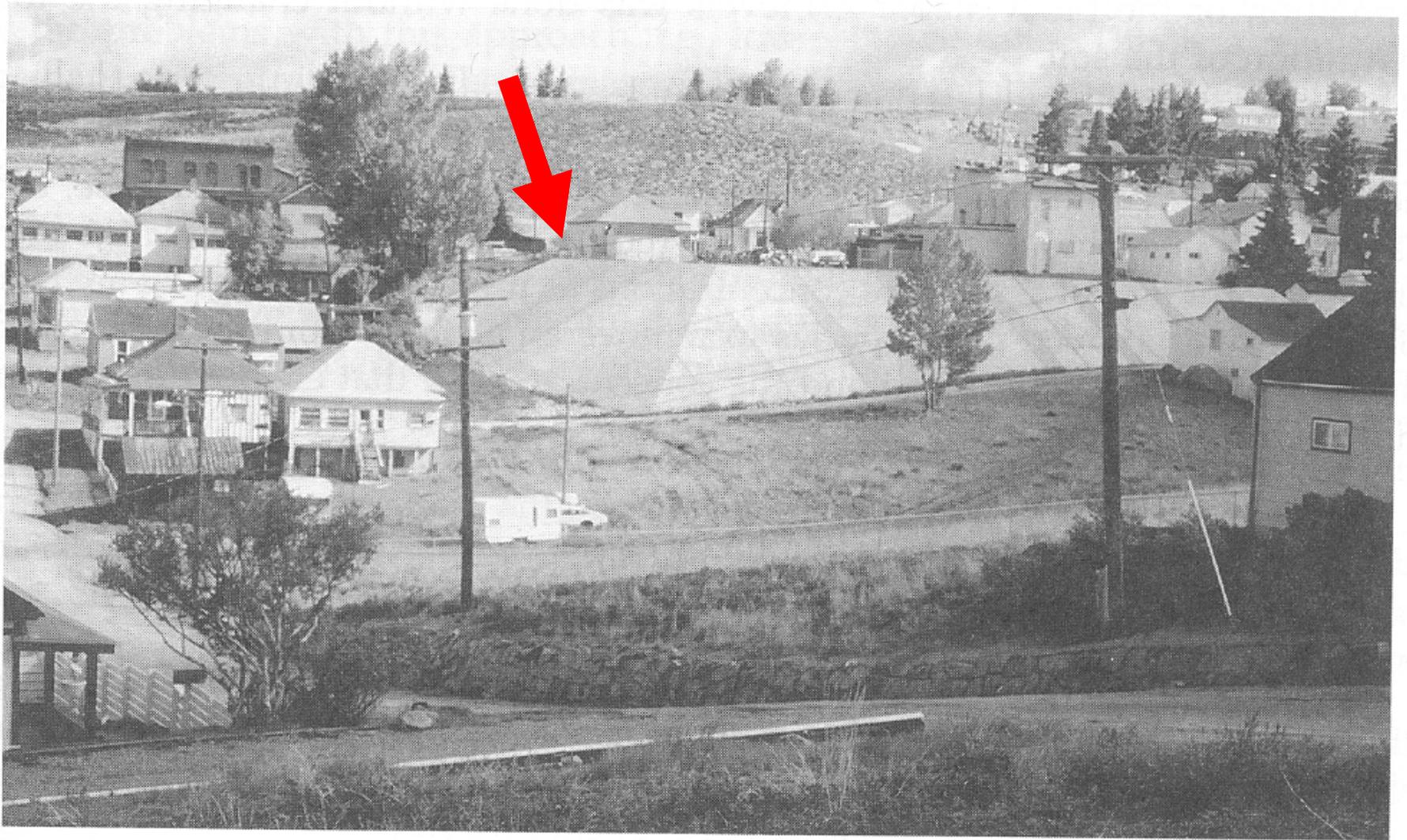
- injection of a non-porous material to soil cracks and voids to eliminate pollutant leaching

## □ Solidification

- cement, gypsum, silicates, resins, asphalt

## □ Isolation

- elimination of pollutant movement
- barriers, walls, covers, encapsulation, capping



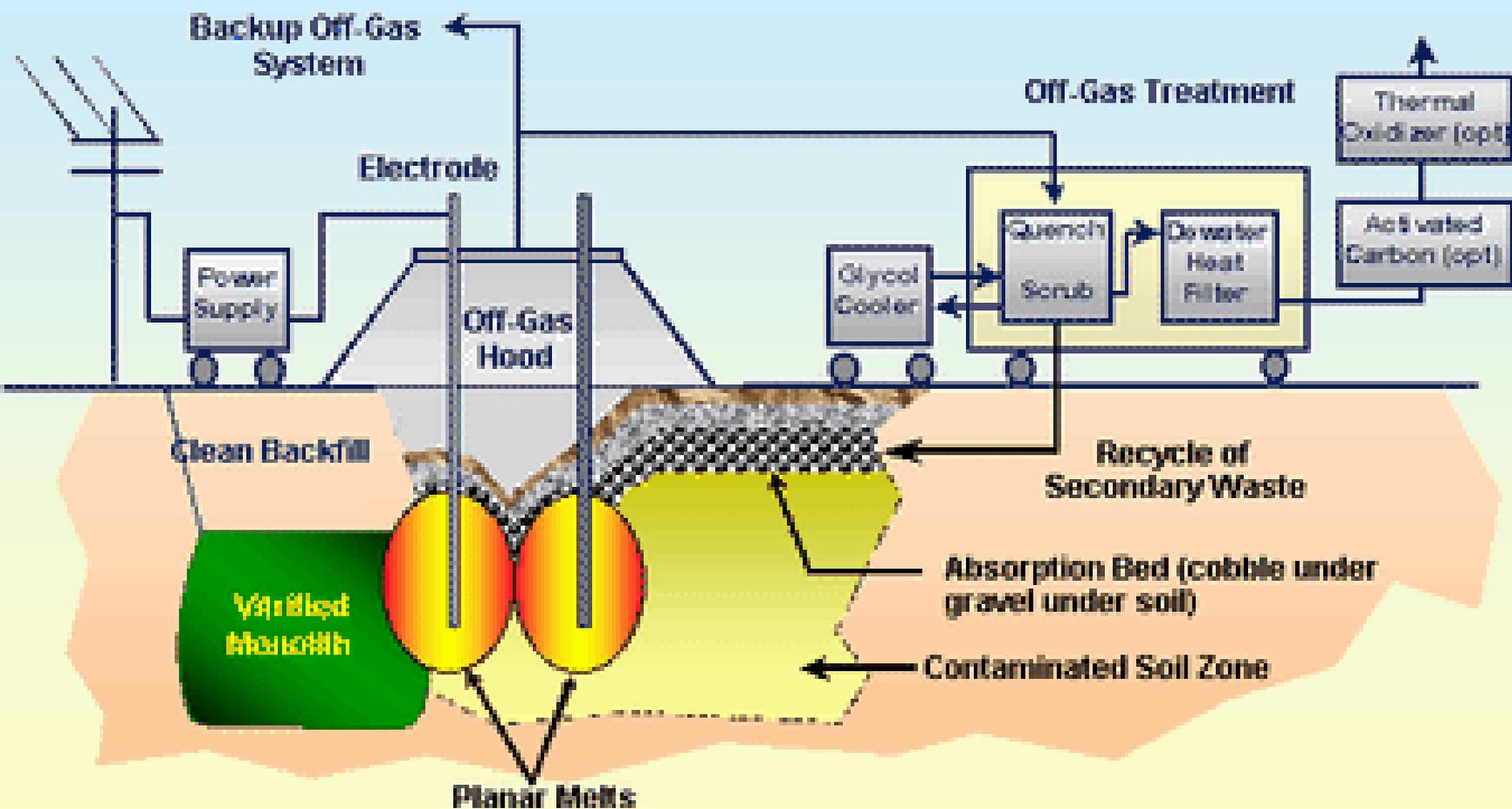
**Isolation – encapsulation** (Butte, MT)

# Remediation *in situ*

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## □ Vitrification

- thermal transformation to a glassy monolith
  - under a strong el. current (graphite electrodes)
  - ~1600-2000°C
  - volume reduction (~ 20-40 %)
  - exhaustion of volatile products necessary
  - costs ~ \$140-290/m<sup>3</sup>



**Scheme of in situ vitrification**

# Bioremediation

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- exploitation of living organisms for soil remediation

## Phytoremediation

- exploitation of higher plants for soil remediation

# Bioremediation - processes

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## **Biodegradation**

- decomposition of high contents of pollutants

## **Biotransformation**

- pollutant transformation to less dangerous forms

# Bioremediation - approaches

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- Natural attenuation (no treatment)
- Stimulated microbial activity
- Inoculation with specific microorganisms
- Treatment with specific enzymes

# Bioremediation - methods

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## **„Land farming“**

- spreading of polluted soil in a thin layer
- biodegradation, biotransformation + dilution
- especially for pesticides

## **Composting**

- stimulation of microbial activity

## **Bioreactors**

- ex situ, controlled conditions

# Bioremediation - methods

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## **Bioventing**

- gas (air) injection into unsaturated soil
- stimulation of natural processes
- can be facilitated by amendments (e.g. nutrients)

## **Air Sparging (Biosparging)**

- gas (air) injection under pressure into saturated soil
- translocation of volatile compounds to unsaturated zone where they can be decomposed

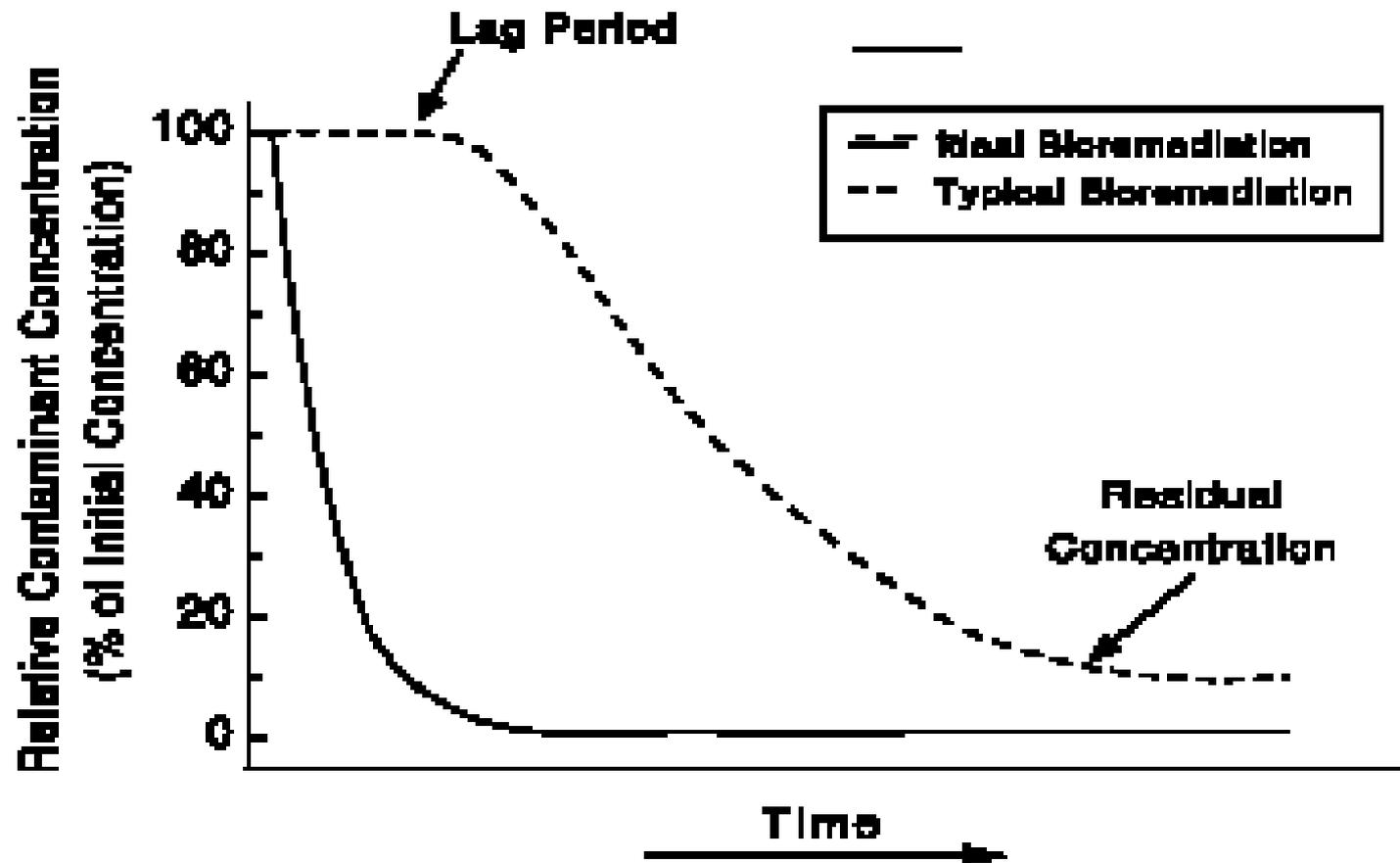


**Stimulated biodegradation – bioventing**



**Stimulated biodegradation**

# Bioremediation running



# Unfavourable factors for bioremediation

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- too high (toxic) pollutant concentrations
- concentration change does not enable adaptation of microorganisms
- insufficient number or type of microorganisms
- soil reaction (too acid/alkaline)
- nutrient, oxygen, enzymes or other deficiency
- unfavourable soil moisture

# Aspects of method selection

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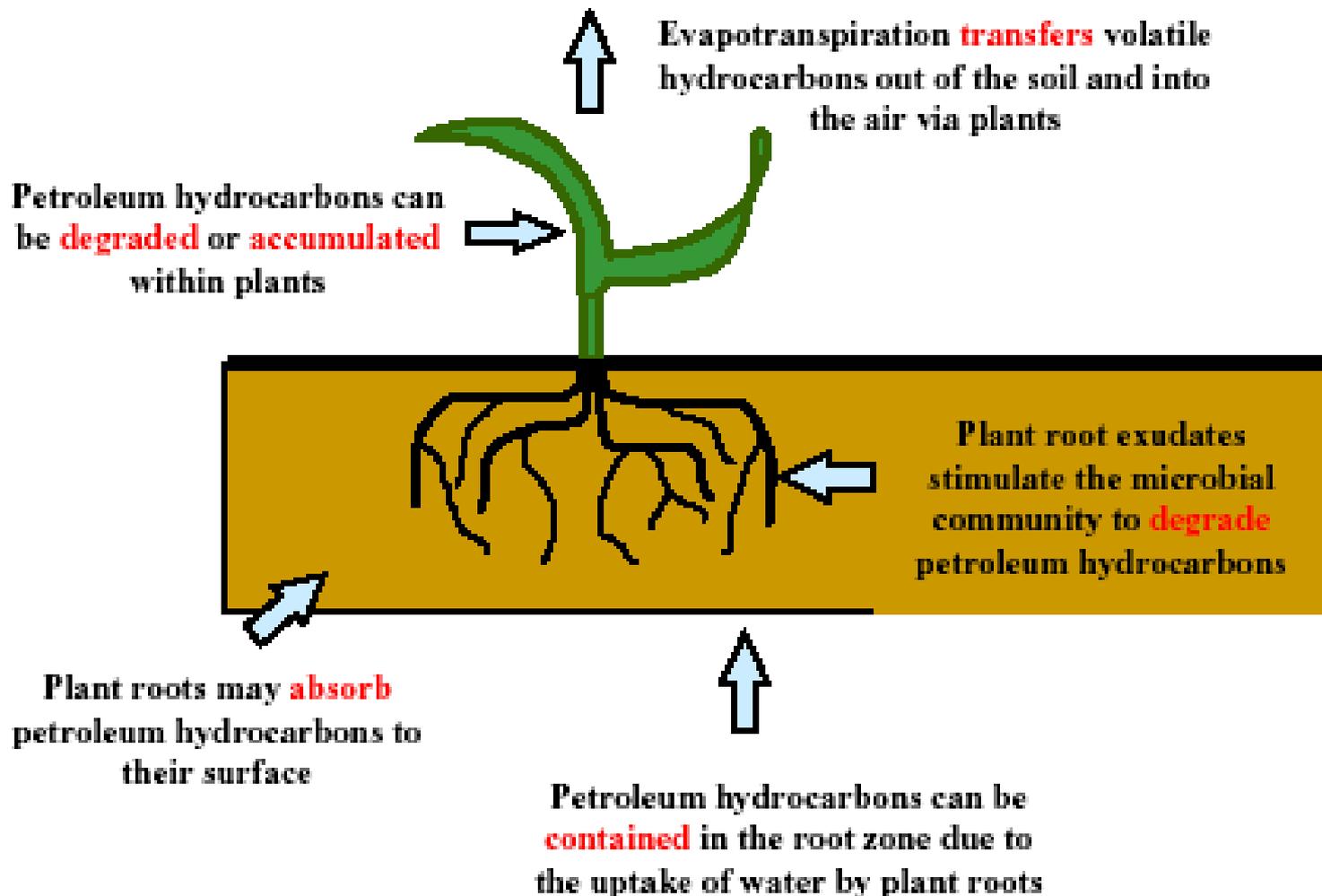
- degradability of pollutant, potential toxic by-products
- pollutant amount and distribution (spatial, profile, between soil phases)
- risk of pollutant leaching
- chemical reactivity
- soil properties, enough O<sub>2</sub> (redox potential)
- presence of other toxic substances
- ability of microorganisms to destroy the pollutant
- depth of water table

# Phytoremediation

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## Applicability:

- PTE (Cd, Cr<sup>6+</sup>, Co, Cu, Ni, Pb, Se, Zn)
- radionuclides (Cs, Sr, U)
- petroleum hydrocarbons
- chlorinated hydrocarbons (e.g. PCB)
- polynuclear aromatic hydrocarbons (PAH)
- pesticides (chlorinated, organophosphates etc.)
- nutrients (N, P)
- surfactants
- salts



## Mechanisms of phytoremediation (petroleum hydrocarbons)

# Phytoremediation - methods

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## **Phytostabilisation, phytoimmobilisation**

- vegetation cover to reduce erosion and leaching
- can be supported by additives

### Plant effects:

- accumulation, chelation, adsorption...
- changes in the rhizosphere:
  - pH, SOM, redox ...
  - element accumulation, precipitation
  - microbial activity

# Phytoremediation - methods

## **Phytostabilisation, phytoimmobilisation**

### Required plant properties:

- tolerance to the pollutant
- high production of root biomass
  - able to immobilise pollutants
- pollutant retention in roots

### Limitations: - low productivity

- unusable or only technical crops

# Phytoremediation - methods

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## **Phytovolatilisation**

- transformation of pollutants (e.g.. Hg, Se) to volatile forms by plant enzymes

## **Phytotransformation**

- pollutant decomposition in plant metabolism

## **Phytoextraction**

- pollutant removal by plant uptake

# Plant classification according to their response to soil pollution with PTE

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- **inadaptable (intolerant)**
- **indicators**
- **excluders**
- **accumulators**
- **hyperaccumulators**
  - > 0.01 g.kg<sup>-1</sup> dry weight in case of Hg
  - > 0.1 g.kg<sup>-1</sup> dry weight in case of Cd
  - > 1 g.kg<sup>-1</sup> dry weight in case of Co, Cr, Cu, Ni, Pb
  - > 10 g.kg<sup>-1</sup> dry weight in case of Zn, Mn (tj. > 1%!)







# Phytoextraction

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## a) Natural:

- exploitation of hyperaccumulators
  - *in total ~ 400 species from at least 45 families*

## b) Induced (enhanced):

- using of chemical compounds to increase plant uptake of risk elements
  - especially chelating agents
    - (EDTA, DTPA, citric acid...)
- x danger of leaching!

# Phytoextraction

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- Advantages:
- rel. low costs (~ \$17-100 per m<sup>3</sup>)
  - environmentally safe

- Problems:
- long duration
  - possible pollutant transfer
  - introduction of non-native organisms
  - biomass liquidation
    - landfills, drying, composting, leaching
    - vitrification, controlled incineration  
(5000 t contam. soil/ha → 25-30 t plant ash)
  - only for shallow pollution (20-100 cm)

# Phytoextraction

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## Applicability:

- PTE
- radionuclides
- some organic substances

„**Phytomining**“ – commercial biomass  
utilisation for metal production

# Phytoextraction

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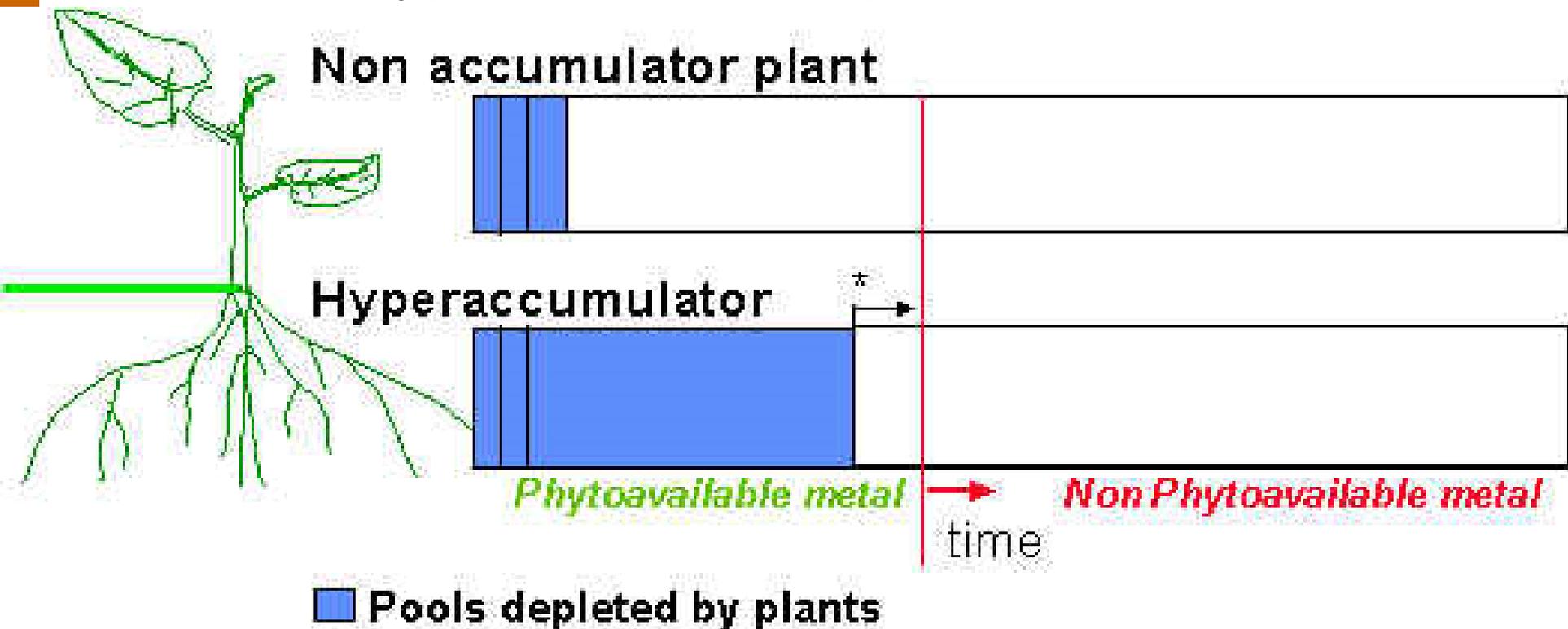
## Required plant properties:

- ❑ tolerance to pollution
- ❑ suitability to given conditions
- ❑ high pollutant uptake and its accumulation in above-ground parts
- ❑ high yield and easy harvesting

*Tolerance to a heavy metal, Cu, was first found at Melandrium album in Piesky, Slovakia (Silvestr Prát, Charles University, 1934)*

# Phytoextraction

Comparison of metal uptake by hyperaccumulator and non-hyperaccumulator plant



\* Limit depends on the plant species and plant growth conditions

# Phytoextraction

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## Effectiveness:

Total amount of removed risk element =  
= (Concentration of RE in plant) x  
x (biomass yield)

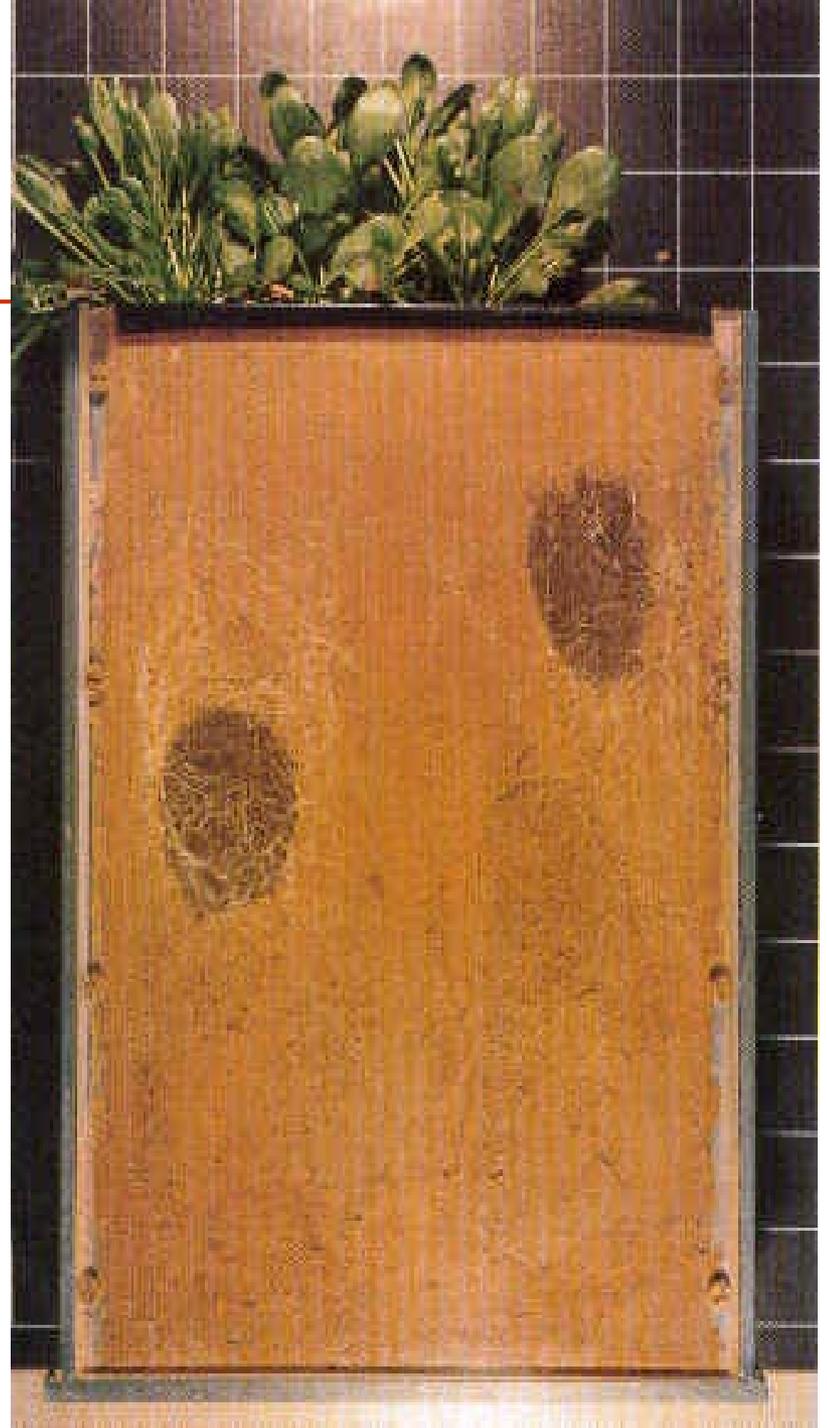


***Thlaspi caerulescens* (Zn, Cd, Pb etc.)**

**Response of *Thlaspi caerulescens*  
to Zn content increase in soil**

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**Basal rosette of  
*Thlaspi caerulescens***





***Salix viminalis***



**Hyperaccumulating  
ferns  
(*Pteris vittata*)**



# QUESTIONS?



# Control questions

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**The most important soil properties controlling behaviour of potentially toxic elements are:**

- a) content of sand and silt
- b) soil pH and content and quality of soil organic matter
- c) composition of soil microorganisms

# Control questions

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## **Extraction as a soil remediation method:**

- a) can be used only on excavated soil
- b) is suitable especially for clayey soils
- c) is applicable only for soluble pollutants

# Control questions

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## **Immobilisation of pollutants as a method of soil remediation:**

- a) can be reached by soil adjustment or soil amendments
- b) aims in removal of the pollutants from soil
- c) ensures complete decomposition of pollutants

# Control questions

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**Which of the following pollutants are readily biodegradable?**

- a) most potentially toxic elements
- b) PCB, PAH
- c) petroleum hydrocarbons

# Control questions

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## **Phytoextraction as a soil remediation method:**

- a) is very fast and effective
- b) is applicable especially for organic pollutants
- c) causes almost no soil disturbance



**Thank you for your attention**