Soil and Water Contamination and Remediation

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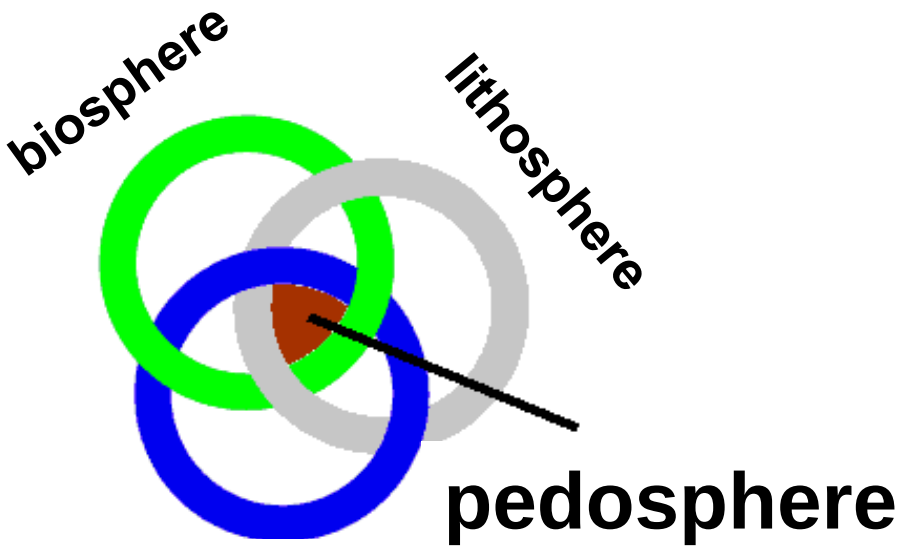
Soil – interface of systems



soil is natural unit generated at the **interface of lithosphere and atmosphere** under mutual process of pedogenetic factors

soil is **binding element** in between anorganic and organic matter and live organisms on the Earth

soil is desribed according to soil horizons

Atmosphere

Vegetation

Carbon binding
Roots
Nutrients
Organic matter

Wind
Heat
Rain
Light

CO_2
H_2O

Nutrients
Water
pH

pores

loosening

Weathering
Nutrient release
Fertility
Texture
Colour

Soil

Bedrock

Ecological functions of soil

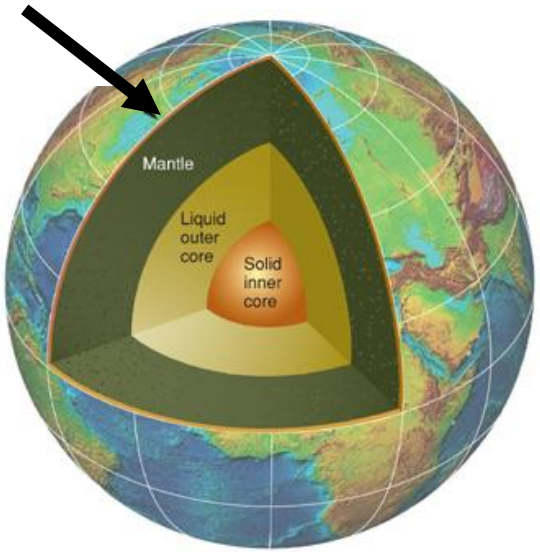
- Supports growth of plants and live of other organisms (phytoedaphon and zooedaphon)
- Recycles nutrients and exhausts
- Governs flow and purity of water
- Serves as building material

Elementary components of soil

Element %	O 49,0	Si 33,0	Al 6,7	Fe 3,2	Ca 2,0	Na 1,1	Mg 0,8
Element %	K 1,8	Ti 0,5	P 0,08	Mn 0,08	S 0,04	C 1,4	N 0,2

(URE a BERROW, 1982)_

- Oxides, hydroxides, organic compounds, soil air
- Silica, silicates, clay minerals
- Clays



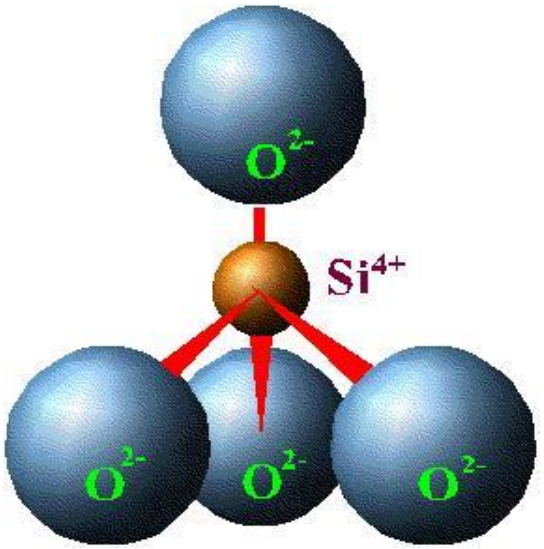
Minerals

- Up to 50% of soil volume
- Made of particles of different sizes
- Determine chemical reaction
- Originate from bedrock material

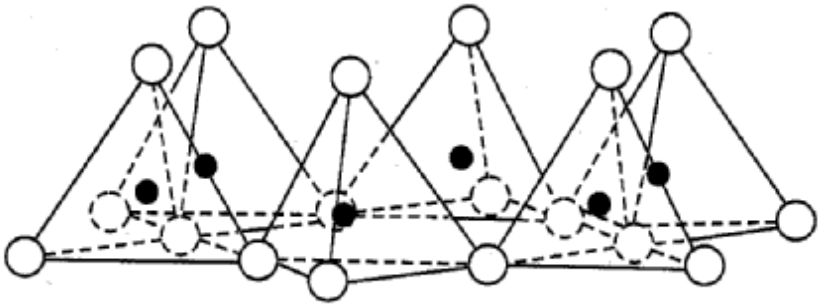
Clay minerals

- silica tetrahedron SiO_4

  one atom of Si is surrounded by 4 anions of O^{2-}



- create layer of tetrahedrons sharing O^{2-}

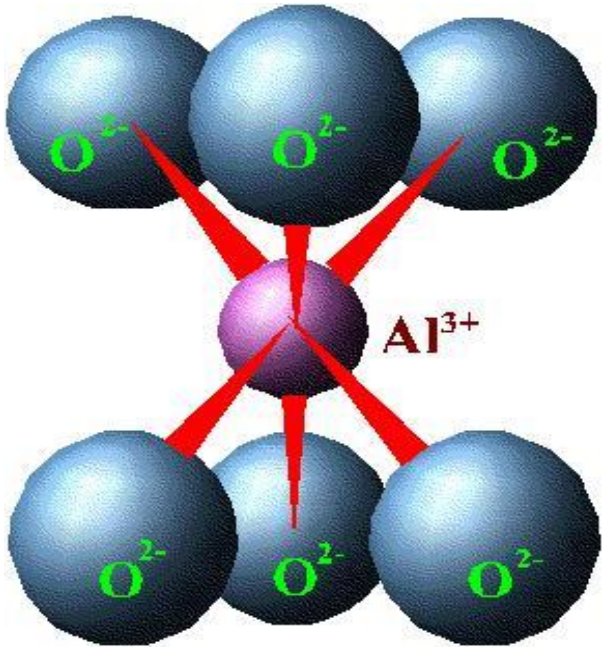


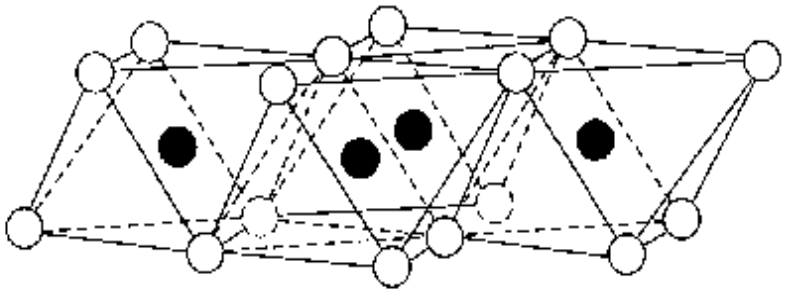
Clay minerals

- aluminium octahedron

  6 oxygens with Al^{3+} atom

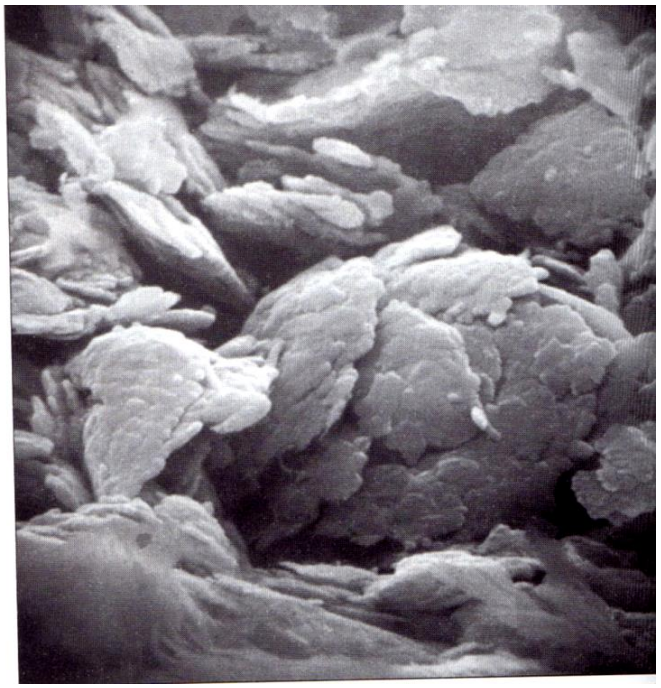
- layer of octahedrons bound with shared O^{2-} or OH^-





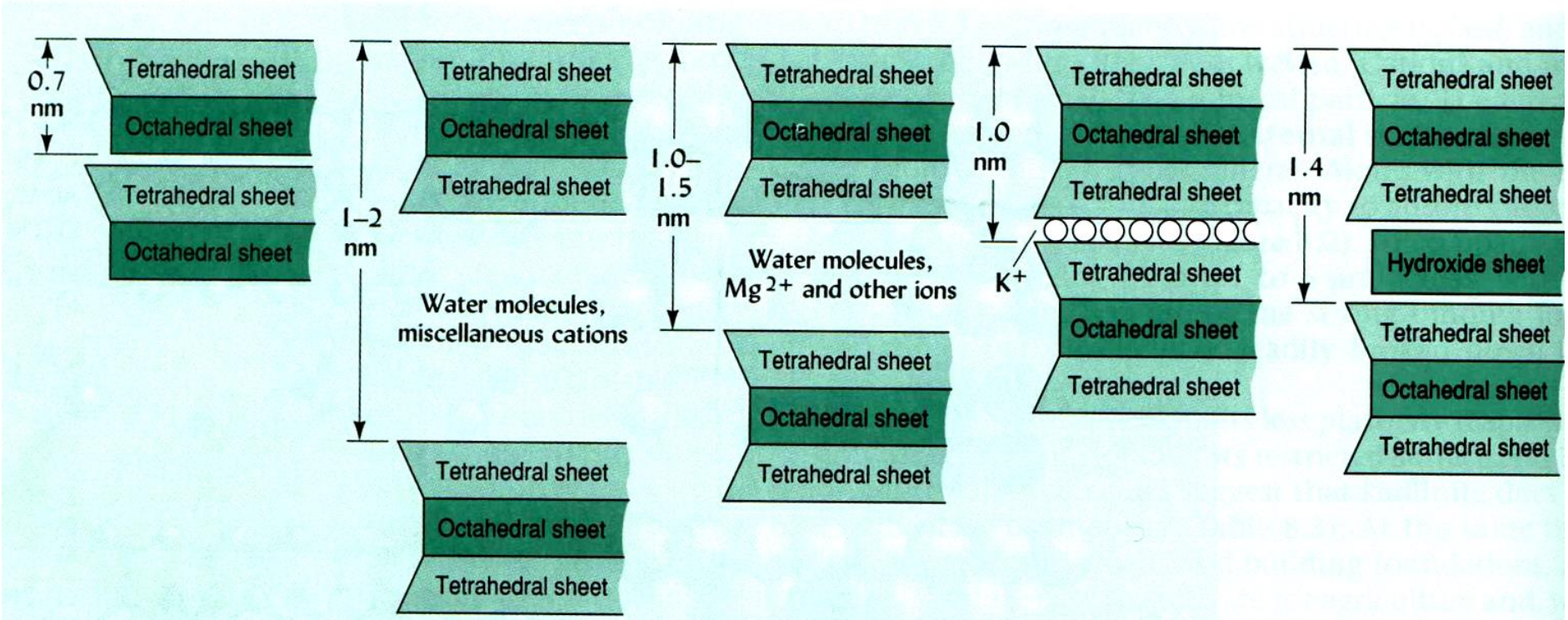
Clay minerals

- Products of **weathering** of rocks (secondary minerals)



- Posses surface charge: attract ions, impact plasticity and adhesion of soil

Types of clay minerals



(Vermiculite (Mica)

Kaolinite 1:1 **Montmorillonite2:1** **Illite 2:1** **Chlorites 2:1**

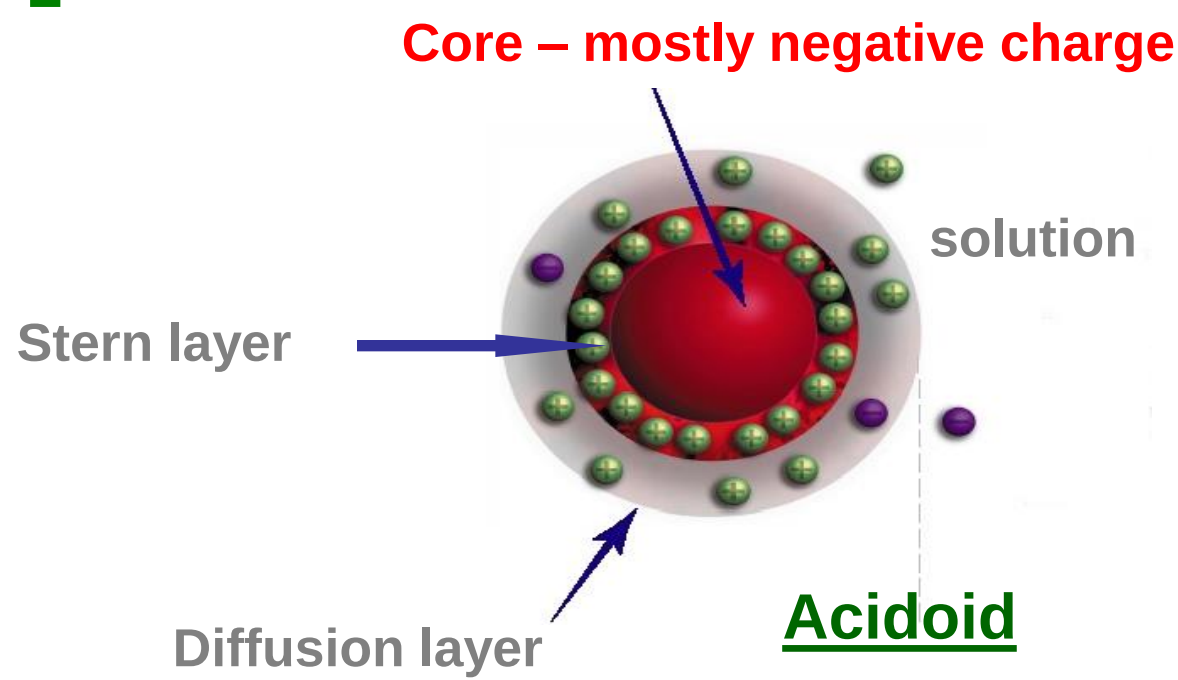
Coloids

Coloids (acc. to charge)

- Acidoids (adsob cations)
- Bazoids (adsorb anions)

Ampholytoids (charge acc. to pH)

- pH ↓ ... bazoids
- pH ↑ ...acidoids



Pedogenetic factors

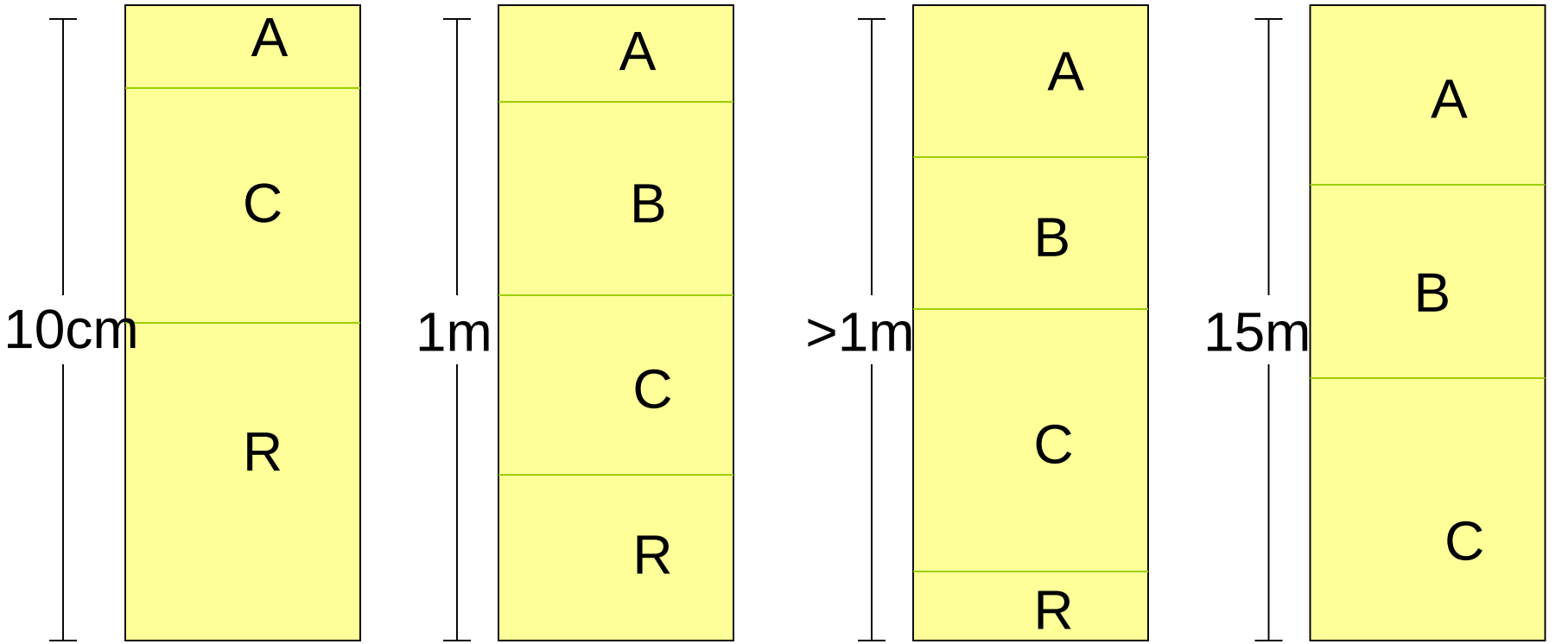
- Bedrock

  (determines properties of soils, important is ability of rock to weather)
- Topography (steepness, orientation, altitude)
- Climate

  (moisture and temperature, precipitation - rainfall)
- Organisms

  (determine creation and existence of soil)
- Time

Impact of climate to soil layering



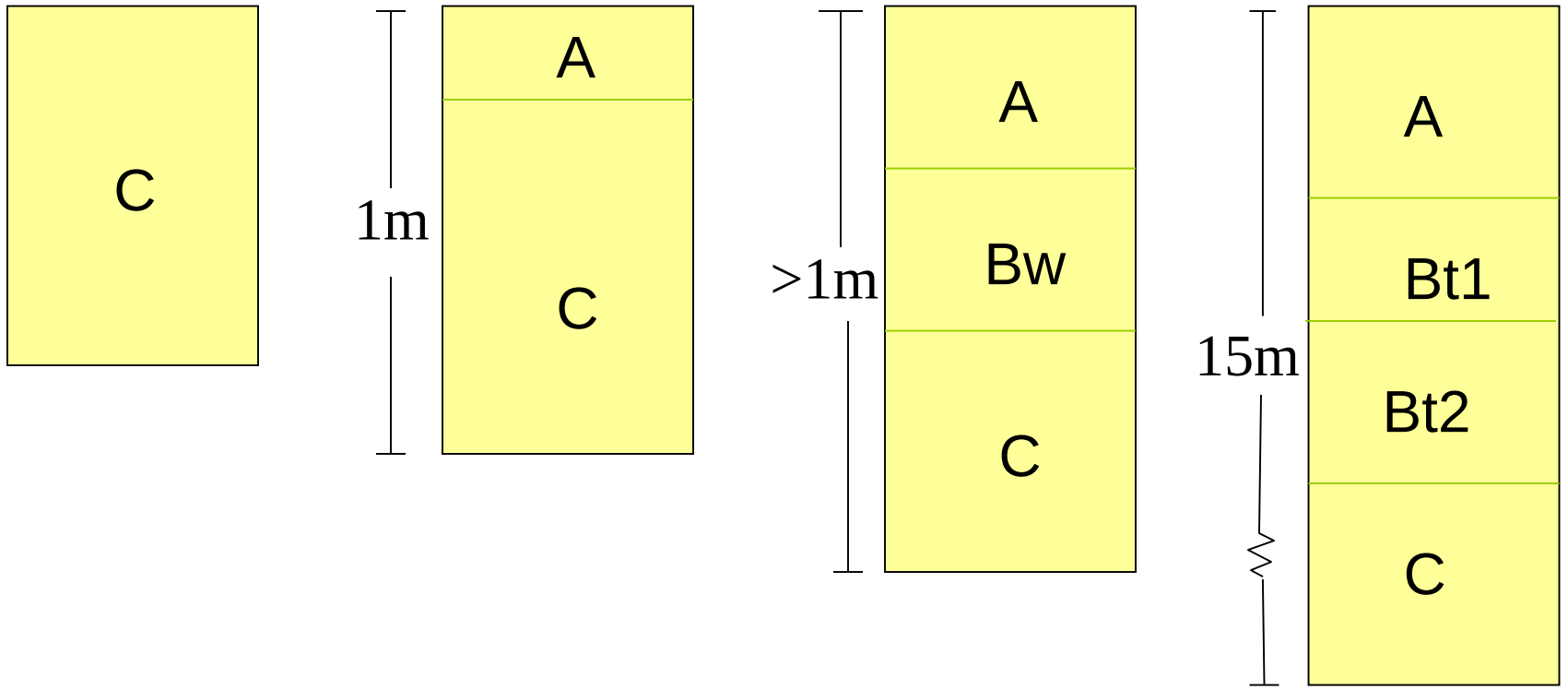
Desert, perma-frost

Arid, semi-arid

warm, wet

rainforest, tropical

Time development of the soil profile



maternal bedrock

“young profile”

“mature profile”

“highly mature profile”

Weathering

physical

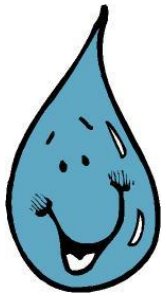
1. Frost
2. Irregular heating
3. Swelling - drying
4. Abrasion (water, wind, ice)
5. Root growth

Weathering

Chemical

1. Hydratation
2. Hydrolysis
3. Dissolution
4. Carbonation
5. Complexation
6. Oxidation-reduction

All processes require water

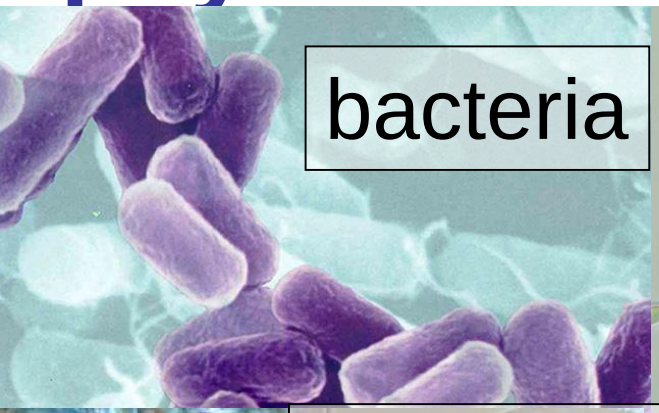


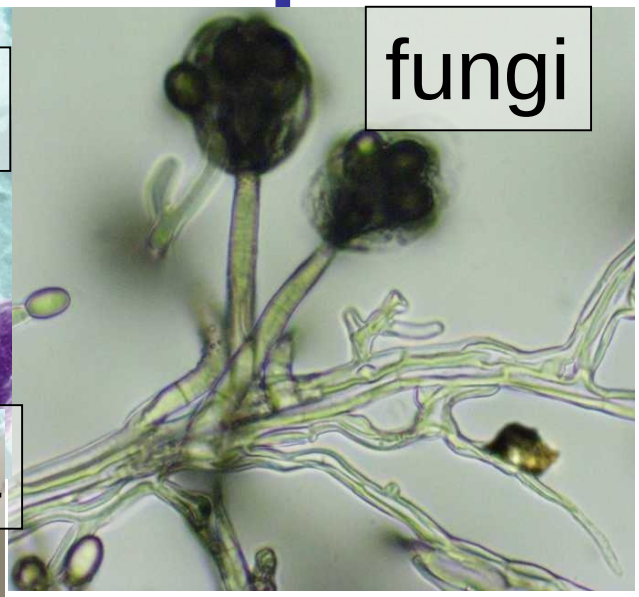
Impact of organisms on the soil formation

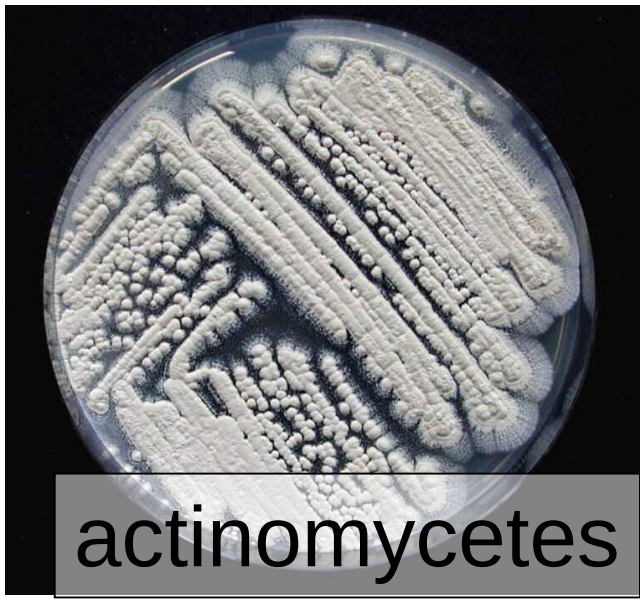
- Vegetation
  - Type of rooting, leaf chemism, amount
- Microbes
  - Decomposition of the organic matter
- Soil animals
  - Building of pathways for water flow
- Humans

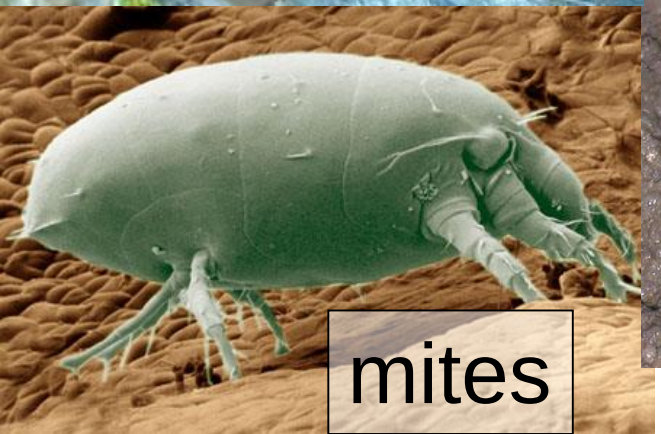
  Tillage, compaction, changes of the landscape – drainage, aplication of chemicals, pollution

phyto- a zoo-edaphon - examples









Human impact on soils

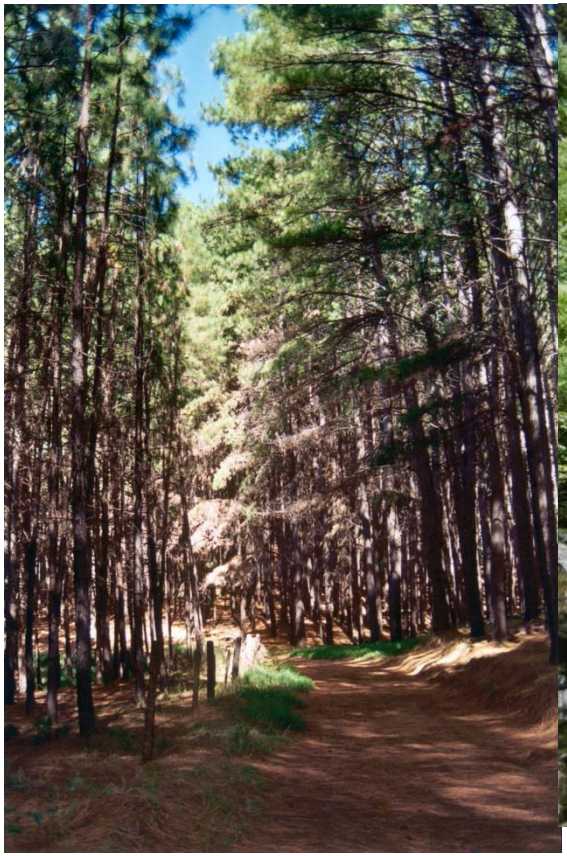
- **intensive agriculture**
  - ✓fertilization
  - ✓pesticides
  - ✓toxic compounds
- **landfills**
- **urbanization**

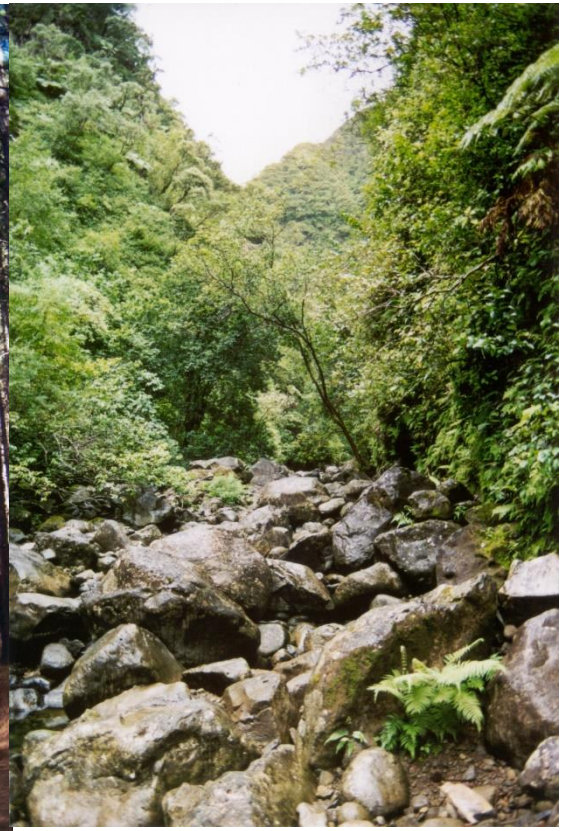
- **deserti-fication**
- **erosion**
  - ✓forest clear-cutting
  - ✓agriculture

Vegetation

natural plants, agriculture crops:
fields, meadows, pastures, forests

trees – forests, rainforests





Basic nomenclature

Soil horizon designations

layers with properties different from other adjacent layers

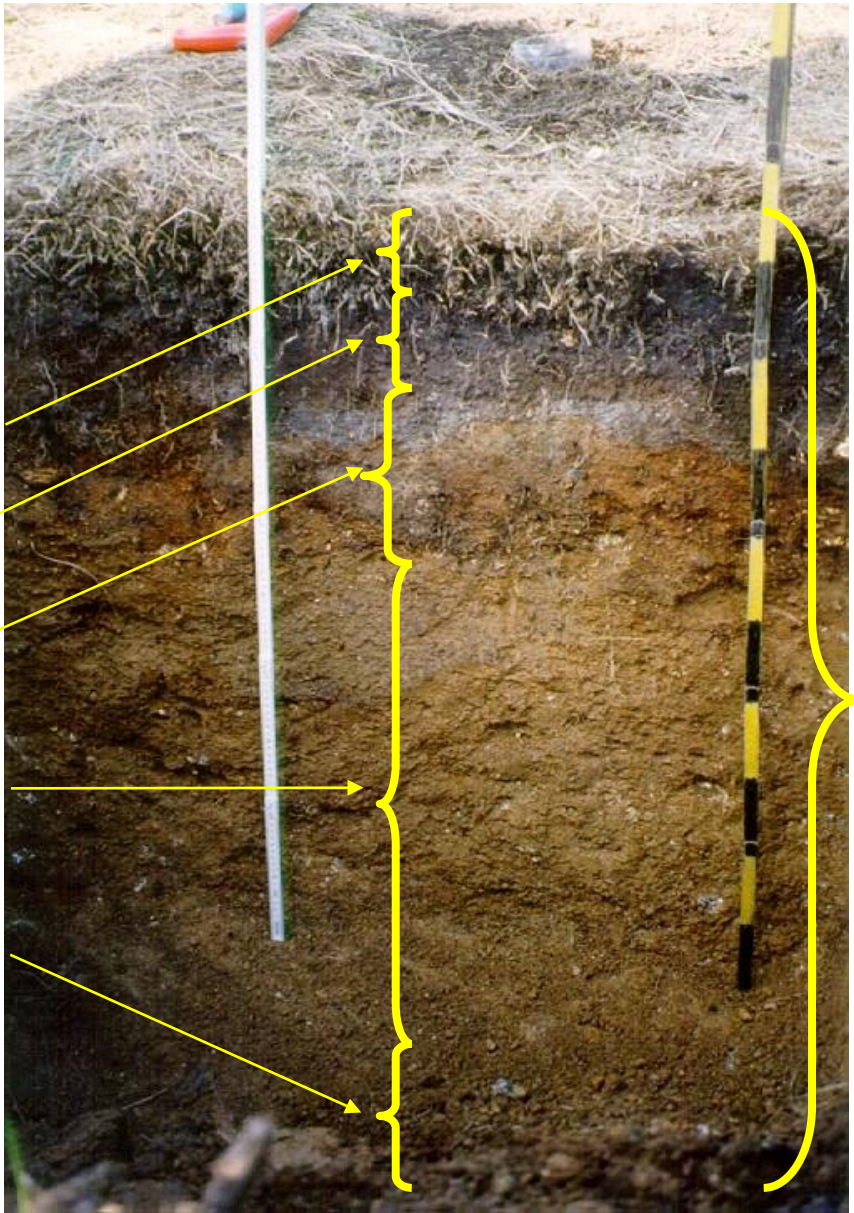
litter layer

A (humus)

B (leached)

C (bedrock substrate)

R (bedrock)

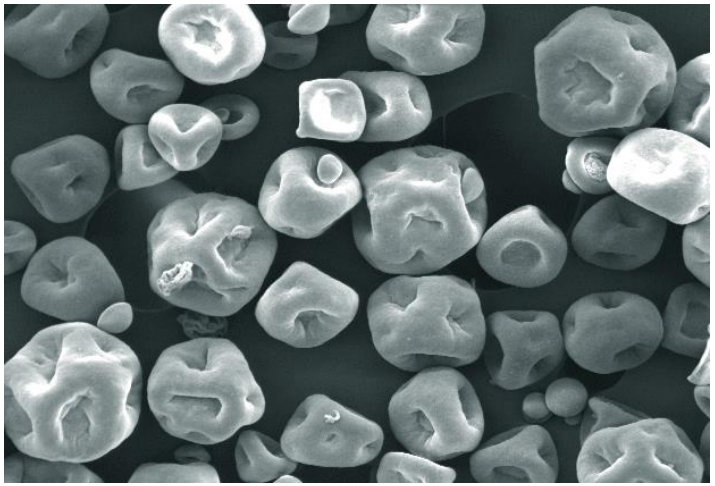


Soil profile – vertical section combining all soil horizons

Soil texture and soil structure

texture – %clay, silt, sand

determined, can not be changed



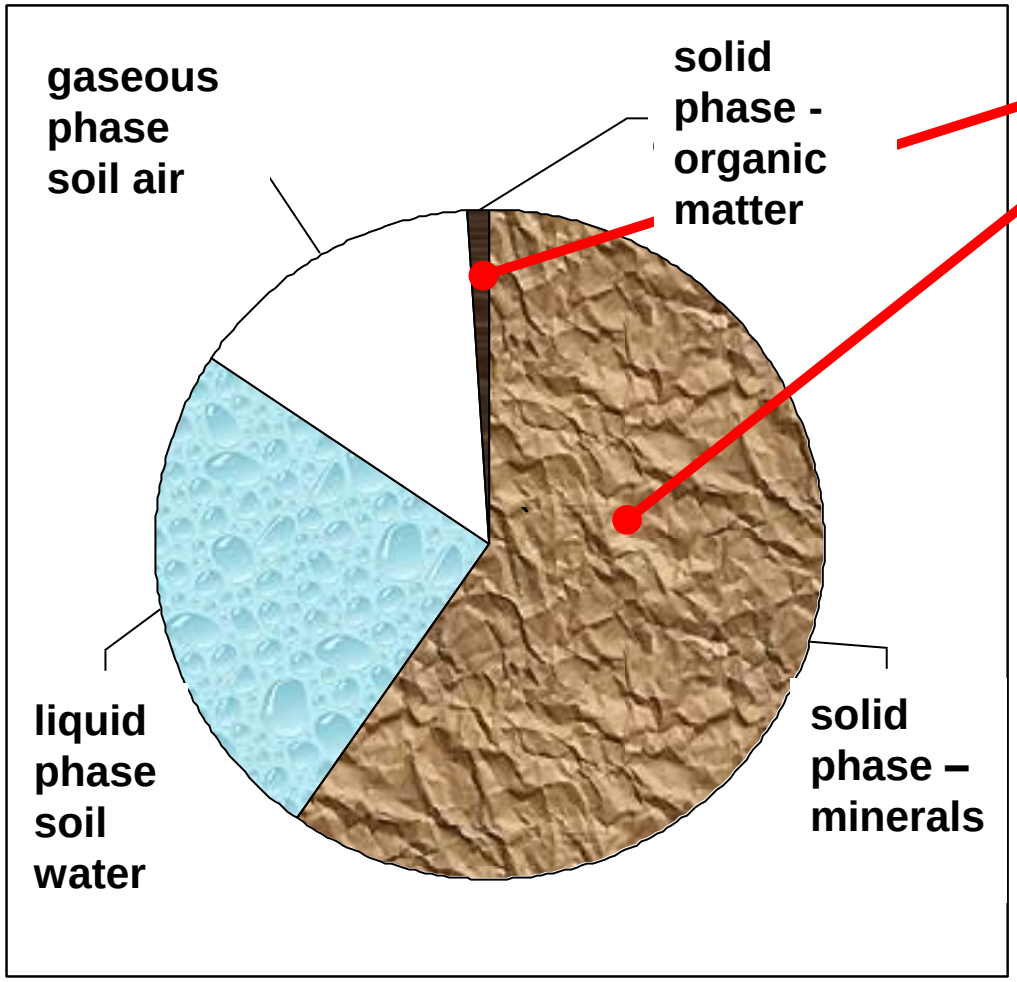
texture classes

aggregates – spatial composition

chemical bonds of humus units at the clay mineralslze ovlivnit can be changed (good/bad)

soil types

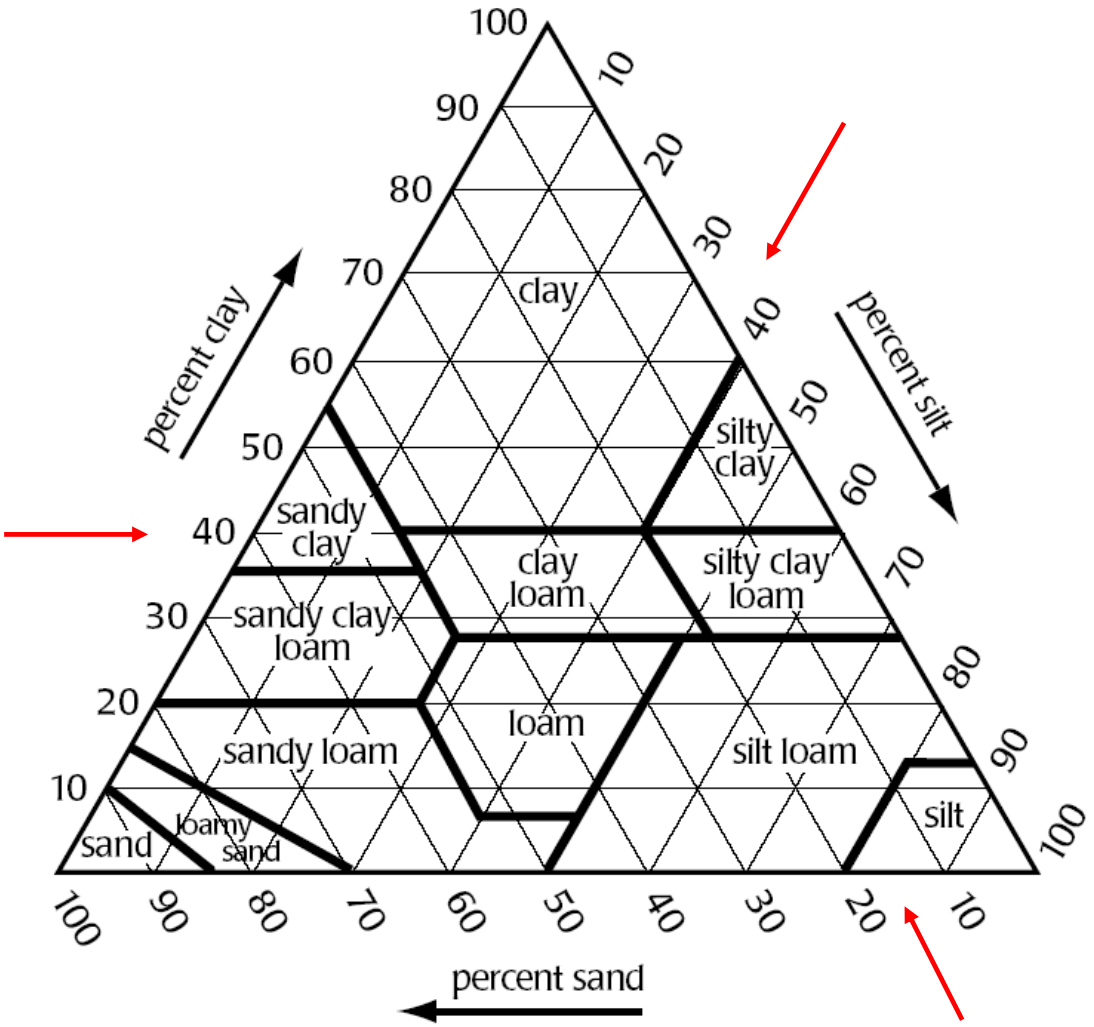
Texture and structure are parameters of soil solids



texture relates to **mineral** part of solid phase only

structure is dependent on **mineral** and **organic** part of solid phase

Texture classes according to clay, silt, sand



Triangle diagram of soil texture (NRSC USDA)

Soil structure

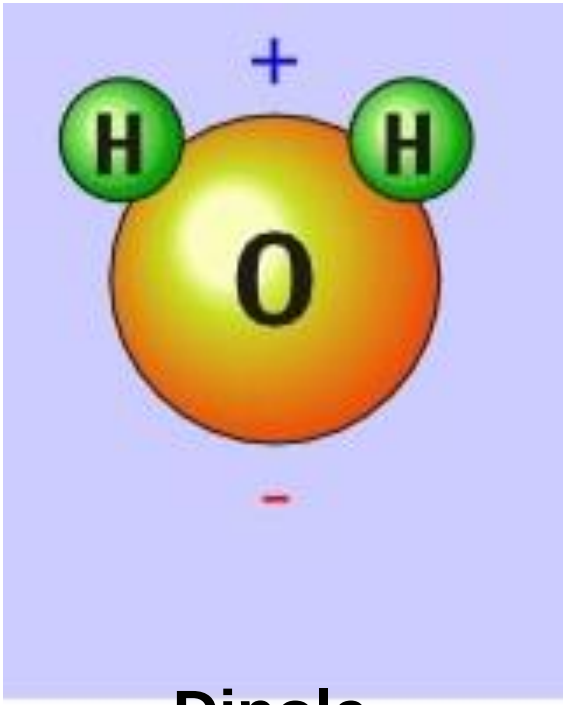
- primary spatial constellation of soil into clumps called aggregates or pedons
- binding factors are plant root (their excrements), organic matter and clay minerals,
- sandy and rocky soils do not create aggregates
- most important factor of aggregation is organic matter
- stability of aggregate is their endurance towards breakdown under external impacts

impact of roots on soil stability

Sulzman

Soil water

- Necessary for plant growth
- Basic medium for transport of matter
- Necessary for clean up of soil
- Is found in soil as
  - chemically bound and
    hygroscopic (grain wrap),
  - **capillary** (capillary forces in pores)
  - **gravitational** (temporal, outflows after cessation of the water source- rain, flood, snowmelt)



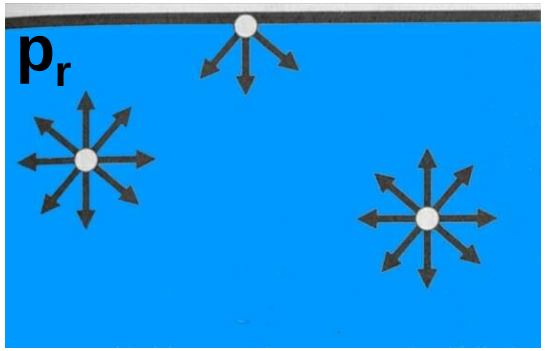
Dipole

extremely good solvent

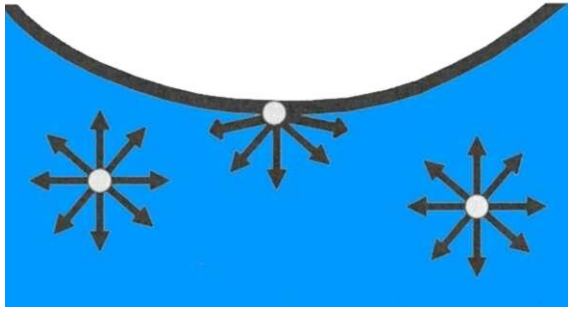
Capillarity

For spherical surface additional (capillary) pressure p_σ causes the curvature:

$$p_\sigma = \frac{2\sigma}{R}$$



At the planar interface water-gas, the pressure is p_r



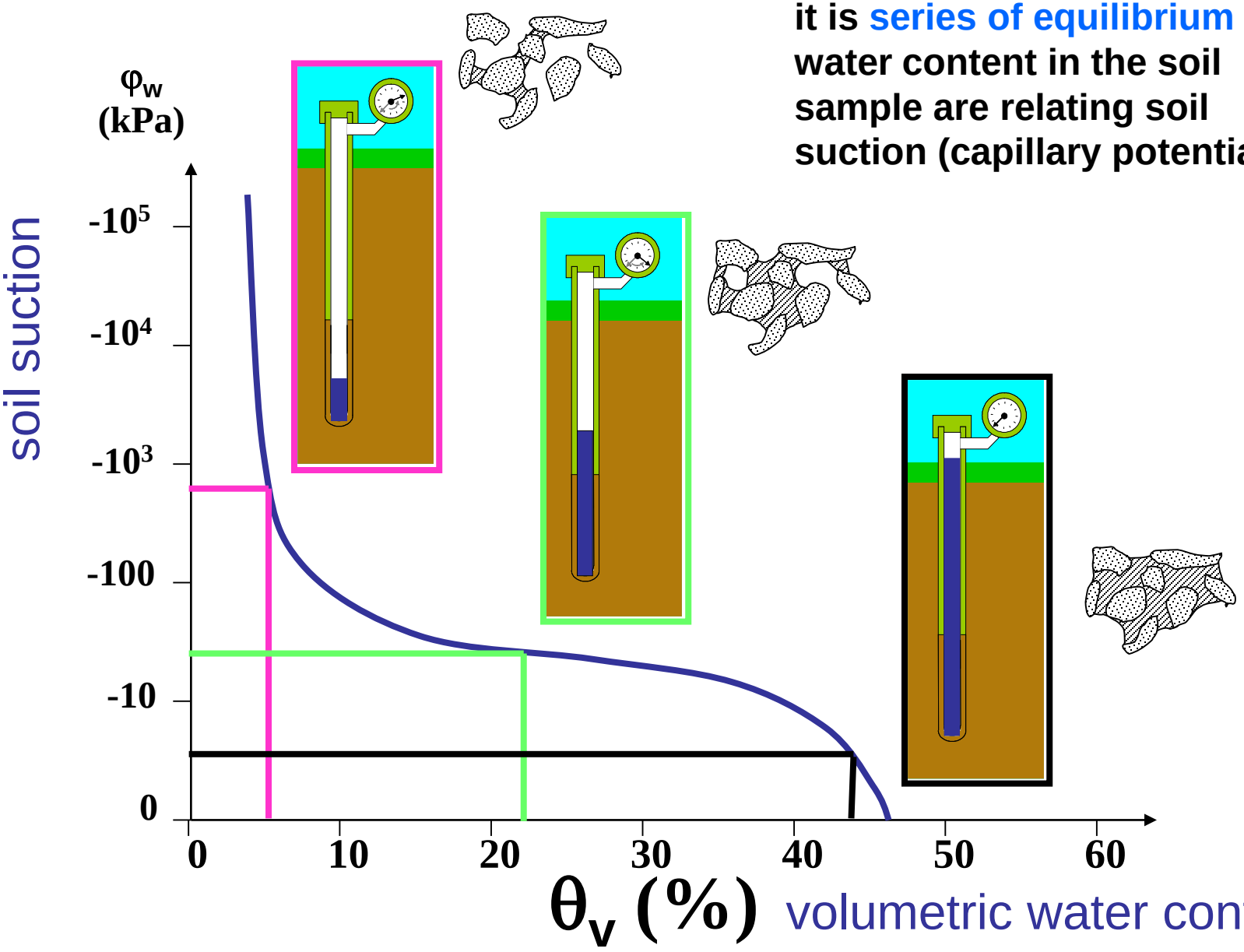
At the curved interface the pressure is $p = p_r \pm p_\sigma$

modfifed from Hotron and Jury 2004

Retention curve of soil moisture

transfers soils suction into moisture – bulk water content

it is series of equilibrium of water content in the soil sample are relating soil suction (capillary potential)



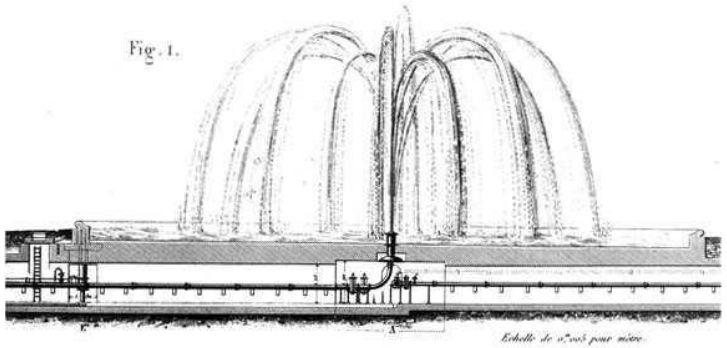
Saturated flow

Henry Darcy

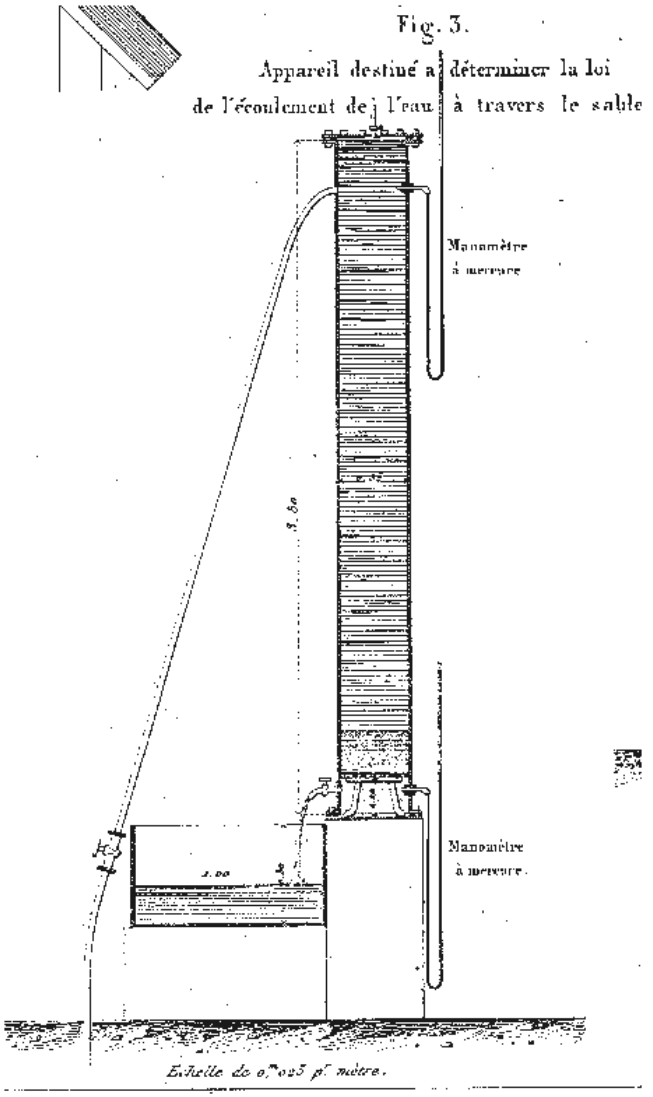
***Henry Darcy (1856)* solved the filtration problem for fountains in Dijon.**

He found that *flow of water* through the column of sand is dependent:

- *proportionally to the difference of hydrostatic pressure at the ends of the column*
- *improportionally to the length of the column*
- *proportionally to the cross-section of the column*
- *depends on the coefficient for the given material*



Darcy, H., 1856. *Les Fountaines de la Ville de Dijon*



Hydraulic conductivity

- is the Darcian coefficient of the material called:

saturated hydraulic conductivity

Darcy law is then

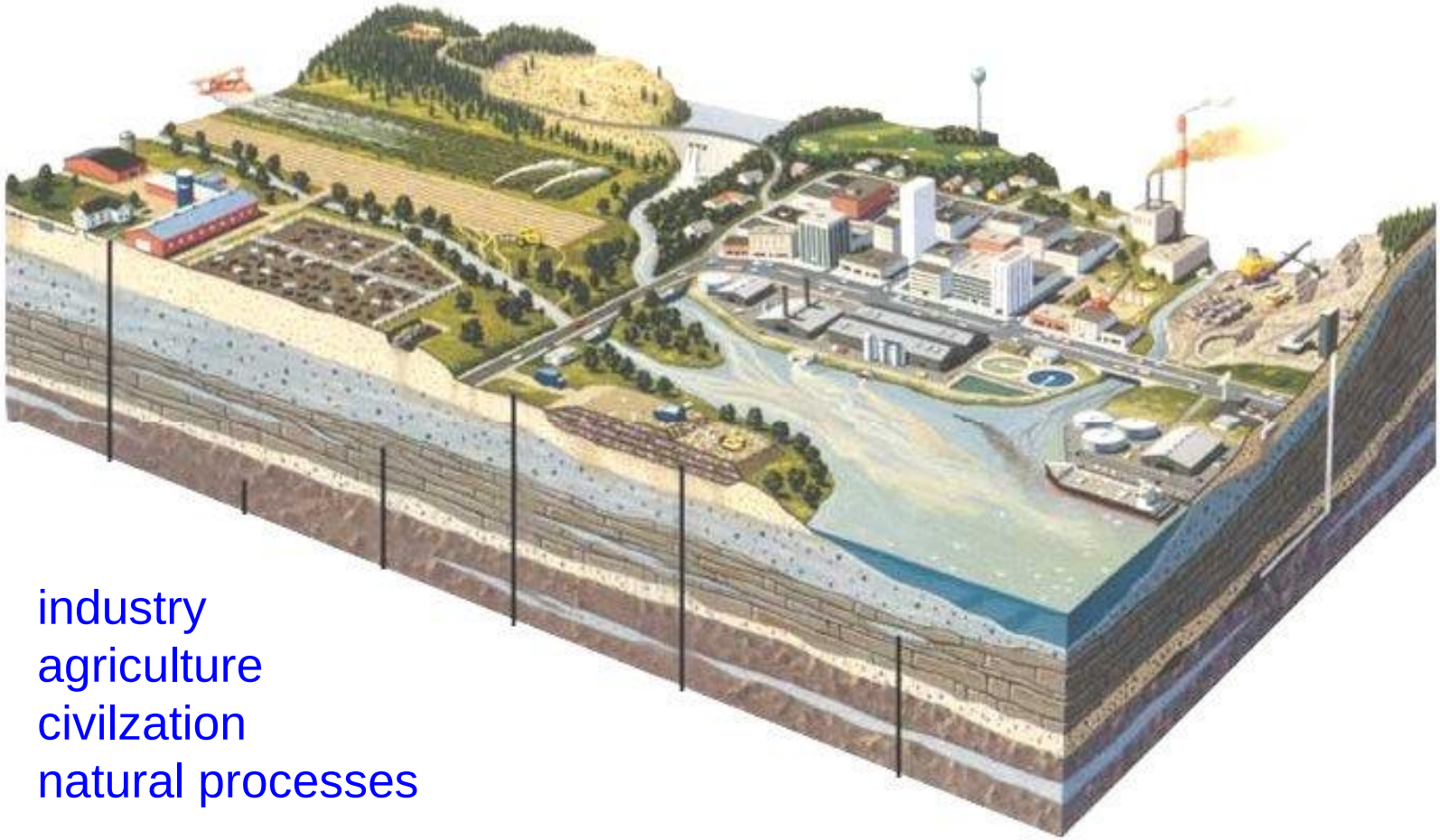
$$\mathbf{v = K_s * i \qquad (m/s)}$$

v – velocity of flow

K_s – saturated hydraulic conductivity (m/s)

i – hydraulic gradient (i = h/L)

Sources of toxic compounds



industry
agriculture
civilzation
natural processes

Source: National Geographic

Sources of toxic compounds

- Point source

  landfills, local sources of contamination on factory premises, petrol station, military areas, fertilizer depositories

- Non-point source

  Agriculture – application of pesticides and fertilizes (and toxic compouds such as heavy metals naturally present in it)

  Industry – pollution of air by exhausts (factories, incineration plants => rain and dry dust atmospheric depositions

- Combined

  civilization activities – river pollution from point and non-point sources

  natural processes – volcano eruption (Hg-mercury), discharge of Earth gases (Ra-radon)

Overview of toxic compounds and their impact on living organisms

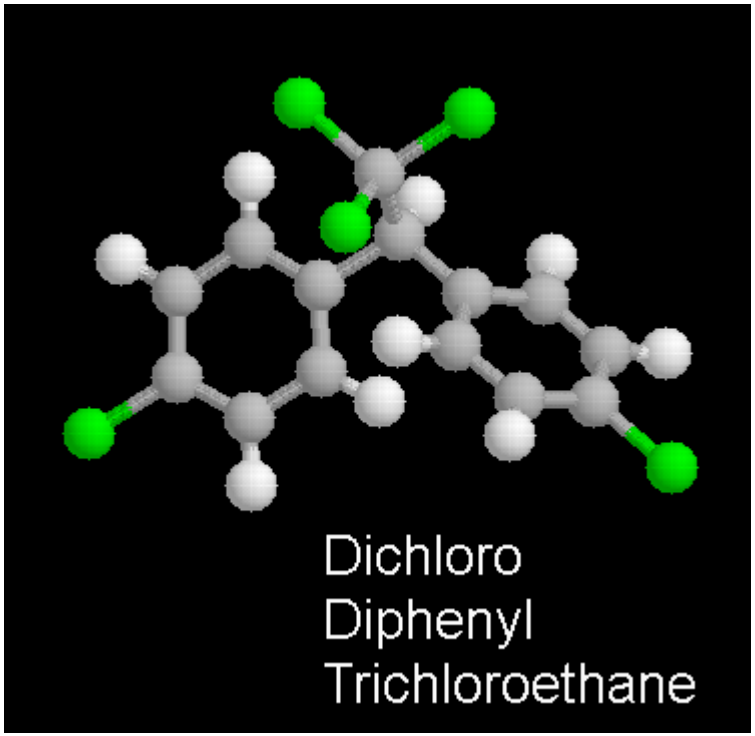
- Inorganic – heavy metals (Hg, Pb, Cd) radioactive elements (Ra), cyanides, asbestos
- Organic – Polyaromatic hydrocarbons, polychlorinated/brominated biphenyls, pesticides

Compound found frequently in soils

Oil products, arsenic, benzene, cadmium, cyanides, lead, mercury, PCB, tetrachlorethylene, trichloroetylene, di-chloroetylene, vinylchloride(PCE-TCE-DCE-VC)

Pesticides – often in agriculture (herbicides, fungicides, insecticides, rodenticides)

- US EPA (Environmental Protection Agency) – any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest.
- The term pest means any harmful, destructive, or troublesome animals, plants, or microorganisms

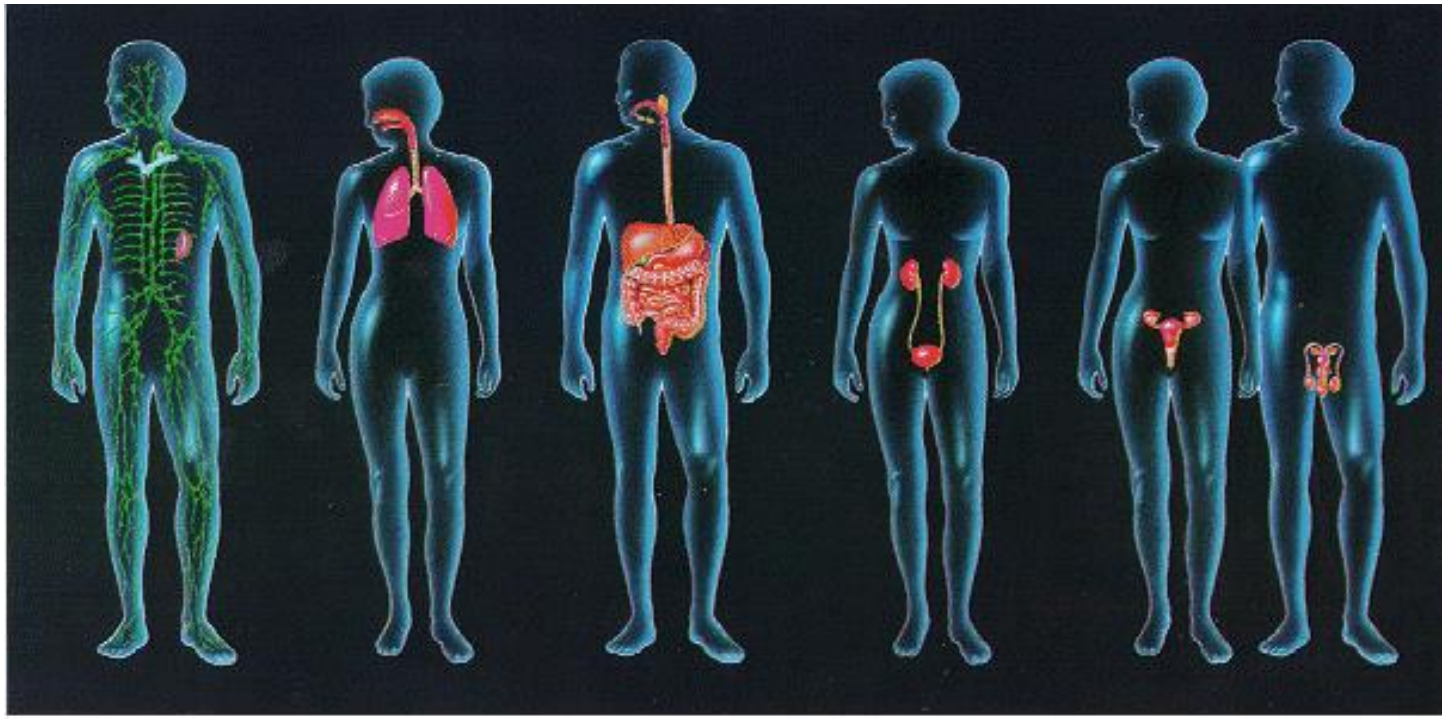


adopted from Muchlinski

Phases of the compouds movement in the human body

Absorption -> Distribution / Digestion -> Secretion

Systems in the human body



circulatory respiratory digestive urinary reproductive

-> Impact on nervous, muscular, endocrine, skeletal systems

Places of toxicant absorption

- Digestive system – most important – food+medicine

  digested amount is dependent on amounts absorbed and metabolized in cells fo the digestive system and secreted by liver

- Lungs

  For low soluble compounds- dependent on blood flow intensity

  For high soluble compounds- frequency of breathing

- Skin

  Skin is not so permeable, despite that selected chemicals can penetrate: nerve gases, pesticide, polyaromatic hydrocarbons

- Other

  intravenous, hypodermic..

adopted from Muchlinski

Technologies according to the processes involved

- **Physical**

  dilution, homogenization, destilation, gravity separation,flotation, solidification, stabilization, sedimentation, filtration, magnetic separation, extraction (by water, steam, air, plants, microbes), microfiltration, termic processes (heat agglomeration, vitrification), venting, stripping
- **Physical-chemical**

  adsorption, dialysis (sorption), chem-sorption, ion exchange, reverse osmosis, solidification, electrochemical processes, termic processes desorption
- **Chemical**

  neutralization, dissolution, precipitation, oxidation (drying, ozonization, burning, aeration, UV light), reduction, coagulation, photosynthesis, dehalogenization
- **Biological**

  aerobic + anaerobic processes, degradation in flow, phytoextraction, bioreactors

Technologies according to site

- **Methods "ex situ“**

  extraction of primary (e.g. subsurface fuel tank) and secondary (contaminated soil) sources to eliminate the origin of contamination of the area

  Elimination is selective – extraction by excavation of soil and its decontamination in **on site** or transporting of the material into certifice decontaminating site - **off site**

- **Methods "in situ"**

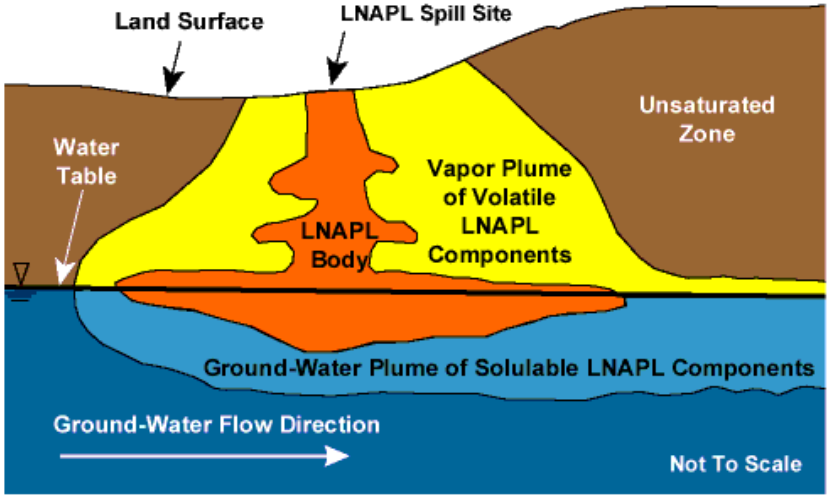
  technological process is applied by non-destructive means into soil or rock environment incl. ground and soil water and air

Technologies In Situ

- Air Sparging
- Bioremediation
- Bioslurping
- Circulation wells
- Solvents/surfactants
- Dual phase extraction
- Dynamical subsurface stripping
- In situ oxidation (Fenton reagent, $KMnO_4$-Potassium permanganate)
- Natural attenuation of non-chlorinated compounds
- Reactive barriers
- Pump and Treat
- Phytoremediation
- Steam flushing
- Vertical barriers

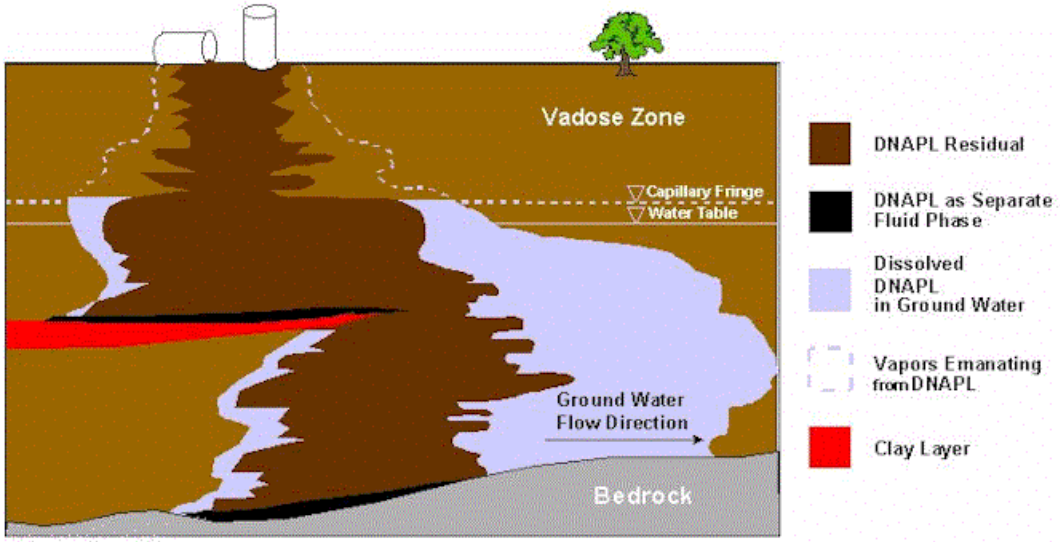
Multiphase flow

- **L-NAPL (Light Non Aqueous Phase Liquid)** – easier extraction from the water table



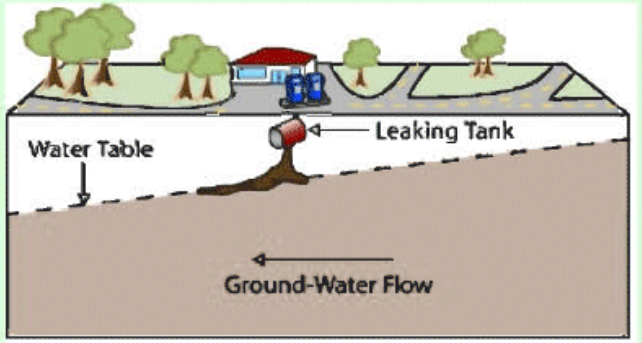
USGS

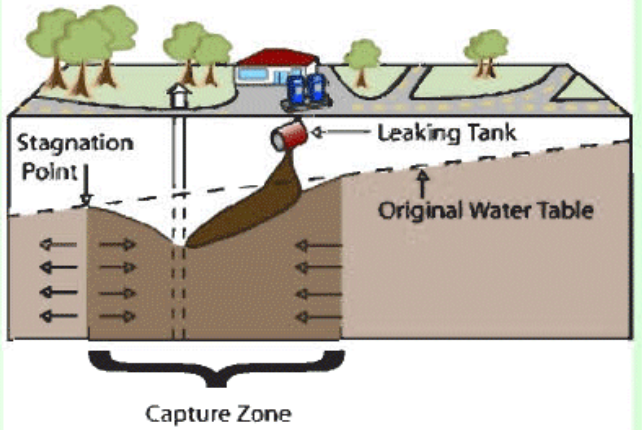
- **D-NAPL (Dense Aqueous Phase Liquid)** – difficult extraction from the bedrock/or low permeable material (e.g. clay lens)



After NRC, 1994

Few selected methods: Pump-and-treat



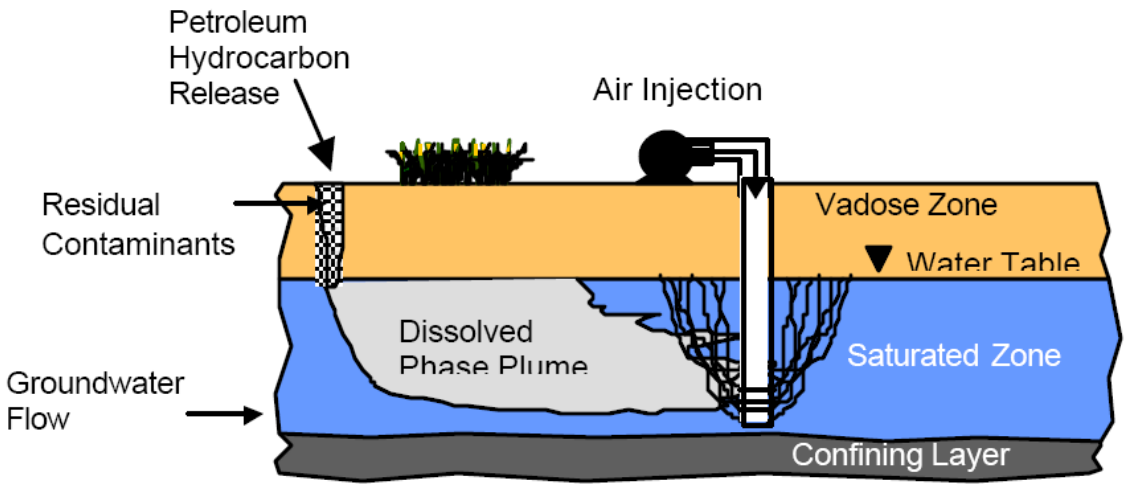


- Basic active method in-situ for clean-up of soil and rock environment
- Retention of contaminated groundwater
- Prevention of contamination propagation of contaminant into clean areas
- Extraction of contamination from the subsurface envrinment and consecutive clean-up of water
- Decrease of contaminant concentration in the groundwater

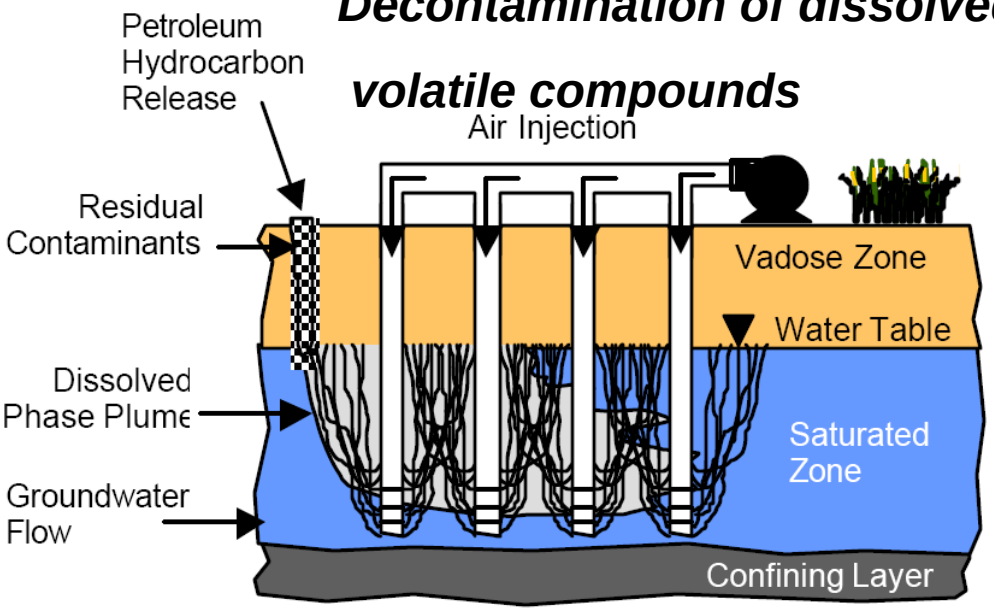
Air sparging

- Air sparging is more efficient than pump-and-treat **but...**
- Saturated aquifer must be relatively thick to make the method efficient
- Available for decontamination both in saturated and vadose zones in contrary to SVE (soil vapor extraction - vadose zone only)

Prevention of contaminant spreading



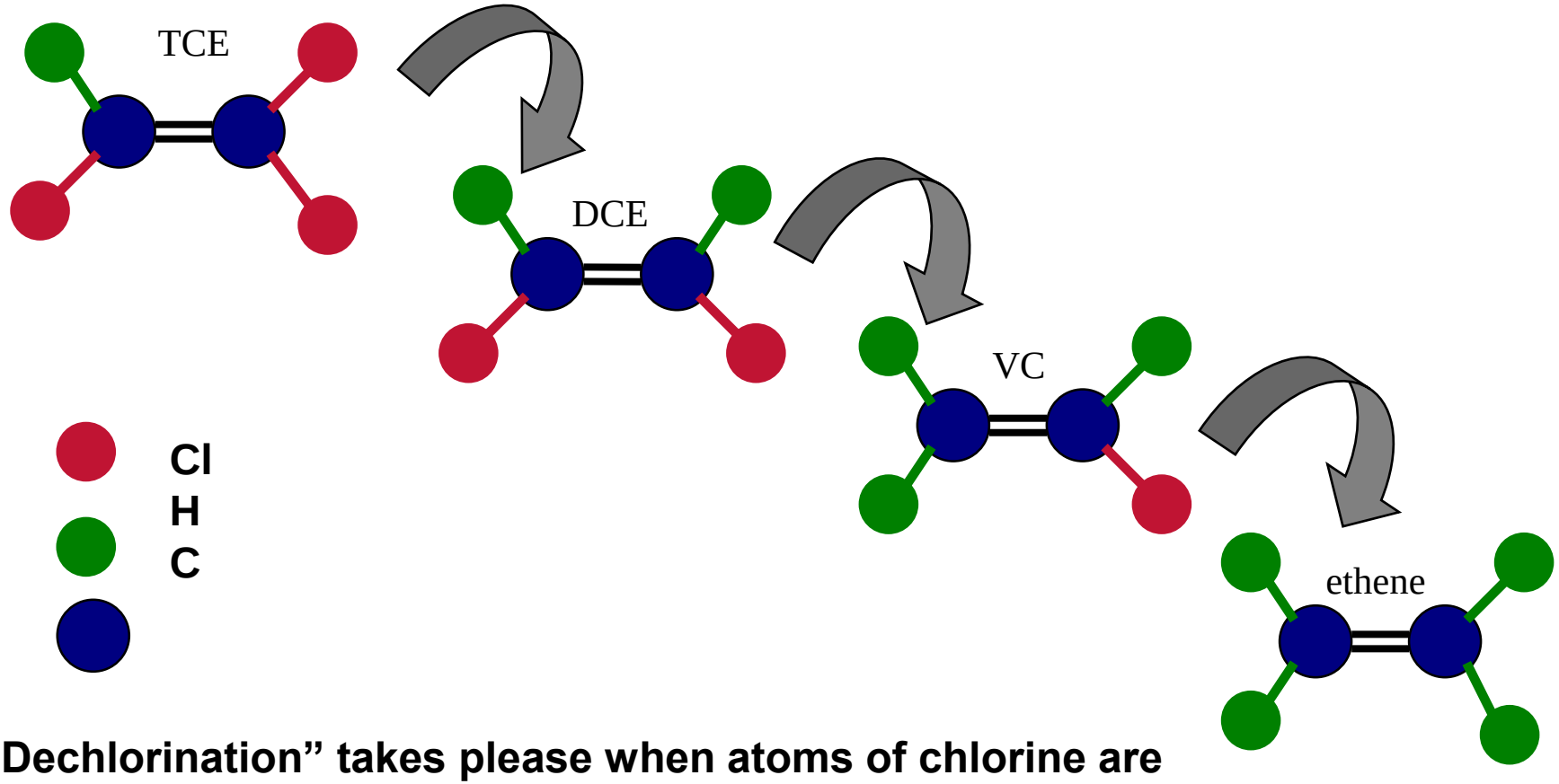
Decontamination of dissolved volatile compounds



MNA - Monitored Natural Attenuation

- attenuation = to diminsh, to decrease
- as fire eats the candle, subsurface consumes the contamination
- definition by EPA: relying on natural processes in reaching goals of remediation for the given site
- it does not mean – to do nothing, leaving alone
- MNA is not basic obvious primary method of decontamination
- As standalone method must be used with the highest caution
- must be evaluated together with other alternatives and chosen only if set goals (limits) can be reached in reasonable time (up to 30 years)
- might be physical, chemical or biological
- processes of attenuation for oil products: biodegradation, dispersion, dilution, chemical reactions, volatilization, sorption, destruction

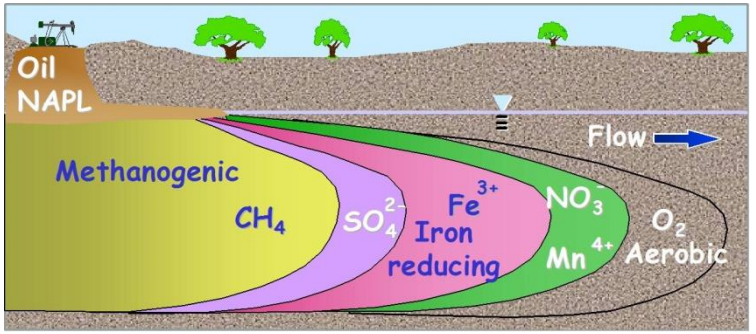
Transformation of chlorinated ethenes



“Dechlorination” takes please when atoms of chlorine are substituted by atoms of hydrogen. In such case harmless ethene is the final product.

components of MNA

- required components of MNA:
  - control – removal of contamination source
  - monitoring of contamination spreading
- required conditions of MNA:
  - data characteristics for the site
  - risk assesment



demonstration of MNA efficiency

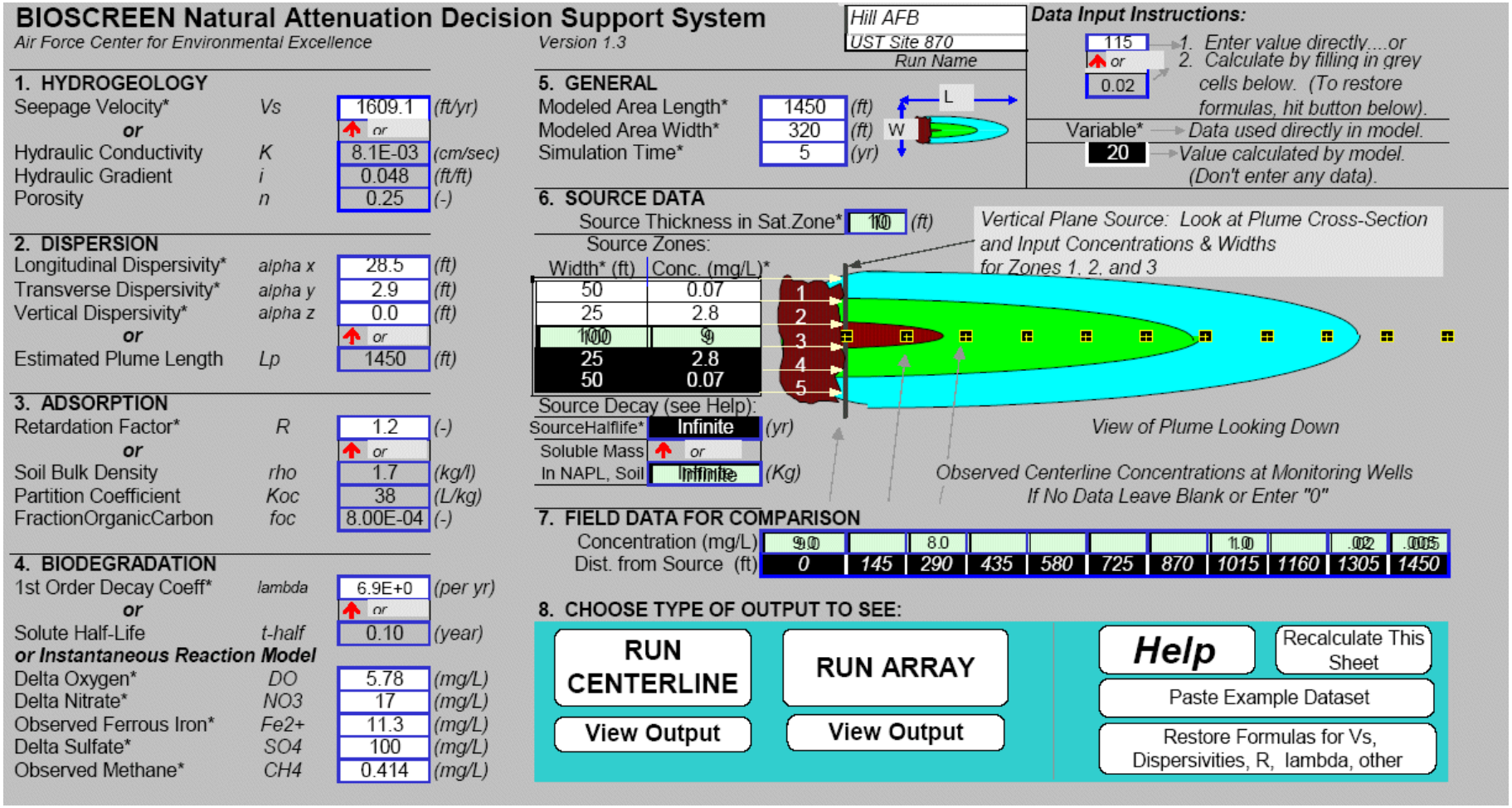
historical chemical data show clear decreasing trend of the compound volume or concentration

hydrogeological or geochemical data demonstrate indirectly processes of MNA

field study of microcosmos, demonstration MNA processes

Bioscreen

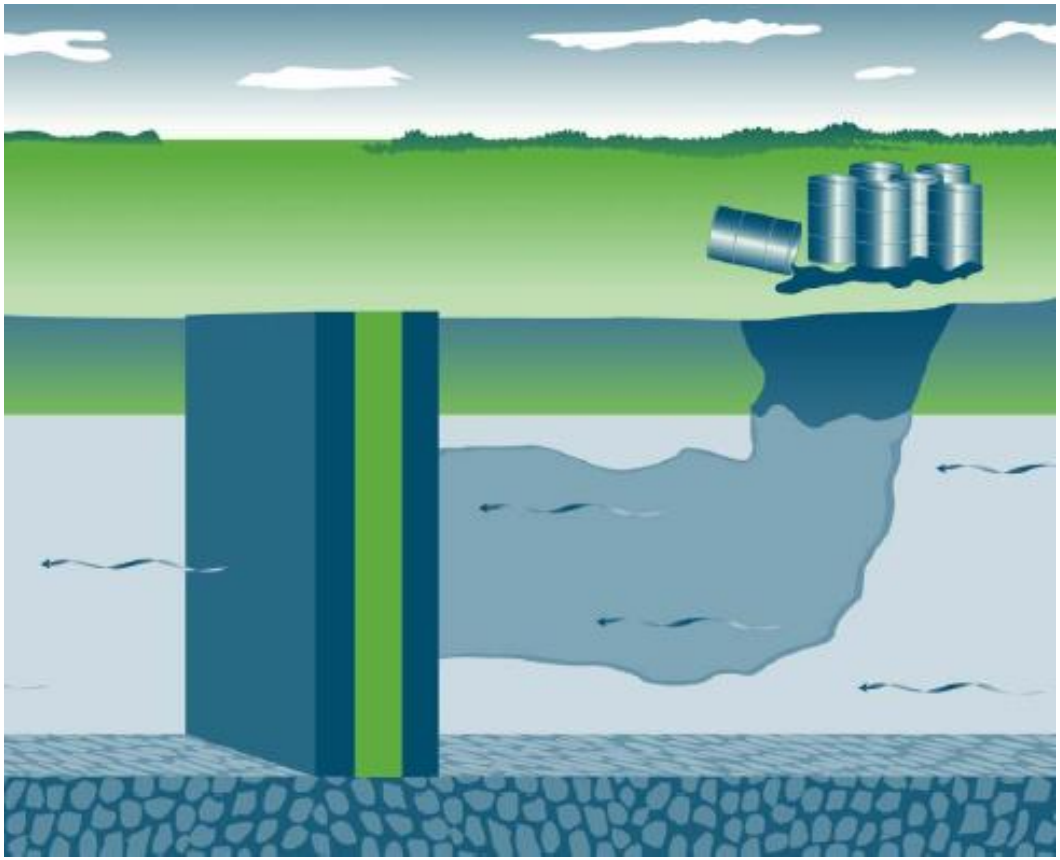
Models of MNA processes estimation



Permeable reactive barriers

or „treatment wall”, “reactive wall” nebo “PRB”

Subsurface wall made from porous materials which, based on various processes, have an ability to reduce contaminant concentration in ground water passing through the wall.

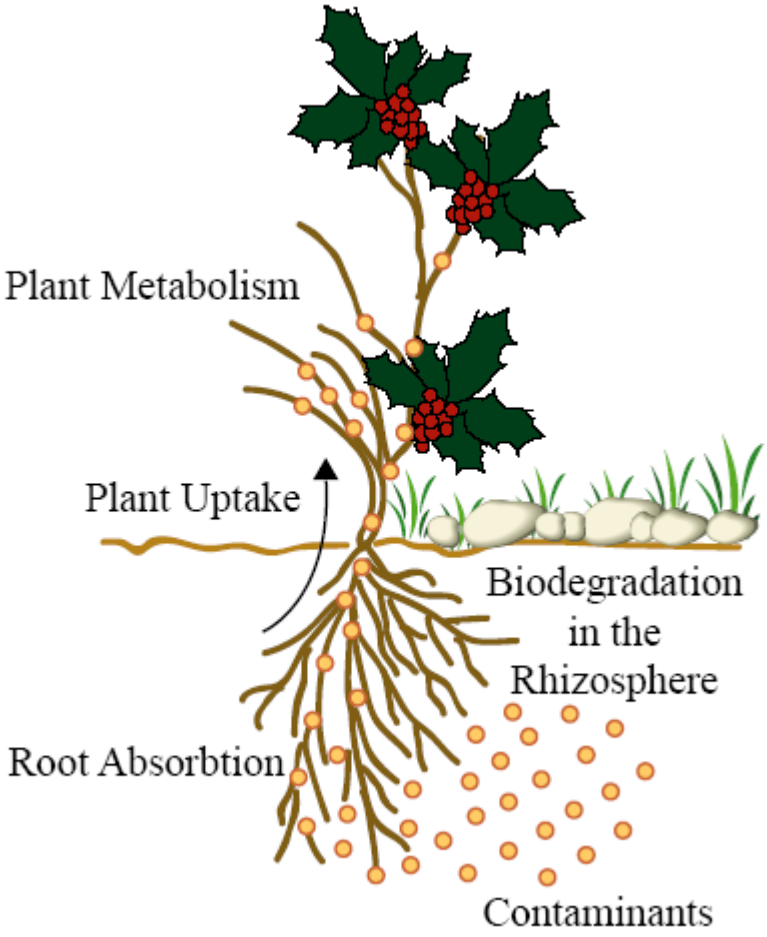


The contaminants are degraded or retained in a concentrated form by the barrier material.

Phytoremediation

Plant enhanced soil cleanup

- phytotransformation – contaminant uptake from soil and groundwater by plants and transformation in plant body
- bioremediation of rhizosphere multiplication of the bacterial processes
- phytostabilization – hydraulic control of water uptake by trees, physical stabilization of soil by plants
- phytoextraction – use of plants capable to bind and concentrate metals in roots, stems or leaves
- rhizofiltration – plant roots help to sorb, concentrate or precipitate metals



Composting

composting – degradation by microorganisms at raised temperature

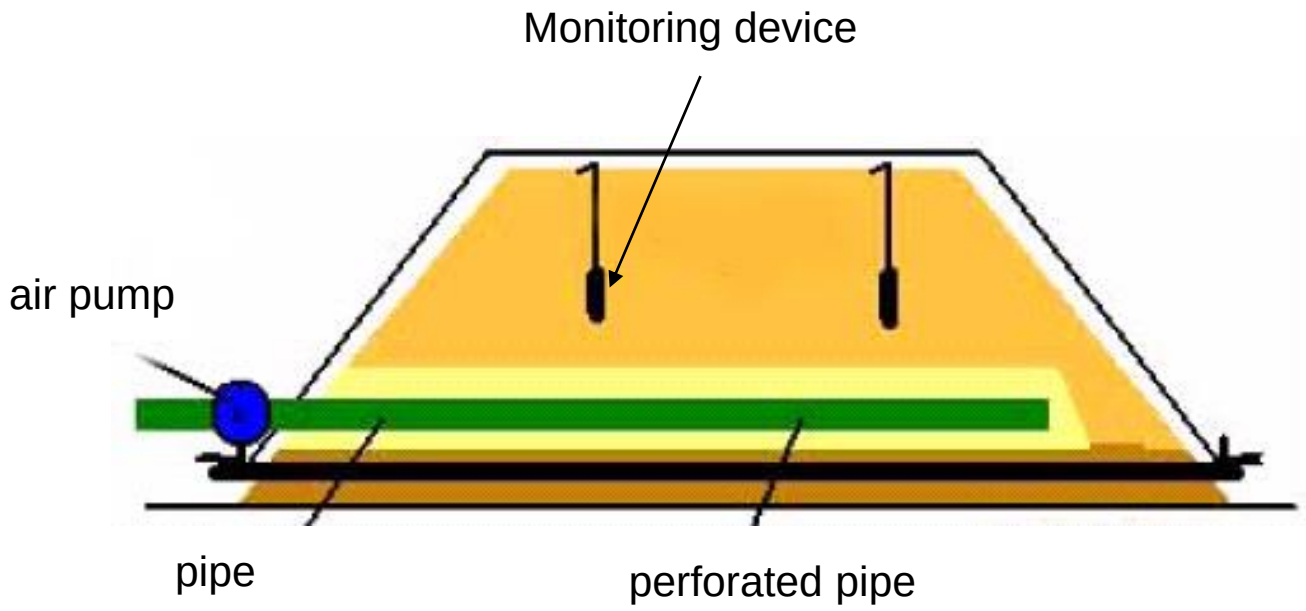
- Typically 55 – 65°C
- Heat is produced by microorganisms
- Decrease of bulk density and supply of organic carbon – straw, alfa-alfa, manure, wood chips
- Spreading into long rows
- Rows are regularly turned over and mixed
- Monitoring of pH, temperature and contaminant concentration

Composting in rows

http://www.rrskw.com/compost_turners.htm

Ex-situ managed bioremediation – Biopiling

- Soil is mixed with additives and placed onto suitable site
- Ventilation device is installed during piling
- Pile is 6 m high (max), covered with PE foil



Ex-situ managed bioremediation – Biopiling