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Design of monitoring of contaminated sites
Components of monitoring of contaminated sites: Soil and Groundwater

Prof. Dr. Ivan Holoubek
holoubek@recetox.muni.cz; holoubek.i@czechglobe.cz
www.recetox.muni.cz; www.czechglobe.cz

REPUBLIC OF TURKEY
MINISTRY OF ENVIRONMENT,
URBANIZATION AND CLIMATE CHANGE

Environment and Climate Action
Sector Operational Programme

Persistent
Organic
Pollutants

UNDP

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Target

Examples of different methods used for determination and monitoring of pollutants in soils and groundwaters

Contents

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Contents

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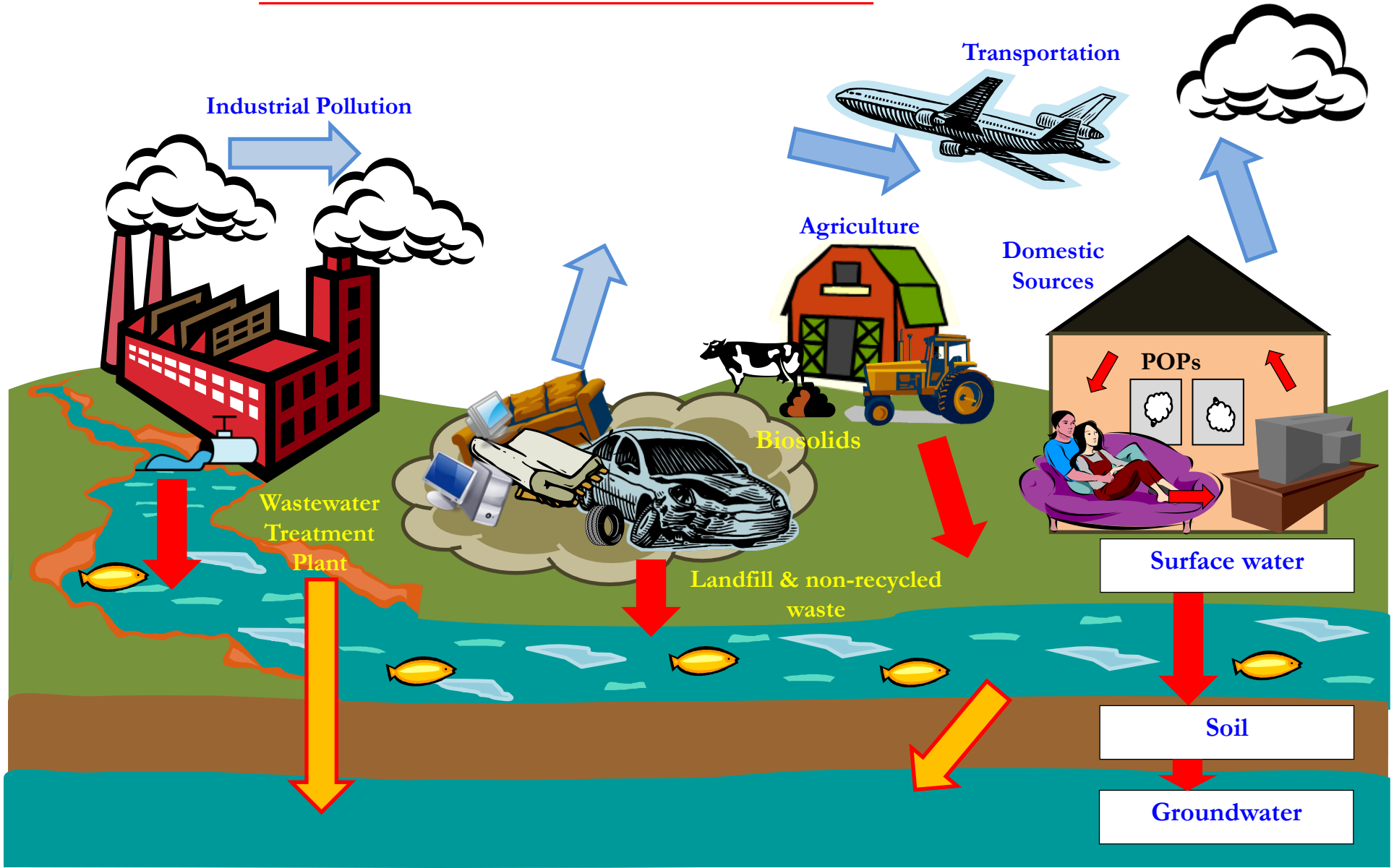
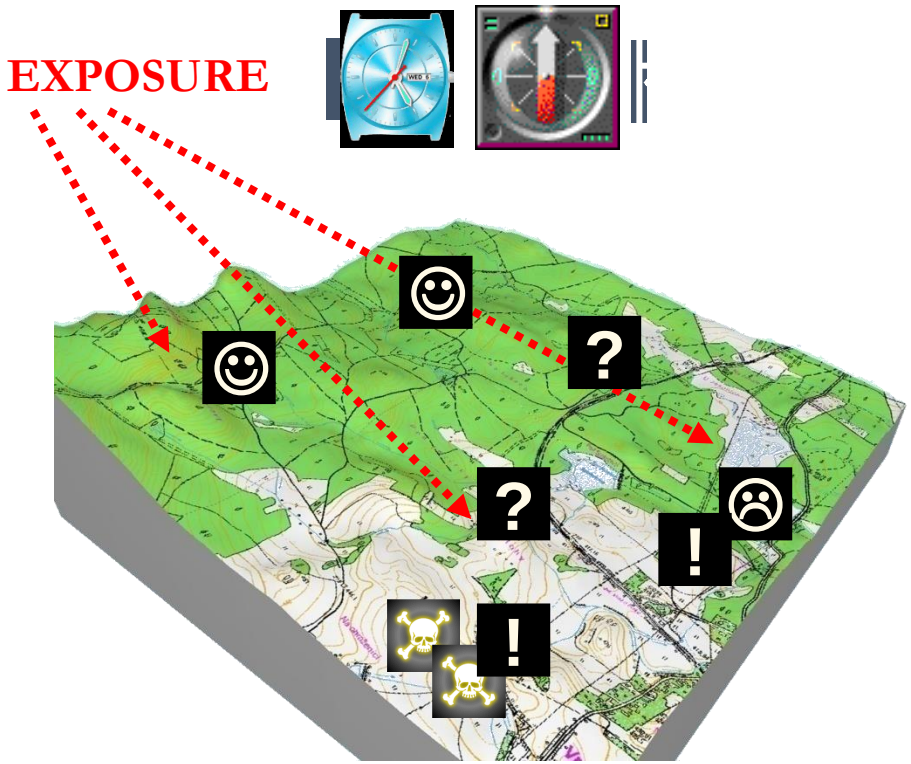
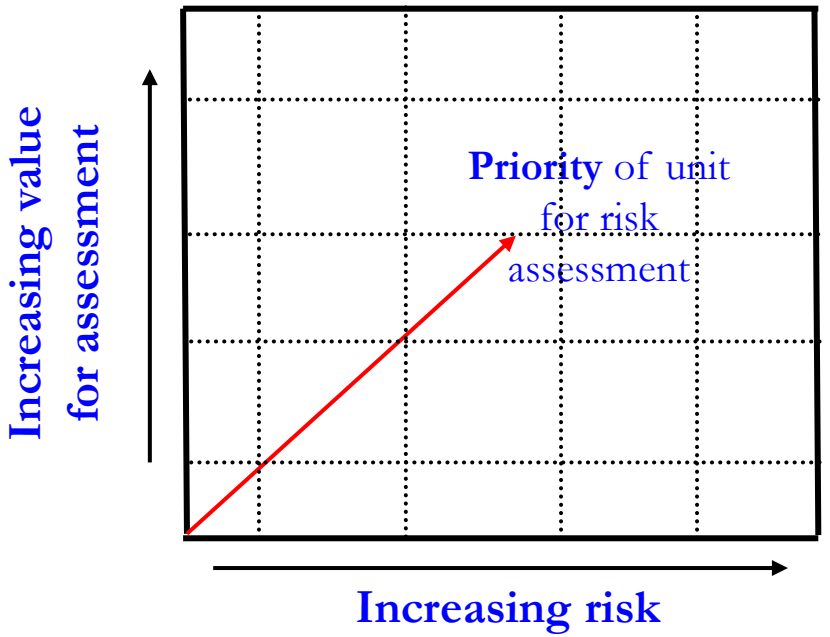
Contaminated sites

Routes of POPs contamination



Problem definition generates comprehensive SITUATION PLAN





☺ Background sites with no influence of exposure

? Uncertain influence and/or uncertain assessment endpoint

! Potentially affected sites, still clean or with negligible effect

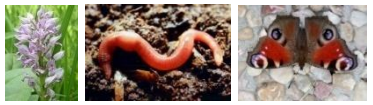
☹ Area with probable and substantial toxic impact

☠ Already strongly affected area with remarkable effects

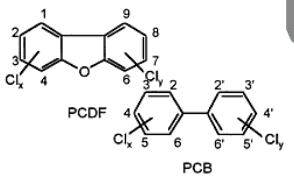
Scenario as milestone of the assessment process

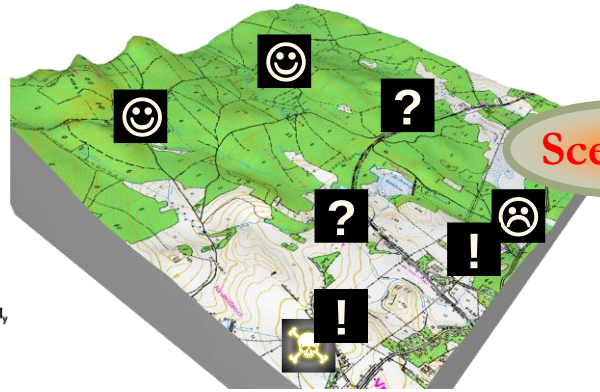
Source of contamination

Environmental characteristics

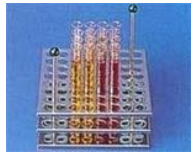


Compounds of interest





SITUATION PLAN



Pilot tests (screening)

Scenario

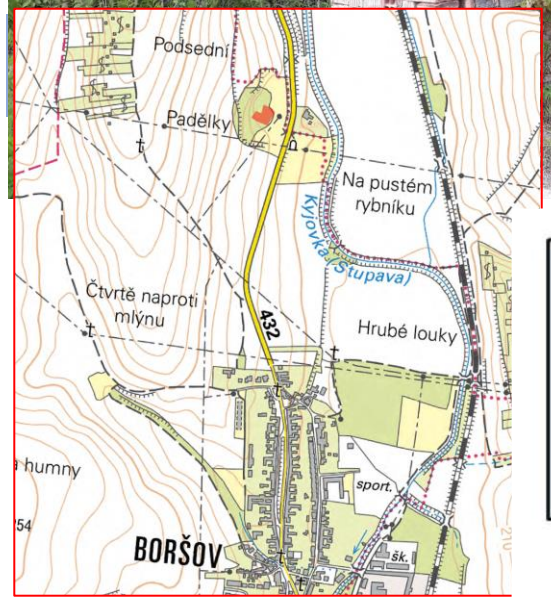
Primary exposure

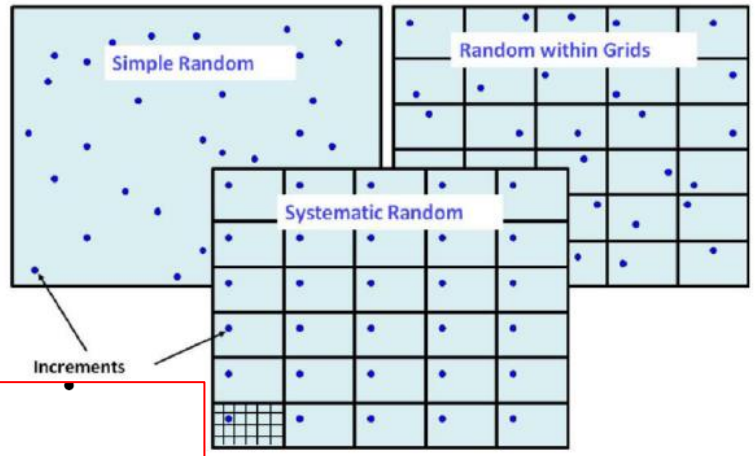
Secondary exposure

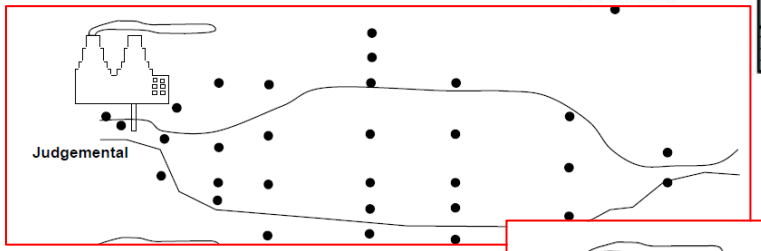
- Soil
- Sediment
- Water
- Air
- Biota

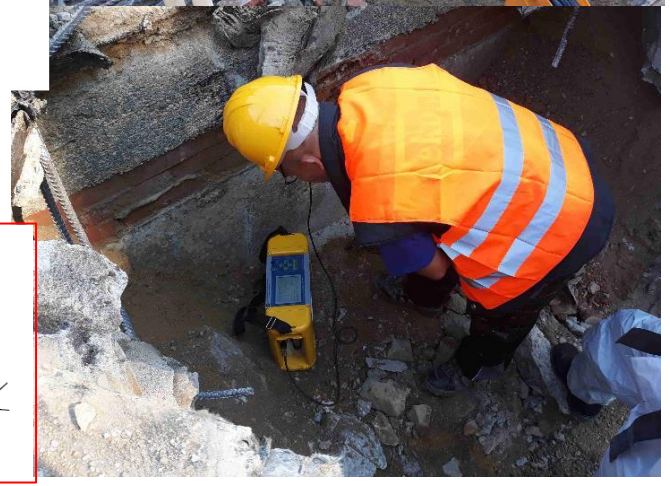
- Soil
- Sediment
- Water
- Air
- Biota

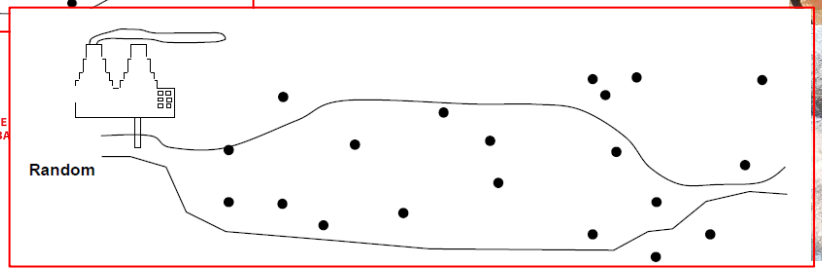
Further tests


Podsední
Padělky
Na pustém rybníku
Kyjovka (Stupava)
Čtvrtě naproti mlýnu
Hrubé louky
432
humny
54
sport.
BORŠOV
šk.


Simple Random
Random within Grids
Systematic Random
Increments


Judgemental




Random

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Monitoring

Data reach, information poor

Monitoring

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- is a long-term consistent observation or measurement of precisely defined indicators well described in the space and time
- is performed in the monitoring network representative for the region
- consists of the observations and measurements, evaluation of the current status, changes as well as future perspectives.

Environmental monitoring is at the very beginning of the environmental information chain:

- it is the basis of environmental data collection,
- environmental reporting and environmental research,
- the basis of understanding of environmental problems and trends.

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Monitoring programmes should

- be developed in accordance with the demands of the current legislature
- monitor the efficiency of the strategic documents such as international conventions and protocols or national measures with respect to the environment

Monitoring outputs

- evaluation of the exposure within systems
- evaluation of the human and ecological risks
- support of decisions
- changes in economic practises, legislature, operation and strategies
- determination of efficiency of accepted measures, funding, etc.

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Environmental monitoring

Environmental monitoring is therefore a powerful tool for

- **supporting a decision-making**
- **enforcing policy decisions**
- **assessing compliance with policy regulations and objectives.**

These programmes are essential in identifying subsequent measures.

The crucial elements in the development of the monitoring program are the measurement methods and standards.

Is monitoring only a rutine procedure or it can be used as a tool for study of environmental processes ?

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Measurement of substances in the environment

Screening - is it possible to detect the substance in environmental samples?

Survey - how big is the problem?

Monitoring - long-term measurements of the temporal trends and/or - large scale measurements of the spatial distribution

Modelling - where is the substance ?

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Monitoring of contaminated sites

- Preliminary phase – collection of basic information
- Phase 2 – collection of detailled information
- Monitoring during remediation process
- Post-remediation monitoring

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Harmonization of monitoring programmes

It is important that data from different sources are comparable for the same parameter

Intercalibration of the analytical laboratories requires significant efforts

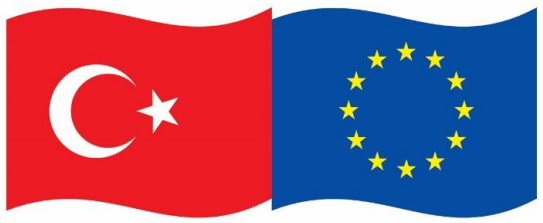
Various approaches of existing monitoring programmes represent currently the major problem (various matrices, frequency, sampling procedures, etc.)

Local – national – regional – global levels

Specific problems of environmental analysis

- low homogenity of samples (soil, wastes)
- low stability of samples (biota)
- various matrices (methods for extraction of analytes from matrices)
- wide range of analytes (method development)
- wide range of concentration (robust methods)
- monitoring on the levels close to the detection limits (high deviations)
- risk of secondary contamination
- price of ultra-trace analysis (instrumentation, chemicals, standards)

What is sampling about?



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Definitions (Oxford dictionary):

- **To sample:** Take a sample or samples of (something) for analysis
  - Example: one hair on a jacket, orange in a supermarket

- **A sample:** A small part or quantity intended to show what the whole is like

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Why do we need to sample?

- To know levels of pollution prior to take specific measures
- To understand emissions of specific pollutants or from specific sectors
- To understand time trends (diurnal, weekly, seasonal variations?)
- To understand specific processes (e.g. air-surface exchange)
- To support legislation

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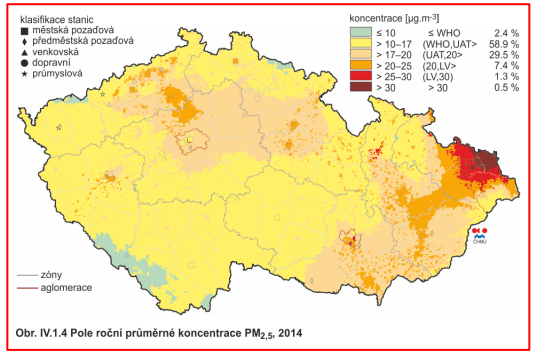
Why do we need to sample?
To know levels of pollution



Obr. IV.1.4 Pole roční průměrné koncentrace $PM_{2.5}$, 2014

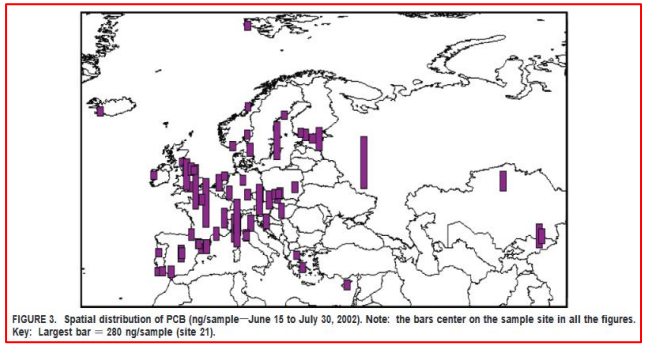


FIGURE 3. Spatial distribution of PCB (ng/sample—June 15 to July 30, 2002). Note: the bars center on the sample site in all the figures. Key: Largest bar = 280 ng/sample (site 21).

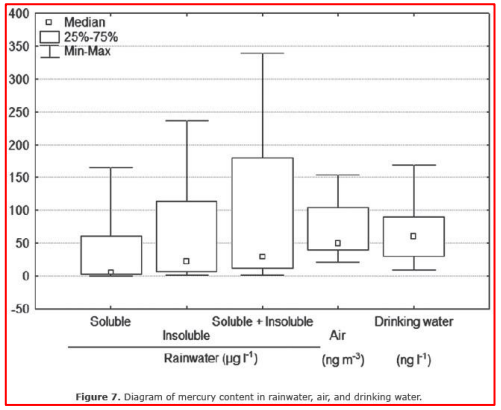


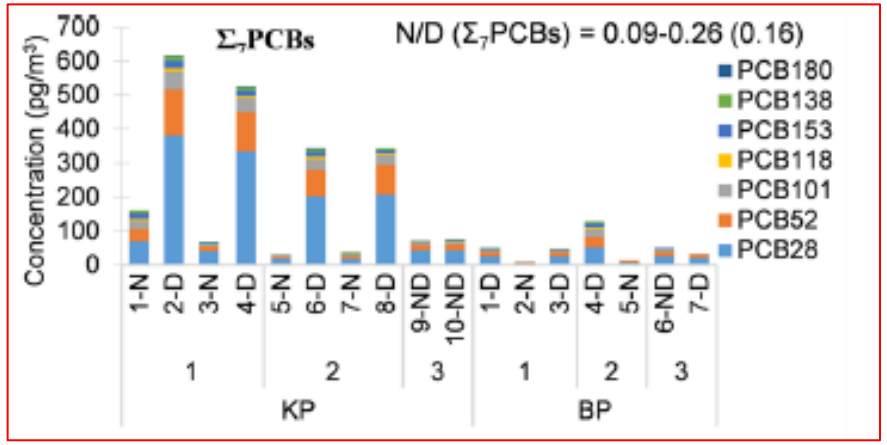
Figure 7. Diagram of mercury content in rainwater, air, and drinking water.

At a national level

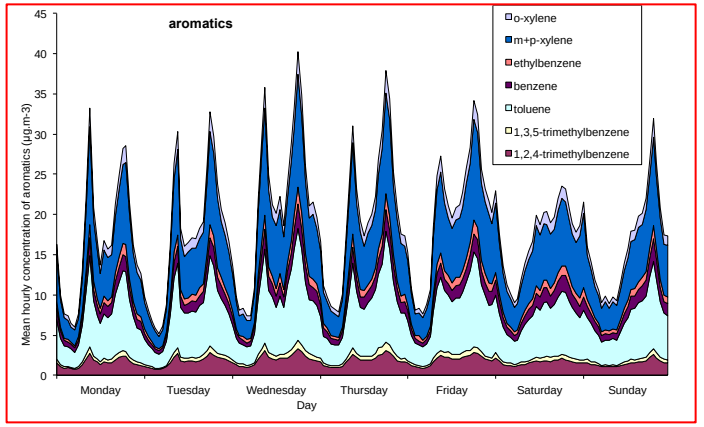
At a European level

Prior to take actions
(e.g. drinking water)

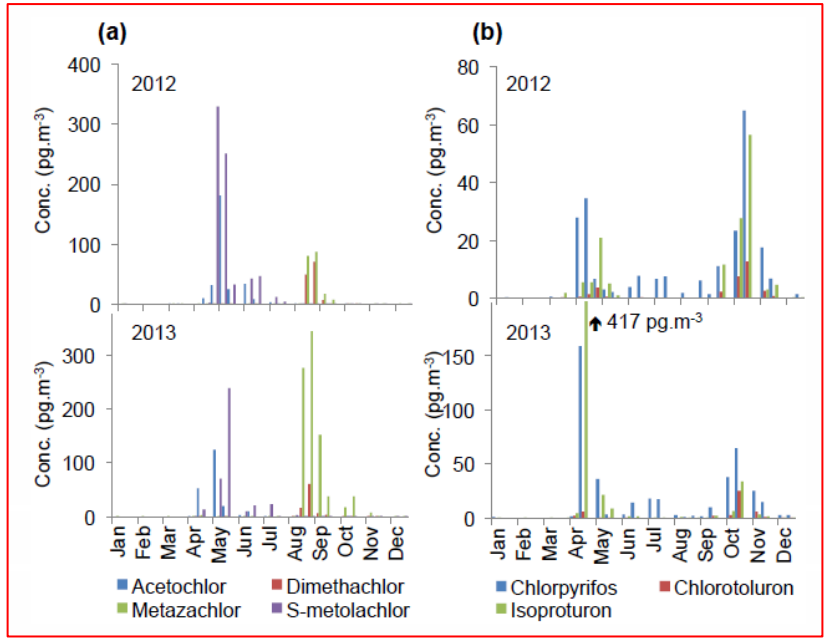
Why do we need to sample?
To understand time trends



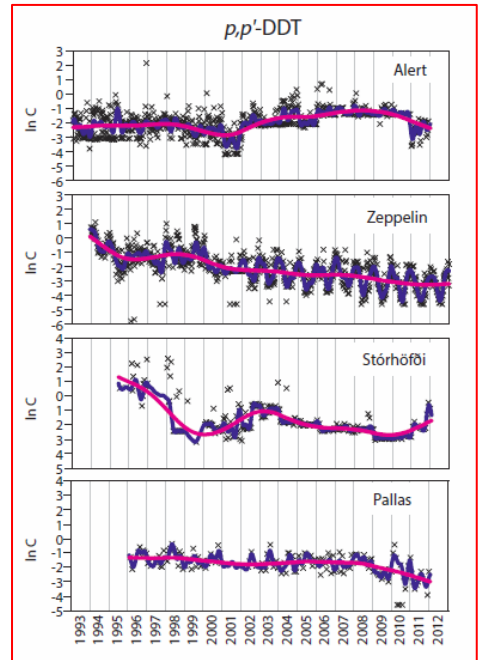
Daily



Weekly

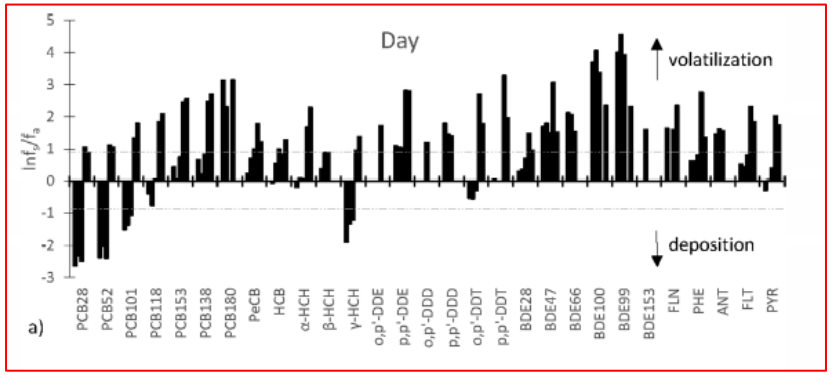


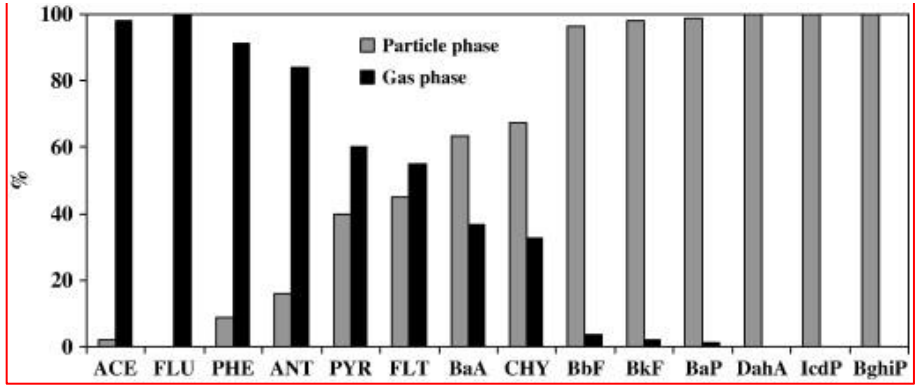
Seasonally



Long-term

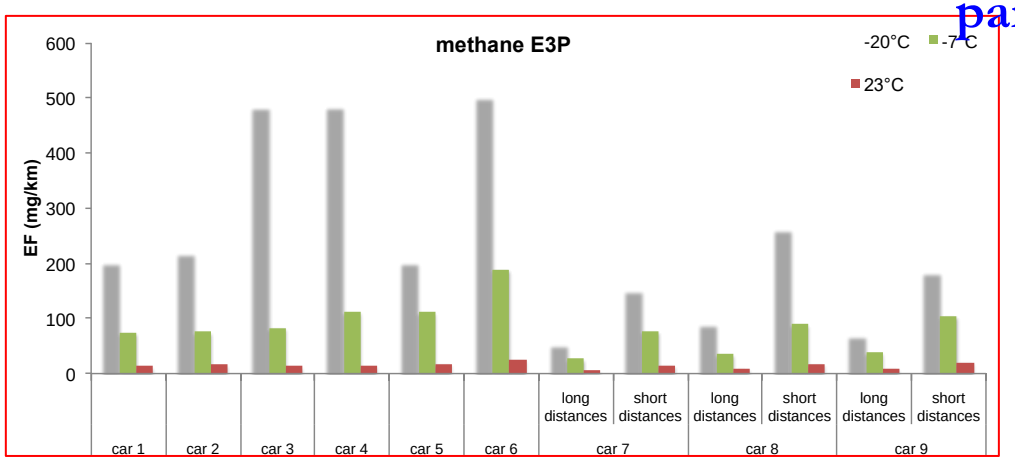
Why do we need to sample?
To understand specific processes





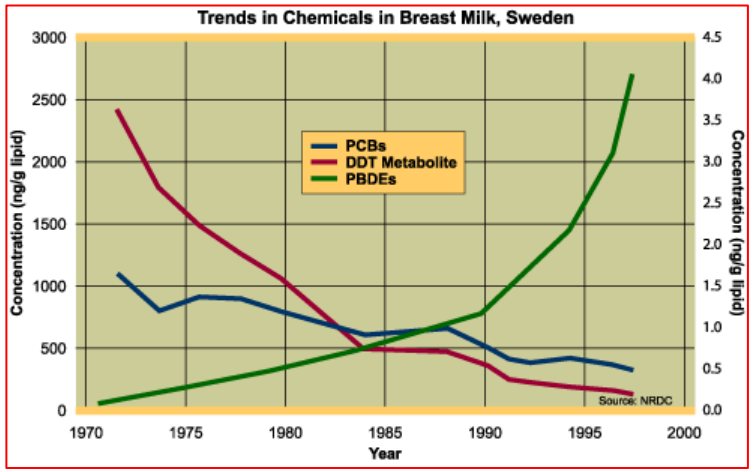
Air-soil exchange

Gas-particle partitioning



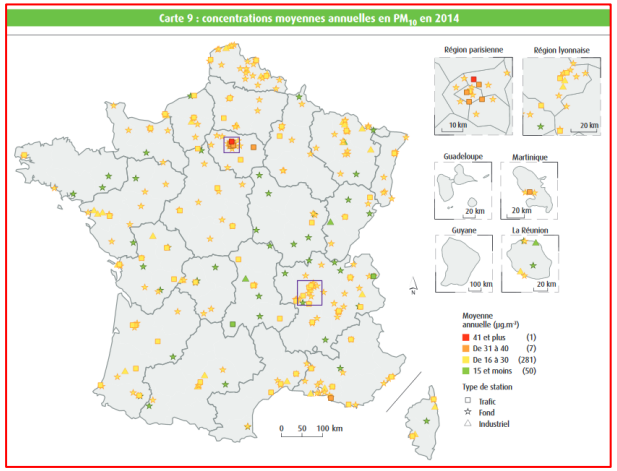
Influence of temperature on cold start emissions from passenger vehicles

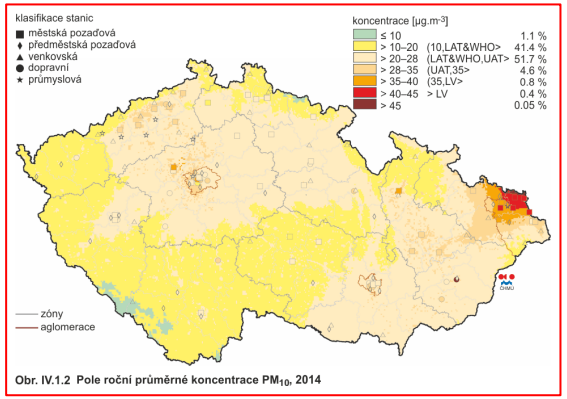
Why do we need to sample?
To support legislation



E.g. Stockholm Convention on Persistent Organic Pollutants

E.g. European regulation about air quality





How to sample?

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Air

Syringes for gas sampling, 1-100 mL

- Ideal for corrosive, radioactive, or sterile materials
- Removable handle minimizes heat transfer from hand to sample, making the syringe easy to hc
- Accurate and reproducible to +/- 1%
- Field repairable

Soil

Water

Environmental monitoring methods

Biomonitoring

- **Chemical Monitoring:** by measuring levels of a selected set of well-known contaminants in abiotic environmental compartments (water, sediment)
- **Bioaccumulation Monitoring:** exposure assessment by measuring contaminant levels in biota or determining the critical dose at a critical site (bioaccumulation)
- **Biological Effect Monitoring:** exposure and effect assessment by determining the early adverse alterations that are partly or fully reversible (biomarkers)
- **Health Monitoring:** effect assessment by examining the occurrence of irreversible diseases or tissue damage in organisms
- **Ecosystem Monitoring:** assessment of the integrity of an ecosystem by making an inventory of species composition, density and diversity

Contents

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Basic soil components

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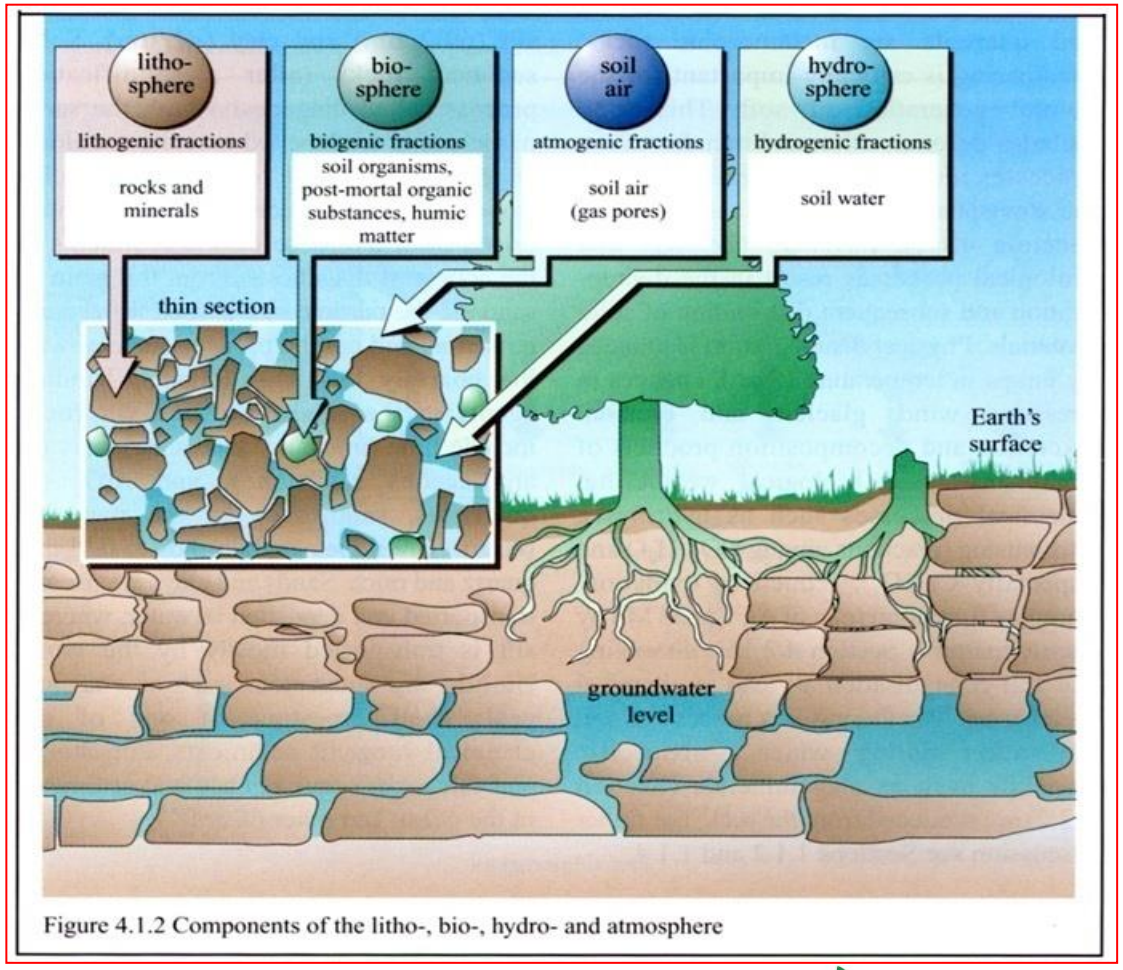


Figure 4.1.2 Components of the litho-, bio-, hydro- and atmosphere

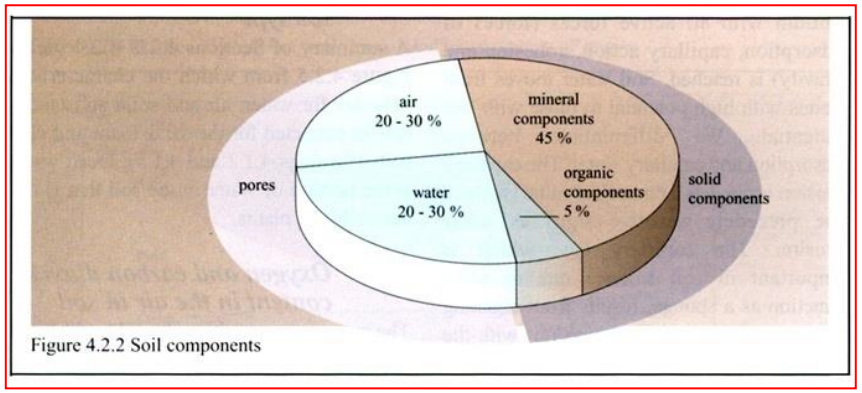
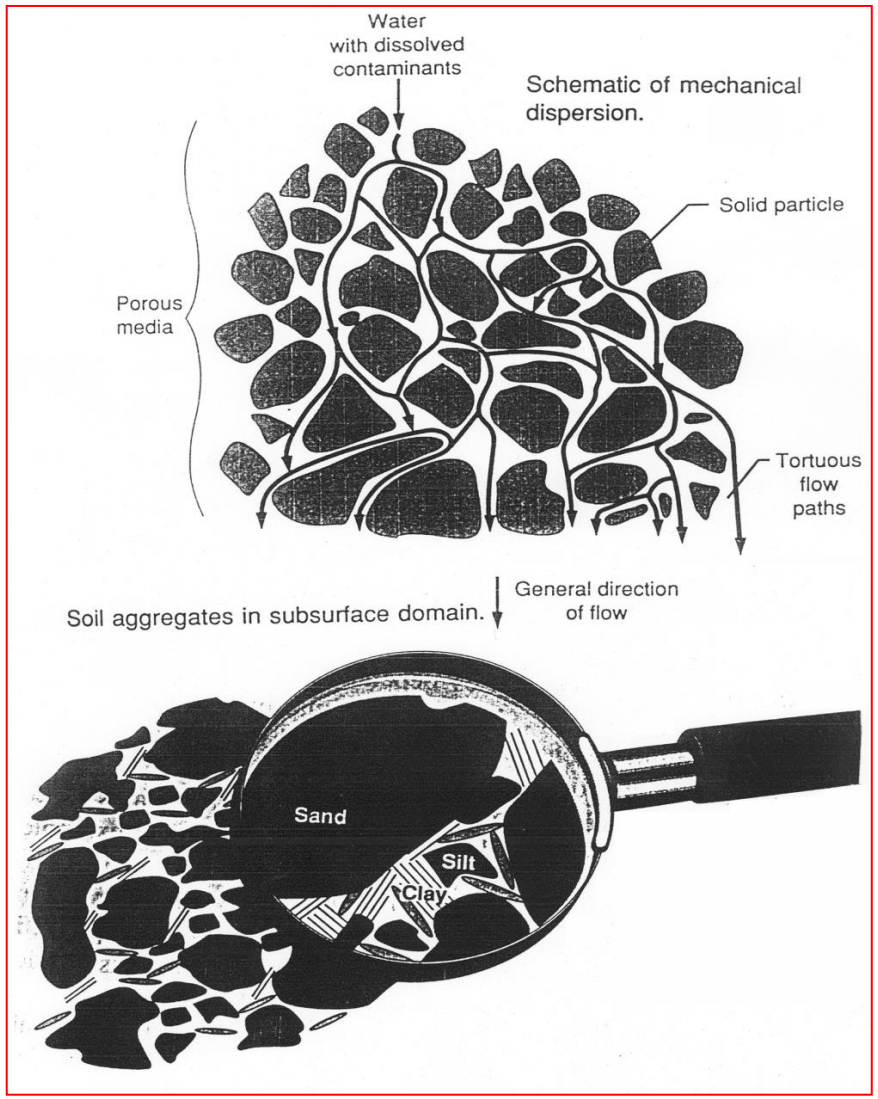


Figure 4.2.2 Soil components

Structure of soil



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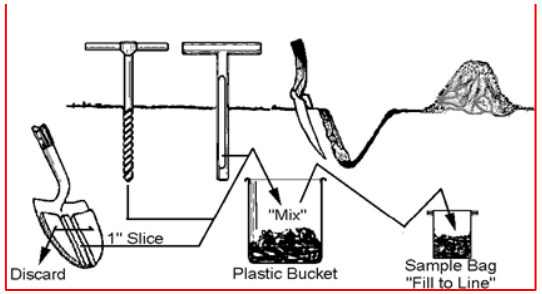
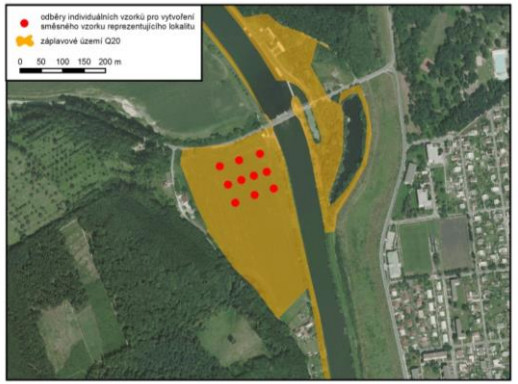
Soil sampling





Considerations for soil sampling

- Soils are very complex! Horizontal and vertical spatial distribution
- The oil sample must be representative
  - Composite sample (homogenization)
    - Aliquots needed, same volume
  - Sampling design and tool used mainly depends on purpose of sampling and type of contamination

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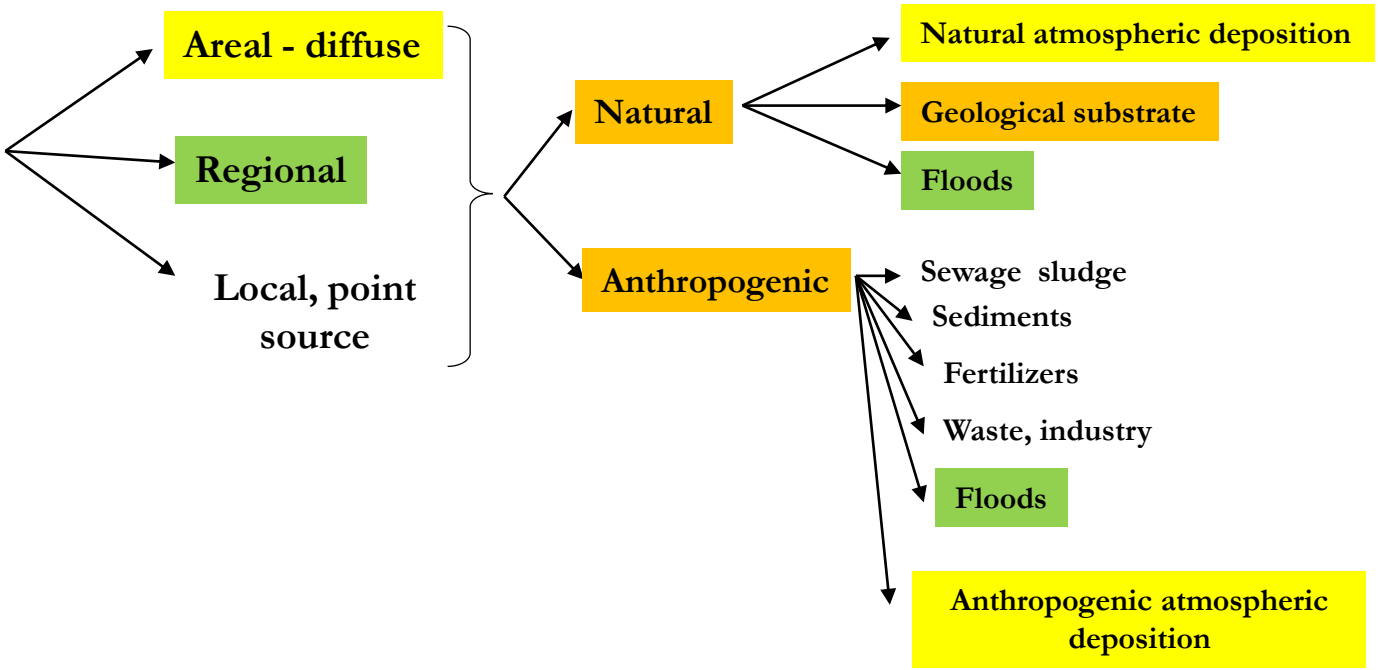
Types of soil contamination



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Types of soil monitoring

- Agricultural, arable soils various types (field, gardens..)
- Grasslands
- Forest soils
- Protected areas
- Industrial areas

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Goals of soil monitoring

- Understanding of level of destruction and contamination
- Determination of trends
- Specification of potential negative changes, quantification
- Make a safe feedback – development of conditions for stopping of negative trends (or improvement of actual state)
- Getting of background information for legislature
- Establishment of database for fundamental and applied research

Soil sampling

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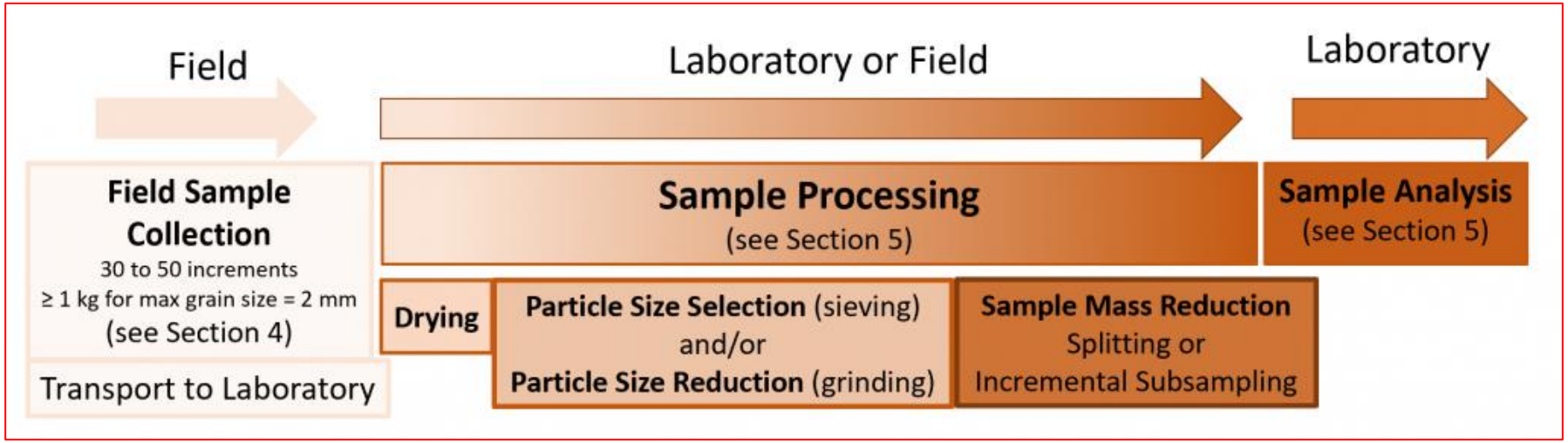

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Methods of soil sampling

Area of sampling:

- Arable soils and grassland – ca 7 - 10 ha (according to soil conditions and production area
- Hop-garden – area for the collection of 1 mixed sample – 3 ha
- Vineyard - 2 ha
- Database – one sample per 1km^2; area for the sampling of 1 mixed samples – at minimum 30 nicks uniformly cover whole investigated area

Depth of sampling:

- Arable land - 30 cm
- Grasslands - 15 cm with removal of upper turf layer
- Hop-garden - 40 cm with removal of upper 10 cm layer
- Vineyards – sampling of two layers 0 - 30 and 30 - 60 cm
- Intensive orchards - 30 cm.

Soil sampling

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Based on the type of analysis

Sampling probe tube, soil borer (mg kg^{-1})

Depth of sampling – based on the goal of monitoring

0 - 5; 5 – 10 cm ....pesticides applied by spraying, ambient air

0 - 30; 30 – 60 cm ....(based on the depth of root systems)

heavy metals, pesticide residua, xenobiotics, nutrients: N, P, K

Average sample - 30 stabs (nicks)

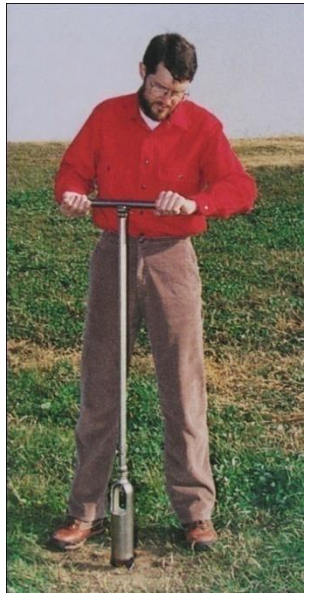
- lowland - 9,5 ha one sample
- mountains - 6,5 ha

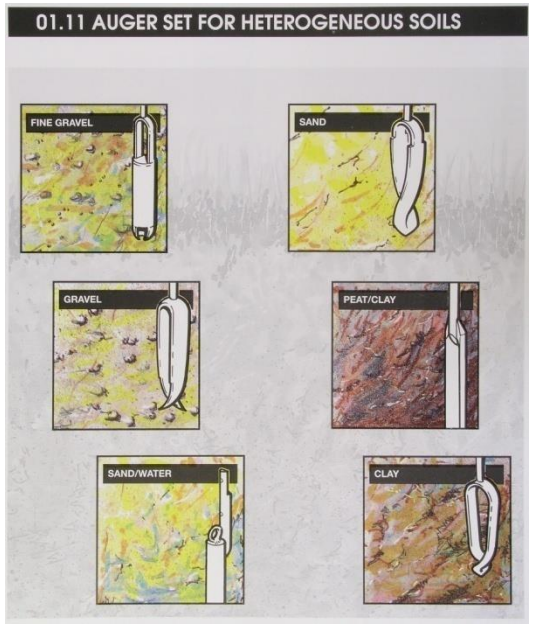
Distribution of stabs regularly whole area (cross the field)

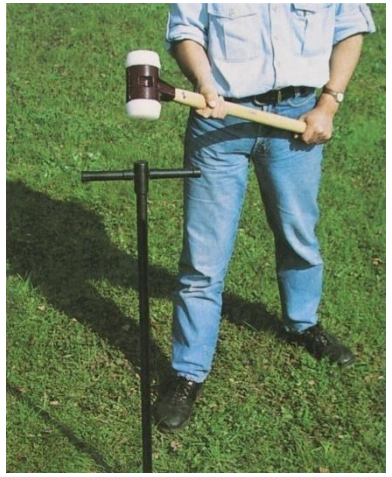
Soil sampling

Sampling sets with various types of probes and soil borer – according to the type of soil

Soil sampling







Soil sampling

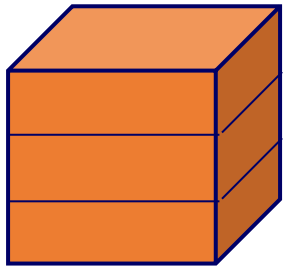
Areal contamination (accidents)

Sampling of ashlars - 30 x 30 x 30 cm - horizons

0 – 5 cm

5 – 15 cm

15 – 30 cm



In exactly selected localities *(with respect of deposition shadow, wind directions, local anthropogennic activities)*

Frequency of sampling – according to the goals of monitoring

Samples - PE (paper) bags with description, dispatch note

In the case when the degradation or transformation can be expected – cooling bags

Soil sampling

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Soil heterogenicity

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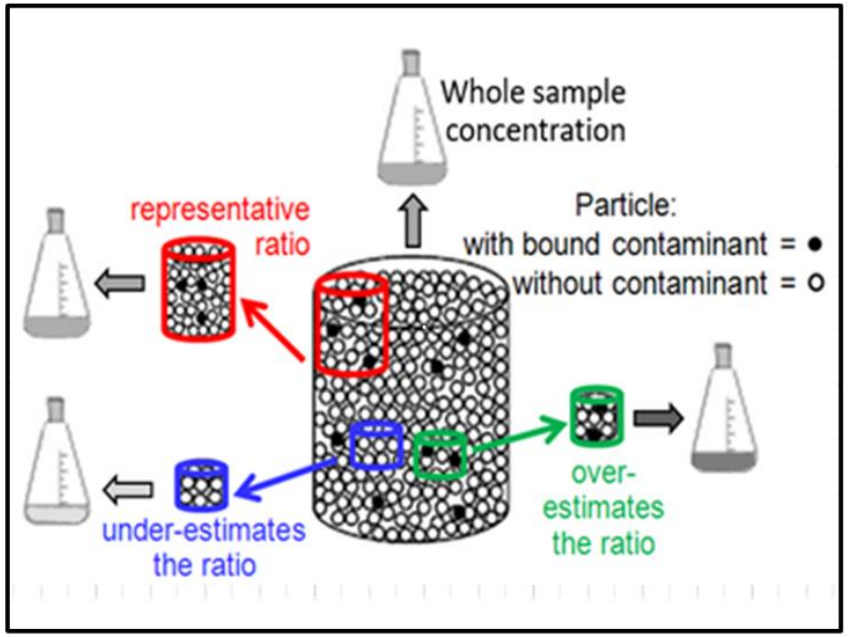

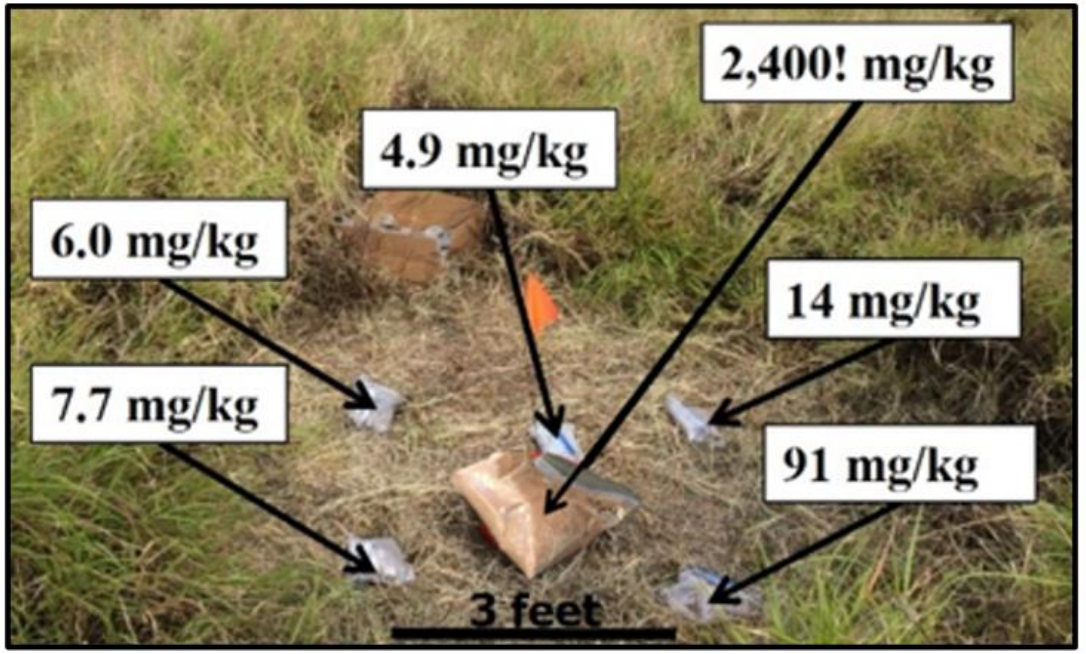

Peat samplers

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04.09 Peat sampler

- Benefits
  - Samples saturated AND unsaturated material
  - Stainless steel sample body for all analyses
  - Simple gouge-with-a-flap principle
  - Effective to sample young peat and sediment
  - Takes point samples at any depth (if very soft)
- Remarks
  - Thick point limits penetration in stiff material
  - Water plant roots will be pushed aside
  - Water and watery top soil will flow out

Peat sampler operation

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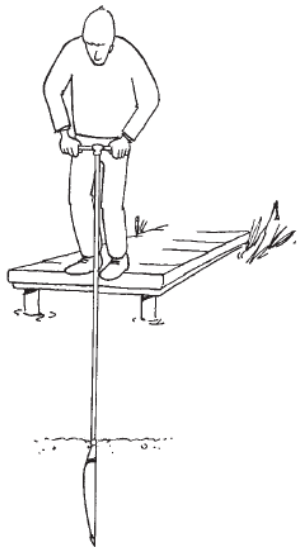
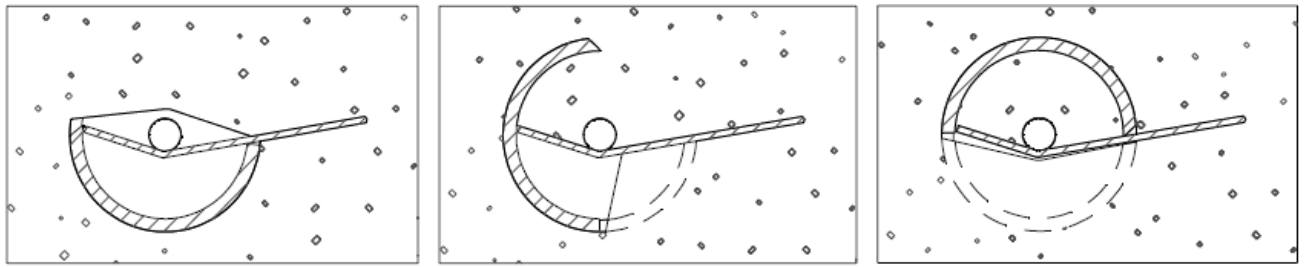
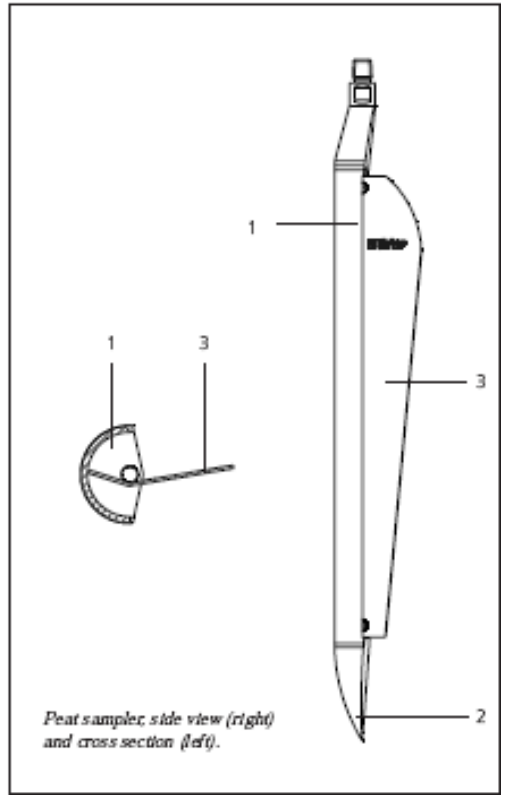
the European Union and the Republic of Turkey.







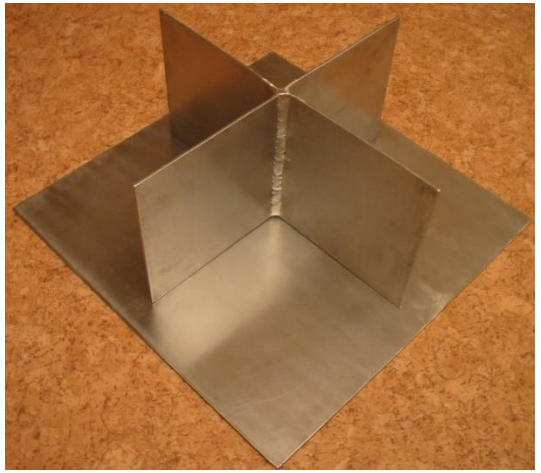
Peat sampler, side view (right) and cross section (left).

Homogenisation, sieving, dividing of samples

Crushing, grinding, homogenization

Sieving

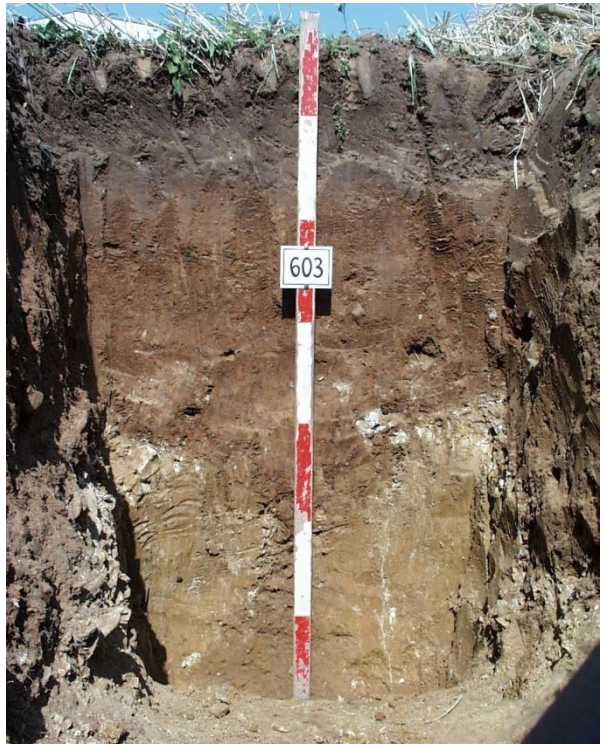
Dividing of sample



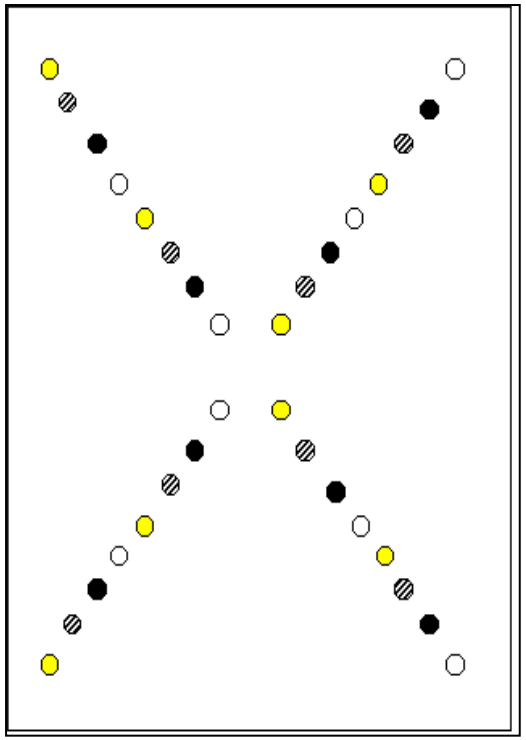
Quarter cruise

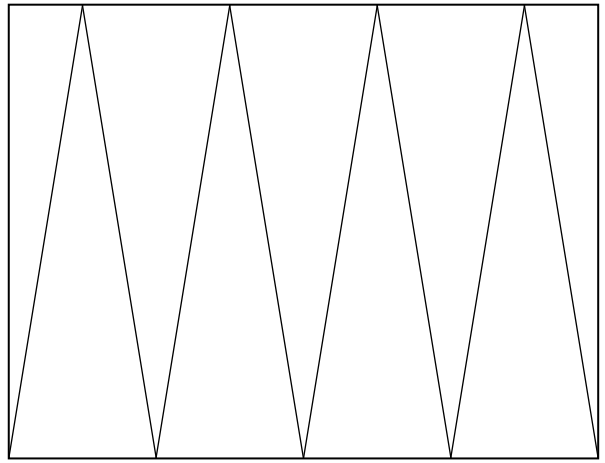
Sampling scheme on the monitoring plot

soil pit



25 m





40 m

no. 1 ● no. 2 ○ no. 3 ● no. 4 ○

individual sampling to get four composite samples

Basal soil monitoring program - setting the soil characteristics

Unrepeated parameters monitored at establishing the monitoring plot

- recording of the identification information of a monitoring plot
- soil pit description
- analyses of physical parameters (complete analyses of disturbed and undisturbed soil samples)

Parameters monitored in six years period

- active and exchangeable soil reaction
- contents of available nutrients - P, K, Mg, Ca analysed by several methods
- contents of microelements (B, Mo, Mn, Zn, Cu, Fe)
- sorption capacity (S, T, V)
- organic matter content (Cox)
- risk element contents in nitric acid (As, Be, Cd, Co, Cr, Cu, Ni, Pb, V, Zn) and aqua regia (Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, V, Zn) extraction and total Hg content

Yearly monitored parameters

- content of mineral nitrogen
- chosen microbiological and biochemical parameters
- contents of selected organic pollutants (persistent organochloric pesticides, PCBs, PAHs, PCDDs/Fs)
- contents of risk elements in plants on contaminated plots

Contents

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Groundwater monitoring

Objectives groundwater monitoring:

- To assess/understand general groundwater quality of the groundwater (ambient + operational monitoring)
- Finding major pollution sources (ambient/effluent monitoring)
- Compliance with regulations/ standards (effluent monitoring)
- Impact of an accidental pollution (early warning monitoring)

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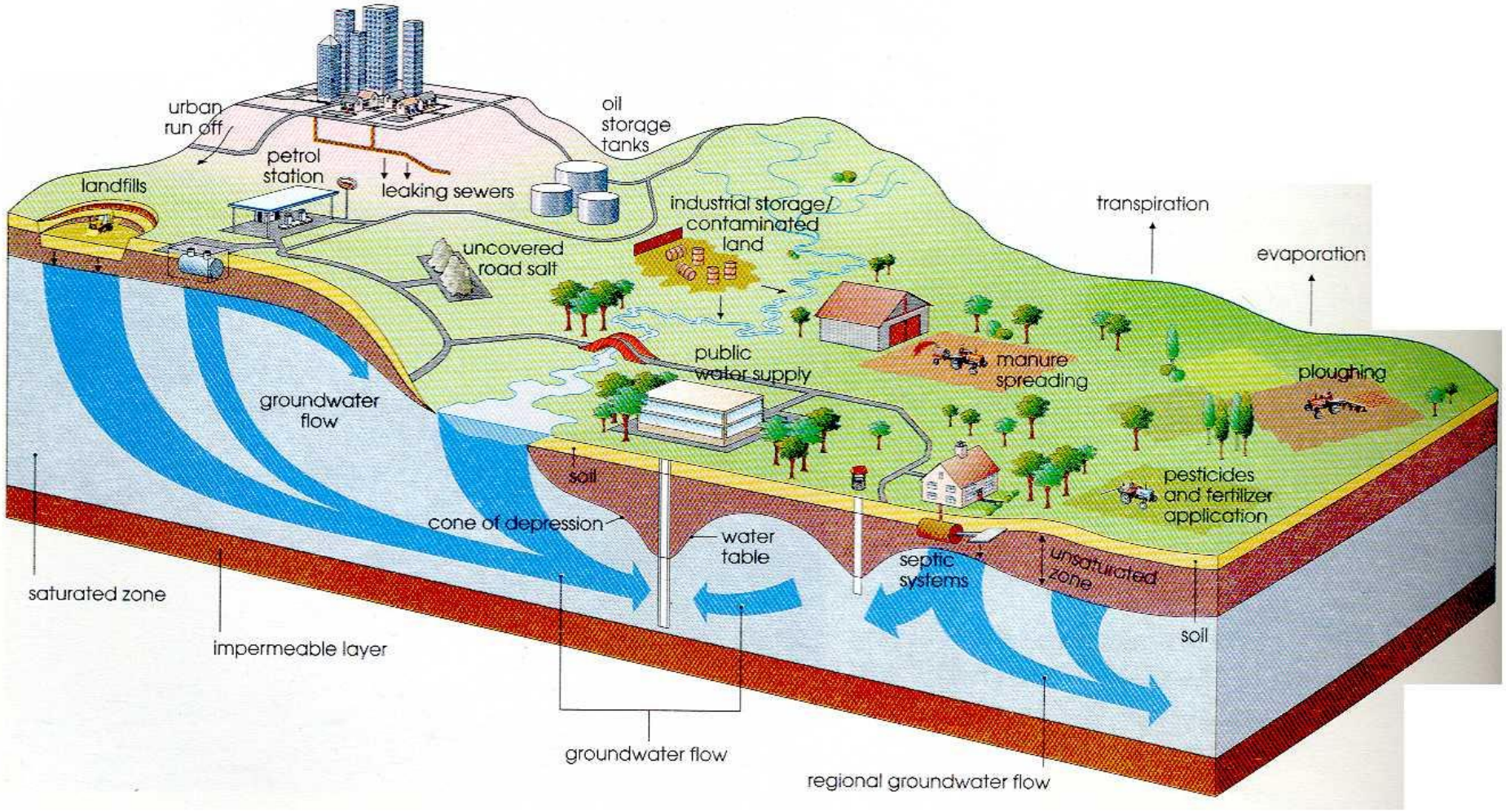
Groundwater pollution

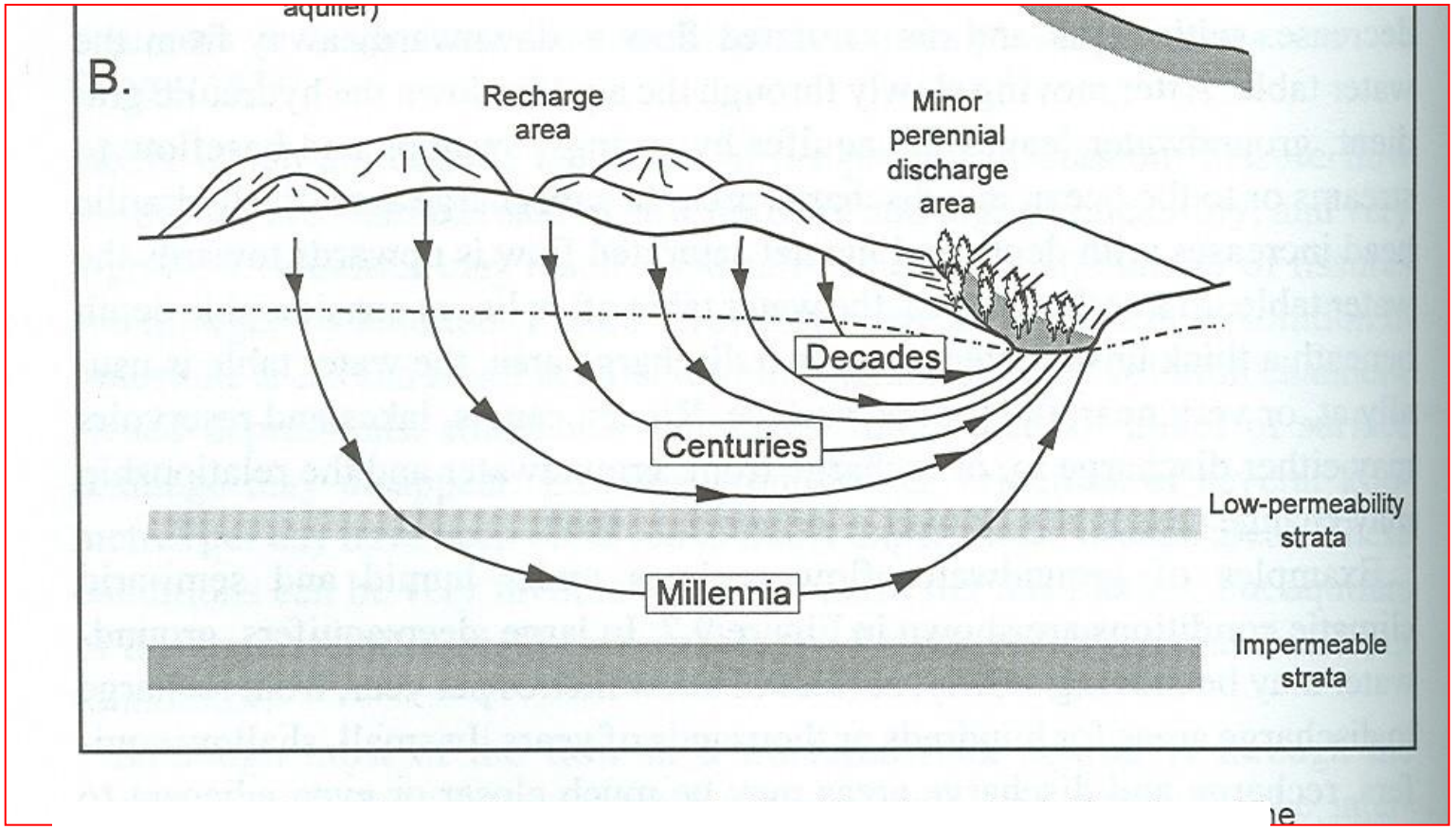
- Input of untreated domestic wastewater (BOD, Suspended solids, nutrients, bacteria and viruses, *etc.)*
- Industrial spills; mining (BOD, SS, micropollutants)
- Agriculture (NO_3^- , pesticides, Cl^- ....)
- Pit latrines and other on-site sanitation systems
- Waste dumps (domestic and hazardous wastes)

Treatment: slow, difficult and very expensive --> prevention!

Groundwater-surface water relationships



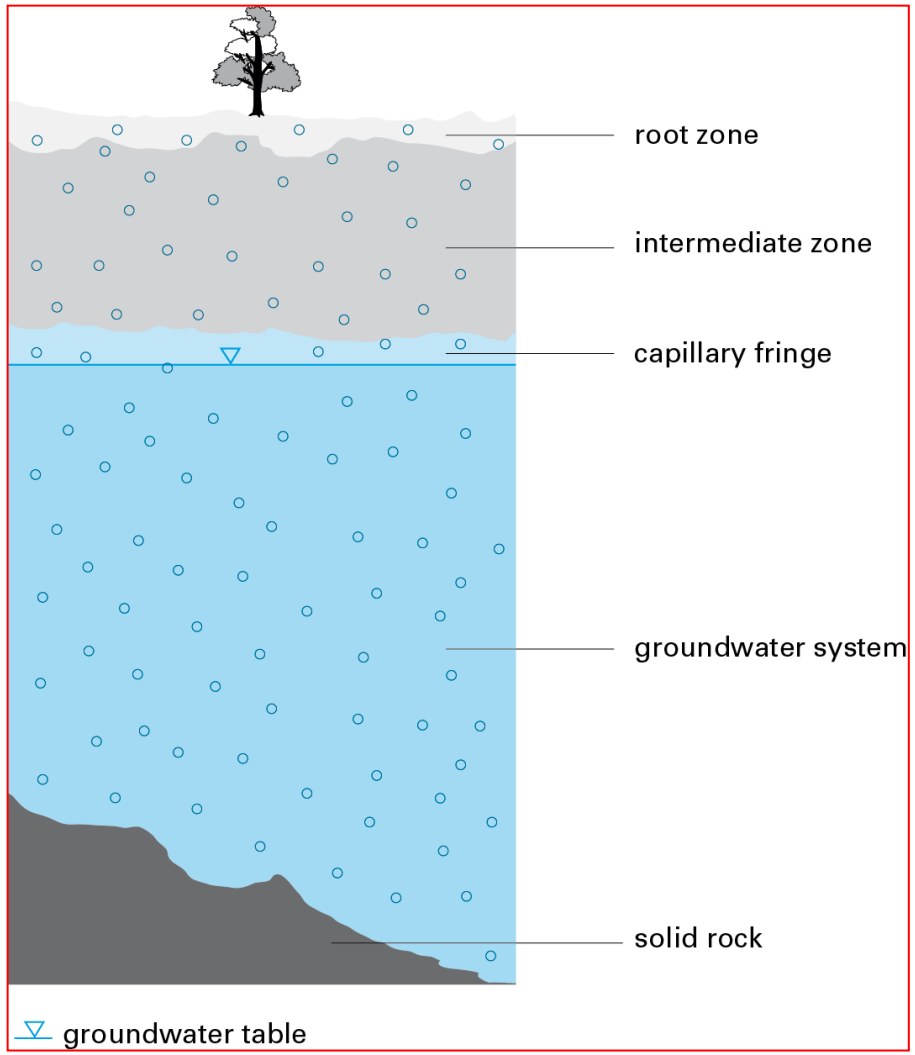
Groundwater flows



May take decades-millenia between recharge → discharge

In arid/semi arid zones often poor quality, *e.g.* high salinity

Unsaturated zone



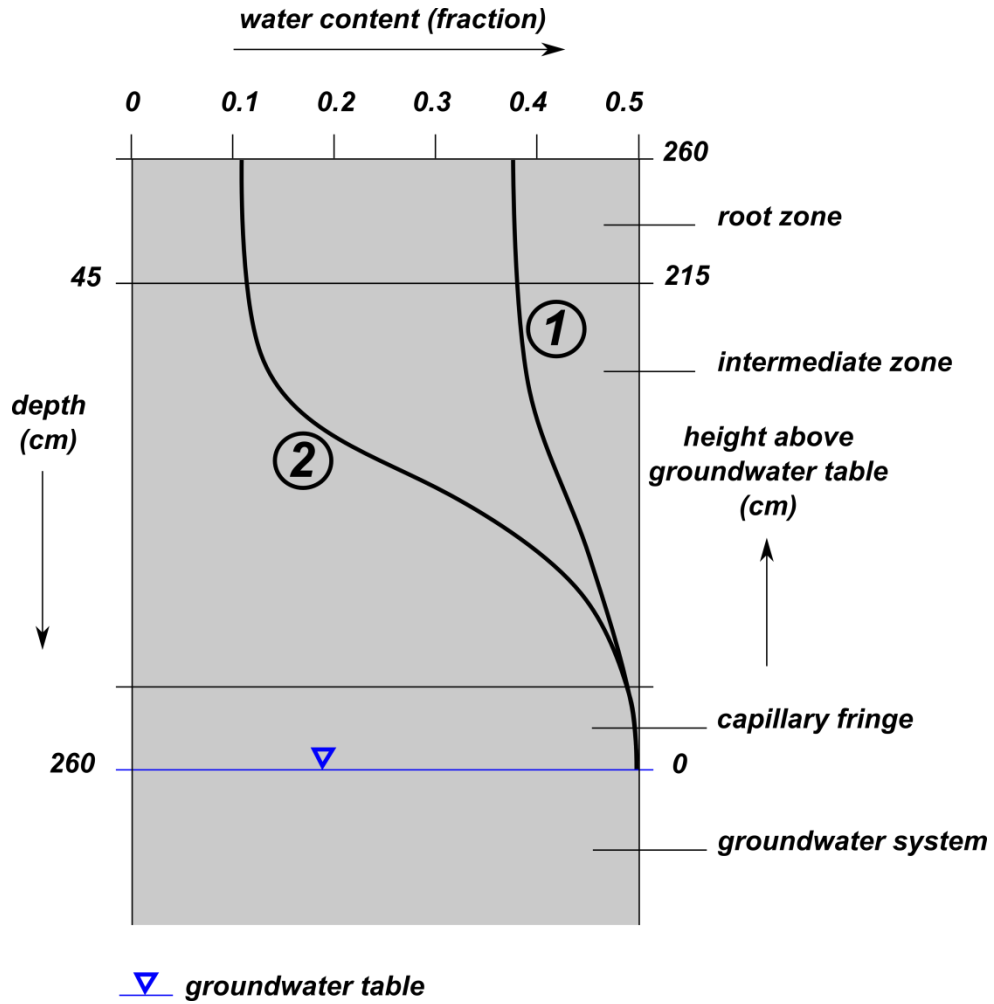
Contains network of plant roots; usually < 2m thick;

Absent in humid areas, but with large thickness in arid areas;

Zone directly above groundwater table; water pressure is less than atmospheric (tension). Thickness ranges from 1-50 cm, dependent on rock type.

Zone with (saturated) groundwater. Pressure at the groundwater table is atmospheric.

Process in the unsaturated zone



Water in unsaturated zone is prone to evapotranspiration and/or downward flow or 'groundwater recharge from precipitation'.

Assuming a precipitation event with groundwater recharge, then after the event stopped, downward flow will continue until field capacity is reached (curve 1). At field capacity, gravity forces acting on water equal surface tensions exterted by the pore structure, and downward flow terminates. Field capacity depends on type of soil. The one shown here is typical for silty loam.

During dry periods, when there is no downward flow, there may be upward flow or capillary flow. When wilting point is reached, roots are not able to extract sufficient moisture for plant survival. Curve 2 shows wilting point conditions for a silty loam.

The structure of rocks: porosity

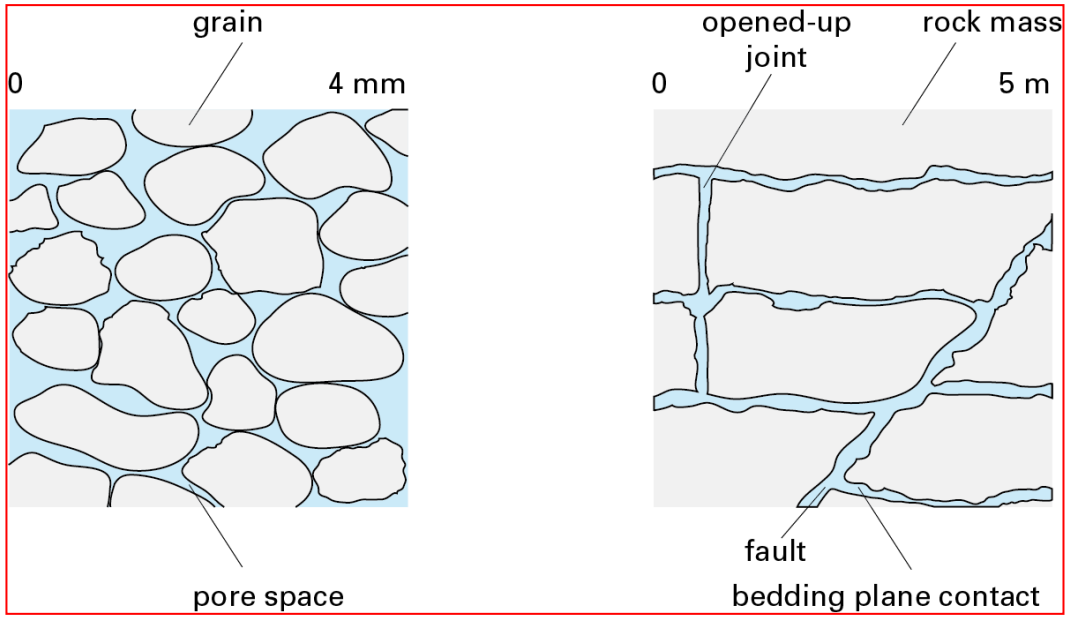
Porosity of rock is the ratio of the volume of open space in the rock and the total volume of rock (including the open space):

$$n = \frac{V_O}{V_T}$$

n rock porosity

V_O volume of the open space (m^3)

V_T total volume of the rock including open space (m^3)



In consolidated rocks, openings are primarily present at fractures, joints, bedding planes, and solution holes. This type of porosity is referred to as secondary porosity.

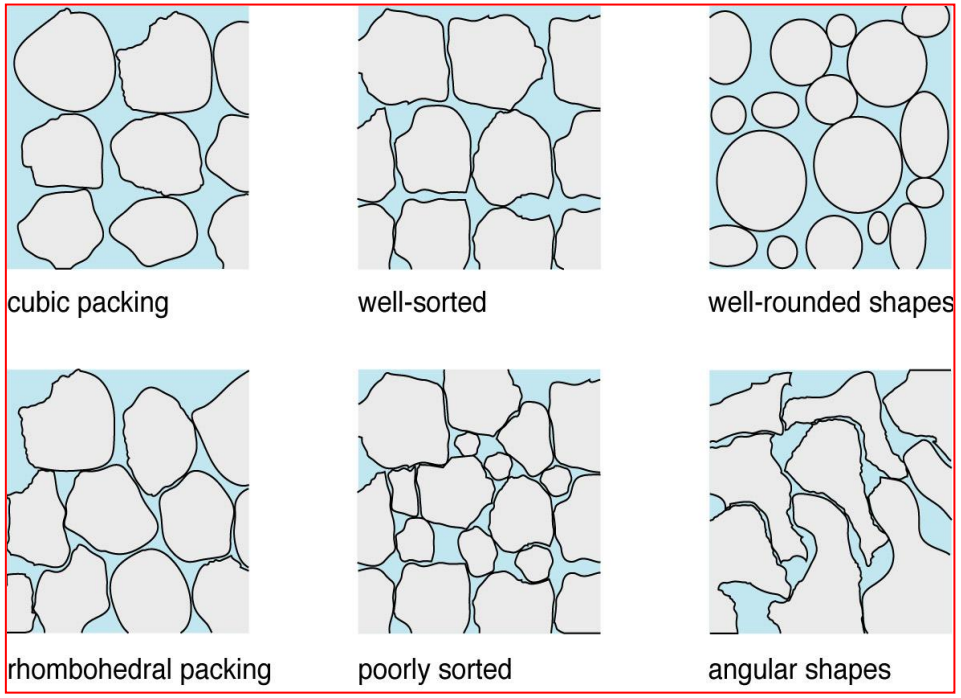
In unconsolidated rocks, openings or pores are present between individual grains. This type of porosity is referred to as primary porosity.

The structure of rocks: porosity

The structure of rocks: porosity

In unconsolidated rocks, (total) porosity ranges from 0.2-0.7.

Rock type	Range of porosities
Unconsolidated rock	
Gravel	0.2-0.4
Sand	0.2-0.5
Silt..→clay	0.3-0.5
	0.3.. -0.7→>0.95



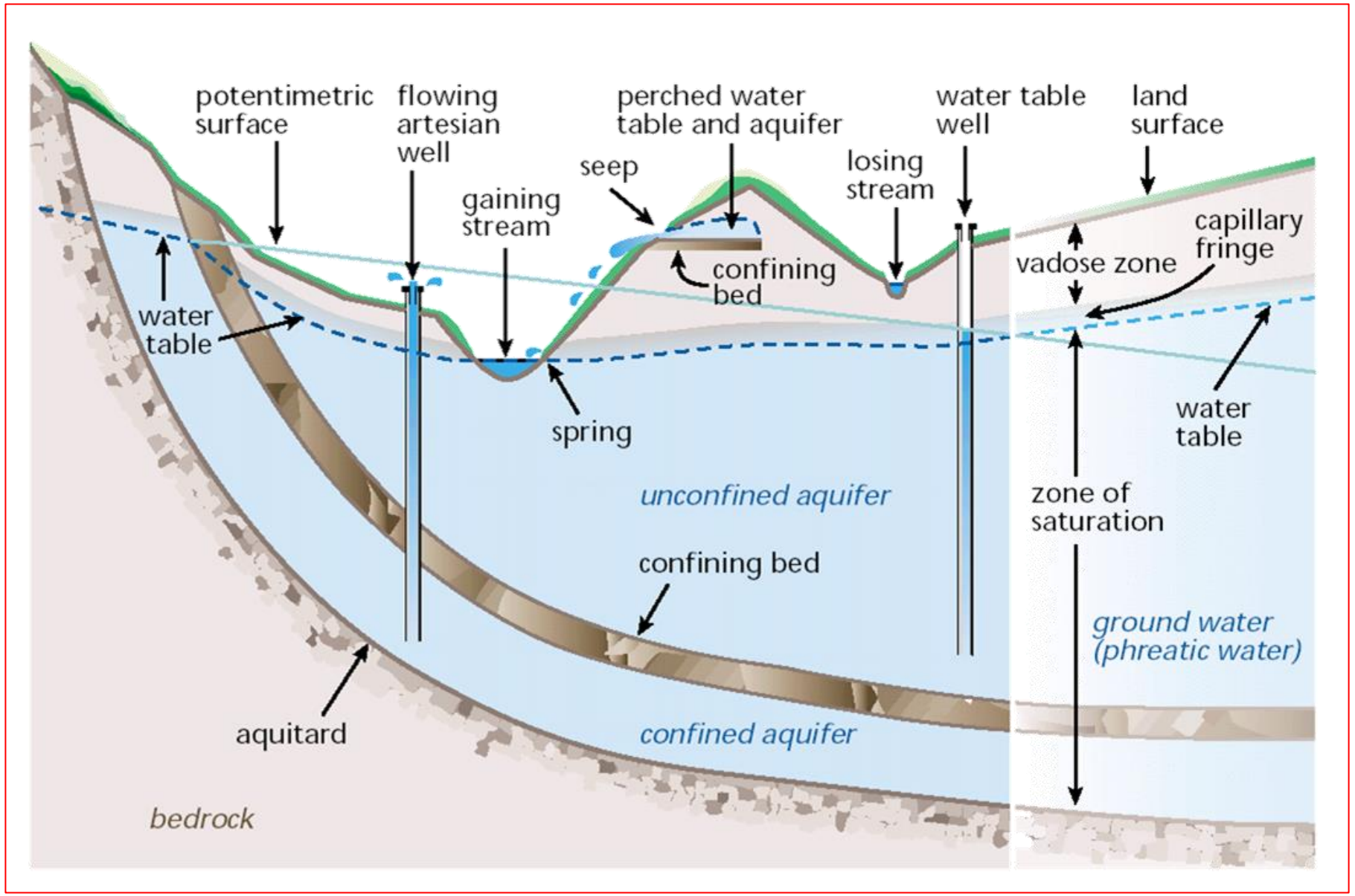
Porosity in this case relates to the packing, sorting, and shape of grains:

Porosity of sediment with cubic packing, well-sorted, well-rounded = ~ 0.48

Porosity of similar sediment, but rhombohedrally packed = ~ 0.26

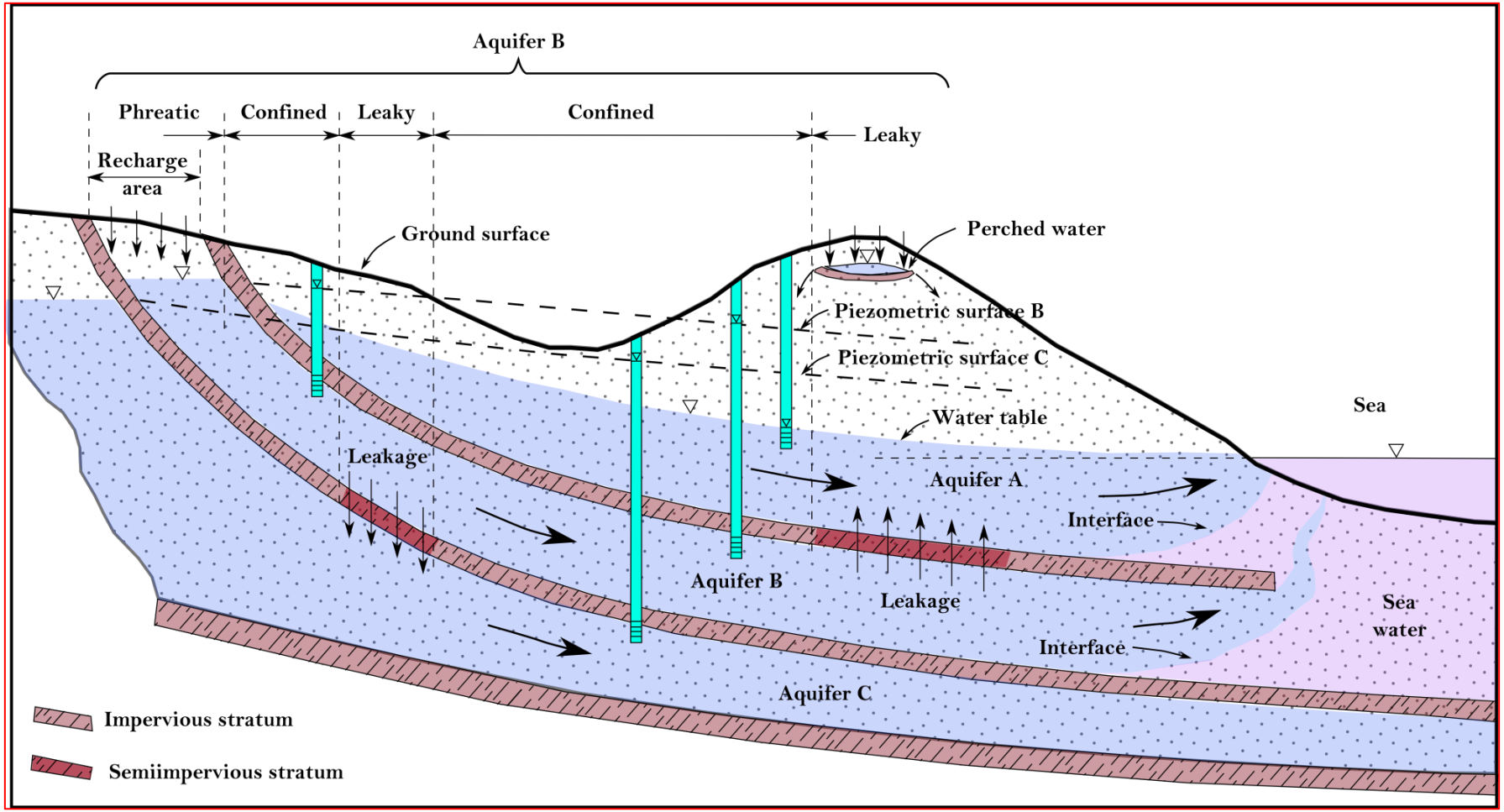
When sorting is poor, and grains are not rounded, porosity decreases further.

Groundwater Terminology

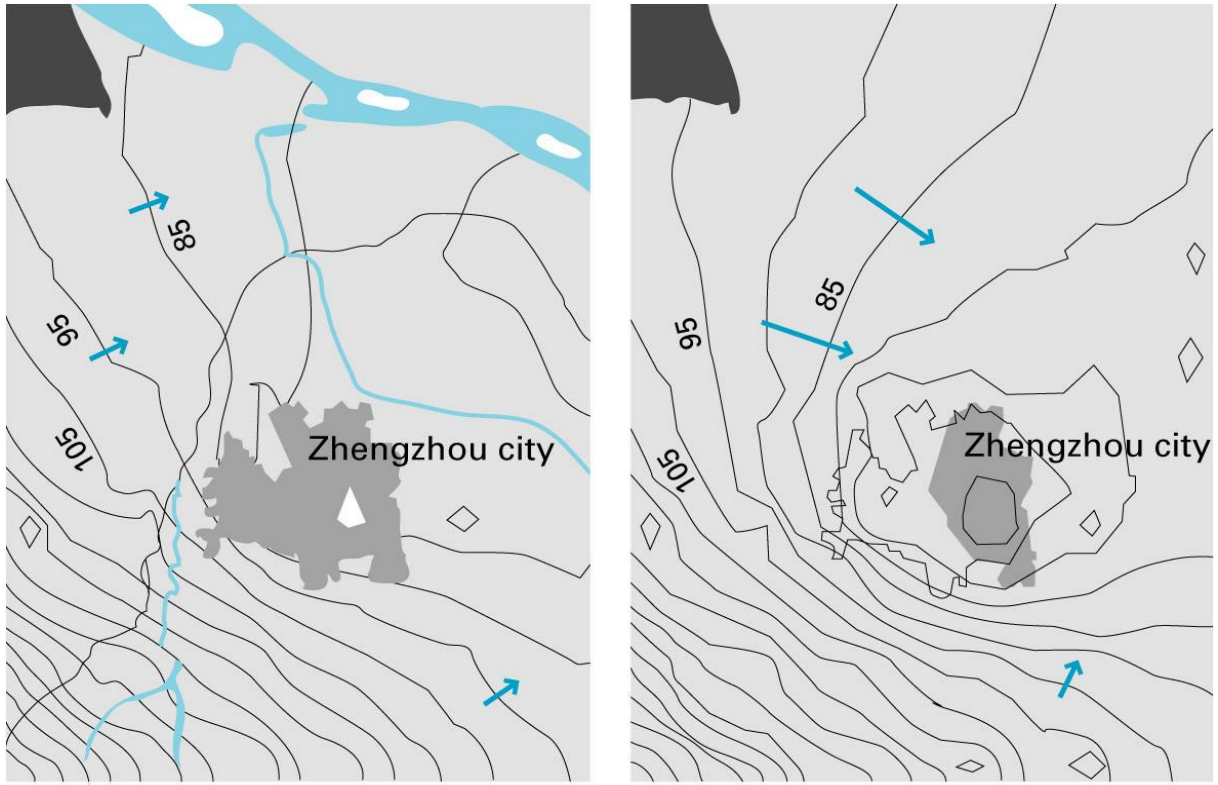


Classifying aquifers: a quite complicated example

From left to right, aquifer B is phreatic, confined, leaky, confined, and finally, leaky again. Please note that, when the piezometric surface is above ground surface, the aquifer is called 'artesian'.



Regional flow and groundwater head contour maps



For shallow aquifer: flow towards river.

For lower aquifer: flow towards the city. Here, a cone of depression is present, caused by excessive pumping below the city.

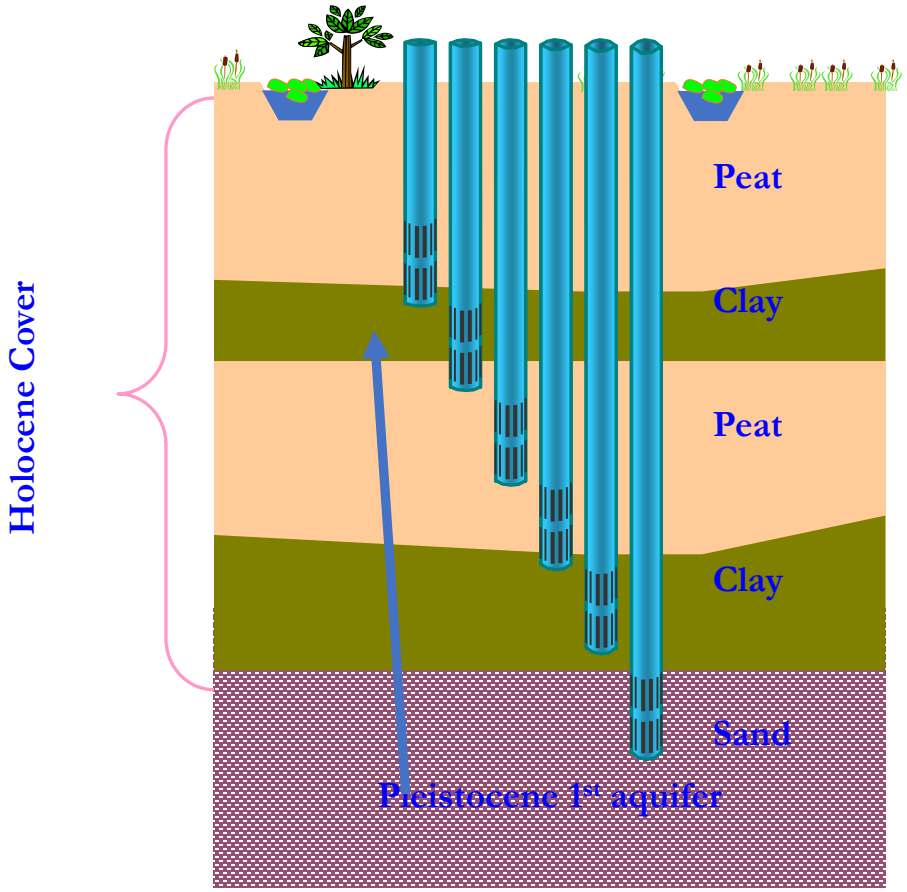
There is also flow from the upper to the lower aquifer through the aquitard.

Left figure: upper aquifer; right figure: lower aquifer (separating aquitard is not shown)

Groundwater sampling/ analysis

Piezometer nests

in Exfiltration area



Groundwater sampling/analysis

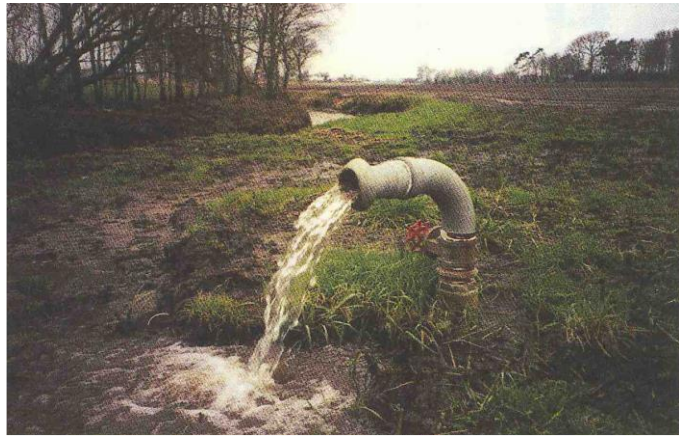
Sampling a 60 m deep groundwater well in
Limburg, The Netherlands

Karst spring, Mount Hermon area, Syria

Dug well in Yemen highland

Hidden in the little hill, a public supply drinking water well, Brixen, Italy

Groundwater seep (with very low electrical conductivity!!)
South-Pare mountains, Tanzania

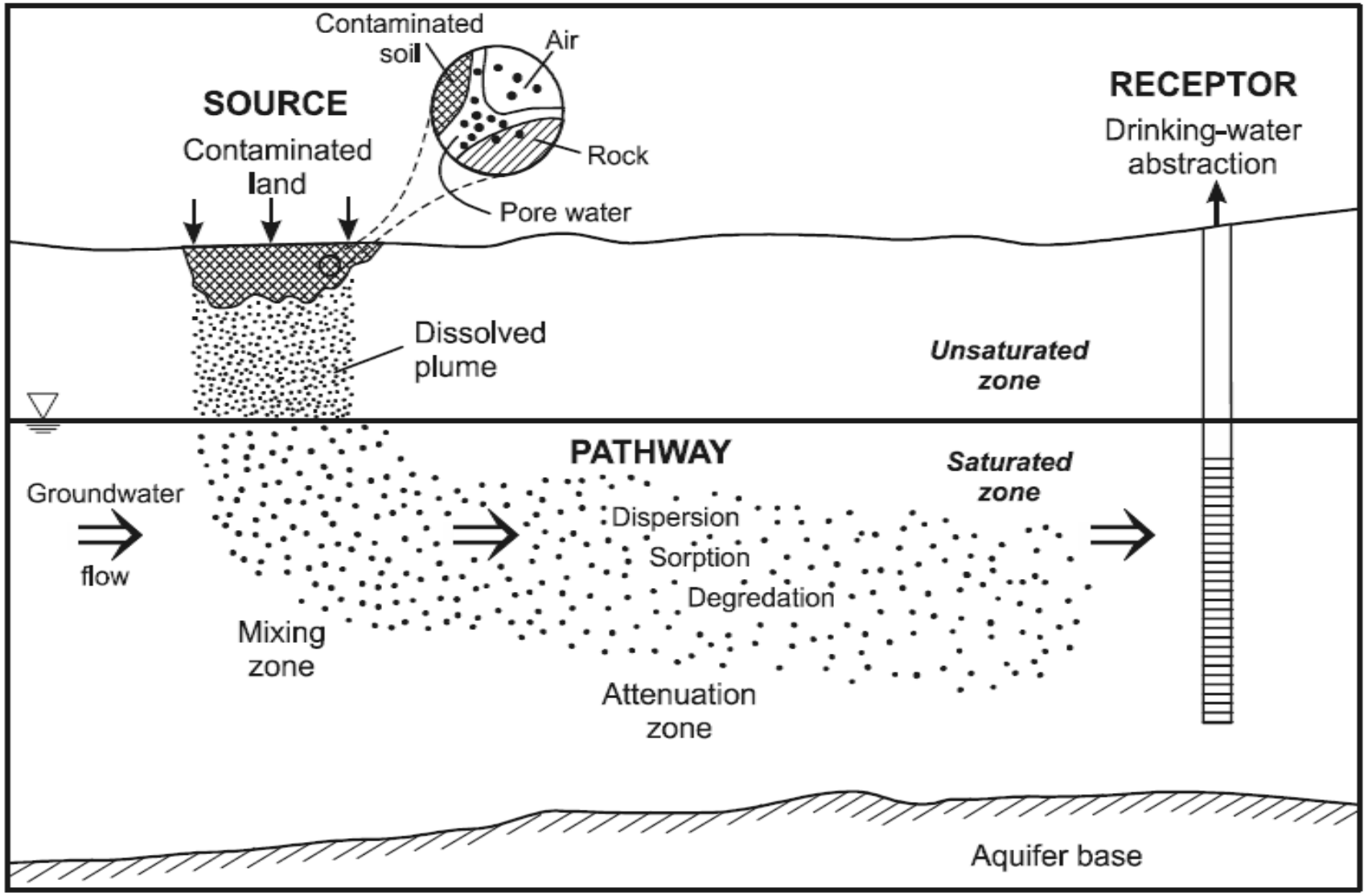


Artesian well, Strijbeekse beek,
The Netherlands

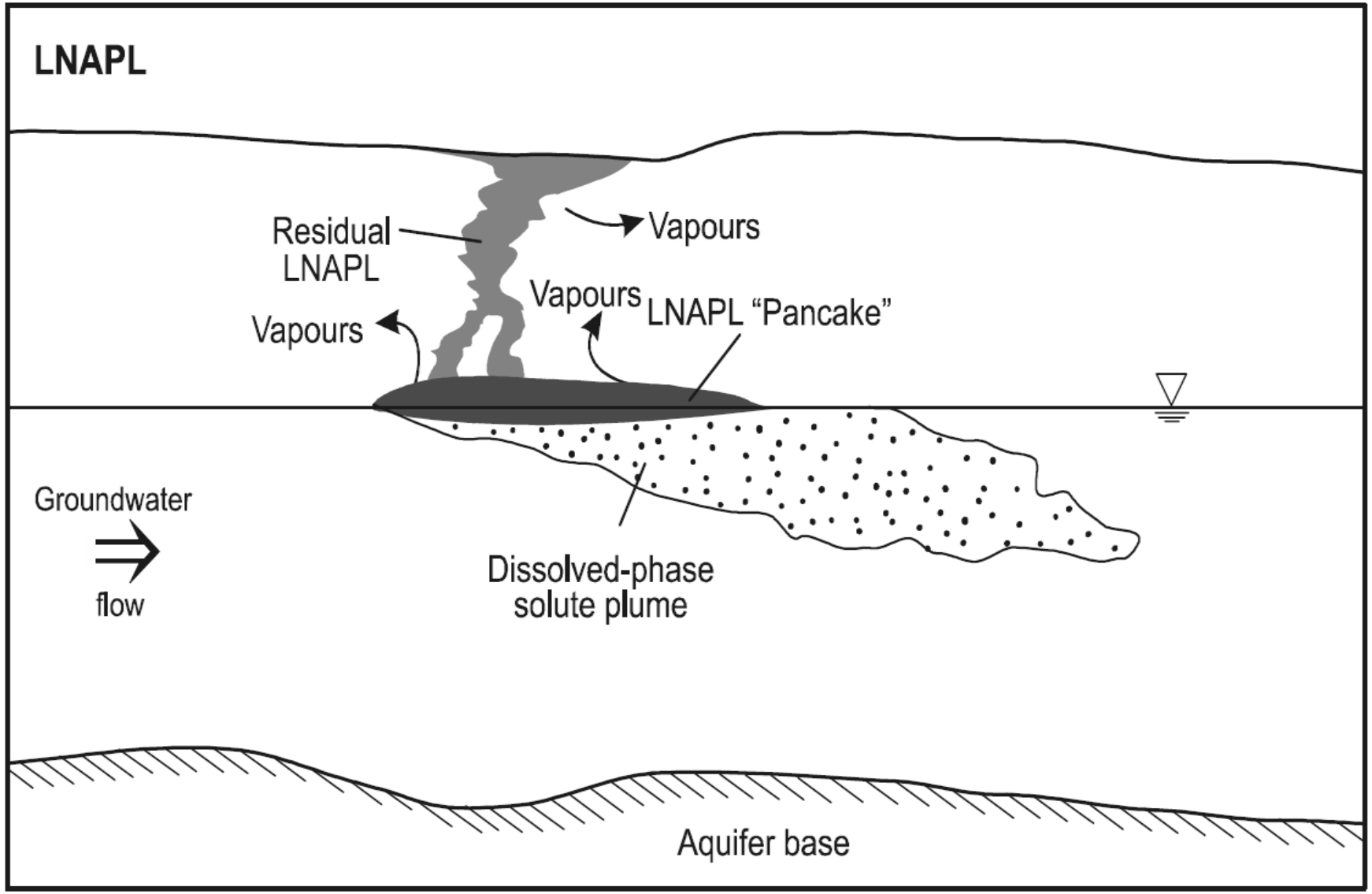
Groundwater sampling/analysis

Maps (GPS)
Field book
Bottles: acidified, non-acidified
Syringe with filter holder and filter paper
EC meter
pH meter
Alkalinity set

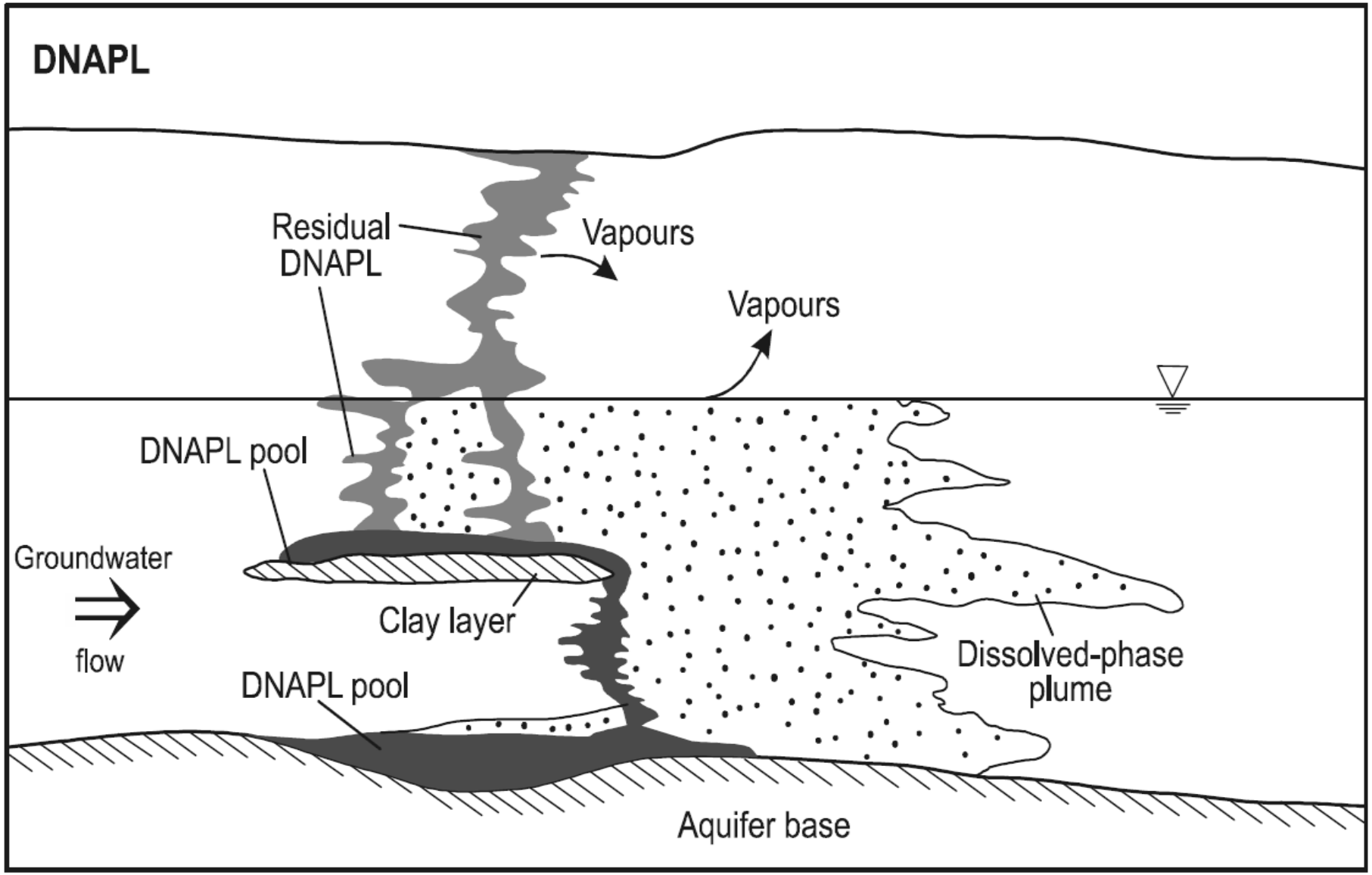
Classical contaminant conceptual model



NAPL (light non-aqueous phase liquid; *e.g.* petrol, benzene)

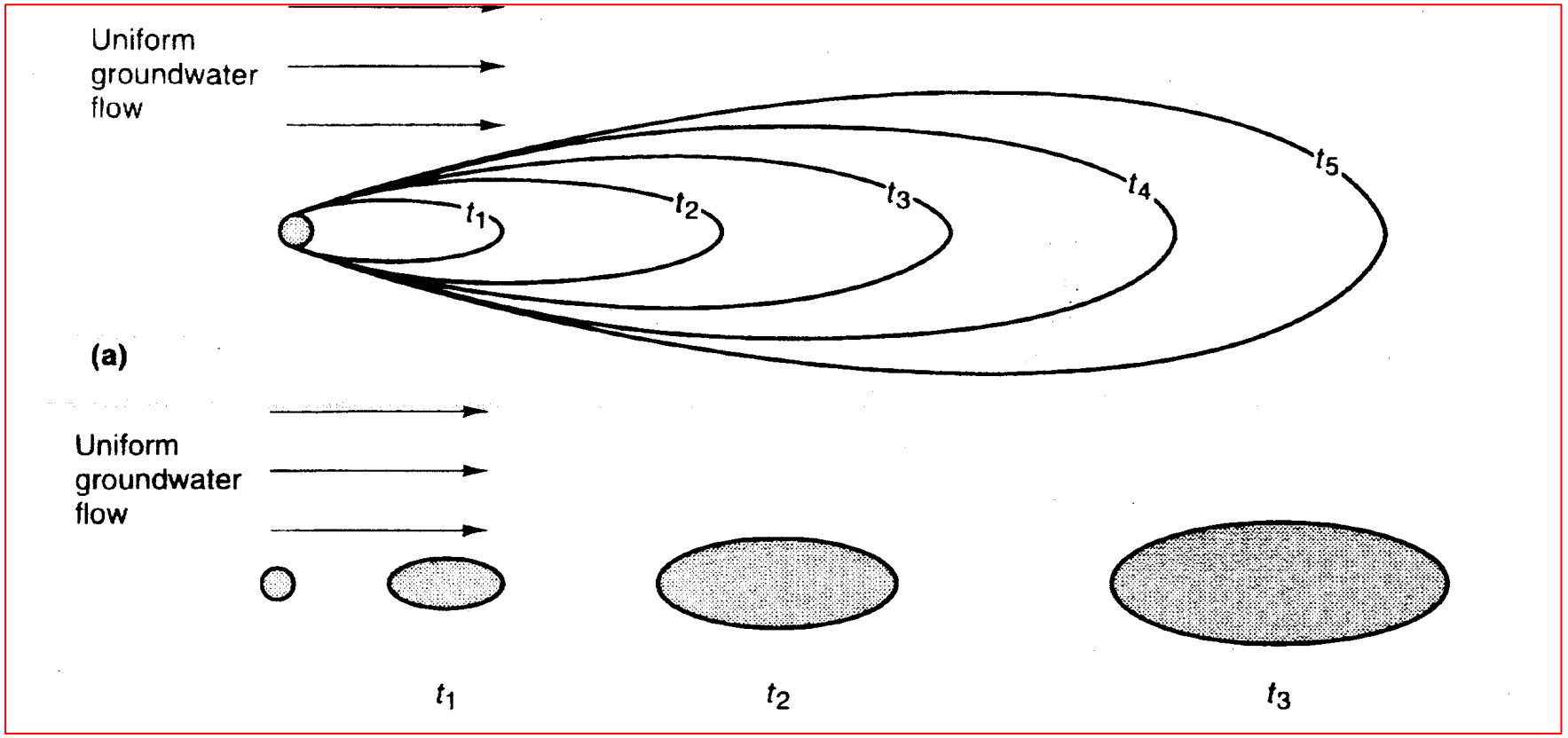


DNAPL (Dense non-aqueous phase liquid, e.g. heavy oils)



Fate of pollutants on groundwater

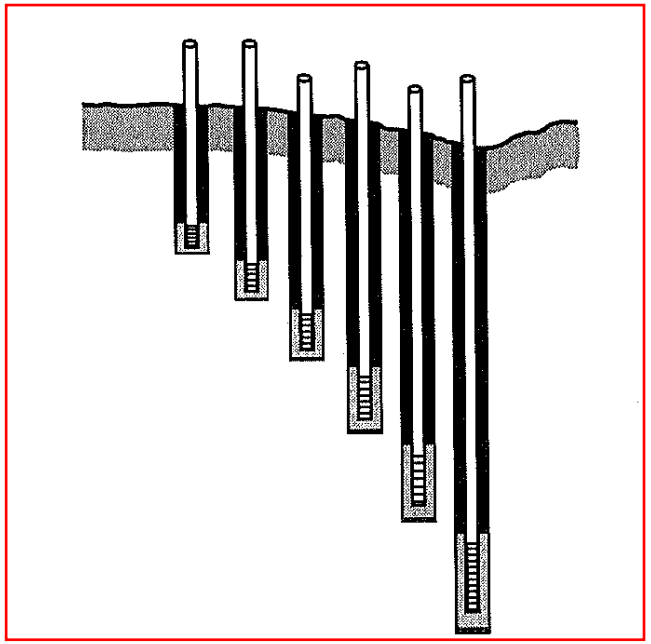
Groundwater flow cm's/day (much less in clay)



- Adsorption/precipitation (but for *e.g.* NO_3^- unhindered flows)
- Microbiological degradation (*e.g.* BOD; also die-off of bacteria)
- Complexation, redox reactions, *etc.* (*e.g.* $Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe(OH)_{3\downarrow}$)

Number, locations, frequency

- Number of stations much dependent on objectives; in The Netherlands: *ca.* 1 per 100 km^2 (near drinking water extractions)
- In many (large and/or less developed) countries: much lower density.
- Location of stations: After surveys. Look at groundwater flows and directions; geology, *etc.* Often special boreholes have to be constructed.



Piezometers installed in a drillhole

Number, locations, frequency

Sampling frequency: about 1-4 times per year; much more for:

- Specific research (see figure hereunder)
- Rapid groundwater flows; high permeability (sand)

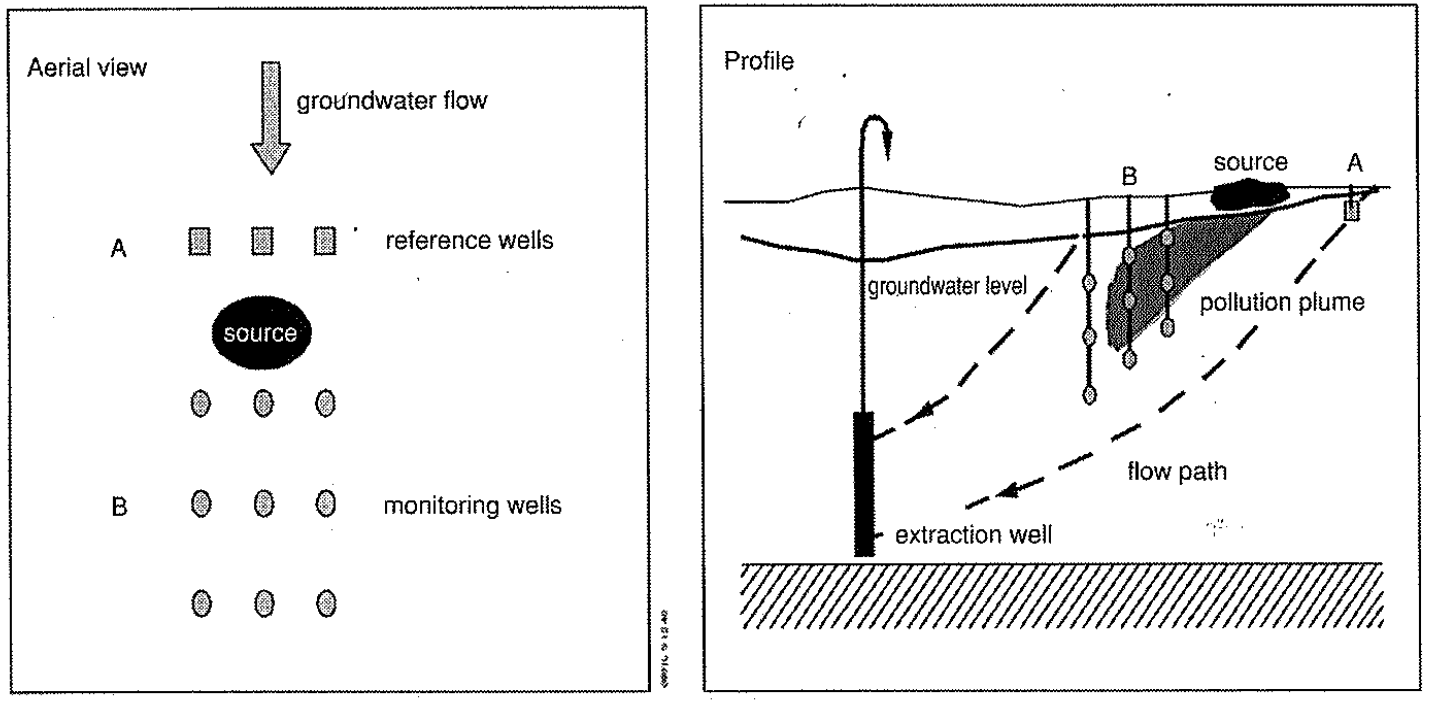


Figure 4: Aerial view (left) and profile (right) of the recommended lay out to monitor point pollution, using reference wells upstream (A) and monitoring wells downstream (B) of the potential source.

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TEŞEKKÜR EDERİM…

REPUBLIC OF TURKEY
MINISTRY OF ENVIRONMENT,
URBANIZATION AND CLIMATE CHANGE

Environment and Climate Action
Sector Operational Programme

Persistent
Organic
Pollutants

UNDP