

Analysis/fractionation and speciation of water samples

KJM3090



Module plan

See:

<https://www.uio.no/studier/emner/matnat/kjemi/KJM3070/h20/timeplan/index.html>

➤ Thursday October 15th:

- **Lecture 1**, Seminar room Avogadro, hr. 08:15 – 10:00
 - Module plan
 - Research strategy
 - Water sampling from different compartments of the environment
 - Sampling strategies for environmental samples
 - Difference between total analysis, fractionation and species
 - The significance of species activities rather than total concentration in terms of mobility and toxicity
 - Chemical analytical speciation and fractionation methods

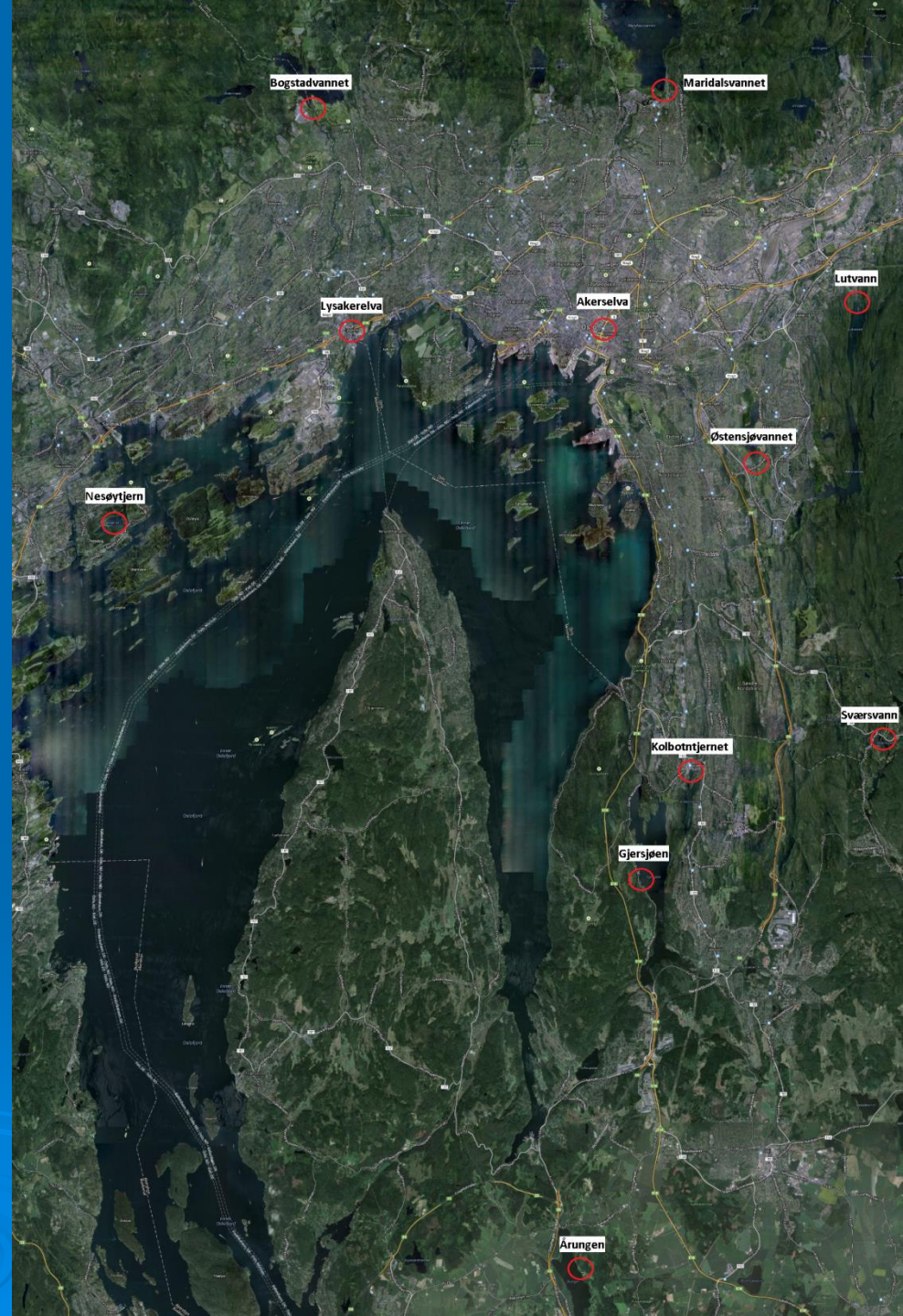
➤ **Thursday, October 22th;**

- **Lecture 2**, Seminar room Avogadro, hr. 08:15 – 10:00
 - HSE protocols
 - Analyses plan
 - Data assessment
 - Central equilibriums in natural water samples

Module plan

➤ Friday, October 23rd;

- **Field work, Lakes and stream around Oslo, hr. 10:15 ~ 18:00**
 - Maridalsvannet (oligotrophic), Akerselva (polluted), Lutvann (oligotrophic), Østensjøvann (eutrophic), Sværsvann (dystrophic), Årungen (eutrophic), Gjersjøen (mesotrophic), Kolbotnvann (eutrophic), Nesøytjern (mesotrophic)



Module plan

➤ Tuesday, October 27th;

- **Labwork, V160 hr. 10:15 ~ 16:00**
 - Sample preparation
 - Filtration, UV oxidation
 - Analysis of:
 - pH, Conductivity, UV/VIS absorbency, Alkalinity, Al fractions
 - Presentation of instruments:
 - Major Anions and Cations on IC, TOC, ICP

Module plan

➤ Thursday, October 29th;

- **Lecture 3**, Seminar room Avogadro, hr. 08:15 – 10:00
 - Challenges with simultaneous equilibrium
 - Speciation programs (MINEQL)
 - Nordic lake assessment

➤ Tuesday, November 3th;

- **PC-stue** Kristine Bonnevie, 1250 hr. 10:15 – 14:00
 - Practice in using MINEQL

➤ Thursday, November 5th;

- **Assignment**, Seminar room Avogadro, hr. 08:15 – 10:00
 - Independent report writing

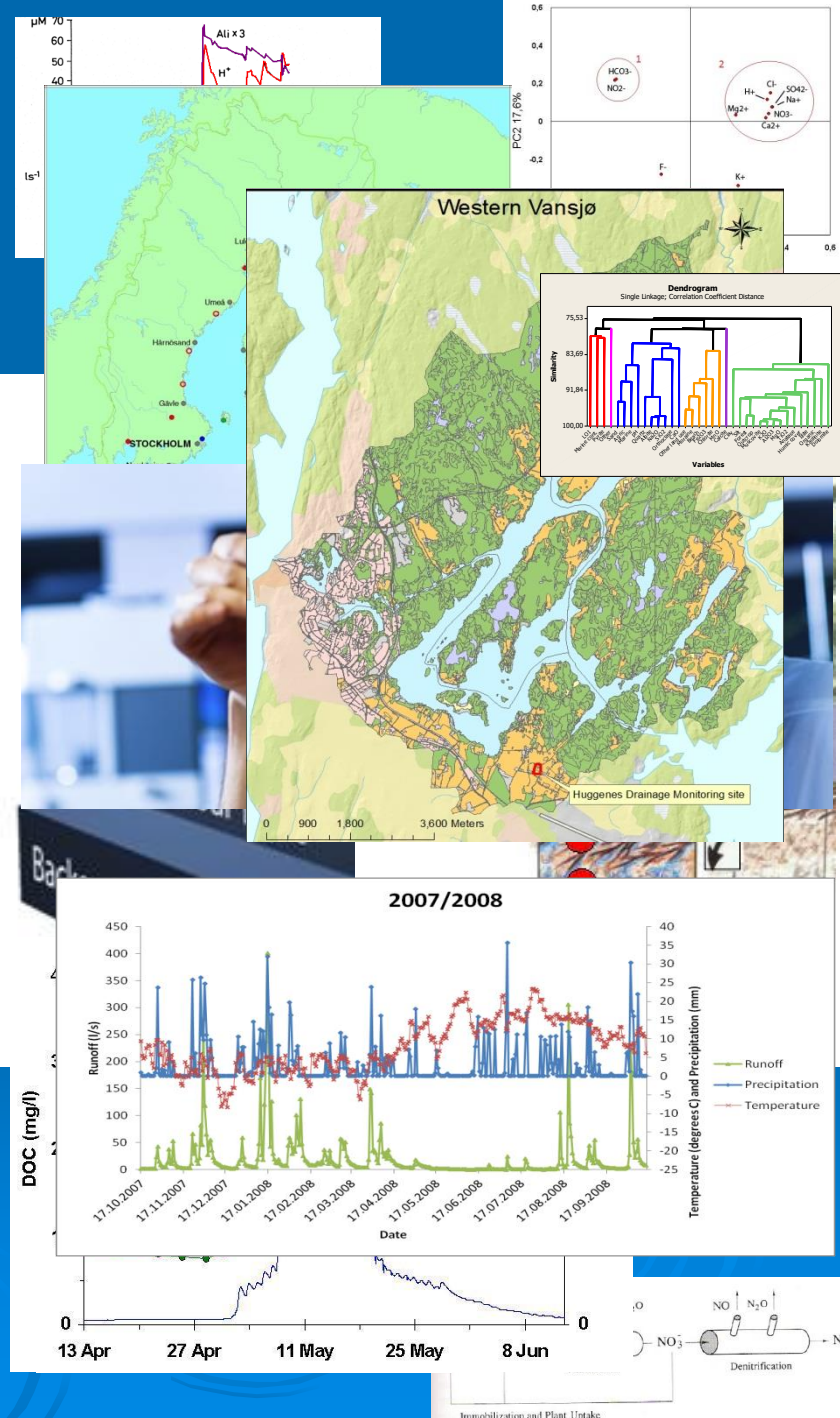
Environmental Research and sampling strategies

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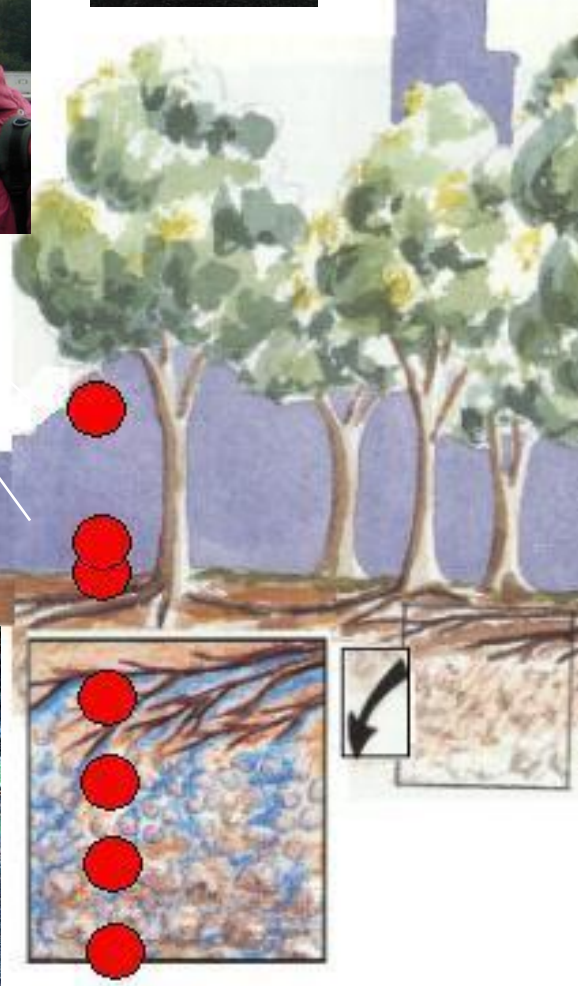
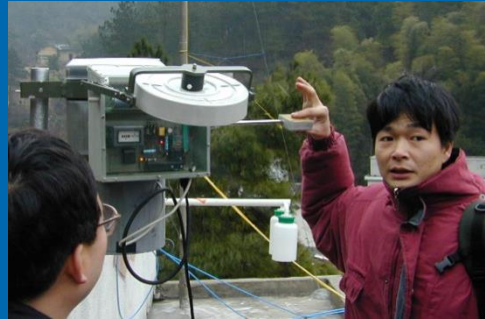
The background of the slide is a solid blue color. In the lower half, there are several faint, concentric circular ripples that resemble water droplets hitting a surface, creating a subtle pattern.

Research strategy

- Collect samples according to a sampling strategy - E.g. capturing the span in parameters to be determined
- Conduct chemical analysis
- Compile other explanatory data (e.g. land-use, runoff) that may provide measures for important pressures
- Deduce empirical relationships between environmental parameters describing the system being studied
 - Assess especially the relationships between explanatory- and response variables
 - Correlation, cluster and PCA
- Induce chemical concepts in the interpretation of the empirical relationships



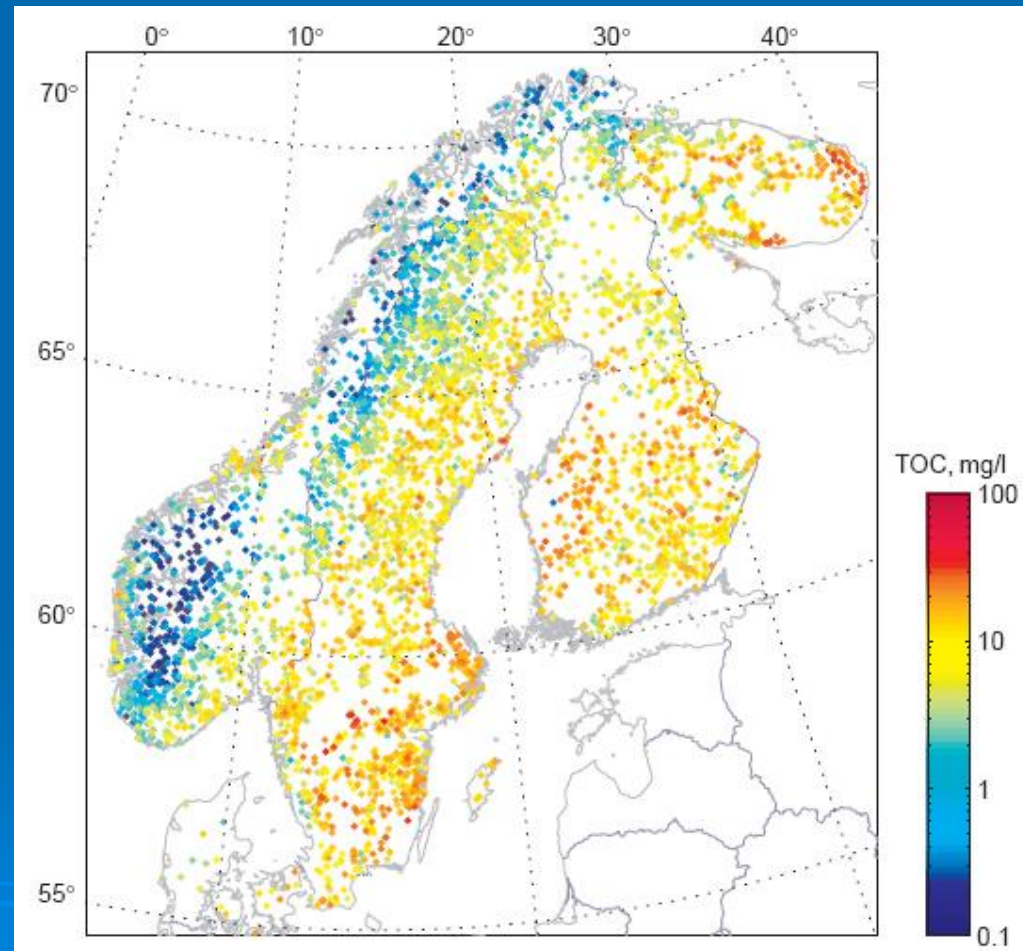
Integrated monitoring



Sampling strategy

Spatial variation

- Large spatial and temporal variation
- Worst case or representative
 - Spatial variation:
 - Regional or Hotspots
- Process studies
 - Capture span in chemistry

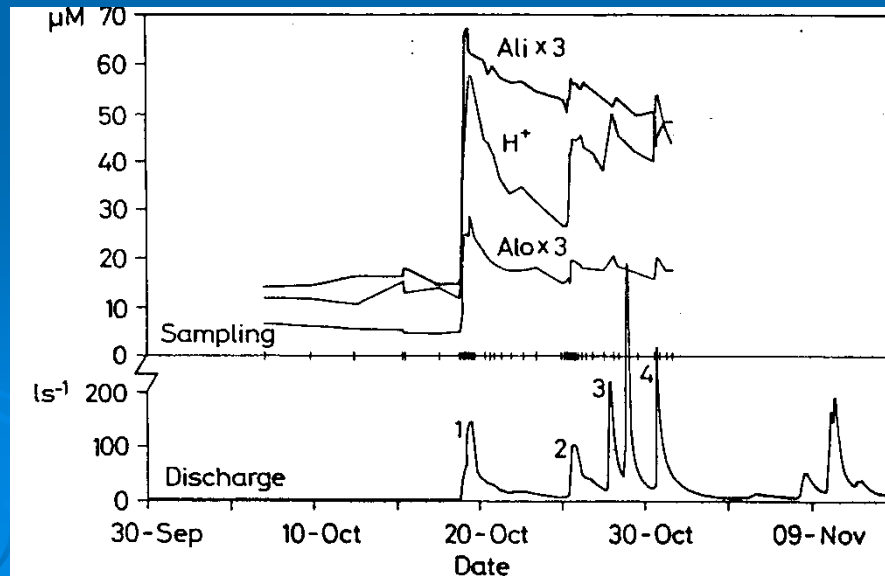
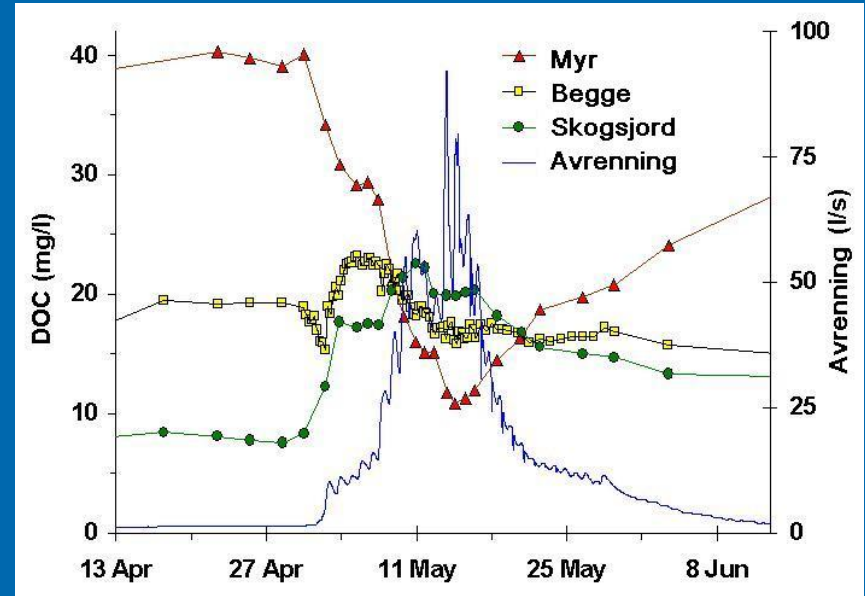


Sampling strategy

Temporal variation

- Seasonal & Climate
- Runoff concentrations of both solutes and suspended material show large variations both seasonal and as a function of discharge

Discharge and concentration measured continuously in runoff water from a small catchments in N Sweden and Norway

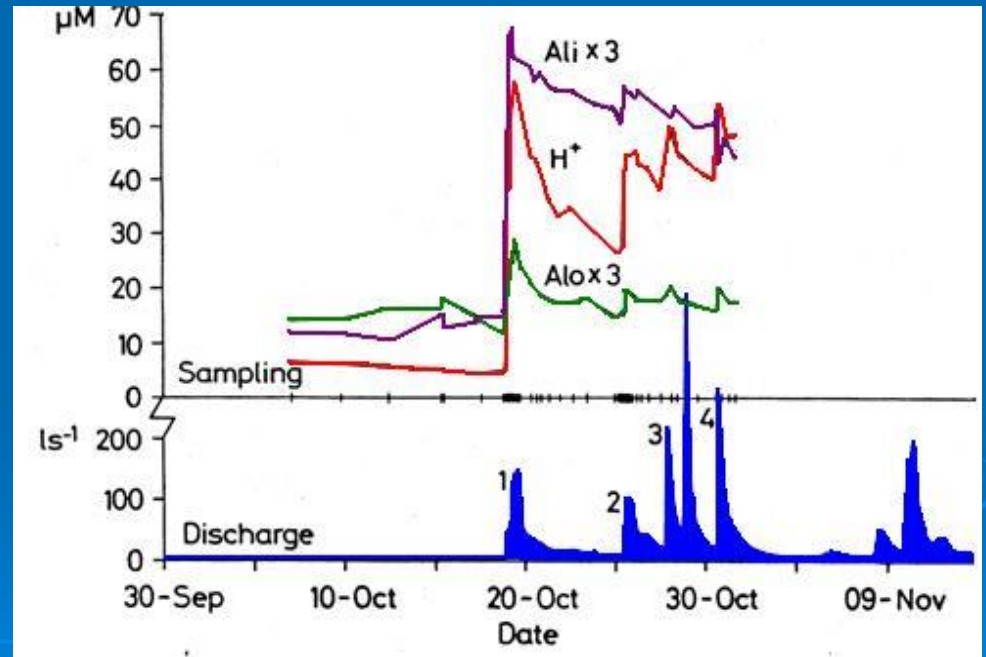


Chemistry vs. flow

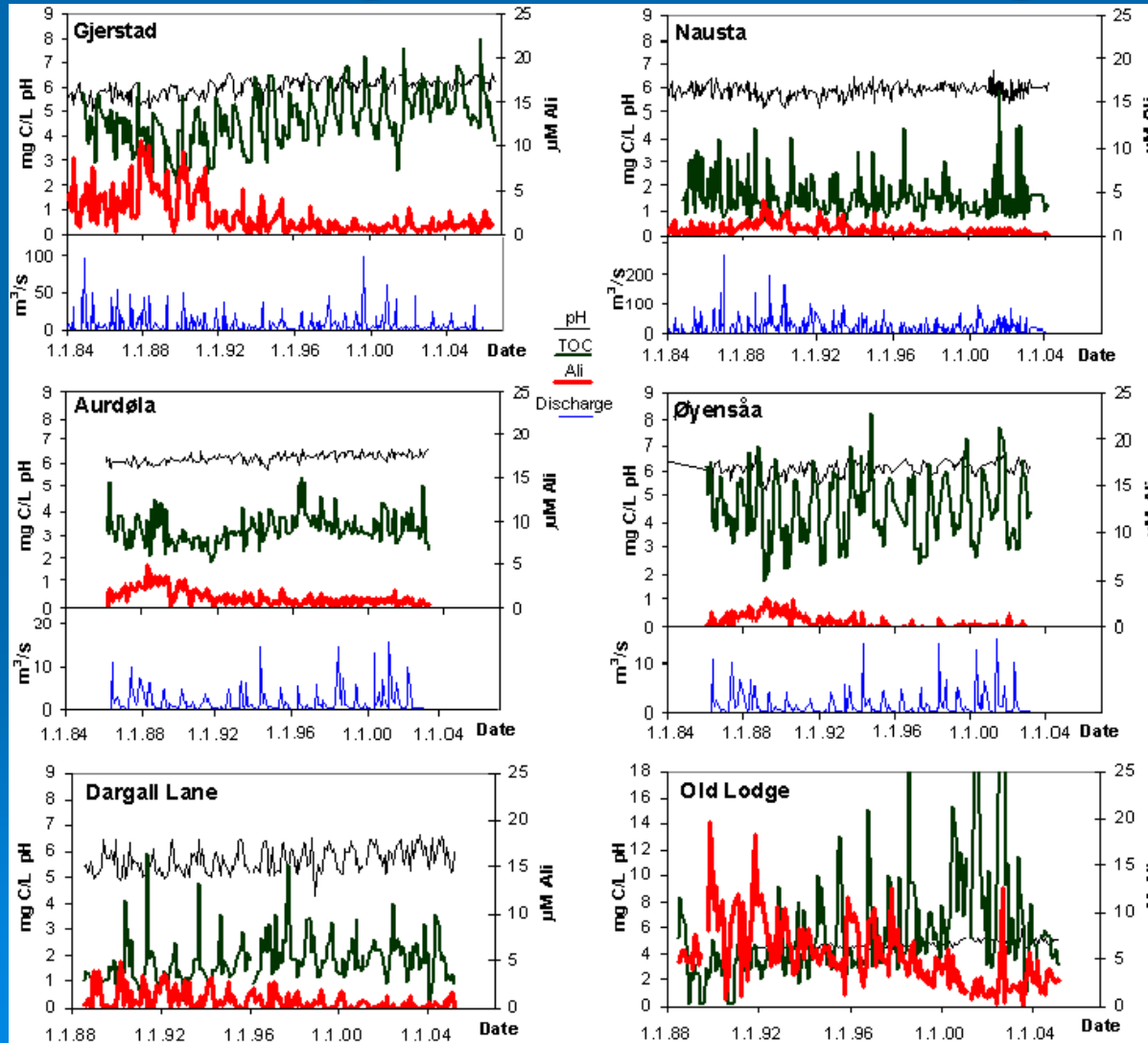
Acidity and labile aluminium

Total Phosphorous

Dissolved Natural Organic Matter



Seasonal variations and long term changes



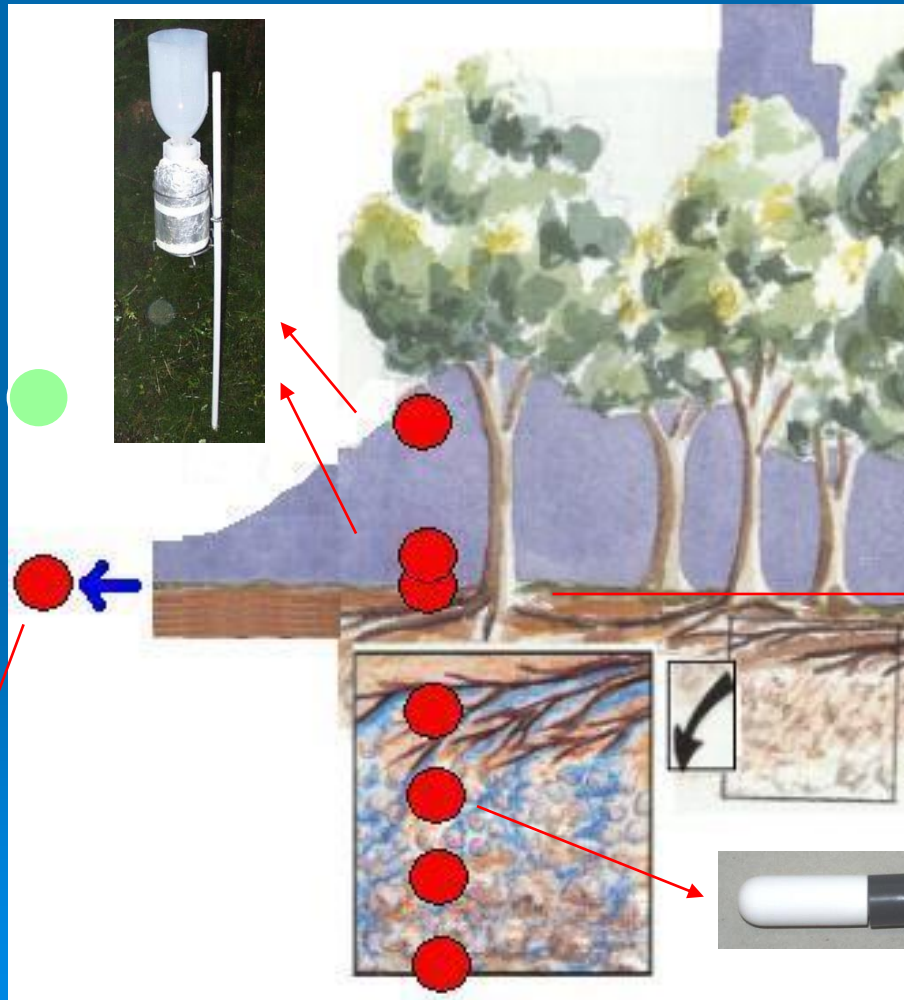
Point sampling strategies

- Choice of water sampling strategy depend on the objectives of the study
 - Study processes
 - E.g. event studies
 - Study of total flux
 - Discharge dependent sampling
 - Study of chemical and/or biological conditions
 - Time averaged sampling

Point sampling strategies

- *Point sampling with variable time interval – Episode studies*
 - Rainfall and snow melt events, which often lead to high soil and nutrient losses, influence to a high degree the sampling frequency
 - Calculations of soil and nutrient losses based on this method are biased
- *Point sampling with fixed time intervals*
 - The accuracy of the result is strongly dependent on the sampling frequency
- *Volume proportional point sampling*
 - Point sampling is triggered each time a certain volume of water has passed the monitoring station. In general, load estimates based on this system leads to an improvement
- *Flow proportional composite water sampling*
 - An alternative to point sampling systems is volume proportional mixed water samples. In this case a small water sample is taken, each time a volume of water has passed the monitoring station
- *Combined sampling*
 - Sampling systems might be combined so as best to suit its purpose

Water sampling from different compartments of the environment



Water sampling equipment

➤ Deposition

1. Bulk precipitation
2. Wet only
3. Throughfall
 - a) Canopy
 - b) Ground vegetation

➤ Soil water

4. Percolation lysimeter
5. Suction lysimeter

➤ Runoff

6. V-notch weir

➤ Lake

7. Nansen collector



Sampling and sample preparation

➤ Soil

- Sample genetic horizons
- Drying
- Sieving (2 mm)
- Storage

➤ Water

- Samples from different environmental compartments
- Filtration (through 0.45 μ m filter)
- Conservation (biocide, acid, cooling)





In solution

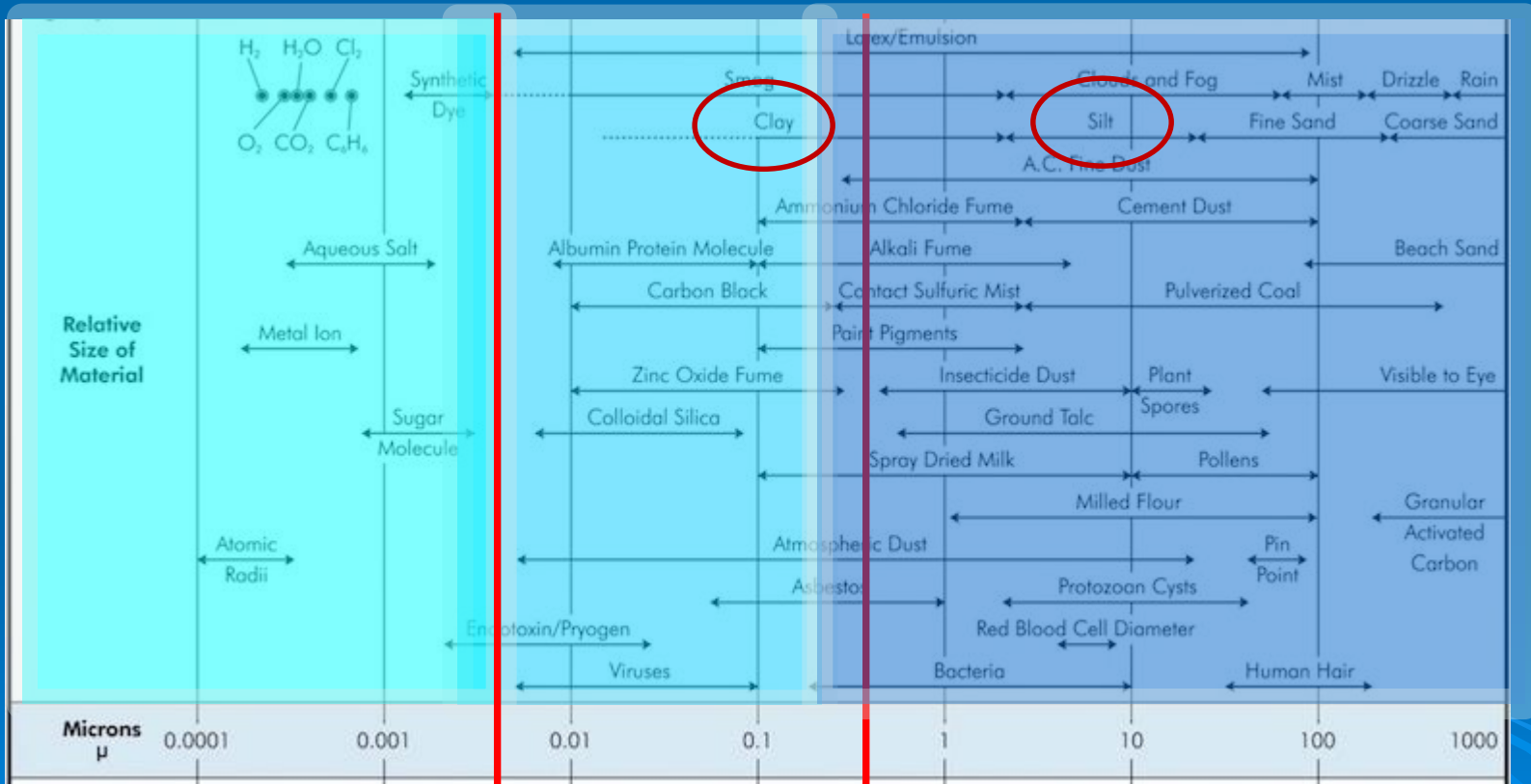


Colloidal



Particulate

Size distribution



1 nm

2nm

0.45 μ m

1 mm

Colloidal matter: Natural organic matter, oxy-hydroxides, clay

Size matters

< 2 nm is in solution

> 200 nm are particles

- Particulate Organic matter (POC) and Soil minerals in the clay and silt size fraction
- Transported especially during periods of high flow

➤ Suspended colloidal particles

- > 2 nm and < 200 nm (0,002 – 0,20 μ m)
 - Colloidal material pass through 0.45 μ m filter!

➤ Heavy metals are adsorbed to the suspended material

- Potential pool
 - Release by ion-exchange or as a result of reductive dissolution



The suspended fraction is a transport vector for a potential pool of type B metals

- Colloidal material, and particles transported during high flow,
 - end up in environments where the contaminant may be released
 - Different ionic strength, pH or redox



Problem associated with sampling, storage and sample preparation for speciation/fractionation

- The procedure *should not disturb* the chemical equilibrium between the different forms of the elements that exist in a given matrix
- Chemical equilibria in water are affected by change in:
 - pH, $p\varepsilon$, temperature (light) and ligand concentrations

Water sample conservation

- Content of labile substances in water sample can be altered due to the chemical, physical, and biological reactions during transport and storage
 - Nutrients: PO_4^{3-} , NH_4^+ , NO_3^- , Silicates
 - Volatile compounds: $\text{HCO}_3^- \rightarrow \text{CO}_2$, may effect pH at pH > 5.5
- Best is to analyse labile parameters immediately upon arrival at lab

Pros and cons of water sample preservation

Conservation method	Pros	Cons
Refrigeration	Slows down metabolism	Effects equilibrium. Temp. differences during analysis
Freezing	Stops metabolism	Hysteresis and lysis effects
Store in dark	Stops photosynthesis	Heterotrophic respiration
Add Biocide (AgCl, HgCl ₂ , NaN ₃)	Stops metabolism	May release nutrients
Filtering through 0,2µm filter	Remove algae and bacteria	Deviate from the 0.45µm standard
Acidify (H ₂ SO ₄ or HNO ₃)	Stops metabolism and avoids precipitation	Changes speciation and fractionation

Trace metal conservation: Acidification to pH<2 with HNO₃
Special: Hg with Cl⁻

Difference between total analysis, fractionation and speciation

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The background is a solid blue color with several faint, concentric circular patterns scattered across it, resembling ripples in water. These patterns are most prominent in the lower right and bottom center areas.

What is speciation and fractionation?

➤ Speciation

Specific form of an element defined as to
electronic or oxidation state,
complex or molecular structure
and isotopic composition

➤ Fractionation

Process of determination of an analyte or a **group of analytes** from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties

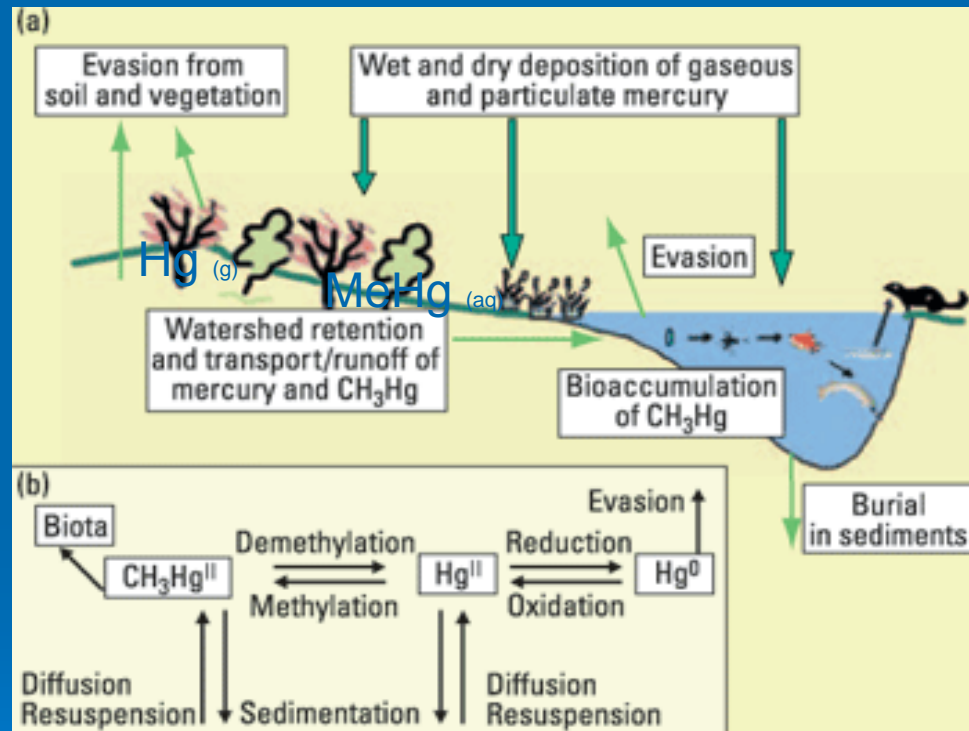
Why is chemical speciation important?

- Determines mobility, transport, fate and impact
- Solubility and **mobility** of a compound depend on in which form it can exist in solution
 - Fe(III) is less soluble and thus less mobile than Fe(II)
- The **bioavailability** of metals and their physiological and toxicological effects depend on the actual species present – not on the total concentration

Mobility

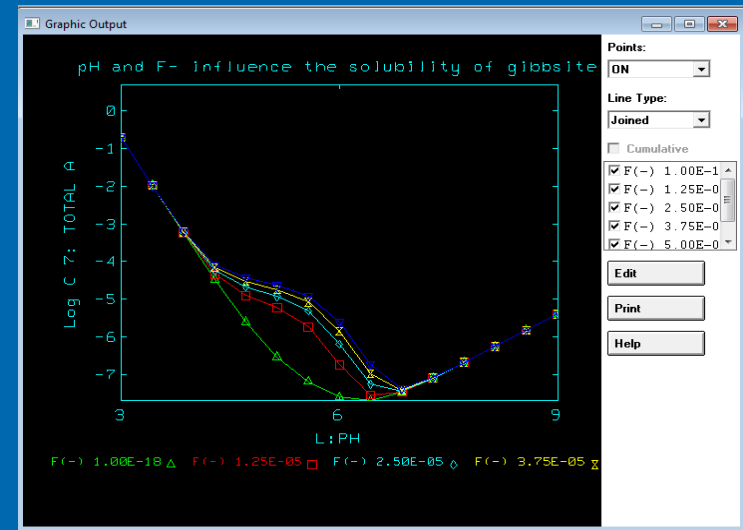
- The distribution of an element among different species profoundly affects its transport by determining such properties as:

- **Solubility and**
- **Partitioning coefficient**

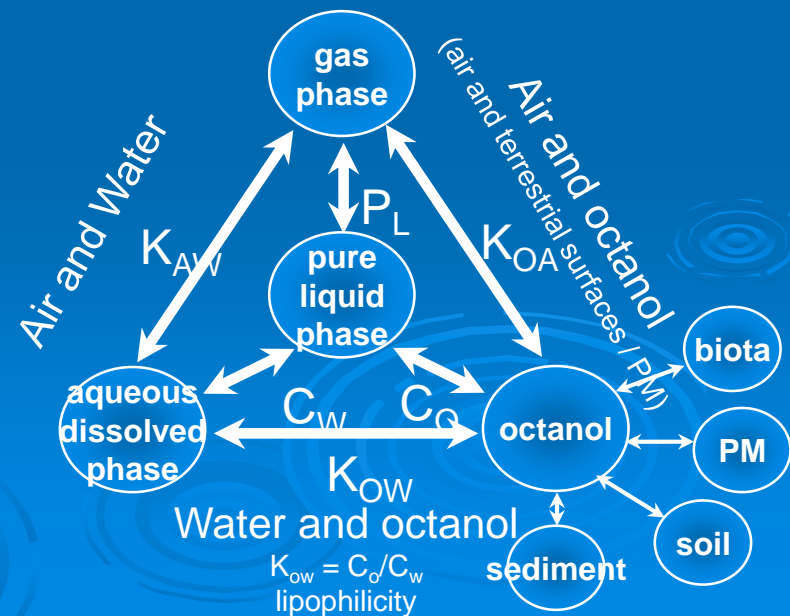


Solubility and Partitioning coefficients

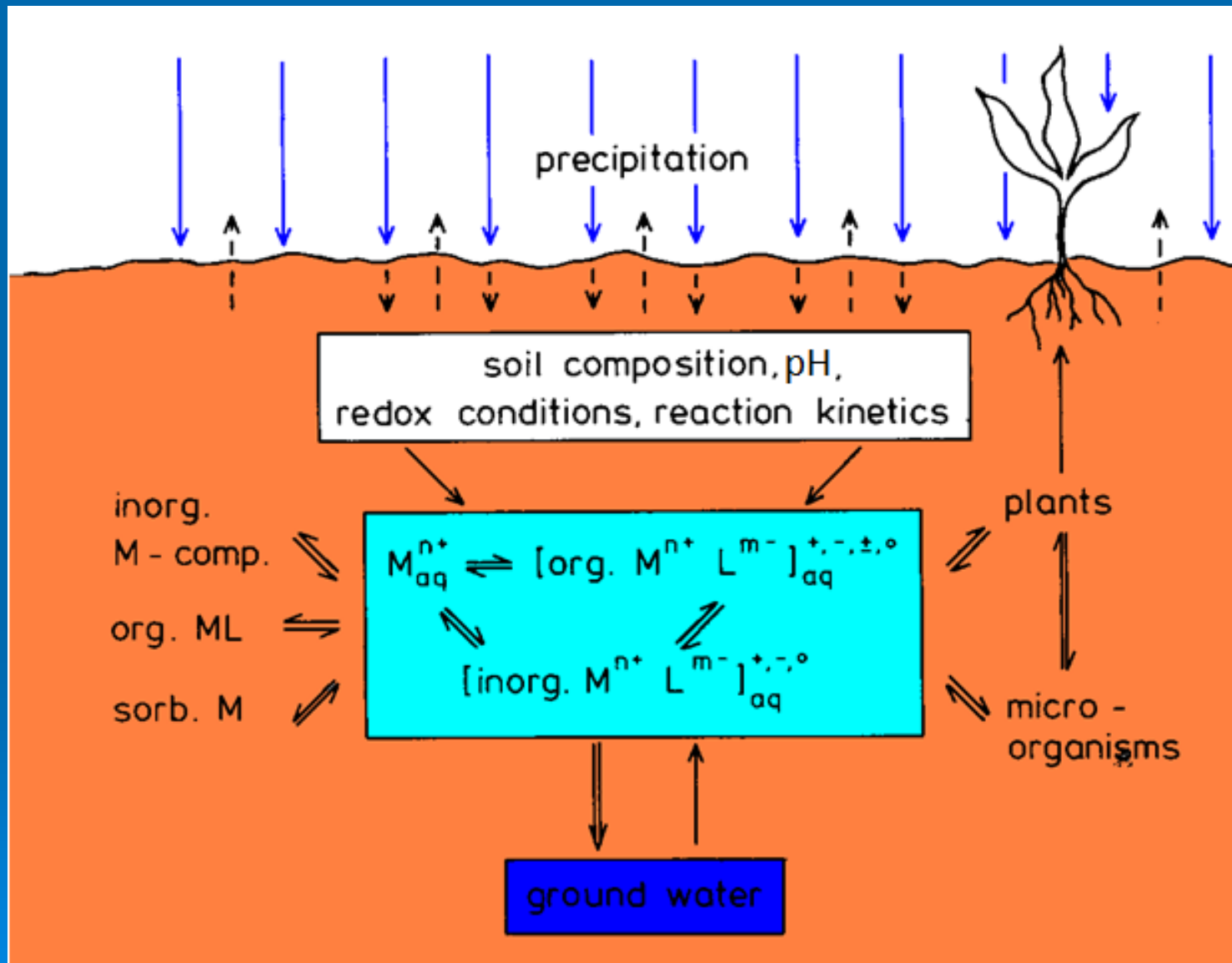
- Mobility of metal ions is determined by its ligands
 - Formation of AlF^{2+} increases solubility
 - Hydrolysis to $\text{Al}(\text{OH})_3$ decreases solubility



- Mobility of POPs are determined by phase partitioning between air, water and organic matter



Mobility of metals in soil and soil solution



Schematic presentation of heavy metal reactions in soils

The significance of species activities

- **Inorganic ligands**

- **Formation of hydroxides is often a key limitation of element solubility**

- **Other inorganic ligands**

- E.g. NiCl_2 and NiSO_4 are water soluble while NiO and Ni_3S_2 are highly insoluble in water
- Fe^{3+} bind PO_4^{3-} stronger than Fe^{2+} so that PO_4^{3-} may mobilized during reducing condition
- PO_4^{3-} bound to Al is a sink

- **Charge and oxidation states**

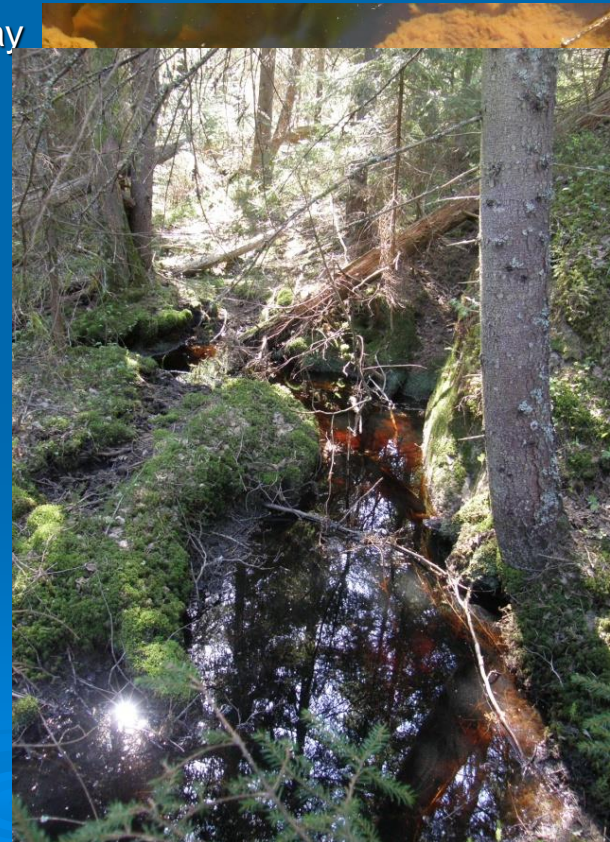
- **Profoundly affect mobility**

- E.g. The Fe(II) ion is soluble, whereas Fe(III) is more prone to hydrolysis and subsequent precipitation
- Elemental Hg^0 may evade to air through evaporation

- **Organic complexes**

- **Macromolecular compounds and complexes**

- Dissolved natural organic matter (DNOM) complex heavy metals and sorb organic micro pollutants enhancing thereby solubility and mobility
 - Mobility of type B (Hg) metals are greatly enhanced by DNOM

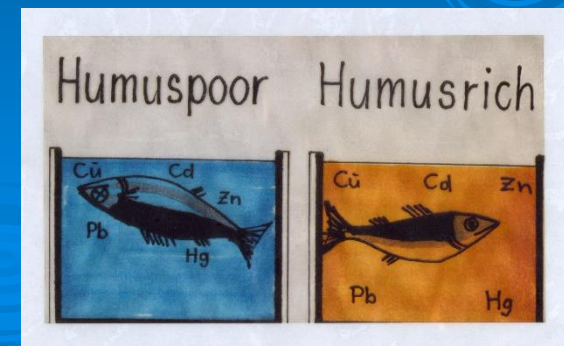
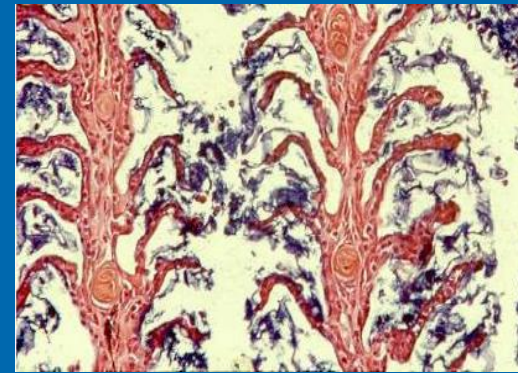


Mobility

Bioavailability

➤ The **bioavailability** (i.e. distribution coefficient; K_{OW}) of metals and their physiological and toxicological effects depend on their **speciation**

- Examples:
 - Al^{3+} , $Al(OH)_3$ and Al-org have different effect on fish
 - Methyl Hg, -Pb, and -Sn are more bioavailable than inorganic forms
 - Methylmercury (CH_3Hg^+) readily passes through cell walls
It is far more toxic than inorganic forms
 - Macro-organometallic Al, As and Cu are less bioavailable than inorganic forms
 - Inorganic Al are more toxic to aquatic organism than Al bound to organic ligand



The significance of speciation in terms of toxicity

➤ Toxicity of a pollutant is affected by

• Oxidation states

- E.g. Cr(III) is an essential element, but Cr(VI) is genotoxic and carcinogenic
- Toxic effect of arsenic (As) and its compound decreases in sequence As (III)>As (V)

• Inorganic compounds

• Aqueous species

- Type B (soft) elements (Cu^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+}) are commonly most toxic in their aqueous form

• Organic complexes

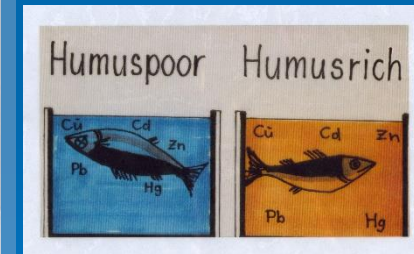
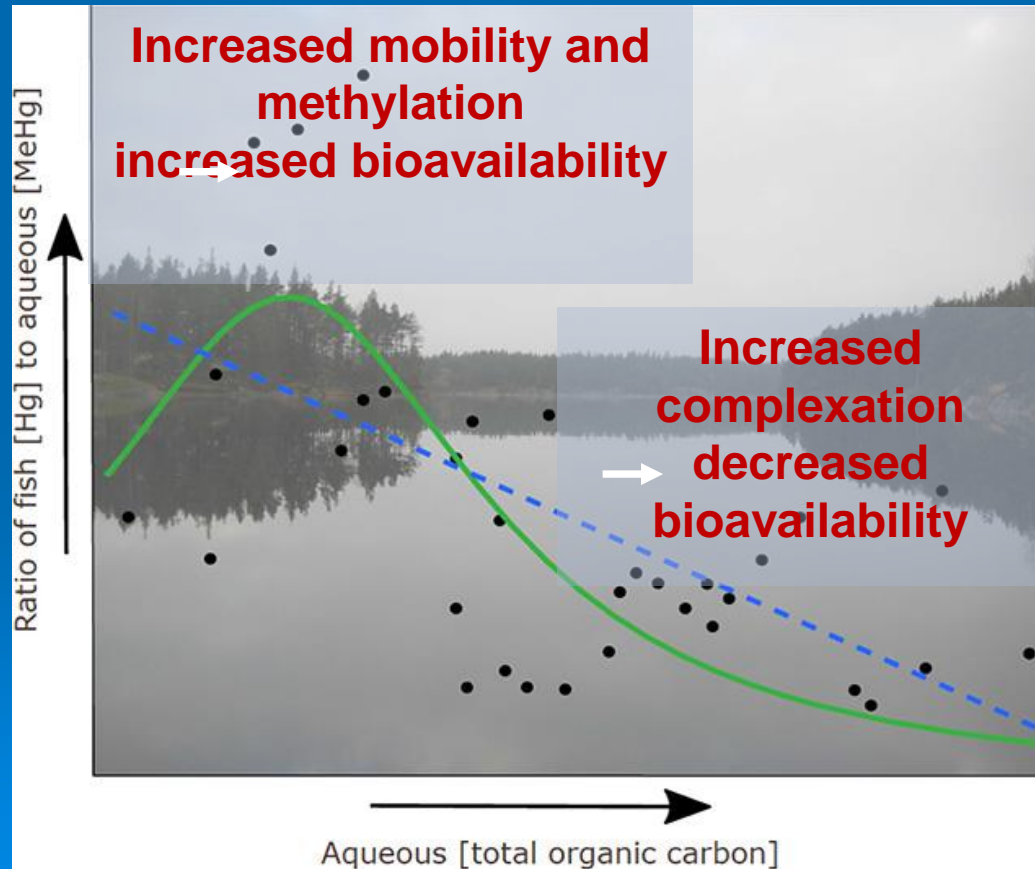
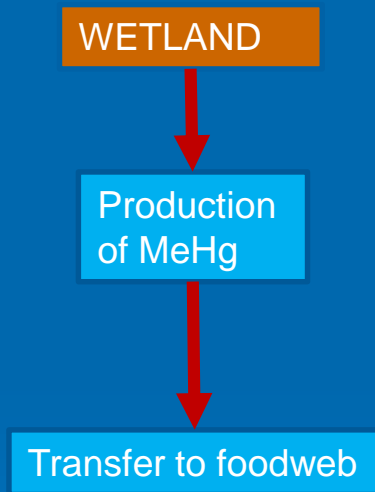
• Organic macromolecular compounds and complexes

- Heavy metals and organic micro pollutants bound to DNOM are generally considered less toxic – too large molecules

• Organometallic compounds

- Hydrophobicity (K_{OW}) is important for bioaccumulation in fatty tissues and penetration of membrane barriers
 - E.g. MeHg

DNOM has a synergistic and antagonistic effect on Hg uptake



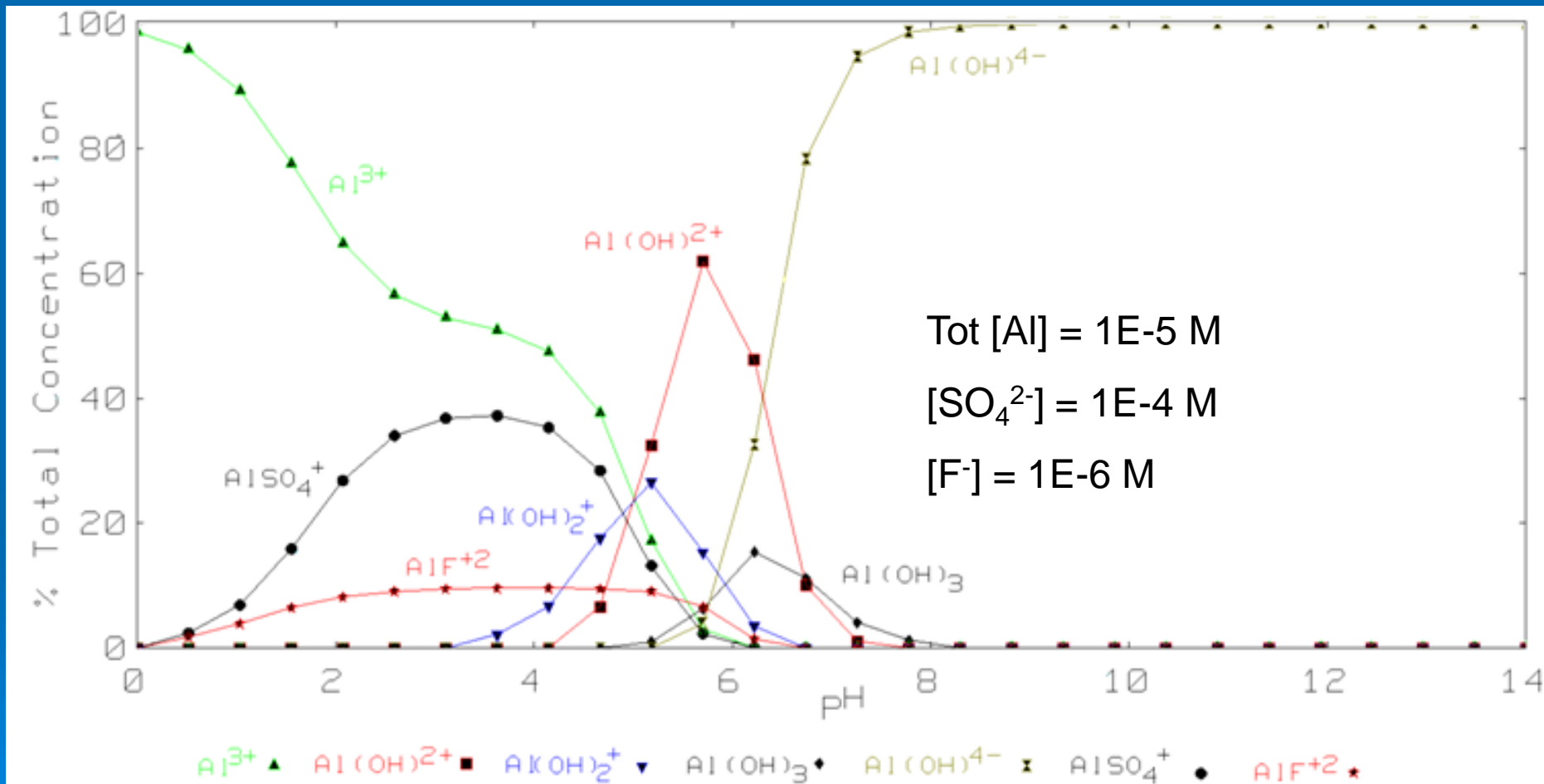
➤ Inorganic compounds

- E.g. The environmental and biological effects of Al ions are associated with the forms present in aquatic system
- In aquatic systems, Al ions exists mainly as:
 - Free aqueous Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})^+$, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$
 - AlF^{2+} , AlF_2^+ , AlF_3
 - monomeric SO_4^{2-} complexes, Al-Org
 - Al speciation depend on soln. pH & conc. of ligand
- **Toxicity:**
 - Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})^+$ are **more toxic**
 - Al-F_x and Al-Org are **less toxic**



pH dependence on Al speciation

MINEQL calculations



Other important factors

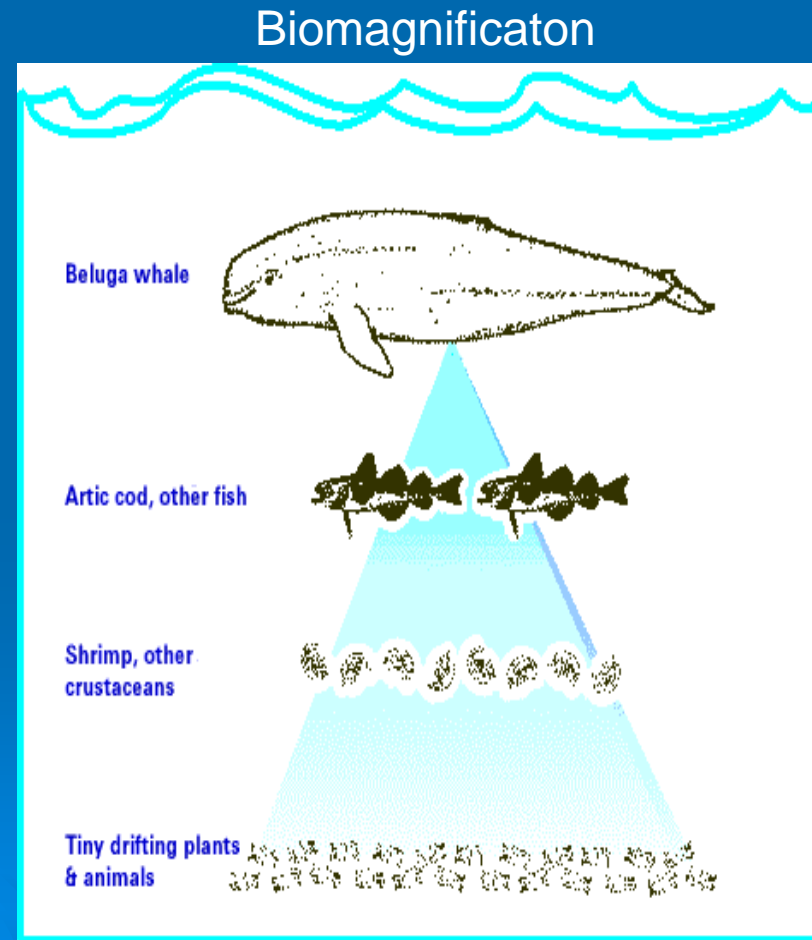
➤ The effect of a pollutant is determined by its concentration and the physical, chemical and biological characteristics of the:

- **Pollutant**

- Solubility in water and organic solvent (K_{ow})
 - Bioconcentration
 - Biomagnification
- Degradability, persistence ($t_{1/2}$)
- Organic complexability (K_{ex})

- **Recipient**

- pH (speciation)
- Stagnant conditions (redox)
- Hardness (Ca+Mg)
- Humic content



Total analysis

- Most standard chemical analytical methods determine the total amount (component) of an element in the sample
 - AAS and ICP
 - Prior to analysis the sample is typically digested where all analyte is transferred to its aqueous form
 - $X\text{-Me} \rightarrow \text{Me}(\text{H}_2\text{O})_{2,4 \text{ or } 6}^{n+}$



Problems with analytical speciation

- Often, chemical species are **not stable** enough to be determined as such
 - During the separation and measurement process the partitioning of the element among its species may be changed
 - New equilibriums are formed
 - Intrinsic properties of measurement methods that affect the equilibrium between species
 - For example a change in pH necessitated by the analytical procedure
- **Detection Limit (DL) problems**
 - When you split an analyte at low concentration then each specie concentration may fall below DL

Solution:

Chemical analytical fractionation

- Isolate various **group of species** of an element and determine the sum of its concentrations in each group

Based on	By means of
Size	Filtration, size-exclusion chromatography
Affinity	Chromatography
Solubility	Extraction
Hydrophobicity	
Charge	Ion-exchange
Reactivity	Complexation to complex-binder

- In some instances, fractionation may be refined by supplementary calculative speciation analysis
 - With further calculations the inorganic fraction can be subdivided into individual species