

Analysis/fractionation and speciation of water samples

Module 19; KJM-MENA4010



Module plan, Week 1

See: http://www.uio.no/studier/emner/matnat/kjemi/KJM-MENA4010/h16/moduler/modul-19/analyser_fraksjonering_vannprover.html

➤ Thursday October 31th;

- **Lecture**, Auditorium 3, hr. 08:15 – 10:00
 - 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
 - Research strategy
 - Water sampling from different compartments of the environment
 - Sampling strategies for environmental samples
- **Field work**, Lakes and stream around Oslo, hr. 10:00 ~ 17:00
 - Maridalsvannet (oligotrophic), Akerselva (polluted), Lutvann (oligotrophic), Østensjøvann (eutrophic), Sværsvann (dystrophic), Årungen (eutrophic), Gjersjøen (mesotrophic), Kolbotnvann (eutrophic), Nesøytjern (mesotrophic), Bogstadsvannet (oligotrophic), Lysakerelva (polluted)



Bogstadvannet

Maridalsvannet

Lysakerelva

Akerselva

Lutvann

Nesøytjern

Østensjøvannet

Sværsvann

Kolbotntjernet

Gjersjøen

Årungen



Module plan, Week 1

➤ Friday, November 4th;

- **Lecture**, Auditorium 3, hr. 08:15 – 09:00
 - Important species in natural water samples
 - Central equilibriums in natural water samples
 - Concentrations and activities
- **Labwork**, V111 hr. 09:15 ~ 17:00
 - HSE protocolls
 - 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, Week 2

➤ Thursday, November 17th;

- **Lecture**, Auditorium 3, hr. 08:15 – 11:00
 - Challenges with simultaneous equilibrium
 - Speciation programs (MINEQL)
- **PC lab**, V152, hr. 10:15 – 16:00
 - Practice in using MINEQL

➤ Friday, November 18th

- Independent report writing

Difference between total analysis, fractionation and speciation

KJM MENA 4010

Module 19

The background features several sets of concentric circles in a lighter shade of blue, resembling ripples in water, scattered across the bottom half of the slide.

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

* D.M. Templeton, F. Ariese, R. Cornelis, L- G. Danielsson, H. Muntau, H.P. Van Leuwen , and R. Lobinski, *Pure Appl. .Chem.*,2000, **72**, 1453

➤ 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

* D.M. Templeton, F. Ariese, R. Cornelis, L- G. Danielsson, H. Muntau, H.P. Van Leuwen , and R. Lobinski, *Pure Appl. .Chem.*,2000, **72**, 1453.

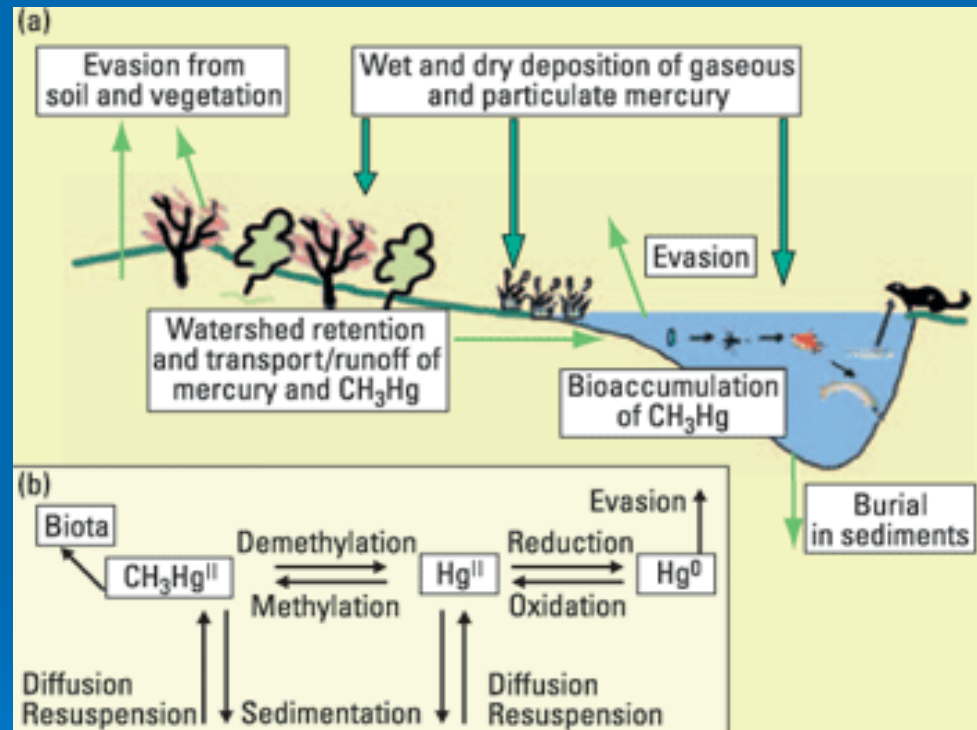
Why is chemical speciation important?

- 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

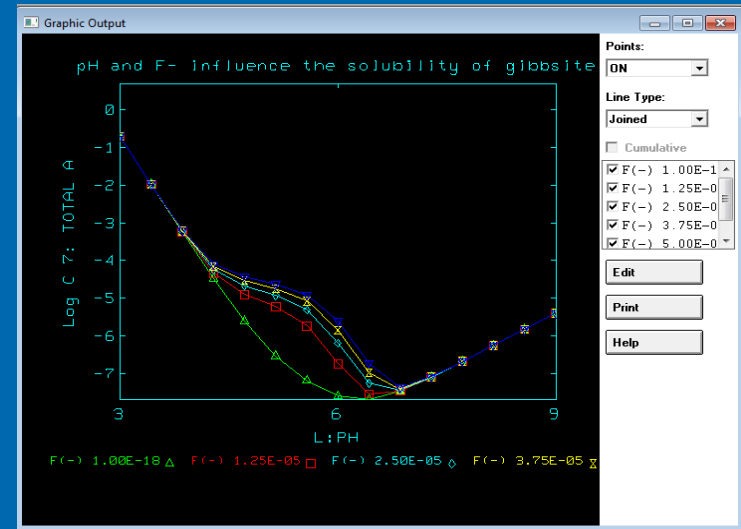
➤ The distribution of an element among different species profoundly affects its transport by determining such properties as:

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

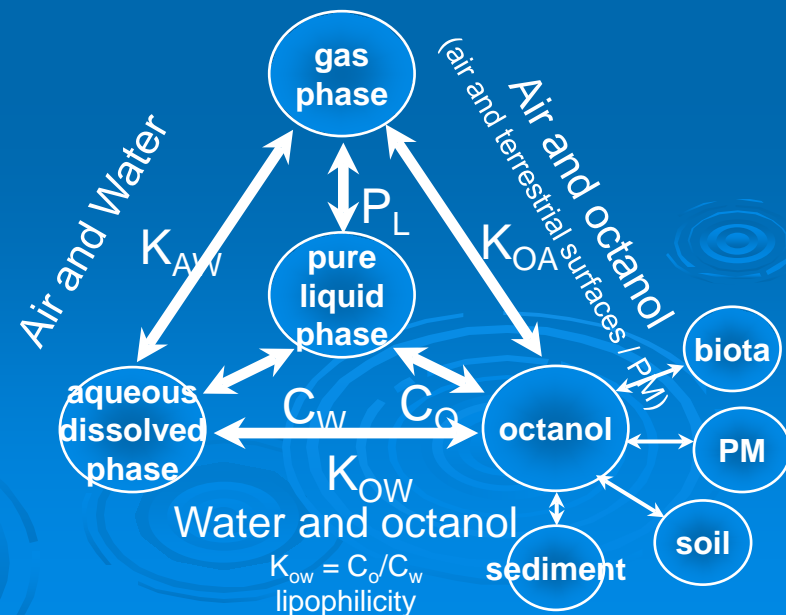


Solubility and Partitioning coefficients

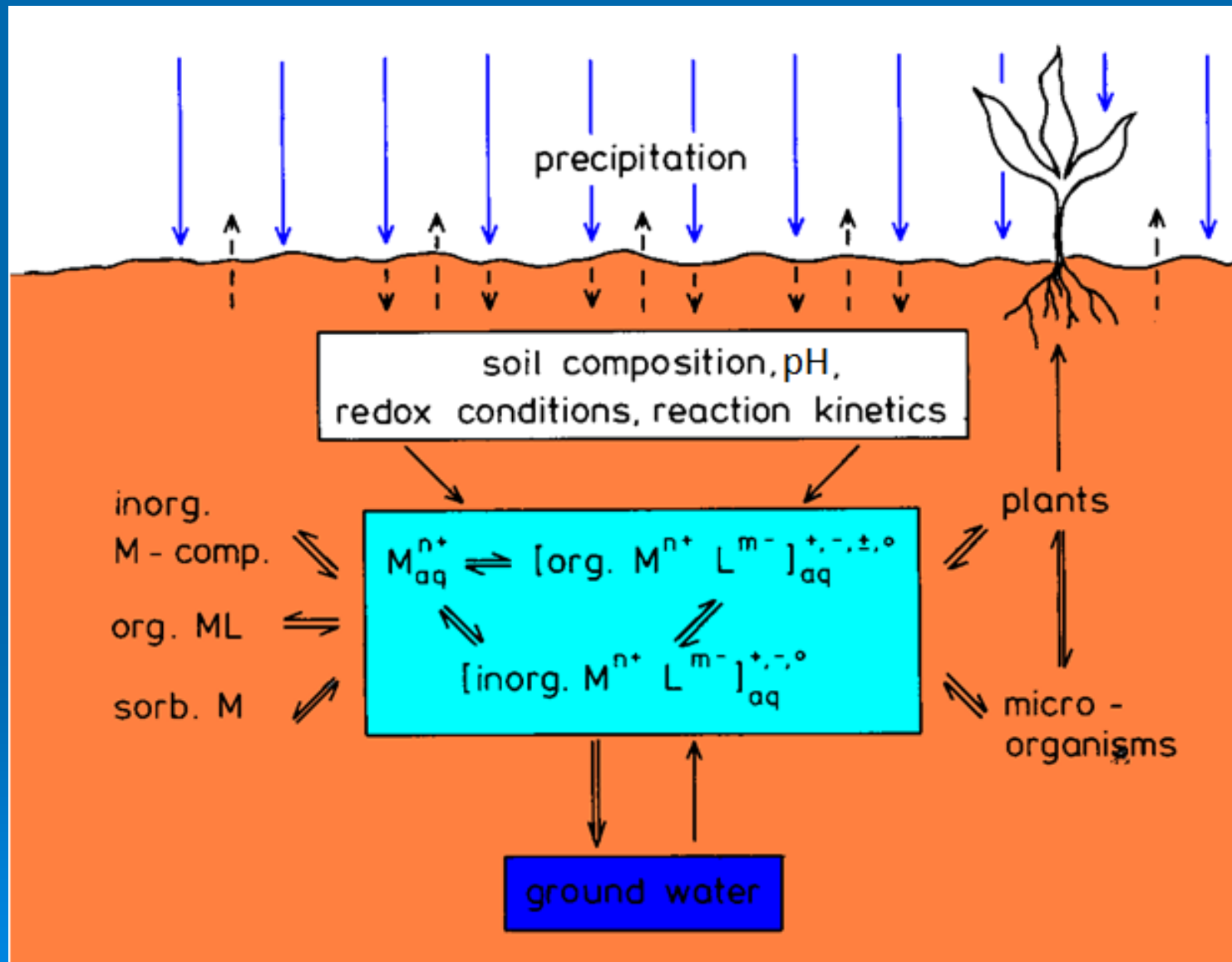
- Mobility of metals is determined by ligands
 - Formation of AlF^{2+} increases solubility
 - Hydrolysis to $\text{Al}(\text{OH})_3$ decreases solubility



- 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**

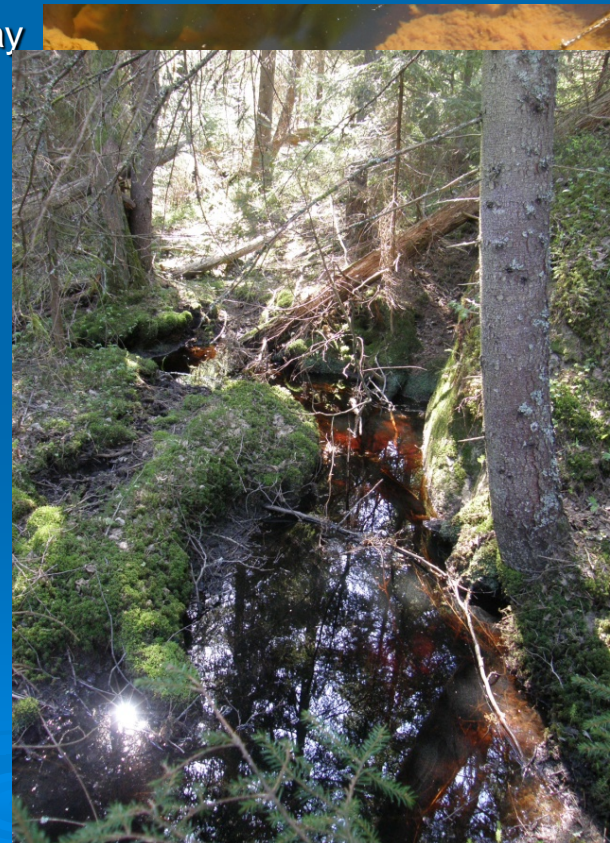
- **Profoundly affect mobility**

- 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**

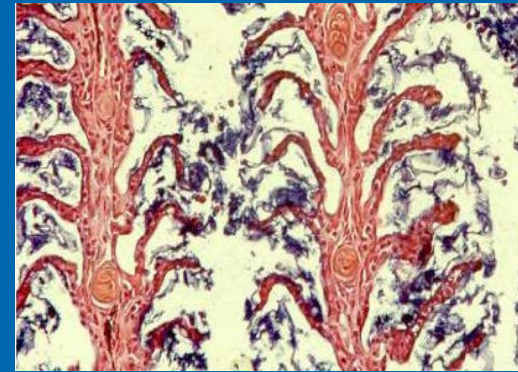
- Dissolved natural organic matter (DNOM) complex heavy metals and sorb organic micro pollutants enhancing thereby solubility and mobility
 - Mobility of type B (Hg) metals are greatly enhanced by DNOM



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
 - Organometallic Hg, Pb, and Sn are more bioavailable than inorganic
 - Methylmercury (CH_3Hg^+) readily passes through cell walls. It is far more toxic than inorganic forms
 - 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**

• **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

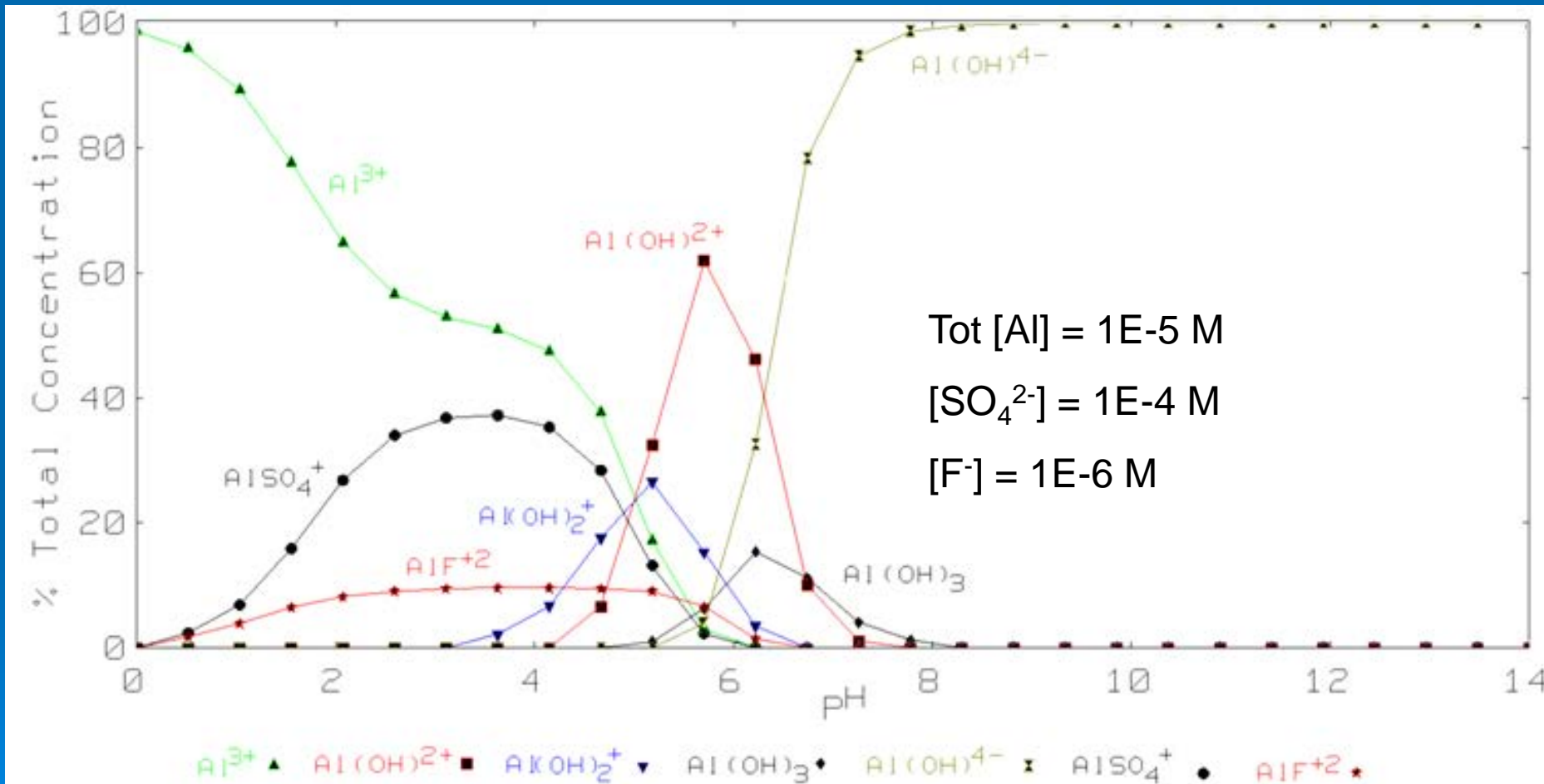
➤ E.g. Aluminum

- 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

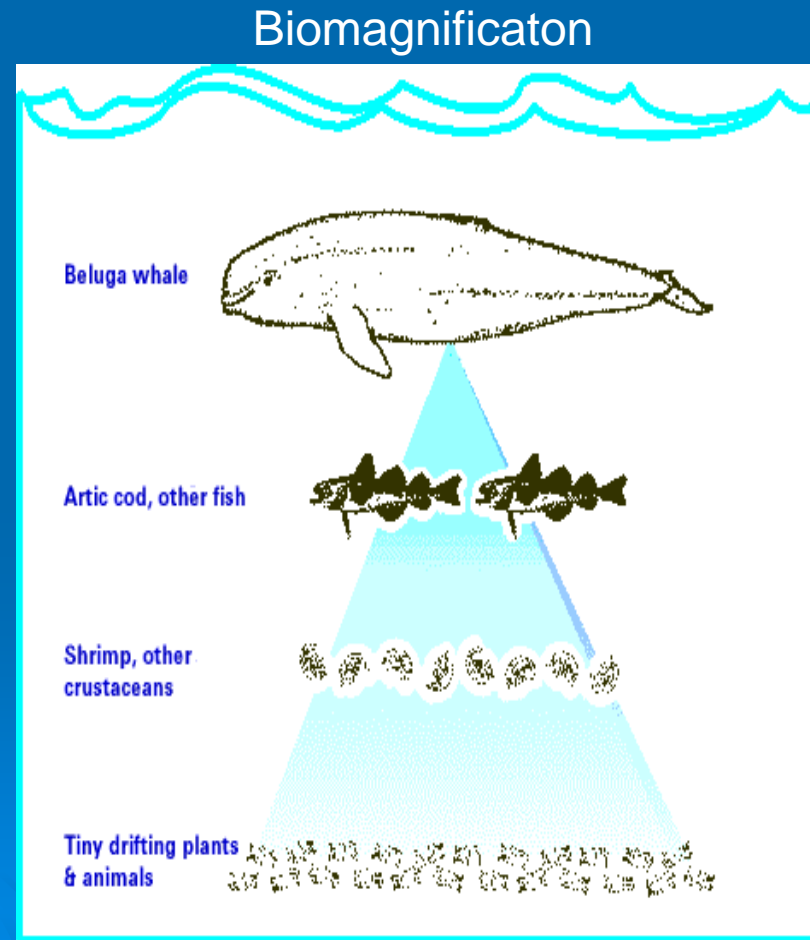
➤ The effect of a pollutant is determined by its concentration and the physical, chemical and biological characteristics of the:

- **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
 - $X\text{-Me} \rightarrow \text{Me}(\text{H}_2\text{O})_{2,4 \text{ or } 6}^{n+}$



Chemical analytical speciation methods

- **Isotopic composition**
 - Mass spectrometry (MS) (e.g. $^{14}\text{C}/^{12}\text{C}$)
- **Charge and oxidation states**
 - Selective organic complexation with spectrophotometric detection
 - Separation with HPLC, detection with e.g. ICP
- **Inorganic compounds and complexes**
 - Potentiometric determination of the activity of Free aqueous species (e.g. ion selective electrodes for H^+ , Free F^- , Ca^{2+})
- **Organic complexes**
 - Anodic stripping voltametry on electroactive species
- **Organometallic compounds**
 - Separation with GC or HPLC, detection with e.g. ICP
- **Macromolecular compounds and complexes**
 - Size exclusion, ion-exchange, affinity and reversed phase chromatography



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

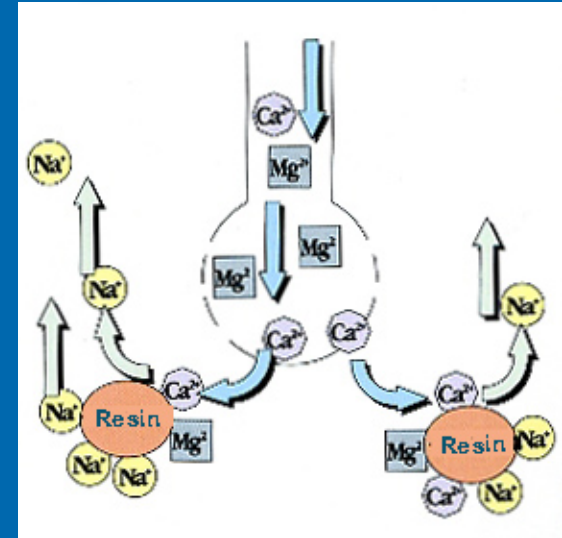
| Based on | By means of |
|----------------|---|
| Size | Filtration, size-exclusion chromatography |
| Affinity | Chromatography |
| Solubility | Extraction |
| Hydrophobicity | |
| Charge | Ion-exchange |
| Reactivity | Complexation to complex-binder |

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

Extraction

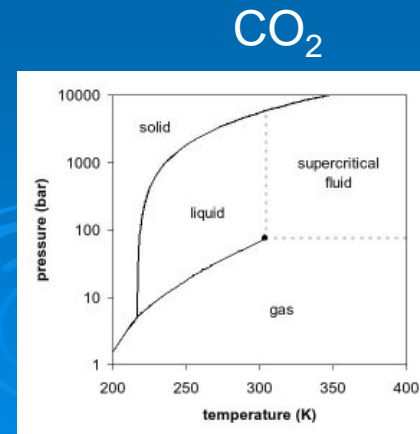
➤ Water sample

- Solvent extraction
- Solid Phase Extraction (SPE)
 - Ion exchange resins



➤ Soil sample

- Leaching method
 - Sonication, stirring, shaking or soxhlet with solvent
- Sequential Extraction (Tessier)
- Supercritical Fluid Extraction (SFE)



Fractionation

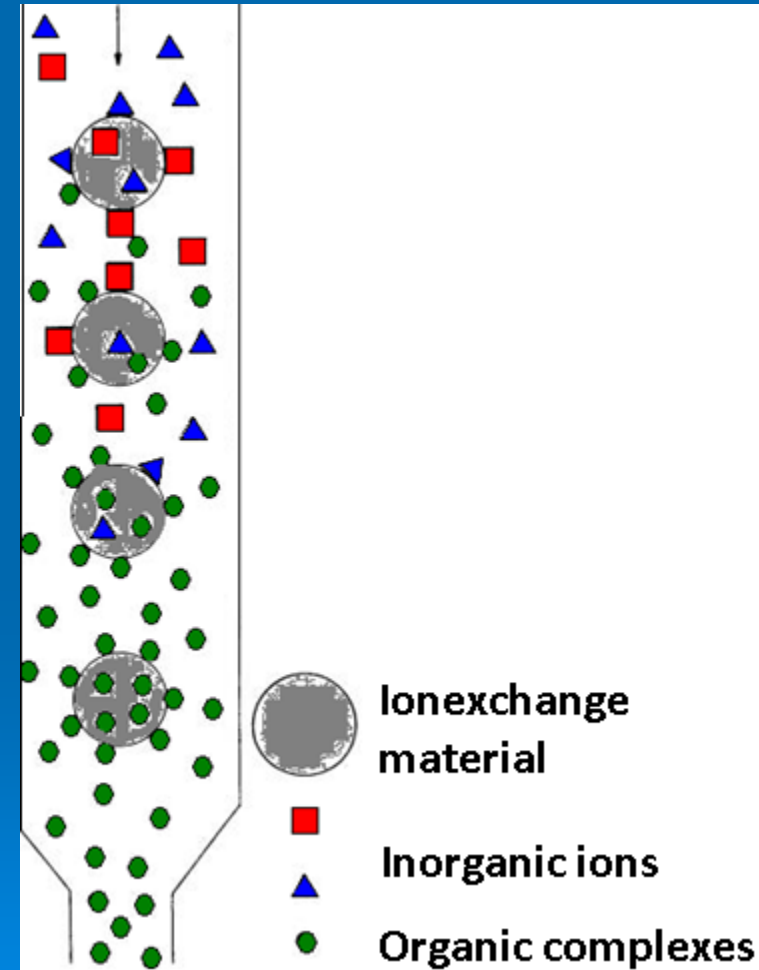
Ion exchange resins for fractionation of metal ions in water

➤ Retains:

- Labile free aqueous metal ions
- Labile inorganic complexes
- Labile metal organic complex

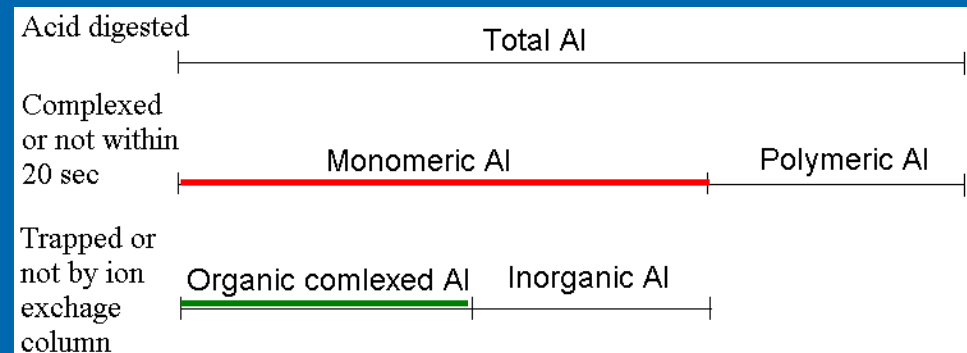
➤ Eluted:

- Non-labile metal complexes
(Strong complexes)



Example; Al fractionation

- Fractionation of **Monomeric aluminium** from polymeric forms is accomplished by 20 sec. complexation

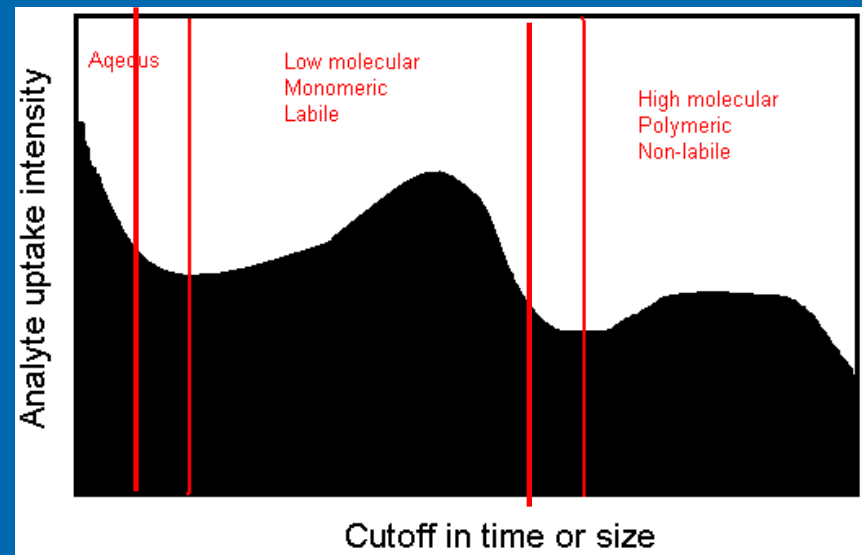


with 8-hydroxyquinoline at pH 8.3 with subsequent solvent extraction into MIBK organic phase

- **Organic bound monomeric aluminium** is separated from inorganic aluminium (mainly labile) by trapping the latter fraction on an Amberlight IR-120 ion exchange column
- The Al concentrations in the organic extracts are determined photometrically

Chemical analytical fractionation; Shortcomings

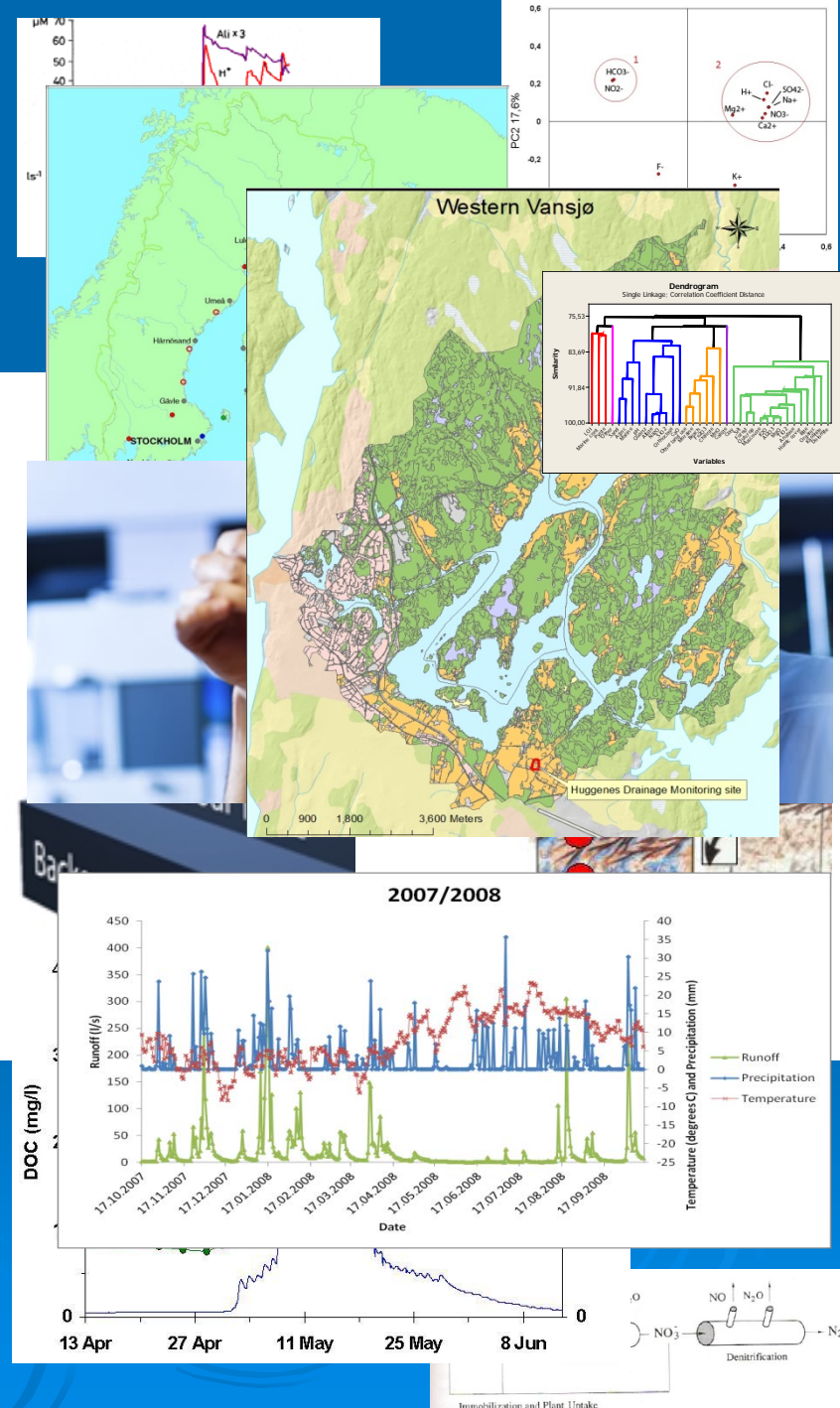
- The discrimination inherent in the method can be more or less selective but it is not absolute
 - Small variations in the methodical cut-off may cause significant variations in the result
- I.e. Operationally defined



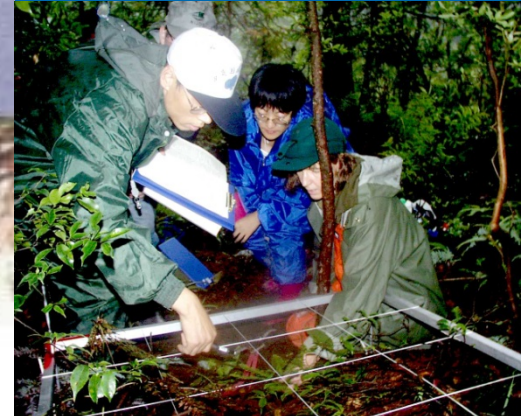
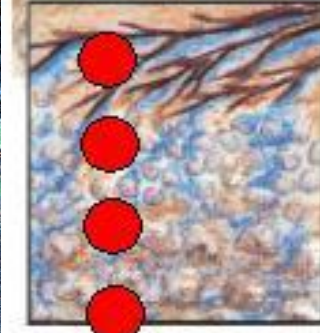
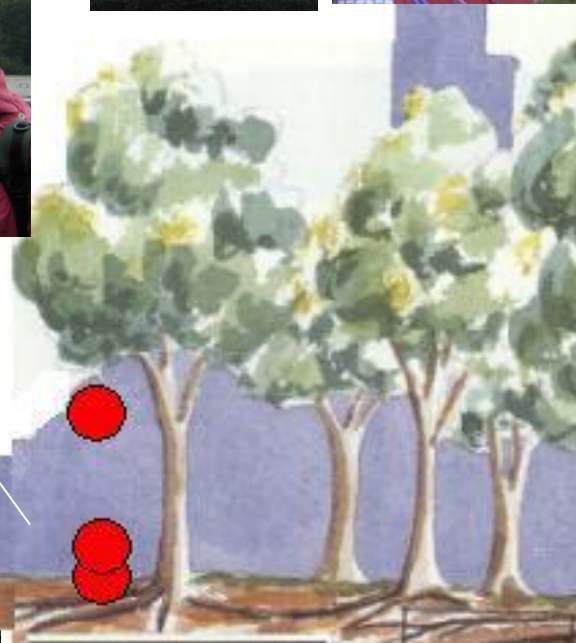
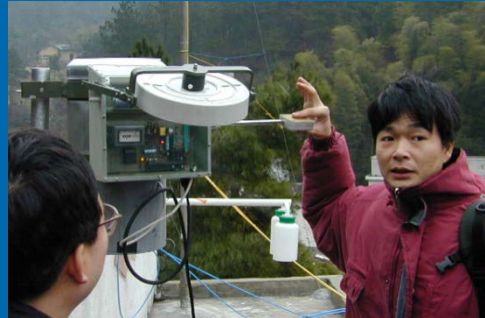
Small variations in the cutoff will often give large variations in the results

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

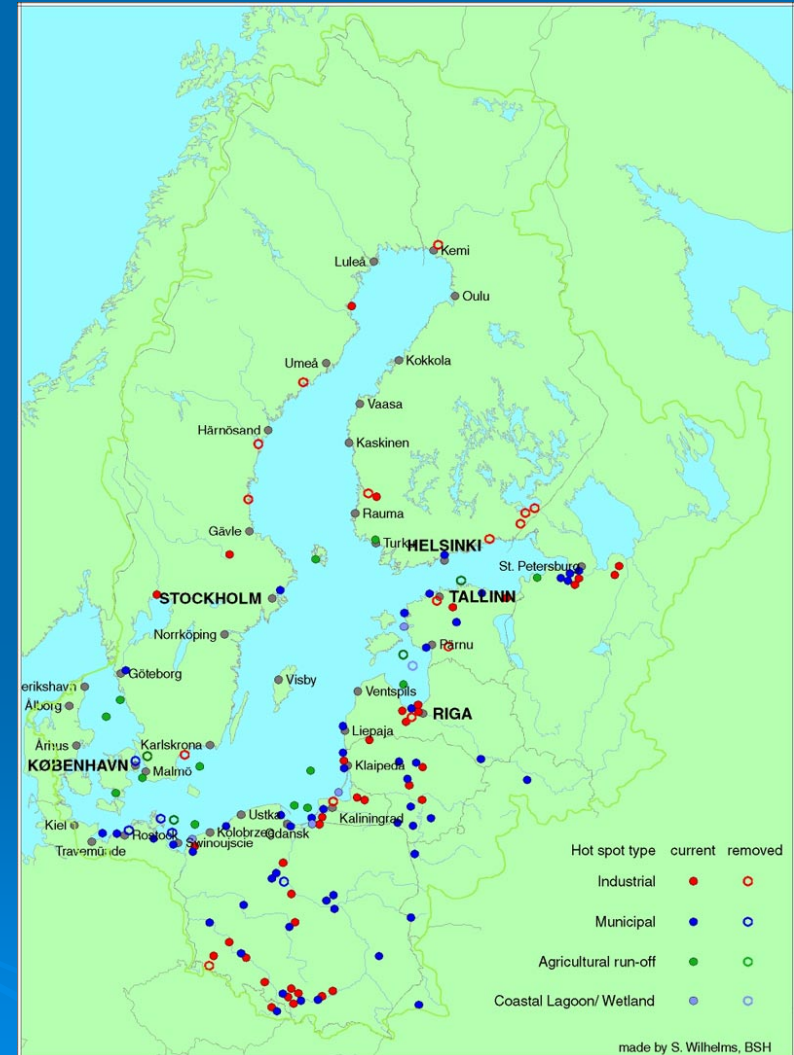


Integrated monitoring



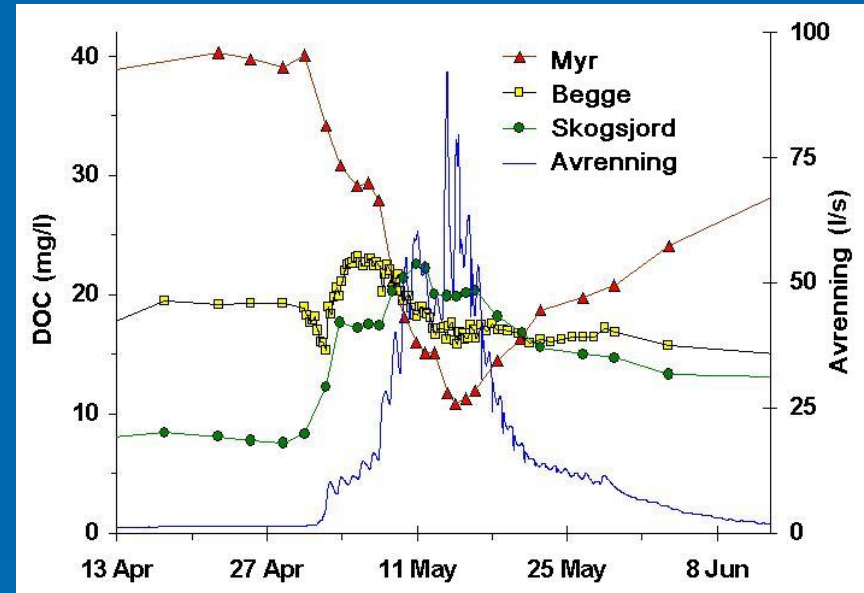
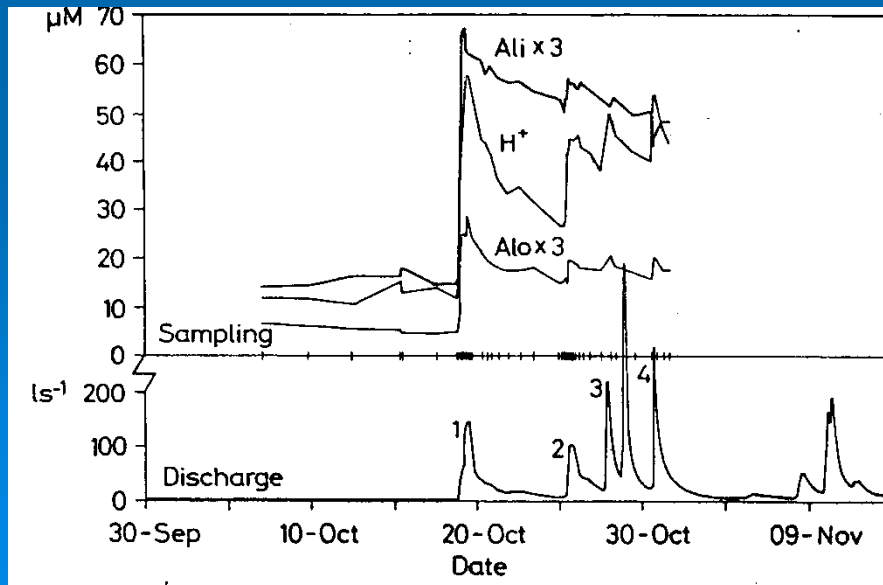
Sampling strategy

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



Temporal variation

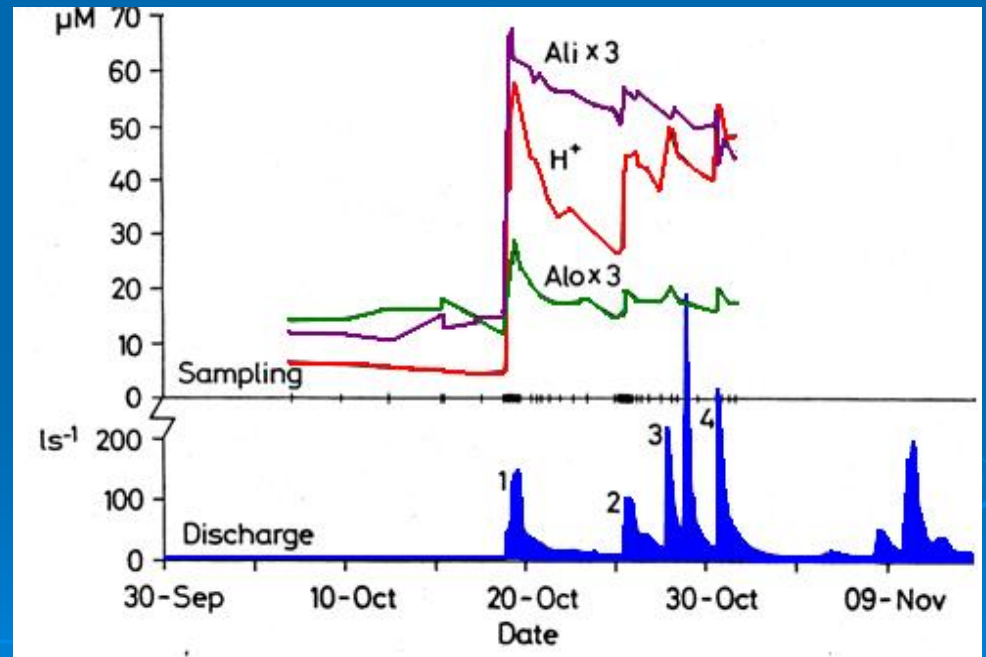
- Seasonal & Climate
- Runoff concentrations of both solutes and suspended material show large variations both seasonal and as a function of discharge



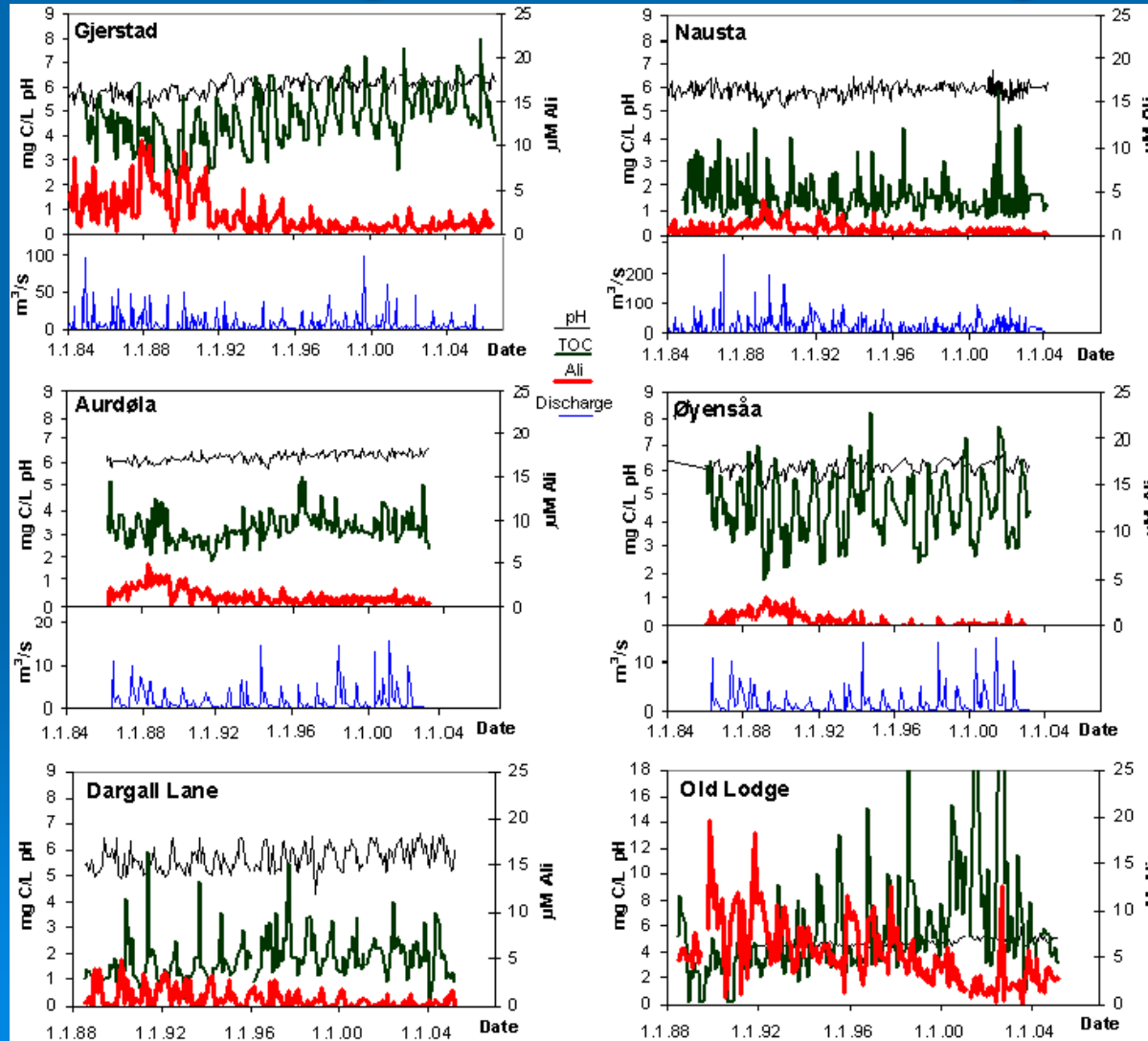
Discharge and concentration measured continuously in runoff water from a small catchment in Norway and N Sweden

Chemistry vs. flow

Acidity and Dissolved Organic Matter



Seasonal variations and long term changes



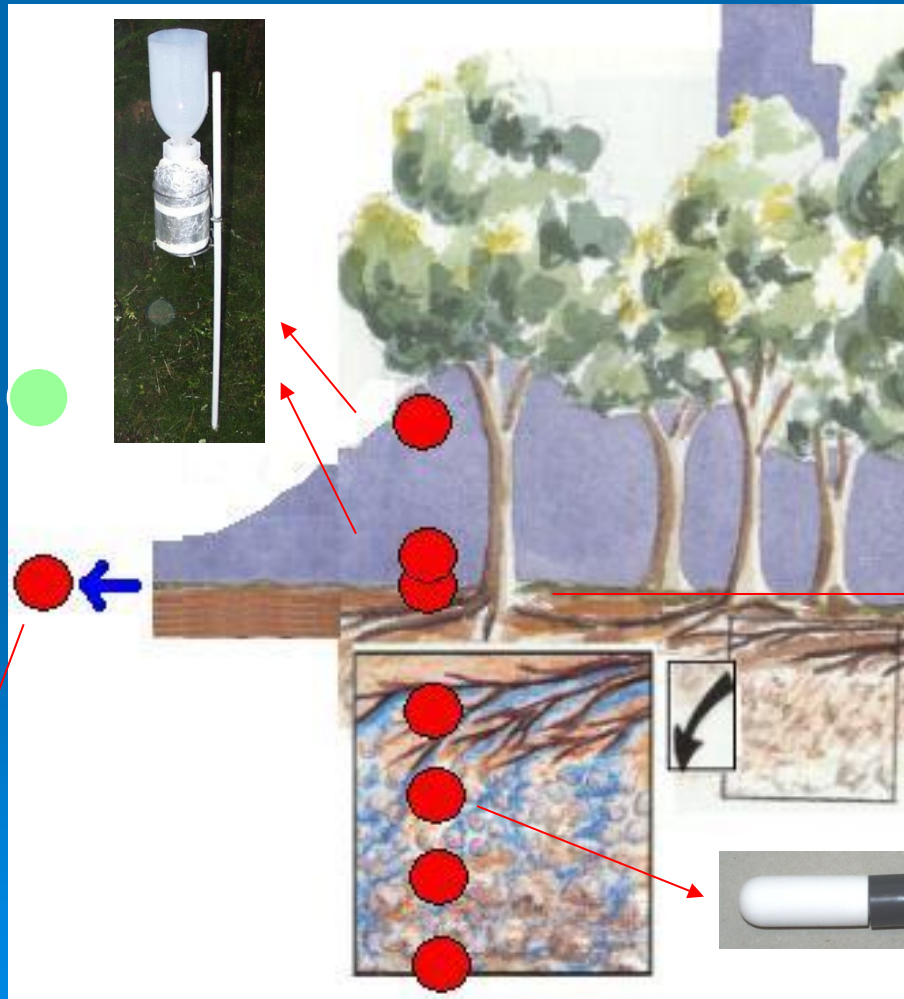
Point sampling strategies

- Different water sampling strategies depending on the objectives of the measurements
 - 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
 - It is assumed that the chemical concentration of runoff water during low flow periods can be considered constant

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

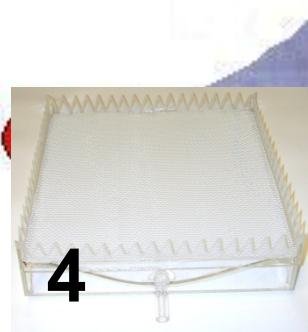
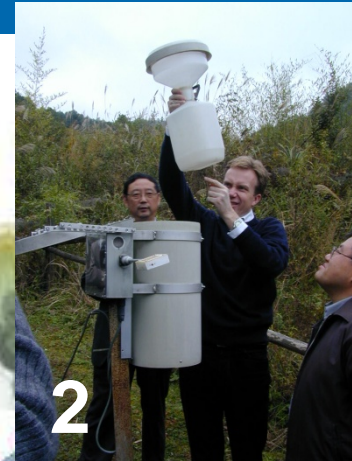
4. Percolation lysimeter
5. Suction lysimeter

➤ 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)



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 effected 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 | |
| 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⁻