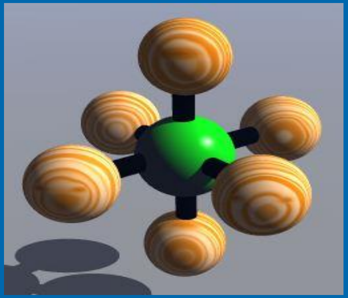
Challenges with simultaneous equilibrium

Speciation programs
(MINEQL)

Inorganic complexes



- Major cations in natural waters
  - H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+
- Common ligands in natural systems:
  - HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-, F^- & organic anions
  - In anoxic environment: HS^- & S^{2-}

- Dominating species in aerobic freshwater at pH 8 are:

Metal ion	Dominating species	% M^{n+}_{aq} of total amount of M
Mg(II)	$Mg(H_2O)_6^{2+}$	94
Ca(II)	$Ca(H_2O)_6^{2+}$	94
Al(III)	$Al(OH)_2(H_2O)_4^+$, $Al(OH)_3(H_2O)_3^0$, $Al(OH)_4(H_2O)_2^-$	$1 \cdot 10^{-7}$
Mn(IV)	$MnO_2(H_2O)_2^0$	-
Fe(III)	$Fe(OH)_2(H_2O)_4^+$, $Fe(OH)_3(H_2O)_3^0$, $Fe(OH)_4(H_2O)_2^-$	$2 \cdot 10^{-9}$
Ni(II)	$Ni(H_2O)_6^{2+}$, $NiCO_3(H_2O)_5^0$	40
Cu(II)	$CuCO_3(H_2O)_2^0$, $Cu(OH)_2(H_2O)_2^0$	1
Zn(II)	$Zn(H_2O)_4^{2+}$, $ZnCO_3(H_2O)_2^0$	40
Pb(II)	$PbCO_3(H_2O)_4^0$	5

Hydrolysis

$$\frac{Z^2}{r}$$

Z = charge
r = radius
The logarithm of the first hydrolysis constant is proportional to $\frac{Z^2}{r}$

- Hydrolysis reactions are important in aqueous systems
  - Hydrolysis reactions are controlled by ionic index and $\{H^+\}$
    - The higher the pH,
      the stronger the hydrolysis of metal cations
    - E.g. Aluminium

$$Al^{3+}{}_{aq} + H_2O \leftrightarrow Al(OH)^{2+}{}_{aq} + H^+ \qquad pK_1 = 4.95$$

$$Al(OH)^{2+}{}_{aq} + H_2O \leftrightarrow Al(OH)_2{}^{+}{}_{aq} + H^+ \qquad pK_2 = 5.6$$

$$Al(OH)_2{}^{+}{}_{aq} + H_2O \leftrightarrow Al(OH)_3{}^{0}{}_{aq} + H^+ \qquad pK_3 = 6.75$$

$$Al(OH)_3{}^{0}{}_{aq} + H_2O \leftrightarrow Al(OH)_4{}^{-}{}_{aq} + H^+ \qquad pK_4 = 5.6$$

$$Al^{3+}{}_{aq} + H_2O \leftrightarrow Al(OH)^{2+}{}_{aq} + H^+ \qquad p\beta_1 = pK_1 = 4.95$$

$$Al^{3+}{}_{aq} + 2H_2O \leftrightarrow Al(OH)_2{}^{+}{}_{aq} + 2H^+ \qquad p\beta_2 = pK_1 + pK_2 = 10.55$$

$$Al^{3+}{}_{aq} + 3H_2O \leftrightarrow Al(OH)_3{}^{0}{}_{aq} + 3H^+ \qquad p\beta_3 = pK_1 + pK_2 + pK_3 = 17.25$$

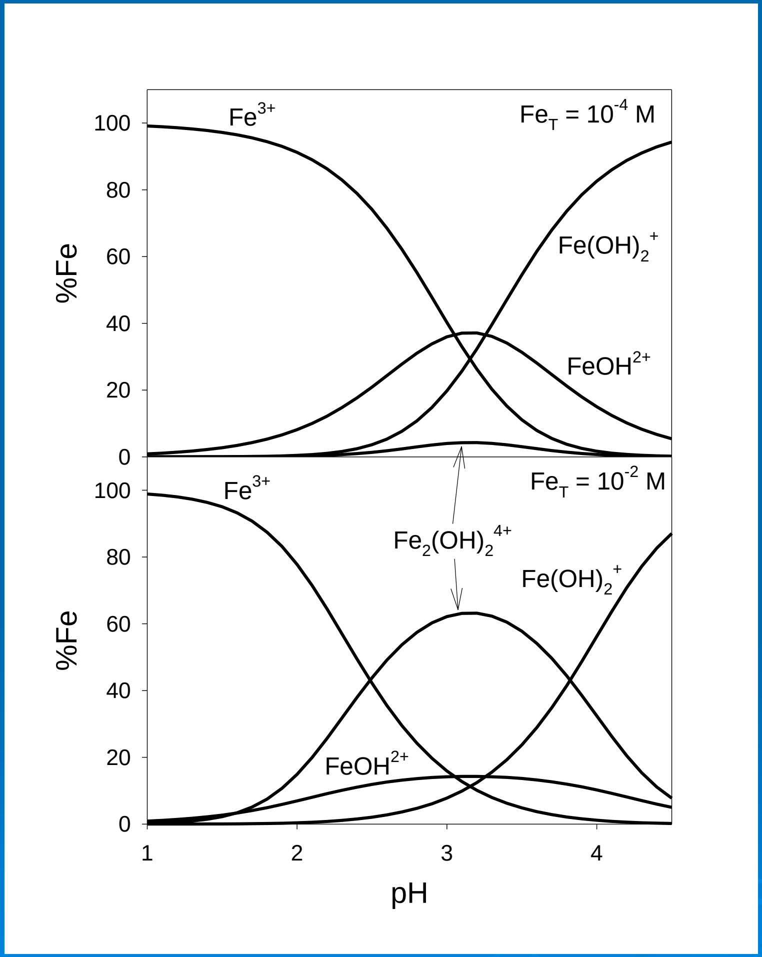
$$Al^{3+}{}_{aq} + 4H_2O \leftrightarrow Al(OH)_4{}^{-}{}_{aq} + 4H^+ \qquad p\beta_4 = pK_1 + pK_2 + pK_3 + pK_4 = 22.85$$

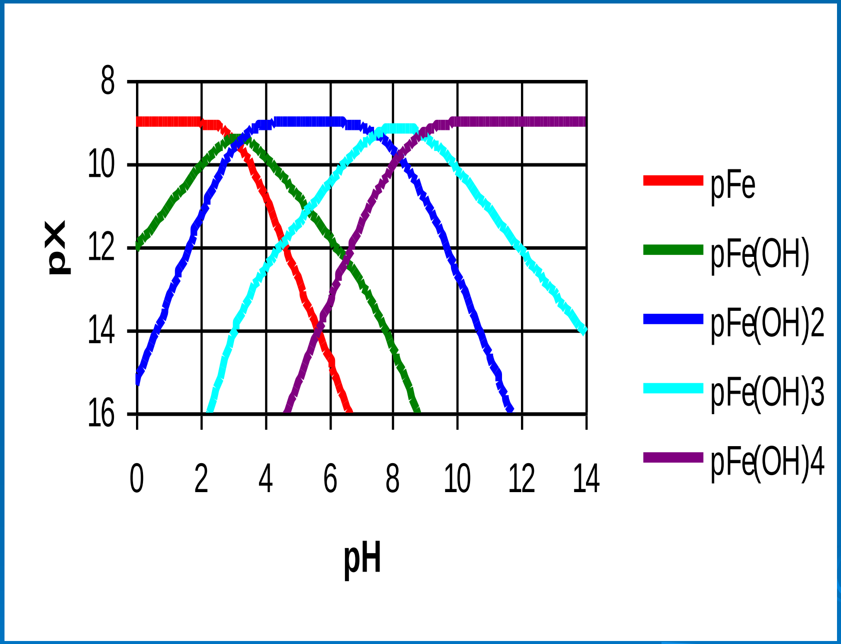
- $Al^{3+}{}_{aq}$ denotes $Al(H_2O)_6{}^{3+}$

Distribution of dissolved Fe^{3+} species

Two total Fe concentrations,

$Fe_T = 10^{-4}M$ and $Fe_T = 10^{-2}M$

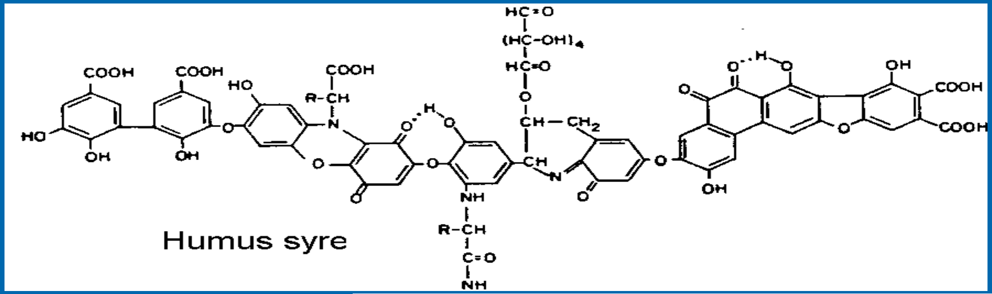




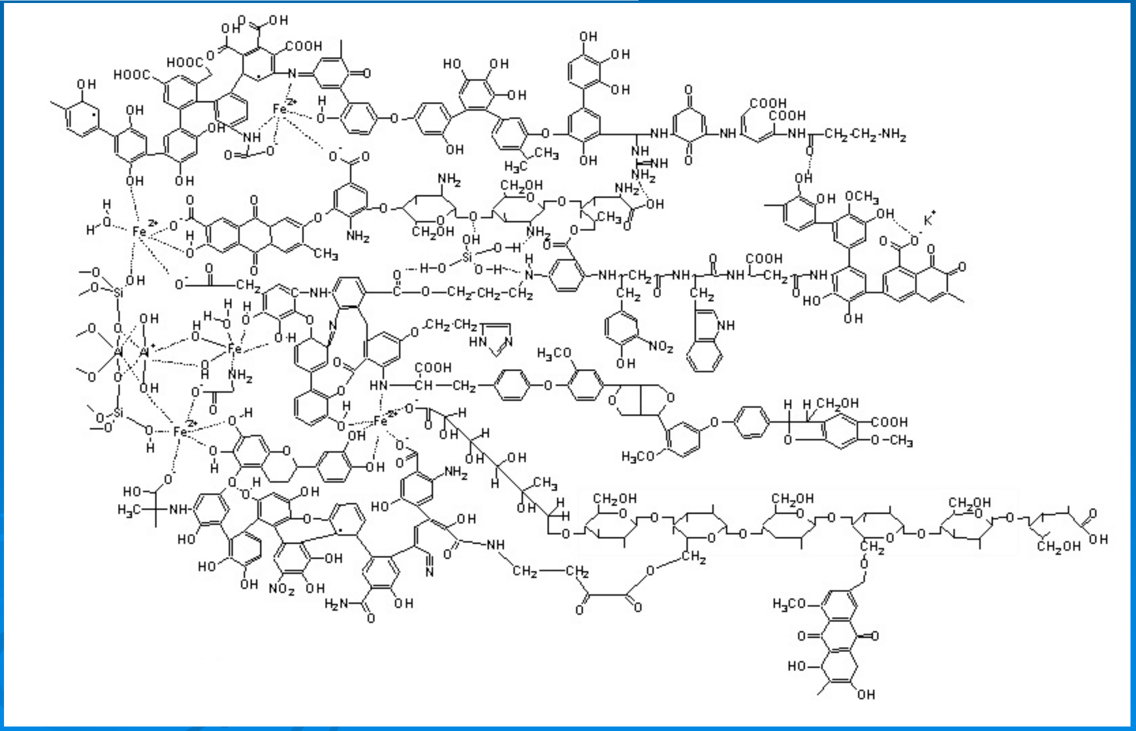
Distribution diagrams

Dissolved Organic Matter

- Low molecular weight (LMW)
  - < 1000Da (e.g. $C_{32}H_{80}O_{33}N_5P_{0.3}$)
  - E.g.:



- High molecular weight
  - 1000 - > 100 000Da
  - Humic substance
    - Very complex and coloured substances

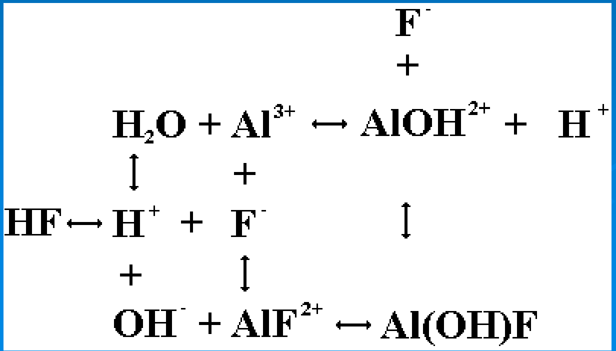


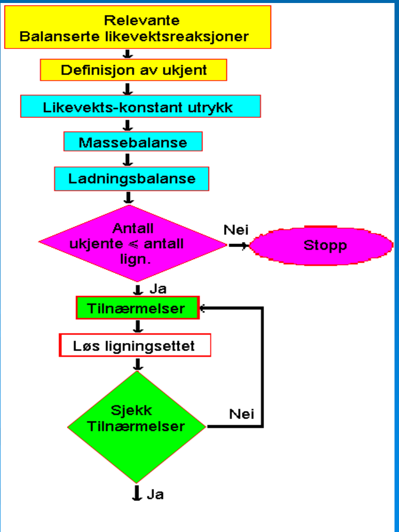
- Measured by TOC/DOC
  - Or by UV absorbency or colour

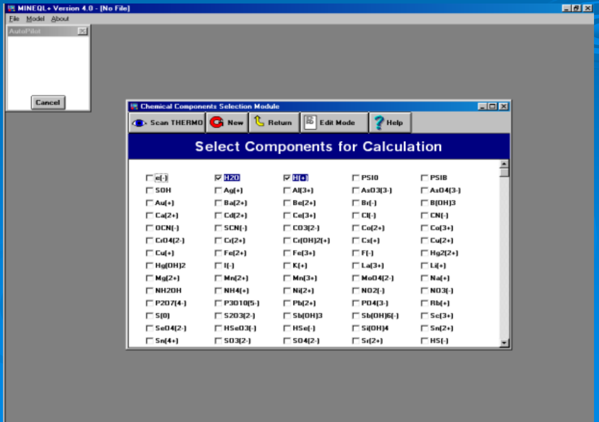
Speciation with different ligands present

- In aqueous solution, containing a number of metal cations and ligand anions, there are several simultaneous equilibriums
  - Important ligands in natural water systems
    - Basic: CO_3^{2-}, OH^-, Org^-, Cl^-
    - Acid: F^-, SO_4^{2-}, Org^-, Cl^-
  - The distribution of species will depend on factors such as ligand concentrations, temperature, pH and ionic strength
- The calculations become very complex where a metal cation have the opportunity to bind to more than one type of ligands
  - Multiple iterations of the calculations are necessary
- For such calculations we apply computer programs as MINEQL+, ALCHEMI or PHREEQ-C

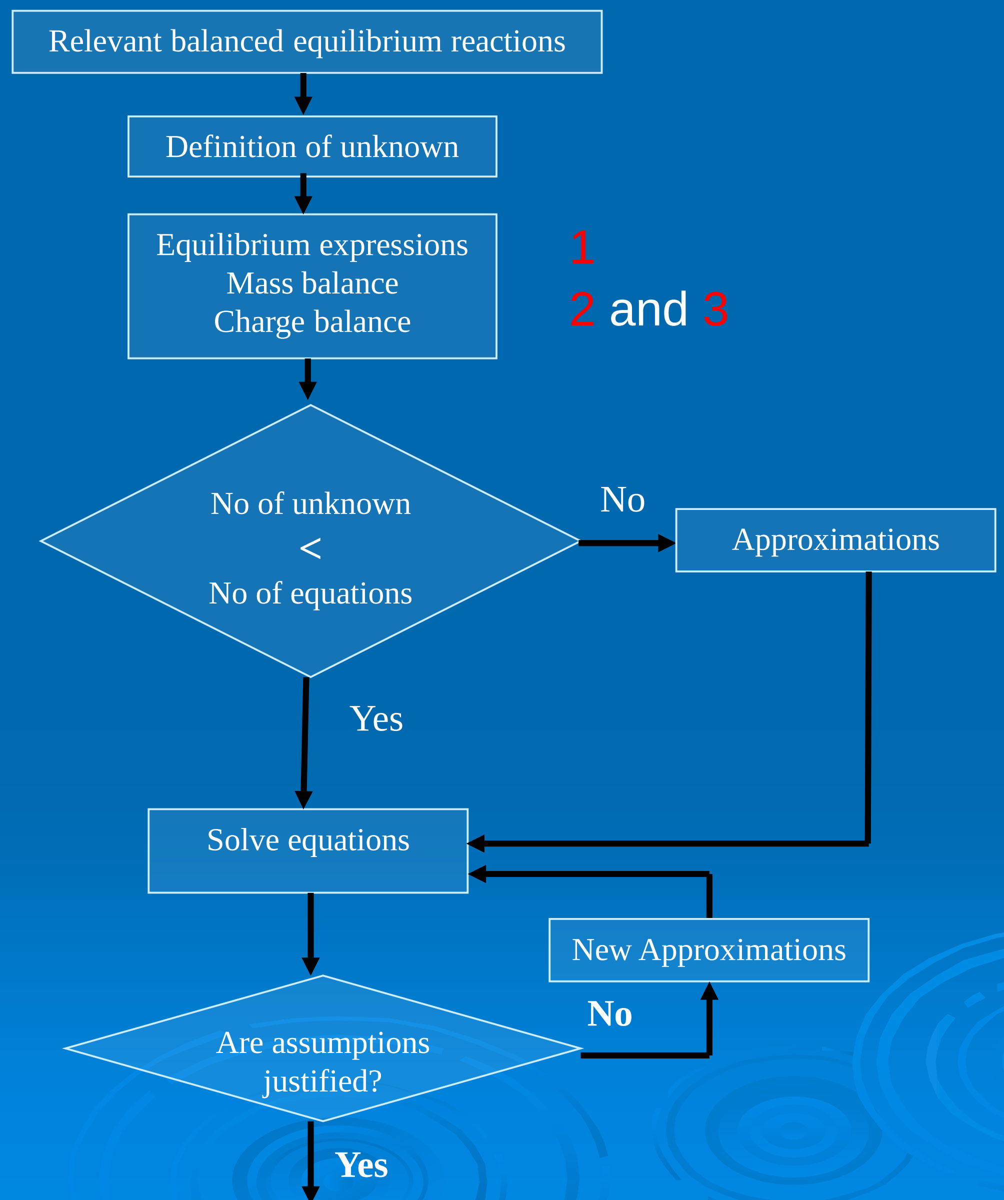
E.g. simple system with only Al^{3+} and F^-







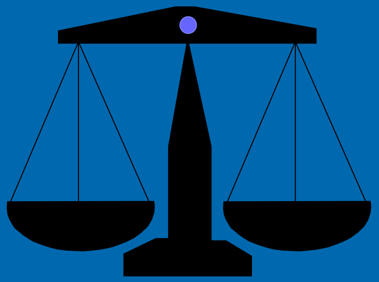
Scheme for chemical equilibrium calculations



Approximations are commonly done by assuming the concentration of specific species are **0 Molar**

Only mass balance and charge balance equations can be simplified

Set of expressions



1. **Equilibrium expressions**
   – K_W, K_{SP}, K_A, K_B, β_n, K_{REDOX}, K_d

2. ***Mass*** (read: concentration) ***balance***
   – Set the equilibrium molarities (M_X) up against each other (M_X vs. M_Y) and against the analytical molarity (M_X vs. c_X)
     – **Analytical concentration** is the concentration of a substance dumped into a solution. It includes all the forms of that substance in the solution.

3. ***Charge balance***
   – Σ eqv./L positive charge = Σ eqv./L negative charge

1. Equilibrium expressions

- K_W, K_{SP}, K_A, K_B, β_n, K_{REDOX}, K_d

$$K_W = [H_3O^+][OH^-]$$

$$K_A = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_{SP} = [Ba^{2+}][SO_4^{\ 2-}]$$

$$K_B = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$$

$$\beta_n = \frac{[Ni(CN)_n^{\ 2-n}]}{[Ni^{2+}][CN^-]^n}$$

$$K_{RedOks} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^{\ -}][Fe^{2+}]^5[H^+]^8}$$

$$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$$

2. Mass balance

- Ex.1: $BaSO_4$ in HCl solution
  - We see from the molecular formula that: $Ba^{2+} : SO_4^{2-} = 1 : 1$
    - So that: $[Ba^{2+}] = [SO_4^{2-}] + [HSO_4^-]$
    - The hydroniumion (H^+) has two sources: HCl ($=c_{HCL}$) and the auto-proteolysis of water ($=[OH^-]$):

$$[H_3O^+] = c_{HCl} + [OH^-]$$

- Ex.2: Ag_2CrO_4 solution
  - We see from the molecular formula that : $Ag^+ : CrO_4^{2-} = 2 : 1$
    - So that : $2[CrO_4^{2-}] = [Ag^+]$

3. Charge balance

- The law of physics demand that
  - Number of positive charge is equal to number of negative charge
    - Charge contribution of a specie = Valens · Molar concentration

$$\Sigma n \cdot [X^{n+}] = \Sigma m \cdot [Y^{m-}]$$

Ex. 1: $2[Ba^{2+}] + [H_3O^{+}] = 2[SO_4^{2-}] + [HSO_4^{-}] + [OH^{-}] + [Cl^{-}]$

– In neutral pH solutions one can disregard the H^+ and OH^- ions

Ex. 2: $[Ag^{+}] = 2[CrO_4^{2-}]$

– No new information

Metal hydrolysis

- The hydrolysis is described by a set of equilibrium reactions

$$Fe^{3+}{}_{aq} + H_2O \leftrightarrow Fe(OH)^{2+}{}_{aq} + H^+ \qquad p\beta_1 = pK_1 = 3.05$$

$$Fe^{3+}{}_{aq} + 2H_2O \leftrightarrow Fe(OH)_2{}^{+}{}_{aq} + 2H^+ \qquad p\beta_2 = pK_1 + pK_2 = 6.31$$

$$Fe^{3+}{}_{aq} + 3H_2O \leftrightarrow Fe(OH)_3{}^{0}{}_{aq} + 3H^+ \qquad p\beta_3 = pK_1 + pK_2 + pK_3 = 13.8$$

$$Fe^{3+}{}_{aq} + 4H_2O \leftrightarrow Fe(OH)_4{}^{-}{}_{aq} + 4H^+ \qquad p\beta_4 = pK_1 + pK_2 + pK_3 + pK_4 = 22.7$$

$$C = \{Fe^{3+}\} + \{Fe(OH)^{2+}\} + \{Fe(OH)_2{}^{+}\} + \{Fe(OH)_3{}^{0}\} + \{Fe(OH)_4{}^{-}\}$$

- $\{Fe^{3+}\}$ is determined by replacing each of the other parts of the mass equation with their equilibrium expression expressed by $\{Fe^{3+}\}$:

$$Fe^{3+}{}_{aq} + 2H_2O \leftrightarrow Fe(OH)_2{}^{+}{}_{aq} + 2H^+$$

$$\beta_2 = \frac{\{Fe(OH)_2{}^{+}\} \bullet \{H^+\}^2}{\{Fe^{3+}\}}$$

$$\{Fe(OH)_2{}^{+}\} = \frac{\beta_2 \{Fe^{3+}\}}{\{H^+\}^2}$$

$$C = \{Fe^{3+}\}\left(1 + \frac{\beta_1}{\{H^+\}} + \frac{\beta_2}{\{H^+\}^2} + \frac{\beta_3}{\{H^+\}^3} + \frac{\beta_4}{\{H^+\}^4}\right)$$

  - Then the other species can be determined from the $\{Fe^{3+}\}$ and β

    E.g.;

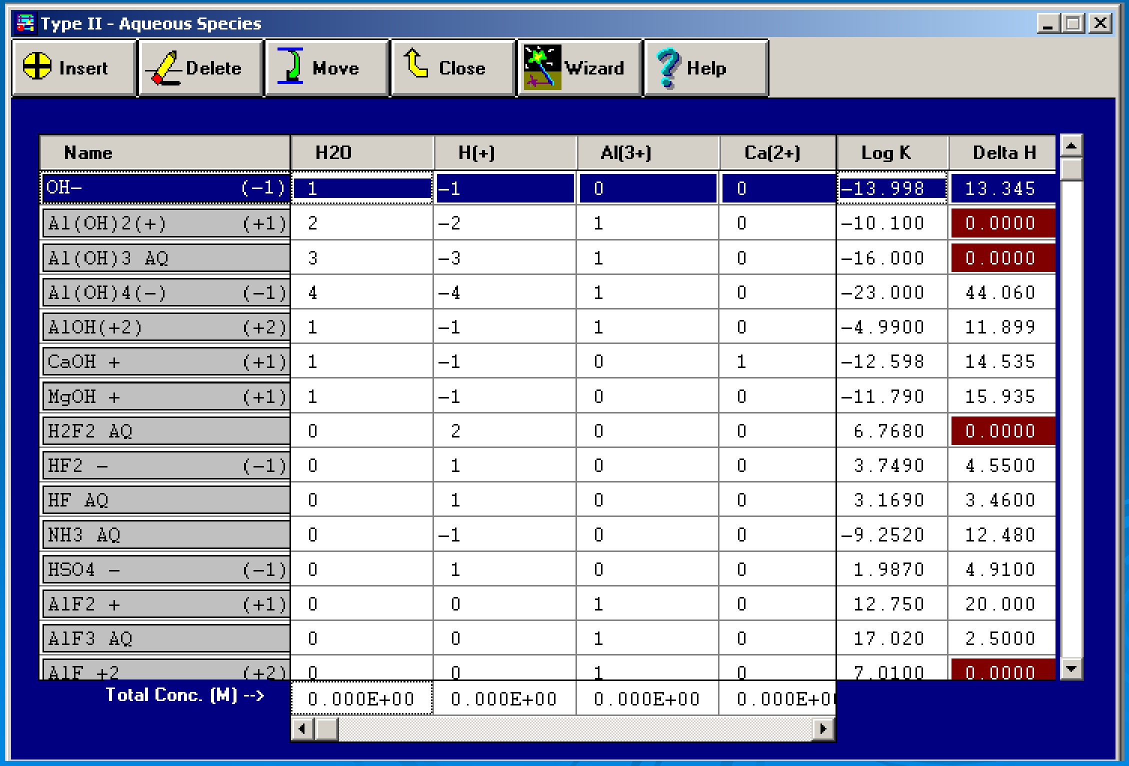
$$Fe(OH)_2{}^{+} = \frac{\beta_2 \{Fe^{3+}\}}{\{H^+\}^2}$$

Speciation programmes

- MINEQL+ is a chemical equilibrium model capable of calculating
  - aqueous speciation
  - solid phase saturation
  - precipitation-dissolution
  - adsorption
- An extensive thermodynamic database is included in the model

Speciation; Shortcomings

- The equilibrium model is based on a choice of complexes and their stability constants, which makes the results questionable



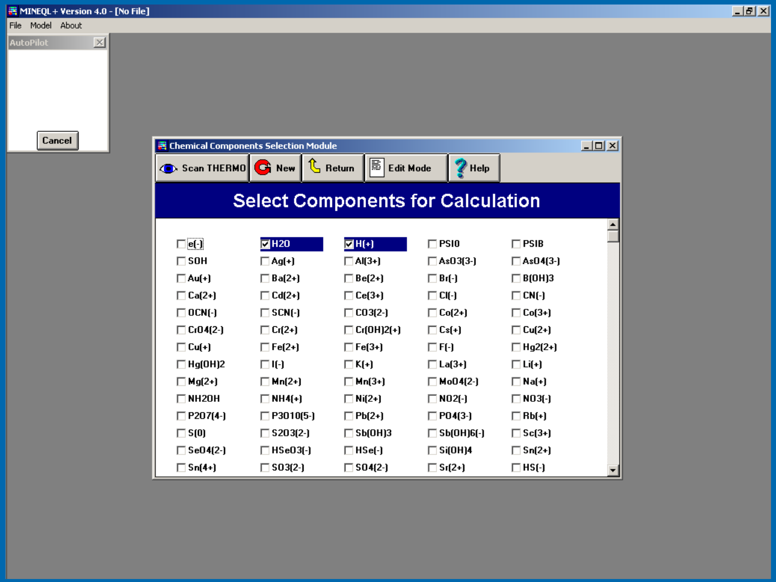
Type II - Aqueous Species

Insert | Delete | Move | Close | Wizard | Help

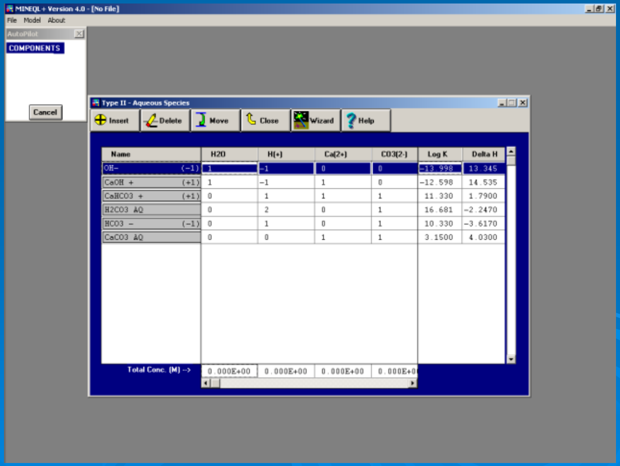
Name		H2O	H(+)	Al(3+)	Ca(2+)	Log K	Delta H
OH-	(-1)	1	-1	0	0	-13.998	13.345
Al(OH)2(+)	(+1)	2	-2	1	0	-10.100	0.0000
Al(OH)3 AQ		3	-3	1	0	-16.000	0.0000
Al(OH)4(-)	(-1)	4	-4	1	0	-23.000	44.060
AlOH(+2)	(+2)	1	-1	1	0	-4.9900	11.899
CaOH +	(+1)	1	-1	0	1	-12.598	14.535
MgOH +	(+1)	1	-1	0	0	-11.790	15.935
H2F2 AQ		0	2	0	0	6.7680	0.0000
HF2 -	(-1)	0	1	0	0	3.7490	4.5500
HF AQ		0	1	0	0	3.1690	3.4600
NH3 AQ		0	-1	0	0	-9.2520	12.480
HSO4 -	(-1)	0	1	0	0	1.9870	4.9100
AlF2 +	(+1)	0	0	1	0	12.750	20.000
AlF3 AQ		0	0	1	0	17.020	2.5000
AlF +2	(+2)	0	0	1	0	7.0100	0.0000
Total Conc. (M) -->		0.000E+00	0.000E+00	0.000E+00	0.000E+0		

Tutorial MINEQL+

- Start out by choosing components that define your system



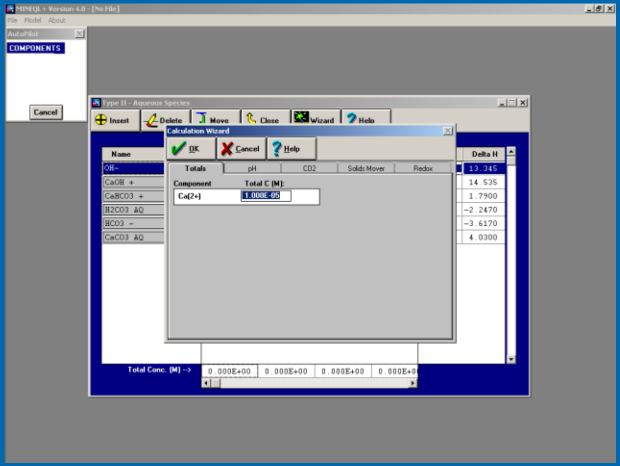
- Find thermodynamic constants in database in "Scan Thermo"

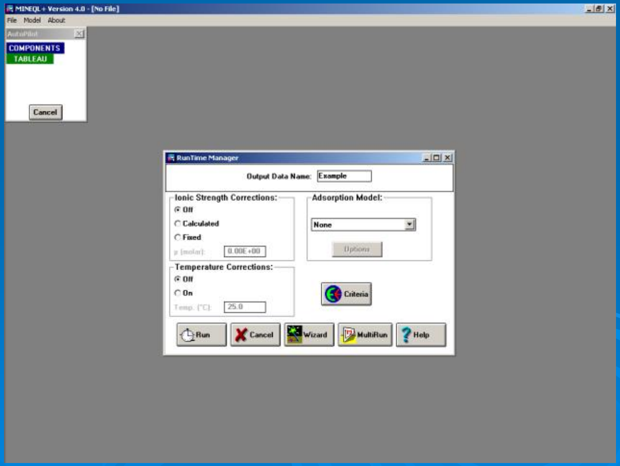


Tutorial

- The Calculation Wizards Tool is a collection of **5** input options to describe the chemistry of the system

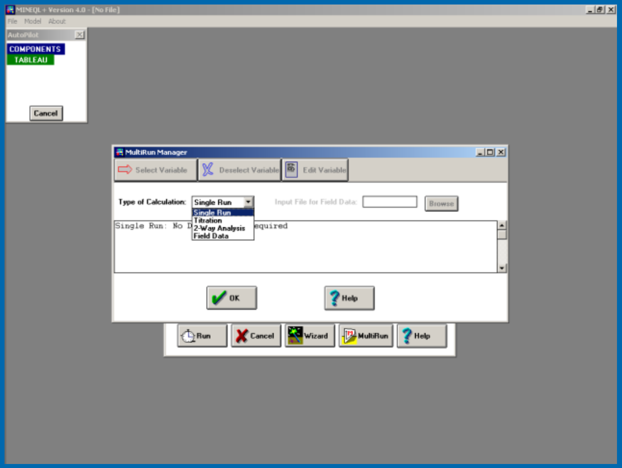
- Running the calculation



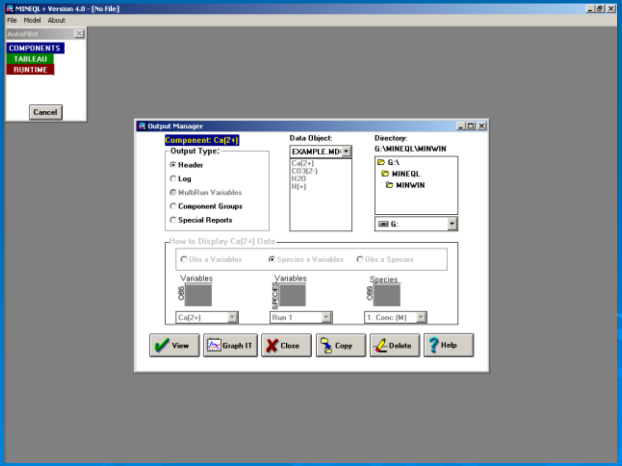


Tutorial

- Multirun manager
  - Titration
  - 2 way analysis
  - Field data

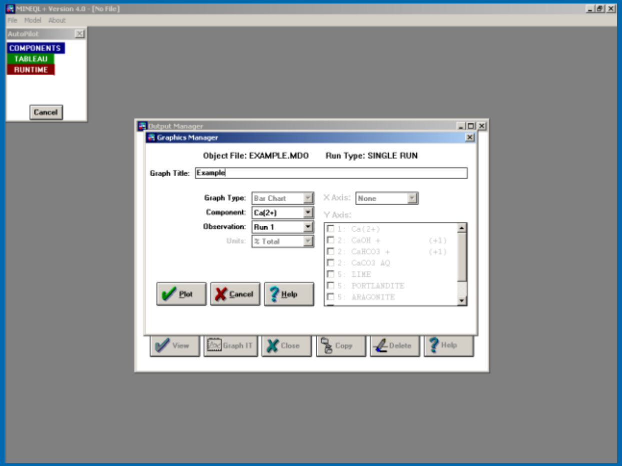


- Output manager
  - Types of Output
    - The Header
    - The Log
    - The MultiRun Table
    - Component Groups
    - Special Reports

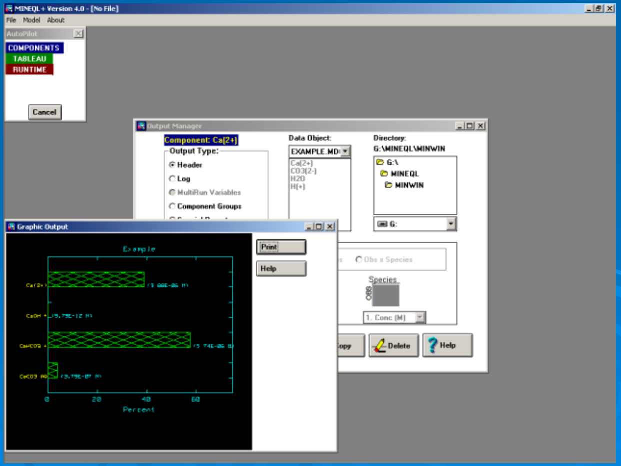


Tutorial

- Graphics manager
  - Bar and X-Y plots



- Run through the 4 problems

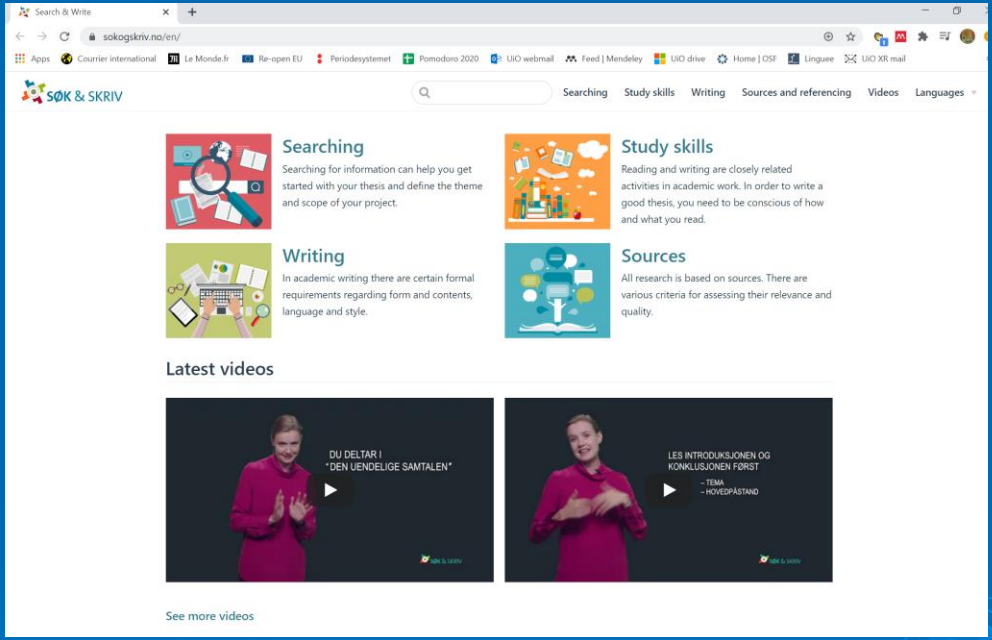


Report

- The report (~ 3p text + graphs/pictures) should include the following paragraphs
  - Abstract
  - Introduction
  - Material and methods
  - Results
  - Discussion
  - Conclusion

Extra tips

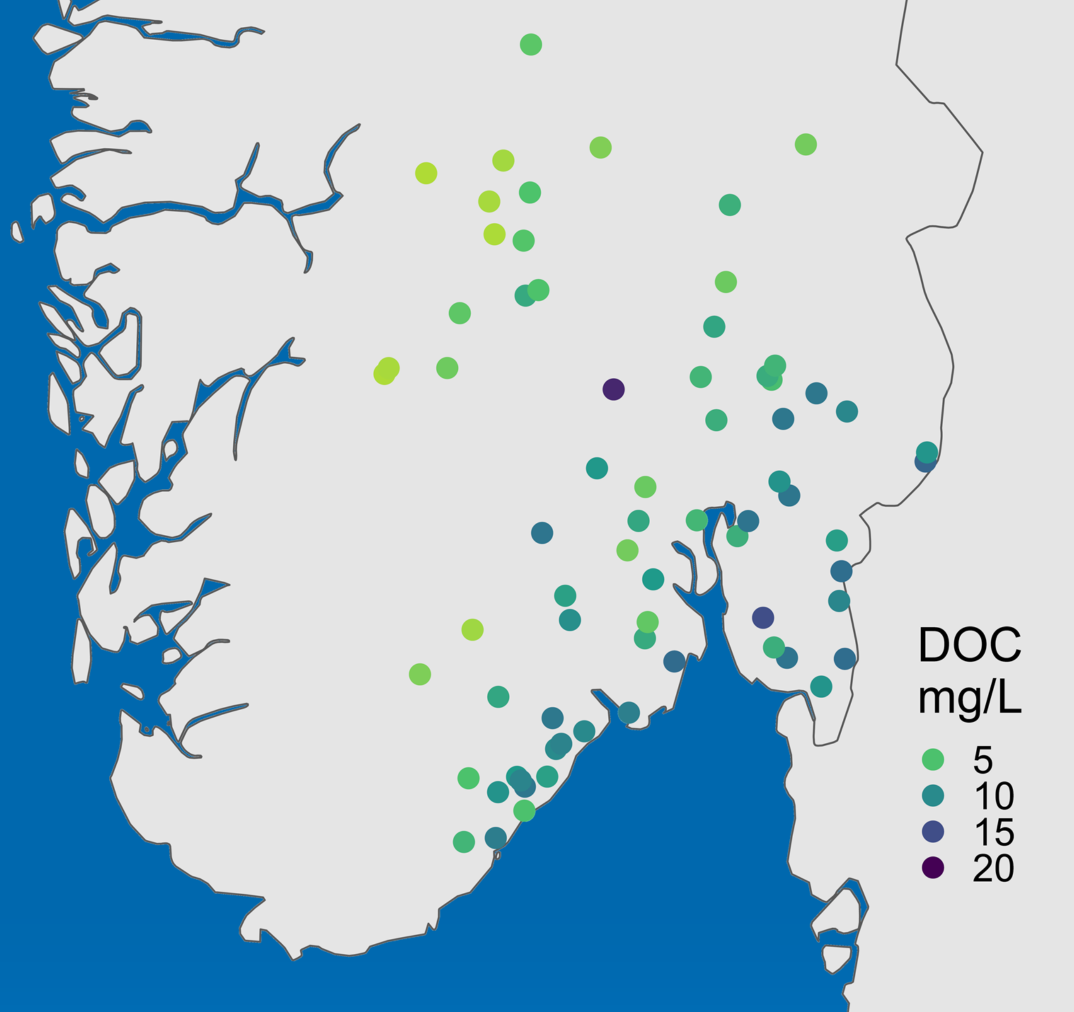
- Report from last year available on Canvas (NB: not perfect!)
- **Søk og skriv**: tips on academic writing



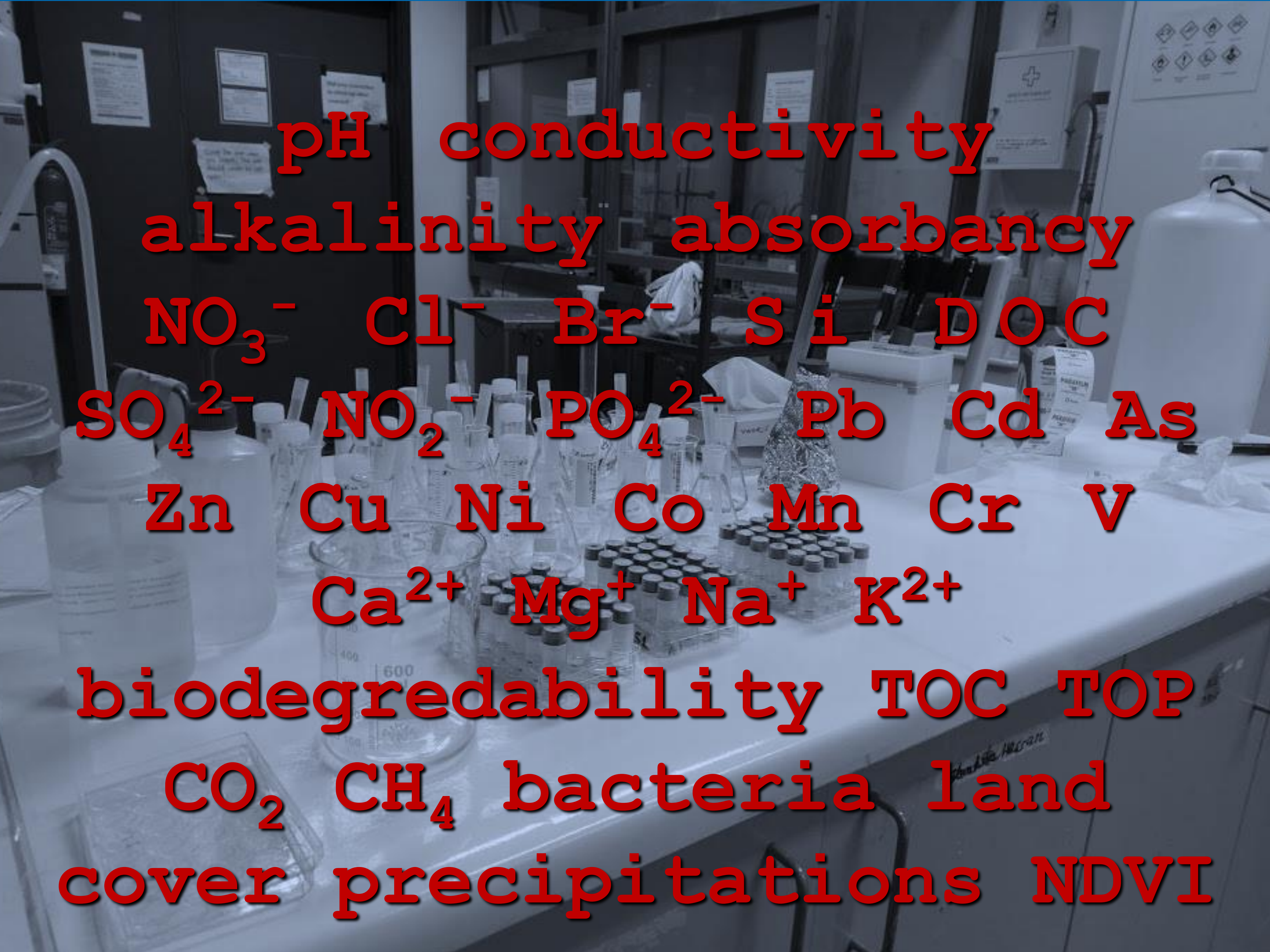
https://sokogskriv.no/en/

The CBA 100 lakes survey

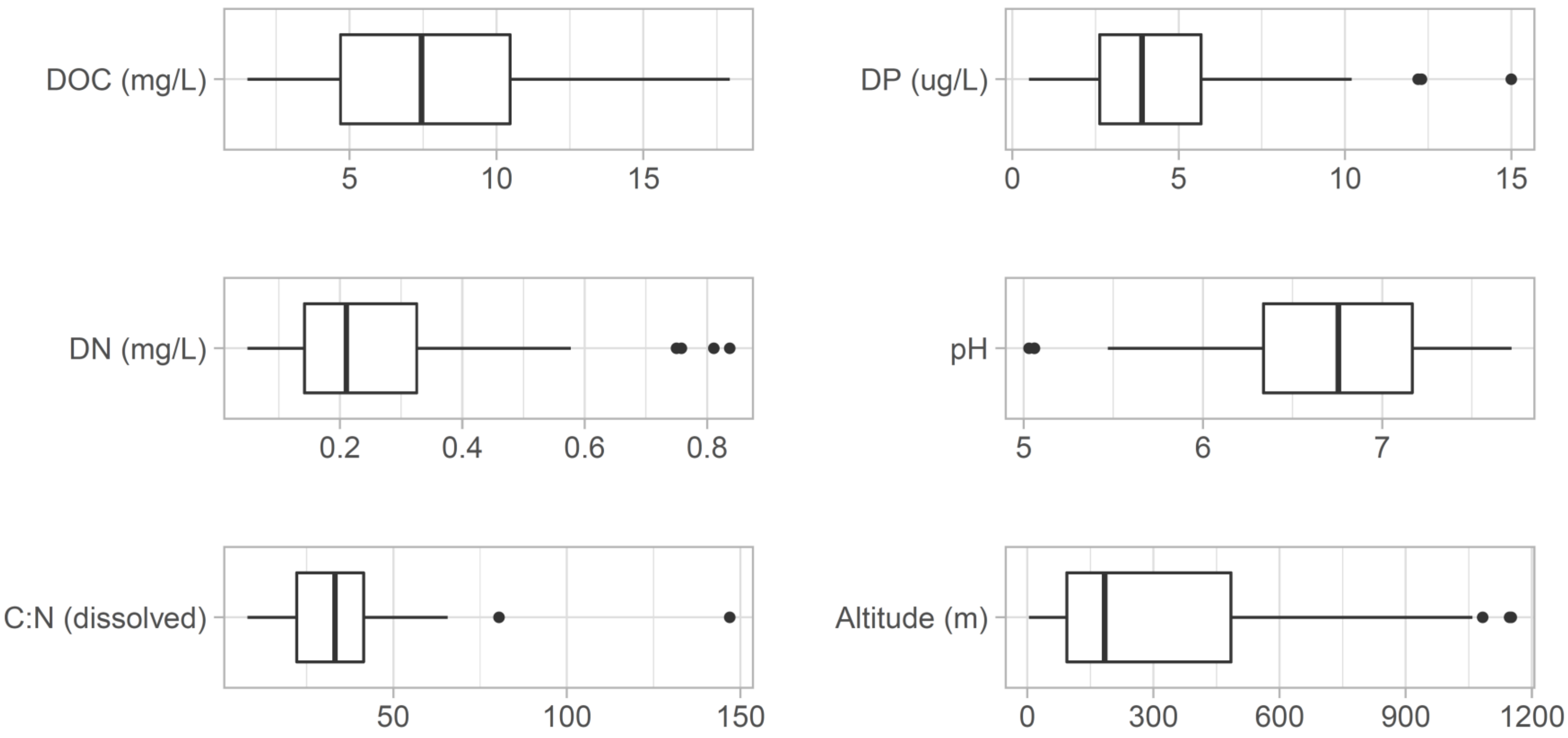
- 81 lakes planned
  - 8 inaccessible
  - 3 discarded during data analysis
- Sampled between October 1st and November 8th 2019
- Cooperation with IBV and NIVA



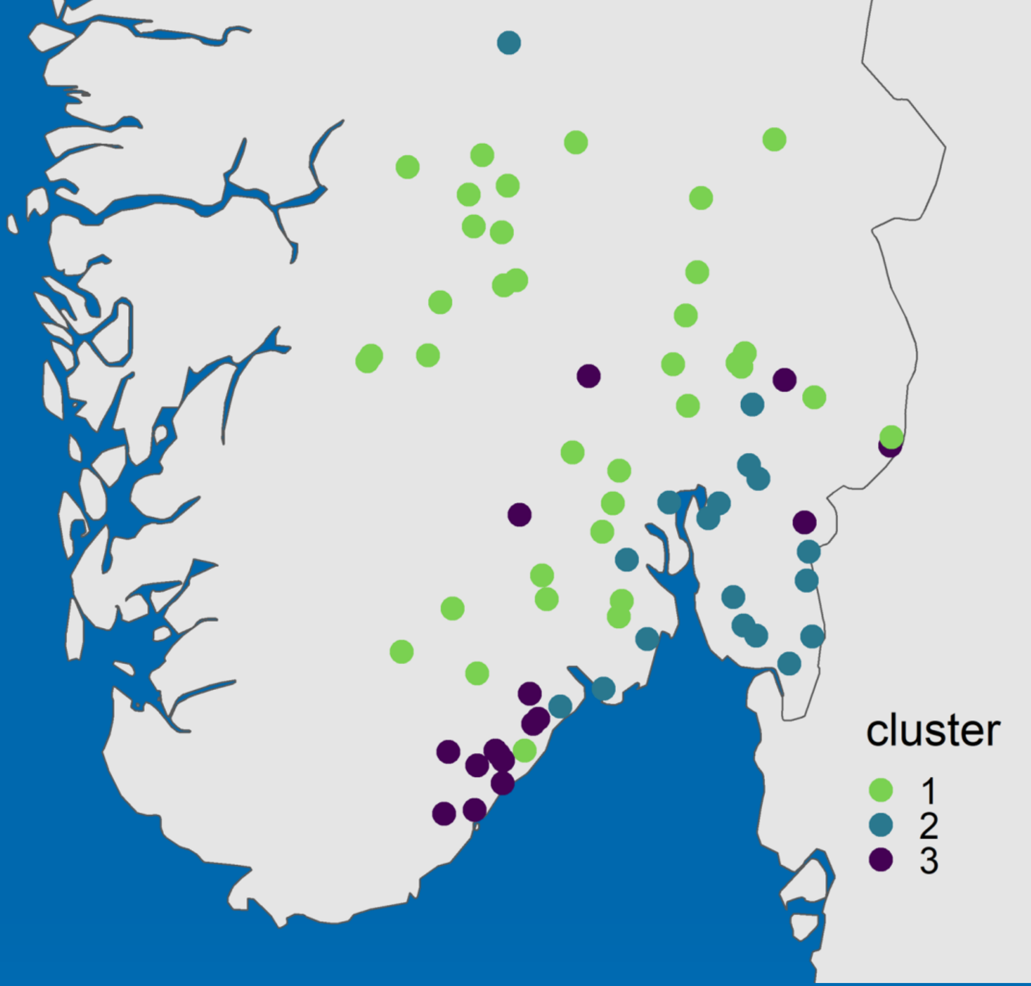
Sampling


pH conductivity
alkalinity absorbancy
NO_3^- Cl^- Br^- Si DOC
SO_4^{2-} NO_2^- PO_4^{2-} Pb Cd As
Zn Cu Ni Co Mn Cr V
Ca^{2+} Mg^+ Na^+ K^{2+}
biodegredability TOC TOP
CO_2 CH_4 bacteria land
cover precipitations NDVI

Characteristics of the lakes



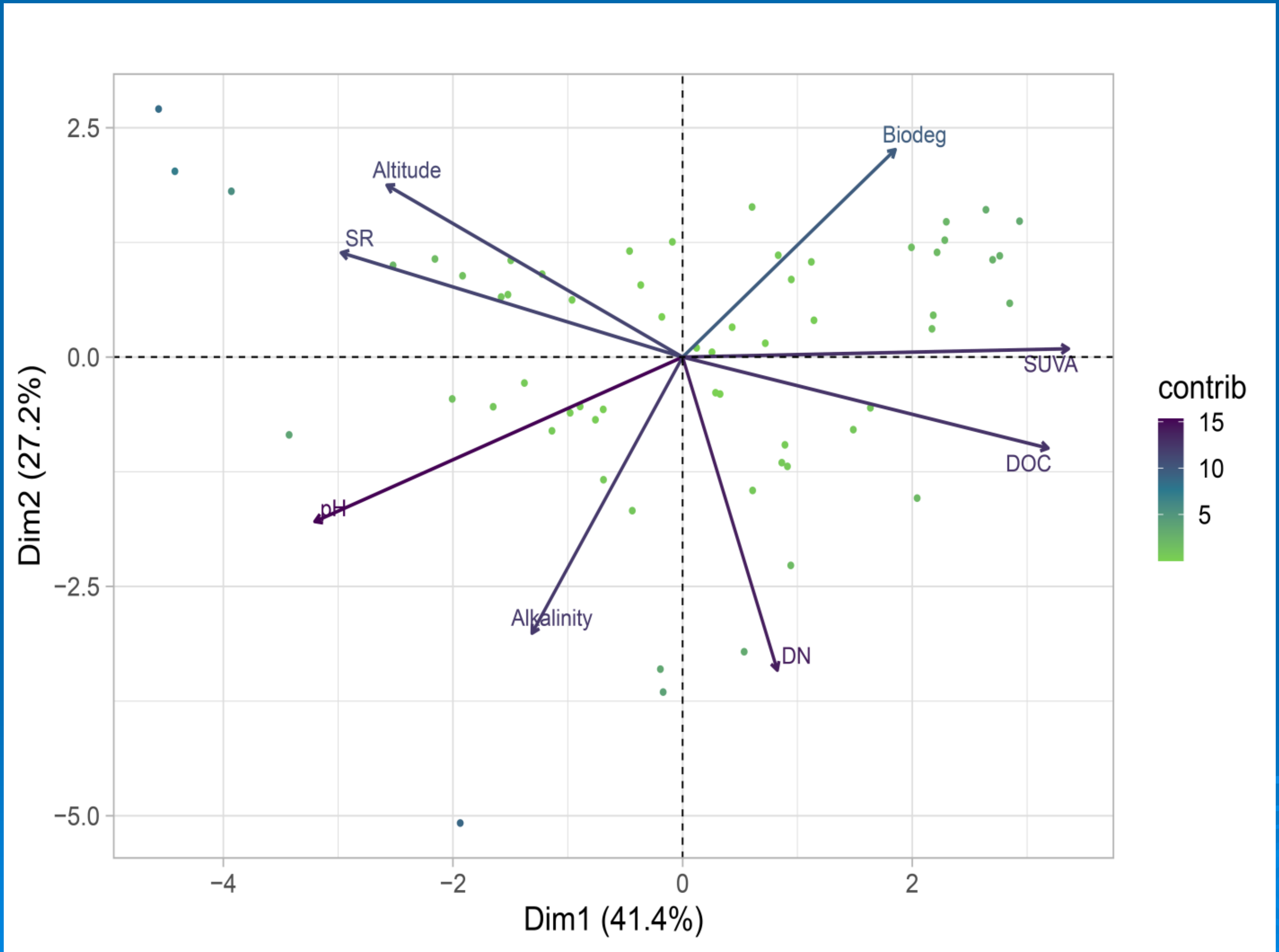
	Cluster 1	Cluster 2	Cluster 3
DOC	-	+	+
Altitude	+	-	-
TN/TP	-	+	-
Mg/K/Na	-	+	-
SUVA	-	+/-	+
CH4	-	+/-	+
CN	-	-	+
pH	+	+	-



Clustering with k-mean method

Differences between cluster: Kruskal Wallis + Wilcoxon tests, p < 005

Principal component analysis



Bacteria

0.3
0.2
0.1
0.0
-0.1
-0.2
-0.2
0.0
0.2
0.4
RDA1
RDA2
T
NO3
Altitude
CH4
CO2
pH
Class
Acidobacteriae
Actinobacteria
Alphaproteobacteria
Anaerolineae
Armatimonadia
Bacteroidia
Bdellovibrionia
Cyanobacteriia
Gammaproteobacteria
Gemmatimonadetes
Omnitrophia
Other
Phycisphaerae
Planctomycetes
Verrucomicrobiae
Vicinamibacteria