Species in natural freshwater

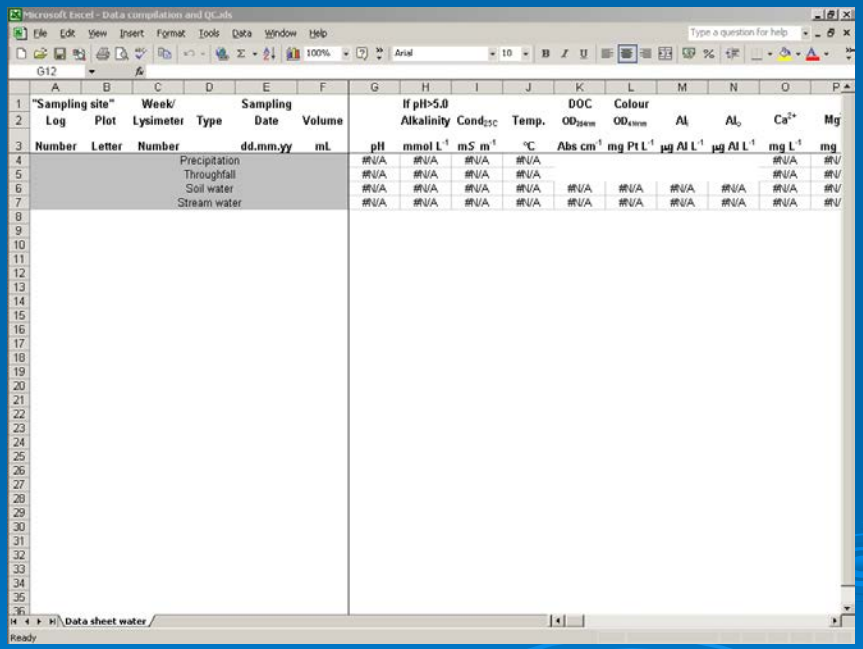
Central equilibriums in natural water samples

KJM MEF 4010

Module 19

Compilation, calculations and QC of data

- After the analysis the data must be:
  - compiled
  - reckoned in terms of **equivalent charge** and
  - **quality controlled** by ion balance and agreement between measured and calculated conductivity



EXAMPLE 1.3: *Estimating the reliability of water analyses*
Your laboratory returns the following water analysis:

pH = 8.22
EC = 290 µS/cm

Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	
13.7	1.18	3.2	42.5	31.2	79.9	39	1.3	mg/l

Is this a reliable analysis?

A basic condition for every analysis is that a reasonable charge balance of cations and anions is present: the solution should be electrically neutral. The analysis is recalculated from mg/l to mmol/l and then to meq/l.

	mg/l		Form. wght (grams)		mmol/l		Charge		meq/l
Ca^{2+}	42.5	/	40.08	=	1.06	×	2	=	2.12
Mg^{2+}	3.21	/	24.31	=	0.13	×	2	=	0.26
Na^+	13.7	/	22.99	=	0.60	×	1	=	0.60
K^+	1.18	/	39.1	=	0.03	×	1	=	0.03
							Σ	=	+3.01
Cl^-	31.2	/	35.45	=	0.88	×	−1	=	−0.88
SO_4^{2-}	39.	/	96.06	=	0.41	×	−2	=	−0.82
HCO_3^-	79.9	/	61.02	=	1.31	×	−1	=	−1.31
NO_3^-	1.3	/	62.0	=	0.02	×	−1	=	−0.02
							Σ	=	−3.03

The difference between cations and anions is 0.02 meq/l, and this is undoubtedly a 'good' analysis. The electrical balance is:

E.N. = (3.01 + − 3.03)/(3.01 − − 3.03)·100 = − 2.00/6.04 = − 0.3%, which is very good indeed.

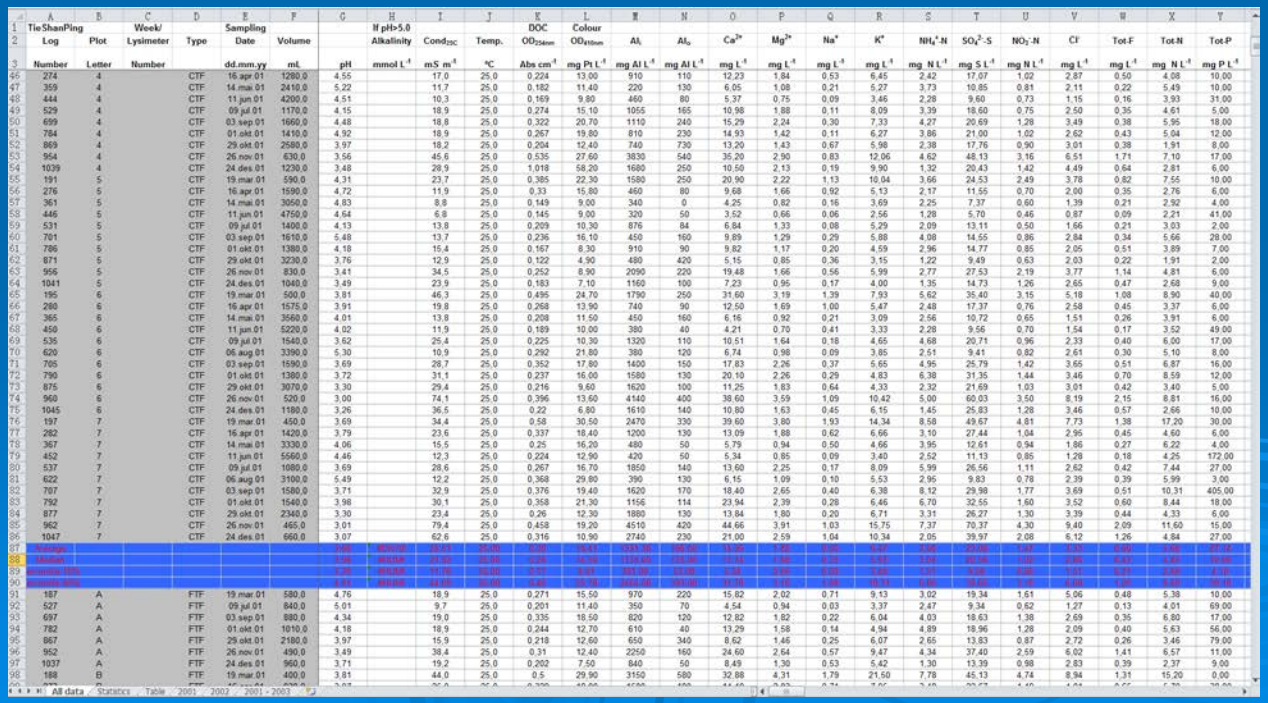
Statistical analysis

- Correlation matrix
  - Identify parameters that are directly correlated or co-variate

	H+	sUVa	SAR	DOC	Ca2+	Mg2+	Na+	K+	SO42-	NO3-	Cl-	Free PO4
sUVa	0,806											
	0,000											
SAR	0,772	0,852										
	0,000	0,000										
DOC	0,842	0,867	0,953									
	0,000	0,000	0,000									
Ca2+	-0,301	-0,177	-0,046	-0,139								
	0,052	0,262	0,774	0,381								
Mg2+	-0,434	-0,344	-0,254	-0,322	0,934							
	0,004	0,026	0,105	0,038	0,000							
Na+	-0,265	-0,179	-0,062	-0,155	0,816	0,822						
	0,090	0,256	0,698	0,327	0,000	0,000						
K+	-0,234	-0,140	-0,031	-0,048	0,834	0,832	0,815					
	0,136	0,378	0,845	0,761	0,000	0,000	0,000					
SO42-	0,365	0,587	0,716	0,641	0,425	0,239	0,444	0,450				
	0,017	0,000	0,000	0,000	0,005	0,128	0,003	0,003				
NO3-	-0,246	-0,140	-0,143	-0,161	0,381	0,539	0,476	0,621	0,186			
	0,116	0,378	0,366	0,308	0,013	0,000	0,001	0,000	0,239			
Cl-	-0,456	-0,405	-0,316	-0,393	0,691	0,764	0,931	0,749	0,213	0,542		
	0,002	0,008	0,041	0,010	0,000	0,000	0,000	0,000	0,176	0,000		
Free PO4	0,356	0,647	0,576	0,479	0,047	-0,086	0,025	0,005	0,655	0,072	-0,186	
	0,021	0,000	0,000	0,001	0,770	0,588	0,873	0,973	0,000	0,651	0,238	
HCO3	-0,500	-0,445	-0,377	-0,431	0,841	0,846	0,608	0,607	0,023	0,222	0,600	-0,202
	0,001	0,003	0,014	0,004	0,000	0,000	0,000	0,000	0,883	0,158	0,000	0,199

Multivariate statistics

- How to interpret information in a data matrix of 1000 samples with typically 20 – 30 parameters



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
1	TieShanPing		Week/		Sampling			If pH>5.0			DOC	Colour													
2	Log	Plot	Lysimeter	Type	Date	Volume		Alkalinity	$Cond_{25C}$	Temp.	OD_{254nm}	OD_{410nm}	Al	Al_o	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+-N	SO_4^{2-}-S	NO_3-N	Cl^-	Tot-F	Tot-N	Tot-P
3	Number	Letter	Number		dd.mm.yy	mL	pH	mmol L^{-1}	mS m^{-1}	°C	Abs cm^{-1}	mg Pt L^{-1}	mg Al L^{-1}	mg Al L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg N L^{-1}	mg S L^{-1}	mg N L^{-1}	mg L^{-1}	mg L^{-1}	mg N L^{-1}	mg P L^{-1}
46	274	4		CTF	16.apr.01	1280,0	4,55		17,0	25,0	0,224	13,00	910	110	12,23	1,84	0,53	6,45	2,42	17,07	1,02	2,87	0,50	4,08	10,00
47	359	4		CTF	14.mai.01	2410,0	5,22		11,7	25,0	0,182	11,40	220	130	6,05	1,08	0,21	5,27	3,73	10,85	0,81	2,11	0,22	5,49	10,00
48	444	4		CTF	11.jun.01	4260,0	4,51		10,3	25,0	0,169	9,80	460	80	5,37	0,75	0,09	3,46	2,28	9,60	0,73	1,15	0,16	3,93	31,00
49	529	4		CTF	09.jul.01	1170,0	4,15		18,9	25,0	0,274	15,10	1055	165	10,98	1,88	0,11	8,09	3,39	18,60	0,75	2,50	0,35	4,61	5,00
50	699	4		CTF	03.sep.01	1660,0	4,48		18,8	25,0	0,322	20,70	1110	240	15,29	2,24	0,30	7,33	4,27	20,69	1,28	3,49	0,38	5,95	18,00
51	784	4		CTF	01.okt.01	1410,0	4,92		18,9	25,0	0,267	19,80	810	230	14,93	1,42	0,11	6,27	3,86	21,00	1,02	2,62	0,43	5,04	12,00
52	869	4		CTF	29.okt.01	2580,0	3,97		18,2	25,0	0,204	12,40	740	730	13,20	1,43	0,67	6,98	2,38	17,76	0,90	3,01	0,38	1,91	8,00
53	964	4		CTF	26.nov.01	630,0	3,56		45,6	25,0	0,535	27,60	3830	540	35,20	2,90	0,83	12,06	4,62	48,13	3,16	6,51	1,71	7,10	17,00
54	1039	4		CTF	24.des.01	1230,0	3,48		28,9	25,0	1,018	58,20	1680	250	10,50	2,13	0,19	9,90	1,32	20,43	1,42	4,49	0,64	2,81	6,00
55	191	5		CTF	19.mar.01	590,0	4,31		23,7	25,0	0,385	22,30	1580	250	20,90	2,22	1,13	10,04	3,66	24,53	2,49	3,78	0,82	7,55	10,00
56	276	5		CTF	16.apr.01	1590,0	4,72		11,9	25,0	0,33	15,80	460	80	9,68	1,66	0,92	5,13	2,17	11,55	0,70	2,00	0,35	2,76	6,00
57	361	5		CTF	14.mai.01	3050,0	4,83		8,8	25,0	0,149	9,00	340	0	4,25	0,82	0,16	3,69	2,25	7,37	0,60	1,39	0,21	2,92	4,00
58	446	5		CTF	11.jun.01	4750,0	4,64		6,8	25,0	0,145	9,00	320	50	3,52	0,66	0,06	2,56	1,28	5,70	0,46	0,87	0,09	2,21	41,00
59	531	5		CTF	09.jul.01	1400,0	4,13		13,8	25,0	0,209	10,30	876	84	6,84	1,33	0,08	5,29	2,09	13,11	0,50	1,66	0,21	3,03	2,00
60	701	5		CTF	03.sep.01	1610,0	5,48		13,7	25,0	0,236	16,10	450	160	9,89	1,29	0,29	5,88	4,08	14,55	0,86	2,84	0,34	5,66	28,00
61	786	5		CTF	01.okt.01	1380,0	4,18		15,4	25,0	0,167	8,30	910	90	9,82	1,17	0,20	4,59	2,96	14,77	0,85	2,05	0,51	3,89	7,00
62	871	5		CTF	29.okt.01	3230,0	3,76		12,9	25,0	0,122	4,90	480	420	5,15	0,85	0,36	3,15	1,22	9,49	0,63	2,03	0,22	1,91	2,00
63	956	5		CTF	26.nov.01	830,0	3,41		34,5	25,0	0,252	8,90	2090	220	19,48	1,66	0,56	5,99	2,77	27,53	2,19	3,77	1,14	4,81	6,00
64	1041	5		CTF	24.des.01	1040,0	3,49		23,9	25,0	0,183	7,10	1160	100	7,23	0,95	0,17	4,00	1,35	14,73	1,26	2,65	0,47	2,68	9,00
65	195	6		CTF	19.mar.01	560,0	3,81		46,3	25,0	0,495	24,70	1790	250	31,60	3,19	1,39	7,93	5,62	35,40	3,15	5,18	1,08	8,90	40,00
66	280	6		CTF	16.apr.01	1575,0	3,91		19,8	25,0	0,268	13,90	740	90	12,50	1,69	1,00	5,47	2,48	17,37	0,76	2,58	0,45	3,37	6,00
67	365	6		CTF	14.mai.01	3560,0	4,01		13,8	25,0	0,208	11,50	450	160	6,16	0,92	0,21	3,09	2,56	10,72	0,65	1,51	0,26	3,91	6,00
68	450	6		CTF	11.jun.01	5220,0	4,02		11,9	25,0	0,189	10,00	380	40	4,21	0,70	0,41	3,33	2,28	9,56	0,70	1,54	0,17	3,52	49,00
69	535	6		CTF	09.jul.01	1540,0	3,62		25,4	25,0	0,225	10,30	1320	110	10,51	1,64	0,18	4,65	4,68	20,71	0,96	2,33	0,40	6,00	17,00
70	620	6		CTF	06.aug.01	1390,0	5,30		10,9	25,0	0,292	21,80	380	120	6,74	0,98	0,09	3,85	2,51	9,41	0,82	2,61	0,30	5,10	8,00
71	705	6		CTF	03.sep.01	1590,0	3,69		28,7	25,0	0,352	17,80	1400	150	17,83	2,26	0,37	5,65	4,95	25,79	1,42	3,65	0,51	6,87	16,00
72	790	6		CTF	01.okt.01	1380,0	3,72		31,1	25,0	0,237	16,00	1580	130	20,10	2,26	0,29	4,83	6,38	31,35	1,44	3,46	0,70	8,59	12,00
73	875	6		CTF	29.okt.01	3070,0	3,30		29,4	25,0	0,216	9,60	1620	100	11,25	1,83	0,64	4,33	2,32	21,69	1,03	3,01	0,42	3,40	5,00
74	960	6		CTF	26.nov.01	520,0	3,00		74,1	25,0	0,396	13,60	4140	400	38,60	3,59	1,09	10,42	5,00	60,03	3,50	8,19	2,15	8,81	16,00
75	1045	6		CTF	24.des.01	1180,0	3,26		36,5	25,0	0,22	6,80	1610	140	10,80	1,63	0,45	6,15	1,45	25,83	1,28	3,46	0,57	2,66	10,00
76	197	7		CTF	19.mar.01	450,0	3,69		34,4	25,0	0,58	30,50	2470	330	39,60	3,80	1,93	14,34	8,58	49,67	4,81	7,73	1,38	17,20	30,00
77	282	7		CTF	16.apr.01	1420,0	3,79		23,6	25,0	0,337	18,40	1200	130	13,09	1,88	0,62	6,66	3,10	27,44	1,04	2,95	0,45	4,60	6,00
78	367	7		CTF	14.mai.01	3330,0	4,06		15,5	25,0	0,25	16,20	480	50	5,79	0,94	0,50	4,66	3,95	12,61	0,94	1,86	0,27	6,22	4,00
79	452	7		CTF	11.jun.01	5560,0	4,46		12,3	25,0	0,224	12,90	420	50	5,34	0,85	0,09	3,40	2,52	11,13	0,85	1,28	0,18	4,25	172,00
80	537	7		CTF	09.jul.01	1080,0	3,69		28,6	25,0	0,267	16,70	1850	140	13,60	2,25	0,17	8,09	5,99	26,56	1,11	2,62	0,42	7,44	27,00
81	622	7		CTF	06.aug.01	3100,0	5,49		12,2	25,0	0,368	29,80	390	130	6,15	1,09	0,10	5,53	2,95	9,83	0,78	2,39	0,39	5,99	3,00
82	707	7		CTF	03.sep.01	1580,0	3,71		32,9	25,0	0,376	19,40	1620	170	18,40	2,65	0,40	6,38	8,12	29,98	1,77	3,69	0,51	10,31	405,00
83	792	7		CTF	01.okt.01	1540,0	3,98		30,1	25,0	0,358	21,30	1156	114	23,94	2,39	0,28	6,46	6,70	32,55	1,60	3,52	0,60	8,44	18,00
84	877	7		CTF	29.okt.01	2340,0	3,30		23,4	25,0	0,26	12,30	1880	130	13,84	1,80	0,20	6,71	3,31	26,27	1,30	3,39	0,44	4,33	6,00
85	962	7		CTF	26.nov.01	465,0	3,01		79,4	25,0	0,458	19,20	4510	420	44,66	3,91	1,03	15,75	7,37	70,37	4,30	9,40	2,09	11,60	15,00
86	1047	7		CTF	24.des.01	660,0	3,07		62,6	25,0	0,316	10,90	2740	230	21,00	2,59	1,04	10,34	2,05	39,97	2,08	6,12	1,26	4,84	27,00
87	[illegible]						[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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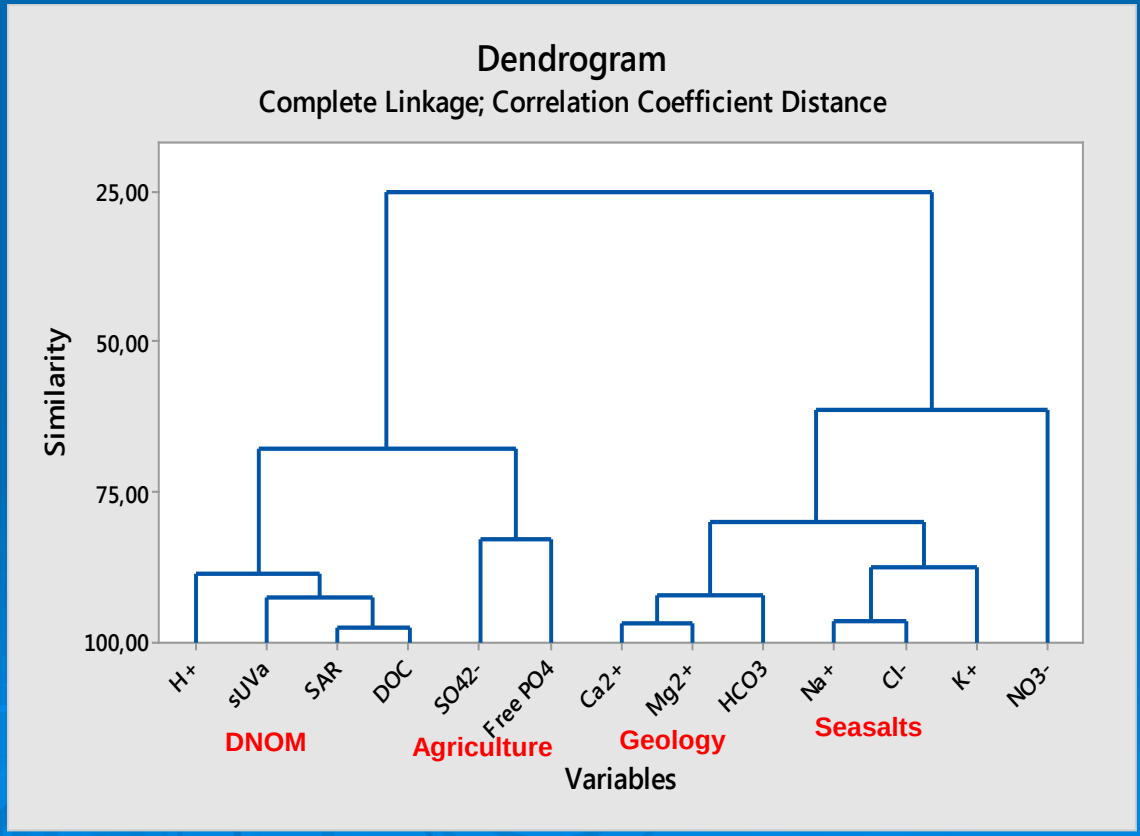
91	187	A		FTF	19.mar.01	580,0	4,76		18,9	25,0	0,271	15,50	970	220	15,82	2,02	0,71	9,13	3,02	19,34	1,61	5,06	0,48	5,38	10,00
92	527	A		FTF	09.jul.01	840,0	5,01		9,7	25,0	0,201	11,40	350	70	4,54	0,94	0,03	3,37	2,47	9,34	0,62	1,27	0,13	4,01	69,00
93	697	A		FTF	03.sep.01	880,0	4,34		19,0	25,0	0,335	18,50	820	120	12,82	1,82	0,22	6,04	4,03	18,63	1,38	2,69	0,35	6,80	17,00
94	782	A		FTF	01.okt.01	1010,0	4,18		18,9	25,0	0,244	12,70	610	40	13,29	1,58	0,14	4,94	4,89	18,96	1,28	2,09	0,40	5,63	56,00
95	867	A		FTF	29.okt.01	2180,0	3,97		15,9	25,0	0,218	12,60	650	340	8,62	1,46	0,25	6,07	2,65	13,83	0,87	2,72	0,26	3,46	79,00
96	952	A		FTF	26.nov.01	490,0	3,49		38,4	25,0	0,31	12,40	2250	160	24,60	2,64	0,57	9,47	4,34	37,40	2,59	6,02	1,41	6,57	11,00
97	1037	A		FTF	24.des.01	960,0	3,71		19,2	25,0	0,202	7,50	840	50	8,49	1,30	0,53	5,42	1,30	13,39	0,98	2,83	0,39	2,37	9,00
98	188	B		FTF	19.mar.01	400,0	3,81		44,0	25,0	0,5	29,90	3150	580	32,88	4,31	1,79	21,50	7,78	45,13	4,74	8,94	1,31	15,20	0,00
99	[illegible]						[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

All data / Statistics / Table 1 / 2001 - 2002 / 2001 - 2003

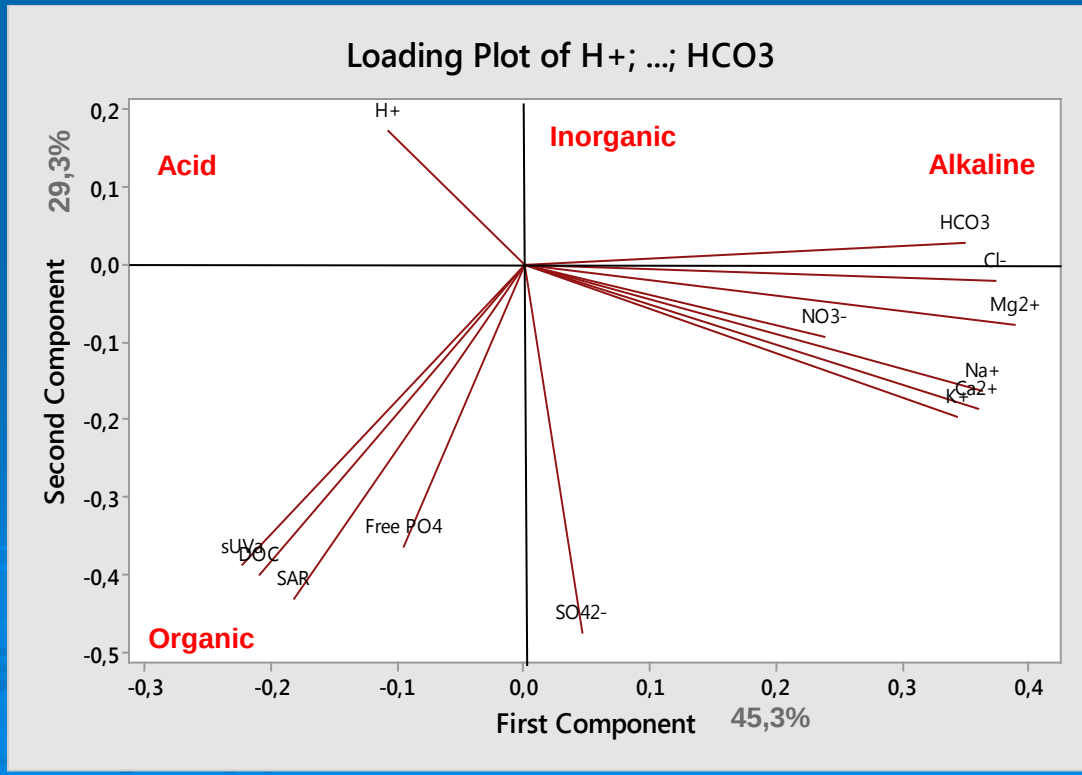
Cluster analysis

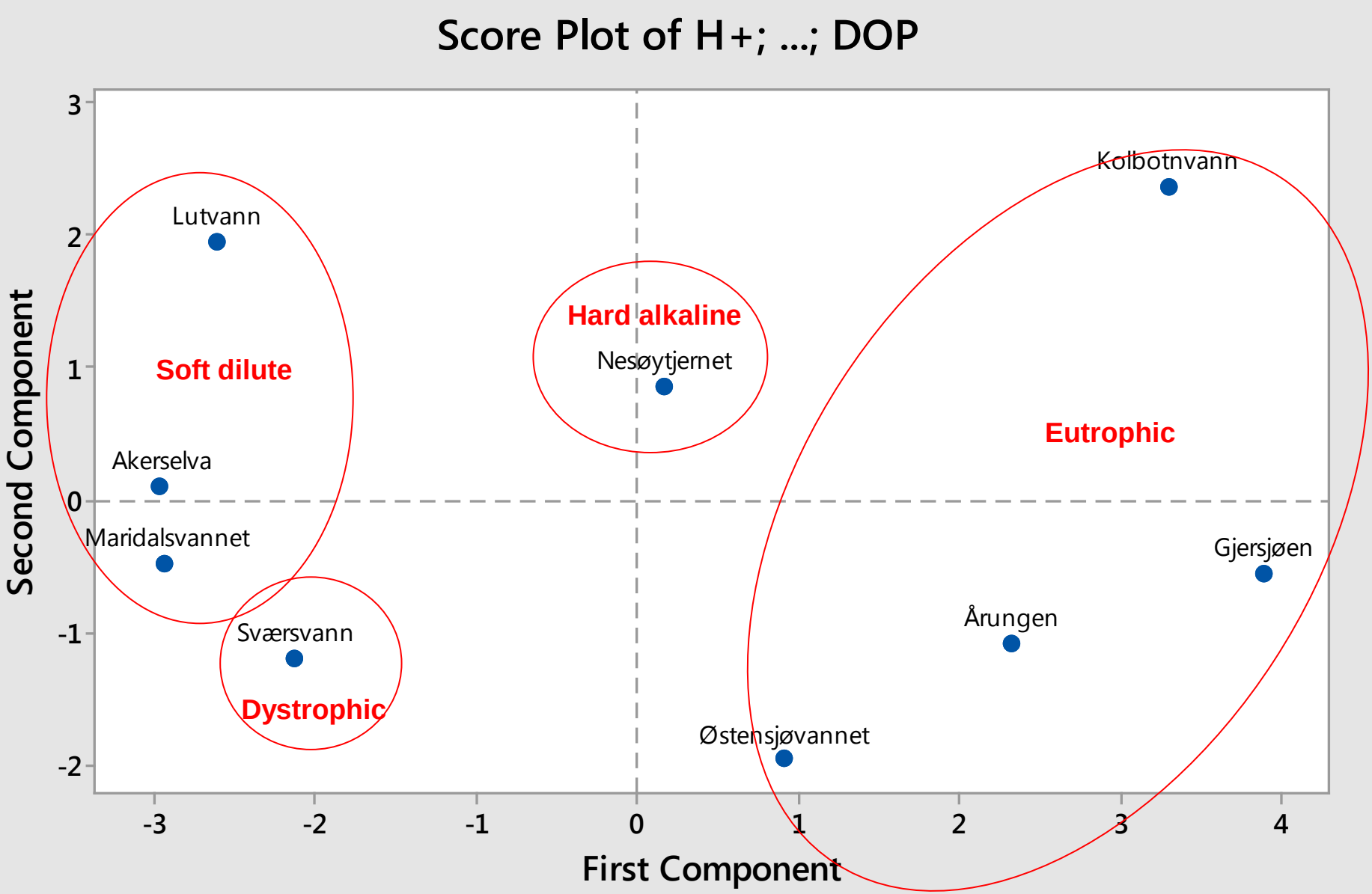
- Organizing parameters that co-variate in clusters
  - Identify
    - Links between parameters and groups of parameters
    - Identify key explanatory factors
    - General patterns

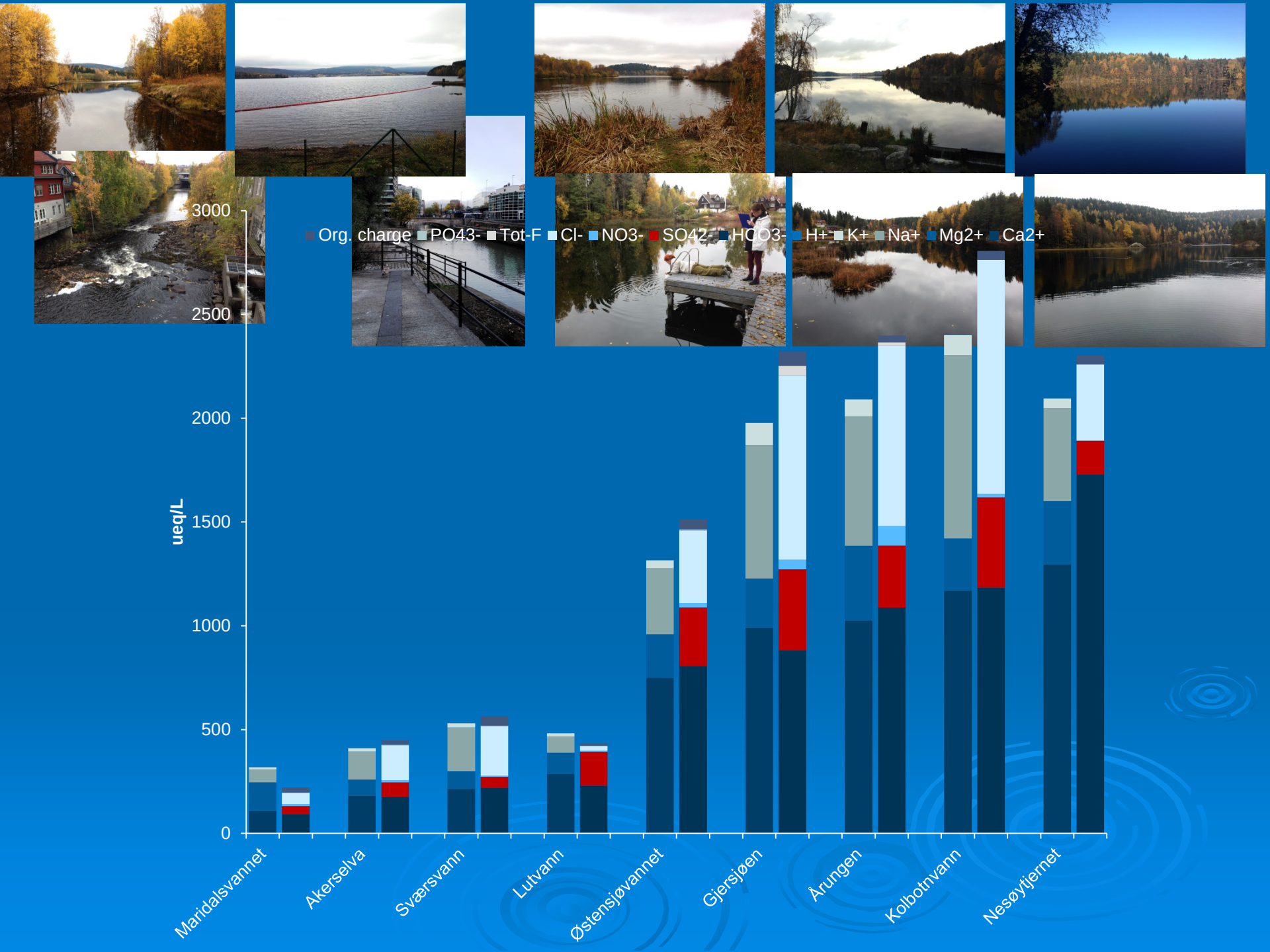


Principal Component Analysis

- Makes an n-dimential graph of your n parameters
- Identifies the greatest variation in the swarm of data points and draws the PC1 through its axis.
- Identifies the next PC perpendicular to the previous
- Produce loading plots that are projections of the points to the PC plane



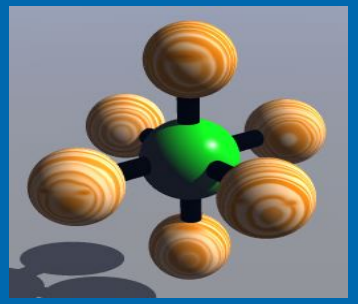

Score Plot of H+; ...; DOP
Second Component
First Component
3
2
1
0
-1
-2
-3
-2
-1
0
1
2
3
4
Lutvann
Akerselva
Maridalsvannet
Sværsvann
Nesøytjernet
Kolbotnvann
Gjersjøen
Årungen
Østensjøvannet
Soft dilute
Dystrophic
Hard alkaline
Eutrophic


Org. charge
PO43-
Tot-F
Cl-
NO3-
SO42-
HCO3-
H+
K+
Na+
Mg2+
Ca2+
ueq/L
3000
2500
2000
1500
1000
500
0
Maridalsvannet
Akerselva
Sværsvann
Lutvann
Østensjøvannet
Gjersjøen
Årungen
Kolbotnvann
Nesøytjernet

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

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

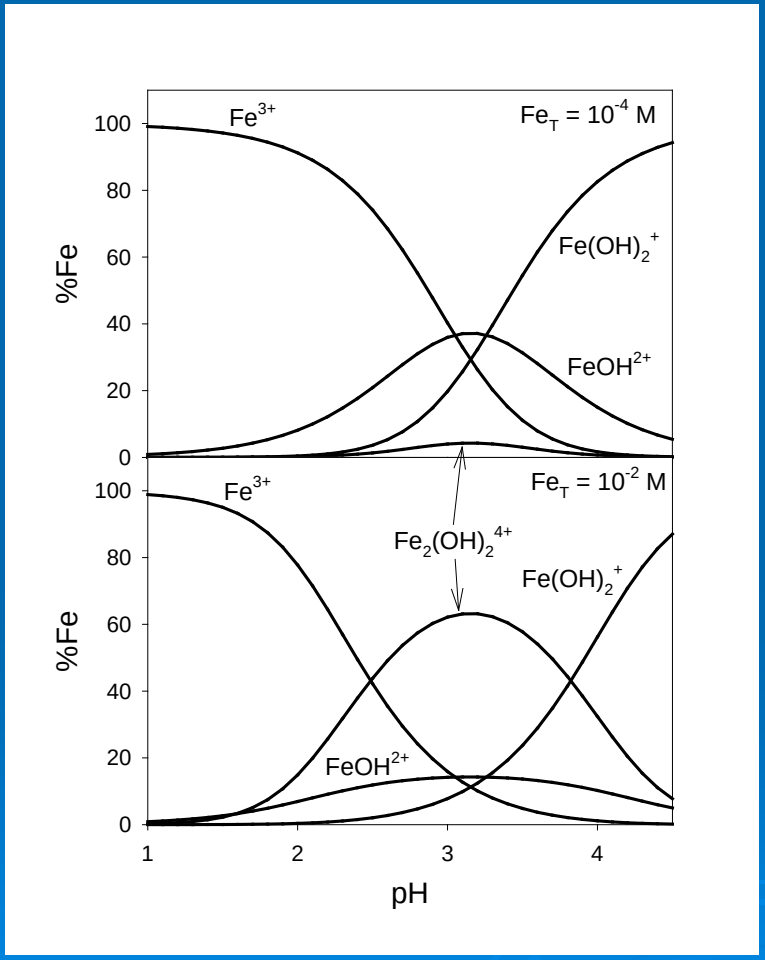
$$Al^{3+}_{aq} + H_2O \leftrightarrow Al(OH)^{2+}_{aq} + H^+ \qquad pK_1 = 4.95$$
$$Al(OH)^{2+}_{aq} + H_2O \leftrightarrow Al(OH)_2{}^{+}_{aq} + H^+ \qquad pK_2 = 5.6$$
$$Al(OH)_2{}^{+}_{aq} + H_2O \leftrightarrow Al(OH)_3{}^{0}_{aq} + H^+ \qquad pK_3 = 6.75$$
$$Al(OH)_3{}^{0}_{aq} + H_2O \leftrightarrow Al(OH)_4{}^{-}_{aq} + H^+ \qquad pK_4 = 5.6$$

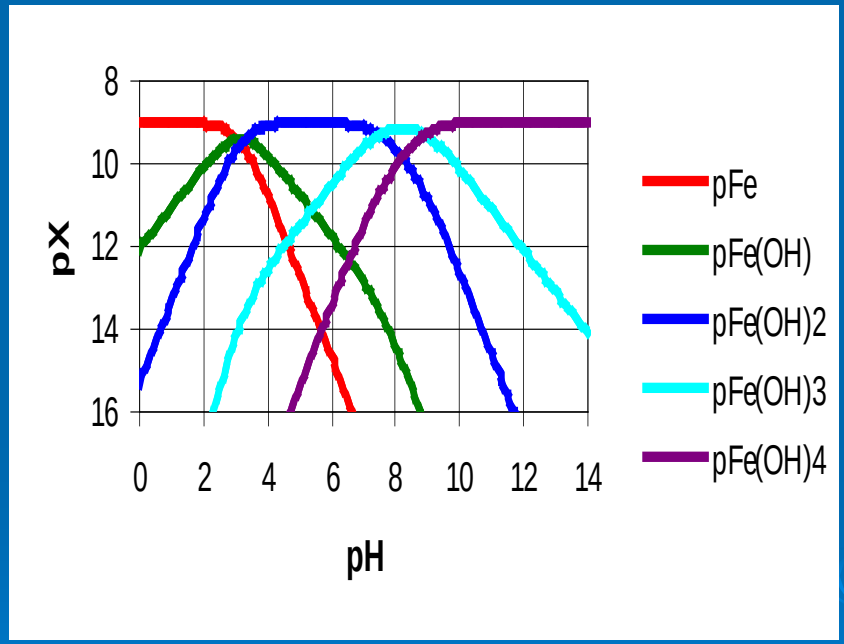
$$Al^{3+}_{aq} + H_2O \leftrightarrow Al(OH)^{2+}_{aq} + H^+ \qquad p\beta_1 = pK_1 = 4.95$$
$$Al^{3+}_{aq} + 2H_2O \leftrightarrow Al(OH)_2{}^{+}_{aq} + 2H^+ \qquad p\beta_2 = pK_1 + pK_2 = 10.55$$
$$Al^{3+}_{aq} + 3H_2O \leftrightarrow Al(OH)_3{}^{0}_{aq} + 3H^+ \qquad p\beta_3 = pK_1 + pK_2 + pK_3 = 17.25$$
$$Al^{3+}_{aq} + 4H_2O \leftrightarrow Al(OH)_4{}^{-}_{aq} + 4H^+ \qquad p\beta_4 = pK_1 + pK_2 + pK_3 + pK_4 = 22.85$$

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

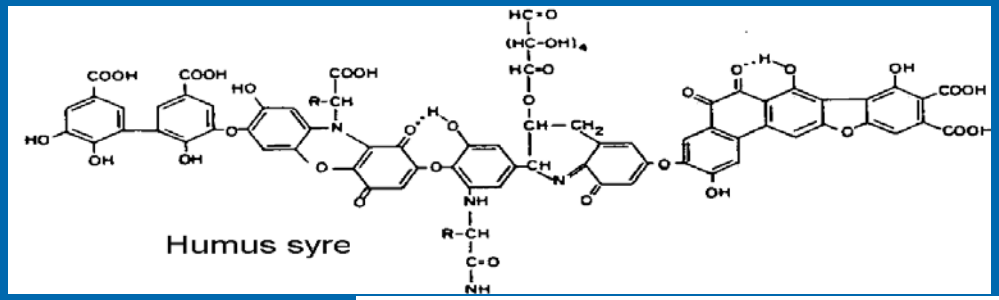




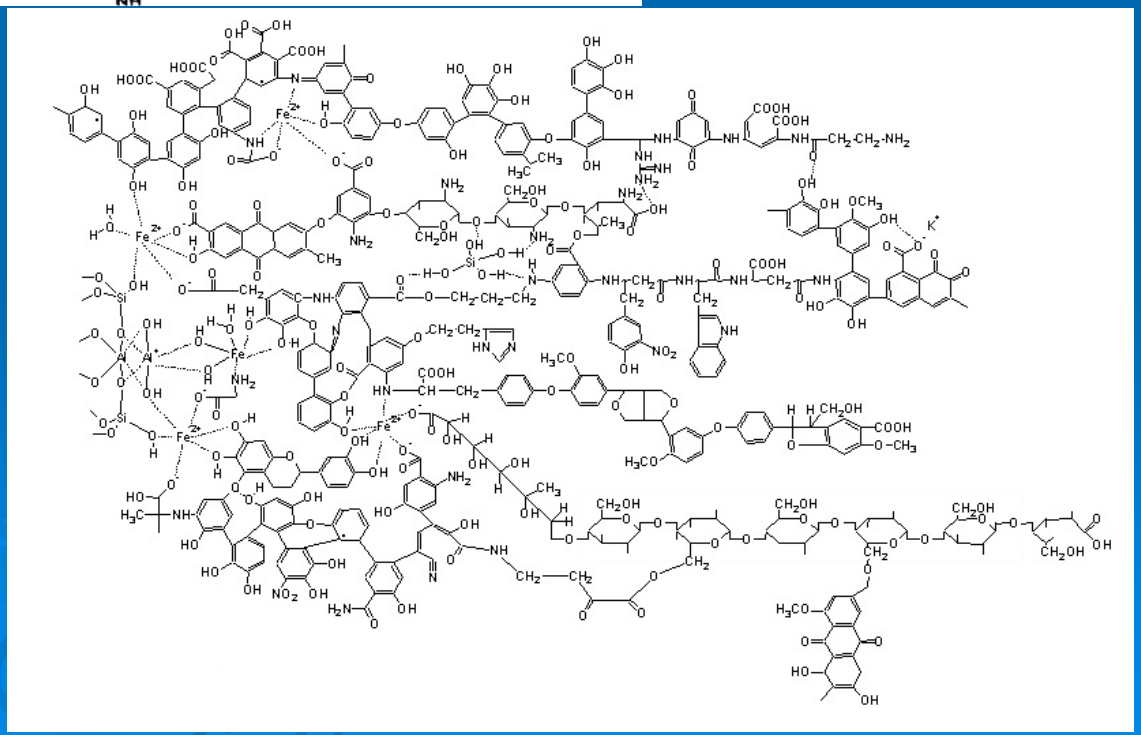
Distribution diagrams

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

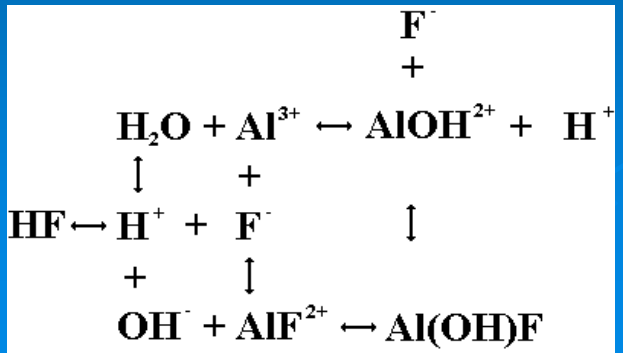


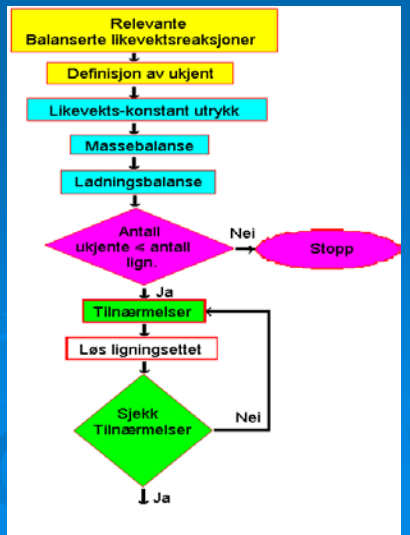
- Measured by TOC/DOC
  - Or by UV absorbency or colour

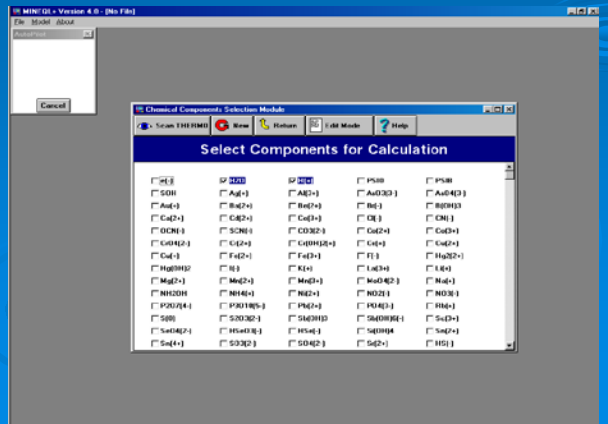
Speciation with different ligands present

- 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

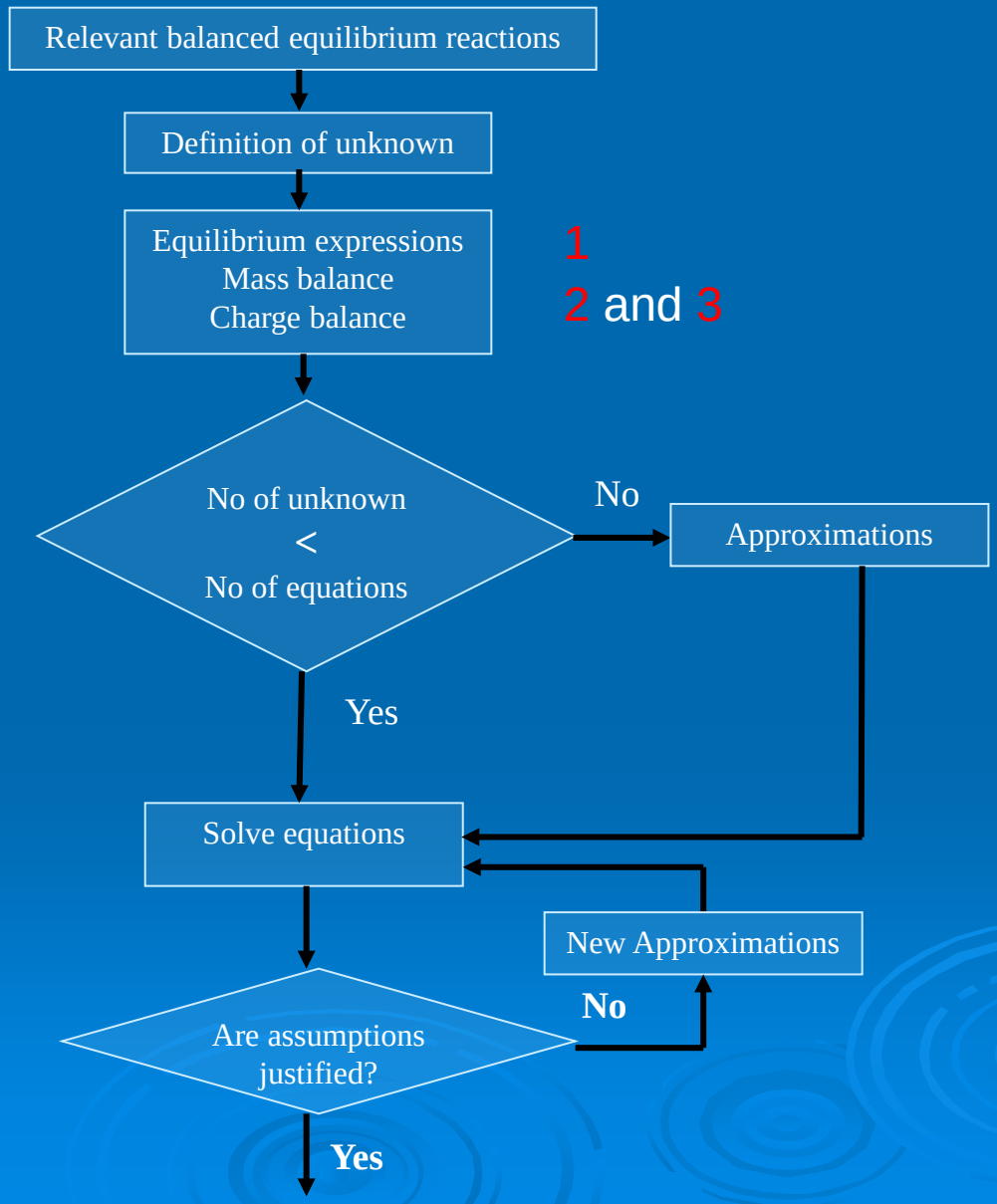
E.g. simple system with only Al^{3+} and F^-







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

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

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

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

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

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

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

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

2. Mass balance

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

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

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

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.;

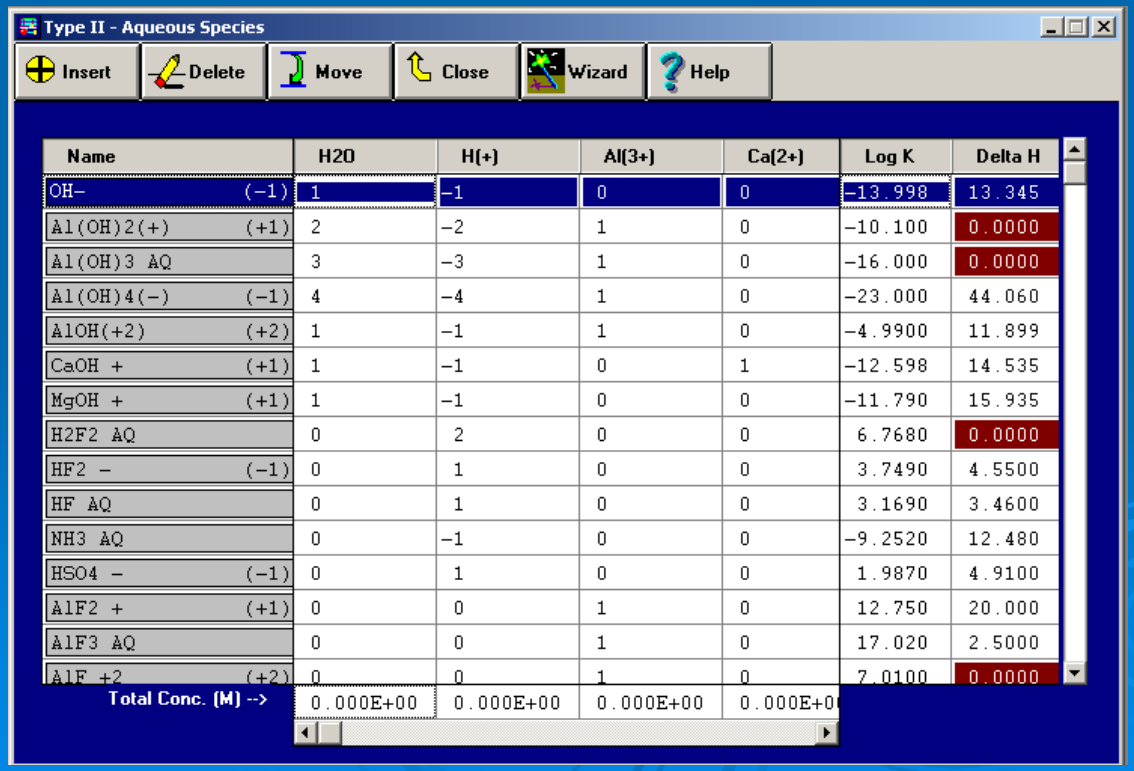
$$Fe(OH)_2{}^{+} = \frac{\beta_2 \{Fe^{3+}\}}{\{H^+\}^2}$$

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

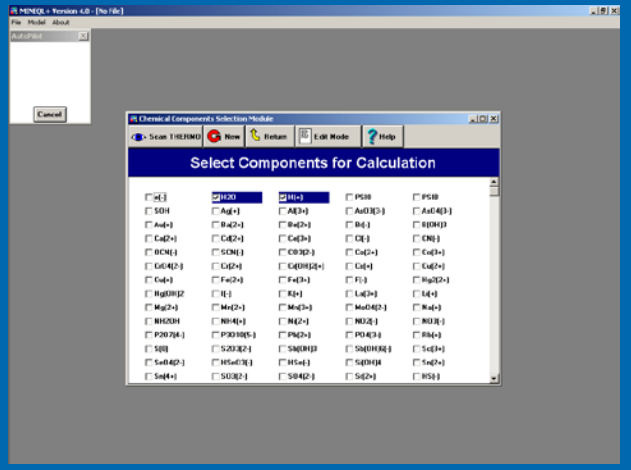
- The equilibrium model is based on a choice of complexes and their stability constants, which makes the results questionable



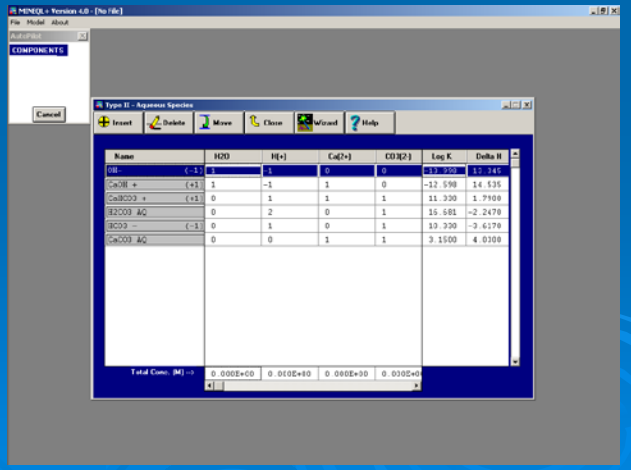
Name	H2O	H(+)	Al(3+)	Ca(2+)	Log K	Delta H
OH- (-1)	1	-1	0	0	-13.998	13.345
Al(OH)2(+) (+1)	2	-2	1	0	-10.100	0.0000
Al(OH)3 AQ	3	-3	1	0	-16.000	0.0000
Al(OH)4(-) (-1)	4	-4	1	0	-23.000	44.060
AlOH(+2) (+2)	1	-1	1	0	-4.9900	11.899
CaOH + (+1)	1	-1	0	1	-12.598	14.535
MgOH + (+1)	1	-1	0	0	-11.790	15.935
H2F2 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+00		

Tutorial

- Start out by choosing components that define your system

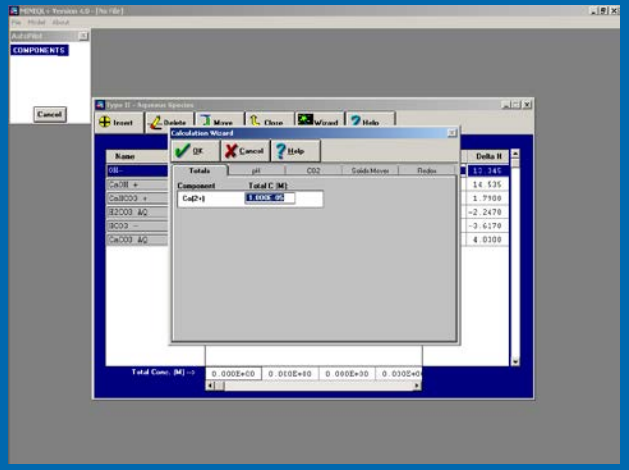


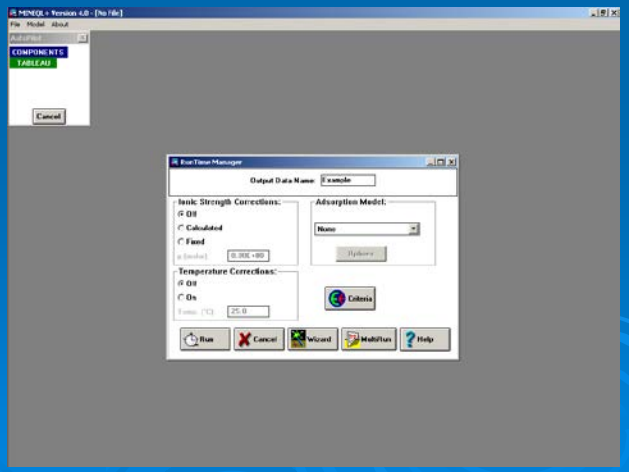
- Find thermodynamic constants in database in ”Scan Thermo”



Tutorial

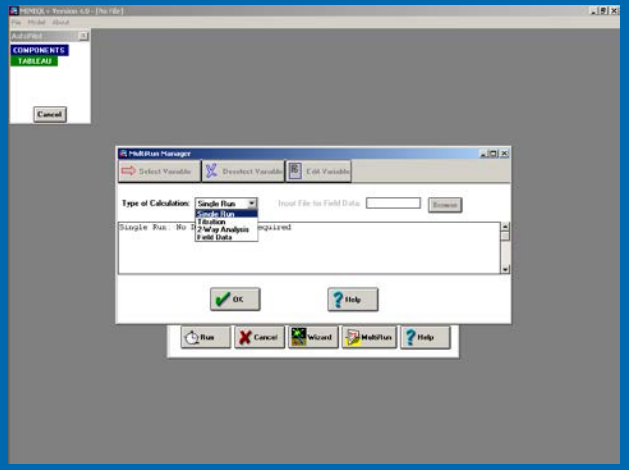
- The Calculation Wizards Tool is a collection of **5** input options to describe the chemistry of the system
- Running the calculation

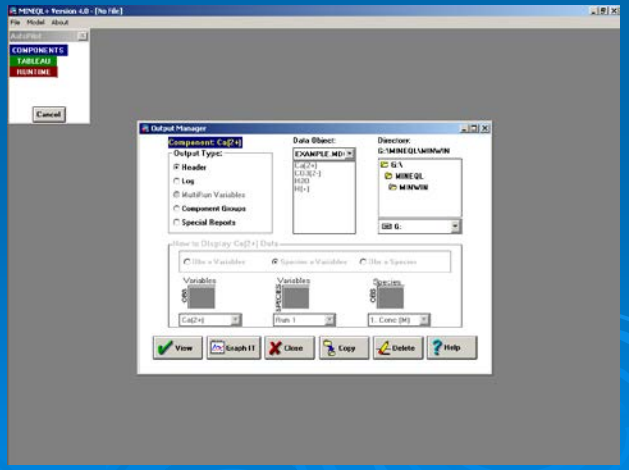




Tutorial

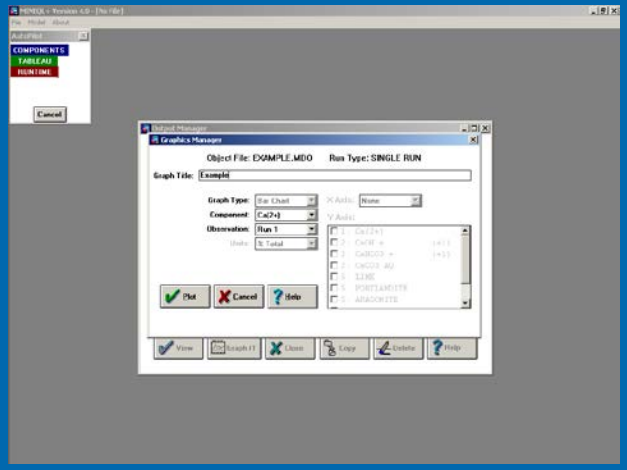
- Multirun manager
  - Titration
  - 2 way analysis
  - Field data
- Output manager
  - Types of Output
    - The Header
    - The Log
    - The MultiRun Table
    - Component Groups
    - Special Reports



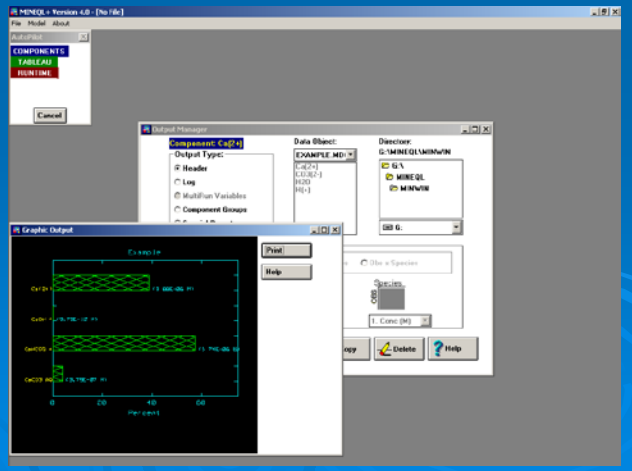


Tutorial

- Graphics manager
  - Bar and X-Y plots



- Run through the 4 problems



Report

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