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# Introduction to hydrogeochemical data evaluation and modeling (*AquaChem, Phreeqc*)

## Part 1

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## Lectures Outline

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- Aqueous geochemical data management
  - Creation of a hydrogeochemical database
  - Graphical illustration of hydrochemical data
  - Simple hydrochemical calculations (e.g. unit conversation, simple mixing...)
- Geochemical Modeling
  - General Approach
  - Modeling Resources
  - Speciation
  - Batch-Reaction
  - One-Dimensional Transport
  - Inverse Geochemical Calculations

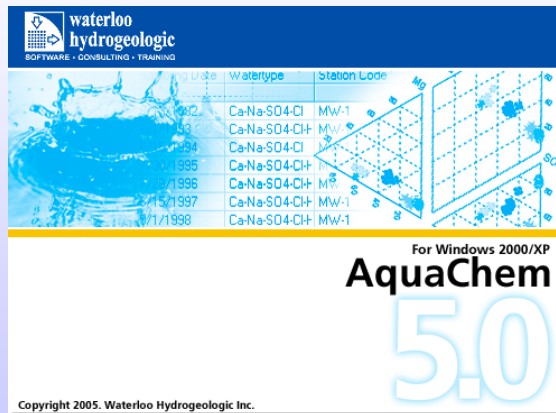
## Useful programs

- **Standard Software**
  - e.g. Excel, Access, ...
    - Easily available but limited possibilities for scientific graphic
- **Special Scientific Software**
  - e.g. Origin, SigmaPlot, MatLab, ....
    - Improved graphic possibilities, but expensive
    - No possibilities for geochemical modelling
- **Special Software for Aqueous Geochemistry**

## Special Geochemical Software

- **Freeware** (USGS, EPA...)
  - NETPATH, **PHREEQC**, **PHREEQCI**, PHRQPITZ, WATEQ4F, MINTEQA2,...
- **Commercial programs** (Rockware; [www.rockware.com](http://www.rockware.com))
  - **AquaChem 5.0®**, price **US\$ 392.50** (Academic Single License)
  - **The Geochemist's Workbench 5.0®**, price \$1599 (Academic License)
    - GWB 5.0 is a set of interactive software tools for solving problems in aqueous geochemistry, including those encountered in environmental protection and remediation, the petroleum industry, and economic geology.
  - **GWB Essentials®**, price \$ 599 (Academic License)
    - GWB Essentials, includes the fundamental tools from GWB 5.0 for work in aqueous geochemistry (e.g. balance chemical reactions, redox-pH and activity diagrams, solution speciation, mineral saturation, plot Piper, Stiff and other aqueous geochemistry diagrams
  - ....

# AquaChem 5.0



## AquaChem - Introduction

### AquaChem

- is a software package developed specifically for graphical and numerical analysis and modeling of water quality data.
- features a fully customizable database of physical and chemical parameters.
- provides a comprehensive selection of analysis tools, calculations and graphs for interpreting, plotting and modeling water quality data.

## AquaChem – Analysis tools

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- AquaChem's analysis tools include:
  - simple unit transformations,
  - charge balances,
  - statistics
  - sample mixing
  - common geochemical calculations
  - correlation matrices
  - geothermometer calculations.

## AquaChem - Data Management

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- Database
  - AquaChem utilizes an MSAccess™ relational data management system and is capable of supporting an unlimited number of parameters.
  - Data Querying and Filtering
  - Two-click access to user-defined data filters for fast isolation and retrieval of selected samples.
- Water Quality Standards
  - Comes with built-in standards from WHO, USEPA, and CCME
- Importing Data
  - Fast, flexible, and easy data entry using tabular views of multiple samples, form views of individual samples, or using the improved data import wizard with automatic matching of CAS Registry Numbers

## AquaChem - Plotting

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- AquaChem - Selection of graphical techniques for representing and interpreting aqueous geochemical data:
  - **Correlation plots:** X-Y Scatter, Ludwig-Langelier, and Wilcox
  - **Summary plots:** Frequency Histogram, Depth Profile, Schoeller, Box and Whisker, Meteoric Water Line, Quantile plot
  - **Trilinear plots:** Piper, Durov, Ternary, and Giggensch
  - **Time-Series plot:** Multiple parameters for a selected station, or a single parameter for multiple stations
  - **Geothermometer plot**
  - **Sample plots:** Radial, Stiff, and Pie
  - **Thematic Map plots:** Bubble, Pie, Radial and Stiff plots at sample locations

## AquaChem - Geochemical modeling

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- Direct link to PHREEQC
  - to calculate the saturation indices, activities or pH for selected water quality samples and seamlessly save the results back into the AquaChem sample database
- Built-in link to the USGS PHREEQC-Interactive program
  - for complex water quality modeling using solutions generated from AquaChem samples

## AquaChem - Overview

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- Installation of the program
  - Hardware Requirements
  - A free demo is available from:  
<http://www.rockware.com/catalog/pages/aquachem.html>
- AquaChem - Main screen
- Other basic screens
  - Input-, text and graphic screen
- Demo database
  - Structure of the database

## Hardware Requirements

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- To run AquaChem you will need the following minimum system configuration:
  - A CD-ROM drive for software installation
  - A hard drive, with at least 35 MB free space
  - A local or network printer installed
  - A Pentium processor or better, with 32 MB RAM
  - Windows 98/2000/XP, or Windows NT 4.0 with Service Pack 4 (or later) installed
  - A Microsoft compatible mouse
  - Minimum 1024 x 768 screen resolution
  - Normal fonts

# Starting AquaChem

## ● Starting AquaChem

- To start AquaChem, you must have it installed on your hard disk.
- Start AquaChem by access in WHI Software/Aquachem 5.0 from your Start > Programs Windows menu. The Open Database dialogue box will be displayed prompting you to choose an existing AquaChem database.
- Select the **Demo.aqc** file to open the demonstration database

# AquaChem - Main window

Main Toolbar

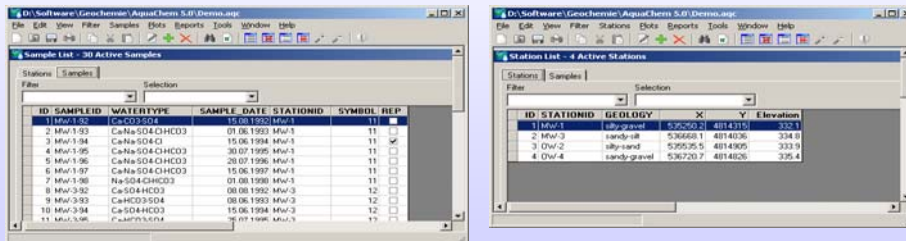
Main Menu Bar

Active Samples/  
Stations  
Window

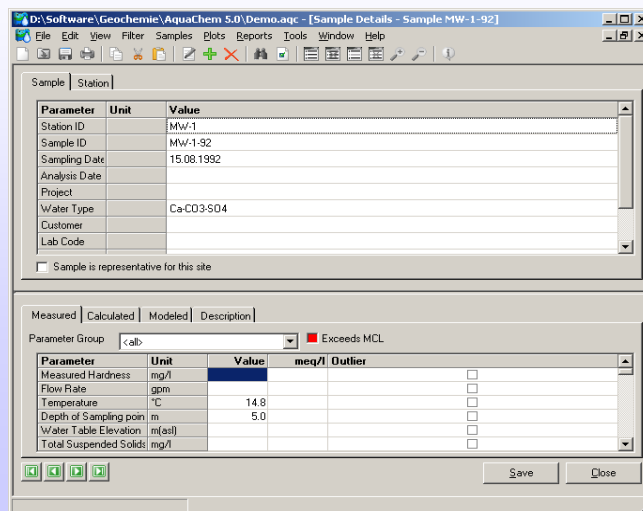
ID	SAMPLEID	WATERTYPE	SAMPLE_DATE	STATIONID	SYMBOL	REP
1	Mw-1-92	CaCO3-SO4	15.08.1992	Mw-1	11	<input type="checkbox"/>
2	Mw-1-93	Ca-Na-SO4-Cl-HCO3	01.06.1993	Mw-1	11	<input type="checkbox"/>
3	Mw-1-94	Ca-Na-SO4-Cl	15.06.1994	Mw-1	11	<input checked="" type="checkbox"/>
4	Mw-1-95	Ca-Na-SO4-Cl-HCO3	30.07.1995	Mw-1	11	<input type="checkbox"/>
5	Mw-1-96	Ca-Na-SO4-Cl-HCO3	28.07.1996	Mw-1	11	<input type="checkbox"/>
6	Mw-1-97	Ca-Na-SO4-Cl-HCO3	15.06.1997	Mw-1	11	<input type="checkbox"/>
7	Mw-1-98	Na-SO4-Cl-HCO3	01.08.1998	Mw-1	11	<input type="checkbox"/>
8	Mw-3-92	Ca-SO4-HCO3	08.08.1992	Mw-3	12	<input type="checkbox"/>
9	Mw-3-93	Ca-HCO3-SO4	08.06.1993	Mw-3	12	<input type="checkbox"/>
10	Mw-3-94	Ca-SO4-HCO3	15.06.1994	Mw-3	12	<input type="checkbox"/>
11	Mw-3-95	Ca-HCO3-SO4	25.07.1995	Mw-3	12	<input type="checkbox"/>
12	Mw-3-96	Ca-HCO3-SO4	02.08.1996	Mw-3	12	<input type="checkbox"/>
13	Mw-3-97	Ca-HCO3-SO4	06.06.1997	Mw-3	12	<input checked="" type="checkbox"/>
14	Mw-3-98	Ca-HCO3-SO4	30.07.1998	Mw-3	12	<input type="checkbox"/>
15	OW-2-92	Na-Cl	01.08.1992	OW-2	13	<input type="checkbox"/>
16	OW-2-93	Na-Ca-Cl-SO4	05.06.1993	OW-2	13	<input type="checkbox"/>
17	OW-2-94	Na-Ca-Cl-SO4	12.06.1994	OW-2	13	<input type="checkbox"/>
18	OW-2-95	Na-Ca-Cl-SO4	01.07.1995	OW-2	13	<input checked="" type="checkbox"/>

# Active Sample/Stations window

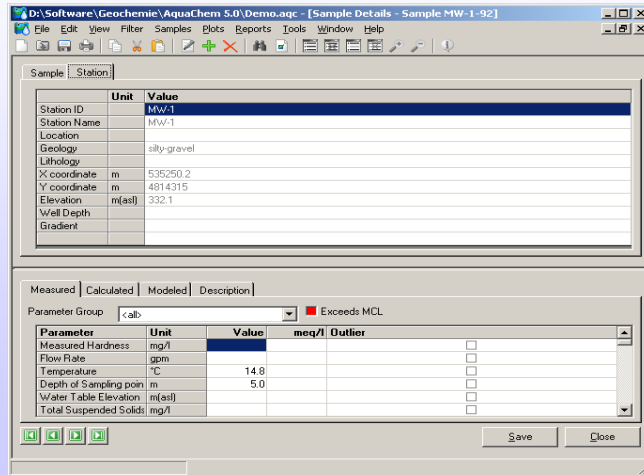
## Samples and Stations



# Sample Details Window



# Station Details Window



# Data Input

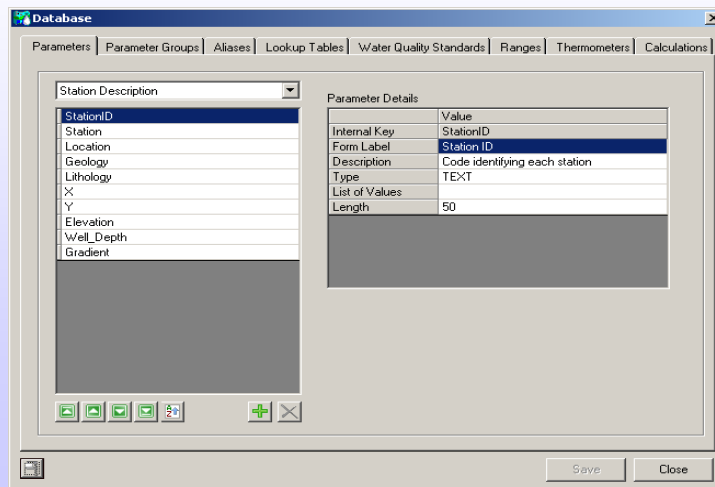
- Data can be entered into the \*.aqc database file by either;
  1. Importing a MS Excel or a tab-delimited ASCII text file;
  2. Using the **input** window, or
  3. Using the **spreadsheet** window.



# AquaChem - Database

- In an AquaChem database there are four categories of parameters:
  - Station Description Parameters
    - station name, ID, location, area, X,Y coordinates, elevation, well depth ...
  - Sample Description Parameters
    - sample ID, geology, sampling date, etc
  - Measured Parameters
    - ex. concentrations for cations, anions, organic contaminants, pH, TDS, etc.).
  - Modeled Parameters
    - Modeled Parameter values are calculated by PHREEQC

## Database - Parameter Details



## How to look at a set of geochemical data with AquaChem

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- **Creating of a hydrochemical data base**

- Check analytical data
- Visual graphics
- Simple calculations
- Thermodynamic calculations
- Geochemical reaction path modeling

## How to look at a set of geochemical data with AquaChem

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- Creating of a hydrochemical data base

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## Analytics

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- Have all **major solutes**?
- Do **electrochemical balance**. If bad figure out why.
- Can you make assumptions based on probable water-rock interaction.
- **pH, water temperature**--master variables.
  - If you don't have it, you can't make geochemical modelling

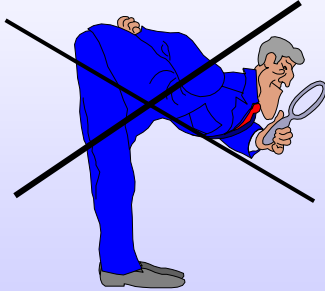
## Analysis control - Introduction

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How good are the chemical data from the Lab?

You didn't think YOU were going to do the analyses, did you?

## Analysis control - What about quality control / quality assurances?



- The analyses were done **randomly**
- The analyses were done according to **"cookbook"**
- The analyses were very often not investigated for **reasonableness**

## Solutes in groundwater

There are major, minor, and trace solutes in groundwater!

### Major (> 5 mg/L)

Ca, Mg, Na, HCO<sub>3</sub>, SO<sub>4</sub>, Cl, Si

### Minor (0.01-10 mg/L)

B, Fe, NO<sub>3</sub>, NH<sub>4</sub>, K, Sr, Mn

### Trace (<0.01 mg/L)

The Rest!!

# Analysis control

## Oxygenated

Calcium  
Magnesium  
Sodium  
Potassium  
Bicarbonate  
Sulfate  
Chloride

## Anoxic

Calcium  
Magnesium  
Sodium  
Potassium  
Bicarbonate  
Chloride  
Sulfide

Iron  
Manganese  
Barium  
Strontium  
Ammonium

## View data as Spreadsheed

The screenshot shows a software window titled 'Data View - Carbon Isotope Analysis - 8.0.0 DataView'. The main area displays a spreadsheet with columns for parameters, sample codes, station codes, pH, TDS, conductivity, temperature, and various chemical elements (Al, Fe, Cu, Mg, Ca, SO4, HCO3, F, Barium, Tokame, Ethylbenzene, Xylene, Vinyl chloride). The data is organized into rows for different samples, with some cells highlighted in red to indicate specific values or anomalies.

Parameter	Sample Code	Sampling Date	Station Code	pH	TDS	El. Conductivity	Temperature	Al	Fe	Cu	Mg	Ca	SO4	HCO3	F	Barium	Tokame	Ethylbenzene	Xylene	Vinyl chloride	
1	Mw-1-92	15/08/1992	Mw-1	7.15	726	1200	14.6	80	1.5	125	22	125	950	125							
2	Mw-1-93	01/08/1993	Mw-1	7.40	1132	1170	19.5	60	1.4	135	28	121	325	104							
3	Mw-1-94	15/08/1994	Mw-1	7.50	1474	1470	15.0	88	2.5	135	23.4	128	325	135	0.01						
4	Mw-1-95	30/07/1995	Mw-1	7.50	1345	1295	13.0	81	1.5	115	26.9	119	215	102.5							
5	Mw-1-96	20/07/1996	Mw-1	7.30	1260	1270	14.2	76	2	105	26.2	115	254	144							
6	Mw-1-97	15/08/1997	Mw-1	7.50	1000	1225	14.0	72	1.8	110	18.3	160	221.5	145							
7	Mw-1-98	01/08/1998	Mw-1	6.99	1105	1310	15.0	75	1.7	110	17.5	111	215.8	126							
8	Mw-1-92	01/08/1992	Mw-3	7.40	620	674	14.0	50	2	256	19	40	360	403							
9	Mw-1-93	01/08/1993	Mw-3	7.30	680	729	15.0	35	2.5	268	20.4	42	346	503							
10	Mw-1-94	15/08/1994	Mw-3	6.80	660	660	12.0	53	1.6	205	19	60	376	459							
11	Mw-1-95	25/07/1995	Mw-3	7.50	480	568	13.0	39	1.7	275	12.5	30	340	493							
12	Mw-1-96	02/08/1996	Mw-3	7.20	464	504	12.9	20	1.5	279	11.8	45	340	432							
13	Mw-1-97	06/06/1997	Mw-3	7.30	700	741	14.8	45	2.5	286	18.2	32	351	500.5							
14	Mw-1-98	30/07/1998	Mw-3	7.40	680	749	13.9	62	2.89	21.6	45	374	601								
15	Dw-2-92	01/08/1992	Dw-2	7.25	1155	1140	14.1	225	1.1	115	5	206	130.5	140.2							
16	Dw-2-93	05/06/1993	Dw-2	7.55	1060	1190	15.4	235	1.3	117.6	23.3	320	315	152.5							
17	Dw-2-94	12/08/1994	Dw-2	7.30	1100	1200	15.7	145	1.5	126	20.7	251	205.2								
18	Dw-2-95	21/07/1995	Dw-2	7.30	1079	1230	15.1	242	1.3	132	21.9	258	300.8	149.8							
19	Dw-2-96	24/07/1996	Dw-2	7.10	1240	1240	15.2	240	1.5	162	24	240	410	125							
20	Dw-2-97	01/06/1997	Dw-2	7.30	1500	1100	15.7	251	2.5	124	23	261	299	146							
21	Dw-2-98	24/07/1998	Dw-2	7.15	1514	1660	15.7	200	1	105	21.4	296	379.2	152.5							
22	Dw-4-92	15/07/1992	Dw-4	7.05	1500	1202	14.5	6.5	2	323	17.6	6.9	732	141.5	.15						
23	Dw-4-93	25/05/1993	Dw-4	7.25	1300	1310	13.9	10	2	324	20.6	12	725	144							
24	Dw-4-94	23/05/1994	Dw-4	7.35	994	1100	14.6	3.1	1.3	203.6	20.6	2.8	560	145.2							
25	Dw-4-95	12/06/1995	Dw-4	6.95	995	1130	12.0	6	2.1	273.6	22.1	8	590	151.3							
26	Dw-4-96	25/07/1996	Dw-4	7.00	1050	1090	15.0	15	2.2	265	20.2	11	550	145.2							
27	Dw-4-97	15/06/1997	Dw-4	7.40	1070	1070	15.3	15	2.2	265	20.2	11	550	145.2							
28	Dw-4-98	12/07/1998	Dw-4	7.40	1040	1140	15.3	2.8	1.3	274	19.7	3	604	152.5							
29	Dw-4-99	12/07/1999	Dw-4	7.40	1040	1140	15.3	2.8	1.3	274	19.7	3	604	152.5							
30	Dw-4-99.3	12/07/1999	Dw-4	6.95	950	950	12.0	-2	-1	1.6	-1	-1	-1	1.2	+0.2						

## Electrical Neutrality

$$\sum_i m_i z_i = 0 \quad !!$$



$$\sum_i m_i^+ z_i^+ = \sum_n m_n^- z_n^-$$

- The sum of the positive charges in solutions must equal the sum of the negative ones!

## Introduction- Charge-balance error I

Aqueous solutions must be electrically neutral. In other words, the sum of all negative charges must equal the sum of all positive charges.

One check on the quality of a water analysis is the **charge-balance error**, calculated as follows:

$$\text{C.B.E.} = \frac{\sum m_c z_c - \sum m_a z_a}{\sum m_c z_c + \sum m_a z_a} \times 100$$

## Introduction- Charge-balance error II

- There is always some error in the measurement of cation and anion concentrations.
- Thus, we cannot expect a charge-balance error of zero for any analysis.
- The C.B.E. may be positive or negative, depending on whether cations or anions are more abundant.
- A reasonable limit for accepting an analysis as valid is  $\pm 5\%$ .

## Analysis control - Calculating electrochemical balance

1. Convert mg/L to mmol/L  $\frac{\text{mg/L}}{\frac{\text{gram formula}}{\text{weight}}} = \text{mmol/L}$
2. Convert mmol/L to meq/l  $\text{mmol/L} \times \text{charge (abs)}$
3. SUM Cations and SUM Anions
4. Apply formula

$$(0.5 \times)^1 \frac{\text{SumCat} - \text{SumAN}}{\text{SumCat} + \text{SumAN}} \times 100 = \% \text{ error}$$

<sup>1</sup> some EU-countries eg. Austria, Germany

# Analysis control - Electrochemical balance (example)

## Major ion composition

Ion	mg/l	mmol/l	meq/l	meq%
Na	5.75	0.25	0.25	0.425
K	2.0	0.051	0.051	0.087
Ca	530.0	13.224	26.447	44.951
Mg	32.1	1.32	2.641	4.489
Cl	10.6	0.299	0.299	0.508
SO4	1139.4	11.862	23.724	40.322
HCO3	323.4	5.3	5.3	9.008

Sum of Anions (meq/l) : 29.37

Sum of Cations (meq/l) : 29.46

Balance:  $100\% \times \frac{\text{Sum of Anions} - \text{Sum of Cations}}{1/2(\text{Sum of Anions} + \text{Sum of Cations})} = 0.2\%$

# Electrochemical balance - Aquachem

The screenshot shows the Aquachem software interface. The 'Sample Summary' window displays the following data:

Parameter	Value
Sample ID	
Sample Date	
Station	
Location	
Geology	silty-gravel
Watertype	Ca-Na-SO4-Cl-HCO3
Temperature (°C)	15.50
pH	7.40
Conductivity	1170.00 uS/cm
Sum of Anions	12.91 meq/L
Sum of Cations	11.88 meq/L
Balance	4.12 %
Total dissolved solids	838.31 mg/L
Total hardness	444.22 mg/l CaCO3
Alkalinity	130.08 mg/l CaCO3

# Electrochemical balance - Aquachem

Sample Designation: MW-1, 15.08.1992

Check	Attention Value	Analysis Value	Pass
Balance (C-A)/(C+A)*100	<5%	48.78	Fail
TDS: (Entered - calculated)/Entered*100	<5%	110.00	Fail
TDS: (Entered - TDS 180 calculated)/Entered*100	<5%	102.13	Fail
TDS Entered/Conductivity	55: ## <75%	51	Pass
Conductivity/sum MEQ Cations	90: ## <110%	103	Pass
K+/(Na+ + K+)	<20%	1	Pass
Mg++/(Ca++ + Mg++)	<40%	22	Pass
Ca++/(Ca++ + SO4--)	>50%	35	Fail
Na+/(Na+ + Cl)	>50%	50	Fail
SI Calcite	<0.2	n/a	
Test for results outside natural occurrence			
Cond	1000	1200	Fail
Mn	0.1	0.6	Fail

## Analysis control - Problems in electrochemical balance calculations

- Organic acids (RCOOH) add unanalyzed negative charge--high positive imbalances;
  - Ex: "Black" swamp waters
- Often won't work if "total" analyses are used;
- Are routinely (contract lab) difficult to get for ground-water with TDS <100 and TDS >5000 (..but there's no excuse!!!).

## REASONS FOR C.B.E. VALUES GREATER THAN $\pm 5\%$

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- An important anion or cation was not included in the analysis.
  - Sometimes this can point out the presence of a high concentration of an unusual anion or cation.
- A serious, systematic error has occurred in the analysis.
- One or more of the concentrations was recorded incorrectly.

## Analysis control - Acceptable error in analysis ?!

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- Typical consulting lab <20%
- USGS/EPA < 7%
- Research Lab <3%

## How to look at a set of geochemical data with AquaChem

---

- Creating of a hydrochemical data base
- Check analytical data
- **Visual graphics**
- Simple calculations
- Thermodynamic calculations
- Geochemical reaction path modeling

## Visual Graphics

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- Do you have only dilution or constant addition of solutes along flow path/in region of study?
  - do bivariate plots (or log solutes) of conservative major solute on axis and other solutes on ordinate: Cl, Br, Si, Mg, B, perhaps other candidates.
- Are the sources of non-redox trace metals the same in the study area:
  - e.g. bivariate metal plots such as Sr vs base metals; Ca versus Mg. Ask what minerals have trace amounts of metals in question.

## Bivariate Plots?

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- **They show water mixtures.**
- They identify dilution
- They can be statistically characterized
- They identify major chemical reactions

## Fundamental Bivariate Mixing Equation

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$$C_1 (1-n) + C_2 n = C_{\text{mix}}$$

**Where:**

**$C_1$  :** Concentration in water-1

**$C_2$  :** Concentration in water-2

**$n$  :** Percent (by volume) of water-2 per liter of water

**$1-n$  :** Percent (by volume) of water-1 per liter of water

## Simple mixing example

$C_1 = 10 \text{ mg/L}$

$C_2 = 250 \text{ mg/L}$

Mix = 75 mg/L

$$C_1(1-n) + C_2n = C_{\text{Mix}}$$

Solving for n..

$$n = \frac{(C_{\text{mix}} - C_1)}{(C_2 - C_1)}$$

$$n = (75-10)/(250-10) = 0.27$$

OR

27% of the mixture is water 2.

## Mixing calculations with AquaChem

- Mixes two samples from your database, in a step wise process

- Simple Mixing mode
- Optimize Mode

Mix Samples

Select Solutions

Mix 36 seawater Na-Cl seawater

With 37 rain Ca-NH4-SO4-HCO3 rain

Parameters: Na, K, Ca, Mg

Mode:  Simple Mixing,  Optimize

Simple Mixing

Add 0.1 to 0.5 Parts of Solution 1 to Solution 2

Number of Steps 5

Set Default OK Cancel

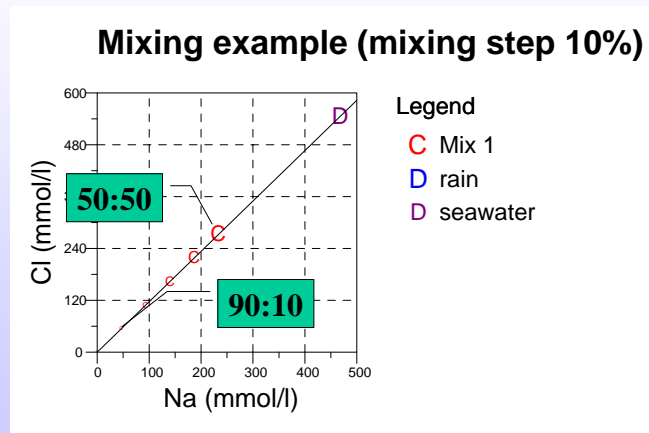
# Result

D:\Software\Geochemie\AquaChem 5.0\Demo.aqc

File Edit View Filter Samples Plots Reports Tools Window Help

Solution 1	seawater						
Solution 2	rain						
Percentage of solution 1 in target solution 10%-50%							
Solution 1	1.0	0.10	0.20	0.30	0.40	0.50	0.0
Solution 2	0.0	0.90	0.80	0.70	0.60	0.50	1.0
Na	10768.0	1076.947	2153.73	3230.514	4307.298	5384.082	0.163
K	399.1	40.2529	80.1248	119.9967	159.8686	199.7405	0.381
Ca	412.3	42.4297	83.5264	124.6231	165.7198	206.8165	1.333
Mg	1291.8	129.4725	258.62	387.7675	516.915	646.0625	0.325
Cl	19353.0	1935.535	3870.809	5806.083	7741.357	9676.631	0.261
HCO3	141.682	3.706769	3.757921	3.815913	3.88286	3.962041	3.661011
SO4	2712.0	274.0152	544.9024	815.7896	1086.677	1357.564	3.128
pH	8.22	4.962	5.324	5.686	6.048	6.41	4.6

## Concentrations in Mixtures are Proportional to Volumes



# Mixing calculations with AquaChem

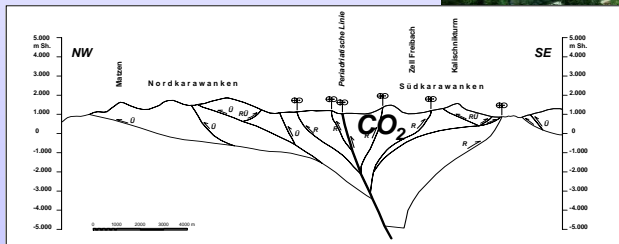
- In addition to mixing two samples, AquaChem also allows you to analyze the composition of a specified sample by choosing the Optimize option. Specify the two initial samples, and specify the resulting sample. AquaChem will mix the two initial samples in 2% increments until the Euclidean distance between the calculated mixture and specified resulting sample is minimized.

## Result

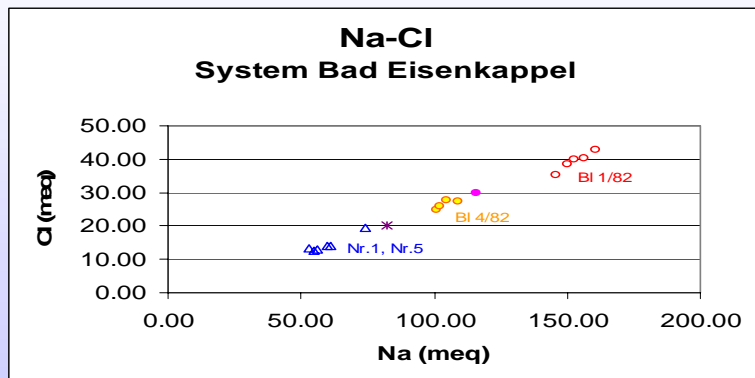
The screenshot displays the AquaChem software interface. On the left, the 'Mix Samples' dialog box is open. It shows two solutions being mixed: '36 seawater' (Na-Cl) and '37 rain' (Ca-NH4-SO4-HCO3). The 'Optimize' section is active, with the 'Calculate the mixing proportions of solutions 1 and 2 that matches best the sample below' field set to '45'. The 'Sample 1' field is set to '30 Na-Cl'. On the right, the 'Sample Mixing Results' window is open, showing a table of results. The 'Optimized sample: Mix 1' row shows a 'Contribution of sample 1' of 30%.

mg/l	Sample 1	Sample 2	Sample 3	Optimized
Na	10768.0	0.163	3230.514	3230.514
K	399.1	0.381	119.997	119.997
Ca	412.3	1.333	124.623	124.623
Mg	1291.8	0.325	387.768	387.768
Cl	19353.0	0.261	5806.083	5806.083
HCO3	141.682	3.661	3.816	45.067
SO4	2712.0	3.128	815.79	815.79
pH	8.22	4.6		

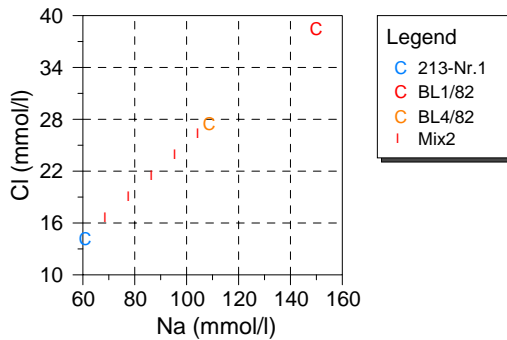
# Example Eisenkappel



## Na/Cl – ratio



## Na/Cl – ratio



## Visual Graphics

- Are there specific geochemical reactions that are releasing solutes stoichiometrically into the water?
  - prepare bivariate plots in mmol/L or meq/L
- Are there specific silicate geochemical reactions that control incongruent geochemical reactions?
- Is a carbonate geochemical system open or closed to carbon dioxide?
  - Plot  $-\log \text{HCO}_3$  versus pH (Langmuir's diagram).
- Does the solubility of a mineral control water chemistry?
  - Prepare bivariate plots of solutes versus total dissolved solids. Data should asymptotically approach a limiting value.

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Simple reaction stoichiometry can be sometimes useful to identify reactions and solute sources

Dissolution of Halite

Dissolving carbonate minerals

Dissolving silicate minerals

Some redox reactions

## Ionic dissolution

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*Halite*



*Gypsum*



## Ionic Dissolution II

### Halite

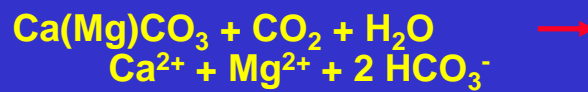
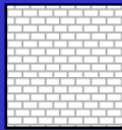


### Gypsum

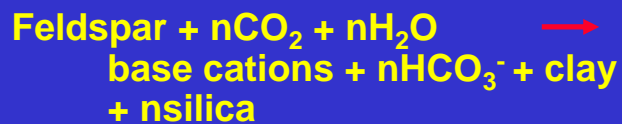
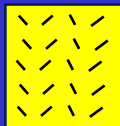


## Hydrolysis

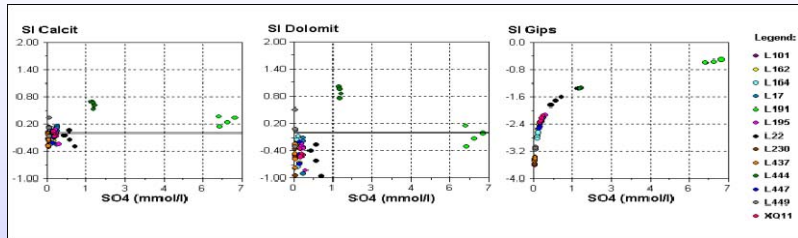
### Carbonates



### Silicates

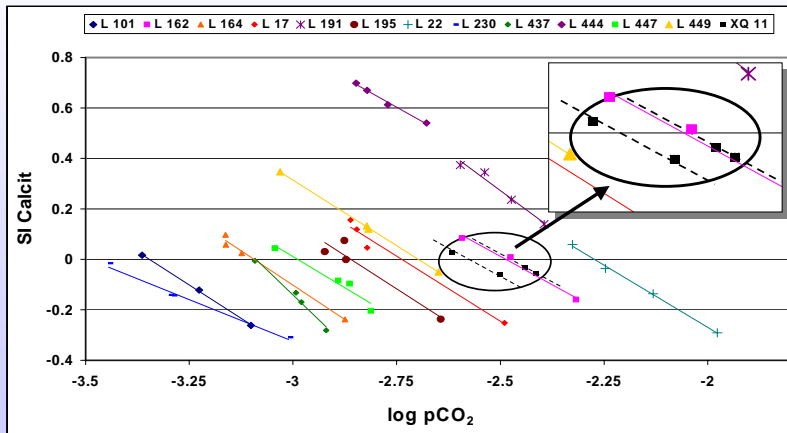


# Scatter plots I

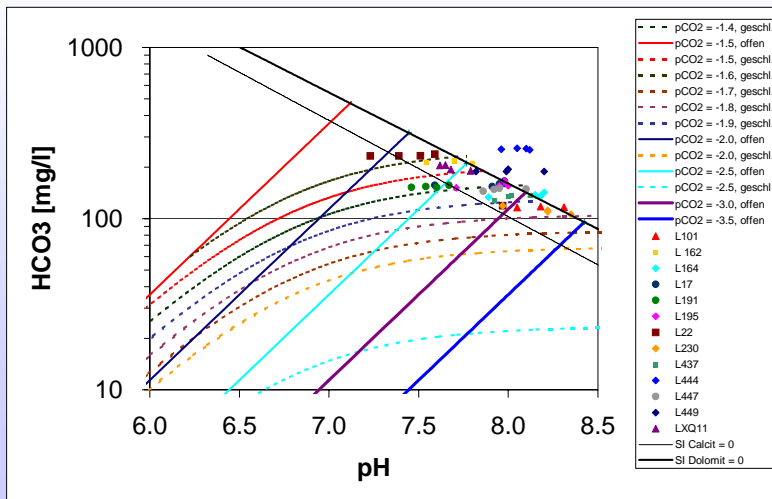


- The X-Y scatter plots are the most simple initial approach to the interpretation of geochemical data.
  - Single plots of ion relationship and parameters that show significant data can be easily created and patterns are quickly identified and easily understood.
  - Both normal scale and log scales are common for the x and y axes
  - Element ratios and sums can also be included for either axes.

# Scatter plots II



## Open or closed carbonate geochemical system



## Visual Graphics

- Are there two different waters mixing?
  - Plot data on ternary or Piper diagrams.
- What is the area distribution of water types?
  - Plot stiff diagrams.
- Can many waters easily be subdivided into facies?
  - Use semilog plots.
- What are the proportions of mixing of two waters?
  - Use Piper diagram or three-component diagram with matrix algebra or factor analysis (STATS).

## PIPER DIAGRAMS - I

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- Consists of two triangles (one for cations and one for anions), and a central diamond-shaped figure.
- Cations are plotted on the Ca-Mg-(Na + K) triangle as percentages.
- Anions are plotted on the  $\text{HCO}_3^-$ - $\text{SO}_4^{2-}$ - $\text{Cl}^-$  triangle as percentages.
- Concentrations are in meq  $\text{L}^{-1}$ .
- Points on the anion and cation diagrams are projected upward to where they intersect on the diamond.

## PIPER DIAGRAMS - II

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### ADVANTAGES

- Many water analyses can be plotted on the same diagram.
- Can be used to classify waters.
- Can be used to identify mixing of waters.

### DISADVANTAGE

- Concentrations are renormalized. Cannot easily accommodate waters where other cations or anions may be significant.

# The four major groundwater types

