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

Part 1

albrecht.leis@joanneum.at

Lectures Outline

- 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

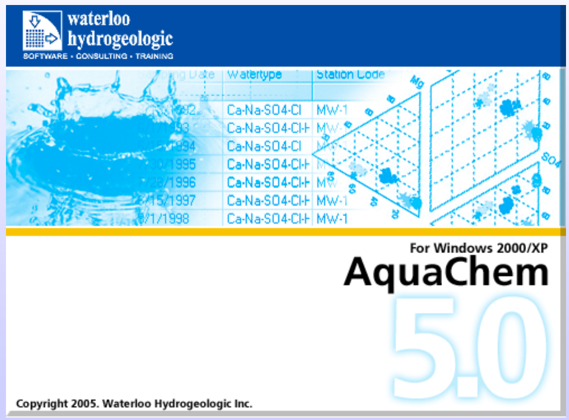
Useful programs

- 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)
  - **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

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

AquaChem - Data Management

- 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

- 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 Giggenbach
  - **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

- 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

- 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

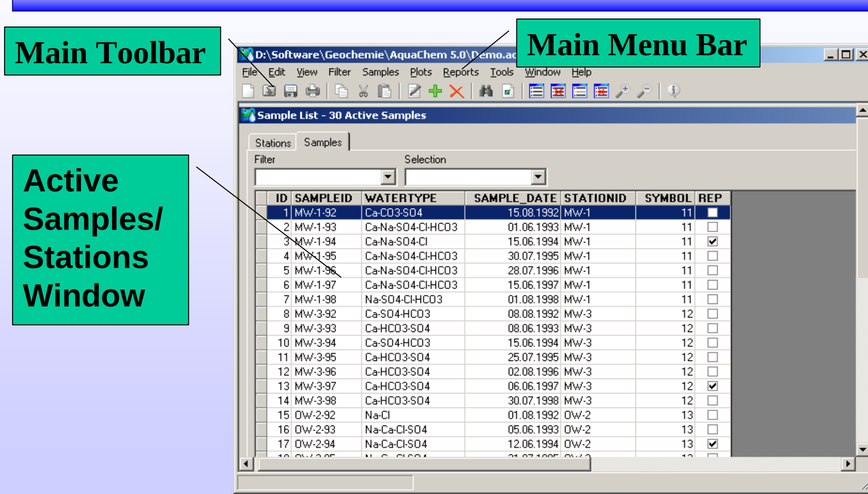
Hardware Requirements

- 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

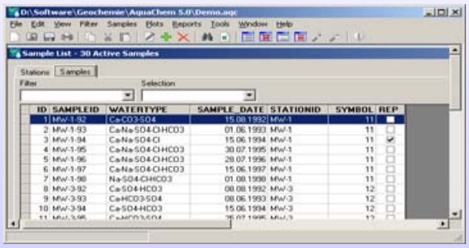
- Starting AquaChem
  - To start AquaChem, you must have it installed on your hard disk.
  - Start AquaChem by access in WHI Software/Aquachem 5.0 from your Start > Programs Windows menu.The Open Database dialogue box will be displayed prompting you to choose an existing AquaChem database.
  - Select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

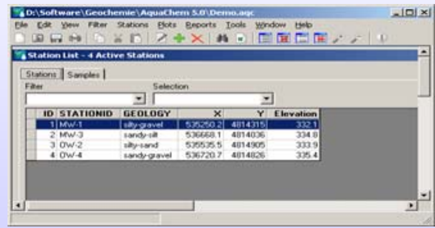
AquaChem - Main window



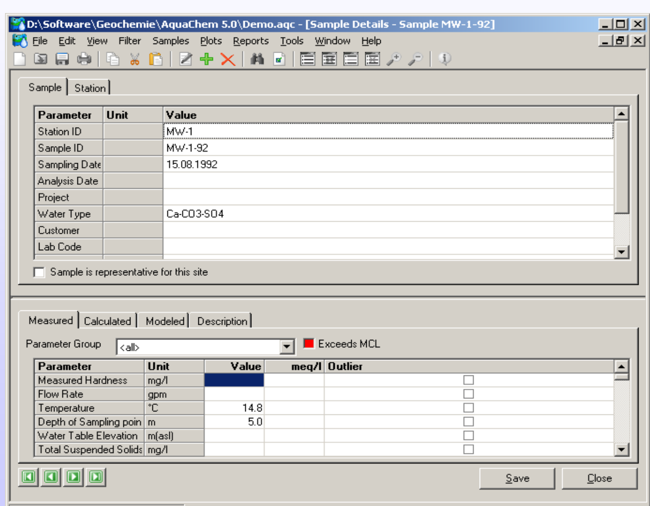
Active Sample/Stations window

Samples and **Stations**

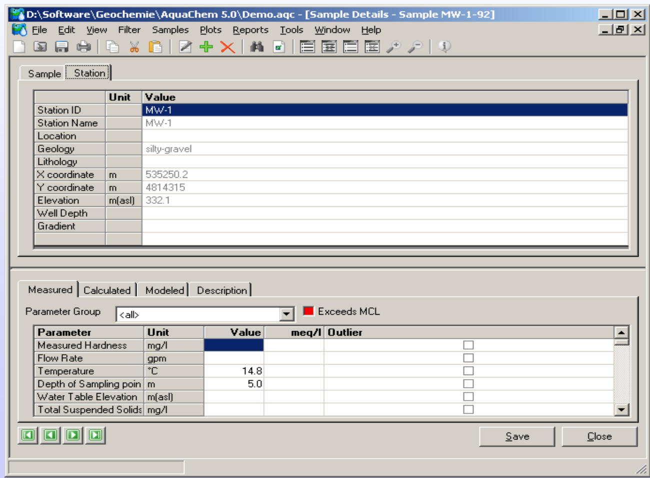




Sample Details Window



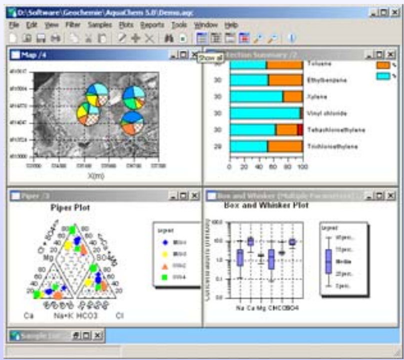
Station Details Window



Data Input

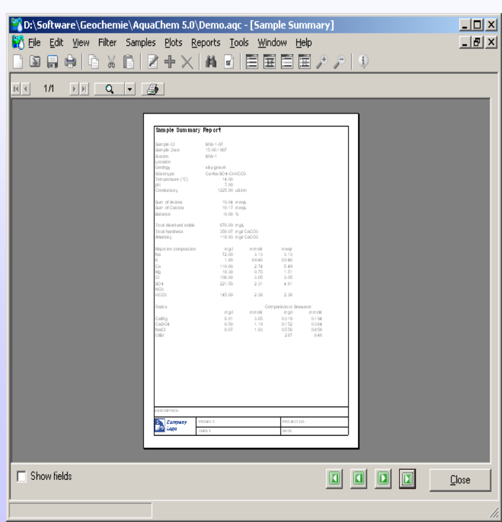
- Data can be entered into the *.aqc database file by either;
  1. Importing a MS Exel or a tab-delimited ASCII text file;
  2. Using the **input** window, or
  3. Using the **spreadsheet** window.

The Plot Window



- AquaChem provides a comprehensive selection of 23 different plotting techniques commonly used for aqueous geochemical data analysis and interpretation.

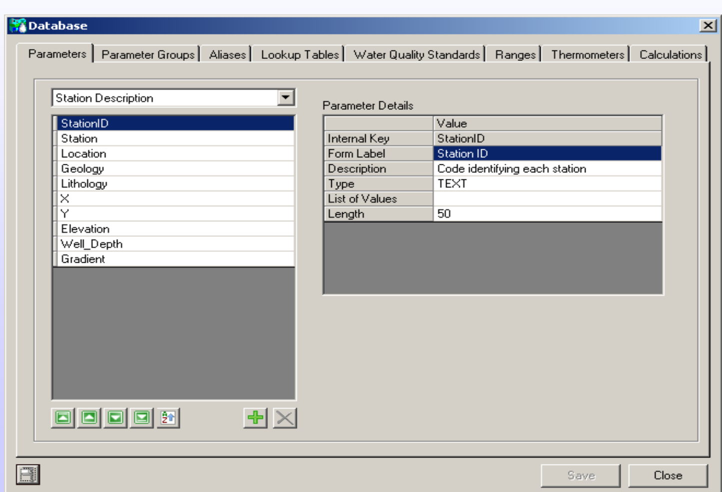
The Reports Window



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

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

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Analytics

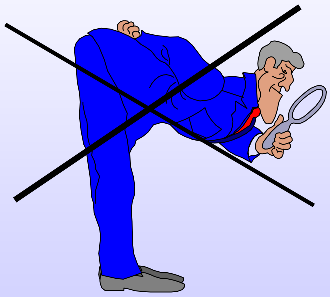
- Have all **major solutes**?
- Do **electrochemical balance**. If bad figure out why.
- Can you make assumptions based on probable water-rock interaction.
- **pH, water temperature**--master variables.
  - If you don't have it, you can’t make geochemical modelling

Analysis control - Introduction

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_3, SO_4, Cl, Si

Minor (0.01-10 mg/L)

B, Fe, NO_3, NH_4, K, Sr, Mn

Trace (<0.01 mg/L)

The Rest!!

Analysis control

Oxygenated

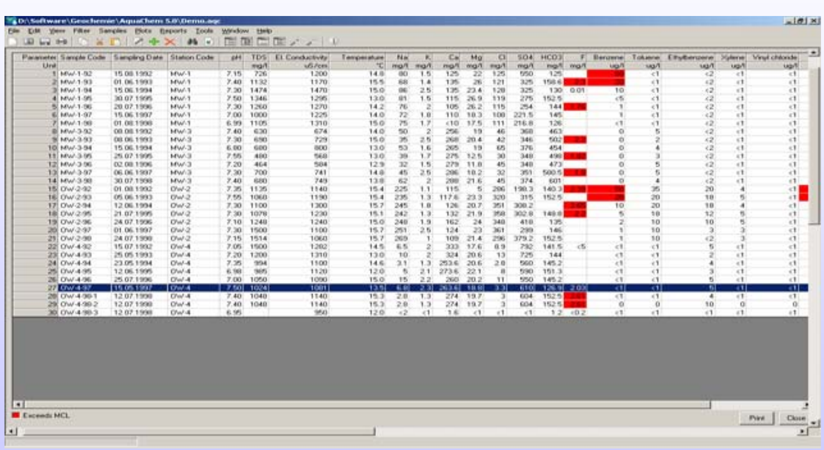
- Calcium
- Magnesium
- Sodium
- Potassium
- Bicarbonate
- Sulfate
- Chloride

Anoxic

- Calcium
- Magnesium
- Sodium
- Potassium
- Bicarbonate
- Chloride
- Sulfide

- Iron
- Manganese
- Barium
- Strontium
- Ammonium

View data as Spreadsheed



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 ±5%.

Analysis control - **Calculating electrochemical balance**

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

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

[1] some EU-countries eg. Austria, Germany

Analysis control - Electrochemical balance (example)

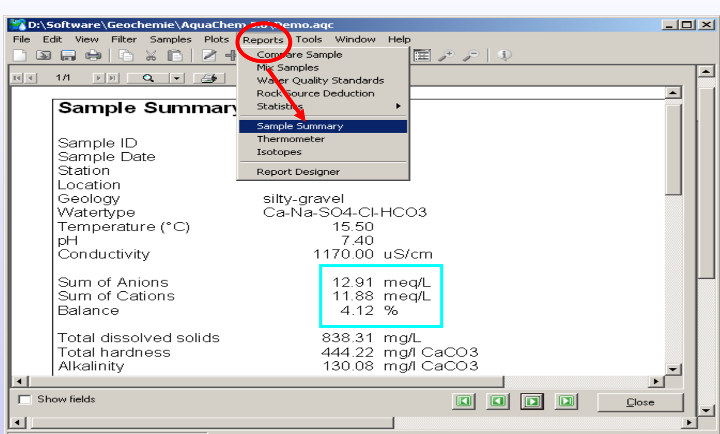
Major ion composition

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

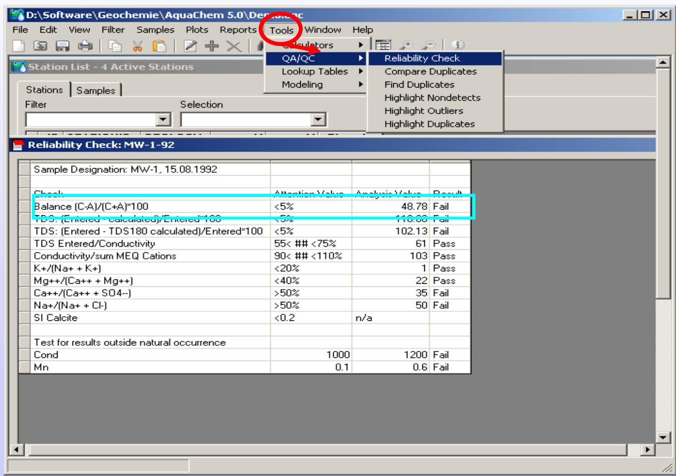
Sum of Anions (meq/l) : 29.37
Sum of Cations (meq/l) : 29.46

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

Electrochemical balance - Aquachem



Electrochemical balance - Aquachem



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 ±5%

- 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 ?!

- 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

- 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?

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

Fundamental Bivariate Mixing Equation

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

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 mg/L

C_2= 250 mg/L

Mix = 75 mg/L

$$C_1(1-n) + C_2 n = C_{Mix}$$

Solving for n..

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

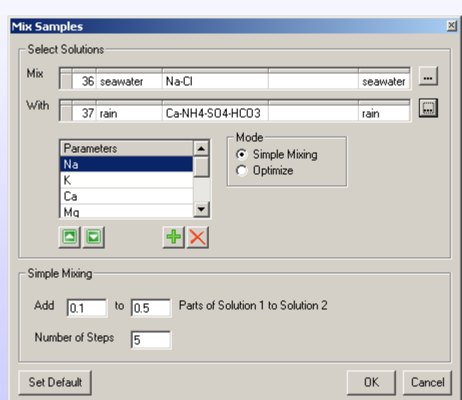
n = (75-10)/(250-10) = 0.27

OR

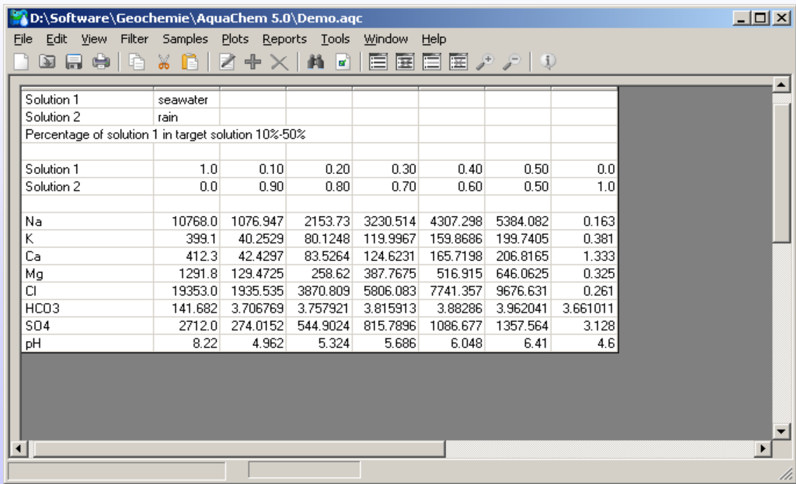
<u>27%</u> of the mixture is water 2.

Mixing calculations with AquaChem

- Mixes two samples from your database, in a step wise process
    - **Simple Mixing** mode
    - **Optimize Mode**

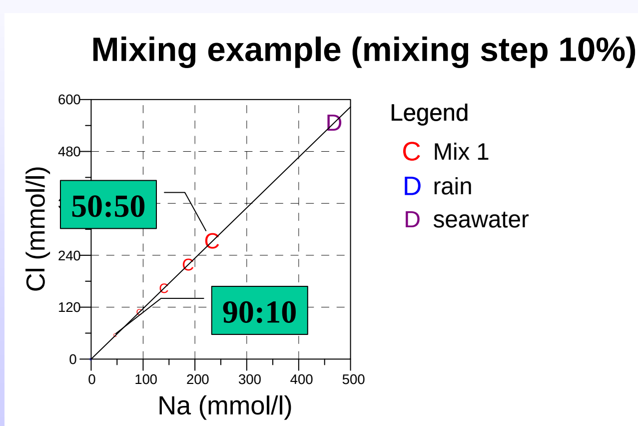


Result



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

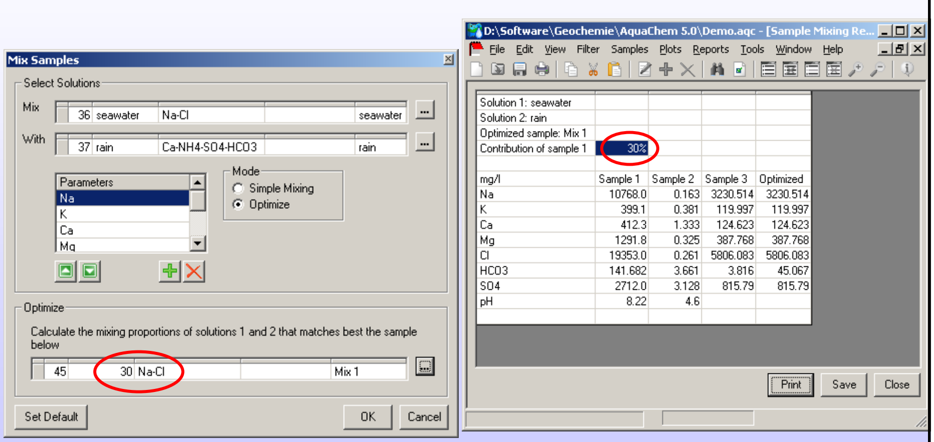
Concentrations in Mixtures are Proportional to Volumes



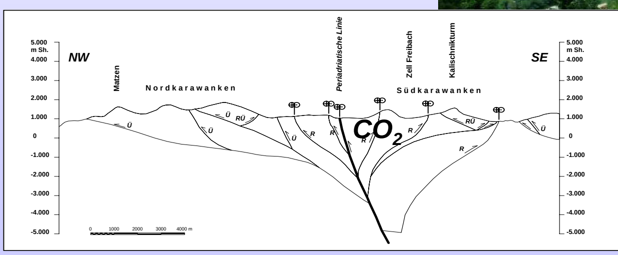
Mixing calculations with AquaChem

- 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.

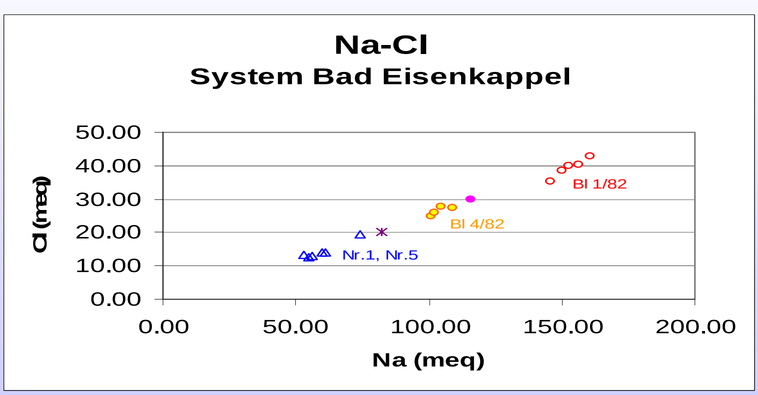
Result



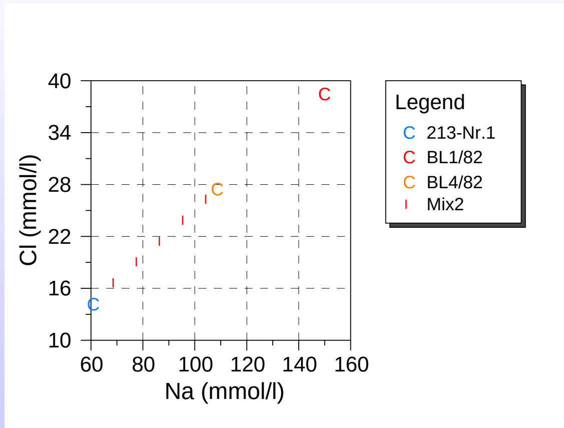
Example Eisenkappel



Na/Cl – ratio



Na/Cl – ratio



Visual Graphics

- Are there specific geochemical reactions that are releasing solutes stochiometrically 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 HCO3 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.

Simple reaction stochiometry can be somtimes useful to identify reactions and solute sources

- Dissolution of Halite
- Dissolving carbonate minerals
- Dissolving silicate minerals
- Some redox reactions

Ionic dissolution

Halite

$$NaCl \longrightarrow Na^{+} + Cl^{-}$$

Gypsum

$$CaSO_4 \longrightarrow Ca^{2+} + SO_4^{2-}$$

Ionic Dissolution II

Halite

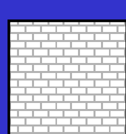
1mmol NaCl $\longrightarrow$ **23mg/L Na^{+} + 35 mg/L Cl^{-}**

Gypsum

1 mmol $CaSO_4$ $\longrightarrow$ **40 mg/L Ca^{++} + 96 mg/L SO_4^{--}**

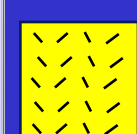
Hydrolysis

Carbonates



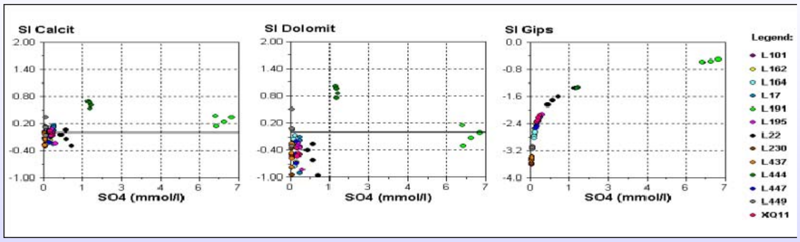
$Ca(Mg)CO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + Mg^{2+} + 2\ HCO_3^-$

Silicates



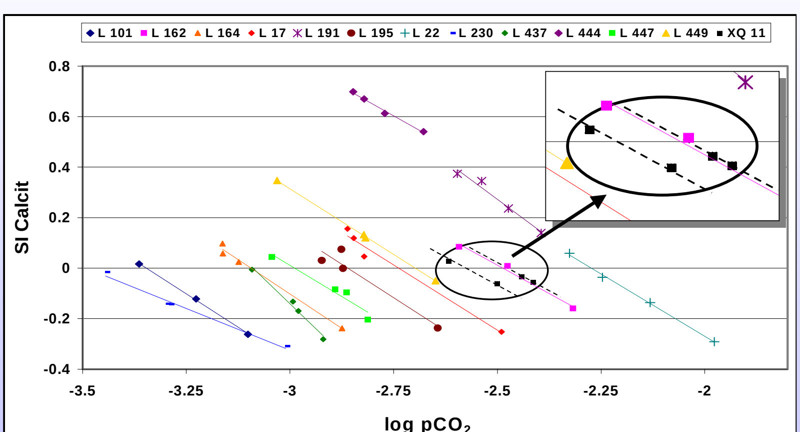
Feldspar + nCO_2 + nH_2O $\longrightarrow$ base cations + $nHCO_3^-$ + clay + nsilica

Scatter plots I

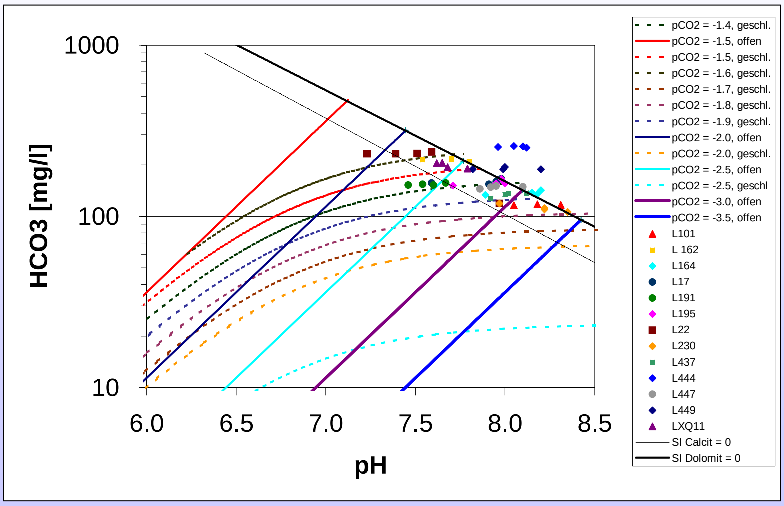


- The X-Y scatter plots are the most simple initial approach to the interpretation of geochemical data.
  - Single plots of ion relationship and parameters that show significant data can be easily created and patterns are quickly identified and easily understood.
  - Both normal scale and log scales 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

- 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 HCO_3^--SO_4^{2-}-Cl^- triangle as percentages.
- Concentrations are in meq L^{-1}.
- Points on the anion and cation diagrams are projected upward to where they intersect on the diamond.

PIPER DIAGRAMS - II

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