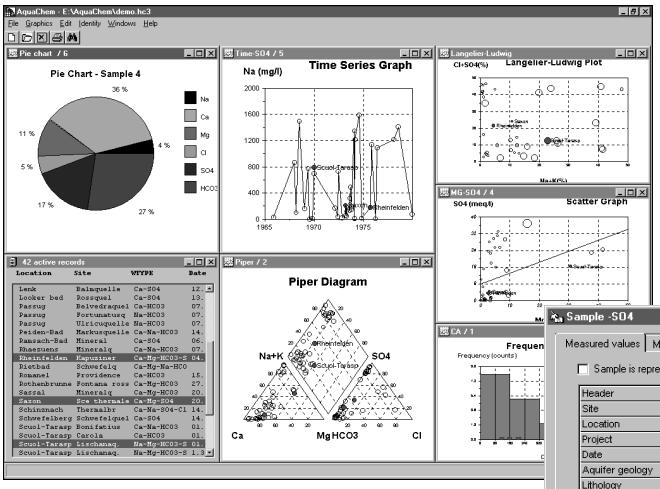
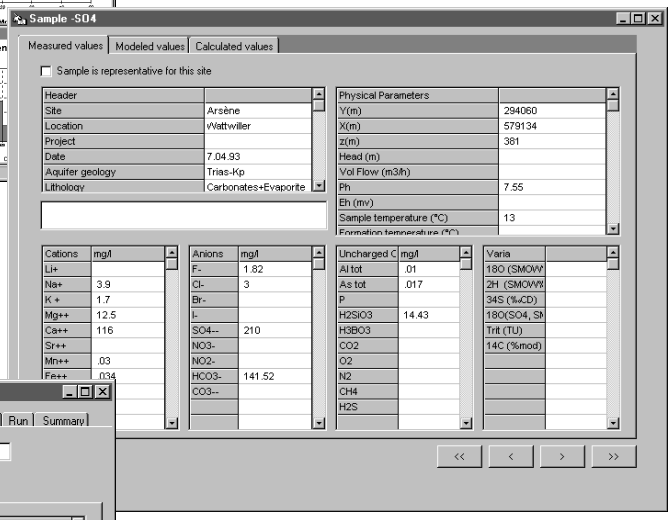
AquaChem v.3.7 *for Windows 95/98/NT*

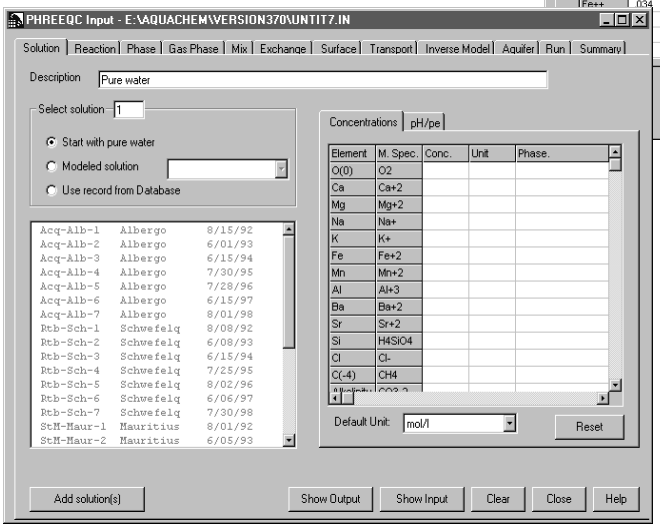
Aqueous Geochemical Analysis, Plotting and Modeling



Comprehensive selection of common graphical methods for interpreting and plotting aqueous geochemical data.



Convenient data entry forms for easily viewing and editing your data.



Graphical interface for geochemical modeling with PHREEQC.

Co-Developed by Lukas Calmbach

and Waterloo Hydrogeologic, Inc.

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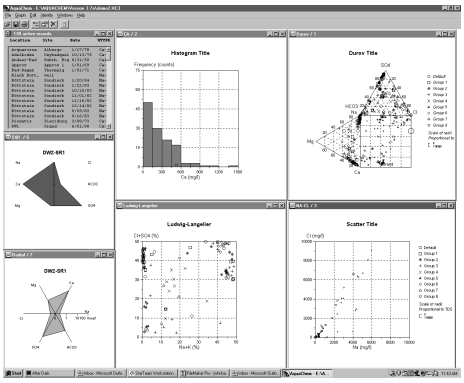
1

Introduction to AquaChem

1.1 Introduction

AquaChem is a software package developed specifically for graphical and numerical analysis and modeling of aqueous geochemical data sets. It features a fully customizable database of geochemical parameters and it provides a comprehensive selection of analysis tools and graphical techniques commonly used for interpreting and plotting aqueous geochemical data.

AquaChem's analysis tools cover a wide range of functions and calculations frequently used for the interpreting and comparing hydrochemical data. These tools include simple unit transformations, charge balances and sample mixing to more complex functions such as correlation matrices and geothermometer calculations. These powerful analytical capabilities are complemented by a comprehensive selection of commonly used graphical techniques to represent the chemical characteristics of aqueous geochemical and water quality data. The graph types available in AquaChem include:



- Piper, Durov, and ternary diagrams,
- Ludwig-Langelier and Schoeller graphs,
- Radial, Stiff and pie diagrams,
- X-Y Scatter graphs, frequency histograms, and time-series graphs,
- Geothermometer plots, and
- Maps plots of sample locations

Each of these graph types provide a unique interpretation of the many complex interactions between the groundwater and aquifer materials.

In addition, AquaChem features a built-in graphical interface to the popular geochemical modeling program PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution.

Once you start using AquaChem, you will see that it is truly one of the most powerful tools available for interpretation, analysis and modeling of simple or complex geochemical data sets.

1.2 How to Contact Waterloo Hydrogeologic Inc.

If, after reading this manual and using AquaChem, you would like to contact Waterloo Hydrogeologic Inc. with comments, suggestions, or if you need assistance, you can reach the technical support team at the following address:

Waterloo Hydrogeologic, Inc.
180 Columbia Street West, Unit 1104
Waterloo, Ontario, Canada, N2L 3L3
Phone: (519) 746-1798
Fax: (519) 885-5262
techsupport@flowpath.com
www.flowpath.com

1.3 Other Products by WHI

Visual MODFLOW for Windows 95/98/NT

The proven standard for professional applications in 3-D groundwater flow and contaminant transport modeling. Visual MODFLOW combines 32-bit Windows 95/98/NT versions of MODFLOW, MODPATH, Zone Budget and MT3D with the most powerful and easy-to-use graphical interface available. For 3-D groundwater flow and contaminant transport modeling Visual MODFLOW is the only software package you need.

FLOWPATH II for Windows 95/98/NT

The next generation of the world's most popular two-dimensional, steady-state, groundwater flow and pathline model. FLOWPATH II includes many radical new improvements including contaminant transport capabilities and enhanced graphical display to give you more power, flexibility and control than ever before.

AquiferTest for Windows 95/98/NT

The fastest and easiest software package available for estimating transmissivity, hydraulic conductivity and storagativity values for confined, unconfined, leaky and fractured rock aquifers. AquiferTest comes with a comprehensive selection of pumping test and slug test solution methods, automatic and manual curve matching, transparent unit conversions and reporting in seven different languages.

Visual Groundwater for Windows 95/98/NT

The most powerful and easy-to-use software package available for 3-D visualization and animation of site characterization data and groundwater modeling results. Visual Groundwater combines state-of-the-art visualization technology with an easy-to-use graphical interface designed specifically for environmental project applications.

Visual HELP for Windows 95/98/NT

A fully-integrated software package for hydrologic evaluation and optimization of landfill design using the latest version of the H.E.L.P. model. Visual HELP's innovative new interface design and powerful graphical features allow the user to have convenient access both the basic and advanced features and analysis capabilities of the HELP model.

SEQUENCE

A powerful new software package for visualization and evaluation of natural attenuation processes. SEQUENCE utilizes a modified radial diagram approach to display chemical concentration, or calculated molarity values, for multiple chemical species. The radial diagrams are then plotted on a site map to simultaneously depict the spatial and temporal trends of each chemical.

WHI UnSat Suite

The WHI UnSat Suite is a compilation of the most popular models for 1-D groundwater flow and contaminant transport through the unsaturated zone. Now VLEACH, PESTAN, VS2DT and HELP are combined in a unified graphical environment for building the model, running the analysis and displaying the results.

FLONET/TRANS

The most complete and easy-to-use cross-sectional groundwater flow and contaminant transport model available. FLONET/TRANS calculates and displays flow nets, velocity vectors, and temporal graphs of concentration at multiple observation points.

AIRFLOW/SVE

The only comprehensive soil-vapour extraction model to simulate the coupled process of soil-vapour flow and multi-component vapour transport in the unsaturated zone.

PRINCE

A compilation of the 10 Princeton Analytical Models which include 7 mass transport models (one-, two-, and three-dimensional) and 3 two-dimensional flow models.

1.4 Waterloo Hydrogeologic Inc. Training and Consulting

Waterloo Hydrogeologic, Inc. offers individually tailored training courses in groundwater modeling. Our highly-acclaimed modeling courses are focussed on providing you with the knowledge and skills you need to build professional groundwater flow and contaminant transport models. Course topics include; (i) How to set up a proper groundwater model (site conceptualization, grid design, boundary conditions, interpretaion of soil properties, etc.), (ii) Calibrating the model; and (iii) Interpretation of results. Customized training courses tailored specifically to your needs can also be arranged.

Waterloo Hydrogeologic, Inc. also offers expert consulting and peer review services for all numerical modeling problems concerning groundwater flow and mass transport. For further information please contact us.

2

Quick Start

This chapter presents information on:

- the necessary hardware requirements
- installation, and
- AquaChem basics.

2.1 Hardware Requirements

To run AquaChem you will need the following minimum system configuration:

- Microsoft Windows 95/98 or NT
- Pentium personal computer
- 16 Mbytes of RAM (in excess of the operating system requirements)
- 20 Mbytes of free hard disk space
- Microsoft compatible mouse
- Minimum screen resolution of 800 x 600 (1024 x 768 recommended)

If you are running Windows NT, you must have Microsoft Windows NT Service Pack 2 or greater installed. However, Windows NT Service Pack 3 is strongly recommended.

The following fonts should be installed on your computer: MS Sans Serif, Arial, and New Courier.

2.2 Installing AquaChem

AquaChem must be installed on your hard disk to run. Please read Section 2.1 to ensure that your system meets the requirements before proceeding with the installation.

The installation procedure outlined here assumes that AquaChem will be installed from drive A: (source drive) to drive C: (destination drive). The default installation directory is **C:\Programs\WHI\AquaChem**, but this may be easily modified to suit your preferences.

> **NOTE:** Since the PHREEQC executable file included with AquaChem is a DOS application, it requires the directory path for AquaChem to follow the DOS directory naming convention (i.e. directory names cannot contain spaces, periods, or names longer than 8 characters).

2.2.1 Installing AquaChem from Floppy Diskettes

To install AquaChem on your hard disk, run the setup application, **SETUP.EXE**, found on Disk #1 of the installation diskettes. To do this,

1) Insert Disk#1 into your floppy disk drive.

2) Run the installation program by clicking **Start** on the Windows taskbar, choosing **Run** and typing **A:\SETUP.EXE** in the dialogue box. Click [**OK]** to start the AquaChem installation program.

3) A diagnostic will be perfomed on your computer to ensure you have the required system files to perform the installation. If you have the required system files, you can proceed to Step 4. If you do not have the required system files, they will be copied to your system and then you will be required to re-boot the computer before proceeding to Step 4. After your computer has re-booted, you will need to re-start the installation procedure.

4) The AquaChem installation program will copy the required initialization files to your computer. If you are running any other applications, you will be advised to close these application before proceeding. To proceed with the installation, press the **[OK]** button.

5) Next you will be prompted to enter the destination directory for the AquaChem program files. The default directory path is **C:\Programs\WHI\AquaChem**. Press the large button on the left-hand side of the dialogue box to begin installing the AquaChem program files on your computer, or press the **[Browse]** button to change the installation directory.

6) The AquaChem installation will copy the contents of Disk#1 onto your computer and then prompt you to remove Disk#1 and insert Disk#2.

7) The AquaChem installation will copy the contents of Disk#2 onto your computer and then prompt you to remove Disk#2 and insert Disk#3

8) After the installation is complete, click **[OK]**.

NOTE: AquaChem has been designed for a screen resolution setting of 1024 x 768 (although full functionality can still be achieved using a screen resolution of 800 x 600). **AquaChem cannot be properly run using a screen resolution setting of 640 x 480.**

2.2.2 Installing AquaChem from a CD-ROM

To install AquaChem on your hard disk, run the setup application, **SETUP.EXE**, found on the CD. To do this,

1) Insert the CD into your CD-ROM drive.

2) Run the installation program by accessing the CD-ROM drive and double-clicking on the file **SETUP.EXE**. Click [**OK]** to start the AquaChem installation program.

3) A diagnostic will be perfomed on your computer to ensure you have the required system files to perform the installation. If you have the required system files, you can proceed to Step 4. If you do not have the required system files, they will be copied to your system and then you will be required to re-boot the computer before proceeding to Step 4.

4) The AquaChem installation program will copy the required initialization files to your computer. If you are running any other applications, you will be advised to close these application before proceeding. To proceed with the installation, press the **[OK]** button.

5) Next you will be prompted to enter the destination directory for the AquaChem program files. The default directory path is **C:\Programs\WHI\AquaChem**. Press the large button on the left-hand side of the dialogue box to begin installing the AquaChem program files on your computer, or press the **[Browse]** button to change the installation directory.

6) The AquaChem installation will copy the AquaChem program files onto your computer.

7) After the installation is complete, click **[OK]**.

NOTE: AquaChem has been designed for a screen resolution setting of 1024 x 768 (although full functionality can still be achieved using a screen resolution of 800 x 600). **AquaChem cannot be properly run using a screen resolution setting of 640 x 480.**

2.3 Contents of the Release

When the installation is complete, the following files will be in your AquaChem directory. The files that are essential for running the program have an asterisk (*) beside them. Other files will be created during the program sessions.

***AQUACHEM.EXE:** Executable file for AquaChem. AQUACHEM.EXE was compiled using Visual Basic. This file must be placed in the working directory.

AQUACHEM.HLP: On-line help file (must be located in the AquaChem directory).

DEMO.HC3: Demo database file containing sample hydrochemical data.

DEMO.MSK: Sample mask file containing the information of the demo database structure (must be located in the same directory as the demo database).

LOGO.BMP: A sample logo bitmap file containing the Waterloo Hydrogeologic logo.

MINTEQ.DAT: Supplementary thermodynamic database file for PHREEQC.

***PARLIST.CSV:** Parameter list file. This is a standard text file containing a list of the parameters which are available in AquaChem.

***PHREEQC.DAT:** The PHREEQC thermodynamic data file.

***PHREEQC.EXE:** The PHREEQC executable file.

SWISS.DXF: A sample .DXF map of Switzerland.

***TEMPLATES.TXT:** Print templates file containing default settings for the page layouts.

WATEQ4F.DAT: Supplementary thermodynamic database file for PHREEQC.

2.4 Starting AquaChem

To start AquaChem, you must have it installed on your hard disk. If you have not yet installed AquaChem, go to Section 2.2 on page 5 for installation instructions. Otherwise click **Start**, choose **Programs**, and click **AquaChem**.

The **Open Database** dialog box will be displayed prompting you to choose an existing AquaChem database. Click **[demo.hc3]** to open the demonstration database.

To open a different database, select **File\Open** from the menu options and select the appropriate database.

AquaChem version 3.7 is compatible with the previous version and can open projects created using version 3.6. However, you should be aware that the date format in version 3.7 has been changed to meet Y2K compliance issues. As such, it now requires valid numeric format date entries in the Date field (or blank entries if sampling date is not an important issue). If you have an existing project database with invalid dates, or text-based date entries (e.g. Jan. 13, 1997) this information will not be recognized in version 3.7.

2.5 Interface Layout

The AquaChem graphical environment consists of the following five types of windows that may be opened. Each window type has a distinct set of menu options associated with it.

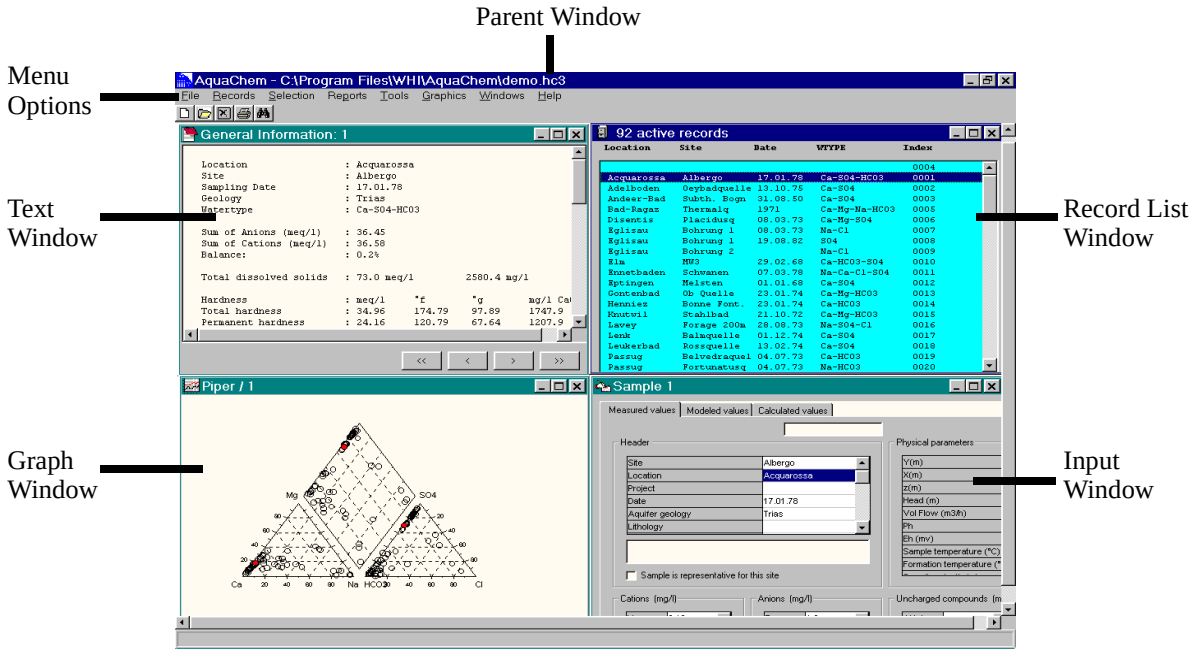


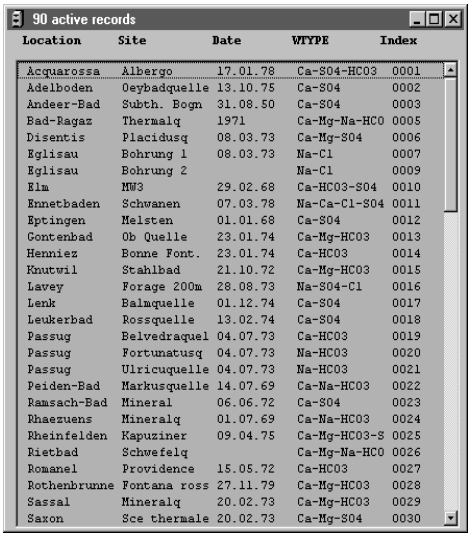
Figure 2.1: The AquaChem interface

NOTE: Multiple windows may be open at the same time, including multiple windows of the same type (e.g. multiple graph windows).

Each type of window has a different set of menu options which appear at the top of the parent window. The menu items for each window type are only display if that window is active (selected). The **Record List** window is considered the **Main Menu**.

AquaChem follows most standard Windows interface conventions. Each window type can be minimized to an icon at the bottom of your parent window and reopened as needed. Windows can be arranged on the parent window using the **Windows\Tile Horizontal** or **Tile Vertical** command, which are available from all menus.The Record List

The **Record List** window (see Figure 2.2) will always appear when you open an AquaChem database and will remain on-screen as long as the project database is open (i.e the **Record List** cannot be closed unless the project database is closed). The **Record List** contains summarized information about every active record in the database.



Location	Site	Date	WTYPE	Index
Acquarossa	Albergo	17.01.78	Ca-SO4-HCO3	0001
Adelboden	Oeybadquelle	13.10.75	Ca-SO4	0002
Andeer-Bad	Subth. Bogn	31.08.50	Ca-SO4	0003
Bad-Ragaz	Thermalq	1971	Ca-Mg-Na-HCO	0005
Disentis	Placidusq	08.03.73	Ca-Mg-SO4	0006
Eglisau	Bohrung 1	08.03.73	Na-Cl	0007
Eglisau	Bohrung 2		Na-Cl	0009
Elm	MW3	29.02.68	Ca-HCO3-SO4	0010
Ennetbaden	Schwanen	07.03.78	Na-Ca-Cl-SO4	0011
Eptingen	Melsten	01.01.68	Ca-SO4	0012
Gontenbad	Ob Quelle	23.01.74	Ca-Mg-HCO3	0013
Henniez	Bonne Font.	23.01.74	Ca-HCO3	0014
Knutwil	Stahlbad	21.10.72	Ca-Mg-HCO3	0015
Lavey	Forage 200m	28.08.73	Na-SO4-Cl	0016
Lenk	Balmquelle	01.12.74	Ca-SO4	0017
Leukerbad	Rossquelle	13.02.74	Ca-SO4	0018
Passug	Belvedraquel	04.07.73	Ca-HCO3	0019
Passug	Fortunatusq	04.07.73	Na-HCO3	0020
Passug	Ulricuquelle	04.07.73	Na-HCO3	0021
Peiden-Bad	Markusquelle	14.07.69	Ca-Na-HCO3	0022
Ramsach-Bad	Mineral	06.06.72	Ca-SO4	0023
Rhaezuens	Mineralq	01.07.69	Ca-Na-HCO3	0024
Rheinfelden	Kapuziner	09.04.75	Ca-Mg-HCO3-S	0025
Rietbad	Schwefelq		Ca-Mg-Na-HCO	0026
Romanel	Providence	15.05.72	Ca-HCO3	0027
Rothenbrunne	Fontana ross	27.11.79	Ca-Mg-HCO3	0028
Sassal	Mineralq	20.02.73	Ca-Mg-HCO3	0029
Saxon	Sce thermale	20.02.73	Ca-Mg-SO4	0030

Figure 2.2: Record List Window

The column headings displayed in the **Record List** window can be any parameter from the project database and are easily modified by selecting **File/Preferences/Startup Defaults** to load the project preferences dialog box. To add a parameter, double-click in the first open cell under the 'Parameter' column and a dropdown list of available parameters will appear. Select the desired parameter and then click in the corresponding 'Length' column and enter a number corresponding to the character length of the parameter as it will appear in the **Record List**. When you are finished, press the **<Enter>** key to accept this new entry and then press the **[Save]** button at the bottom of the dialogue box to apply the changes to the **Record List**.

The Parameters displayed in the **Record List** are sorted in ascending order according to the parameter in the first column. The columns headings can be changed by selecting **File\Preferences\Startup Defaults** from the menu options and using the arrow buttons to change the order of the parameters displayed in the **Record List** columns.

To work with a subset of the whole database, you can temporarily omit selected samples by choosing **Selection\Omit Selected**. Omitted samples will not be included in any plots or calculations performed. Any samples that you omit can by re-instated by choosing **Selection\Show All**.

2.5.1 The Input Window

Individual database records can be created, edited, or viewed using the **Input** window (see Figure 2.3). To display this window for a record in your database you can either:

- double click the sample in the **Record List**
- click a record in the **Record List** and select **Records\Edit** from the **Main Menu**, or
- Right-click a record in the **Record List** and select **Edit**.

You can view the **Input** window for other records by selecting **Record\Previous** or **Record\Next** from the top menu bar. This can also be done by clicking on the push buttons at the bottom of the text window or by using the **<F8>** and **<F9>** keys.

To edit a parameter on the **Measured values** tab in the **Input** window, click on the cell that you want to edit and type the changes. Save the changes to the record by pushing the **[Save]** button at the bottom of the form or by advancing to the next **[>]** or previous **[>]** record. The values in the **Calculated values** tab are internally calculated by AquaChem and cannot be edited.

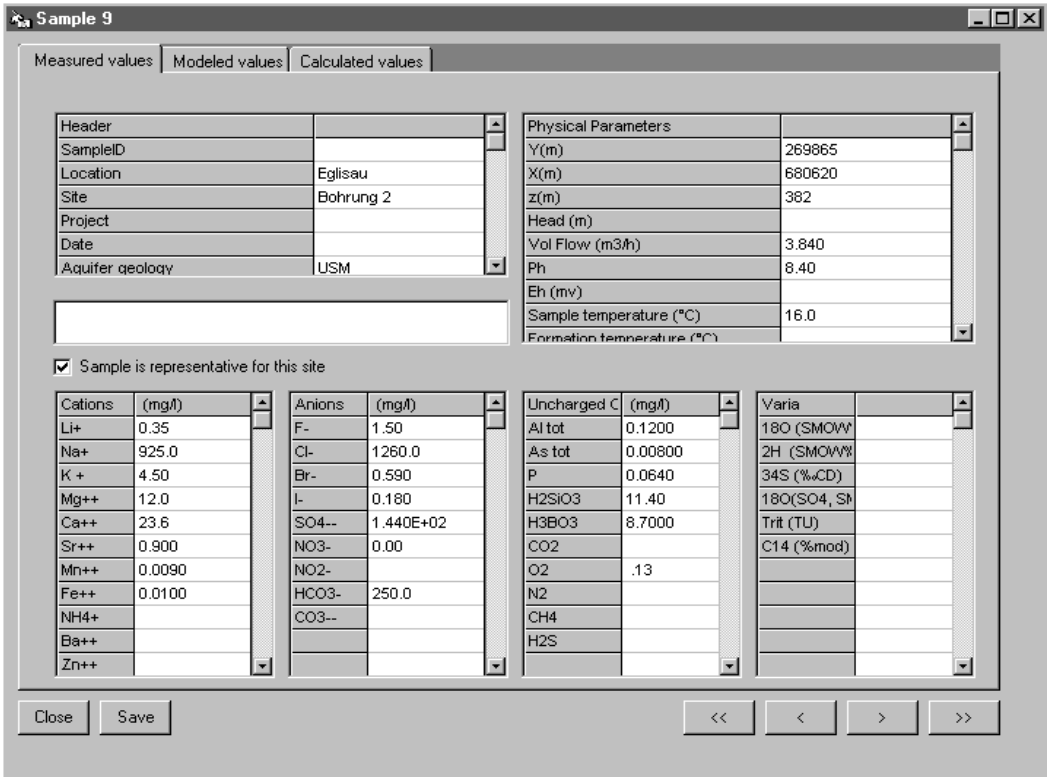


Figure 2.3: Input Window

2.5.2 The Text Window

The **Text** windows provide reported and/or calculated information on a selected sample, or group of samples, from the database (see Figure 2.4). The reports can be produced by selecting a sample in the **Record List** and then selecting one of the reports from the **Reports** menu option.

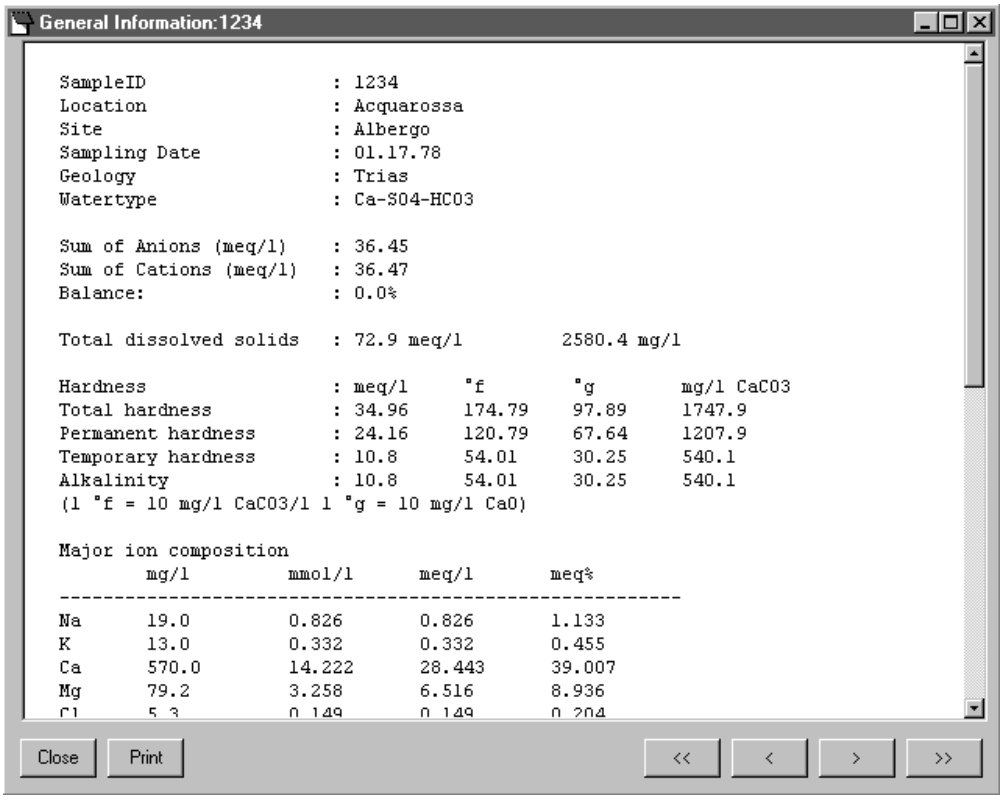


Figure 2.4: General Report Text Window

AquaChem generates ten different types of reports dealing with information on a selected sample, or information on all active samples in the database.

A sample **General Report** is shown in Figure 2.4. The General Reports for other samples can be viewed by selecting the **Record\Previous** or **Record\Next** menu option to automatically update the report for the next/previous record in the database. This can also be done by clicking on the push buttons at the bottom of the text window or by using the **<F8>** and **<F9>** keys. The text reports can be edited, printed, saved to a text file, or copied and pasted to another Windows application for inclusion in a report document.

A detailed description of each report and the calculations involved is provided in Section 4.2.4 on page 55.

2.5.3 Graph Window

AquaChem provides a comprehensive selection of 13 different plotting techniques commonly used for aqueous geochemical data analysis and interpretation. Each of these plot types can be used to graphically represent information from all samples in the **Record List**, or for selected samples only. To create a graph, follow the instructions listed below:

- Select **Graphics\New\Piper** from the **Main Menu**
- A **Piper Graphic Options** dialogue box will appear
- Click [**Apply]** or [**Ok]** to accept the default settings

REMINDER: The **Record List** window must be selected to access the **Graphics** menu option.

This will create a **Graph** window displaying the Piper graph for all sample records displayed in the **Record List** (see Figure 2.5). Note that any records selected in the Record List are highlighted on the Piper plot. These sample points can be labelled as shown in the following figure, and the shapes and sizes of the symbols can also be modified.

It is important to remember that the data plotted on all open graphs are directly linked to the database records. Any changes to the data are immediately reflected in each of the open graphs. Clicking a data point on the graph will highlight the corresponding record in the **Record List** window (the corresponding data point in all other open **Graph** windows will also be highlighted). Similarly, selecting a record in the **Record List** will highlight the corresponding data point on all open graphs. Changing the number of records in the **Record List** automatically updates all open graphs.

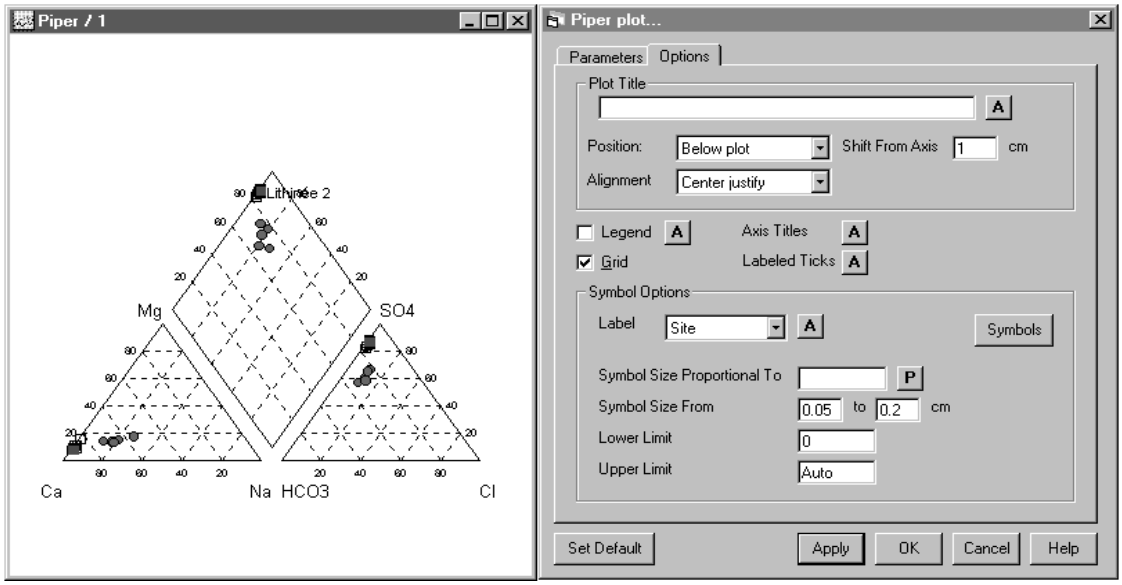


Figure 2.5: Piper Plot

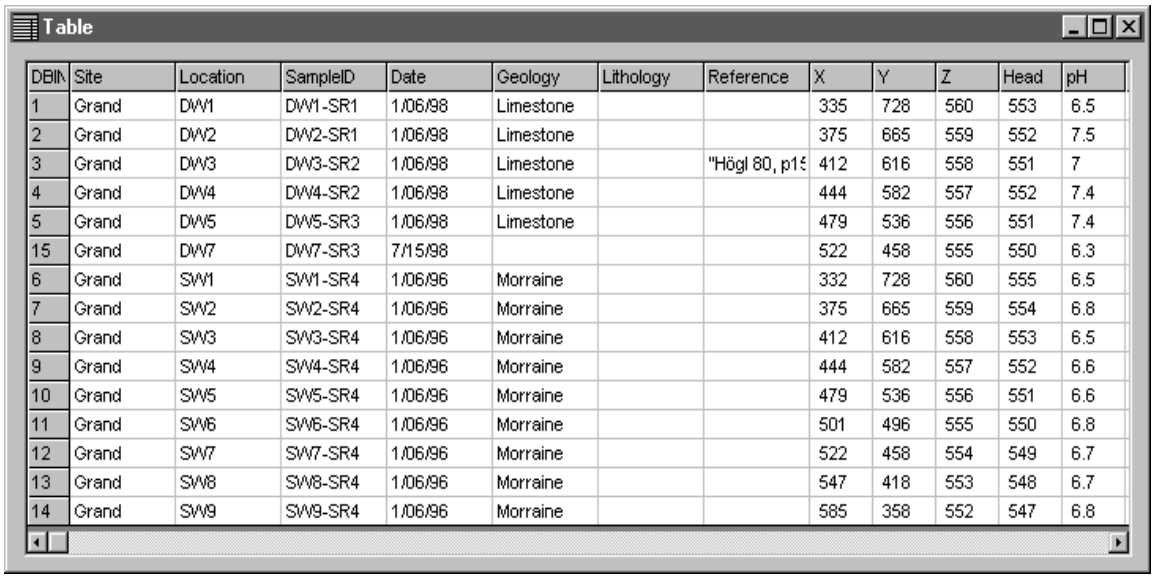
2.5.4 The Spreadsheet Window

AquaChem allows you to edit or view data in a tabular spreadsheet-like format containing all sample records currently displayed in the **Record List**. This is a more convenient method of handling a series of data or comparing selected parameter values for multiple samples. To create a spreadsheet view of the database, select **Record/View as Spreadsheet** from the **Main Menu**. A **Spreadsheet Settings** dialogue box will appear listing the parameters that will be included in the columns of the spreadsheet (each record in the **Record List** will always be included in the spreadsheet view). The spreadsheet settings can be used to select only those parameters you are interested in viewing/editing in a spreadsheet format.

Select **[OK]** to accept the default spreadsheet settings.

A **Spreadsheet** window will appear listing all of the selected paremeters (one per column) and all of the active records in the database (one per row).

Since building and loading spreadsheets for long record lists (<500 records) can be time-consuming, you should minimize the tables as icons when they are not in use rather than closing them.



Table

DBIN	Site	Location	SampleID	Date	Geology	Lithology	Reference	X	Y	Z	Head	pH
1	Grand	DW1	DW1-SR1	1/06/98	Limestone			335	728	560	553	6.5
2	Grand	DW2	DW2-SR1	1/06/98	Limestone			375	665	559	552	7.5
3	Grand	DW3	DW3-SR2	1/06/98	Limestone		"Högl 80, p15	412	616	558	551	7
4	Grand	DW4	DW4-SR2	1/06/98	Limestone			444	582	557	552	7.4
5	Grand	DW5	DW5-SR3	1/06/98	Limestone			479	536	556	551	7.4
15	Grand	DW7	DW7-SR3	7/15/98				522	458	555	550	6.3
6	Grand	SW1	SW1-SR4	1/06/96	Morraine			332	728	560	555	6.5
7	Grand	SW2	SW2-SR4	1/06/96	Morraine			375	665	559	554	6.8
8	Grand	SW3	SW3-SR4	1/06/96	Morraine			412	616	558	553	6.5
9	Grand	SW4	SW4-SR4	1/06/96	Morraine			444	582	557	552	6.6
10	Grand	SW5	SW5-SR4	1/06/96	Morraine			479	536	556	551	6.6
11	Grand	SW6	SW6-SR4	1/06/96	Morraine			501	496	555	550	6.8
12	Grand	SW7	SW7-SR4	1/06/96	Morraine			522	458	554	549	6.7
13	Grand	SW8	SW8-SR4	1/06/96	Morraine			547	418	553	548	6.7
14	Grand	SW9	SW9-SR4	1/06/96	Morraine			585	358	552	547	6.8

Figure 2.6: Sample Speadsheet Window

2.6 The AquaChem Database

The AquaChem database files (***filename.hc3***) have a proprietary binary format. Each record has a fixed length, depending on the number of parameters defined in the maskfile (***filename.msk***). Every record is composed of string header fields containing descriptive text information (Location, Site, Date etc.), and a user-defined number of parameter fields, each of which occupies 4 bytes.

The structure for each database is defined in the maskfile (***filename.msk***). A database can contain an unlimited number of samples, depending on the number of parameters it uses and

the amount of memory on your PC. Working with too many samples can slow some operations even though you are only working with a portion of the database. Working with several databases containing less than 1,000 samples is more efficient than using one large database. Databases should be stored separately from the C:\AQUACHEM directory, and one directory should be created for each project database.

The AquaChem database design always contains ten distinct parameter groups. Nine of these parameter groups consist of parameters that need to assigned by the user:

- **Header Info (Project, Location, Date, SampleID, etc.)**
- **Physical Data (Location coordinates, Ph, Conductivity, etc.)**
- **Cations (Na, Ca, Mg, etc.)**
- **Anions (Cl, HCO_3, SO_4, etc.)**
- **Uncharged Compounds (Al, CO_2, O_2, CH_4, etc.)**
- **Variable (2H, tritium, 18O, etc.)**
- **PHREEQC Description**
- **PHREEQC Minerals**
- **PHREEQC Activities**

The other parameter group is the **Calculated Parameters** (sum of cations, sum of anions, ion balance, hardness, alkalinity, etc.) which are automatically calculated by AquaChem based on the values of the required parameter fields.

Data can be entered into the database (***filename.hc3***) by either; (i) importing a tab-delimited ASCII text file; (ii) using the **Input** window, or (iii) using the **Spreadsheet** window. Once the data is entered into the AquaChem database, it may be conveniently viewed and modified using either the **Input** window or the **Spreadsheet** window. The **Input** window is typically used to view and edit all of the data from a single record, while the **Spreadsheet** window is used to compare data for all records in the Record List.

Data Classes

AquaChem uses both alphanumeric and numeric parameters. The **Header Info** parameters are stored in an alphanumeric format, while all the other parameter groups are stored using a numeric format. These data classes are described in the following sections.

The alphanumeric fields accept both text and numeric data, while the numeric fields require numeric data. The numeric fields must use a point "." demical and not a comma "," decimal. The numeric parameter fields do not accept text values such as "ND" or "NA" and will return a value of zero for any text entry. However, AquaChem does accept "greater than" and "less than" values (e.g. <0.01). In addition, AquaChem allows you to recognize or ignore the "greater than" and "less than" values on graphs (see **File/Preference/Startup Defaults**).

2.6.1 Alphanumeric Parameters

The following fields provide a text description of each sample record in the database:

Name	Length	Description
Site	30	Name of the borehole or spring
Location	30	Location of the sampling site
Date	8	Sampling date, format is "DD.MM.YY" "D.M.YY" is also accepted
SampleID	15	Identification tag associated with each individual sample
Geology	15	Name of the aquifer formation e.g. Jura-u for upper Jurassic
Lithology	20	Aquifer lithology e.g. sandstone, granite etc...
Reference	30	Either the laboratory sample label or the reference if the analysis is copied from literature
WType	20	Water type is automatically calculated according to the composition of the major elements
Comment	40	Additional remarks
Project	10	Name of the project

2.6.2 Numeric Parameters

The numeric parameters in AquaChem include Measured Parameters, Calculated Parameters and Modeled parameters.

Measured Parameters

The Measured parameters consist of parameters that are either measured at a sampling location, or derived from a laboratory analysis of a water sample taken from that location. The Measured parameters are sub-divided according to the following parameter groups.

- Physical data (e.g. location coordinates, temperature, pH),
- Cations (e.g. Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}),
- Anions (e.g. Cl^{-}, F^{-}, SO_4^{2-}),
- Uncharged compounds (e.g. CO_2, SiO_2), and
- Variable (e.g. isotopes, bacteria),

Although AquaChem allows you to modify the parameters in the database, you should not change the spelling of the Internal names of existing parameters since many of them are used for calculating hardness, alkalinity, ion balance, etc. For example, the name for silicon is always SiO_2, whether you enter your data as SiO_2, H_2SiO_3, or Si. The aqueous species is specified by the formula weight and the charge of the ions, not by its name.

Calculated Parameters

AquaChem includes a number of common calculation for determining common geochemical parameters. Each calculated parameter is described in Table 1 below.

Table 1: Calculated Parameters

Name	Required Parameters	Description
Sum Cations	major cations	sum of major cations in milliequivalents
Sum Anions	major anions	sum of major anions in milliequivalents
Molality	major ions	molal sum of all elements
Charge Balance	major ions	charge balance between anions and cations
Total hardness mmol	Ca, Mg	Ca+Mg in mmol
Total hardness, ° f	Ca, Mg	Ca+Mg in French degrees
Total hardness, ° g	Ca, Mg	Ca+Mg in German degrees
Alkalinity, mmol	HCO_3^-	HCO_3^- in mmol/L
Alkalinity ° f	HCO_3^-	HCO_3^- in French degrees[1]
Alkalinity ° g	HCO_3^-	HCO_3^- in German degrees[2]
SAR	Na, Ca, Mg	sodium adsorption ratio
Adjusted SAR	Na, Ca, Mg, HCO_3^-	adjusted Sodium adsorption ratio
TDS	major ions	sum of chemical elements
z(^{18}O)*	^{18}O	estimated infiltration height based on ^{18}O conc.
z(^{2}H)*	^{2}H	estimated infiltration height based on ^{2}H conc.
T(^{18}O)*	^{18}O	estimated average annual temperature of recharge area based on ^{18}O concentration
T(^{2}H)*	^{2}H	estimated average annual temperature of recharge area based on ^{2}H concentration
H_H_2Ol J/g	temperature	enthalpy of liquid water
H_H_2Ov J/g	temperature	enthalpy of steam

[1] 1.0 German degree = 17.8 mg $CaCO_3$/L

[2] 1.0 French degree = 10 mg $CaCO_3$/L

* Needs the coefficients of the equations which describe the altitude and temperature isotope relation.

The calculated parameter are treated by AquaChem as regular database parameters with respect to plotting, searches, or statistical calculations. However, in order for the built-in calculations to work, their corresponding database parameters must be included in the database. For example, the database must include Ca and Mg in order to calculate hardness, and both of these parameters must be identified with an Internal Name of 'Ca' and 'Mg' respectively.

Modeled Parameters

AquaChem provides an integrated graphical interface for geochemical modeling using PHREEQC where the sample the sample data for each record in the database can be used as input data for the PHREEQC simulations. The Modeled Parameters consist of parameters that are required by PHREEQC in order to run the simulation. These parameters are sub-divided into the following parameter groups:

- PHREEQC Description (e.g. ionic strenght, pe),
- PHREEQC Minerals (e.g. gypsum, siderite), and
- PHREEQC activities

Although AquaChem allows you to modify the parameters in the database, you should not change the spelling of the Internal names of existing Modeled parameters since they are linked to the PHREEQC thermodynamic data file.

2.7 Creating a New Database

To create a new project database file,

- Close the open database by selecting **File\Close** from the **Main Menu**
- Select **File\New** from the **Main Menu**
- Type the name of the new database, and click **[Save]**
- A pop-up **Database Template** window will appear prompting you to either;
- **Use an existing database template**, or
- **Create a new database template**

NOTE: When you first start using AquaChem it is highly recommended that you use the existing database template provided in the ***demo.msk*** maskfile until you become comfortable with creating a customized database structure.

2.7.1 Use An Existing Database Template

If you choose to use an existing database template you must select a maskfile containing the desired data structure for the new database. The default maskfile is ***demo.msk*** which contains the same data structure as the demo database. If you want to choose a different maskfile, use the **[...]** button to browse your computer for the target maskfile. Once you have selected the desired maskfile click **[OK]** to create the new AquaChem project database.

AquaChem will then automatically create an Aquachem database file (***filename.hc3***) and the associated maskfile (***filename.msk***) containing the data structure for each record in the database.

NOTE: If you select the ***demo.msk*** maskfile, then your data structure may contain some parameters which do not apply to your data set, while others may be missing. Use the **File/Preferences/Data Structure** options to modify the selected maskfile.

2.7.2 Create a New Database Template

If you choose to create a new database template, a **New database template** window will appear and you can select the various descriptions and numeric parameter fields that you would like to include in your Aquachem project database (see Figure 2.6).

The **Parameter Group** field contains a list of each AquaChem Parameter Group as described in Section 2.6. By default, the first Parameter Group displayed is the **Header Info**. The empty box on the left-hand side of the window labeled **Destination (maskfile)** displays a list of parameters that will be included in the selected Parameter Group. By default, each **Destination maskfile** (parameter list) is empty to start with.

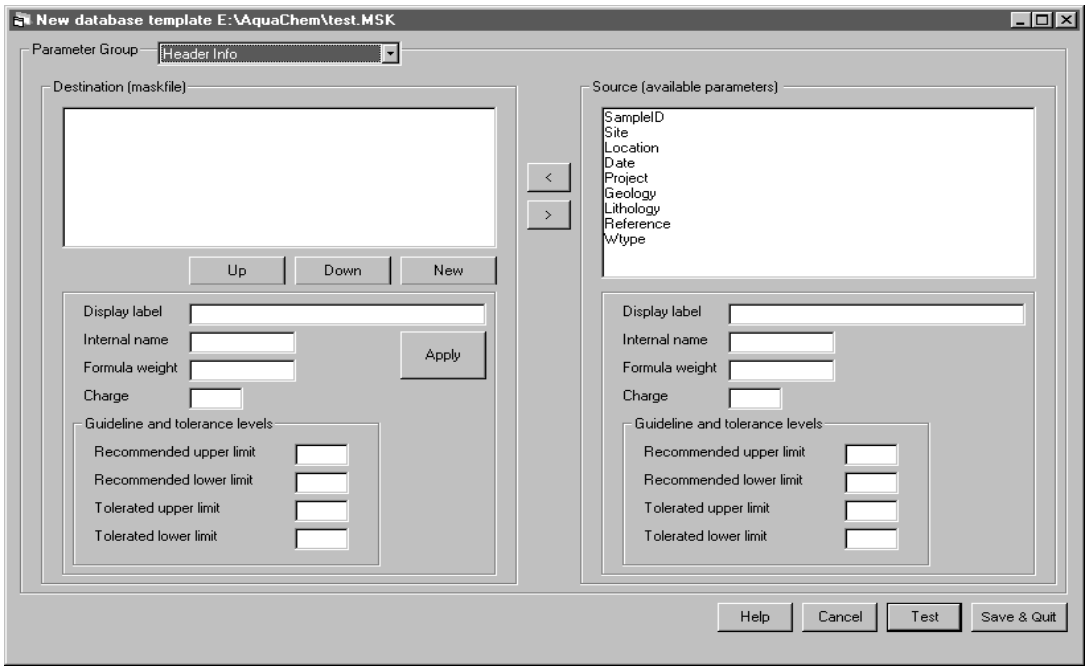


Figure 2.7: New database template window

The box on the right-hand side of the window labelled **Source (available parameters)** contains the default selection of parameters from each Parameter Group that can be added to the **Destination maskfile**. Each available parameter has an associated **Display label** that is used in the **Input** window, and an **Internal name** that is used to identify the parameter for internal calculations. If you choose to edit the **Internal name** of a parameter, it should have less than eight characters and should be unique. However, if possible, you should always use the proposed default name since certain parameters are used for internal calculations (e.g. ion balance, geothermometers, isotope reports, etc.). If you refer to a parameter used in one of the internal calculations by a different name, AquaChem will not recogize it and some calculated parameters will be incorrect or omitted. All chemical parameters should have a formula weight specified. Ions must be accompanied by their valence (which is always a positive number). Upper and lower Guideline and tolerance levels should be specified for chemical elements that are involved with health issues.

Adding a Parameter from the Source List

To add one of the available parameters from the **Source** list to the **Destination** list

- select the parameter from the **Source** list (by clicking on it)
- click the left arrow **[<]** button.

To add several parameters press the **<Ctrl>** button while you select multiple parameters from the **Source** list.

Creating a New Parameter

To create a new parameter that is not included in the **Source** list:

- click the **[New]** button,
- enter the appropriate information (Display label, Internal name, etc.)
- click the **[Apply]** button to add the new parameter to the **Destination** list

To remove a parameter from the **Destination** list, simply select the parameter from the **Destination** list and then click the right arrow **[>]** button.

To set up the database template for your new AquaChem project you must choose the parameters that you want to include for each of the nine Parameter Groups.

> **NOTE:** The number of Parameter Groups and the names of the Parameter Groups cannot be changed.

Once you have finished selecting the parameters for each Parameter Group you can test the database template by clicking the **[Test]** button on the bottom left-hand corner of the **New database template** window. This will load a sample **Input** Window showing the layout of the database template that you have selected. If this is suitable, click **[OK]** and then click **[Save and Quit]**.

AquaChem will then automatically create an Aquachem database file (***filename.hc3***) and the associated maskfile (***filename.msk***) containing the specified data structure for each record in the database.

2.7.3 Entering Data in the Database

Once you have created your AquaChem project database, the next step is to begin entering the sample information. Data can be imported from a tab delimited text file, or manually entered directly into AquaChem using either the **Input** window or the **Spreadsheet** view.

Importing Data

To import data from an external tab-delimited ASCII text file:

- select **File/Import ASCII**
- match the columns of the ASCII file to the AquaChem data fields
- select the appropriate concentration units
- click the **[OK]** button to start importing

See Section 4.2.1 on page 39 for a more detailed description of importing ASCII files.

Creating a New Record

To create a new record, select **Records\New** from the **Main Menu**. The **Input** window will appear with blank cells for each parameter. Click the mouse in the upper cell of the **Header Group** and then enter the appropriate information. Use the **<Enter>** key to accept the value and advance to the cell below. Select **Record\Save** to add the new record to your database.

NOTE: AquaChem requires you to use a point "." decimal for all numeric data!

2.8 Printing

AquaChem generates two types of output; (i) text-based reports containing specific information or summaries of the data; and (ii) graphical reports containing one or more open graphs. To setup the printer, select **File/Printer Setup** and a **Print** dialogue box appears that allows you to select the appropriate printer, network path, # copies, other properties.

2.8.1 Printing a Text Report

To print one of the text-based reports generated by AquaChem, simply click on the report window to make it the active window, and then select **File/Print**. The contents of the text window will be printed to the printer. Many of the report windows also have a **[Print]** button on the lower left-hand side of the window that can also be used to print the report.

2.8.2 Printing a Graph

To print one or more of the onscreen graphs, select **File\Print** from the **Graphics Menu**. A **Print Preview** window will appear with a **Print Options** dialogue box as shown in the following figure.

The **Print Options** dialogue box allows you to select which plots to print, and then set the size and location of each plot on the page. To print one (or more) plots you must select the desired plot(s) from the list of **Available Plots** and then move it to the list of **Selected Plots** by clicking the left arrow **[<]** button. The selected plot(s) will appear in the **Print Preview** window and will be automatically sized and arranged to fit the screen. To remove a plot from the **Print Preview** window, click on the plot under the **Selected Plots** list and then click the right arrow **[>]** button.

Arranging the Plots

The position and size of the plots can be easily modified using the **Arrangement** tab provided in the **Print Options** dialog box. The position/size of a single plot can be modified by clicking on the plot in the **Selected Plots** list (make sure only one plot is selected) and then making the desired changes to the position and/or size. Press the **<Ener>** key or click the **[Preview]** button to update the print preview. See Section 5.15 for a more detailed explanation of the plot arrangement options.

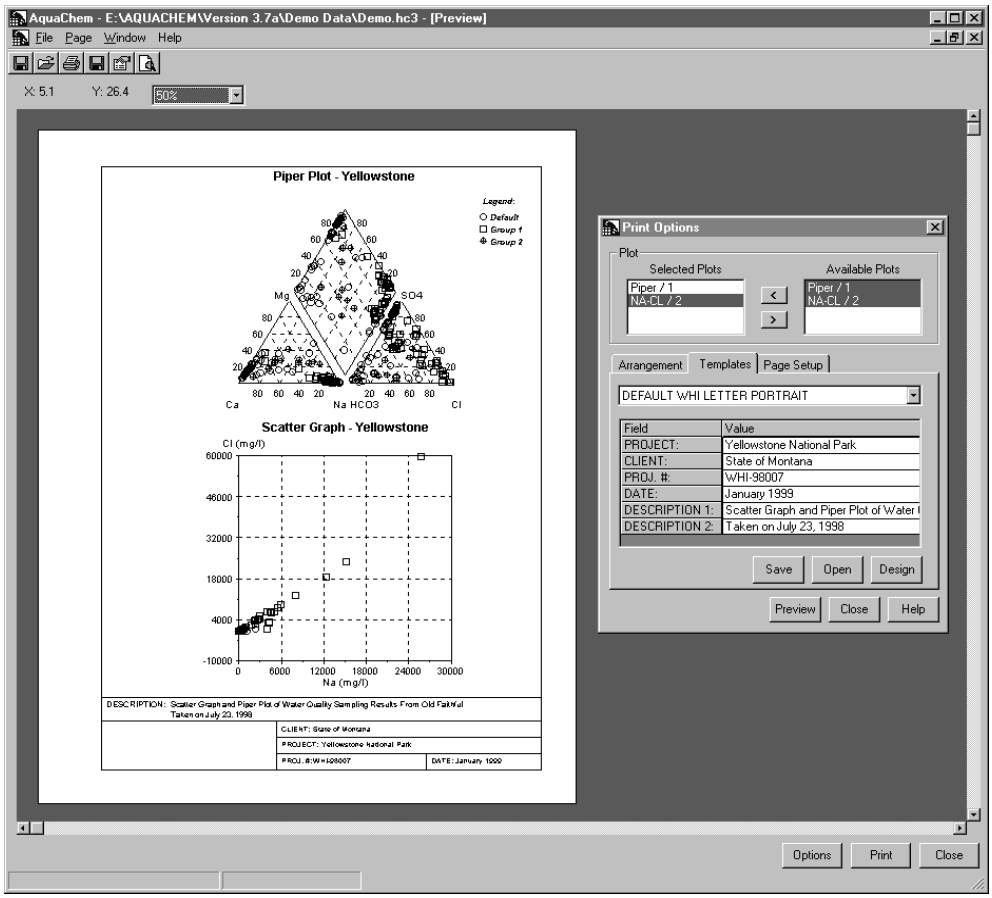


Figure 2.8: Graphics Printing Options

Selecting a Print Template

The **Templates** tab provided in the **Print Options** dialog box allows you to select from a list of pre-defined print templates that allow you to add more detailed descriptions of the plot(s), the project, and the client. The list of available templates provided with AquaChem includes:

- None
- Default A4 Portrait
- Default Letter Portrait
- Default Letter Landscape
- Default Tabloid Landscape

The default template selection is "None" (meaning no template has been selected). If "None" is selected you can enter a two line title at the top of the page plus a footer at the bottom of the page. In addition, all of the **Page Setup** tab options are available for adjusting the page margins and turning the page border on or off.

If you select one of the pre-defined WHI print templates, a list of available descriptor fields will appear and the **Print Preview** window will be updated to reflect the layout of the selected template. The information you enter in the descriptor fields can be saved to a

project template file (***templatename.tpl***) to avoid re-entering repetitive information for each printed page (e.g. project name, client name, project number).

If the pre-defined print templates are not satisfactory for your needs, you can easily create your own customized print templates using the **[Design]** option in the **Templates** tab. For a detailed description of the template design features, please refer to Section 5.15.

Printing to a Windows Metafile

With this latest version of AquaChem you can now export the graphic in the Print Preview window to a Windows metafile for pasting in a report or for further graphic enhancements. To create a metafile of the print preview graphics, select File/Export to metafile.

2.9 Obtaining Technical Support

If you have a problem using AquaChem, please feel free to contact Waterloo Hydrogeologic Inc. for free technical support via phone, fax or e-mail (available only to registered users of AquaChem). Our contact information is as follows:

Waterloo Hydrogeologic, Inc.
180 Columbia Street West - Unit 1104
Waterloo, Ontario, Canada, N2L 3L3
Tel. (519) 746-1798
Fax (519) 885-5262
E-mail techsupport@flowpath.com
Web http://www.flowpath.com

Generally, we reply to all technical support questions within one business day, however please allow up to two business days for a response.

In addition to a brief description of your problem, on all correspondence please provide your

- name,
- company and office,
- telephone and fax numbers,
- email address (if you have one),
- serial number, and
- the build date of your version.

The build date of your version can be found by choosing the **About AquaChem** menu option under **Help** in the **Main Menu**.

If your question is of a "How do I...?" type, the above information is generally sufficient. However, if you are reporting a bug (especially one that causes a system crash) or are having technical problems with the program please provide the following additional information:

- a list of your current hardware setup, and operating system details
- a copy of your autoexec.bat, and config.sys,
- the amount of RAM you have on your system,
- the amount of free hard disk space remaining on your machine, and
- a detailed description of when and how the problem occurs.

If we are unable to reproduce your problem, or are otherwise unable to solve it, we may ask you to send us a copy of your project files.

3

Tutorial

3.1 Learning Objective

To use AquaChem to compare and analyze groundwater samples.

3.2 Introduction

This exercise is a step-by-step example of some of AquaChem's key features and analysis capabilities. You will use AquaChem to query the database, calculate various hydrochemical properties, and create a variety of common aqueous geochemical graphs. The example study seeks to characterize water samples from two mineral springs that are fed by the Muschelkalk aquifer located in Alsace, France. The water from the Lithinee mineral spring is used for mineral water, while the water from the Arsene site is a mixture of ascending mineral water and surficial water

3.3 Terms and Notation

The following terms and notations will be used:

type	Type in the given word or value
select	Click the left mouse button where indicated
↦	Press the **<Tab>** key
↵	Press the **<Enter>** key
☞	Click the left mouse button where indicated
☞☞	Double-click the left mouse button where indicated

The **bold faced type** indicates menu or window items to click, or values to type.

[...] denotes a button to click.

...\...\... denotes a menu selection.

The **Main Menu** is displayed when the Records List window is active.

The **Graphics Menu** is available when a graph window is active.

The **Input Menu** is available when the Input window is active.

3.4 Start AquaChem

To start AquaChem, you must have it installed on your hard disk. If you have not yet installed AquaChem, go to section 2.2 on page 5 for installation instructions. Otherwise, click **Start**, and choose **Programs/WHI/AquaChem**.

An **Open Database** dialog box will prompt you to select an AquaChem database to open.

Select **demo.hc3** (in the Open Database dialog box)

☞ **[Open]**

A **Record List** window will appear with some summary information for the sample records provided in the demo database. As you can see from the information displayed in the **Record List**, there are 28 sample records in total, with seven samples collected from four different sites. A single sample was collected annually from each site from 1992 until 1998. It should be noted that, while the locations for the samples are real, the sample information has been fabricated for the purpose of this demonstration tutorial.

3.4.1 Customizing the Record List

The summary information displayed in the Record List can be customized by selecting **File/ Preferences** from the **Main Menu** and adding or subtracting items from the **Record List Columns** frame. The parameters displayed in the **Record List** are listed under the **Parameter** column, while the field length is indicated under the **Length** column. To change a parameter in the **Record List**, simply double-click on the target parameter and select a new parameter from the drop-down list. For this example, you will change the field marked 'Geology' to 'Date'.

☞☞ **Geology**

☞ **Date**

Press **<Enter>**

☞ **[Save]**

To change the order of the parameters in the **Record List**, select the target parameter and then use the **[Up]** and **[Down]** buttons. To remove a parameter from the **Record List**, double-click on the target parameter and use the backspace key to delete the parameter name and field length.

Once you have customized the **Record List** to your liking, click the **[Save]** button to save the changes and then press the **[Close]** button to return to the **Main Menu**.

3.4.2 Editing Data

To activate the **Input** window simply double-click on any record in the **Record List** (or right-click on a record and select **Edit**). The **Input** window should appear as shown in the following figure.

The **Input** window displays all of the data for a single record in the database including **Measured values**, **Modeled values** and **Calculated values**. You can navigate through all of the records in the database using the previous **[<]** and next **[>]** push buttons at the bottom of the window.

To change one of the parameter values simply click in the cell, type a new value and press the **<Enter>** key. Use the arrow keys to navigate up and down the parameter lists.

To change the displayed concentration units select **Unit/meq/L** from the top menu bar. All of the measured values for the Cations, Anions and Uncharged compounds will be immediately updated to reflect the new concentration units.

In some instances you may not have information on one of the major ions. AquaChem allows you to calculate the concentration of the missing ion based on a valence balance. To see how this works you must first delete the sodium (Na**)** value for the open record and press the **[Save]** button.

Now calculate the concentration of sodium by selecting **Calculate/Missing/Na** from the top menu bar. The calculated value should be quite close to the original value. Similarly, you can also calculate the missing concentrations of any of the major ions.

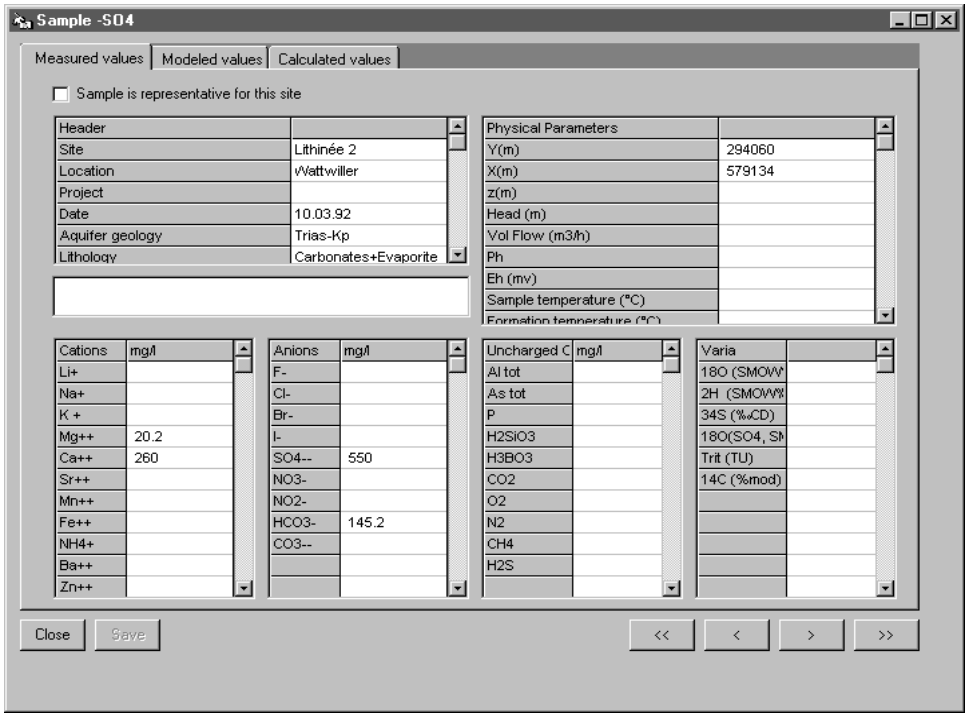


Figure 3.1: Input window

Close the **Input** window by clicking the **[Save]** button to save the new data and then press the **[X]** short cut button in the top right corner of the **Input** window.

3.5 Assigning Symbol Groups

In order to easily identify the data points from each sample location, you can assign a specific symbol to each sample group. Each symbol group is associated with a specific number, shape and color for easily identifying the associated sample records in the **Record List** and on a graph.

Follow the steps described below to assign symbol groups to each sampling location.

- Use the mouse to select each of the first seven sample records (click-and-drag the mouse over each record, or hold the **<Ctrl>** key down and click on each record)
- Right-click on the selected records and a pop-up menu will appear
- Select **Assign Symbol**
- An **Assign Symbol** dialogue box will appear with a list of available Symbol Groups and the default symbol shape associated to the selected group
- Select **Group 1 (01)** and then click the **[Assign]** button

  NOTE: This will assign each of the samples collected from the Albergo site to Group 1. In the **Record List**, each sample from the Albergo site now has '(01)' under the Group heading indicating it belongs to Group 1. On a plot, each sample from Group 1 will be represented by a square symbol. However, both the name of the group and the associated symbol shape, color and size can be customized to your liking.

- Now repeat these steps and assign symbol groups to the sample records from the Schwefelq site (Group 2), the Mauritius site (Group 3) and the Lithinee site (Group 4)

When you are finished, each of the sample records in the **Record List** should be assigned to the appropriate symbol group.

3.6 Querying the Database

The database querying function in AquaChem allows you to search and select a single record or groups of records satisfying a specified search criteria. To use the AquaChem database querying option, select **Records\Search** from the **Main Menu**.

The **Search Records** dialog box will appear as shown in Figure 3.2.

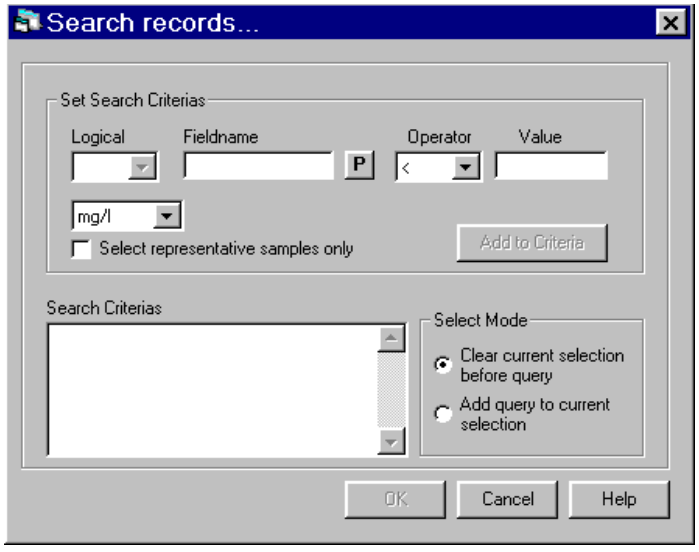


Figure 3.2: Search Records window

In this example you will search the database for all sample records with sodium concentrations greater than 100 mg/l.

AquaChem will allow you to search for a parameter based on the Internal name of that parameter. In many instances you will not remember the exact Internal name of the parameter that you want to search for, so AquaChem provides a parameter list of all available parameters in the open database. To activate and display the Parameters window:

☞ **[P]** (under Set Search Criterion)

Now click and drag **'Na'** from the **Parameter List** window into **Fieldname** text box. The parameter **'Na'** should now appear in the **Fieldname** text box.

Click the arrow button under **Operator**, and choose the **'>'** symbol from the drop down menu.

type **100** (in the **Value** text box)

☞ **[Add to Criteria]**

'NA < 100' should now appear in the **Search Criterion** text field.

☞ ⊙ **Clear current selection before query**

☞ **[OK]**

All of the samples from the Mauritius site should now be selected in the **Record List**. This tells you that all of the samples from the Mauritius site contain sodium concentrations in excess of 100 mg/l.

If you are interested in dealing only with this subset of data, you can temporarily remove the other samples from the database by selecting **Selection/Omit not selected**. Now only the samples from the Mauritius site will be listed in the **Record List**. All calculations, reports and plots will only consider this subset of the data.

Select **Selection/Show All** to restore the entire dataset.

3.7 Analyzing the Data

3.7.1 General Reports

The General Report provides a summary of the measured and calculated parameters for the selected sample record. To create a General Report,

☞ **Acq-Alb-1** (in the Record List)

Select **Reports\General** (from the **Main Menu**)

The **General Information** report window will be displayed as shown in Figure 3.2.

To view the **General Information** report for other samples, select **Records\Previous** and **Records\Next** from the menu bar or click the push buttons **[<] [>]** on the bottom right-hand side of the **General Information** window.

The **General Report** can be printed, saved to a text file or copied and pasted into a spreadsheet or report document for formatting.

☞ **[Close]** (to close the General Information window)

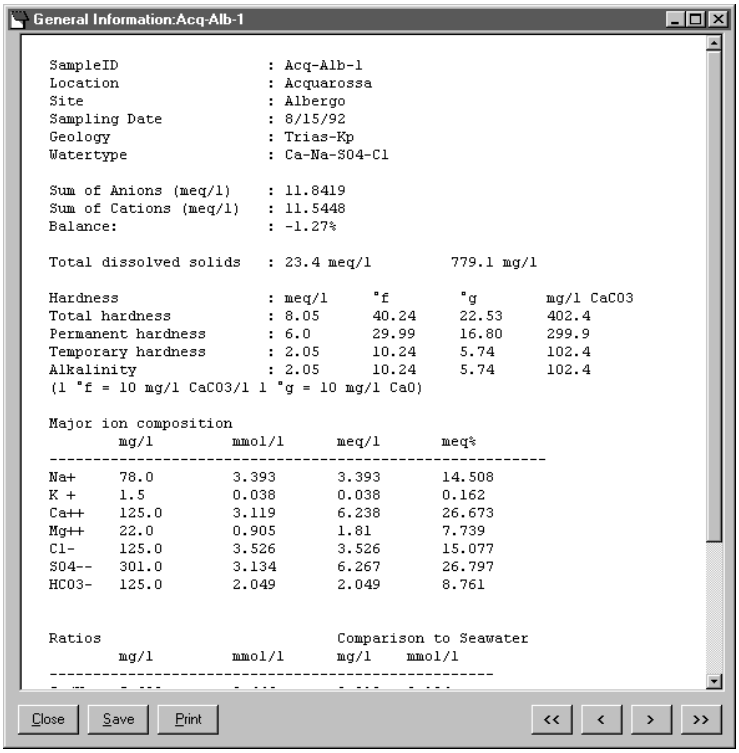


Figure 3.3: General Information window

3.7.2 Statistics Report

The Statistical Report provides a statistical summary of selected parameters for all active sample records. To view a Statistical Report for all samples in the Record List:

Select **Tools/Statistics** (from the **Main Menu**)

☞ **[OK]** (to accept the default settings)

The minimum, maximum, arithmetic mean, standard deviation, as well as other values of interest will be calculated for the selected database parameters. The parameters selected for statistical analyses can be easily customized and saved using the **[Set Defaults]** button.

3.7.3 Correlation Matrix

To calculate a correlation matrix for the major ions from all active sample records:

Select **Tools\Correlation matrix** (from the Main Menu)

☞ **[OK]** (to accept the default settings)

A **Correlation** window will appear listing correlation coefficients, y-axis intercepts, regression slopes and number of samples for each of the selected parameters (see Figure 3.4). Notice the high correlation between Na and Cl.

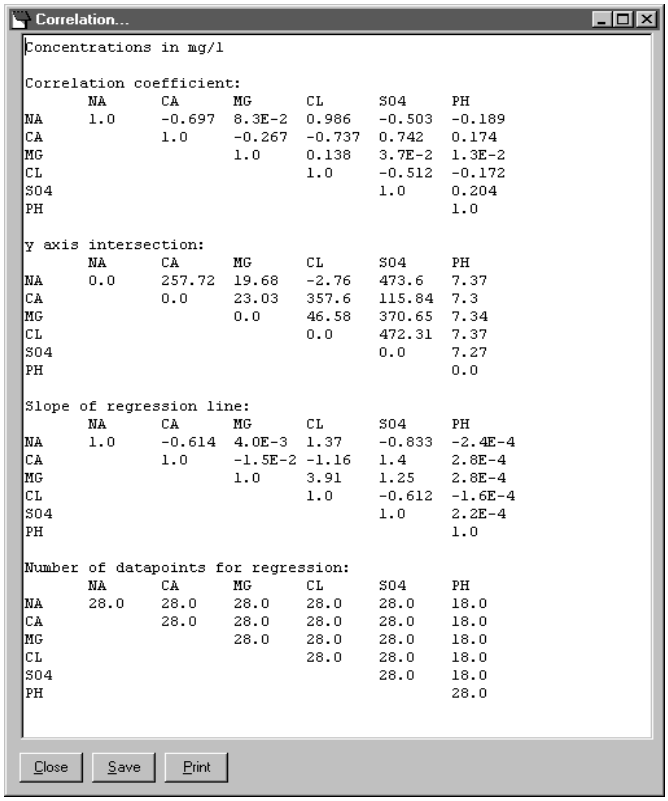


Figure 3.4: Correlation Matrix

Please close all report windows before proceeding to the next section of the tutorial (click the 'X' in the top right-hand corner of the report windows).

3.8 Graphing the Data

AquaChem allows you to create 13 different types of graphs commonly used for aqueous geochemical data analysis and interpretation. The following sections of the tutorial will describe how you can easily create, customize and display multiple graph types.

3.8.1 Piper Graph

Piper graphs provide an overview of the chemical composition of the samples. You will usually find it useful to start your analysis with a Piper graph.

- From the **Main Menu**,
- Select **Graphics\New\Piper**

A Piper Plot dialogue box will appear with default settings for which parameters will be plotted. These parameters can be modified at any time, but for this example we will accept the default parameter settings.

☞ **[OK]** (to accept the default settings)

A **Piper** plot graphics window will appear as shown in Figure 3.5. Enlarge the graphics window to make it easier to view. This plot clearly indicates that there are four distinct groups of samples, each with distinctly different water chemistry.

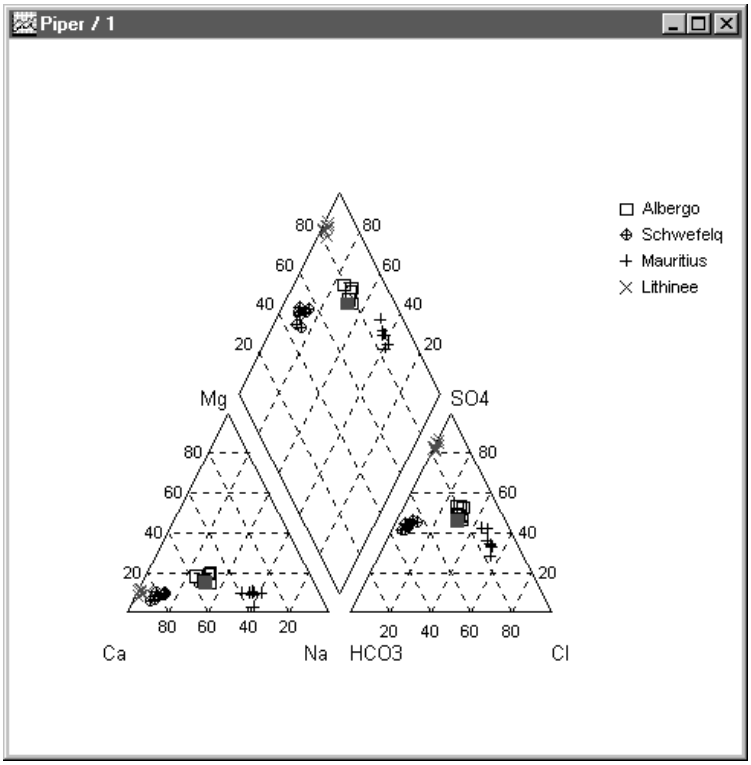


Figure 3.5: Piper Plot

Notice that if you click on a sample point in the graph, the corresponding record will be selected in the **Record List**. In addition, you can also place a label beside each of the selected sample points.

To open the graphic options dialogue box you must right-click on the open graph window (in this case, right-click on the Piper plot). A **Piper plot** graphic options dialogue box will then appear. Notice that each graphic options dialogue box has a **[Set Defaults]** button that allows you to save the appearance settings for each of the graph types.

☞ **Options** tab

The **Options** tab allows you to modify the appearance of the graph by adding a title, changing the fonts, adding a legend, or removing the grid. The **[Symbols]** button provides options for customizing the appearance of the graph symbols.

To label the symbols,

☞ **Label** (in the Symbol Options frame)

☞ **Site** (from the list of available symbol labels)

☞ **[Apply]** (to accept this change)

Now all of the highlighted symbols on the Piper plot will have labels beside them. The font type, size and style of the symbol label can be customized to your liking.

You can also change the name, shape and color of the symbols.

☞ **[Symbols]**

A **Define Symbol or Line** dialogue box will appear as shown below.

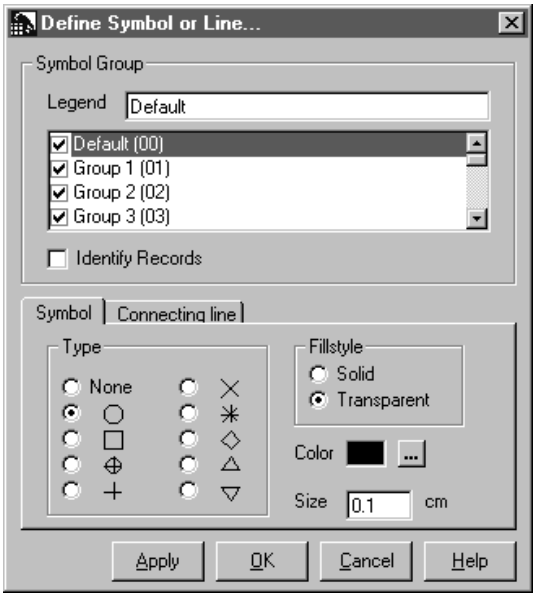


Figure 3.6: Define Symbol or Line dialogue box

The list of available symbol groups is shown in the list box. There is a maximum of 50 available symbol groups. Unless otherwise specified, all sample records are automatically assigned to the Default symbol group. The checkbox beside each symbol group is used to indicate which groups are active and which groups are inactive (only active groups are plotted on the graphs). The names of the groups will be displayed in the legend of each plot. These names can be easily changed by clicking on the group name and entering a new name in the **Legend** text box.

- Select **Group 1 (01)** and change the name to Albergo.
- Press **<Enter>** to accept the change.
- Select **Group 2 (02)** and change the name to Schwefelq.
- Press **<Enter>** to accept the change.
- Select **Group 3 (03)** and change the name to Mauritius.
- Press **<Enter>** to accept the change.
- Select **Group 4 (04)** and change the name to Lihinee.
- Press **<Enter>** to accept the change.
- Deactivate the **Default** symbol group since all samples now belong to a defined symbol group

The symbol shape for each group is indicated in the **Symbol** tab in the bottom half of the dialogue box. The symbol shape associated with each group can be easily changed to any of the symbol shapes and colors provided. For this example you will not adjust the symbol shapes.

☞ **[OK]** (to accept the remaining symbol settings)

To display a legend on the Piper plot,

☞ **Legend** (to activate the checkbox)

☞ **[Apply]** (to apply these changes to the Piper plot)

☞ **[Set Defaults]** (to save the Piper plot settings)

☞ **[OK]**

The legend will be plotted along the right-hand side of the Piper plot graphics window as shown in Figure 3.5.

3.8.2 Schoeller Graph

The Piper plot provided a good overview of the data. Next you will plot a Schoeller graph to get more details on the concentrations of the major ions for each record in the database.

From the **Main Menu**, select **Graphics\New\Schoeller**.

A **Schoeller plot** graphic options dialogue box will

☞ **[Apply]** (to accept the default settings)

A Schoeller graph will appear as shown in the figure below.

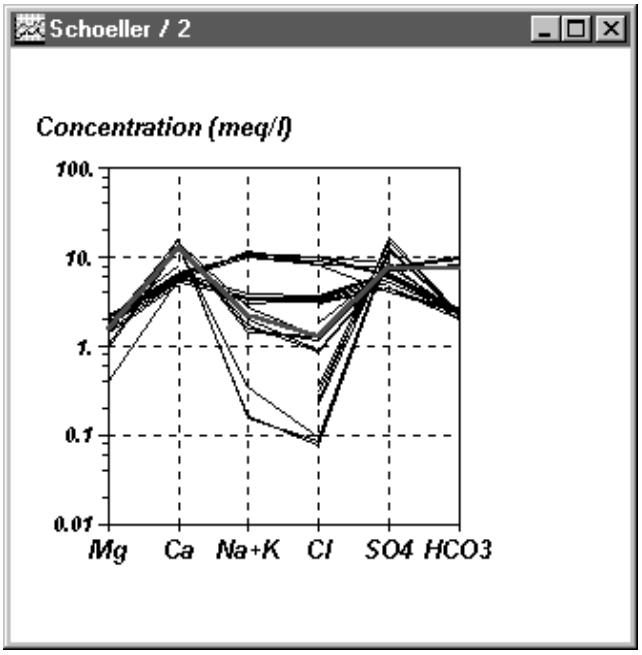


Figure 3.7: Schoeller graph for sample data

This graph provides a comparison of the log of the concentrations of the major ions for each sample record in the database. The highlighted line on the graph corresponds to the selected record in the **Record List**.

To display the legend and the symbols for each record, select the **Options** tab in the **Schoeller plot** graphic options dialogue box.

☞ **Legend**

☞ **Symbols**

☞ **[Apply]**

To modify the line settings,

☞ **[Symbols]**

The **Define Symbol or Line** dialogue box will appear.

Select the **Connecting Line** tab to access the line appearance options as shown in the following figure.

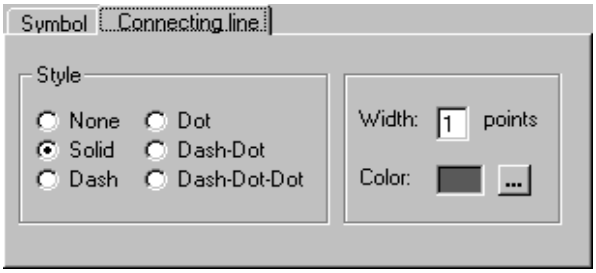


Figure 3.8: Connecting Line options frame

☞ **Albergo (01)** (in the list of groups)

☞ **Dash**

☞ **[...]**

A color selection dialogue box will appear. Choose one of the blue shades.

☞ **[OK]**

☞ **[OK]**

The Schoeller graph should now appear with a legend on the right-hand side and blue lines representing the Arsene sample records.

Now you should have both a Piper plot and a Schoeller graph displayed on your screen. Notice that if you select a record in the **Record List**, this record is highlighted on both the Piper plot and the Schoeller graph. In addition, any changes that are made to the sample data will be immediately reflected on both of these plots.

3.8.3 Scatter Plots

The correlation analysis showed a high-correlation between the Ca and SO4 concentrations. It might be interesting to plot the relationship between these two parameters using an X-Y Scatter graph.

From the **Main Menu**, select **Graphics\New\Scatter**.

A **Scatter plot** graphic options dialogue box will appear with the default settings for plotting an X-Y Scatter graph for Na vs. Cl. You will need to change these default settings.

Then double-click in the **X-Parameter** text box to highlight **Na** and replace it with **Ca**

Next double-click in the **Y-Parameter** text box to highlight **Cl** and replace it with **SO4**.

☞ **[Apply]** (to accept the new settings)

A scatter graph will appear as shown in the figure below.

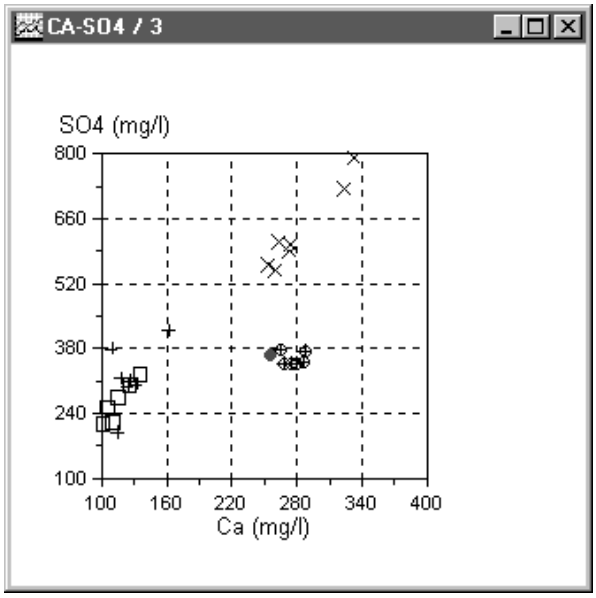


Figure 3.9: Scatter graph for sample data

This graph clearly indicates a much higher ratio of Ca to SO_4 for those samples taken from the Schwefelq site. However, this is not the only relationship that you can show on this graph (or any graph for that matter). AquaChem also allows you to easily plot the symbol sizes relative to the concentration of any parameter in the database.

☞ **[P]** (to load the **Parameter List**)

Now search the **Parameter List** for '**TDS**' and drag it into the text box labelled **Symbols Size Proportional To:**. The symbol sizes for both the Arsene samples and the Lithinee samples will now be plotted relative to the Total Dissolved Solids (TDS) value for each sample.

☞ **[Apply]** (to accept the new settings)

The scatter graph should clearly show that the samples from the Albergo site and the Mauritius site have a higher level of TDS than the samples from the Lithinee site and the Schwefelq site.

3.8.4 Radial Plots

The first step is to select any two records from the **Record List** (preferably from different sites). To select two records you must click on one records and then press the **<Ctrl>** key while you select another record.

To create a radial plot,

☞ **Graphic/New/Radial**

☞ **[OK]** (to accept the default settings)

Two radial plot will appear for the two records that you selected. To edit the appearance of either of these radial plots simply right-click on them and a **Radial plot** graphic options dialogue box will appear.

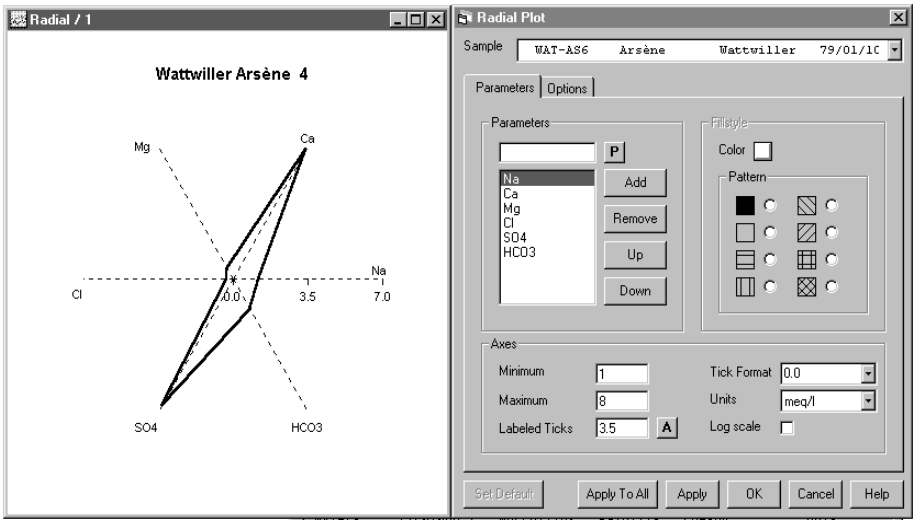


Figure 3.10: Radial plot and graphic options dialogue box

At the top of the **Radial plot** graphics option dialogue box there is a combo box that provides a list of the samples that are displayed as radial plots. To view the graph settings for a particular sample you simply select that sample from the list, and all of the graphic options will be displayed for the selected sample.

Now you should have four **Graphics** windows and the **Record List** window displayed on your screen. To arrange these windows,

☞ **Windows/Tile Vertical**

All of the open windows will be automatically arranged to fit the screen.

3.9 Printing the Graphs

From the **Graphics Menu**, select **File\Print** (one of the graphs must be selected first).

A list of **Available plots** will appear on the right-hand side of the **Print Options** dialogue box. This list represents the plots which are currently open in AquaChem and are available to be printed or output to a graphics file. In this example you will print only the Piper plot.

The first step, before you select the plots to print, is to select the page layout or to choose a print template. To choose a print template,

- Select the **Templates** tab
- The default template setting is **NONE**
- Click on the dropdown menu and select the **DEFAULT LETTER PORTRAIT** template

A list of plot descriptors will appear in the **Print Options** dialogue box and the print preview window will be automatically updated to reflect the template settings (see Figure 3.11). The plot descriptors contain information that is both project specific and plot specific. The project specific information can be saved to a print template configuration file (.TPL extension) to avoid re-typing it each time.

> **NOTE:** The Waterloo Hydrogeologic logo shown in the bottom left-hand corner of the page can be easily replaced with your own company logo (see section 6.4 on page 128).

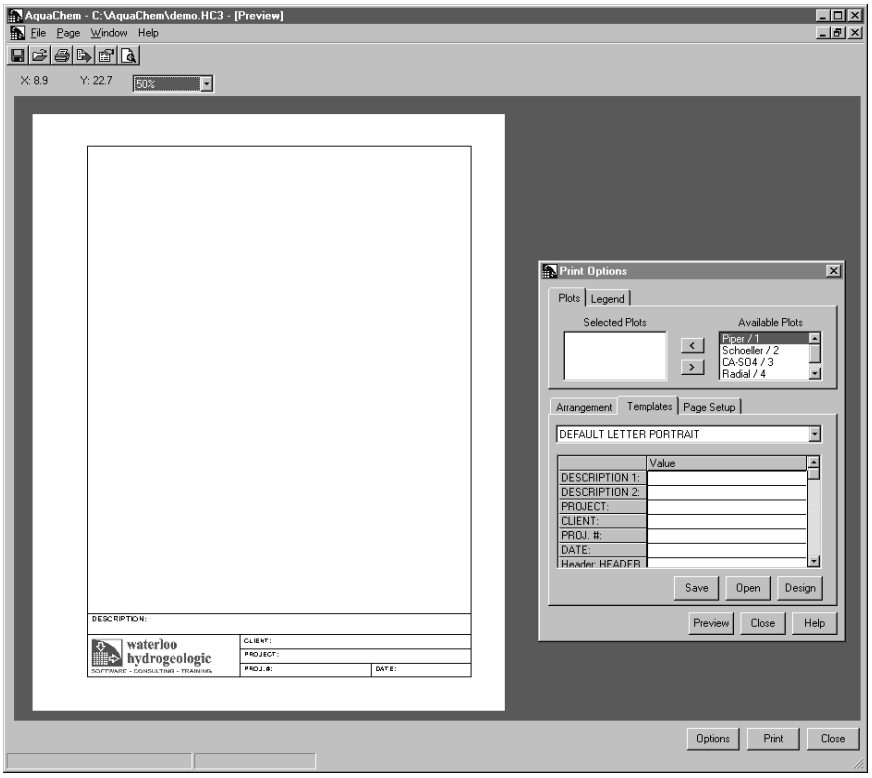


Figure 3.11: Print Preview window

Next, fill in the project specific plot description fields as follows (press the **<Enter>** key after each entry):

PROJECT: Demo Project

CLIENT: ACME Industry

PROJ #: 99-10024

DATE: current date

Leave the **HEADER** and **FOOTER** fields blank.

- To save these template description settings,
- Press the **[Save]** button in the Templates tab
- A **Save Template Settings** dialogue box will prompt you for a file name
- Press the **[Save]** button to accept the default name of DEMO.TPL.

These template description settings can now be easily recalled during future printing sessions using the same project data.

Next you must select which plot(s) to print. For this example you will select only the Piper plot. However, you can plot multiple plots on the same page if desired.

- Scroll to the top of the **Available plots** list and click on **Piper**
- Click on the left arrow **[<]** button to move the Piper plot to the **Selected plots** list.

The plot will be automatically sized to fit the page layout as shown in Figure 3.12. If the default page settings are not acceptable, you can manually change the individual size and position of each plot using the options provided in the **Arrangement** tab, and you can easily change the page layout using the options provided in the **Page Setup** tab.

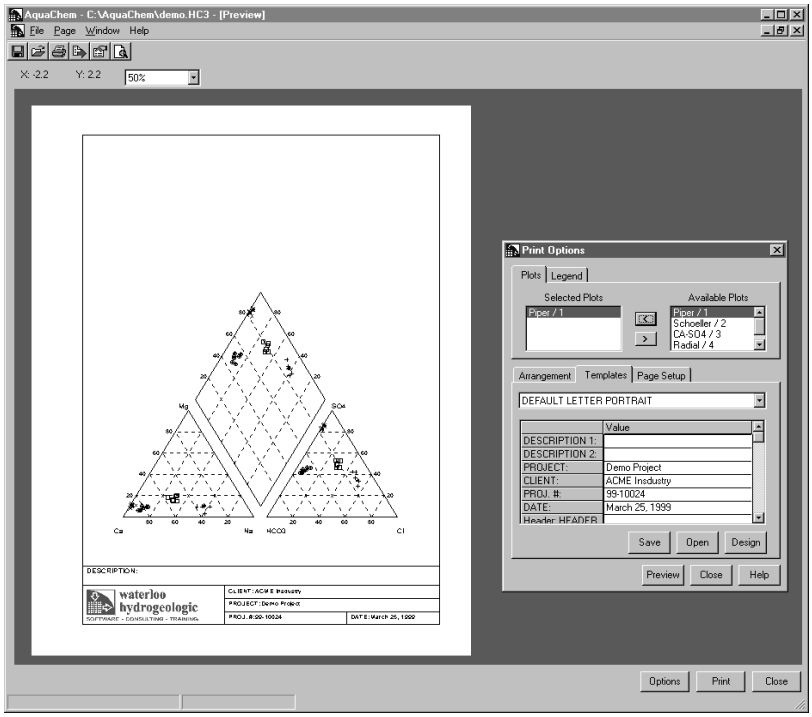


Figure 3.12: Print Preview of Piper Plot

Next, you must select the Piper plot legend and positon it on the page.

- Select the **Legends** tab at the top of the **Print Options** dialogue box
- A list of **Available legends** will be provided for all graphs currently open in AquaChem
- Click on **Piper** and then click the left arrow **[<]** button
- The Piper plot legend will appear at the top left-hand corner of the page
- Click in the **Positon X** field and enter a value of **13**

- Click in the **Postion Y** field and enter a value of **19**
- Press the **[Preview]** button to preview the legend position on the page
- Now return to the Plots tab and enter the following plot description (press the **<Enter>** key to register each entry):

  DESCRIPTION 1: Piper plot of annual water quality monitoring

  DESCRIPTION 2: Samples collected from 1992 to 1998

- Press the **[Preview]** button to preview the page.
- Press the **[Print]** button on the bottom right-hand corner to print the plot to a printer.

This concludes the tutorial guide for AquaChem.

Although the purpose of this tutorial guide is to highlight some of the key features and analysis capabilities of AquaChem, it really only scratches the surface of the potential applications for this software package for managing, analyzing, interpreting and plotting aqueous geochemical data. Please continue to explore the program and discover for yourself how truly powerful it is.

If you have any specific questions regarding the features and analysis capabilities of AquaChem, please contact a Waterloo Hydrogeologic technical representative at:

Tel. (519) 746-1798

Fax (519) 885-5262

E-mail techsupport@flowpath.com

4

Menu Commands

4.1 All Menus

4.1.1 Windows

Open AquaChem windows are listed in the **Windows** drop down menu, and can be activated by clicking the window's title in the **Windows** drop down menu.

Tile Horizontal

Arranges open windows one above the other.

Tile Vertical

Arranges open windows side by side.

Cascade

Cascades open windows.

Arrange Icons

Organizes icons of minimized windows along the bottom of the parent window.

4.1.2 Help

On-line help and general information are available from the drop down **Help** menu.

4.2 Main Menu

The **Main Menu** can be accessed when the **Records List** window is active.

4.2.1 File

New

Creates a new Aquachem project database file (***filename.hc3***). See Section 8.2 on page 167 for detailed instructions on how to create a new AquaChem project database. If any **Graph** windows are open on your workspace, you will be prompted to close them.

Open

Opens an existing AquaChem project database file (***filename.hc3***). The directory of the selected database becomes the default directory for all further read and write operations. It is recommended that all project data files be separated from the application directory. If you work with different databases, each one should have its own directory. If there are graph

windows open on your workspace, you will be prompted to close them before opening a different project database file.

Close

Closes the current database and empties the Record List. All open **Graphic** windows, **Text** windows, **Input** windows, and dialog boxes will be closed.

Save As

Saves the current database under a different name or to a different directory. This operation is useful for creating a backup copy before making substantial changes to the database.

Import ASCII

The Import ASCII option imports data from a tab-delimited text file (***filename.txt***) with the following file structure: sample records as rows, sample parameters as columns. The first row of the tab-delimited ASCII text file must contain the parameter labels for each column of data in the spreadsheet.

The **Import ASCII file** dialogue box is shown in Figure 4.1 below.

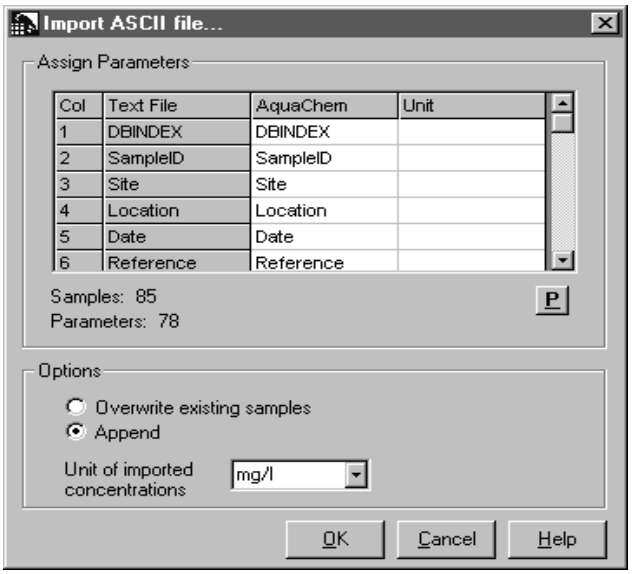


Figure 4.1: Import ASCII File Window

The **Assign Parameters** frame contains a table listing the column numbers, the ASCII Text File column headers, the corresponding AquaChem field labels, and the appropriate units for each imported parameter. The total number of samples in the text file, and the total number of parameters is shown below the table. Before proceeding with the import routine, check to make sure that the ASCII Text File column headers correspond to the appropriate AquaChem field labels.

The imported data can be either written over the existing records in the database by selecting the **Overwrite** radio button, or additional records can be appended to the end of the existing database by selecting the **Append** radio button. The **Overwrite** option can also be used to import data for blank field in the existing database records.

The **Units** field is used to select a 'default' concentration unit that will be applied to all of the imported parameters where a concentration unit is not otherwise indicated in the table. If all of the chemical parameters in the database have the same concentration units, you can simply use this field to select the appropriate concentration unit for all of the imported data.

How To ??? Hints

Matching Imported Data Fields

If the fields listed under the **Text File** column do not correspond to the fields listed under the **AquaChem** column, you can manually match the fields as follows:

- Double-click in the grid cell under the AquaChem column and a combo box will appear listing all of the available parameters in your AquaChem database.
- Select the appropriate parameter to match to the import Text File column.

OR

- Click on **[P]**, the button below the parameter table to load the **Parameter List** window containing all of the available in your AquaChem database.
- Click on the target cell under the AquaChem column heading
- Drag the target parameter from the **Parameter List** window into the target cell.

Selecting Concentration Units

AquaChem allows you to select either a uniform concentration unit for all imported chemicals, or variable concentration units for selected chemicals. Unless otherwise specified, the imported concentration units will be as indicated in the **Units** field. To change the default units, click on the down arrow in the Units field and you will see a selection of available units (mmol/l, mol/l, mg/l, ug/l and ppm).

To select different concentration units for individual parameters, double-click in the corresponding grid cell under the **Units** column and select the desired unit.

Export ASCII

The **Export ASCII** menu item exports all parameters from selected samples to a text file. This procedure is much faster than the **Main Menu\Record\View as Spreadsheet** command. However, the **Export** command does not give you all the options you have in the spreadsheet environment. You can not select which parameters to export, the unit of the exported data is always mg/l and you cannot export anything other than database parameters (for example you cannot export calculated parameters such as sums, ratios, geothermometer temperatures etc.). For more flexibility you should use the **Records/View as Spreadsheet** option and then save the spreadsheet as a text file.

Printer Setup

The **Printer Setup** allows you to select the destination printer location and customize the printer properties such as number of copies to print, landscape or portrait format, paper source, etc.

Preferences

The **Preferences** option is used to edit the default configurations and parameter settings that are used for most calculations and graphic displays. The **Preferences** dialogue box contains four separate tabs as shown in the Figure 4.2.

- **Startup Defaults** - Miscellaneous defaults settings
- **Thermometers** - Thermometer calculations and equations
- **Calculations** - Internal calculations and references
- **Data Structure** - Database parameters included in project file

The new preference settings can be applied to the database by clicking the **[Save]** button at the bottom of the dialogue box. Pressing the **[Save]** button will apply the new preference settings for the open AquaChem database and will save these settings to the ***filename.cfg*** file and/or the ***filename.msk*** file for future sessions.

Startup Defaults Tab

The **Start-up Defaults** tab allows you to specify some of the general/miscellaneous settings pertaining to the PHREEQC model settings and the appearance of the **Record List** window (see Figure 4.2).

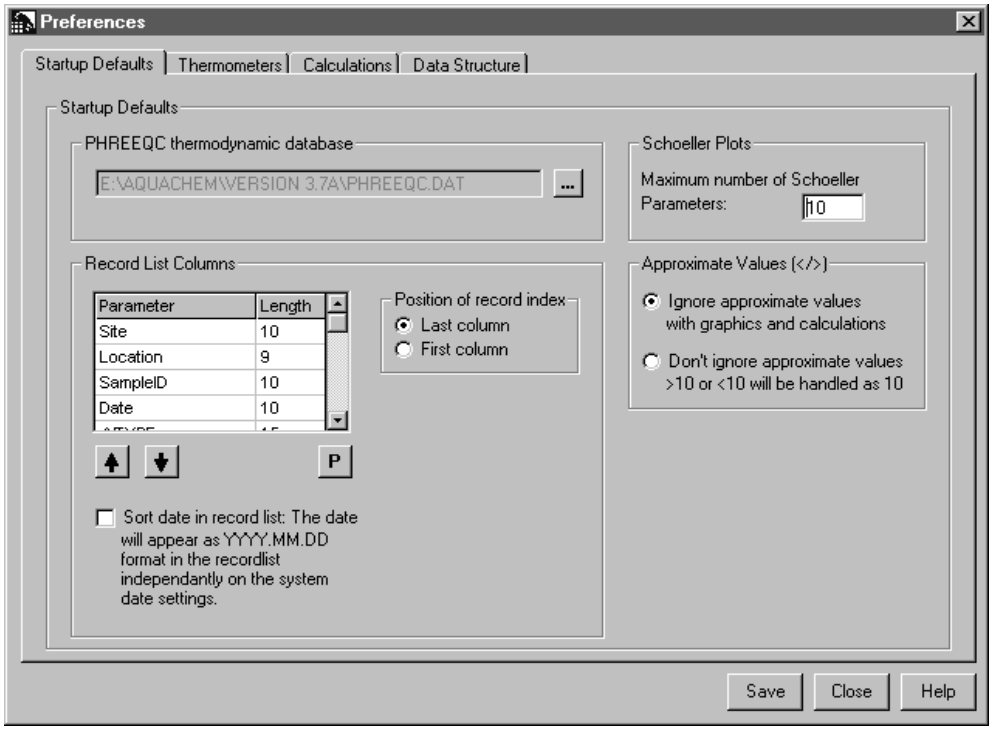


Figure 4.2: Start-up Defaults

PHREEQC Thermodynamic database

The PHREEQC program comes with three separate thermodynamic database files; ***phreeqc.dat*** (recommended); ***wateq4f.dat***; and ***minteq.dat***. The AquaChem interface for PHREEQC requires a 'link' to one of the available thermodynamic database files in order to obtain the parameters necessary to create the PHREEQC input data files. Refer to Chapter 7 for a more detailed explanation of the PHREEQC thermodynamic database files.

Each of the thermodynamic database files provided with AquaChem are essentially the same as the files that you get with the original programs, except they each contain some additional information required to link the parameters to the AquaChem database.

One of these files must be selected in order to perform a PHREEQC simulation and it must be located in the same directory as the PHREEQC.EXE file. The default setting is C:\PROGRAMS\WHI\AQUACHEM\PHREEQC.DAT. If you have installed AquaChem in directory other than the default installation directory, please update the default settings.

> **NOTE:** If you are running AquaChem under Windows NT, the PHREEQC.EXE file must be located in a directory that follows the DOS directory naming convention (e.g. 8 character names and no spaces).

Record List Columns

The **Record List** window is always sorted in ascending order according to the parameter in the first column. The **Record List Columns** table allows you to customize the appearance of the **Record List** window by selecting the parameters that appear under each column heading, and setting the field length of each parameter.

The first parameter in the Record List Columns table represents the first column in the **Record List**. The field length describes the number of character spaces that a parameter occupies in the **Record List**.

The **Record List** will always display the record index number (database index) of each record. This record index number can be displayed in either the first or the last column of the **Record List** window. If you choose to display the record index in the first column, the records will be sorted in ascending order according to the record index number.

The **Sort date** option is used to sort the **Record List** according to the date when the sample was collected. The date format as it appears in the **Record List** will automatically be changed to YYYY/MM/DD. This date format is required in order to sort the dates and will only appear in the **Record List**. To sort the **Record List** according to the sample date, you must move the **Date** field to the top of the **Parameter** list.

Schoeller Plots

The text box in the **Schoeller Plots** frame allows you to set the maximum number of parameters allowed in the Schoeller plots.

Approximate Values

AquaChem allows you to enter and store approximate measured values using the less than ('<') and greater than ('>') symbols. The approximate values options requires you to specify whether the approximate values will be ignored or included in the graphs. If you choose to ignore the approximate values, they will be treated as null entries. If you choose not to ignore these values, they will be interpreted as the values they are approximating (e.g. <0.01 will be treated as 0.01)

How To ??? Hints

Modifying the appearance of the Record List,

- Double-click on the parameter that you would like to change and a drop-down list of all available parameters will appear
- Select the parameter you would like to appear in the **Record List**
- Click in the **Length** cell and enter the desired field length
- Use the **[Up]** and **[Down]** arrow buttons to adjust the position of the parameter(s)

Thermometers Tab

Geothermometers are used to estimate the original subsurface reservoir temperature of ascending groundwater which underwent conductive cooling during their ascent. They reflect the temperature dependence of most rock-water reactions. The reactants, which remain dissolved during the journey to the surface, are, ideally, proportional to their original aquifer temperatures. For example, SiO_2 (Quartz or chalcedony dissolution or Na/K for albitisation). The original reference and the temperature range for which the thermometer is valid (most thermometers only work above 100 °C) can be viewed and edited.

Geothermometers are generally derived from the van't Hoff equation and have the form:

$$T(^\circ C) = \frac{a}{b + \log(K)} - 273$$

where:

a and *b* are constants describing a straight line in the 1000/T-log(K) plot, and

K depends on the reaction used for the geothermometer (SiO_2 for all SiO_2 thermometers, Na/K for the Na/K thermometer, etc.)

As thermometers are usually developed from empirical data, different coefficient values are found in the literature. AquaChem includes a compilation of most currently used geothermometers as shown in Figure 4.3. The equations for each of the thermometers are stored in the project configuration file (***filename.cfg***) and can be customized and modified. Each thermometer record includes the formula's coefficients, the reference (author and year), and the range within which the formula was calibrated. Refer to Section 5.3 on page 97 for more information about how to interpret geothermometers.

The **Thermometers** tab contains a list of available geothermometers that can be plotted on a geothermometers plot. If the thermometer is active (checked) it will be available for the geothermometers plot. If it is de-activated (not checked) it will not be available for the geothermometers plot and it will not appear in the geothermometer report.

The specific equation, reference and calibration range for each geothermometer can be viewed and modified by selecting the desired geothermometer from the list.

The **Formula** text fields contain the coefficients a, b, elements and their exponents as shown in the formula above.

The **Short Name** refers to the list name of the selected geothermometer.

The **Label** refers to the reference name of the geothermometer.

The **Reference** refers to the author and year of the original publication.

The **Range** refers to the temperature range within which the thermometer is supposed to provide reliable data. This normally corresponds to the range of the calibration data.

How To ??? Hints

Creating a New Geothermometer

You can add published thermometers from the literature or create your own thermometer if the formula structure corresponds to one of the pre-defined thermometers provided by Aquachem. For example, to create a new Na/K thermometer:

- select an existing Na/K geothermometer
- click the **[+]** button to create a new Na/K geothermometer
- select the new geothermometer
- enter a new **Short Name**, **Label** and **Reference**
- replace the formula parameters from the original geothermometer with the parameters from the new geothermometer
- press the **[Save]** button to save the changes

This new thermometer is automatically included in thermometer calculations or can be visualized as a thermometer plot.

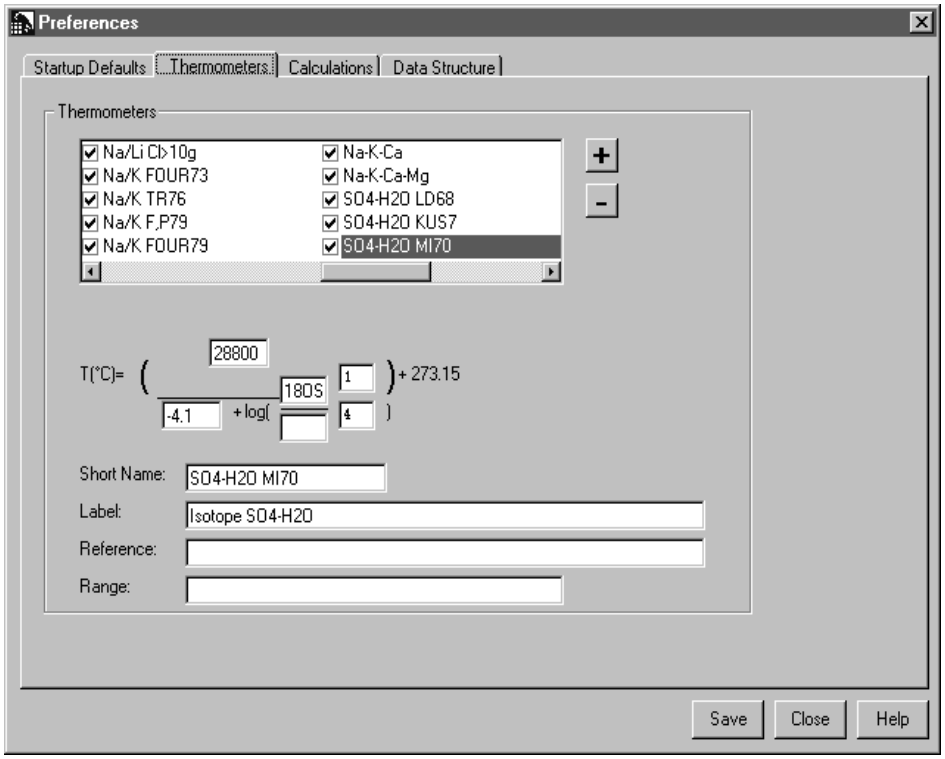


Figure 4.3: Thermometers Tab

Calculations Tab

The **Calculations** tab (see Figure 4.4) allows you to set the equation coefficients and parameters that are used in the isotope and geothermometer calculations. It also provides information on the various calculations that are automatically calculated by AquaChem.

Isotopes

Contains the parameters for oxygen 18 and deuterium equations: meteoric waterline, altitude-isotope and altitude-mean annual temperature relations. All of these functions are derived empirically. The coefficients for the isotope-altitude and the isotope-temperature functions are regional and should be used only in the area of calibration. Indicate the area of application of these functions in the window provided.

Any changes made to the isotope equations should be registered with AquaChem by pressing the **[Save]** button prior to closing the **Preferences** dialogue box.

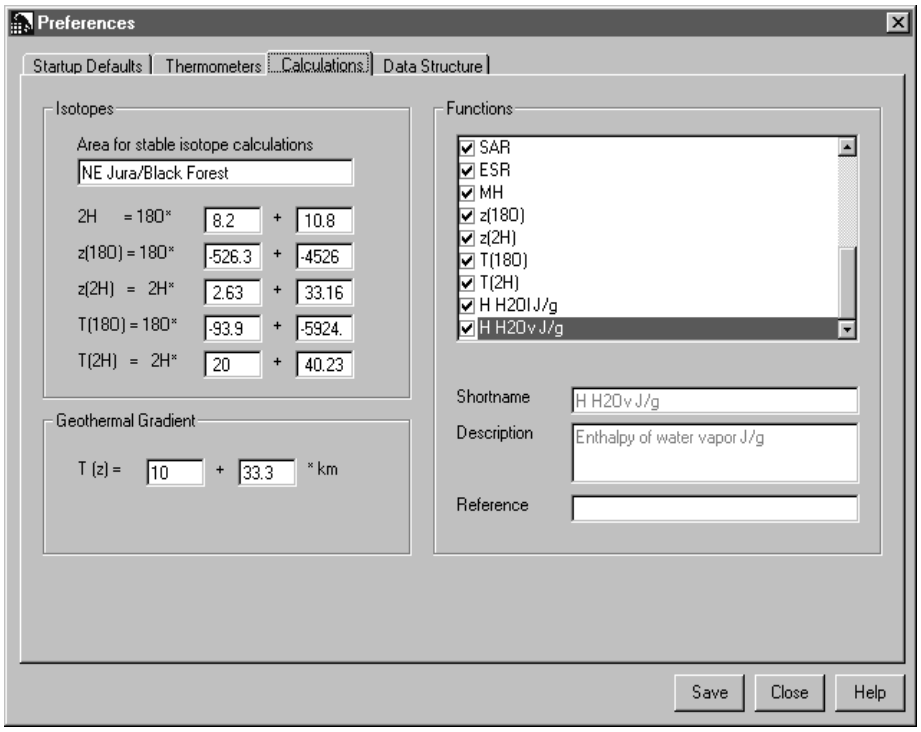


Figure 4.4: Calculations Tab

Geothermal gradient

The Geothermal Gradient is Specify the parameters to calculate the temperature at a given depth. The geothermal gradient is used in the geothermometer output window. It allows the user to estimate the subsurface temperature of waters produced by a borehole if the depth of the inflow zone is known. This temperature is then compared to geothermometer temperatures for the respective sample.

$T = T_D x \times z$

T_0= mean annual temperature

x = geothermal gradient (°C/km)

z = depth (m)

Any changes made to the Geothermal gradient equation should be registered with AquaChem by pressing the **[Save]** button prior to closing the **Preferences** dialogue box.

Functions

The **Functions** frame lists all of the built-in calculations performed by AquaChem, with reference information for each calculation provided in the fields below the list of functions. All of the active functions (as indicated by a checkmark) will be available as database parameters which can be included in statistical comparisons and for plotting data.

> **NOTE:** If your database does not include some of the required parameters, or if some of the required parameters are not properly named, then the applicable function(s) requiring these parameters will contain null values or erroneous information.

Data Structure Tab

The **Data Structure** tab allows you to modify the data structure of the current AquaChem database project by adding or deleting parameter fields from each of the nine parameter groups. The **Data Structure** tab can also be used to modify the attributes of each parameter in trhe database (e.g. Display label, Internal name, Molecular weight, Charge, and Guideline/Tolerance levels).

> **WARNING:** When modifying the data structure be careful NOT to change the Internal names for any of the major ions and isotopes. These parameters are used in many of the built-in calculations performed by AquaChem and are required to have a specific format in order for the calculations to function properly.

Each of the nine available parameter groups can be selected from the **Parameter Group** dropdown list at the top of the dialogue box. Once you have selected a Parameter Group, the relevant parameters from the selected group will appear in the underlying listbox as shown in Figure 4.5. The order of the parameters in the list box is the order they will appear in the **Input** window.

The **Display label** is the parameter label that is displayed in the **Input** window, in text reports and on graphs.

The **Internal Name** is the parameter name that is used by AquaChem to locate data from fields that are used for internal calculations (e.g. alkalinity, hardness, ion ratios, etc.).

The **Molecular Weight** is the numeric value for the molecular weight of the parameter (where applicable).

The **Charge** is the numeric value for the valence state (where applicable) of the selected parameter. The Charge value should always be a positive integer value.

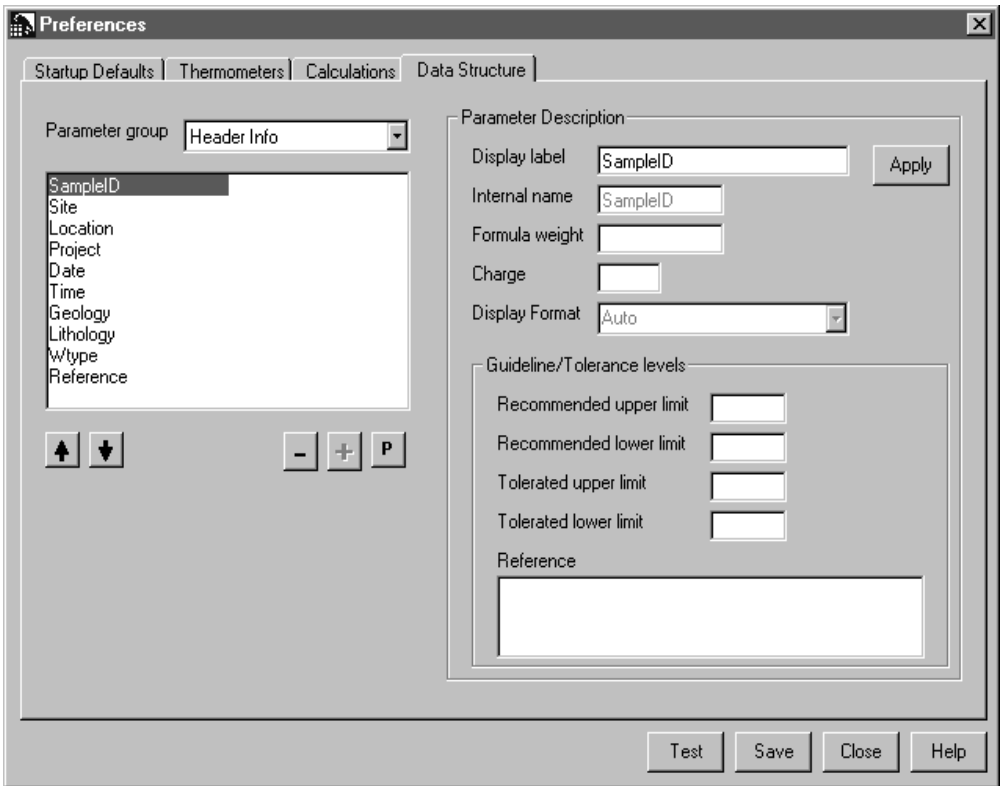


Figure 4.5: Data Structure Tab.

Guidelines/Tolerance Levels

The **Guidelines/Tolerance Levels** refer to published or commonly applied minimum and maximum allowable levels of each parameter. The reference documentation for each guideline/tolerance level can be entered for each parameter as well.

The **[Test]** button will preview the new data structure settings as they will appear in the **Input** window. This is only a test window and is not functional.

How To ??? Hints

Modifying the Parameter Listing Order

- Click on the parameter that you would like to move
- Click the **[Up]** or **[Down]** arrow button to change the position of the parameter

Modifying the Parameter Attributes

- Click on the parameter from the parameter list
- The selected parameter attributes will appear in the adjacent fields
- Enter any modifications in the appropriate field(s)
- Click on the **[Apply]** button to register the changes

Adding a Parameter from the Database

- Select the appropriate parameter group
- Click on the **[P]** button
- Drag the target parameter into the **Parameters** list
- The new parameter will be appended to the end of the **Parameters** listbox

Creating a New Parameter for the Database

If you would like to add a new parameter to the list, but it is not listed in the **Parameters** window, you can easily create a new parameter:

- Click on the **[New]** button below the **Parameters** listbox
- Fill in the appropriate information for the new parameter in the parameter attributes fields (e.g Display label, Internal name, Charge, Molecular weight, etc.)
- Click on the **[Apply]** button next to the parameter attributes fields

Removing a Parameter from the Database

- Click on the target parameter that you would like to remove
- Click the **[Remove]** button to remove the parameter from the list

Compress Database

The **Compress Database** option will permanently remove records that you have deleted from your database. Deleted records can always be recovered until the database is either compressed or closed. To recover a deleted file select **Records/Undelete**, click on a deleted record, **[Undelete]**.

Exit

The **Exit** menu option closes the current AquaChem session.

4.2.2 Records

New

The **New** menu option creates a new record and opens the **Input** window for entering the new data in the appropriate database fields.

Edit

The **Edit** menu option opens the **Input** window for the database record selected in the Record List. If multiple records are selected, the record closest to the top of the **Record List** window will be selected.

View as spreadsheet

The **View As Spreadsheet** menu option allows you to display the active samples in a spreadsheet table format. The **Spreadsheet Settings** dialogue box (see Figure 4.6) prompts you to choose the parameters to be included in each column of the spreadsheet table (the rows of the spreadsheet are always reserved for each active record in the database). Spreadsheet columns may contain any measured parameter (Na, Ca, Cl...) or calculated parameter (e.g. ion ratios, total hardness, or geothermometer temperatures).

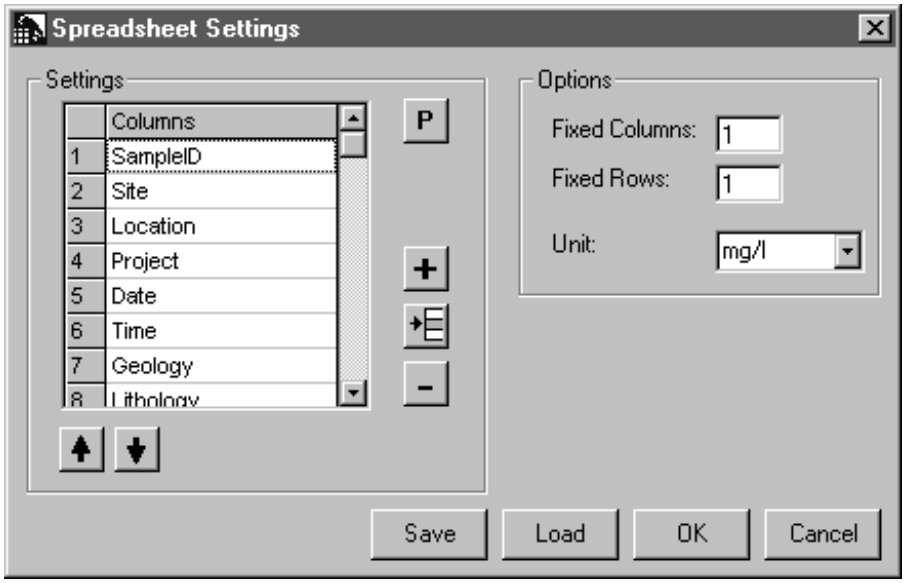


Figure 4.6: View as Spreadsheet dialog box

The **Settings** frame contains a table of spreadsheet headers that lists all parameters that will be included on the spreadsheet, in the order that they will be displayed (i.e. the parameter in the first row will be displayed in the first column of the spreadsheet). The default Spreadsheet Setting will include all of the project database parameters.

Typically, one row and one column containing the row and column titles will be 'fixed' on the spreadsheet so the column and row headings always appear at the top and far right of the **Spreadsheet** window as you scroll through the rows and tables of the spreadsheet. However, more than one column and row can be 'fixed' if you wish.

The **Fixed Rows** field is used to specify the number of rows to fix.

The **Fixed Columns** field is used to specify the number of columns to fix.

The **Units** field allows you to select the concentration units that you want to display on the spreadsheet. Concentrations can be displayed in mg/l, mmol/l, meq/l, and mol/l.

If you work with the spreadsheet view quite often, you may have several different spreadsheet settings you use most often. AquaChem allows you to save the spreadsheet setting in a report file (***filename.rpt***) for fast recall of the spreadsheet formats you use most often.

The **[Save]** button saves the current **Spreadsheet Settings** in a report file, and the **[Load]** button loads an existing **Spreadsheet Settings** report file

The **[OK]** button accepts the current settings and loads the **Spreadsheet** window.

Changes to the spreadsheet configuration are automatically saved and will be remembered the next time you use the **View as spreadsheet** option. See Section 4.5 for a detailed description of the **Spreadsheet** window menu options.

Once the spreadsheet is loaded, any change to a measured parameter value in the spreadsheet is automatically saved to the database. However, the database is not affected by editing calculated values such as ion ratios, hardness, geothermometers, etc.

Although the spreadsheet may contain up to 200 columns (parameters) and 2000 rows (samples), it is recommended that no more than 400 samples be loaded at a time, as the operation will likely take too long and consume too much memory.

How To ??? Hints

Adding a Parameter to the Spreadsheet Settings

- Click on the **[P]** button to load the **Parameters** window
- Click on the target parameter in **Parameters** window
- Click on the **[+]** button to append the new parameter to the table

Changing a Parameter in the Spreadsheet Settings

- Double-click on the parameter that you would like to change
- Select the new parameter from the list of available parameters
- Press the <Enter> key to register the changes

Search

The **Search** menu option is used to perform queries of the AquaChem project database. The **Search records** dialogue box (see Figure 4.7) allows you to create SQL-like queries of the records in the AquaChem database. All found records matching the search criteria will be selected (highlighted) in the **Record List** window after the search operation is completed. This feature is very useful for filtering the active records in the **Record List** to include only those sample records which meet a set criteria.

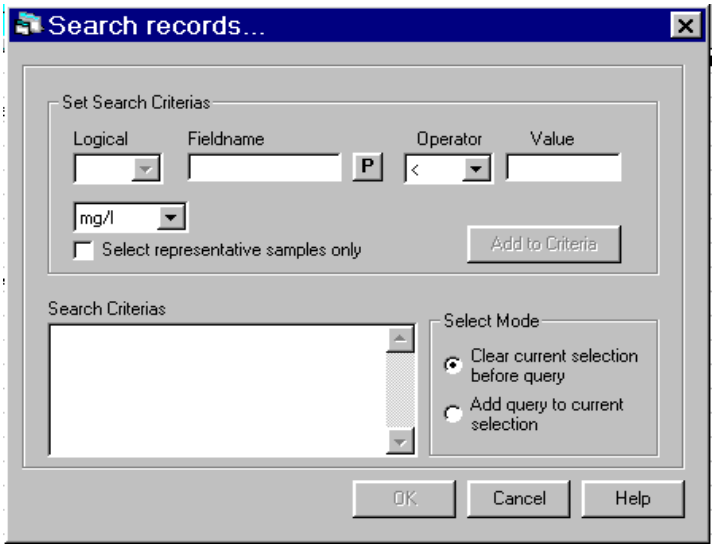


Figure 4.7: Search Records window

The **Logical** field is a dropdown menu containing 'AND' and 'OR'. These logical operators are used to link multiple search criteria. This field is only available after you have entered at least one search criterion.

The **Fieldname** text field is used to specify a database parameter on which to base the query. To prevent spelling mistakes, you can drag the parameter from the parameter list and drop it in the **Fieldname** text field. Press **<F4>** to open the **Parameters** window, or click on the **[P]** button next to the **Fieldname** field.

The **Operator** field is a drop-down menu to select from the list of comparison operators (>, <, =, and LIKE). Searches for strings that use the = operator return exact matches, whereas searches that use the **LIKE** operator return matches that contain the substring you have specified in the **Value** text field. Searches for character strings are not case sensitive.

The **Value** text field is the value to compare to the parameter you specified in the **Fieldname** text field. For queries based on dates, refer to the examples below for syntax.

The **Units** field is used to select a unit system for searches based on chemical elements.

The **Select Representative Samples Only** checkbox is used if your project database contains several sites and many analyses from each site. In this case the graphs comparing all records can become crowded, so you might prefer to display only one representative sample per site. You can assign a representative sample for each site when entering the data in the **Input** window. If you select the **Select Representative Samples Only** option, only the records which are representative of each site, and which satisfy the search criterion, are returned.

The **[Add to Criteria]** button is used to transfer the specified search criteria to the **Search Criterion** list box. You can also type the query expression directly into the **Search Criterion** text field if you are familiar with the syntax.

Only the criterion listed in the **Search Criterion** text field will be searched for when you click **[OK]**.

Examples

Search Criterion	**Search Results**
Location = Baden	Returns all records with location "Baden"
Location **LIKE** Baden	Returns all records with location containing the substring "Baden" (e.g. Baden, Badenweiler, Baden Baden, etc.)
Date > 01.01.1960	Returns all records sampled after January 1st, 1969
Na/Cl > 0	Returns all records with non-zero concentrations of Na/Cl Choose units of mmol/l when using ion ratios

Copy

Copies the selected record(s) to a different database. If the destination database has a different data structure, only parameters which are spelled identically are copied.

Delete

Deletes the selected record(s) from the database. Deleted files are permanently deleted from the database once the project is either closed or the database is compressed (select **File/ Compress Database**)

Undelete All

Information from deleted records is only overwritten when new records are added to the database. Until new records are added to the database, some deleted records may be recovered. Select **Main Menu\Records\Undelete All** to display a list of the records which can still be recovered. Select the records you wish to delete permanently, then click **Main Menu\Records\Delete**, and **Main Menu\Records\Show All**.

Representative ON

Sets the "**Select representative samples only**" flag for the selected record(s). When you perform a search or calculation, or create a graph, you may choose to use only samples in the **Record List** which are representative of each site. A representative sample is indicated by the solid square on the right side of the index number.

Representative OFF

Turns off the "**Select representative samples only**" flag for the selected record(s).

4.2.3 Selection

Show All

Use this command to restore your **Record List**. All of the samples in the database file will be displayed.

Omit All

Clears all of the database records from the **Record List**.

Omit Selected

Hides all selected records from the **Record List**. The records are not deleted. They are simply not shown in the **Record List** window, so that you may work with a subset of the database.

Omit Non-selected

Hides all non-selected records from the Record List.

Invert Selection

Use this command to select all records not selected, and de-select all records currently selected.

Save Selection

Saves the indexes of all selected samples in the **Record List** to a selection file (***filename.sel***). Selection files can be opened in later sessions to work with the same portion of the database again.

Open Selection

Opens a selection file. All samples in the selection file will then be highlighted in the **Record List**. If you want to work exclusively with the samples from the selection file, select **Main Menu\Selection\Omit Not Selected** after opening the selection file. Selection files can only be opened in the database in which they were created.

When selecting records in the **Record List** with the mouse, remember that AquaChem supports the standard Windows selection functions: press **<Shift>** or **<Ctrl>** to select multiple records.

Assign Symbol

Opens the **Assign Symbol** dialogue box listing all of the available symbol groups as shown in Figure 4.8. Each symbol group is identified by a specific symbol shape and color when plotted on a graph. The symbol shape associated with each symbol group is displayed in the lower left-hand portion of the **Assign Symbol** dialogue box.

All records are automatically assigned to the **Default** symbol group whenever you start a new database. However, once you assign a record to different symbol group, it is removed from the **Default** symbol group. Each record can belong to only one symbol group at a time.

The default naming convention for the symbol groups is shown in Figure 4.8 (Group 1, Group 2, Group 3, etc.). These symbol group names can be easily modified (see Section 4.2.6 Define Symbol or Line) and will appear on the legend of any plots. The number in brackets beside each group is displayed in the **Record List** and is used to identify which group each record belongs to. The number in brackets will not appear in the plot legend.

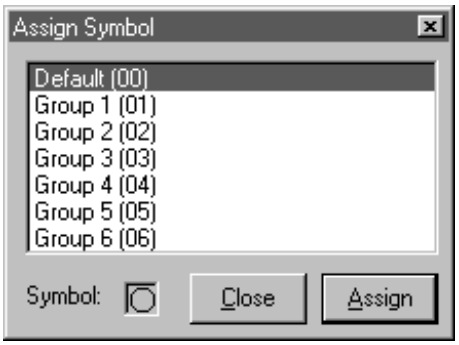


Figure 4.8: Assign Symbol dialogue box

The **[Assign]** button is used to assign selected records to the target symbol group.

The **[Close]** button is used to close the Assign Symbol dialogue box.

How To ??? Hints

Assigning a record to a symbol group

To assign a record(s) to a specific symbol group,

- Click-on (highlight) the record(s) from the **Record List** window
- From the top menu bar choose **Selection/Assign Symbol** (or right-click on the selected records in the **Record List** and choose **Assign Symbol**)
- Select the desired symbol group
- Click the **[Assign]** button

Now repeat this with the other records you want to group together.

4.2.4 Reports

AquaChem generates ten different types of reports:

1) **Compare** - correlation coefficient and the Euclidean distance between a selected sample and all other active samples
2) **Correlation Matrix** - correlation matrix for specified sample parameters which are common to all active sample records
3) **Geothermometers** - original subsurface reservoir temperature of hot ascending groundwater which underwent conductive cooling or boiling
4) **Mixing** - solution concentrations resulting from the step-wise mixing of specified proportions of two selected samples from the project database
5) **Statistics** - statistical analyses of specified parameters which are common to all active sample records
6) **General** - summary of general information about the major ions, hydrochemical facies (e.g. Na-Cl), calculated hardness, ion balance, ion ratios, etc.
7) **Isotopes** - information about the stable and radioactive composition of the water and of dissolved components
8) **Drinking Water Regulations** - a summary of parameters exceeding the established Guideline/Tolerance levels for the selected sample
9) **List of headers** - a listing of all information displayed in the **Record List**
10) **Data** - listing of all database parameters and their value for the selected sample record

These reports are all generated in a separate **Report** window as unformatted ASCII text. These reports can be printed 'as is' using the **[Print]** button on the lower left-hand corner of the windows, or the information can be easily 'cut-and-pasted' into a formatted report document.

The following are more detailed descriptions of the various reports generated by AquaChem.

Compare Sample

The **Compare Sample** report uses a linear regression algorithm to generate the correlation coefficient and the Euclidean distance between a selected sample and all other active or selected records. Sample records having a chemical composition similar to the selected sample record will have a correlation coefficient close to 1. The correlation coefficient is a

function of ratios rather than absolute values. The difference in absolute concentrations is expressed by the Euclidean distance:

$$d_{ij} = \frac{\sum_{k=1} x_{ik} - x_{jk}}{n}$$

where x_{ik} denotes the kth variable measured on sample i and x_{jk} is the kth variable measured on sample j. For each sample, n variables are measured. The distance between sample i and sample j is d_{ij}.

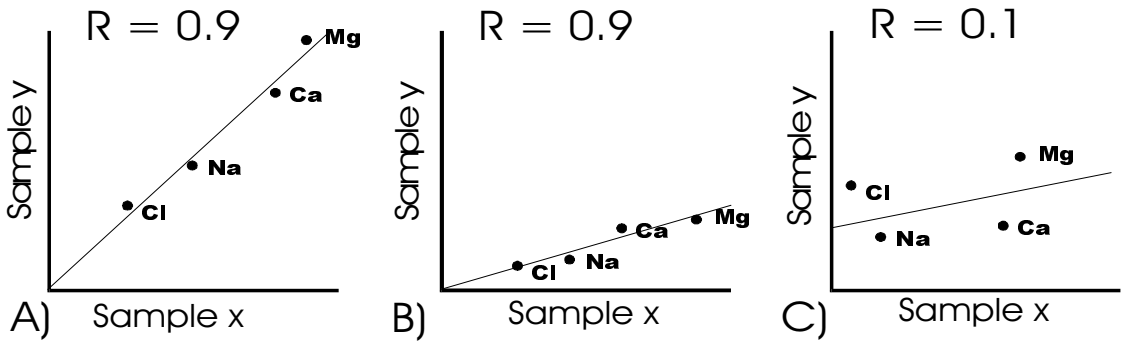


Figure 4.9: Comparing sample **x** to sample **y**: a) high similarity
b) high similarity but sample **y** is diluted with respect to sample **x**
c) low similarity

The following is a description of the **Compare sample** dialogue box (see Figure 4.10).

The **Compare sample to active records** field is a dropdown menu of all active records in the **Record List**. This field is used to select the sample record that will be compared against all other active records.

> **NOTE:** You can also include element ratios, sums or differences (e.g. Na/Cl, Ca+Mg, Cl-SO_4) in the **Parameters** field.

The **Parameters** field contains a list of the parameters that will be used in the comparison analysis. The default parameter settings for this project can be changed by modifying the parameters field and pressing the **[Set Default]** button Figure 4.10). Additional parameters may be added to the parameters field by dragging and dropping the parameters from the database **Parameter List** (press the **[P]** to load the **Parameter List**).

The **Select records with r >** checkbox is used to select samples with a correlation coefficient greater than the specified value. These samples will be highlighted in the **Record List** once the comparison is completed.

A typical Sample Comparison report is provided in Figure 4.11.

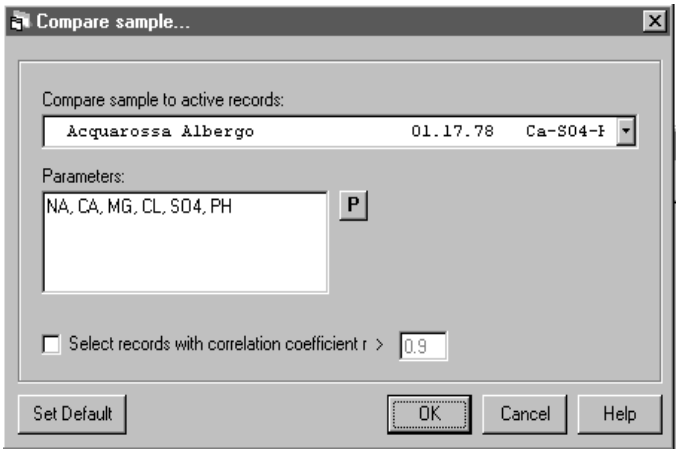


Figure 4.10: Compare Samples Dialogue Box

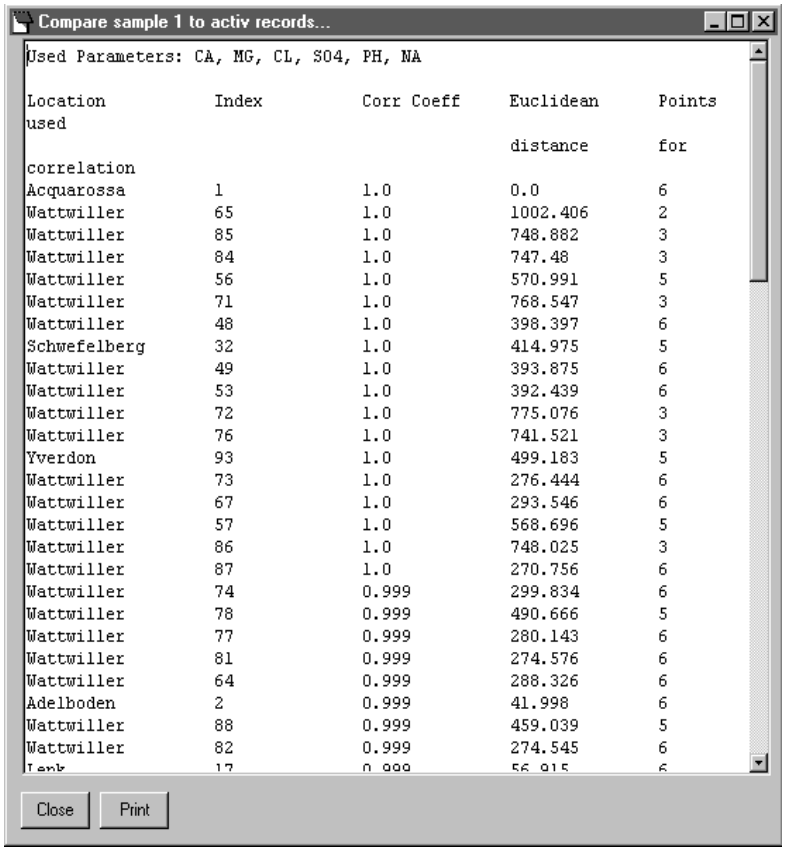


Figure 4.11: Compare Samples Report

Correlation Matrix

The **Correlation Matrix** report generates a correlation matrix for a specified number of sample parameters that are common to all samples. A linear regression routine calculates the regression coefficient (r), and the slope and intercept of the regression line. Figure 4.12 shows the correlation of Ca against SO_4 for three different scenarios.

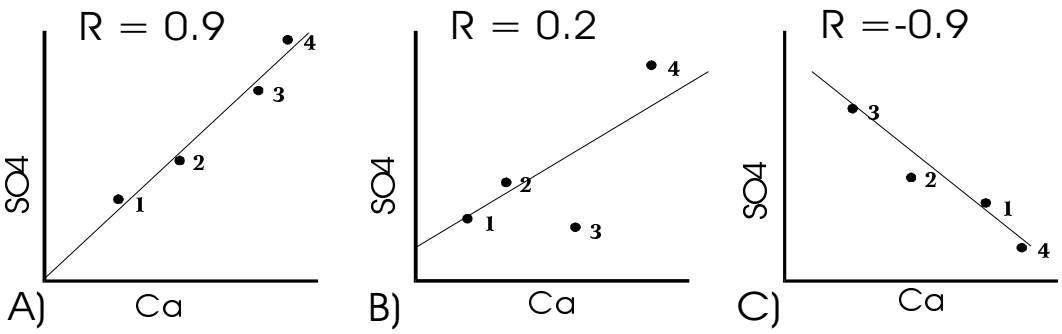


Figure 4.12: Correlation of Ca and SO_4 in three samples:
a) high correlation b) low correlation c) high negative correlation

The following is a description of the **Parameter Correlation** dialogue box as shown in Figure 4.13.

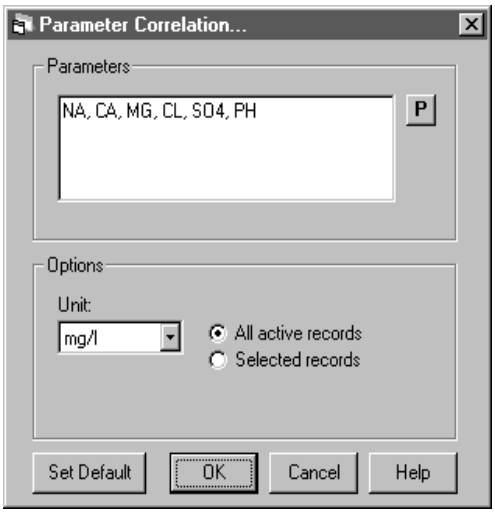


Figure 4.13: Parameter Correlation dialogue box

The **Parameters** field contains a list of the parameters that will be used in the correlation analysis. The default parameter settings for this project can be changed by modifying the parameters field and pressing the **[Set Default]** button. Additional parameters may be added to the parameters field by typing the Internal names directly, or by clicking the **[P]** button

and dragging the parameters from the **Parameters** window into the **Parameters** field (each parameter must be separated by a comma).

> **NOTE:** You can also include element ratios, sums or differences (e.g. Na/Cl, Ca+Mg, Cl-SO_4) in the **Parameters** field.

The **Units** field contains a dropdown list of the available concentration units for the correlation of the chemical parameters. Units of mol/l are often more suitable for correlating than mg/l because it gives you an idea of which minerals have been dissolved.

The parameter correlation can be calculated for **All active records** in the **Record List**, or for **Selected records** only.

It is often useful to check the correlation results graphically in a scatter plot to easily identify outliers. Select **Main Menu\Graphics\New\Scatter** to plot the data, then select **Graphics Menu\Edit\Function** to calculate the regression curve.

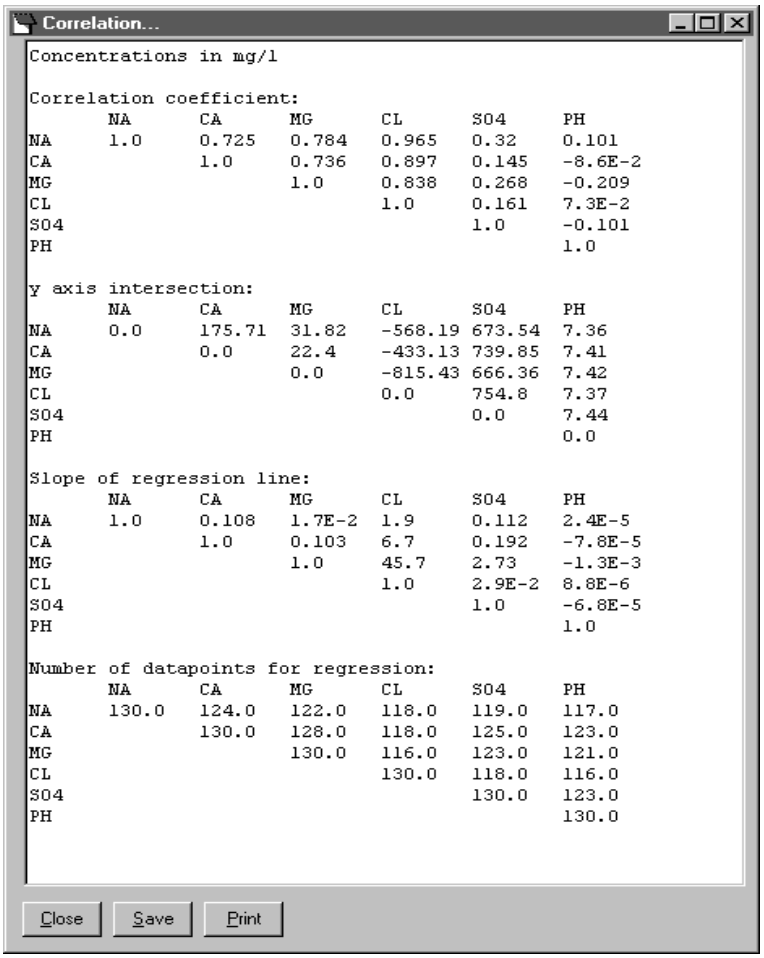


Figure 4.14: Sample correlation report

Geothermometers

The **Geothermometers** report generates the original subsurface reservoir temperature of hot ascending groundwater which underwent conductive cooling or boiling. Reactants which remain metastably dissolved during the journey to the surface are proportional to their original aquifer temperatures. An example of this is SiO_2 (Quartz or chalcedony dissolution or Na/K for albitisation).

This subject is discussed in more detail in Section 5.3 on page 97. The original bibliographic reference and the temperature range for which the thermometer is valid can be viewed and edited from the **Main Menu\File\Preferences** window. Thermometer data can also be displayed graphically by selecting **Main Menu\Graphics\New\Geothermometer**. The formulas of the thermometers, listed below, can be edited from the **Main Menu\File\Preferences** window. You can also add new thermometers from the **Preferences** window. The following thermometers are included with AquaChem:

- SiO_2
- Mg/Li
- Mg/Ca
- Na/K
- Na-K-Ca
- Na-K-Ca Mg corrected
- $^{18}O\ SO_4$-H_2O

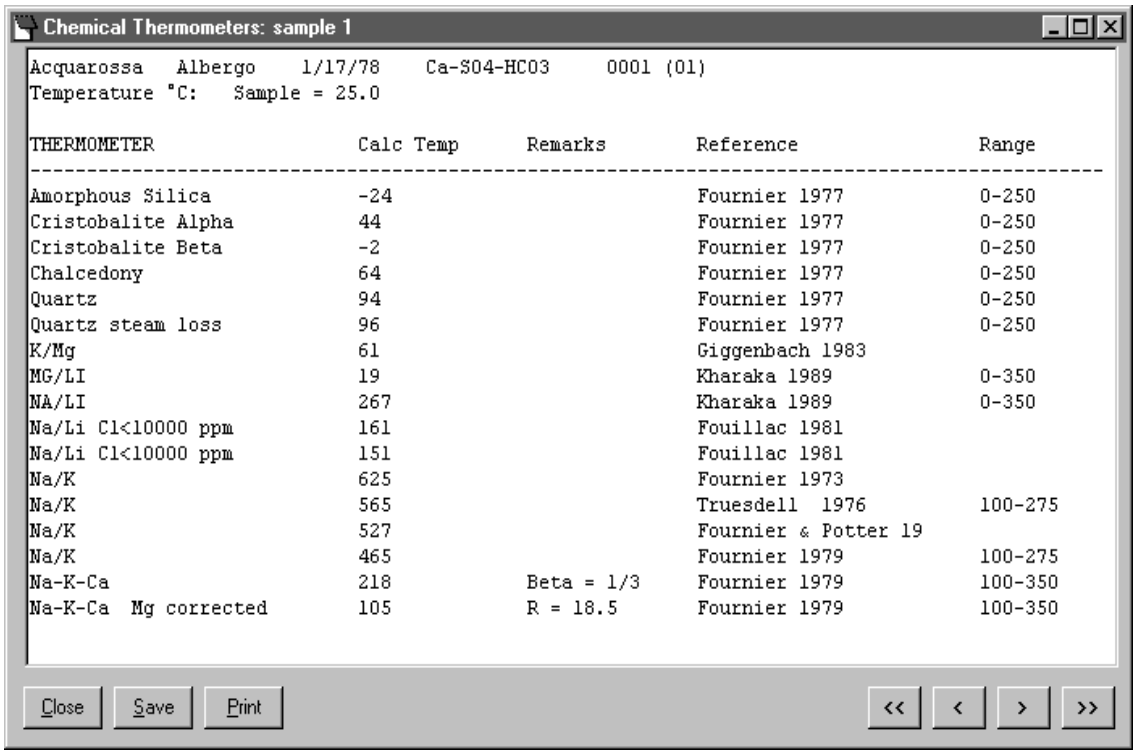


Figure 4.15: Geothermometer report

Mix Samples

The **Mix samples** report generates solution concentrations resulting from the step-wise mixing of specified proportions of two selected samples from the project database. The mixtures resulting from each step can be saved as separate AquaChem records, which can then be graphed or manipulated in the same way as any other sample. The **Mix samples** dialogue box is shown in Figure 4.16.

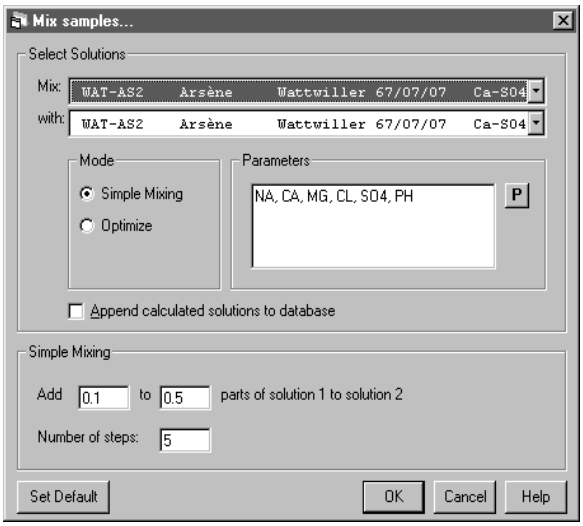


Figure 4.16: Mix samples dialogue box

Select Solution

The **Mix** and **with** fields are drop-down menus of the available solutions that can be used in the mixing of two samples. Each field contains a complete list of all active records in your AquaChem database project.

The **Parameter** text field allows you to select the parameters that will be included in the mixing calculations. Typically you would select parameters that you know are common to each sample. To add a parameter to the list, click **[P]** and drag parameters from the **Parameter List** window into the list box. The default parameter settings for this project can be changed by modifying the parameters field and pressing the **[Set Default]** button (Figure 4.16)

Simple Mixing Mode

In the simple mixing mode, AquaChem will mix the two selected samples in a step-wise process.

The **Add** text field is the starting proportion (*m*) of Solution 1 in the mixture solution, while the **to** text field is the final proportion (*n*) of Solution 1 in the mixture solution.

The **Number of steps** text field is the number of uniform steps in which to get from (*m)* to (*n)* parts of Solution 1 in the mixture solution.

Starting with (*m*) parts of Solution 1 and (*1.0 - m*) parts of Solution 2 in the mixture solution, AquaChem will begin uniformly decreasing the proportion of Solution 1 in the mixture

solution while maintaining a total proportion value of 1.0. The final mixture solution has (*n*) parts of Solution 1 and (*1.0 - n*) parts of Solution 2.

Figure 4.17 shows the results of mixing two solutions. The concentrations of each parameter in the first column are the concentrations for Solution 1. The concentrations of each parameter in the second column are the concentrations for a mixture of 0.1 parts Solution 1 with 0.9 parts Solution 2. The concentrations of each parameter in the third column are the concentrations for a mixture of 0.2 parts Solution 1 with 0.8 parts Solution 2. etc.

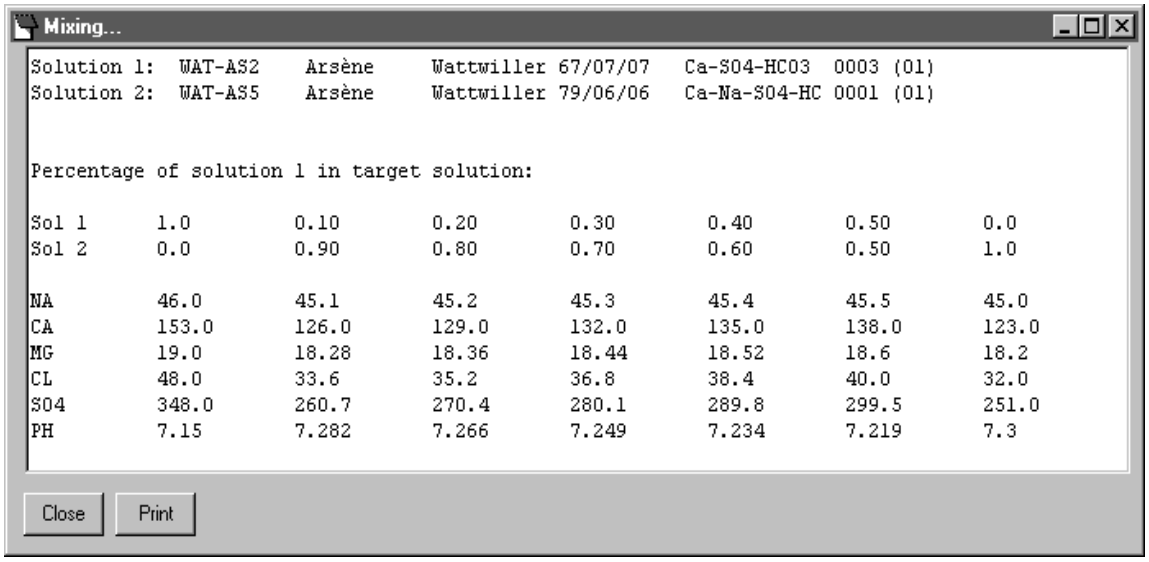


Figure 4.17: Mix Samples report

Optimize Mode

In addition to simple mixing of two samples, AquaChem also allows you to determine the optimal mixing ratio of the two select samples that most closely matches a target sample from the database. When you select the **Optimize** mode you will be prompted to select a sample that you would like to match. AquaChem will mix the two initial samples in 2% increments until the Euclidean distance between the calculated mixture and specified resulting sample is minimized.

The Optimize Mode is used in a situation where you have 3 samples (groundwater, seawater and freshwater) and you suspect that the groundwater is a mixture of the freshwater and the seawater. The Optimize Mode can be used to estimate the percentage of freshwater and the percentage of seawater required to obtain the groundwater composition of selected parameters.

Statistics

The **Statistics** option calculates basic statistics for all visible or selected records. You can choose the units for the chemical concentrations. This is useful for analyzing ion ratios. The average values can be saved as a record and appended to the database.

- Maximum, Minimum(Min, Max)
- Average ($\bar{x}$)
- Standard deviation: $\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}}$
- Variance coefficient: $\frac{\sigma}{\bar{X}} \cdot 100$
- Variability: $Var\% = \left(\frac{Max - Min}{\bar{x}} \cdot 100 \right)$

The **Statistics** dialogue box is shown in Figure 4.18 and is described as follows.

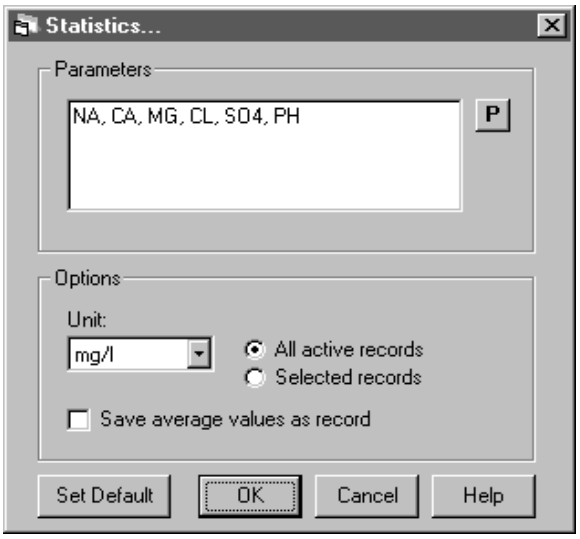


Figure 4.18: Statistics dialogue box

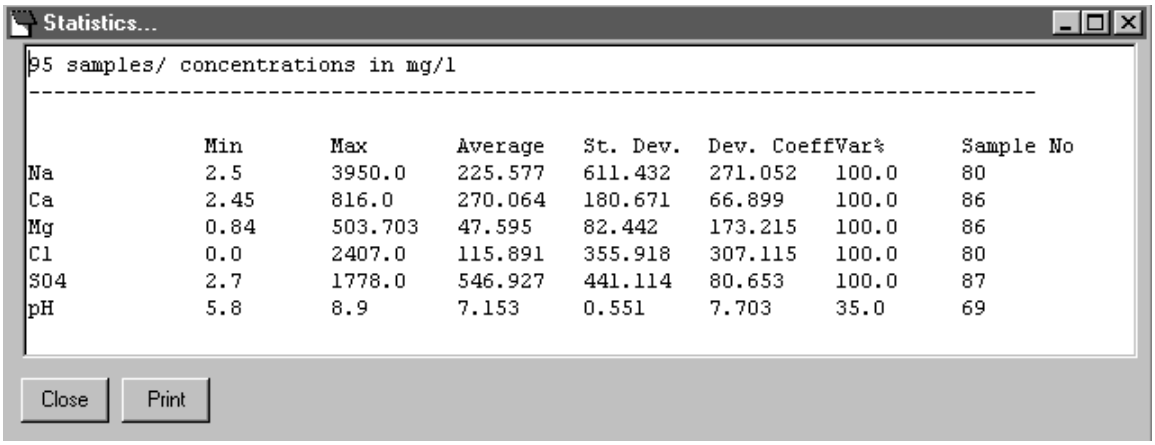
The **Parameters** text field contains a list of the parameters that will be used in the statistical analysis. New parameters can be typed in the text field, or dragged from the Parameters window. Click **[P]** to load the Parameters window. Each statistical parameters must be separated by a comma. The default parameter settings for this project can be changed by modifying the parameters field and pressing the **[Set Default]** button.

NOTE: You can also include element ratios, sums or differences (e.g. Na/Cl, Ca+Mg, Cl-SO_4) in the **Parameters** text field.

The **Units** field contains a drop-down list of the chemical concentration units to be used in the statistical analysis. Chemical concentrations can be expressed in mg/l, mmol/l, meq/l, ppm or mol/l.

Statistics may be calculated for **All active records** in the **Records List**, or only for **Selected records**. To study the influence of specific samples in your database, you can create multiple statistical reports using different selections of records.

The **Save average values as record** option allows you to save the average parameter values calculated in the statistical report as a new record in your database.



	Min	Max	Average	St. Dev.	Dev. Coeff	Var%	Sample No
Na	2.5	3950.0	225.577	611.432	271.052	100.0	80
Ca	2.45	816.0	270.064	180.671	66.899	100.0	86
Mg	0.84	503.703	47.595	82.442	173.215	100.0	86
Cl	0.0	2407.0	115.891	355.918	307.115	100.0	80
SO4	2.7	1778.0	546.927	441.114	80.653	100.0	87
pH	5.8	8.9	7.153	0.551	7.703	35.0	69

Figure 4.19: Statistics report

General Report

A sample **General Information** report is shown in Figure 4.20. The following is a description of each parameter that is calculated for the General report.

Water type

Chemical facies that determine the water type are calculated by first converting the milli-equivalents per litre of the major cations (Na, Ca, Mg) and anions (Cl, SO_4, HCO_3) to percentages. All ions with concentrations surpassing 10% of the molar concentration in the solution are considered to be major ions. The Water Type expression is formed by listing the major ions in order from highest composition to lowest composition, with cations listed first and anions listed second.

Example

Ions	Percentage (meq%)	Resulting Water Type
Na	0.4%	
Ca	37.9%	
Mg	11.5%	
Cl	0.4%	Ca-Mg-SO_4
SO_4	40.3%	
HCO_3	9.5%	

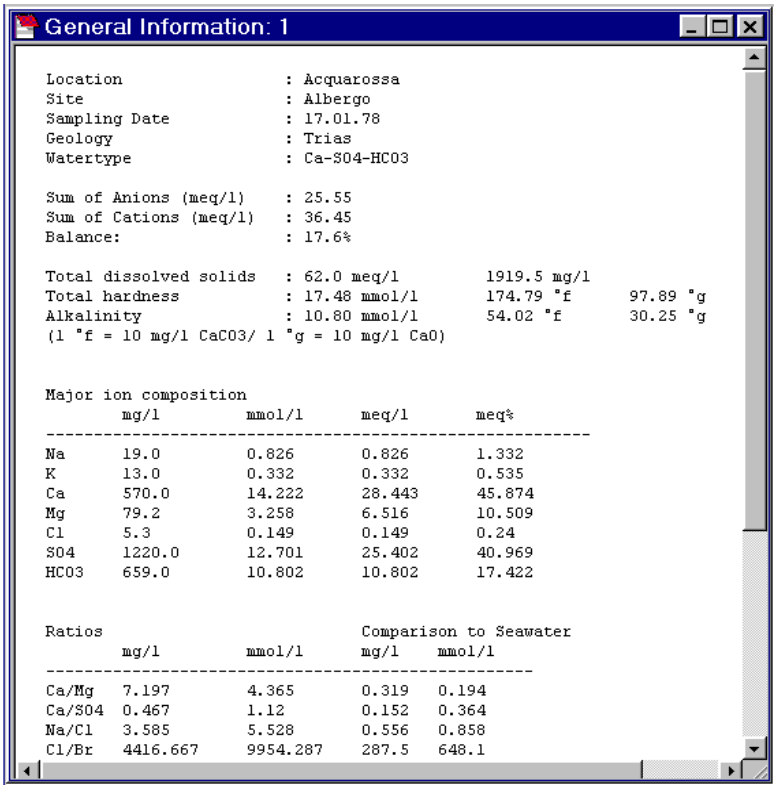


Figure 4.20: General Information Report

Ion balance

Balance between sum of anion and cation equivalent charges. This value is useful for evaluating the quality of the analysis (value should be < 5%) and for finding errors in the input data.

Hardness

Total hardness: The sum of the ions that can precipitated from water as hard particles. Generally, the sum of Ca and Mg, expressed in meq/l or $CaCO_3$/l, or in degrees.

100 mg $CaCO_3$/l =1mmolCa^{2+}/l = 2meq Ca^{2+}/l

Hardness degrees: 1 german degree = 17.8 mg/$CaCO_3$/l,

1 french degree = 10 mg $CaCO_3$/l

Permanent hardness (or noncarbonate hardness):

Parts of Ca^{2+} and Mg^{2+} in excess of HCO_3^-

Temporary hardness (carbonate hardness):

Parts of Ca^{2+} and Mg^{2+} which are balanced by HCO_3^- and thus can precipitate as $CaCO_3$

Alkalinity: Acid neutralizing capacity. Generally equal to the concentration of $HCO_3^- + 2*CO_3^{2-}$.

Concentrations

Concentration of major elements in mg/l, mmol/l, meq/l and meq%.

Ion Ratios

Na/Cl, Ca/SO_4 and Ca/Mg Cl/Br compared to corresponding ratios in seawater

Gas Composition (if gas analysis present)

Composition of gas phase: N_2, O_2, CO_2, Ar, He, CH_4 in mg/l, mmol/l, and mmol%. Comparison to the theoretical composition of saturated air at 1 atm pressure (data from Schmassmann, 1992):

O_2: S_0 (mg/l) = 14.60307 - T * 0.4021469 + T^2 * 0.00768703 - T^3 * 0.000692575

N_2: S_0 (mg/l) = 14.01*(-21.3539 + 37.2477 * (100/T) 1 24.3639 log(T/100))

Ar: S_0 (mg/l) = 39.948*(-21.5520+35.6235*(100/T) + 22.5929 log(T/100))

These concentrations are valid for 1 atm pressure. They decrease at higher elevations as a function of the pressure. The saturation value for a given pressure can be calculated:

$$t(K^\circ) = \frac{a}{b + \log(x)}$$

for example at 1000 m:

$$s_{1000m} = \frac{s_0 \cdot p_0}{p_{1000m}}$$

Dissolved Minerals

Weight in mg/l of the following minerals: halite, sylvite, anhydrite, calcite, chalcedony (quartz) or Na feldspar. Precipitation of these minerals is numerically simulated according the following procedure:

Generate sylvite (KCl), subtract Cl

Generate halite (NaCl), subtract Na, Cl

Generate anhydrite ($CaSO_4$), subtract Ca, SO_4

Generate dolomite (($CaMg(CO_3)_2$), subtract Ca, Mg

Generate calcite ($CaCO_3$) with the remaining amount of Ca

Generate either quartz (SiO_2) or Na feldspar ($NaAlSi_3O_8$)(if any Na still available) with SiO_2

Isotopes Report

Oxygen and deuterium

Distance from meteoric waterline, average height and average annual temperature of the recharge area if $\delta^{18}O$ and $\delta^{2}H$ data are available, and if the following local relationships are given:

$\delta^{2}H=a_1\ \delta^{18}O + b_1$ (meteoric waterline)

$z\ (\delta^{18}O)=c_1\ \delta^{18}O + d_1$

$z\ (\delta^{2}H)=c_2\ \delta^{18}O + d_2$

$T(\delta^{18}O)=e_1\ \delta^{18}O + f_1$

$T(\delta^{2}H)=e_2\ \delta^{2}H + f_2$

The empirical coefficients c_1, c_2, d_1, d_2, e_1, e_2, f_1, f_2, are generally only valid for a restricted geographic area. They must be specified in the **Main Menu\File\Preferences** window, under the **Calculations** tab. Unfortunately these coefficients have only been established for a few areas in the world. The meteoric waterline can be applied globally.

Sulfur and oxygen from sulfates

Sulfur and oxygen isotopes in sulfates are widely used to distinguish the source of dissolved sulfate. Information about the selected record is displayed, as well as a table of values of different evaporates.

Drinking Water Regulations Report

The **Water Quality Regulations** report lists all the parameters of the selected records that lie outside the recommended limits (see Figure 4.21). Each line of the report contains the actual value, a recommended tolerance interval and a maximum tolerance interval. The default settings for the report are in accordance with the WHO guide of drinking water requirements. These values can be edited in the **Main Menu\File\Preferences** window, under the **Data Structure** tab.

Parameters for irrigation waters

From Lloyd and Heathcote (1985):

Sodium Adsorption Ratio:

$$SAR = \frac{Na^{+}}{\left(\frac{Ca^{2+} + Mg^{2+}}{2}\right)^{2}}$$

Exchangeable Sodium Ratio:

$$ESR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$$

Magnesium Hazard:

$$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100$$

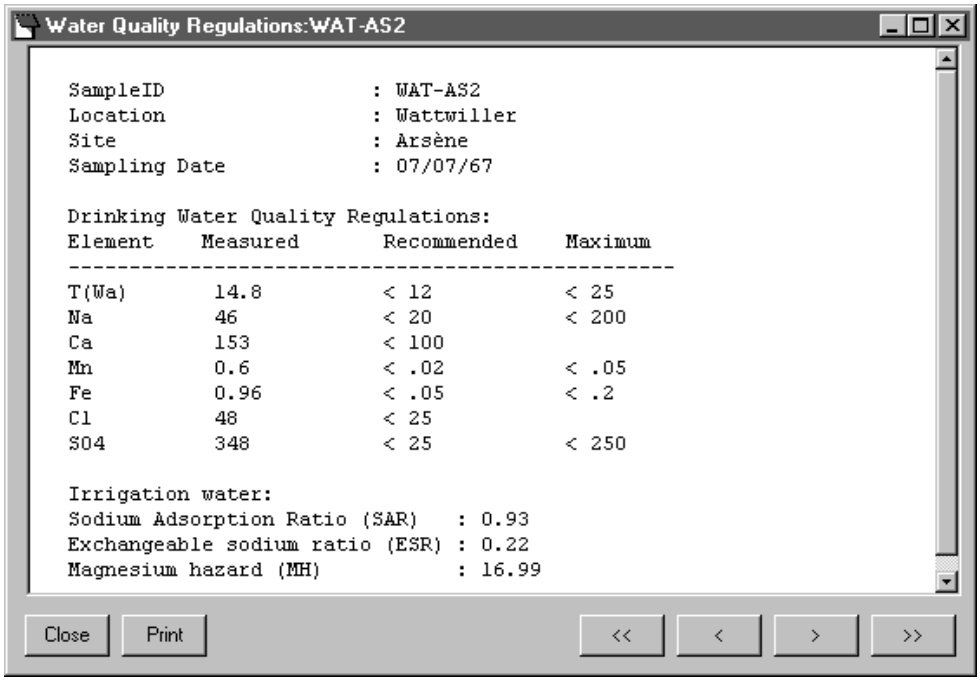


Figure 4.21: Drinking Water Regulations Report

The following are some examples of groups of irrigation water based on electrical conductivity (µS/cm at 25°C):

C1:Low salinity water:< 200

C2:Medium salinity water:250-750

C3:High salinity water:750-2250

C4:Very high salinity water:>2250

List of Headers Report

The **List of Headers** report displays the headers of all records in the current **Record List** window to a text screen where the contents can be cut and pasted to a text editor or sent to the printer (see Figure 4.22).

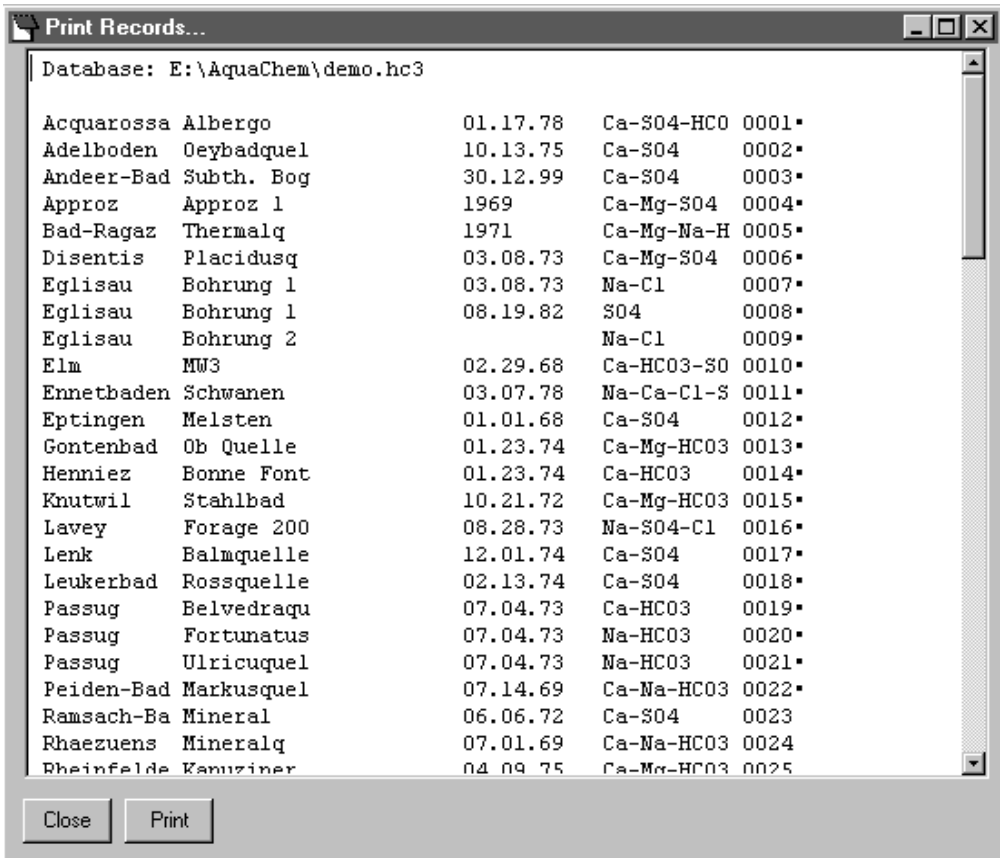


Figure 4.22: List of Headers Report

Data Report

The **Data** report option displays the data for all selected records in a text window where the contents can be cut and pasted to a text editor or printed (see Figure 4.23). The default units for chemical concentrations are printed in both mg/l and meq/l.

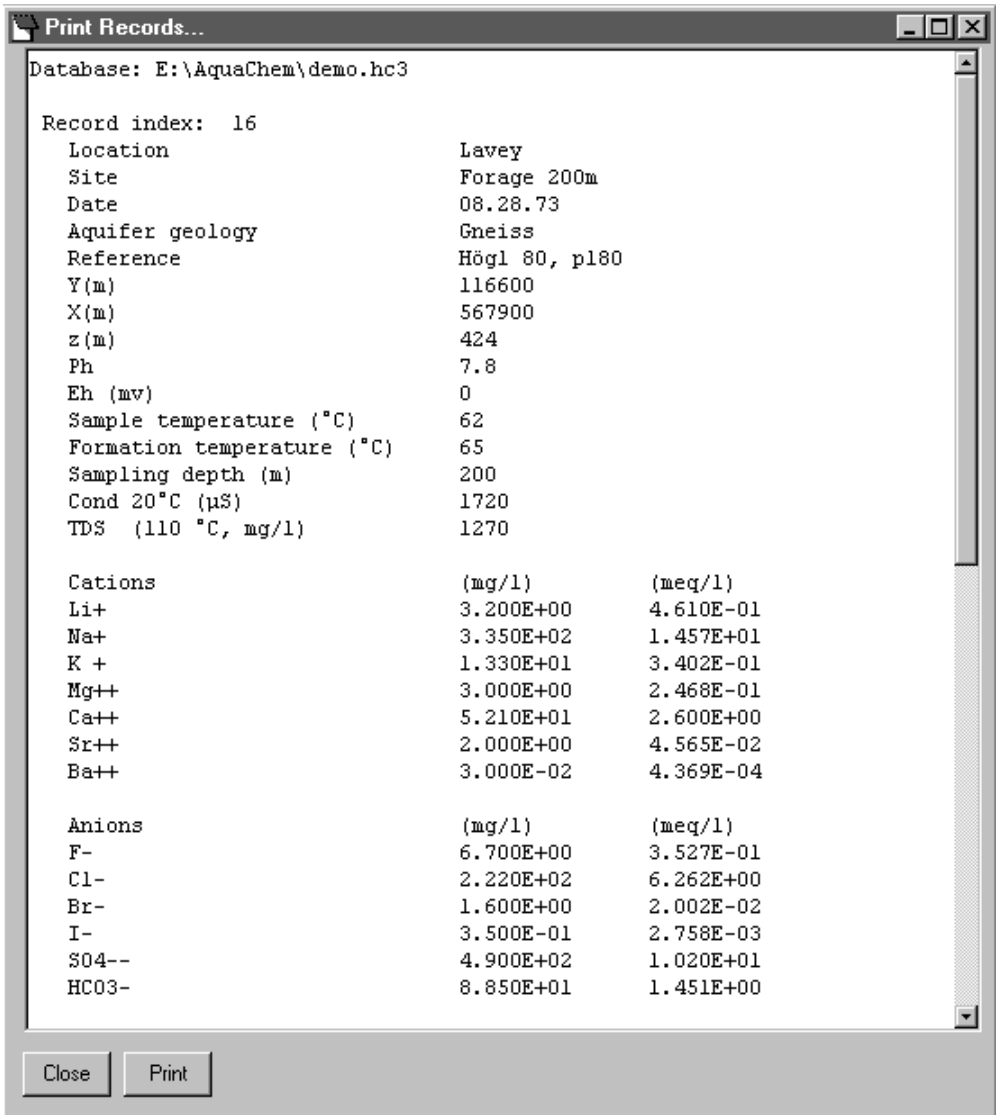


Figure 4.23: Data Report

4.2.5 PHREEQC

Import PHREEQC Results

AquaChem allows you to import PHREEQC simulation results files (***filename.pun***) into a spreadsheet, and import solutions from your PHREEQC results into your AquaChem database. This is ideal for statistically analyzing the PHREEQC output.

To import your ***.pun*** file, type the ***.pun*** filename in the text field at the top of the window, or click the browse button to locate and select the appropriate ***.pun*** file. The results will be displayed in the spreadsheet on the **Import PHREEQC Results** window as shown in Figure 4.24. Results can be copied and pasted to other Windows applications, or can be imported into your AquaChem database.

To import a solution from your spreadsheet into your database, you must ensure that a record with an index number equal to the solution number already exists in your database. If you used database records as input solutions for the PHREEQC simulation, then the index numbers and solution numbers will automatically match. However, if you saved your PHREEQC results as new solutions, then you will need to create a dummy record for each new solution. You must create these dummy records before importing the PHREEQC results. It is best to create dummy records before running your PHREEQC simulation so you can be certain to save your new solutions with solution numbers equal to the index numbers of the dummy records.

When you import a solution to the database, it is important to note that you may only import those parameters which are currently defined in the database structure under the parameter groups PHREEQC minerals, PHREEQC activities or PHREEQC descriptions (e.g. if you want to import the saturation index of calcite, you must have a parameter "#calcite_si" defined in the PHREEQC Minerals parameter group).

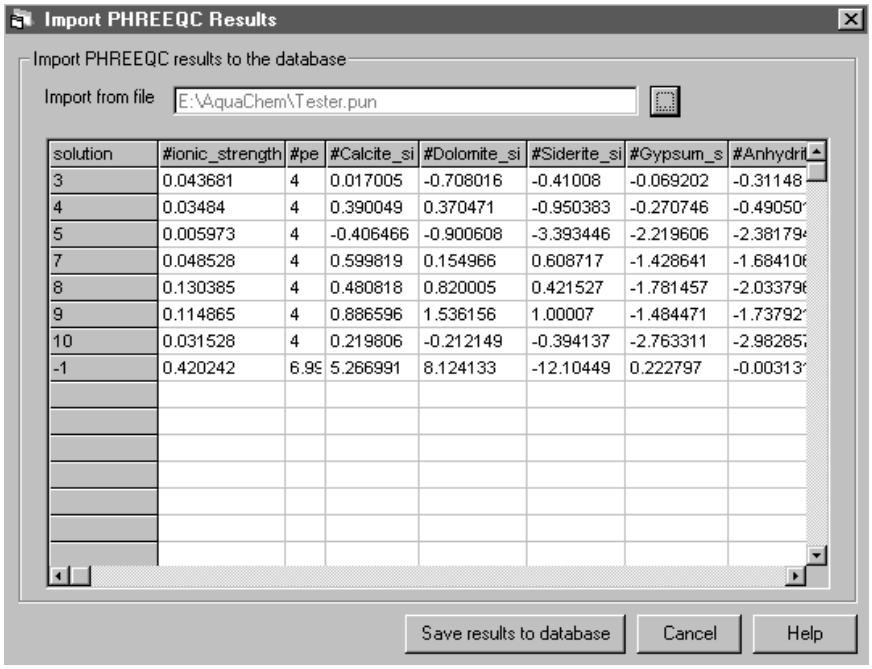


Figure 4.24: Import PHREEQC Results window

Create PHREEQC Input File

The AquaChem PHREEQC interface allows you to quickly and easily create input files for running PHREEQC simulations in a Windows environment. This unique graphical environment facilitates rapid development of simple or complex PHREEQC simulations. All of the latest PHREEQC analysis options are supported and presented in an intuitive and logical structure. In addition, AquaChem provides direct access to your AquaChem project database records for selecting solutions and building the input files. New solutions can be easily defined as needed, or existing solutions from previous simulations can be conveniently selected. AquaChem also supports the use of flexible units for the various chemicals in solution. Several simulations can be defined in one input file and processed in a single run. Reactions such as heating, evaporating, dissolving, or precipitating minerals can be conveniently simulated in step wise simulations, with all model parameters calculated for each step.

Once the PHREEQC input files have been prepared, the PHREEQC simulation can be launched directly from AquaChem (the PHREEQC executable file is automatically installed in the AquaChem working directory). When the PHREEQC simulation is completed you can import the results back into AquaChem for further processing and analysis.

The **PHREEQC Input** window is shown in Figure 4.25. The operation and functionality of the PHREEQC interface is too involved to deal with in this section of the user's manual. Refer to Section 7.3 on page 141 for detailed instructions for creating PHREEQC input files.

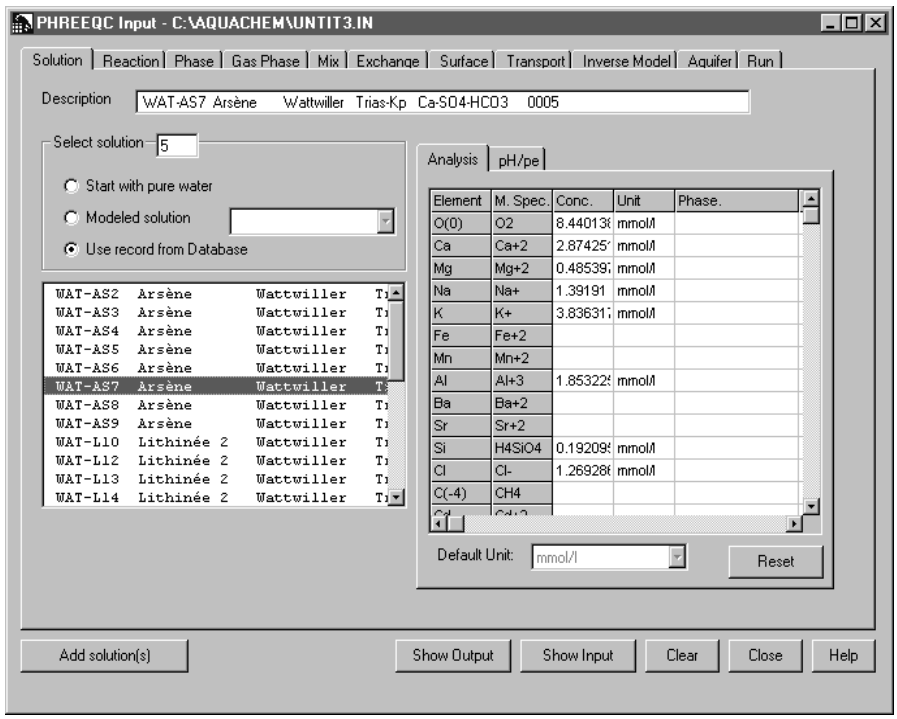


Figure 4.25: Create PHREEQC Input File window

4.2.6 Graphics

Open Configuration

The **Open Configuration** menu option opens an existing graphics configuration file (***filename.grf***) containing a previously defined plot, or set of plots. This graph file is linked to the database in which it was created and should not be opened from other AquaChem database projects. The graph configuration file saves the plot settings like titles, fonts, parameters, symbol labels, etc. for fast recall of the set of plot at a later time.

New

The **New** menu option is used to create a new graph by selecting from a list of 13 different plotting techniques commonly used to graphically present and interpret aqueous geochemical data. By selecting one of the 13 plot types, a **Graphics Options** dialogue box will appear with default settings for the specific plot type you selected. Select **[OK]** to accept the default settings and create a new **Graphics** window.

Define Symbol or Line

The **Define Symbol or Line** menu option opens a dialogue box (see Figure 4.26) where you define the names and status (active/inactive) of the symbol groups, the shape and color of the symbols, and the line-type and color of lines that appear in the graphs (see “Assign Symbol” on page 54 for instructions on assigning symbol groups to sample records). AquaChem allows you to assign up to 50 different symbol groups.

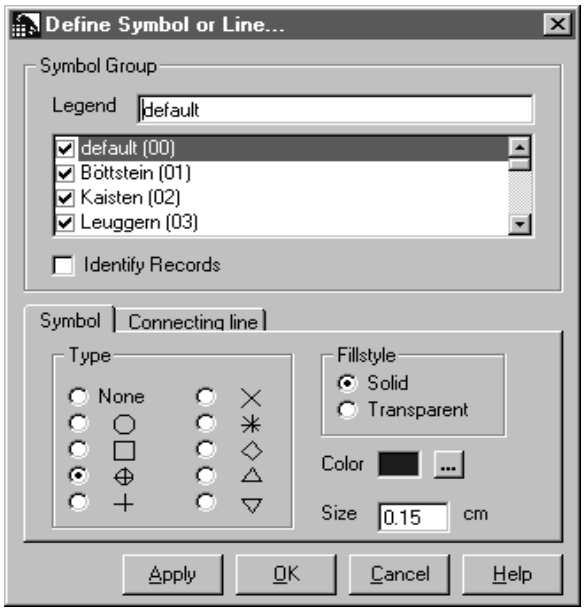


Figure 4.26: Define Symbol or Line dialogue box

The name and active status of the available symbol groups is listed in the **Group** list box. The groups with a check mark beside them are active and the sample records associated with these groups will be displayed in the open graphs. To remove a group of sample data points from all of the open graphs, simply click-on the appropriate checkbox to de-activate the symbol group.

The name of each symbol group will appear on the legend of each graph (if the legend is active). These names can be customized by selecting a symbol group and then entering a new name in the **Legend** text field. You must press the **<Enter>** key to accept the new name.

The number in parentheses beside each symbol group (e.g. **Group 1 (01)**) is used to identify the records belonging to this group. The symbol group number for each record is always displayed in the **Record List** in the far right-hand column.

The **Identify Records** checkbox is used to highlight the records associated with the selected symbol group.

Symbol Tab

The **Symbol** tab is used to select/customize the shape, size and color of the graph symbols as they appear for each symbol group.

There are 10 symbol types to choose from. The default color setting for each symbol type is **Transparent**, meaning it will appear on the graph in black lines with no color fill. The color of the symbols can be changed by selecting the **Solid** color setting and choosing a color by clicking the **Color [...]** button.

Connecting Line Tab

The **Connecting Line** tab displays a selection of six line styles, a line width and a line color that can be displayed in the Schoeller graph and the time-series graph to connect associated data points.

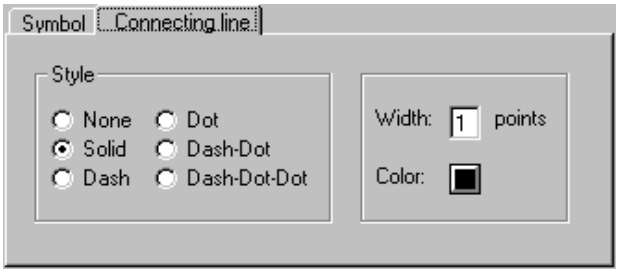


Figure 4.27: Connecting Line tab

Each symbol group is associated with a particular line style. This line style, the width of the line and the line color can be customized for each symbol group.

Close All Graph Windows

Closes all of the open **Graphics** windows. **Graphics** windows must be closed when performing an operation which will change the number of records in the open database.

4.3 Graphics Menu

The **Graphics Menu** is displayed when any **Graphics** window is the active window selection (see Figure 4.28). The **Graphics** window menu options are discussed in the following sections.

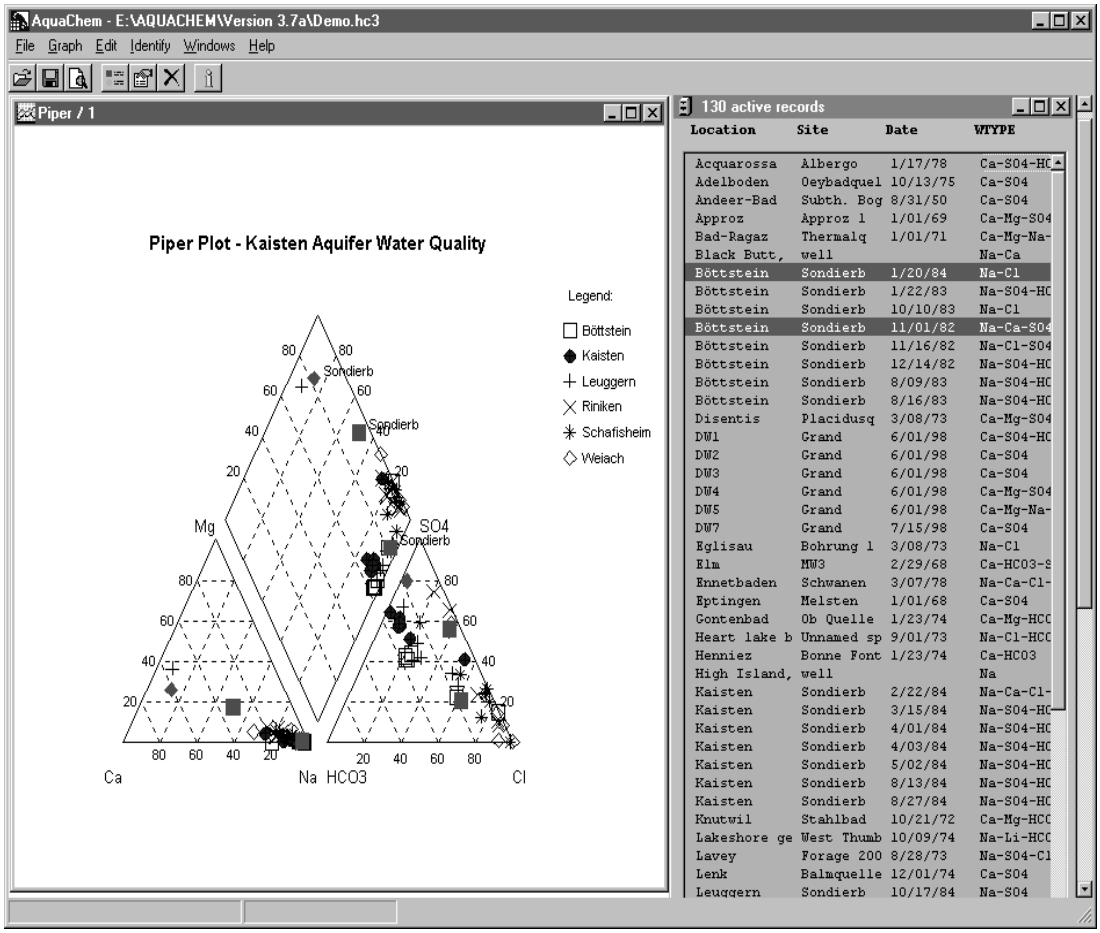


Figure 4.28: Graphics Window

4.3.1 File

Display Graph Data

Displays the Cartesian coordinates of the active graph in a spreadsheet format as shown in Figure 4.29). The data can then be saved to an ASCII file. This function is useful if you want to recreate triangular plots (e.g. Piper, Ternary, Durov) with programs such as Excel, Grapher or Lotus Freelance.

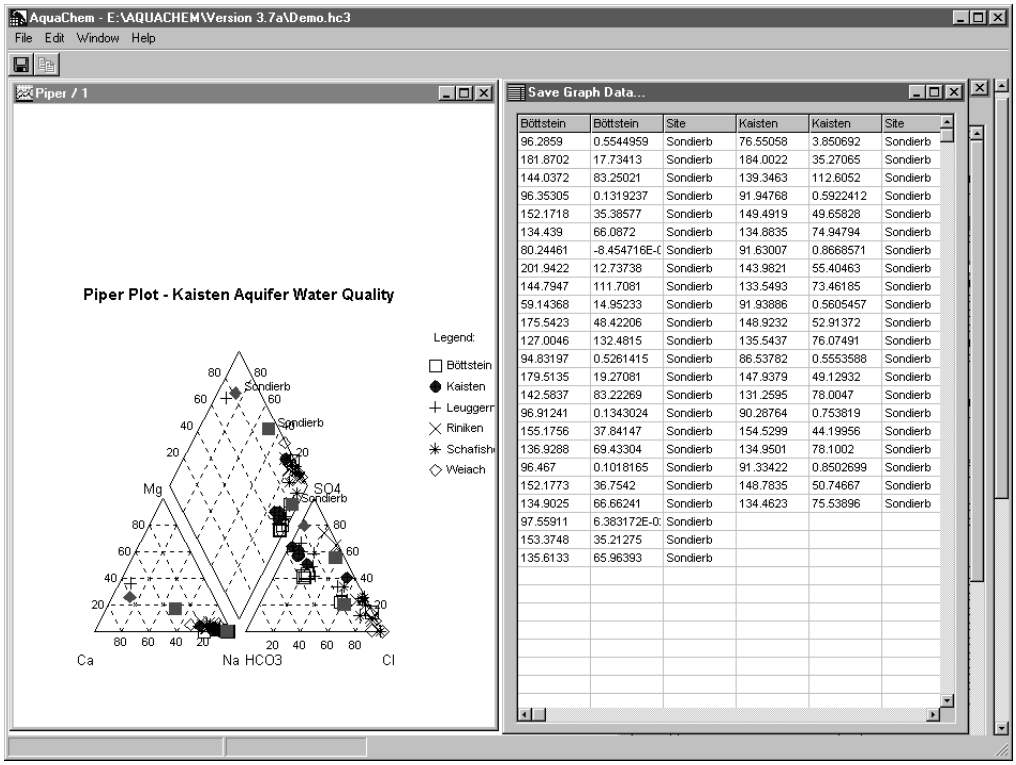


Figure 4.29: Scatter Graph and Graph Data

The data is displayed in spreadsheet form. It can be saved to a file or cut-and-pasted to another Windows application. If the samples are grouped by symbols, a separate x and y column is produced for every symbol group. The first row contains the titles for every column. The cells can be edited by clicking the cell, and typing in the text field located at the top of the window.

If you are planning to use a different program to plot the data, you may find it helpful to add a third column containing a label for each data set to help you identify the points. Typical labels are: the database index, the site, or the location name. Right click the graph and select the **Options** tab. Select one of the labels from the label list. This label will be used to specify selected points in the graph and to fill the third column if you extract the data to a spreadsheet.

Data for Ternary, Piper, and Durov plots are also provided in Cartesian form. If you choose to re-create these plots with other graphing programs, you will need to super-impose the triangular grid lines on your graphs. The information required to plot the triangular grid lines is provided in the table below.

Use a square grid to avoid distortions in your plots. The domain of X values and the range of Y values are given in the table below. For example, Ternary data will have a domain of X values lying between X=0 and X=100, and a range of Y values between Y=0 and Y=86.6. The first grid line you need to draw connects the points (0, 0) and (100, 0). The second connects (100, 0) and (50, 86.6), and the third connects (50, 86.6) and (0, 0).

You can construct the grids for Durov and Piper graphs in a similar fashion, using the information below.

Graph Type	Min X	Max X	Min Y	Max Y	Grid Lines	Start Coord. (X,Y)	End Coord. (X,Y)
Ternary	0	100	0	86.6	Main Triangle	(0, 0)	(100, 0)
						(100, 0)	(50, 86.6)
						(50, 86.6)	(0, 0)
Piper	0	210	0	186.6	Left Triangle	(0, 0)	(100, 0)
						(100, 0)	(50, 86.6)
						(50, 86.6)	(0, 0)
					Right Triangle	(110, 0)	(210, 0)
						(210, 0)	(160, 86.6)
						(160, 86.6)	(110, 0)
Durov	0	186.6	0	186.6	Lower Triangle	(0, 50)	(86.6, 0)
						(86.6, 0)	(86.6, 100)
						(86.6, 100)	(0, 50)
					Upper Triangle	(86.6, 100)	(186.6, 100)
						(186.6, 100)	(136.6, 186.6)
						(136.6, 186.6)	(86.6, 100)

Save Configuration

The **Save Configuration** menu option saves the configuration of the open graphs to a graph file (***filename.grf***). This configuration can be only be loaded in a the AquaChem project database in which it was created. The configuration includes axis settings, selected records, symbol settings, etc.

Open Configuration

The **Open Configuration** menu option opens an existing graph file (***filename.grf***). This graph file is linked to the database in which it was created and cannot be opened from other AquaChem database projects.

Print

The **Print** menu option allows you to print the contents of any or all of the open graphics windows. When you select the **Print** menu option a **Print Preview** window will open with a floating **Print Options** dialogue box as shown in the following figure. The **Print Options** dialogue box is used to select the plots, to customize the arrangement of the plots on the page, and to customize the appearance of the page itself.

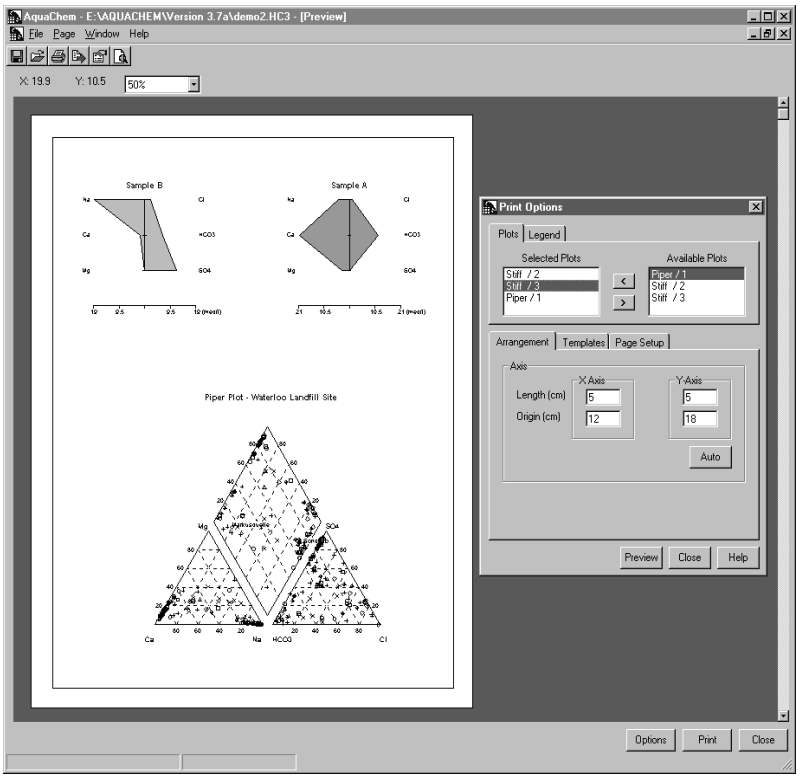


Figure 4.30: Print Graph dialog box

The **Print Options** dialogue box allows you to select which plots to print, and then set the size and location of each plot on the page. To print one (or more) plots you must select the desired plot(s) from the list of **Available Plots** and then move it to the list of **Selected Plots** by clicking the left arrow **[<]** button. The selected plot(s) will appear in the **Print Preview** window and will be automatically sized and arranged to fit the screen. To remove a plot from the **Print Preview** window, click on the plot under the **Selected Plots** list and then click the right arrow **[>]** button.

To print one or more of the open plots, select the desired plots from the list of **Available Plots** and then move them to the list of **Selected Plots** by clicking on the **[<]** arrow. Plots can also be removed from the **Selected Plots** list using the **[>]** arrow.

The following sections describe the basic features of the Print Preview screen. Please refer to Section 6.1 on page 124 for a more detailed description of the various plot printing options.

Arrangement Tab

The selected plots will be automatically sized and arranged on the page according to the number of plots and the type of plots selected. However, the default arrangement of plots does not consider the presence of plot titles or legends. Therefore, you may want to customize the size and location of each plot to produce a more desirable arrangement of the plots on the page.

The position and size of the plots can be easily modified using the **Arrangement** tab provided in the **Print Options** dialog box. The position/size of a single plot can be modified by clicking on the plot in the **Selected Plots** list (make sure only one plot is selected) and then making the desired changes to the position and/or size of the selected plot. Press the **<Enter>** key to update the print preview. The **[Auto]** button will prompt you to select a layout design (# rows, # columns) for the plots (a default layout style will be suggested depending on the number of plots selected). Once the layout style is selected, the plots will be automatically resized and positioned on the page using uniform spacing and sizing for each plot.

If the plots you selected have a legend associated with them, you must select the **Legends** tab and move the appropriate legends from the list of **Available Legends** to the list of **Selected Legends**. The position and font size of the selected legends can be easily customized using the options provided.

How To ??? Hints

Changing the Size of a Plot

- Select a plot from the **Selected Plots** list or click on the target plot in the **Print Preview** window (make sure only the plot you are interested in is highlighted in the **Selected Plots** list)
- Enter the new length dimension (X-Axis or Y-Axis)
- Press the **[Apply]** button or press the **<Enter>** key

NOTE: You can simultaneously change the X or Y axis length for more than one plot at a time by selecting multiple plots from the **Selected Plots** list.

Changing the Position of a Plot

- Select a plot from the **Selected Plots** list or click on the target plot in the **Print Preview** window (make sure only the plot you are interested in is highlighted in the **Selected Plots** list)
- Enter the new position (X-Axis or Y-Axis)
- Press the **[Apply]** button or press the **<Enter>** key

NOTE: You can simultaneously change the X or Y position for more than one plot at a time by selecting multiple plots from the **Selected Plots** list. However, you should be particularly careful not to assign the same X and Y origin to each plot.

Print Template Tab

The **Templates** tab provided in the **Print Options** dialog box allows you to select from a list of pre-defined print templates that allow you to add more detailed descriptions of the plot(s), the project, and the client. The list of available templates provided with AquaChem includes:

- None
- Default A4 Portrait
- Default Letter Portrait
- Default Letter Landscape
- Default Tabloid Landscape

The default template selection is "None" (meaning no template has been selected). If "None" is selected you can enter a two line title at the top of the page plus a footer at the bottom of the page. In addition, all of the **Page Setup** tab options are available for adjusting the page size and margins, and turning the page border on or off.

If you select one of the pre-defined WHI print templates, a list of available descriptor fields will appear and the **Print Preview** window will be updated to reflect the layout of the selected template. The information you enter in the descriptor fields can be saved to a project template file (***templatename.tpl***) to avoid re-entering repetitive information for each printed page (e.g. project name, client name, project number).

If the pre-defined print templates are not satisfactory for your needs, you can easily create your own customized print templates using the **[Design]** option in the **Templates** tab. For a detailed description of the template design features, please refer to Section 6.4.2 on page 130.

How To ??? Hints

Selecting a Blank Page Design

The default page design is to display only the border around the edge of the page and to have the option for simple titles and a footer (as shown in the following figure).

To add a title at the top of the page, select **Title1** from the dropdown **Title** list and type the desired description in the text box provided. To add a second line to the title, select **Title2** from the dropdown Title list and type the desired description in the text box provided (note: when **Title2** is selected, the text from **Title1** is removed from the textbox, but the information is saved). The font and alignment of the titles and footer can be customized using the **[F]** button and the **Align** selection list, respectively.

Selecting a Page Design Template

If one of the available (or customized) page designs is selected, the selected page design will be displayed in the **Print Preview** window and the corresponding text description fields will be provided below the Page Design selection field (as shown in the following figure). To enter a value in one of the text descriptor fields, simply double-click in the target field and enter the text description.

Saving/Opening a Page Design Template

The text descriptions entered in the descriptor fields can be saved in a page design template file (***filename.tpl***) for fast recall at a later date and to avoid repetitive entry of similar information. To save a page design template file press the **[Save]** button and enter an appropriate name for the file. To open a page design template file, select the **[Open]** button and choose the desired template (***filename.tpl***) file.

Page Setup Tab

The **Page Setup** tab contains options for setting the page margins and selecting the desired paper size and orientation. If a print template page design has been selected, the page setup options are disabled to avoid conflicts with the template settings.

Quit

The **Quit** menu option closes the active graph window.

4.3.2 Graphics

New

The **New** menu option allows you to creates a new plot in a new **Graphics** window. See Chapter 5 for a description of the available plot types.

Close All Graph Windows

The **Close All Graph Windows** menu option closes all open **Graphics** windows. Graphics windows that are not in use should be closed before making changes to the current selection in the **Records List**, to avoid recalculating the position of every point on every graph.

Parameters

The **Parameters** menu option opens the **Parameters** window listing all of the parameters in the open database. These parameters can be 'dragged' from the **Parameters** window and 'dropped' into parameter fields in most dialog boxes requiring parameter names for plots, reports or calculations.

4.3.3 Edit

Copy Graph

The **Copy Graph** menu option copies the plot in the active **Graphics** window to the clipboard in bitmap format. The graph can then be pasted to most graphics or word processing programs.

Axes

The **Axes** menu option allows you to modify the axes settings for the active plot. Each plot type has a graphic options dialogue box that is specifically designed to accommodate the special features of each plot. The graphic options for each plot type are described in detail in Chapter 5. The graphic options dialogue box for any plot can accessed by right-clicking in the graph area on the open **Graphics** window.

Symbol or Line

The **Symbol or Line** menu option opens the **Define Symbol or Line** dialogue box where you define the names and active status of the symbol groups, the shape and color of the symbols, and the line-type and color of lines that appear in the graphics. The symbol groups are described on page 54, while the **Define Symbol or Lin**e options are described on page 73.

Function

The **Function** menu item will open the **Curves** dialogue box (see Figure 4.31) where you can create and edit regression lines in XY-scatter graphs. You can manually enter the curve coefficients or use AquaChem to calculate the equation of the line by means of a linear regression algorithm. The regression can be based on all records in the **Record List**, on currently selected records, and on pre-defined groups of records.

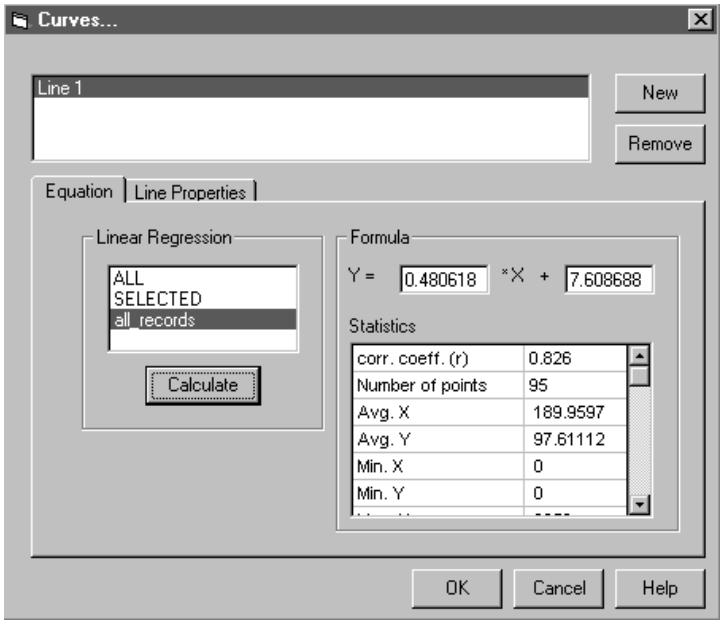


Figure 4.31: Edit Function dialog box

Equation Tab

The linear regression analysis can be performed on **All** active records in the **Record List**, on currently **Selected** samples, or on one of the active groups of sample records. To calculate a linear regression analysis on the selected data, click the **[Calculate]** button and AquaChem will display the equation of the line passing through the selected data points. The resulting formula and associated statistical analysis of the selected data is displayed in the **Formula** frame.

Line Properties Tab

The **Line Properties** tab is used to specify line style, width, colour and start and end co-ordinates for the regression line as it appears in the scatter plot.

4.3.4 Identify

There are three options available for selecting and identifying points on a graph: **None**, **Selected Graph**, and **Linked**. The default mode to identify points is the **Linked** mode, where all data points on all graphs are linked to the database. All three options are described in the following section.

None

The data points on the graphs are not linked to the database which means that samples are not identified if you click on a data point in a plot. When you have several open graphs and a large database with many records, it may be convenient to have no link between the graphs and the database in order to increase the speed of the various AquaChem operations.

Selected Graph

Only the data points in the active graph are linked to the database. This mode is useful if you are working with a large data set and several open graphs and the **Linked** mode is too slow.

Linked

This is the default mode to identify points. If you are working with several graphs, you can identify a sample in all plots as well as in the **Record List** by clicking near a point in any of the plots, or by clicking on a sample in the **Record List**. The record will become selected in the **Record List**, and the corresponding data points will become red in all the open graph windows.

Info

Pops up an information window which displays plot coordinates associated units of the data point selected on a graph (see Figure 4.32).

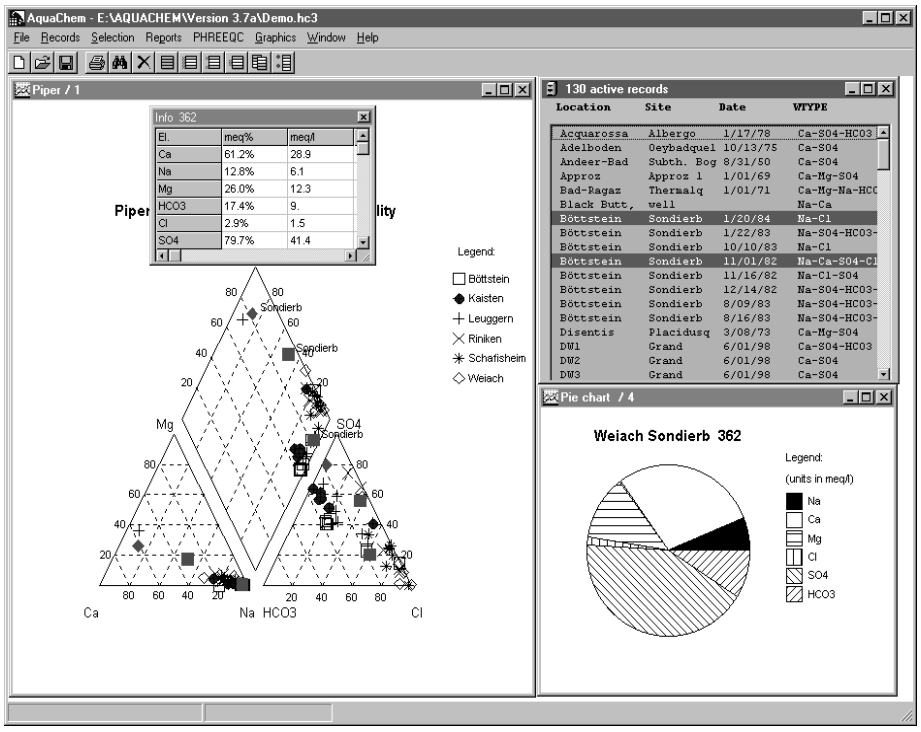


Figure 4.32: Graph Info window

4.4 Input Menu

The **Input Menu** is displayed when the **Input** window is the active window (see Figure 4.33). The **Input** window can be opened by either;

(i) selecting **Main Menu\Record\Edit;**

(ii) double-clicking a record in the **Record List;** or

(iii) right-clicking on a selected record in the **Record List** and choosing **Edit**.

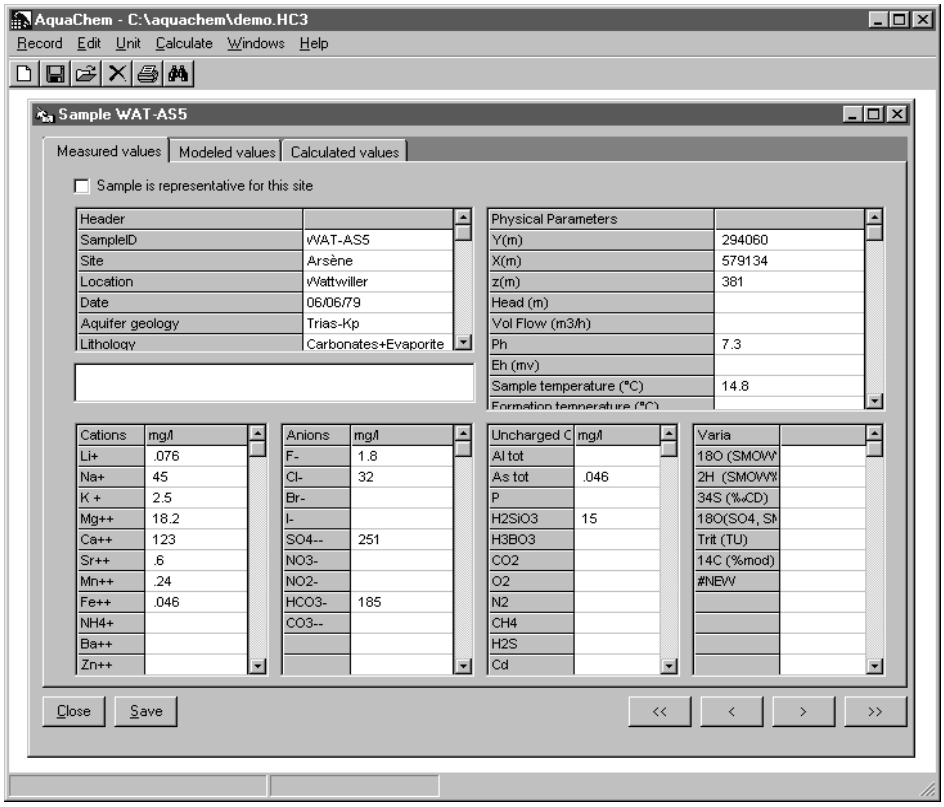


Figure 4.33: Input Window

The **Input** window displays all of the data for a single record in the database. The data for each record is displayed in the **Input** windows using three different tabs:

- **Measured values**
- **Modelled values**
- **Calculated values**

The **[Close]** button closes the **Input** window and returns to the **Main Menu.**

The **[Save]** button saves any changes to the parameter values and updates all graphs and calculated parameter values.

The **[<<]** button displays data for the first record in the **Record List**.

The **[<]** button displays data for the previous record in the **Record List**.

The **[>]** button displays data for the next record in the **Record List**.

The **[>>]** button displays data for the last record in the **Record List**.

How To ??? Hints

Entering data using the Input window

- Select the cell of the parameter that you would to edit
- Type in the value
- Press the **<Enter>** key

The new value is not actually saved to the database until you press the **[Save]** button or until you advance to the next or previous record.

Changing the numeric format in the Input window

- Return to the **Main Menu** by closing the **Input** window or clicking on the **Record List**
- Select **File/Preferences/Data Structure**
- Select the target **Parameter Group** (e.g. Cations)
- Select the target parameter (e.g. Na)
- Choose the desired numeric format from the **Format** selection field
- Press the **[Apply]** button beside the **Display label** field
- Press the **[Save]** button at the bottom of the **Preferences** dialogue box

4.4.1 Record

New

The **New** menu option creates a new record. All graph windows must be closed to create a new record.

Duplicate

The **Duplicate** menu option creates a new record with the same header information and coordinates as the selected record. All graph windows must be closed to create a duplicate record.

Save

The **Save** menu option saves the record to the database. All graph windows must be closed to save a record to the database.

Delete

The **Delete** menu option deletes the selected record(s).

Next

The **Next** menu option displays the data for the next record in the **Record List**.

Previous

The **Previous** menu option displays the data for the previous record in the **Record List**.

Print

The **Print** menu option displays the data for the selected record in a text window. The information can then be sent to the printer or copied and pasted to another Windows application.

Close

The **Close** menu option closes the Input window.

4.4.2 Edit

The **Cut**, **Copy** and **Paste** menu options are used to cut, copy, and paste individual cell values into other text fields or to other Windows applications.

4.4.3 Unit

The Units menu option is used to select the desired concentration units to be displayed in the Input window. The available concentration units include mg/l, mmol/l, meq/l, mol/l or ppm. Conversion factors are calculated using the formula weights as defined in the mask file (see **File/Preferences/Data Structure**). Switching between units can result in small rounding errors. If possible, save files with the units used when the data was originally obtained.

4.4.4 Calculate

Find Missing

Theoretically, every sample has a perfect charge balance of anions and cations in meq/l. If information for one of the major anions or cations (Na, Ca, Mg, Cl, SO_4, HCO_3) is missing from a database record, you can choose **Calculate/Find Missing** to estimate the concentration of the missing major element. The concentration of the missing ion is calculated using the theoretical ion balance between the major ions. This does not work if more than one of the major cations or anions is missing in the analysis.

In order to calculate the missing values for one of the major ions, each of the remaining major ions must be present. The major ions are as follows:

Parameter Group name	Internal name
Cations	Na, Ca, Mg
Anions	Cl, SO4, HCO3

TDS

TDS, or Total Dissolved Solids, is a measure of the evaporation residue at a given temperature. It can also be thought of as the mass of all ions. It is important to note that the calculated TDS is only an approximation and it is always better to have a measured value.

First the sum in mg/l of $Na+K+Mg+Ca+Cl+SO_4$ is calculated. Then the program checks if $(Ca+Mg-SO_4) > (HCO_3+CO_3)$. This is done because TDS is not simply the sum of ions but the weight of residue you would expect if you evaporate the entire sample. In waters that contain in excess carbon $(Ca+Mg-SO_4) < (HCO_3+CO_3)$ you may not add all carbon since bicarbonate will partly outgas as CO_2 during evaporation. Only the quantity of HCO_3 which can be precipitated as calcite and dolomite is added to the estimate of the TDS. SO_4 is

deduced from Ca+Mg because gypsum is built first and the Ca that is used up by this process cannot be used any more to build calcite. If ($Ca+Mg-SO_4$) > (HCO_3+CO_3) then all HCO_3 and CO_3 can be added to the TDS because there is enough Ca+Mg to build calcite and dolomite.

In order to calculate the TDS of a given sample, you need to have TDS specified in the **Physical Data** Parameter Group with an **Internal name** of **TDS**.

Calculator

The AquaChem **Calculator** allows you to easily convert quantities from one unit system to another (see Figure 4.34). Use the **In** field to choose the original unit system, and type the value in the underlying text field. Then use the **Out** field to choose the desired conversion units, and click the arrow **[>]** button. The converted quantity will be displayed below the **Out** field. Text can be cut and pasted from the **Calculator** to the **Input** window, by using the menu options under **Edit**. To close the **Calculator**, select **File\Close**.

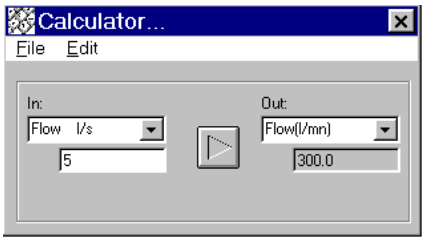
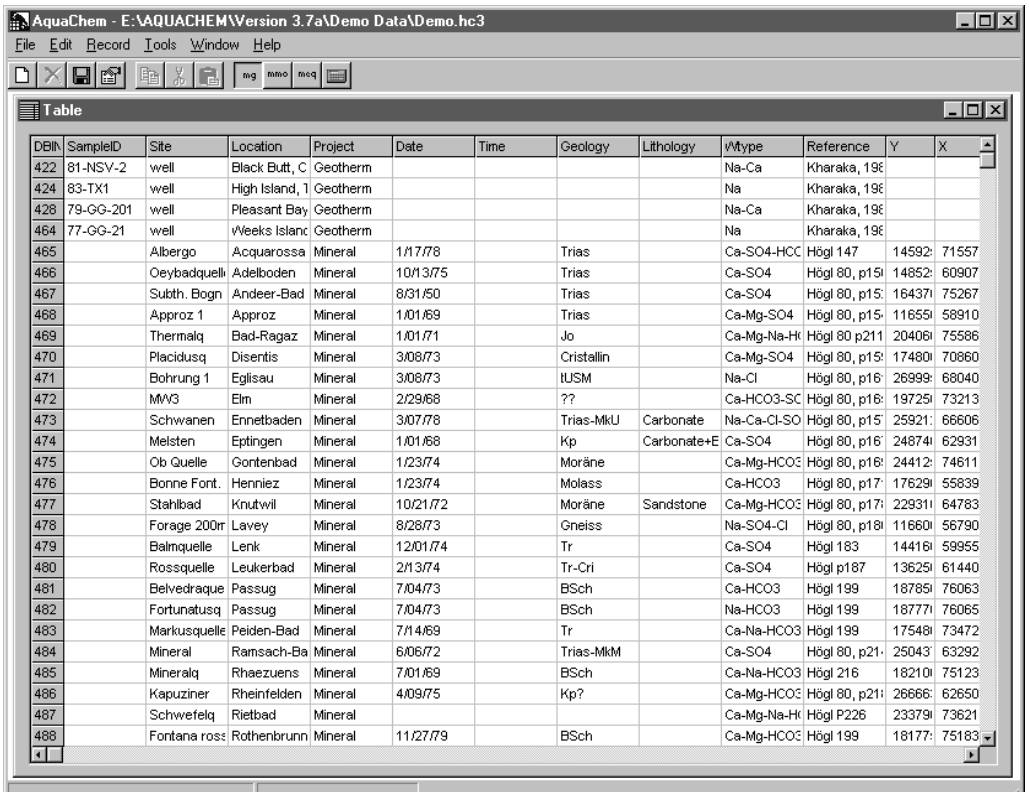


Figure 4.34: Calculator

4.5 Spreadsheet Menu

The **Spreadsheet** menu items are available when the AquaChem **Spreadsheet** window is active (see Figure 4.35). The **Spreadsheet** window provides a convenient tabular display of selected sample data from the active records in the **Record List**.

The AquaChem spreadsheet table works similar to most spreadsheet tables in that you can edit and modify the contents of the individual grid cells. To replace the contents of a grid cell simply click on the grid cell and type in a new value. To modify the existing contents of a grid cell, double-click on the grid cell and use the **<Backspace>** or arrow keys to navigate inside the grid cell. If you wish to import data from an existing spreadsheet format (e.g. Excel or Lotus), it is best to save the existing spreadsheet as a tab-delimited text file and then use the AquaChem data import utility to bring that information into AquaChem.



DBIN	SampleID	Site	Location	Project	Date	Time	Geology	Lithology	Wtype	Reference	Y	X
422	81-NSV-2	well	Black Butt, C	Geotherm					Na-Ca	Kharaka, 198		
424	83-TX1	well	High Island, T	Geotherm					Na	Kharaka, 198		
428	79-GG-201	well	Pleasant Bay	Geotherm					Na-Ca	Kharaka, 198		
464	77-GG-21	well	Weeks Islanc	Geotherm					Na	Kharaka, 198		
465		Albergo	Acquarossa	Mineral	1/17/78		Trias		Ca-SO4-HCC	Högl 147	14592	71557
466		Oeybadquell	Adelboden	Mineral	10/13/75		Trias		Ca-SO4	Högl 80, p15	14852	60907
467		Subth. Bogn	Andeer-Bad	Mineral	8/31/50		Trias		Ca-SO4	Högl 80, p15	16437	75267
468		Approz 1	Approz	Mineral	1/01/69		Trias		Ca-Mg-SO4	Högl 80, p15	11655	58910
469		Thermalq	Bad-Ragaz	Mineral	1/01/71		Jo		Ca-Mg-Na-H	Högl 80 p211	20406	75586
470		Placidusq	Disentis	Mineral	3/08/73		Cristallin		Ca-Mg-SO4	Högl 80, p15	17480	70860
471		Bohrung 1	Eglisau	Mineral	3/08/73		tUSM		Na-Cl	Högl 80, p16	26999	68040
472		MW3	Elm	Mineral	2/29/68		??		Ca-HCO3-SC	Högl 80, p16	19725	73213
473		Schwanen	Ennetbaden	Mineral	3/07/78		Trias-MkU	Carbonate	Na-Ca-Cl-SO	Högl 80, p15	25921	66606
474		Melsten	Eptingen	Mineral	1/01/68		Kp	Carbonate+E	Ca-SO4	Högl 80, p16	24874	62931
475		Ob Quelle	Gontenbad	Mineral	1/23/74		Moräne		Ca-Mg-HCO3	Högl 80, p16	24412	74611
476		Bonne Font.	Henniez	Mineral	1/23/74		Molass		Ca-HCO3	Högl 80, p17	17629	55839
477		Stahlbad	Knutwil	Mineral	10/21/72		Moräne	Sandstone	Ca-Mg-HCO3	Högl 80, p17	22931	64783
478		Forage 200m	Lavey	Mineral	8/28/73		Gneiss		Na-SO4-Cl	Högl 80, p18	11660	56790
479		Balmquelle	Lenk	Mineral	12/01/74		Tr		Ca-SO4	Högl 183	14416	59955
480		Rossquelle	Leukerbad	Mineral	2/13/74		Tr-Cri		Ca-SO4	Högl p187	13625	61440
481		Belvedraque	Passug	Mineral	7/04/73		BSch		Ca-HCO3	Högl 199	18785	76063
482		Fortunatusq	Passug	Mineral	7/04/73		BSch		Na-HCO3	Högl 199	18777	76065
483		Markusquelle	Peiden-Bad	Mineral	7/14/69		Tr		Ca-Na-HCO3	Högl 199	17548	73472
484		Mineral	Ramsach-Ba	Mineral	6/06/72		Trias-MkM		Ca-SO4	Högl 80, p21	25043	63292
485		Mineralq	Rhaezuens	Mineral	7/01/69		BSch		Ca-Na-HCO3	Högl 216	18210	75123
486		Kapuziner	Rheinfelden	Mineral	4/09/75		Kp?		Ca-Mg-HCO3	Högl 80, p21	26666	62650
487		Schwefelq	Rietbad	Mineral					Ca-Mg-Na-H	Högl P226	23379	73621
488		Fontana ross	Rothenbrunn	Mineral	11/27/79		BSch		Ca-Mg-HCO3	Högl 199	18177	75183

Figure 4.35: Spreadsheet window

4.5.1 File

Export

The Export menu option will export the data from the spreadsheet table to a tab-delimited text data file (***filename.dat***).

Settings

The **Settings** menu option opens the **Spreadsheet Settings** dialogue box where you can modify the column selections and arrangement of the spreadsheet table (see Figure 4.36).

The **Spreadsheet Settings** dialogue box prompts you to choose the parameters to be included in each column of the spreadsheet table (the rows of the spreadsheet are always reserved for each active record in the database). Spreadsheet columns may contain any measured parameter (Na, Ca, Cl...) or calculated parameter (e.g. ion ratios, total hardness, or geothermometer temperatures).

The **[Delete]** button is used to delete a selected parameter from the table.

The **[Save]** button saves the current **Spreadsheet Settings** in a report file (***filename.rpt***).

The **[Load]** button loads an existing **Spreadsheet Settings** report file (***filename.rpt***).

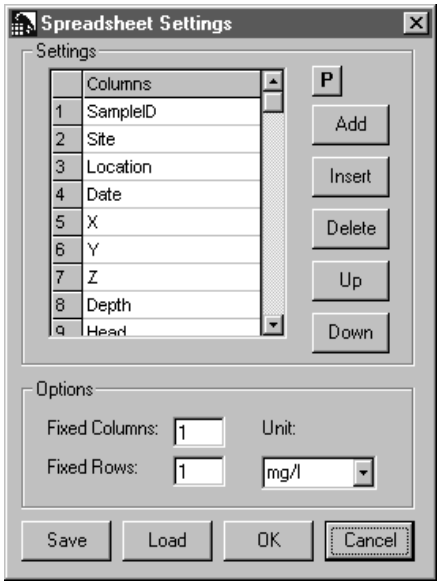


Figure 4.36: Spreadsheet Settings dialogue box

Select **[OK]** to accept the settings and view the spreadsheet. Changes to the spreadsheet configuration are automatically saved and will be remembered the next time you use the **View as spreadsheet** option.

Typically, one row and one column containing row and column headings will be fixed on the spreadsheet so the column and row headings always appear at the top and far right of the Spreadsheet window as you scroll through the spreadsheet. More than one column and row can be 'fixed'.

The **Fixed Rows** field is used to specify the number of rows to fix.

The **Fixed Columns** field is used to specify the number of columns to fix.

The **Units** field allows you to select the concentration units that you want to display on the spreadsheet. Chemical concentrations can be displayed in mg/l, mmol/l, meq/l, and mol/l.

Every change to a cell in the spreadsheet is automatically saved to the database. The database is not affected by editing calculated values such as ion ratios, hardness, geothermometers, etc.

How To ??? Hints

Adding a Parameter to the Spreadsheet Settings

- Click on the **[P]** button to load the **Parameters** window
- Click on the target parameter from **Parameters** window
- Click on the **[Add]** button to append the new parameter to the end list

Changing a Parameter in the Spreadsheet Settings

- Double-click on the parameter that you would like to change
- Select the new parameter from the list of available parameters
- Press the **<Enter>** key to register the new parameter selection

Quit

The **Quit** menu option closes the **Spreadsheet** window and returns you to the **Main Menu**.

4.5.2 Edit

Cut, Copy and Paste

The **Cut**, **Copy** and **Paste** menu options will cut, copy and paste data from selected fields to the Windows clipboard (or vice versa). If you are copying information from an existing Excel spreadsheet or a tab-delimited ASCII file, into the AquaChem spreadsheet, you must first highlight the appropriate fields in the AquaChem spreadsheet where the information will be copied. For example, if you are copying data from a 3 rows and 4 columns of an Excel spreadsheet, you must highlight all of the appropriate destination rows and columns in the AquaChem spreadsheet before you paste the information from the Windows clipboard.

4.5.3 Record

New

The **New** menu option will create a new (blank) sample record and add it to the last row of the spreadsheet table.

Delete

The **Delete** menu option will delete the selected record from the spreadsheet table. The **Delete** option will not be available unless the entire row is selected by clicking on the first column of the spreadsheet listing the table row.

4.5.4 Tools

Units

The **Units** menu option allows you to select the display units of the Cations, Anions and Uncharged compounds as either **mg/l**, **mmol/l** or **meq/l**.

Calculator

The AquaChem **Calculator** allows you to easily convert concentrations from one unit system to another. Use the **In** field to choose the original unit system, and type the value in the underlying text field. Then use the **Out** field to choose the desired conversion units, and click the arrow **[>]** button. The converted quantity will be displayed below the **Out** field. Text can be cut and pasted from the **Calculator** to the **Input** window, by using the menu options under **Edit**. To close the **Calculator**, select **File\Close**.

5

Graph Types

5.1 Common Features

When you select **Graphics\New**, from either the **Main Menu** or the **Graphics Menu**, a drop down menu will appear with an alphabetical list of the 13 available graph types. Although each graph type has unique characteristics, there are also many similar graphical features and options for each one. When you select any of the graph types to plot, a graphic options dialog box will appear with default settings for all of the necessary parameters. The graphic options dialog box for each graph type is divided into two separate sections as shown in Figure 5.1.

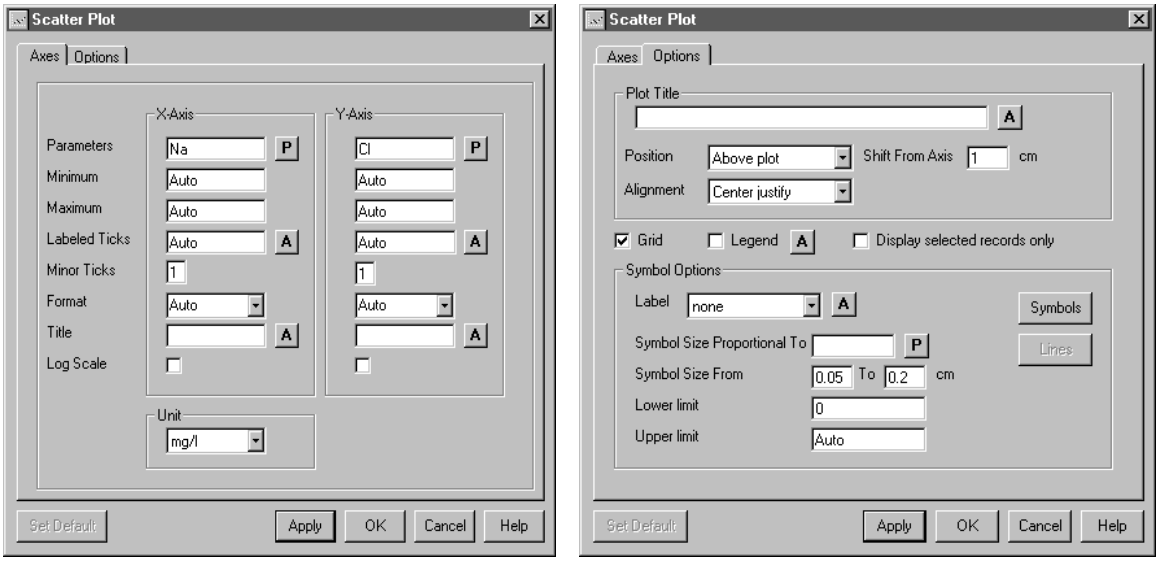


Figure 5.1: Graphic options dialog boxes

The **Axes** tab is for assigning the parameters that will be plotted on the graph axes, while the **Options** tab is for modifying the appearance of the graph (e.g. graph title, symbol label, symbol size, grid lines, etc.).

> **NOTE:** Since the triangular plots (Piper, Durov and ternary) do not have typical axes, the corresponding tab is labelled as **Parameters** instead of **Axes**.

The **[Set Defaults]** button will save the current settings for the selected parameters and the appearance of the graph type. These default settings will be applied every time you select that graph type in the current project. Each graph type can have different default settings that are saved in the database configuration file (***filename.cfg***). Each AquaChem database project has it's own configuration file.

The **[Apply]** button will apply the current graphic option settings to the selected graph type.

The **[OK]** button will apply the current graphic option setting to the selected graph type and will close the Graphic Options dialog box.

5.1.1 Axes Settings

Parameter Fields

Most graph dialog boxes have several fields for assigning chemical or physical parameters. These parameters can be typed directly into the text fields or dragged from the **Parameters** window. Click the **[P]** button to load the **Parameters** window listing all of the available parameters that can be added to the parameter field. Most of the parameter fields can also accommodate operators and functions (e.g. Na+K or Na/Cl), but multiple parameters (e.g. Na,Cl) will not be accepted.

Minimum/Maximum

Allows you to customize the minimum/maximum axes values. AquaChem will determine a default minimum/maximum value based on all of the data plotted on the graph. If you enter a new value and you wish to return to automatic calculation, enter a value of "A".

Labelled Ticks

Defines the value of the labelled ticks for the corresponding axis. AquaChem will determine a default value for the labelled ticks such that the plot will have 5 labelled ticks on the corresponding axis. If you enter a new value and you wish to return to automatic calculation, enter a value of "A".

Minor Ticks

Defines the number of minor ticks between each of the labelled ticks. The default value is 1. Only integer values are accepted.

Format

Sets the numeric format for the labels on the axes (e.g. 0.0, 0.00, 0.000, 0e+0. etc.). Click the down arrow to select from a list of available numeric formats.

Title

Defines the title of the corresponding axis. If a title field is left empty, a default title equal to the Internal name of the parameter will be selected by AquaChem. If you want to omit one or both axes titles, type a space in the text field(s).

Units

Defines the units for the parameters that will be plotted on the selected graph (mg/l, mmol/l, mol/l, meq/l, ppm). AquaChem will perform an automatic unit conversion on each data point before it is plotted on the graph.

Fonts

The default fonts for axes title and labels can be modified by selecting the **[F]** button. The Font dialog box provides a selection of all available Windows true type fonts, font sizes and font styles.

5.1.2 Display Options

Plot Title

Defines the title of the selected graph type. Enter the plot title in the text field provided. If no text is entered, then no title will be plotted

Position

Defines the position of the Plot Title as either above the plot or below the plot.

Alignment

Defines the alignment of the Plot Title as either left justified, centre justified, or right justified in the Graph Window.

Shift From Axis

Defines the vertical distance of the Plot Title above or below the plot.

Grid

Displays a grid on the plot with the same interval as the labelled ticks.

Legend

Displays a legend on the right-hand side of the plot listing all of the active symbol groups and the symbol shape associated with each. By default, all records are plotted with the same symbol. The symbol shape and the legend label for each symbol can be edited by selecting **Graphics Menu\Edit\Symbol or Line,** or by clicking the **[Symbols]** button.

If you have symbol sizes plotted proportional to a parameter value, the legend will also include a scale for the proportional symbol sizes.

Symbol Labels

Data points can be labelled on the plots using any of the Header Info parameters (e.g.Sample ID, Location, Site, Date, etc.). Press the down arrow to select from a list of available label parameters. Only records that are selected (highlighted) will be labelled. To label all sample points on the graph, select all records in the Record List (if you have many sample points, this may create a cluttered graph).

Symbol Size Proportional To:

AquaChem allows you to plot the size of the symbols on the graph relative to the value of a selected parameter. The **Symbol Size Proportional To:** text field defines the parameter that will be used to plot proportional symbol sizes. This parameter can be entered directly into the text field, or you can drag a selected parameter from the **Parameters** window (press the **[P]** button to load the **Parameters** window).

Symbol Size

Defines the minimum and maximum radius of the symbols. The minimum symbol size will be plotted for the lower limit of the proportional parameter value, while the maximum symbol size will be plotted for the upper limit of the proportional parameter value. The minimum radius ensures that all symbols will be visible even if the proportional parameter value it zero.

Lower/Upper Limit

Defines the minimum/maximum value of the proportional parameter to use for plotting a proportional symbol size.

Symbol Button

The **[Symbol]** buttons opens the **Define Symbol or Line** dialog box (see Figure 5.2) where you define the names and active status of the symbol groups, the shape and color of the symbols, and the line-type and color of lines that appear in the graphics (please refer to “Assign Symbol” on page 54 for a description of the symbol groups).

The name and active status of the available symbol groups is listed in the **Group** list box. The groups with a check mark beside them are active and will be displayed in the open graphs. To de-activate a group of samples simply click-on the appropriate checkbox and all associated sample points will be removed from all of the open graphs.

You can specify up to 50 different symbol groups. The name of each symbol group will appear on the legend of each graph. These names can be customized by selecting a symbol group and entering a new name in the **Legend** text field. You must press the **<Enter>** key to accept the new name.

The number in parentheses beside each symbol group (e.g. Group 1 (01) is used to identify the records belonging to this group. The symbol group number for each record is always displayed in the **Record List**, but it does not appear in the plot legend.

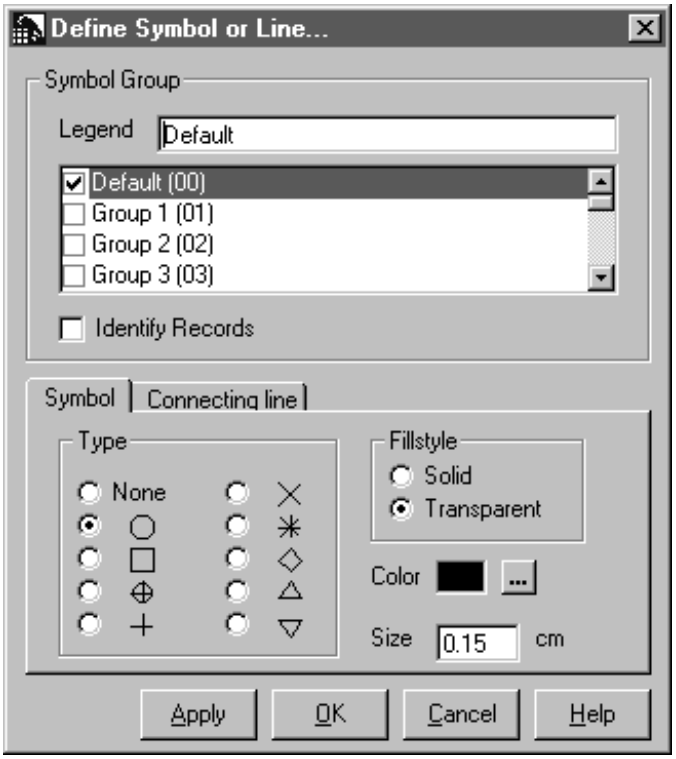


Figure 5.2: Define Symbol or Line dialog box

The **Identify Records** checkbox is used to highlight the records associated with the selected symbol group.

Symbol Tab

Displays a selection of 10 symbol types (shapes), the symbol color, and the symbol size.

To change the default symbol selections,

- Select the target symbol group
- Select the desired symbol type
- Press the **[Apply]** button

The symbol color selection applies only to the circle and the square symbols. To change the color of the circle or square symbols,

- Select the circle or the square symbol type
- Select the **Solid** colour option
- Click-on the color box to load the color palette
- Select a color from the color palette and press **[OK]**
- Press the **[Apply]** button

Connecting Line Tab

Displays a selection of six line styles, a line width and a line color that can be displayed in the Schoeller graph and the time-series graph to connect data points.

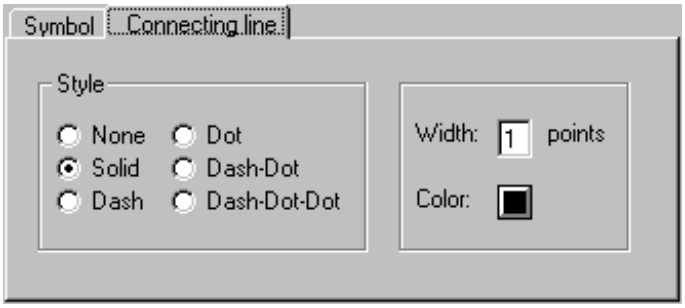


Figure 5.3: Connecting Line tab

Each symbol group is associated with a particular line style. This line style, the width of the line and the line color can be customized for each symbol group.

To change the line style of a symbol group

- choose the symbol group
- select the corresponding line style
- enter the desired line width
- click on the **Color** button and choose an appropriate color
- click **[OK]**

5.2 Durov Plot

The trilinear Durov diagram is based on the percentage of major ion milliequivalents. The cation and anion values are plotted on two separate triangular plots and the data points are projected onto a square grid at the base of each triangle. The Durov plot is an alternative to the Piper plot which is described in section 5.8 on page 115. Since the data points are projected along the base of the triangle, which lies perpendicular to the third axis in each triangle, information about the concentration of the vertex element (the third element) is lost in the square grid. Changing the orientation of elements in both triangles may improve your ability to detect distinct groups. The following section describes some of the features and options of the Durov plot that are not covered in the Common Features section.

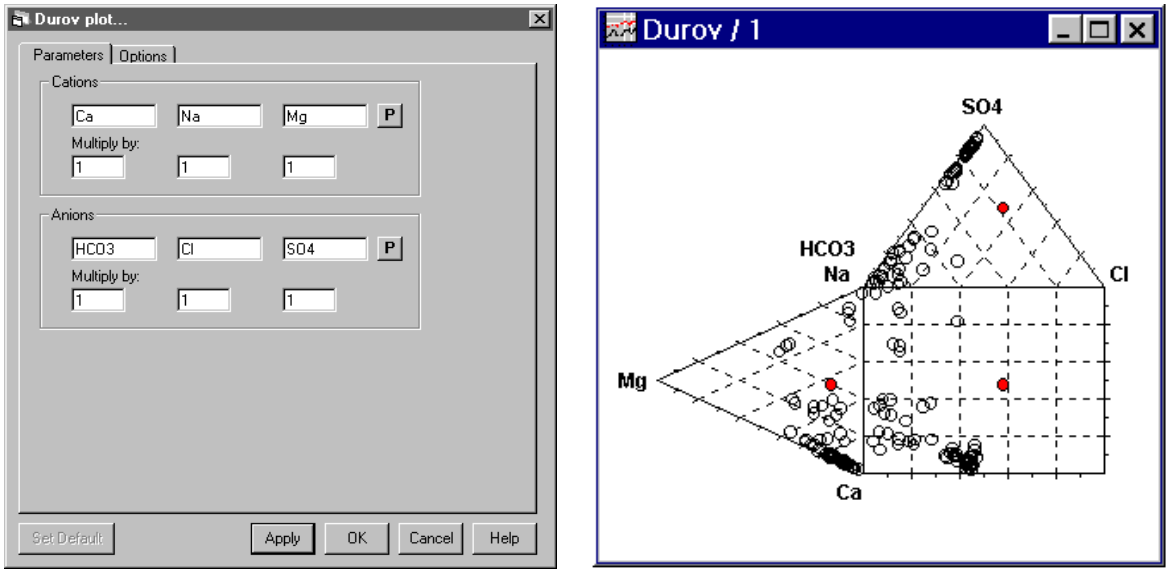


Figure 5.4: Durov dialog box and Graph window

Parameters

Cations

Specify the parameters of the left triangle. Default settings are the major cations Na, Ca, and Mg, but any other element can be selected (e.g. gas composition, trace elements etc.). Type or drag the new parameters from the **Parameters** window into the text fields. Click **[P]** to load the **Parameters** window.

Data from poorly concentrated elements can be multiplied by a common factor to prevent data point accumulation on a base line. Type the multiplication factor in the text field below the parameter.

Anions

Specify parameters for the upper triangle. Default settings are the major anions Cl, SO_4, and HCO_3, but any other parameter can be selected. Type or drag the new parameter from the **Parameters** window into the text fields. Click **[P]** to pop up the Parameters window.

5.3 Geothermometer Plot

Geothermometer plots can be used to test the quality of geothermometer estimates for a given geological and hydrogeological situation.

Different geothermometers can furnish very different results, when applied to the same water samples. Each geothermometer has a set of conditions which must exist for reasonable values to be calculated. For example, if the *in situ* temperature was not sufficient to attain rock-water equilibrium, the aquifer composition may be different from the one assumed by the geothermometer. Using conventional geothermometer graphs (log K-1000/T plots), you can check the quality of the calculated temperature if you have precise *in situ* temperature measurements. You should collect all analyses from the literature for which *in situ* temperatures have been measured. Also note the aquifer lithology of the samples. One excellent source of data is Kharaka et al. 1989. When you start a geothermal study, search for references to samples which compare closely with the aquifer of the water you are studying, and check which geothermometer gives the most reliable estimates. This thermometer is likely to give the most reliable results for the water you are studying as well.

The following section describes some of the features and options of the Geothermometer plot that are not covered in the Common Features section.

Plot Type

Under the Plot Type tab, click **Log(K)-1000/T** to plot a log(K)-1000/T graph. Click **K-Mg-Na Triangle** to plot a Giggenbach Triangle.

K-Mg-Na Triangle

The Giggenbach triangle representation allows you to check the extent that water-rock equilibrium has been attained. The theoretical background of this representation is explained in detail by Giggenbach (1988). The triangle is comprised of three zones:

1) immature waters (at the base),
2) partially equilibrated waters in the middle, and
3) fully equilibrated waters along the upper curve.

Depending on where the composition of a given sample lies within this triangle, you can estimate the extent of rock-water equilibrium. For mature waters falling near the upper curve, you can estimate the temperature as well.

To plot the K-Mg-Na triangle, enter the division factors for Na and K in the text fields provided and press **[OK]**.

Log(K)-1000/T

The linear log(K)-1000/T plots can be used for samples from boreholes, where the *in situ* temperature is known. Of course, in geothermal investigations, you rarely know the formation temperature and if you do there is no need to apply a geothermometer. If you follow the technique explained above you will be able to decide which geothermometer to use in other projects with similar water chemistry and aquifer lithology settings. If the geothermometers provided in AquaChem do not meet your needs, you can also develop your own geothermometers and save them for each project (see **Files/Preference/ Thermometers**).

Geothermometers are generally expressed by the formula:

$$t(K^\circ) = \frac{1000 \cdot a}{b + \log(x)}$$

Where, x is the SiO_2 concentration or Na/K, etc.

log(x) values plot on a straight line as a function of 1000/T.

The coefficients a and b are obtained from the linear regression curve.

This graph can be used to:

- Check the usability of a thermometer on a set of samples.
- Plot the chemistry versus the formation temperature for samples produced from a borehole.
- Search for the geothermometer for which you observe the best fit.
- Develop new chemical thermometers for parameters or parameter ratios which show linear behavior in this plot.

Available geothermometers are:

- SiO_2
- Na/Li
- Mg/Li
- Mg/Ca
- Na/K

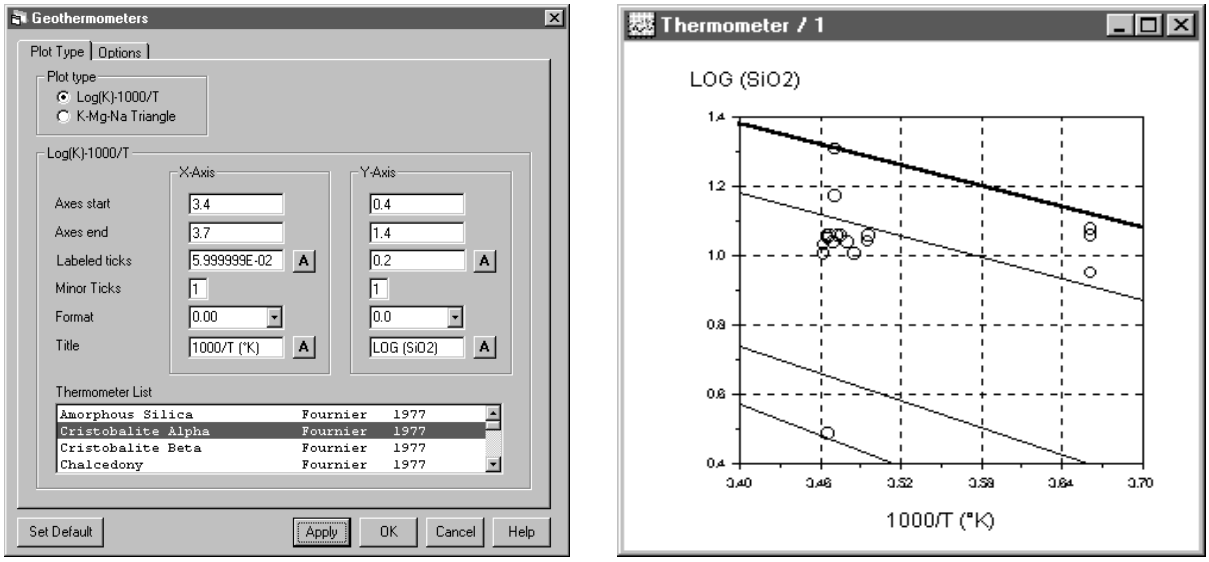


Figure 5.5: LogK-1000/K dialog box and Graph window

5.4 Histogram

Histograms are primarily used to check the population of data within a given range of values. Histograms allow a large number of samples to be represented without causing the diagram to becoming too difficult to interpret. You can easily identify a single sample in a multi-sample histogram plot by clicking on the sample record in the **Record List**. A red triangle will be displayed on the histogram, indicating the range interval of the selected sample (this is a unique feature of AquaChem and is not normally found in other histogram plotting software). Clicking a bar on the graph will select all the samples in the **Record List** which are included within the interval range defined by the histogram bar you selected.

The following section describes some of the features and options of the Histogram plot that are not covered in the Common Features section.

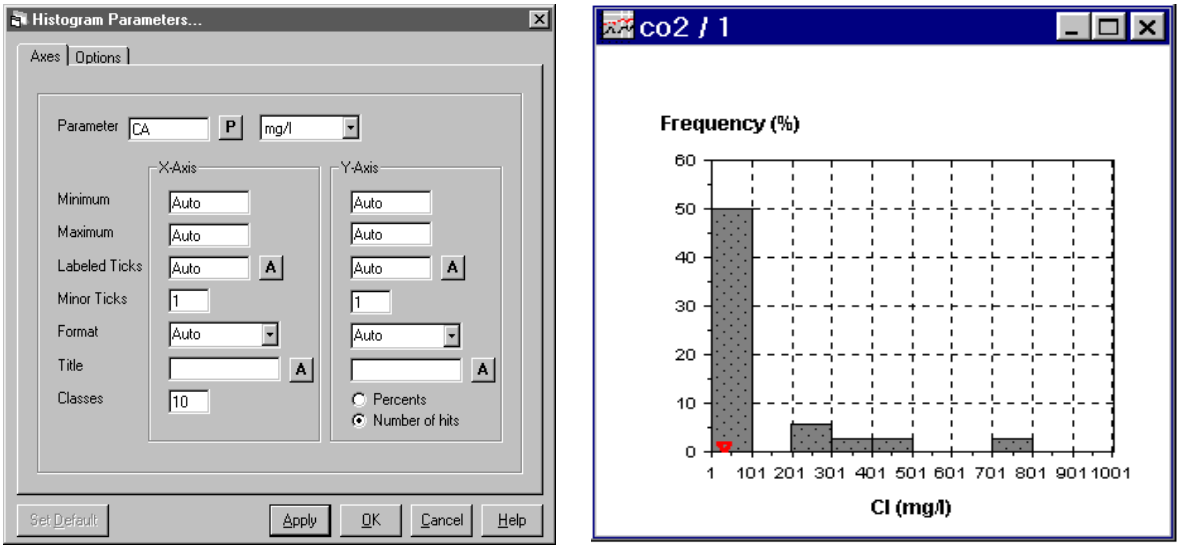


Figure 5.6: Histogram dialog box and graph window

Axes Settings

The **Parameter** field requires the **Internal name** of the parameter of interest for the Frequency Histogram. The parameter of interest can be typed in directly if you know the Internal name, or you can drag it in the field from a **Parameters** window. Click **[P]** to pop up the **Parameters** window. This field can also handle parameter ratios, sums, or differences (e.g. Na/Cl, Ca+Mg, Cl-SO_4).

The **Classes** field defines the number of data classes (or intervals) into which the range of parameter values will be subdivided. Each data class will be represented by a single bar on the histogram. Type the number of classes (bars in the histogram) in the text field provided.

The number of sample records within each data class is referred to as the frequency of occurrences. This can be expressed as either a percentage of the total number of records (**Percents**), or as the number of records within each data class (**Number of hits**).

5.5 Langelier-Ludwig Plot

The Langelier-Ludwig square diagram is similar to the projection areas of the Piper and Durov plots. By convention, the sums of selected cations are plotted on the y-axis and the sums of selected anions are plotted on the x-axis. Each axis ranges from 0 to 50 meq%. Sample points are calculated as follows:

$$\Sigma_{an} = e_{Cl}+e_{SO4}+e_{HCO3}$$

$$\Sigma_{cat} = e_{Ca}+e_{Mg}+e_{Na}+e_{K}$$

$$\%Na = 50\ e_{Na}/\Sigma_{cat}$$

$$\%Cl = 0\ e_{Cl}/\Sigma_{an}$$

Suitable groupings of cations and anions are selected and plotted as percentages. Generally this type of graph is used to plot %Na+%K against $\%HCO_3+\%SO_4$. In this plot, %Ca+%Mg and %Cl are also fixed:

$$\%Ca+\%Mg = 50 - (\%Na+\%K)$$

$$\%Cl = 50 - (\%HCO_3 + \%SO_4)$$

Changing the groupings of anions and cations often improves the identification of water with a particular chemical type. For instance:

- %Na+%K+%Mg against $\%HCO_3$, cold, low salinity calcium bicarbonate waters (limestones).
- %Na+%K+%Ca against $\%HCO_3$, cold, low salinity magnesium bicarbonate waters (mafic and ultramafic rocks).
- %Na+%K+%Mg against $\%HCO_3+\%Cl$, cold, calcium sulfate waters (gypsum and/or anhydrite).

All major elements can be displayed in one plot with the Langelier-Ludwig diagram, however, like the Piper and Durov plots, it displays relative ratios rather than absolute concentrations.

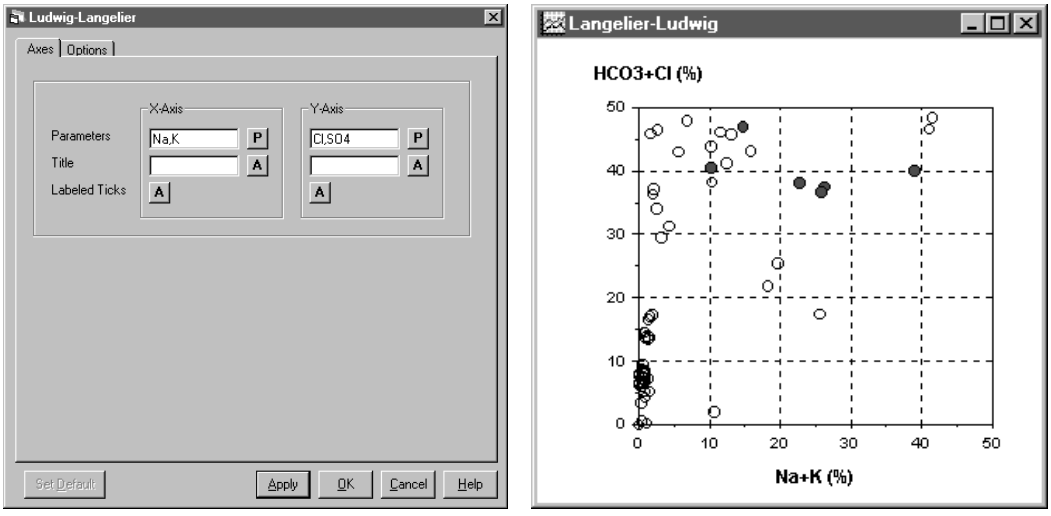


Figure 5.7: Langelier-Ludwig dialog box and Graph window

5.6 Map Plot

The Map plots display the sampling position in a Cartesian coordinate system. The Map plot can import and overlay an AutoCAD .dxf file as a basemap of the site or study region defining the major physical and geographical boundaries and geological characteristics (see Figure 5.8). The Map plots can be used to simply display the sample locations throughout the study region, or you can use the Map plot to interpret spatial trends in the physical or chemical characteristics of each plot using proportional symbol sizes, or by plotting Pie, Stiff or Radial graphs at each sample location.

NOTE: You must have at least one record in your database with X and Y co-ordinates in order to create a Map plot.

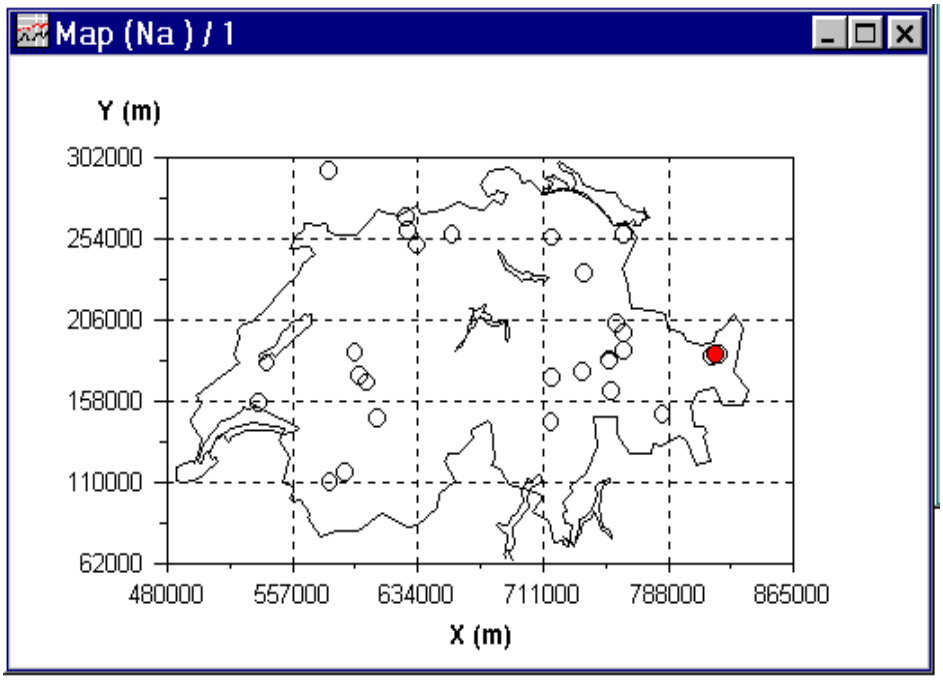


Figure 5.8: Map plot showing sample locations

The following section describes some of the features and options of the Map plot that are not covered in the Common Features section.

Axes Settings

AquaChem allows you to import and overlay AutoCAD ***.dxf*** files as a basemap for your site or study region. Press the **[...]** button in the **Base Map** frame to locate and select the ***.dxf*** file to use as a basemap. The ***.dxf*** file reader currently supports AutoCAD version 12 ***.dxf*** file formats. Please note that this option is intended to relatively small files (.dxf site maps larger than 1 Mb can take a long time to load).

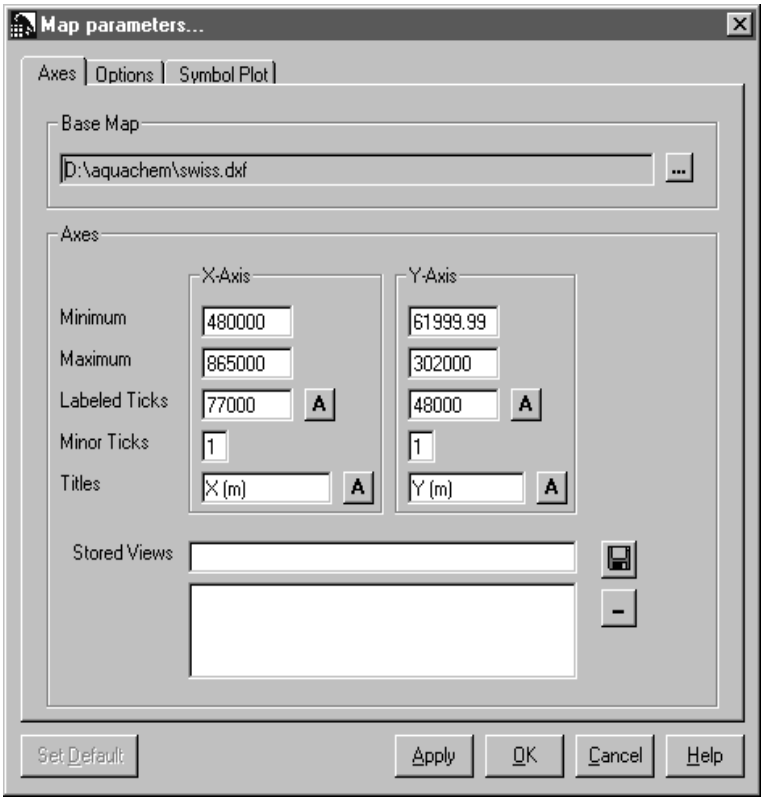


Figure 5.9: Map plot axes settings dialogue box

The start and end coordinates of the base map are automatically displayed after you have imported the ***.dxf*** base map file. These coordinates correspond to the minimum and maximum X and Y coordinates of the ***.dxf*** file you selected. You may edit the start and end coordinates to zoom in on part of your base map. Since each record in the database is referenced with X and Y coordinates, the range specified in the **Axes** frame will determine which records will be plotted on the graph. If the coordinate locations of the samples does not correspond to the coordinate dimensions of the basemap, none of the samples will appear on the Map plot.

You may save sets of start and end coordinates in map limits files. These start and end coordinates are essentially 'saved views' of the map. Existing map limits file entries are listed in the **Stored Limits** list. Map limits files are helpful if you often need to regularly zoom-in on certain areas of your study region. To load a map limits file, select it from the **Stored Limits** list. The coordinates will automatically be displayed in the Axes frame.

To create a new map limits entry(i.e. to create a new map view), type the start and end coordinates of the new map view in the **Axes** frame. Type a filename (no extension) in the **Stored Limits** text field and click the **[Save]** button. The map limits file will be added to the **Stored Limits** list.

Map limits files can be removed from the list by selecting the file and clicking the **[-]** button.

Display Options

The display options tab of the Map Parameters dialogue box is shown in Figure 5.10. The map plot display options contain a selection of seven different symbol types as described in the following section.

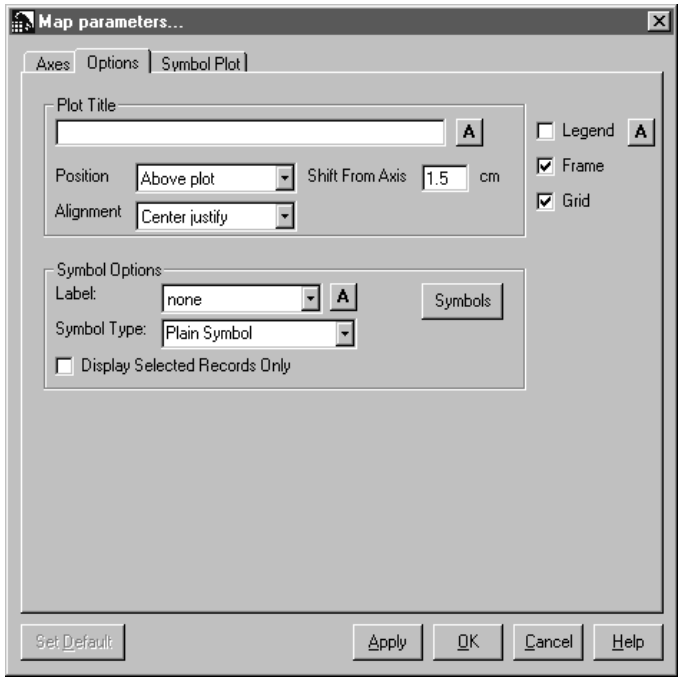


Figure 5.10: Map plot display options dialogue box

The **Symbol Type** option is used to select the type of symbol that will be plotted at each sample location. There are seven different symbol types available:

- Plain Symbol
- Proportional Size
- Proportional Greyscale
- Water Facies
- Pie Chart
- Radial Diagram
- Stiff Diagram

The following section describes the various symbol types and the display options available for each one.

Plain Symbol

The **Plain Symbol** symbol type will plot the symbol shapes, sizes and colors as they are defined by the user for each sample group. Press the **[Symbols]** button to view/modify the symbol settings for the active database. A sample map plot with plain symbols is shown in Figure 5.11.

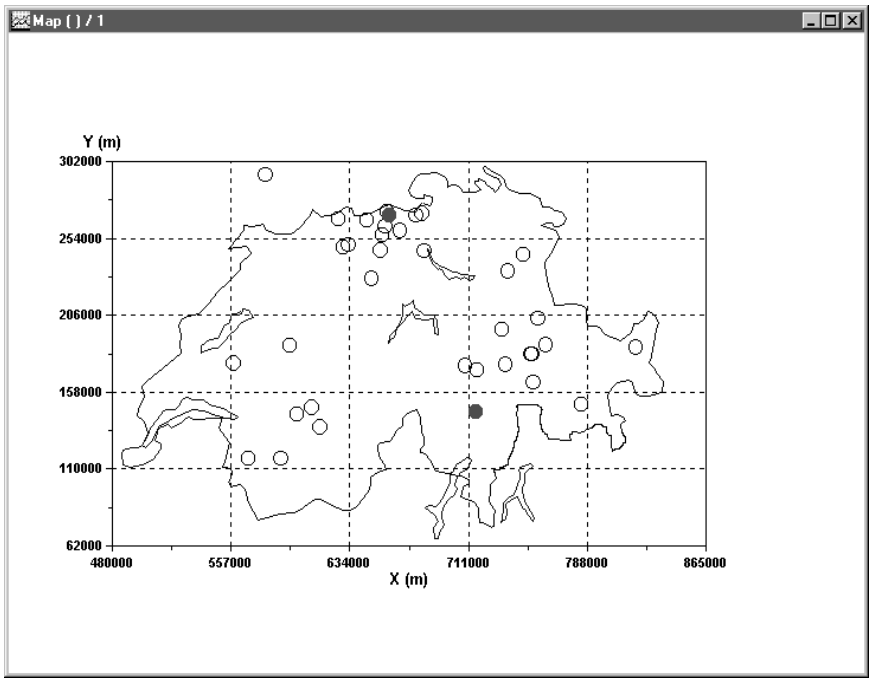


Figure 5.11: Sample map plot of plain symbols

Proportional Size Symbols

The **Proportional Size** symbol type will plot the defined symbols at each sample location with a symbols size determined by the sample concentration of a selected parameter. If **Proportional Size** symbol type is selected, the following information will appear in the display **Options** dialogue box.

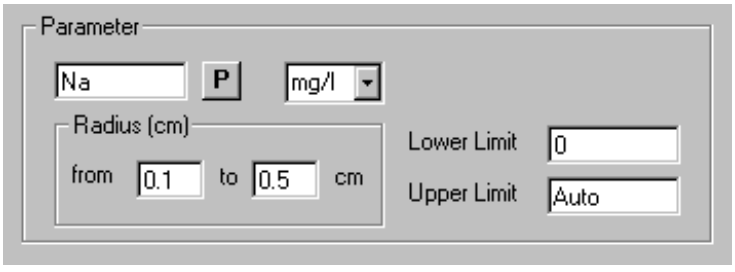


Figure 5.12: Proportional Symbol Size Display Options

By default, AquaChem selects 'Na' as the proportional parameter. The sample values for the proportional parameter will be used to determine the radius of the symbol at each sample location (e.g. samples containing higher values of the proportional parameter will have a larger radius). To change the proportional parameter, simply type in the **Internal name** of the desired parameter in the **Parameter** field, or click the **[P]** button and drag the desired parameter into the **Parameter** field.

The **Radius** fields are used to set the minimum and maximum symbol radius. The minimum symbol radius corresponds to the **Lower Limit** value of the proportional parameter, while the maximum radius corresponds to the **Upper Limit** value. Use a non-zero minimum radius to plot symbols at sample locations containing very low values of the proportional parameter. The symbol radius at each sample location is determined using a linear interpolation between the **Upper Limit** value and the **Lower Limit** value.

A sample map plot of proportional size symbols is provided in Figure 5.13.

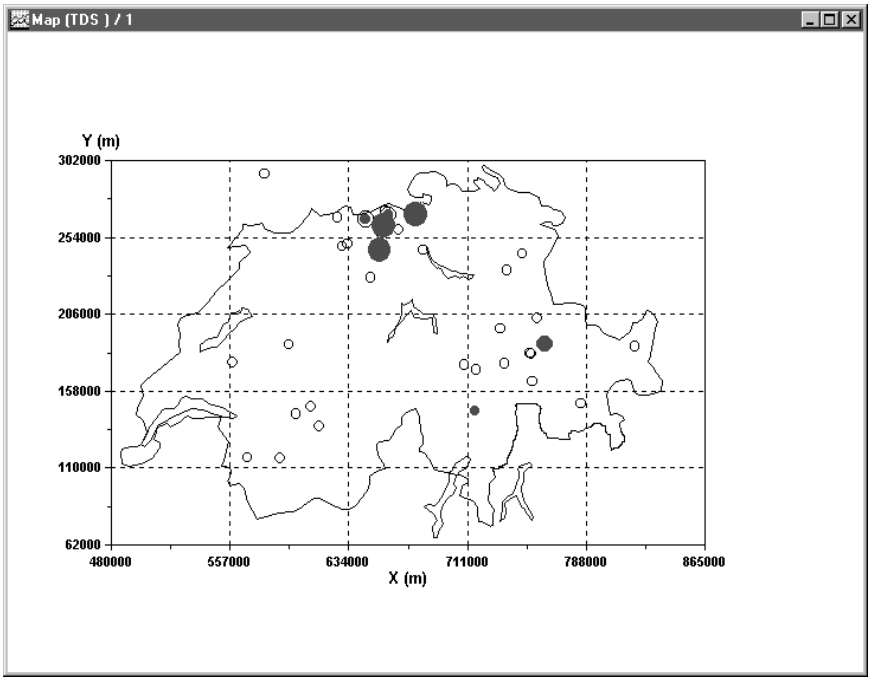


Figure 5.13: Sample map plot of proportional size symbols

Proportional Greyscale

The **Proportional Greyscale** symbol type will plot the defined symbols at each sample location with a Greyscale determined by the sample concentration of a selected parameter. If **Proportional Greyscale** symbol type is selected, the following information will appear in the display **Options** dialogue box.

By default, AquaChem selects 'Na' as the proportional parameter. The sample values for the proportional parameter will be used to determine the greyscale color of the symbol at each sample location (e.g. samples containing higher values of the proportional parameter will have a darker greyscale). To change the proportional

parameter, simply type in the **Internal name** of the desired parameter in the **Parameter** field, or click the **[P]** button and drag the desired parameter into the **Parameter** field.

Sample with values less than the **Lower Limit** value are assigned a white symbol colour, while points with values equal to or greater than the **Upper Limit** value are assigned a black colour fill.

A sample map plot with proportional greyscale symbols is provided in Figure 5.14.

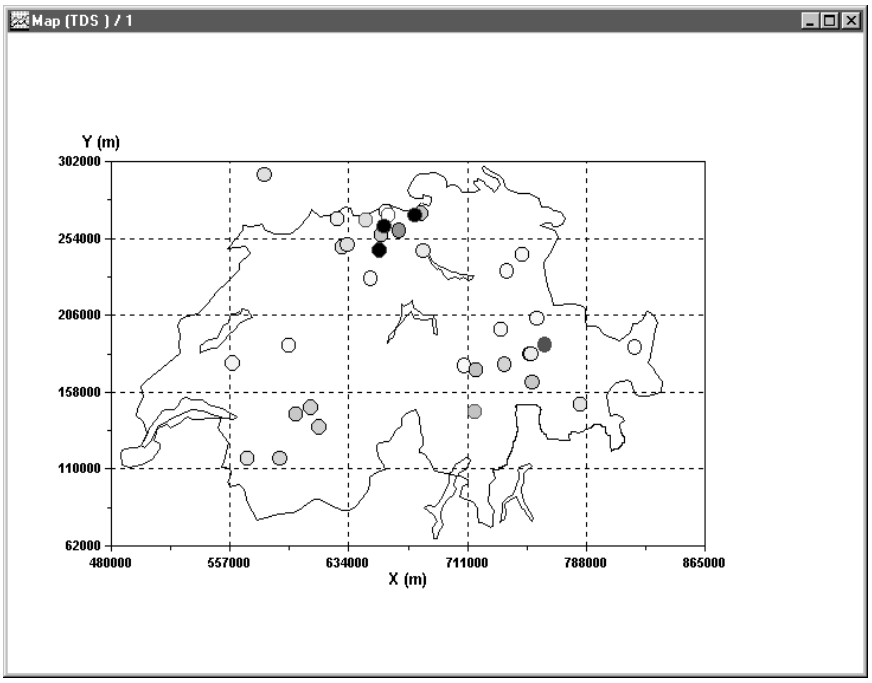


Figure 5.14: Sample map plot of proportional greyscale symbols

Water Facies

The **Water Facies** symbol type plots the calculated water type for each sample as a distinct symbol type. Symbols will be created which combine the symbol for the dominant anion with the symbol for the dominant cation. The following water-types are automatically calculated by AquaChem and are distinguished with different symbols: Ca-HCO_3, Ca-Cl, Ca-SO_4, Na-HCO_3, Na-Cl, Na-SO_4. The data points can be plotted on a base map (***.dxf*** file format) containing the main geographical and geological features of the area.

A sample map plot with water facies symbols types is shown in Figure 5.15.

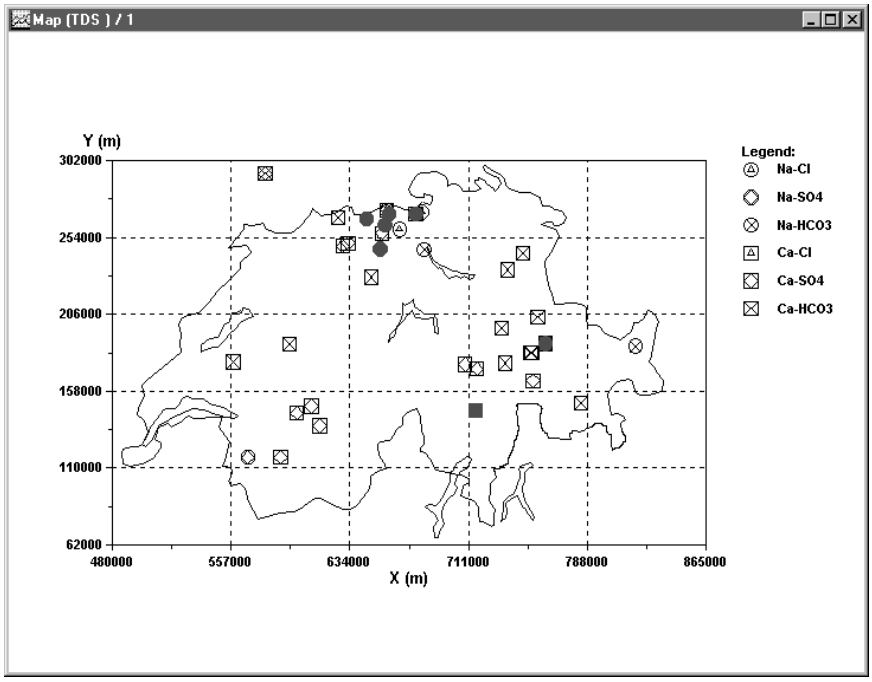


Figure 5.15: Sample map plot with water facies symbol types

Pie Chart

The **Pie Chart** symbol type plots a pie chart of the selected parameters at each sample location. If the **Pie Chart** symbol type is selected the display **Options** dialogue box will display a schematic diagram of the pie chart as shown below.

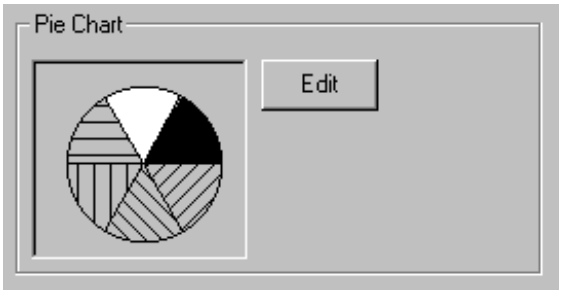


Figure 5.16: Sample Pie chart

To view or modify the pie chart display settings, press the **[Edit]** button, or click the **Symbol Plot** tab on the **Map Parameters** dialogue box as in Figure 5.17.

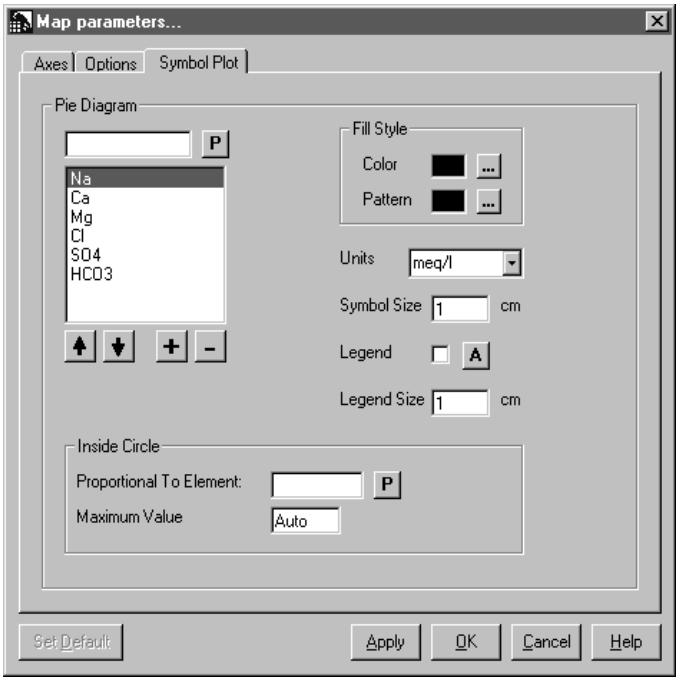


Figure 5.17: Symbol plot settings for pie charts

The parameters plotted on the pie charts are shown in the parameter list box on left-hand side of the dialogue box. The parameters are plotted in counter-clockwise order, where the first parameter in the list starts at the three o'clock position in the circle. The order of the parameters in list box can be modified by selecting the parameter and using the **[Up]** and **[Down]** arrow buttons to move the position of the selected parameter.

Additional parameters can be added to the list by typing the **Internal name** of the parameter in the blank text field and then pressing the **[+]** button. Alternatively, you can click the **[P]** button and then drag the desired parameter from the **Parameters** window into the parameter list box.

The **Fill Style** (fill color and fill pattern) for each parameter can be viewed by clicking on the target parameter. The **Fill Style** can be modified by clicking on the **[...]** button beside the **Color** or the **Pattern** boxes and then selecting the desired color or pattern.

The **Symbol Size** field contains the setting for the size of the pie charts plotted at each sample location.

The **Legend Size** field contains the setting for the size of the pie chart legend.

The **Units** field contains a selection of available concentration units for the selected pie chart parameters.

The **Inside Circle** option plots an open circle at the centre of the pie chart where the radius of the open circle is proportional to the concentration of the **Proportional Element**. The maximum radius of the inside circle is one-half of the radius of the pie chart circle. The samples containing a **Proportional Element** concentration equal or greater than the **Maximum Value**, will have an inside circle with the maximum radius.

The inside circles for samples with **Proportional Element** concentrations less than the **Maximum Value** will have a proportionally smaller radius.

A sample map plot with pie chart symbol types is shown in Figure 5.18.

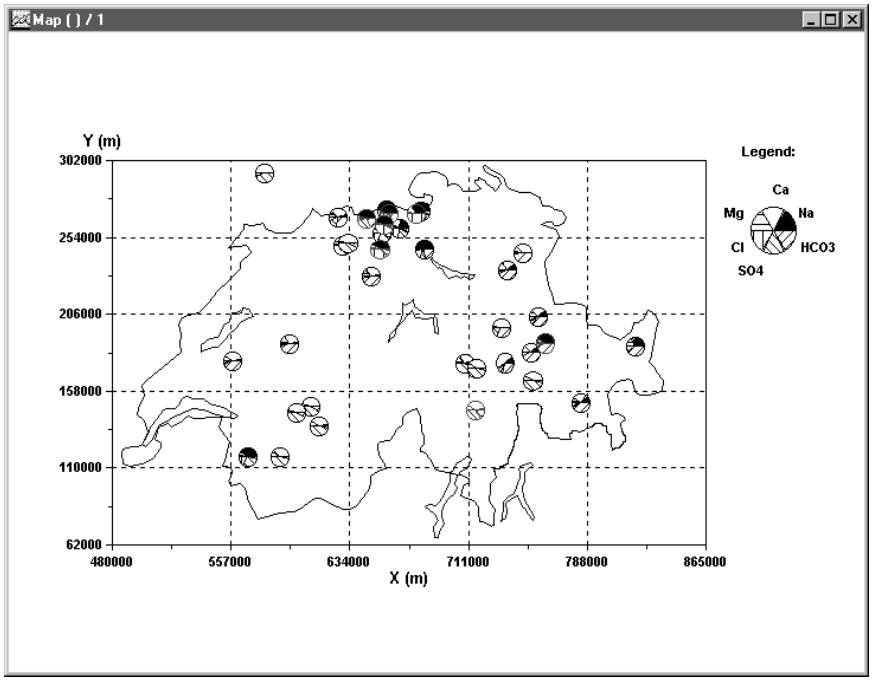


Figure 5.18: Sample map plot with pie chart symbol types

Radial Diagram

The **Radial Diagram** symbol type plots a radial diagram of the selected parameters at each sample location. If the **Radial Diagram** symbol type is selected a schematic drawing of a sample radial diagram is displayed in the lower left-hand corner as shown below.

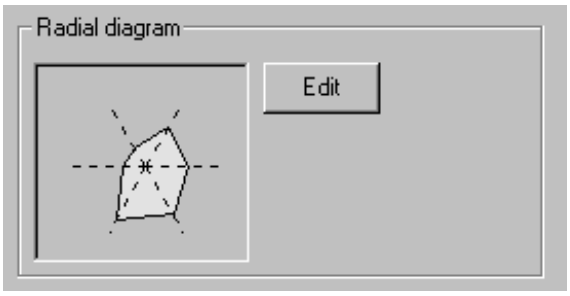


Figure 5.19: Sample Radial Diagram

To view or modify the radial diagram display settings, press the **[Edit]** button, or select the **Symbol Plot** tab on the **Map Parameters** dialogue box as shown in the following figure.

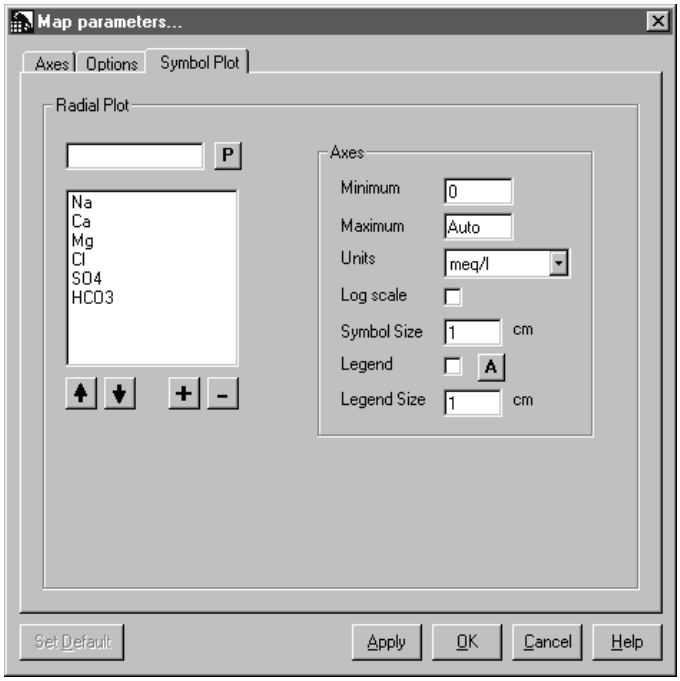


Figure 5.20: Symbol Plot Settings for Radial Diagrams

The parameters plotted on the radial diagram are shown in the parameter list box on left-hand side of the dialogue box. The parameters are plotted in counter-clockwise order, where the first parameter in the list starts at the three o'clock axis position. The order of the parameters in list box can be modified by clicking on the parameter and using the **[Up]** and **[Down]** arrow buttons to move the position of the selected parameter.

Additional parameters can be added to the list by typing the **Internal name** of the parameter in the blank text field and then pressing the **[Add]** button. Alternatively, you can click the **[P]** button and then drag the desired parameter from the **Parameters** window into the parameter list box.

The **Fill Style** (fill color and fill pattern) for each parameter can be viewed by clicking on the target parameter. The **Fill Style** can be modified by clicking on the **[...]** button beside the **Color** or the **Pattern** boxes and then selecting the desired color or pattern.

The **Minimum** and **Maximum Axes** values will apply for all radial diagram symbols plotted on the map. The minimum axes value will reflect the parameter value at the centre of the radial diagram, while the maximum axes value will represent the uniform maximum parameter value at the end of each axis. The minimum value is zero by default, and maximum value is uniform for each axis of the radial diagram.

The **Units** field contains a selection of available concentration units for the selected radial diagrams chart parameters.

The **Log Scale** checkbox allows you to set the scale of the radial diagram axes to a log scale instead of the default normal scale. The minimum and maximum values of the axes will be automatically adjusted to find the most appropriate log scale values.

The **Symbol Size** field contains the setting for the size of the radial diagrams plotted at each sample location.

The **Legend** checkbox allows you to show/hide the legend on the map plot, while the **[A]** button allows you to customize the font settings (type, style and size).

The **Legend Size** field contains the setting for the size of the radial diagram legend.

A sample map plot with radial diagram symbol types is shown in Figure 5.21.

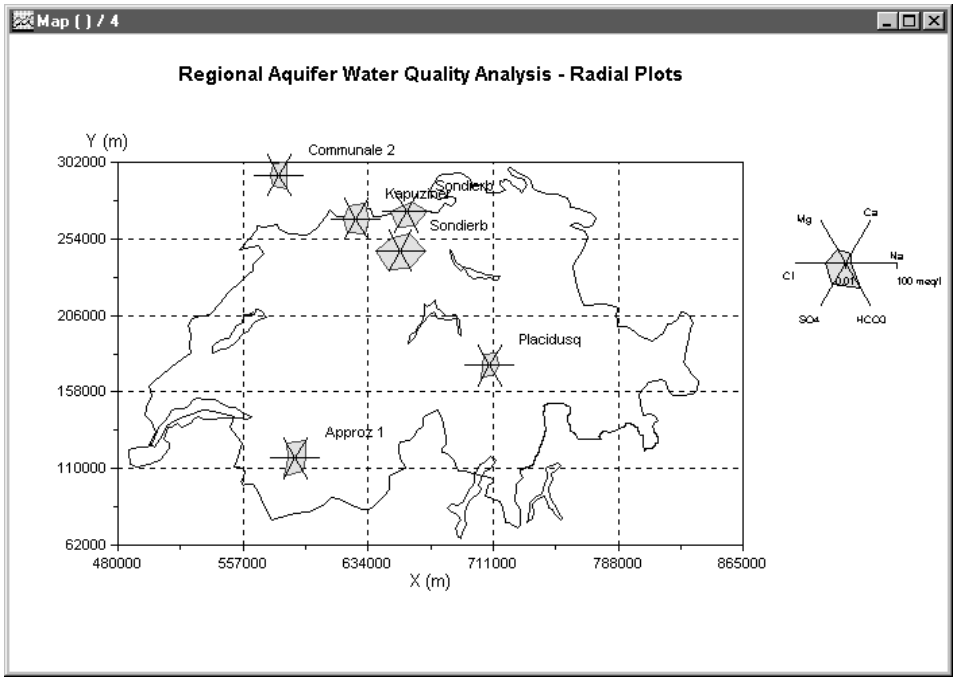


Figure 5.21: Sample map plot using radial diagram symbol types

Stiff Diagram

The **Stiff Diagram** symbol type plots a Stiff diagram of the selected parameters at each sample location. If the **Stiff Diagram** symbol type is selected a schematic drawing of a sample stiff diagram is provided in the lower left-hand corner as shown in Figure 5.22.

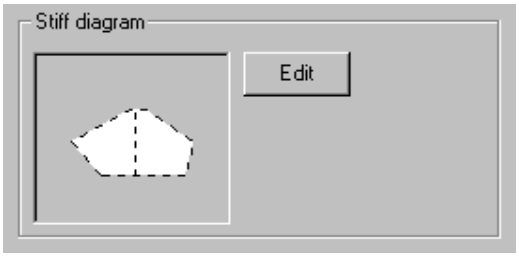


Figure 5.22: Sample Stiff Diagram

To view or modify the radial diagram display settings, press the **[Edit]** button, or select the **Symbol Plot** tab on the **Map Parameters** dialogue box as shown in the following figure.

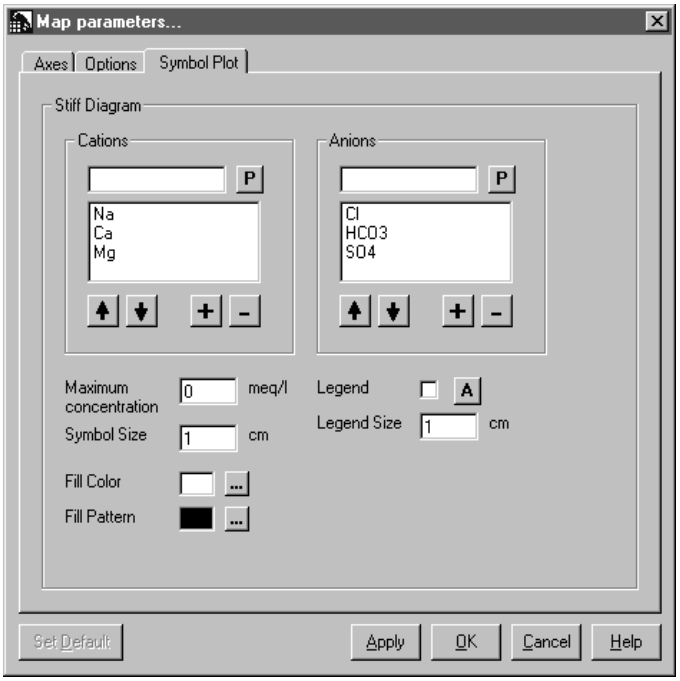


Figure 5.23: Symbol Plot Settings for Stiff Diagrams

The parameters plotted on the Stiff diagrams are shown in the parameter list boxes labelled Cations and Anions. By default, the six major ions are included in the stiff diagram. The parameters at the top of the list will appear on the top of the Stiff diagram. The order of the parameters in list box can be modified by clicking on the parameter and using the **[Up]** and **[Down]** arrow buttons to move the position of the selected parameter.

Additional parameters can be added to the list by typing the **Internal name** of the parameter in the blank text field and then pressing the **[+]** button. Alternatively, you can click the **[P]** button and then drag the desired parameter from the **Parameters** window into the parameter list box. Parameter combinations can also be used (e.g. Na+K).

The **Fill Style** (fill color and fill pattern) for each parameter can be viewed by clicking on the target parameter. The **Fill Style** can be modified by clicking on the **[...]** button beside the **Color** or the **Pattern** boxes and then selecting the desired color or pattern.

The **Maximum Axes** values will apply for all radial diagram symbols plotted on the map (the minimum axes value is always zero). The maximum axes value will represent the uniform maximum value for each parameter. This value cannot vary for each axis of the Stiff diagram.

5.7 Pie Chart

The **Pie** menu option creates a Pie chart for every selected sample in the Record List (to a maximum of 10 selected records). Before using this option, make sure that only the samples you want to plot are selected. The following section describes some of the features and options of the Pie plot that are not covered in the Common Features section.

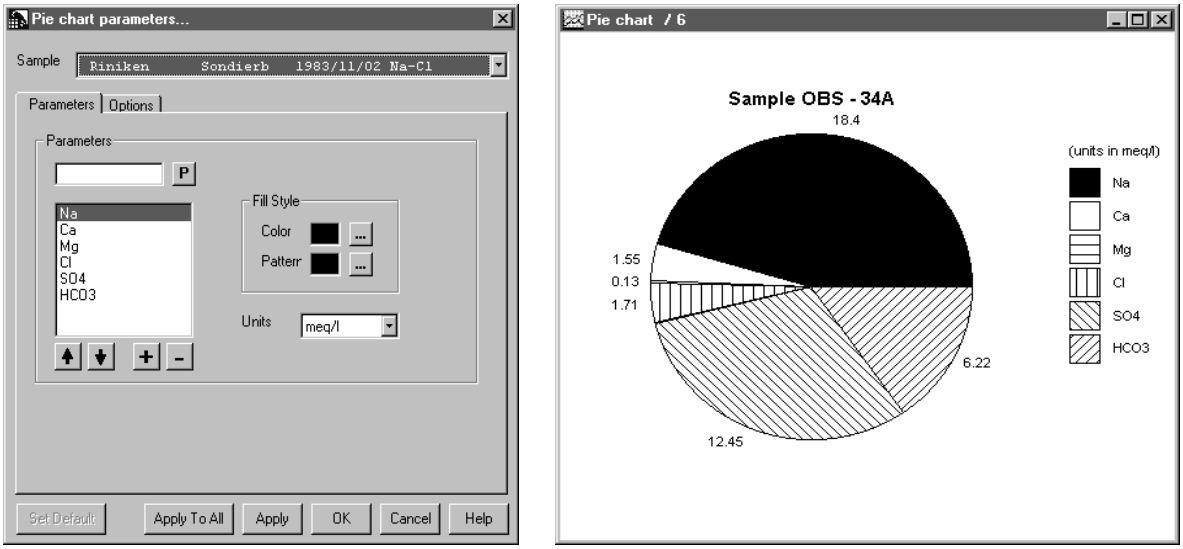


Figure 5.24: Pie Chart dialog box and Graph window

Sample

Each of the Pie, Radial and Stiff graphs will produce a single plot for each record that is selected. The **Sample** field identifies the active sample record associated with the graphic options dialog box. If you have several Pie charts open, you can use the **Sample** field to select and modify the settings for each one.

Parameters

The **Parameters** list contains the parameters that will be plotted on the Pie chart. New parameters can be added to the list by typing the parameter name in the text field and clicking the **[Add]** button, or by dragging the parameter into the **Parameters** list from the **Parameters** window (press the **[P]** button to load the **Parameters** window). The order of the parameters in the list can be adjusted using the **[Up]** and **[Down]** button. Parameters can be removed from the list by selecting the parameter and clicking the **[-]** button.

The **[Apply to All]** button is a feature that is available for the Pie, Radial and Stiff graphs since they plot one graph for each record that it selected. This is used for normalizing the axes scales, units, and general formats in each of the open Pie charts. The **[Apply to All]** button applies to most of the graph settings that affect the appearance of the Pie chart, with the exception of the plot title.

Select a parameter from the **Parameters** list, then select the fill pattern and the fill colour you wish to assign to that parameter on the pie chart. Repeat for all the parameters in the list.

Display Options

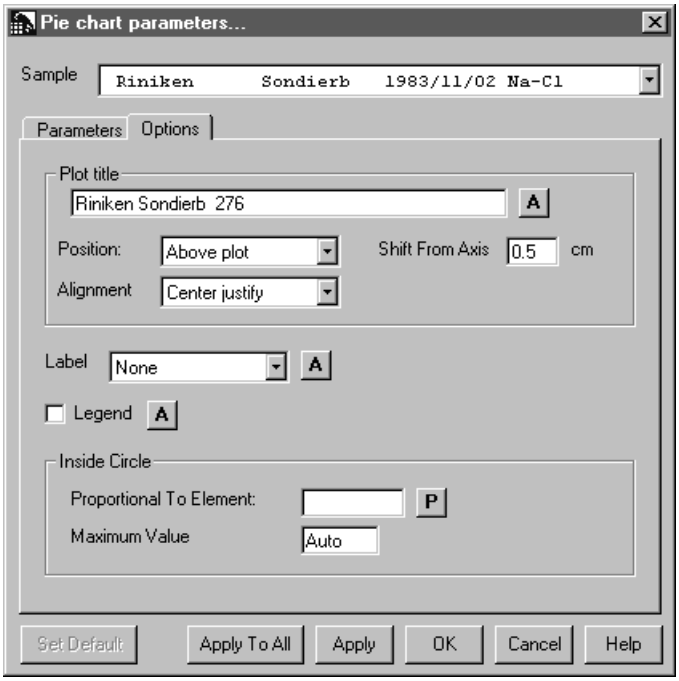


Figure 5.25: Pie chart display options

The inside circle is used to represent the concentration of a single parameter (or combination of parameters) that is not included in the Pie Chart parameters. CO_2 content and SIO_2 concentration are most commonly displayed in the inside circle. However, you can specify any chemical or physical parameter that reveals the most comprehensive information about the sample.

Type a valid parameter in the **Proportional To Element** text field to create an inside circle on your pie chart. Type a maximum value in the **Maximum Value** text field. If several pie charts are created, it is recommended that you choose 3 to 4 times the average value of the inside parameter as the maximum value. All values that are greater than or equal to the maximum value are displayed with the maximum diameter.

The inside circle will have a radius between zero and the specified maximum radius. Type the maximum radius in the Maximum Radius text field. The inside circle diameter is expressed as:

$$\frac{\text{r(inside circle)}}{\text{R(pie chart)}}$$

5.8 Piper Plot

In Piper plots, major ions are plotted as cation and anion percentages of milliequivalents in two base triangles. The total cations in meq/l, and the total anions in meq, are set equal to 100%. The data points in the two triangles are then projected into the square grid. The projection reveals certain useful properties of the total ion relationships. Every sample is represented by three data points; one in each triangle and one in the square grid. The Piper diagram allows comparisons between a large number of samples. Like all trilinear diagrams, it does not portray absolute ion concentrations. The main purpose of Piper plots is to show clustering of samples.The following section describes some of the features and options of the Piper plot that are not covered in the **Common Features** section.

Parameters

A typical Piper diagram plots cations and anions. The default settings in AquaChem plot the major cations (Na, Ca, and Mg) against the major anions (Cl, SO4 and HCO3), but any other parameters, or combination of parameters, can be easily selected (e.g. gas composition, trace elements etc.).

The parameters can be modified by typing the Internal name of the parameters in the appropriate fields, or dragging the new parameters from the **Parameters** window into the desired fields. Click **[P]** to load the **Parameters** window. You may also multiply or divide the concentrations by a factor if you need to compare elements which are systematically very different in concentration (e.g. comparing a trace element together with major ions).

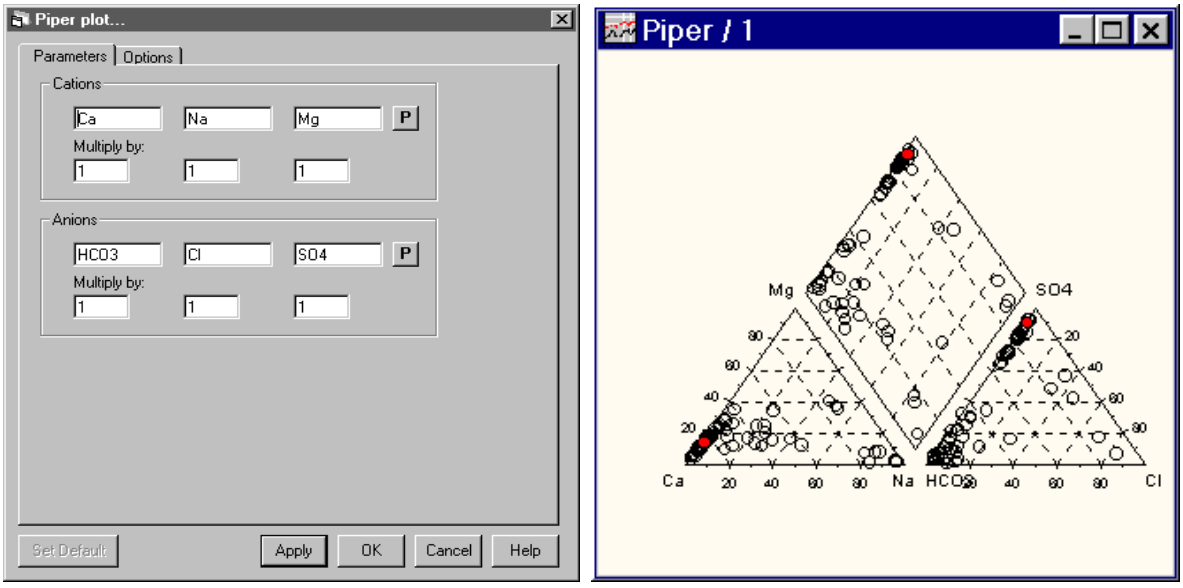


Figure 5.26: Piper dialog box and Graph window

5.9 Radial Plot

The Radial plot is used to compare multiple parameter values for a single sample, and to compare the ratios of these values for many different sample records. The Radial plot can be used to plot from three to ten different parameter values for a single sample record. Radial plots can be used to evaluate the change in water quality at a single location over a period of time, or they can be used to evaluate the change in water quality as the water passes through different geologic formations or different subsurface conditions.

The **Radial** menu option creates a Radial plot for every selected sample in the **Record List** (to a maximum of 10 selected records in a single step). Before using this option, make sure that only the samples you want to plot are selected. The following section describes some of the features and options of the Radial plot that are not covered in the Common Features section.

Sample

Each of the Pie, Radial and Stiff plots will produce a single graph for each record that is selected. The **Sample** field identifies the active sample record associated with the graphic options dialog box. If you have several Radial plots open, you can use the **Sample** field to select and modify the settings for each one.

Parameters

The **Parameters** list contains the parameters that will be plotted on the Radial plot. New parameters can be added to the list by typing the parameter name in the text field and clicking the **[+]** button, or by dragging the parameter into the **Parameters** list from the **Parameters** window (press the **[P]** button to load the **Parameters** window). The order of the parameters in the list can be adjusted using the **[Up]** and **[Down]** button. Parameters can be removed from the list by selecting the parameter and clicking the **[-]** button.

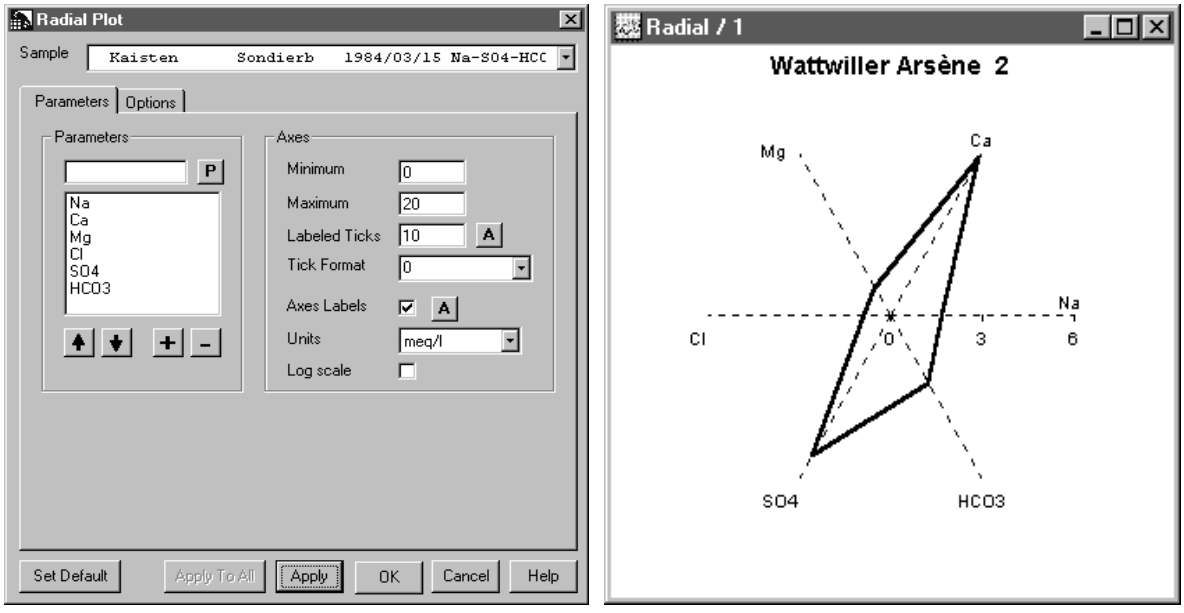


Figure 5.27: Radial diagram graphic options dialogue box and sample plot

The **Log Scale** checkbox allow you to switch all of the axes on the radial plot to a log scale. This is often used when the parameters that are plotted range through several orders of magnitude (e.g. when plotting major and minor or trace elements).

The **[Apply to All]** button is a feature that is available for the Pie, Radial and Stiff graphs since they plot one graph for each selected record. This is used for normalizing the axes scales, units, and general formats in each of the open radial diagrams. The **[Apply to All]** button applies to most of the graph settings that affect the appearance of the radial diagram, with the exception of the plot title.

5.10 Scatter Plot

X-Y Scatter plots are the most simple approach to the interpretation of hydrochemical data. Multiple plots of single ion relationships and parameters that show significant correlations can be easily created and regression analyses can be quickly performed to obtain average molal ratios for all data of for selected groups of data. The following section describes some of the features and options of the Scatter plot that are not covered in the Common Features section.

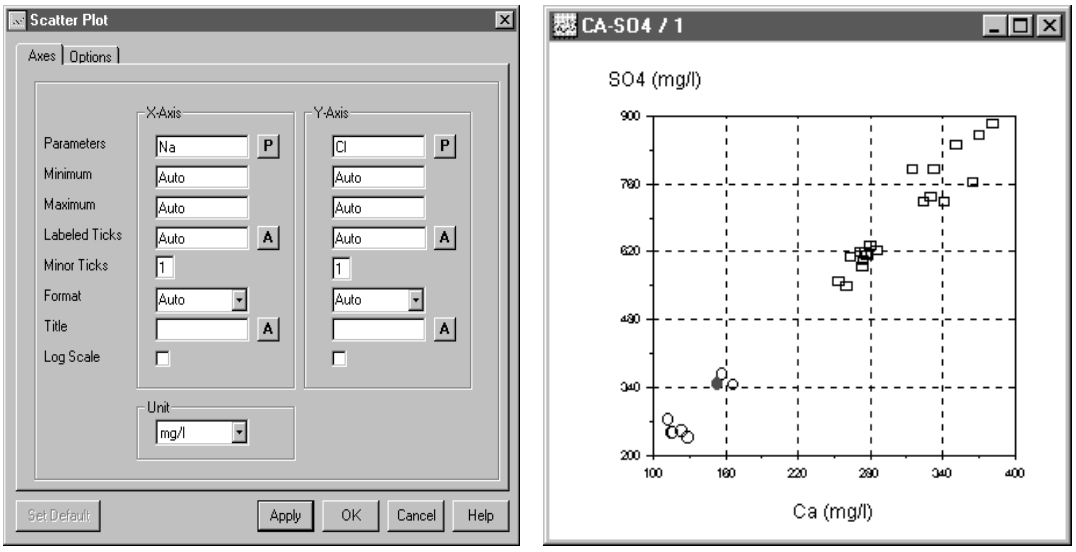


Figure 5.28: Scatter graph window

Axes Settings

The **Log Scale** checkbox allows you to change the scale of the axis to log scale. This is often used when you have parameter values that range through several orders of magnitude.

Display Options

The **[Lines]** button opens the **Lines** dialog box that allows you to perform a regression analysis on all of the data in the **Record List**, or on selected groups of data only.

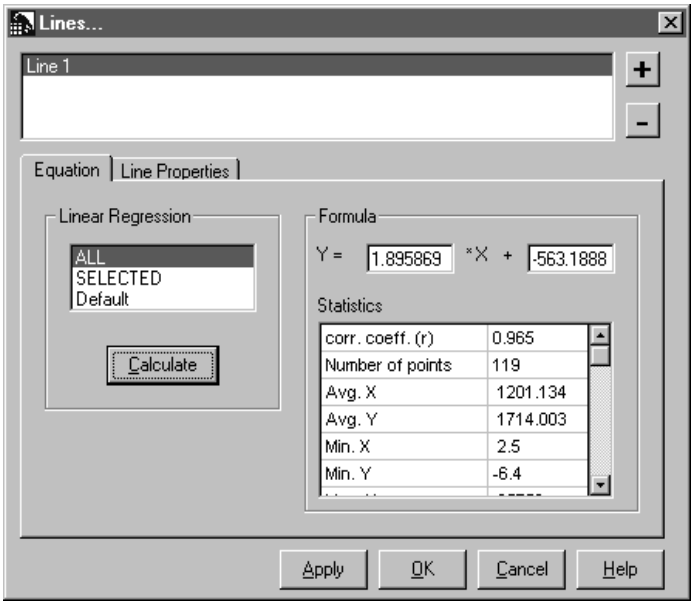


Figure 5.29: Lines dialogue box

Equation Tab

The equation of the straight line is displayed under the Equation tab. If the equation is calculated by the regression routine rather than entered manually, the regression coefficient 'r' is displayed in the Formula frame.

Linear Regression

The linear regression analysis can be performed on **All** active record in the **Record List**, on currently **Selected** samples, or on the defined groups of samples.

To calculate and plot a line on the graph, click the **[+]** button and 'Line1' will appear in the list of lines (more than one line can be plotted on each graph). Then choose whether you want to calculate the linear regression using All sample records, Selected sample records, or a selected group of sample records. Finally, click the [Calculate] button to calculate the equation of the line through the selected data points. The resulting formula appears in the Formula frame. Descriptive statistics including the regression coefficient for the points selected will appear in the Statistics text box below the equation.

Line Properties Tab

The **Line Properties** Tab allows you to select the line type, thickness and color as well as the start and end coordinates of the line in the X-Axis Limits frame.

5.11 Schoeller

Semi-logarithmic diagrams were developed by Schoeller (1962) to represent major ion analyses in milliequivalents per liter and to demonstrate different hydrochemical water types on the same diagram. The number of analyses that can be illustrated at one time is limited because of the lines. The diagram has the advantage that, unlike trilinear diagrams, actual parameter concentrations are displayed. The following section describes some of the features and options of the Schoeller plot that are not covered in the Common Features section.

Parameters

Defines the parameters that will be plotted on the X-axis of the Schoeller plot. New parameters can be added to the list by typing the parameter name in the text field and clicking the **[Add]** button, or by dragging the parameter into the Parameters list from the **Parameters** window (press the **[P]** button to load the **Parameters** window). The order of the parameters in the list can be adjusted using the **[Up]** and **[Down]** button. Parameters can be removed from the list by selecting the parameter and clicking the **[Remove]** button. Parameters can include ratios, sums, or differences (Na/Cl, Ca+Mg, Cl-SO_4).

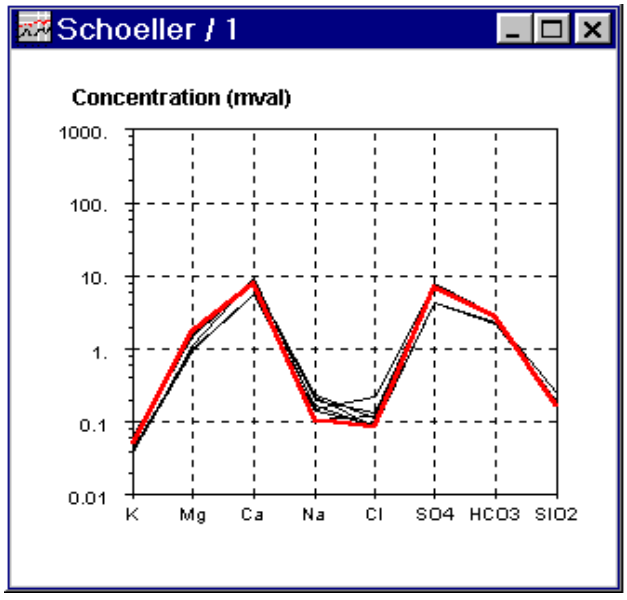


Figure 5.30: Schoeller Graph window

5.12 Stiff

The Stiff diagram belongs to the group of pattern diagrams (see Hem 1985, p. 175). It is constructed by plotting the milliequivalents per liter of three or more anions and three or more cations. Stiff plots can be used to evaluate the change in water quality at a single location over a period of time, or they can be used to evaluate the change in water quality as the water passes through different geologic formations or different subsurface conditions.

The **Stiff** menu option creates a Stiff plot for every selected sample in the Record List (to a maximum of 10 selected records). Before using this option, make sure that only the samples you want to plot are selected. The following section describes some of the features and options of the Stiff plot that are not covered in the Common Features section.

Sample

Each of the Pie, Radial and Stiff plots will produce a single graph for each record that is selected. The **Sample** field identifies the active sample record associated with the graphic options dialog box. If you have several Stiff plots open, you can use the **Sample** field to select and modify the settings for each one.

Parameters

The **Parameters** list contains the parameters that will be plotted on the Stiff plot. New parameters can be added to the list by typing the parameter name in the text field and clicking the **[+]** button, or by dragging the parameter into the **Parameters** list from the **Parameters** window (press the **[P]** button to load the Parameters window). The order of the parameters in the list can be adjusted using the **[Up]** and **[Down]** button. Parameters can be removed from the list by selecting the parameter and clicking the **[-]** button.

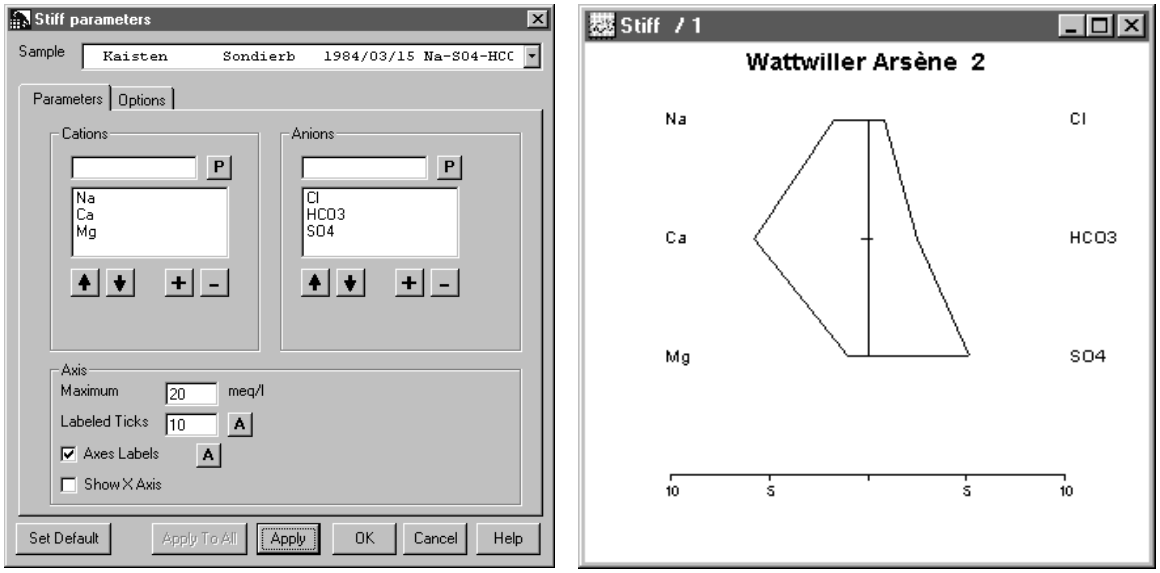


Figure 5.31: Stiff dialog box and Graph window

The **Show X Axis** checkbox allows you to show/hide the X-Axis of the Stiff plot.

The **[Apply to All]** button is a feature that is available for the Pie, Radial and Stiff graphs since they plot one graph for each record that it selected. This is used for normalizing the axes scales, units, and general formats in each of the open Pie charts. The **[Apply to All]** button applies to most of the graph settings that affect the appearance of the Pie chart, with the exception of the Plot Title.

5.13 Ternary Plots

Ternary diagrams are used to determine the relationship between the concentrations of three different parameter in multiple sample records. Like the Piper and Durov plots, the Ternary plot displays relative concentrations of each parameter with respect to the sum of the concentrations of each parameter. Each vertex of the Ternary plot represents a relative concentration of 100% for the parameter at the respective vertex, while the base represents a relative concentration of 0% for the parameter plotted at the opposite vertex.

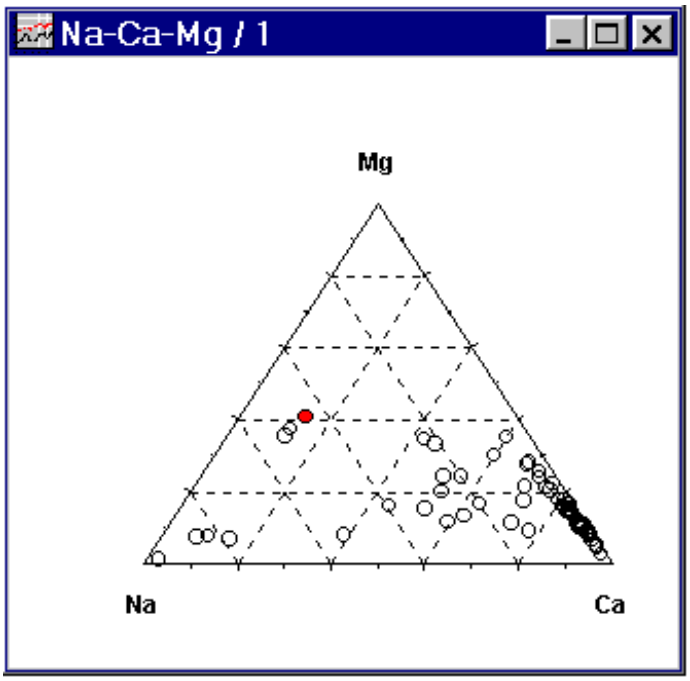


Figure 5.32: Ternary graph window

5.14 Time Series

The evolution of chemical and physical parameters for a given sampling point as a function of time is a standard technique for interpreting hydrochemical and hydrogeological processes in natural waters. The current version of AquaChem only allows you to plot a time series graph for a single parameter. Future versions of AquaChem will allow you to plot multiple parameters and have dual X and Y axes. In the meantime, you will need to create one plot for each parameter you wish to evaluate.

Date Format

The date format for the database must match the data format in your Windows 95/98 or NT Regional Settings. The date format for the database is set in the **File/Preferences** dialog box under the **Startup Defaults** tab. For Windows 95/98 or NT, the date format is configured in the Windows **Control Panel** under **Regional Settings**. If the date settings in your AquaChem database do not correspond to the Windows Regional Settings, you will get an error stating "**Axes End < Axes Start**".

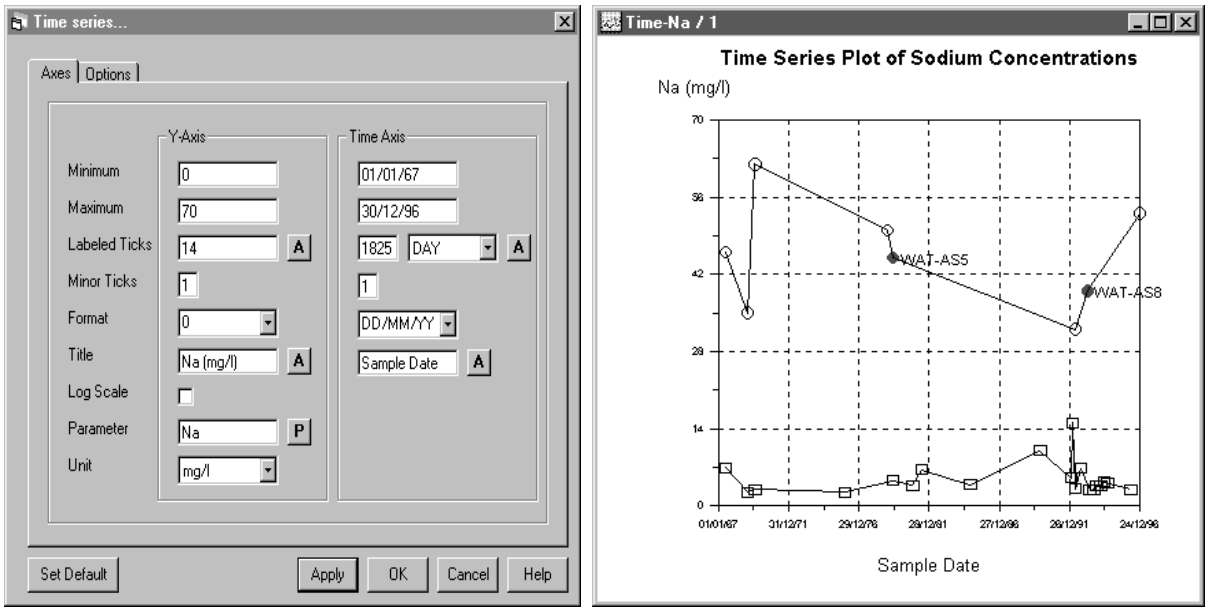


Figure 5.33: Time Series dialog box and Graph window

6

Printing Graphs

This chapter describes the various print options available for printing graphs generated by AquaChem. The topics discussed in this chapter include:

- Selecting the graphs for printing
- Setting up the page layout
- Arranging the selected graphs on the page
- Selecting a print template
- Designing a print template

Once you have generated one or more graphs, you can print these graphs to a printer or to a Windows metafile (***.wmf***) graphics file by selecting **File/Print** from the **Graphics** window menu. A **Print Preview** window will appear showing a blank page, and a floating **Print Option** dialogue box will appear as shown in Figure 6.1.

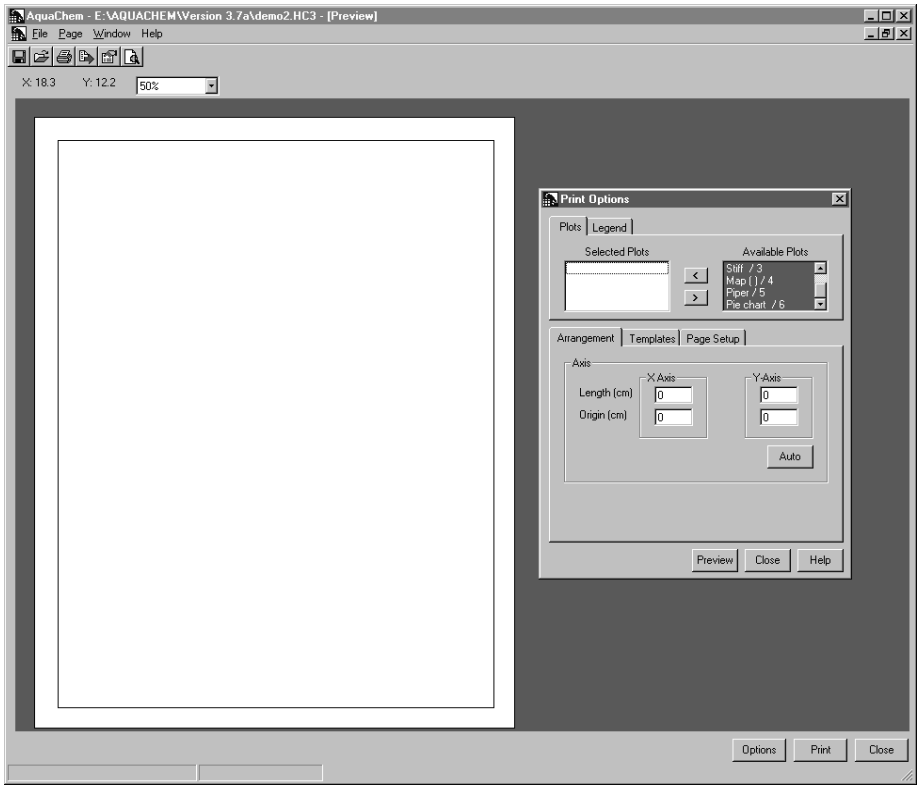


Figure 6.1: Print Preview window and Print Options dialogue box

The **Print Preview** window provides a What You See Is What You Get (WYSIWYG) preview of the printed page. The page magnification value is displayed above the page preview together with the page coordinates (cm) for the mouse pointer location. The page magnification value can be adjusted to enlarge or shrink the appearance of the page preview on your screen.

The **Print Options** dialogue box is automatically displayed every time the Print Preview window appears. However, if you close the Print Option dialogue box you can easily retrieve it by one of the following selections:

- clicking on the **[Options]** button at the lower right-hand corner of the window
- clicking the **Options** icon on the toolbar menu, or
- selecting **Page/Options** from the top menu bar

The remaining sections of this chapter describe the various options available for printing the graphs generated by AquaChem

6.1 Selecting Plots

The **Print Options** dialogue box allows you to select which plots to print, and then set the size and location of each plot on the page. To print one (or more) plots you must select the desired plot(s) from the list of **Available Plots** and then move it to the list of **Selected Plots** by clicking the left arrow **[<]** button (see Figure 6.2).

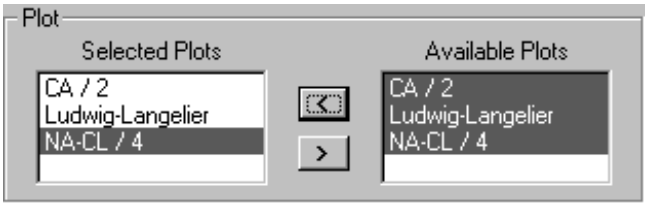


Figure 6.2: Plot Selection

The selected plot(s) will automatically appear in the **Print Preview** window and will be sized and arranged to fit the screen. To remove a plot from the **Print Preview** window, click on the plot under the **Selected Plots** list and then click the right arrow **[>]** button.

6.2 Arranging Plots

The selected plots will be automatically sized and arranged on the page according to the number of plots and the type of plots selected. However, the default arrangement of plots does not consider the presence of plot titles or legends. Therefore, you may want to customize the size and location of each plot to produce a more desirable arrangement of the plots on the page.

The position and size of the plots can be easily modified using the **Arrangement** tab provided in the **Print Options** dialog box.

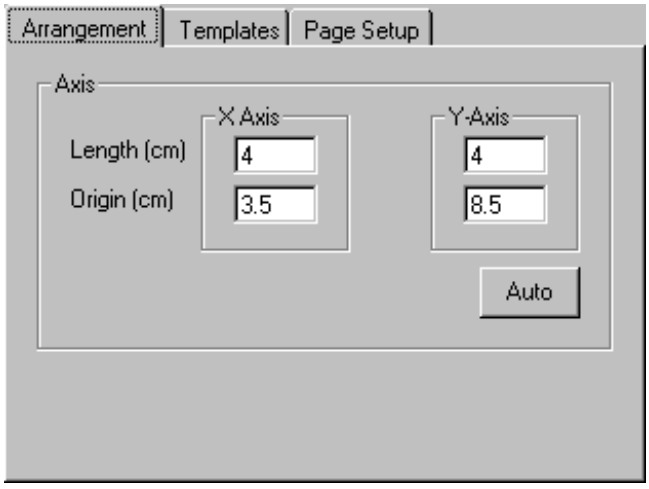


Figure 6.3: Graph arrangement options

The **Length (cm)** fields describe the length of the selected plot(s) in the X and Y direction on the printed page.

The **Origin (cm)** fields describe the co-ordinate locations of the lower right-hand corner of the selected pot(s) on the page.

The position/size of a single plot can be modified by selecting the plot in the **Selected Plots** list (make sure only one plot is selected) and then making the desired changes to the origin and/or length dimensions of the plot. Press the **<Enter>** key or click the **[Preview]** button to update the print preview.

Multiple plots can be simultaneously re-sized or aligned by selecting the plots from the Selected Plots list and then making the desired modifications. However, you should use caution when modifying multiple plots because you may inadvertently move plots on top of each other. If you do encounter a situation where the plots become unmanageable, use the **[Auto]** to return the plots to the default size and positions.

The **[Auto]** button will prompt you to select a layout design (# rows, # columns) for the selected plots (a layout style will be automatically suggested depending on the number of plots selected).

How To ??? Hints

Changing the Size of a Plot

- Select a plot from the **Selected Plots** list or click on the target plot in the **Print Preview** window (make sure only the plot you are interested in is highlighted in the **Selected Plots** list)
- Enter the new length dimension (X-Axis or Y-Axis)
- Press the **[Apply]** button or press the **<Enter>** key
- **NOTE:** You can simultaneously change the X or Y axis length for more than one plot at a time by selecting multiple plots from the **Selected Plots** list.

Changing the Position of a Plot

- Select a plot from the **Selected Plots** list or click on the target plot in the **Print Preview** window (make sure only the plot you are interested in is highlighted in the **Selected Plots** list)
- Enter the new position (X-Axis or Y-Axis)
- Press the **[Apply]** button or press the **<Enter>** key

> **NOTE:** You can simultaneously change the X or Y position for more than one plot at a time by selecting multiple plots from the **Selected Plots** list. However, you should be particularly careful not to assign the same X and Y origin to each plot.

6.3 Plotting Legends

Since AquaChem allows you to plot multiple graphs on the same page, it is often redundant to include a legend for each of the selected plots. Therefore, AquaChem now gives you the opportunity to select which legends to plot on the page, and it allows you to customize the location and font sizes for each of the selected legends.

6.3.1 Selecting Plot Legends

The **Print Options** dialogue box allows you to select which legends to print, and then set the font size and location of each legend on the page. To print one (or more) legends you must select the desired legend(s) from the list of **Available Legends** and then move it to the list of **Selected Legends** by clicking the left arrow **[<]** button (see Figure 6.4).

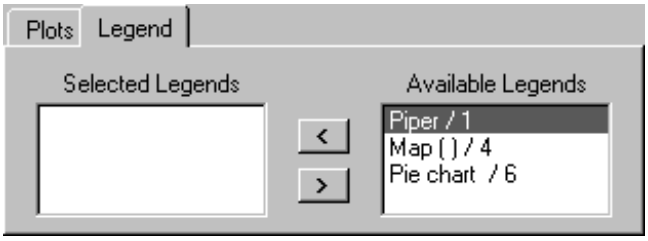


Figure 6.4: Legend Selection

The selected legend(s) will automatically appear in the top left-hand corner of the **Print Preview** window. If you have selected more than one legend, the selected legends will initially overlap one another, but this can be easily fixed by positioning each legend adjacent to the plot it is associated with (see Section 6.3.3 Positioning Legends).

To remove a legend from the **Print Preview** window, click on the target legend in the **Selected Legends** list and then click the right arrow **[>]** button to remove it from the list.

6.3.2 Customizing the Legend Appearance

AquaChem provides you with a comprehensive selection of tools for customizing the appearance of the selected legend.

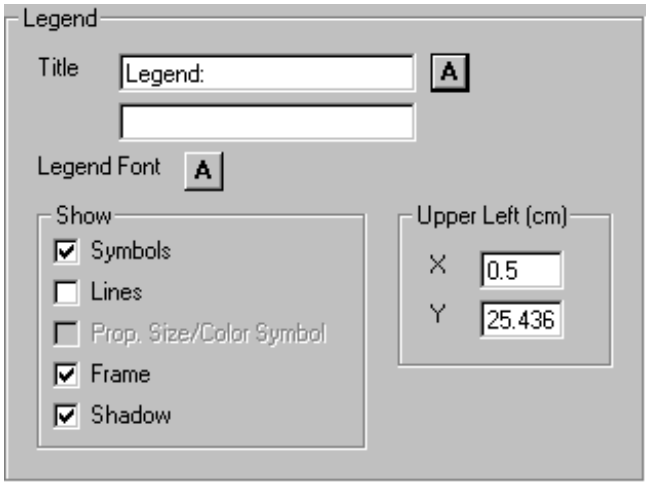


Figure 6.5: Legend Display Options

The **Legend Title** fields allow you to give the legend a customized title (one-line or two-lines) and select the font for the **Legend Title**.

The **Legend Font [A]** button sets the font size, type and style for the legend text. The default font setting is obtained from the associated plot settings.

The **Symbols** checkbox shows/hides the plot symbols in the selected legend (if relevant).

The **Lines** checkbox shows/hides the plot lines in the selected legend (if relevant).

The **Prop. Size/Color Symbol** checkbox show/hides the Proportional To information in the selected legend (if relevant).

The **Frame** checkbox shows/hides the line framing the selected legend.

The **Shadow** checkbox shows/hides the shadow on the selected legend.

6.3.3 Positioning the Legend

Each of the selected legends can be positioned anywhere on the page layout using the fields labeled **Position: X** and **Y**. The X and Y coordinates describe the position of the top left-hand corner o the legend. To change the position of a legend:

- Click-on the target legend in the **Selected Legends** list
- Move the mouse to the page location where you would like to position the legend and read the page coordinates from the upper-left corner of the Print Preview window
- Click in the X field and type the desired X location
- Click in the Y field and type the desired Y location
- Click the [Preview] button to see the new legend location

NOTE: Changing page sizes or selecting a different print template will clear any changes to the legend location and will return the selected legends to the upper-left-hand corner of the page layout.

6.4 Print Templates

6.4.1 Using Default Print Templates

The **Templates** tab provided in the **Print Options** dialog box allows you to select from a list of pre-defined print templates. These templates have a pre-defined form layout containing borders and text boxes for adding more detailed descriptions of the plot(s), the project, the client and even for importing a bitmap of your company logo. The list of available templates provided with AquaChem includes:

- None
- Default WHI A4 Portrait
- Default WHI Letter Portrait
- Default WHI Letter Landscape
- Default WHI Tabloid Landscape

The default template selection is "None", meaning no template has been selected (see Figure 6.6). If "None" is selected you have the option of entering a one line or two line title at the top of the page plus a footer at the bottom of the page. The alignment and font for each of the titles and footer can be customized using the **Align** options and the **Font [A]** button respectively. In addition, all of the **Page Setup** options are available for adjusting the page size, orientation and margins.

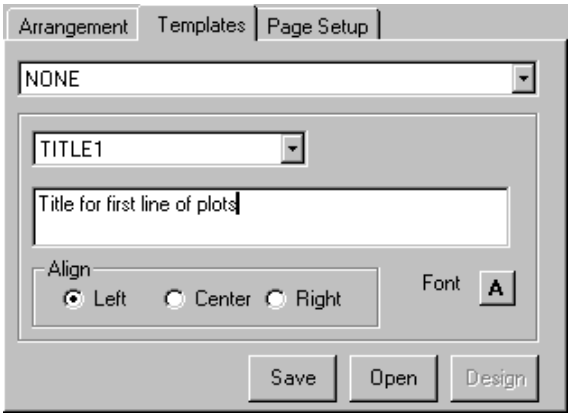


Figure 6.6: Blank template title options

If you select one of the pre-defined WHI print templates, a Template Grid will appear in the **Print Options** dialogue box and the **Print Preview** window will be updated to reflect the layout of the selected template (see Figure 6.7). The Template Grid allows you to enter text values for the available plot description fields. The Template Grid for each of the default templates will allow you to enter field values for:

- The Client
- The Project
- The Project No.
- The Date
- A Description of the Plots

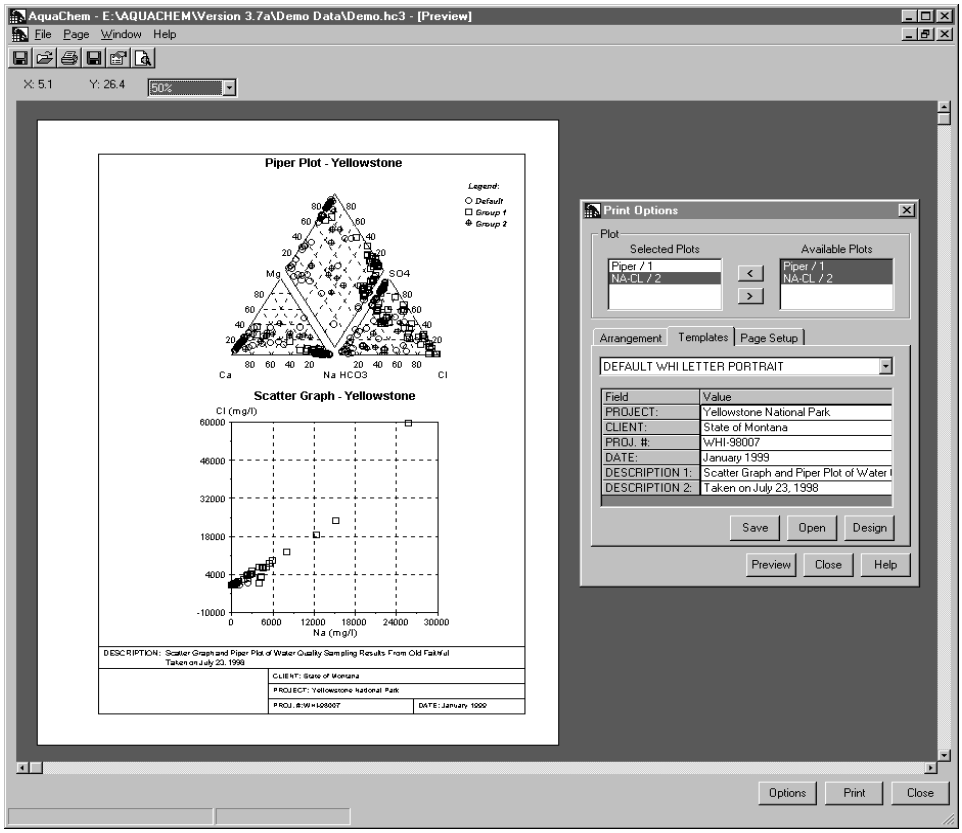


Figure 6.7: Print Preview of Sample Print Template (Default WHI Letter Portrait)

To enter the appropriate text in the title blocks, click once in the text box beside the title descriptor and type the relevant information. Press the **<Enter>** key to register the information, or use the cursor key to advance to the next field below. Depending on the template you select, the plot Description may allow you to enter either two or three lines of text.

The **[Save]** button is used to save the selected template configuration to avoid re-entering repetitive information for each printed page (e.g. project name, client name, project number). All of the information in the descriptor fields can be saved to a template configuration file (***filename.tpl***) that can be easily re-loaded the next time you want to print a report for the same project.

The **[Open]** button is used to load a template configuration file (***filename.tpl***) containing previously defined template settings and project information. The selected template configuration file will load the associated Print Template layout and restore the title block information.

6.4.2 Designing a Print Template

If the pre-defined print templates built-in to AquaChem are not satisfactory for your needs, you can easily create your own customized print templates using the **[Design]** option in the **Templates** tab or edit an existing template.

To create a customized Print Template, you must first choose one of the default print templates. Once you have selected a default print template the **[Design]** button will be activated. Press the **[Design]** button to access the Print Template design options as shown in Figure 6.8.

The Print Template design options allow you to:

- Select the page size, orientation and margins,
- Draw lines and borders
- Define and position text block descriptors
- Position user-entry fields
- Add headers and footers
- Position and size a bitmap image

Although you have the option of modifying the default template designs, it is strongly advised that you either duplicate the selected template (use the **[Duplicate]** button), or create a new blank template (press the **[New]** button. This avoids damaging or losing the original template designs and ensures you will always have a standard set of default Print Templates.

The duplicate Print Template will have the same layout and characteristics as the originally selected Print Template. If it is your first time creating or customizing a Print Template it is likely easier to modify an existing template file than to start from the beginning. Please note that each Template must have a unique name.

The New Print Template will start with a blank page and default page settings.

The **[Delete]** button will delete any of the Print Templates from the list. It is not advisable to delete the default Print Templates.

The **[Save]** button saves all current template settings. All of the templates and the template design settings are saved to a TEMPLATE.TXT file located in the AquaChem installation directory. It is not advisable to move this file, delete this file, or edit this file using a text editor.

The **[Back]** button closes the Print Template design tab and returns to the Print Template Selection tab where the title block information is entered.

Any modification or new template designs can be previewed on the **Print Preview** window by pressing the **[Preview]** button.

The following section describes the Print Template design options and how to use them to build your own customized Print Templates.

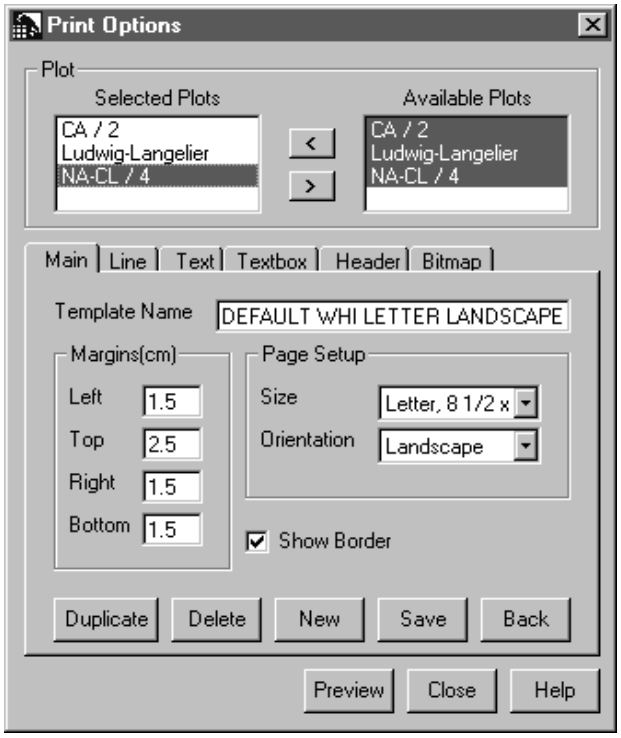


Figure 6.8: Print Template design options

Template Page Setup

The **Main** tab (as shown in Figure 6.8) allows you to set or modify the following template characteristics:

- Template Name (must be unique)
- Page Margins
- Page Setup (size and orientation)
- Border

It is advised to name the template according to the page size and orientation for easy reference at a later date.

The page margins will correspond to the location of the page border. The page dimensions inside the margins will be used to automatically locate and size the selected plots.

The bottom-left corner of the page border serves as the origin for the Print Template design. For example, if you selected page margin settings as indicated in Figure 6.8, the point located 1.5 cm from the bottom of the page and 1.5 cm from the left side of the page would be the Print Template origin with X-Y coordinates of (0.0 cm, 0.0 cm). Remember that you can always use the mouse pointer to check the page coordinates in the upper left-hand section of the Print Preview screen.

The **Page Setup** options allow you to select a Portrait or Landscape page orientation and choose from a complete selection of page sizes.

The **Show Border** checkbox shows/hides the page border lines.

Designing the Template Form

The **Line** tab (as shown in Figure 6.9) allows you to create the Print Template form by drawing lines indicating the borders of the template Title Blocks. Each line has a starting coordinate (X1, Y1), an ending coordinate (X2, Y2), and a line width. The coordinates units are in cm and are measured from the page border origin defined by the bottom left margin.

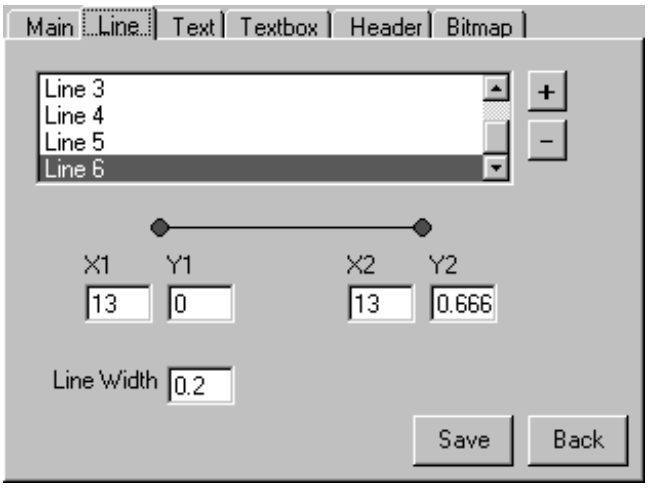


Figure 6.9: Print Template design options - Line tab

To create a new line,

- Press the **[+]** button and a new line will be added to the list.
- Enter the desired start and end coordinates for the new line
- Enter the desired width of the new line
- Press the **[Save]** button to save the new line settings

To edit an existing line, select the line from the list and enter the new coordinates.

To delete a line from the list, select the line from the list and then press the **[-]** button.

To preview line locations, press the **[Preview]** button at any time to see the new line setting on the page layout.

Creating Fixed Text Fields

AquaChem allows you to plot multiple Fixed Text field at any location on the page. These Fixed Test fields generally contain static project information pertaining to the contents of each Title Block (see Figure 6.10).

The **Text** tab (as shown in Figure 6.11) allows you to create, position and customize the Fixed Text fields on the page.

The **Position** fields refer to the X-Y coordinates of the lower left corner of the selected Fixed Text field. Typically, each Fixed Text field should be positioned inside the borders of the associated Title Block as shown in Figure 6.10.

The **Text** field contains the actual text value for the selected Fixed Text field. The font for each Fixed Text field can be customized by pressing the **[A]** button to select the desired font type, size and style.

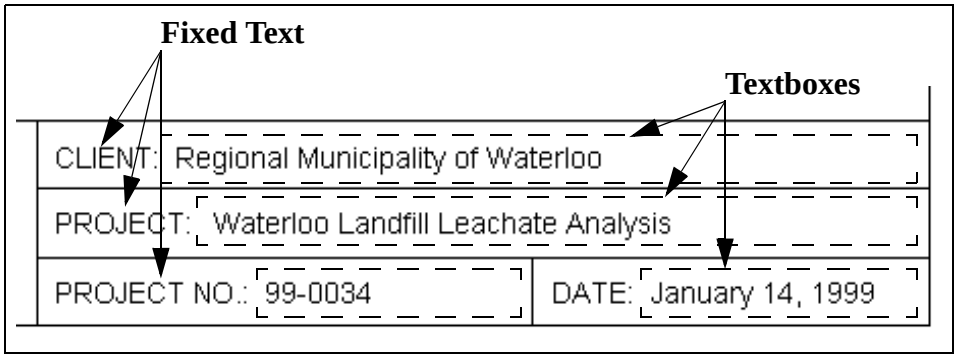


Figure 6.10: Sample Title Block

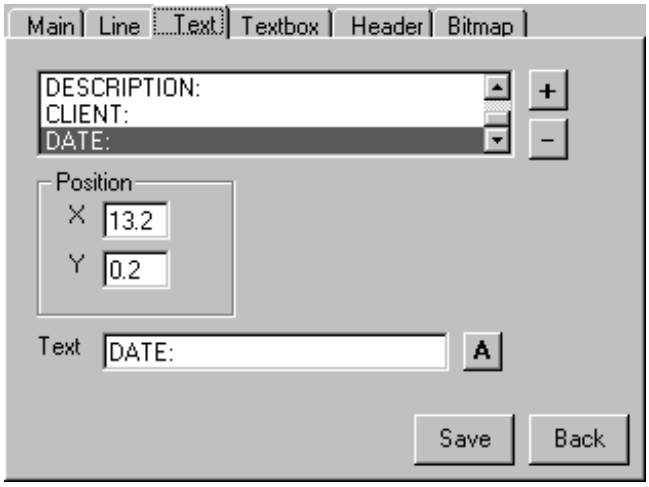


Figure 6.11: Print Template design options - Text tab

To create a new Fixed Text field,

- Press the **[+]** button and a new Fixed Text field will be created with the name "text#"
- Click in the **Text** field to enter the desired text value for the new Fixed Text field
- Enter the appropriate page coordinates

The **[-]** button can be used to remove existing Fixed Text fields from the list.

To modify an existing Fixed Text field, select the title from the list and make the desired changes to the position, text value and/or font.

Press the **[Save]** button to save any additions and/or modifications to the Print Template.

Press the **[Preview]** button to see the new Print Template settings on the page layout.

Creating Textboxes

The **Textbox** tab (as shown in Figure 6.12) is used to create, position and label the Textboxes containing the Template Grid field values (see Figure 6.7). The Textboxes are typically positioned next to the Fixed Text fields as shown in Figure 6.10 (i.e. the Fixed Text fields typically serve as titles for the Plot Description field Values).

The Textbox **Position** refers to the page coordinate location for the bottom-left corner of the Textbox.

The Textbox **Label** refers to the internal label of the Template Grid fields. The Textbox Label appears under the 'Fields' column in the Templates Grid. This label will not appear on the plot or anywhere else in the program.

Multiple lines in a single Title Block can be accommodated by creating two or more Textboxes which are positioned one above the other within the same Title Block border.

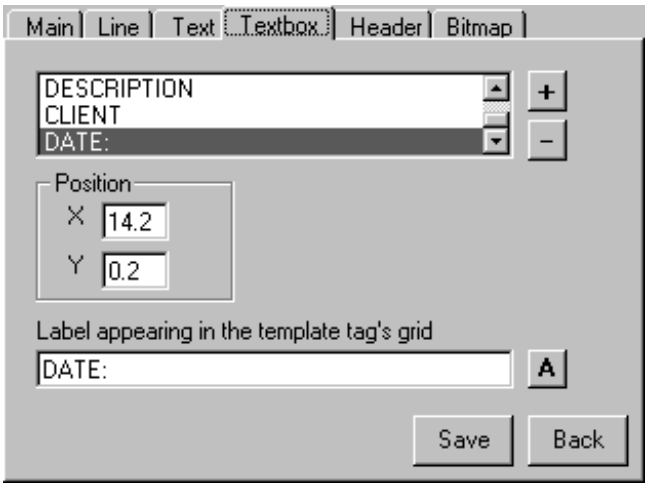


Figure 6.12: Print Template design options - Textbox tab

To create a new Textbox,

- Press the **[+]** button and a new Textbox field will be created with the name "textbox#"
- Click in the **Label** field to enter the desired internal label for the new Textbox field
- Enter the appropriate page coordinates

The **[-]** button can be used to remove existing Textbox fields from the list.

To modify an existing Fixed Text field, select the title from the list and make the desired changes to the position, text value and/or font.

Press the **[Save]** button to save any additions and/or modifications to the Print Template.

Press the **[Preview]** button to see the new Print Template settings on the page layout.

Adding Template Headers and Footers

The Fixed Text fields and Open Text fields are plotted inside the page border, but in some cases you may want to include some header and/or a footer text (e.g. Appendix titles or page numbers). The **Header** tab (see (see Figure 6.13)) allows you to create Header fields and place them in a header or footer position. These Header fields are included in the list of Plot Description fields associated with the selected template.

The **Position** of the selected Header field can be in either the Header position (top of the page) or the Footer position (bottom of the page).

The **Alignment** of the Header field can be either left, right or centre justified.

The **Label** of the Header field is the internal name that appears in the Template Grid. This label will not appear on the plot or anywhere else in the program.

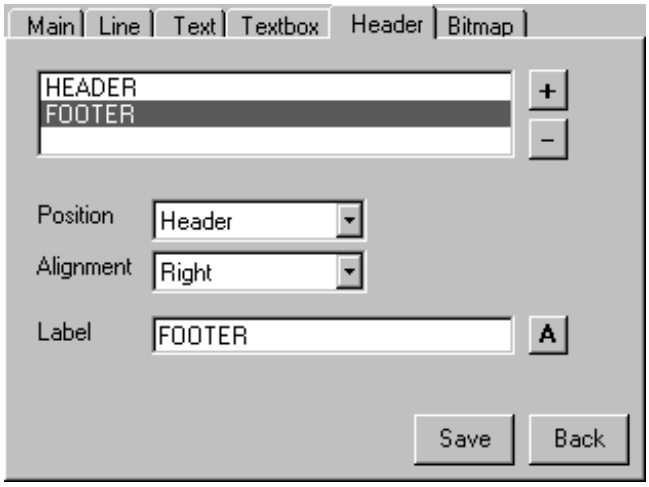


Figure 6.13: Print Template design options - Header tab

The **Default Value** is the initial Value of the Header field. This Value will automatically appear in the Value field of the Template Grid, but you will be able to modify it directly from the Template Grid dialogue box.

To create a new Header field,

- Press the **[+]** button and a new Header field will be created with the name "header#"
- Click in the **Label** field to enter the desired internal label for the new Header field
- Select the appropriate page position and alignment.

The **[-]** button can be used to remove existing Header fields from the list.

To modify an existing Header field, select the title from the list and make the desired changes to the position, text value and/or font.

Press the **[Save]** button to save any additions and/or modifications to the Print Template.

Press the **[Preview]** button to see the new Print Template settings on the page layout.

Importing a Bitmap Image

Each of the default Print Templates has been designed to accommodate an imported bitmap image of your company logo or your client's logo (or any bitmap image). The **Bitmap** tab (as shown in (see Figure 6.14)) allows you to import a bitmap image file, set the position the image on the page, and specify the size of the image as it will appear on the page.

> **NOTE:** AquaChem currently supports only bitmap image files (***filename.bmp***) and does not import other graphics file formats.

The **[+]** and **[-]** buttons are used to add/delete bitmaps from the list of bitmap files.

The **Position** of the bitmap refers to the X-Y page coordinates for the top-left corner of the bitmap image.

The **Dimensions** of the bitmap image refers to the Width and Height of the bitmap image as it will appear on the page. The bitmap image will be automatically re-sized (e.g. stretched or compressed) to fit the dimensions.

The **File [...]** button is used to browse your computer to select the bitmap image file (**filename.bmp**) to import.

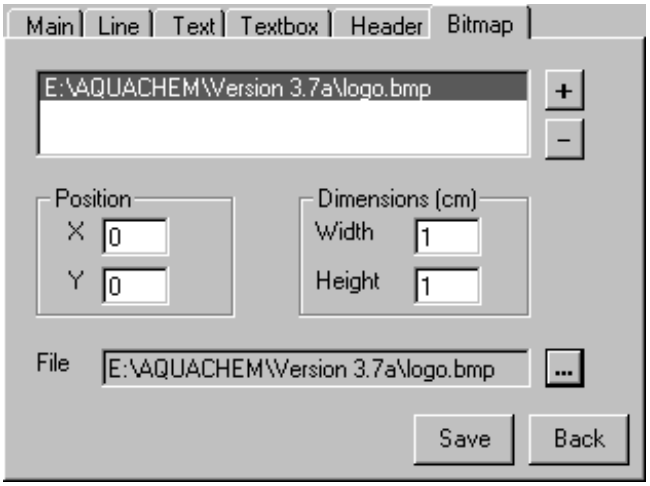


Figure 6.14: Print Template design options - Bitmap tab

To import a new bitmap image file,

- Press the **[+]** button and a new bitmap entry will be created with the name "bitmap#".
- Click on the **File [...]** button to select the desired bitmap image.
- Enter the position coordinates of the bottom-left corner of the bitmap
- Enter the dimensions of the selected bitmap file

The **[-]** button can be used to remove existing Header fields from the list.

To modify the position or dimensions of an existing bitmap file, select the title from the list and make the desired changes to the position, text value and/or font.

Press the **[Save]** button to save any modifications to the Print Template.

6.4.3 Exporting to a Graphics File

The selected graphs appearing in the Print Preview window can be printed directly to a printer or they can be exported to a Windows Metafile graphics file by selecting **File/Export to metafile** from the top menu bar. The exported image will the same as it appears in the Print Preview window (including any borders, headers and template graphics and text).

The .wmf file can then be easily imported or inserted into any Microsoft Word document file where further modifications and enhancements can be made using the built-in image editor. Unfortunately, the .wmf graphics file format is not compatible with all graphics packages, and the interpretation of the .wmf format can be different from one version of a program to another. However, it has been tested with Microsoft Word without any difficulties.

To insert a .wmf file into and Microsoft Word document,

- Select **Insert/Picture/File**
- Choose the .wmf file created by AquaChem
- The .wmf file will be inserted into the document file and the MS Word picture editor screen will appear
- Select the **[Draw]** button from the toolbar along the bottom of the screen
- Select the **Ungroup** option to ungroup the different elements of the image (you may have to ungroup the image twice to separate all of the image elements).

Now each of the image components can be moved, resized, modified or deleted.

7

PHREEQC Interface

7.1 Introduction

PHREEQC[1] is derived from the FORTRAN program PHREEQE, which has been one of the most commonly used hydrochemical modeling programs for nearly 15 years. As the name implies, the original FORTRAN code has been entirely rewritten in the C programming language and this new version has eliminated many of the deficiencies and limitations of earlier version of PHREEQE, while adding many new powerful analytical capabilities.

The PHREEQC program is based on an ion pairing aqueous model and is used to calculate pH, redox potential, ion exchange, surface reactions and mass transfer (e.g. solution or precipitation of minerals). You can also use PHREEQC to perform inverse modeling to estimate the chemical changes that occur as a water sample evolves along a flow path.

AquaChem comes with the PHREEQC DOS executable file (***phreeqc.exe***) and three thermodynamic database files (***phreeqc.dat, wateq4f.dat and minteq.dat***). The PHREEQC user's manual and source code may be downloaded from the ftp site:

ftp://brrcrftp.cr.usgs.gov (connect as anonymous),

or it can also be downloaded from the web site:

http://water.usgs.gov/software/phreeqc.html.

Although this chapter describes the AquaChem interface to PHREEQC, it is recommended that you download and read the detailed PHREEQC user's manual before performing any complex hydrochemical simulations.

AquaChem provides a very user-friendly interface for generating the PHREEQC input files and running the simulations. The direct link from the AquaChem database to the PHREEQC interface lets you read sample information directly and avoid the tedious task of retyping water sample information. For simple problems such as speciation and saturation calculations, dissolving or precipitating minerals, and mixing solutions, you do not need special knowledge of PHREEQC to run simulations with AquaChem. Since PHREEQC supports sequential processing of a unlimited number of simulations, you may calculate the saturation indices for your entire database in only a couple of minutes. If you are familiar with the PHREEQC input syntax, you may choose to view and edit the generated input files after each simulation step. Although the AquaChem interface does not support all PHREEQC capabilities, the built-in text editor can be used to manually edit the input files to fully exploit all of the PHREEQC simulation capabilities.

The concept of hydrochemical modeling and the PHREEQC program will not be discussed in detail in this manual. This chapter presents an introduction to the AquaChem-PHREEQC interface, as well as an overview of the modeling capabilities of PHREEQC.

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1. pH redox-equilibrium-equations

7.2 Setting Up your AquaChem-PHREEQC Interface

Instructions in this manual will be based on the assumption that you are using the PHREEQC executable file (***phreeqc.exe*** - PHREEQC version 1.6) included with AquaChem. By default, the PHREEQC executable file and the PHREEQC thermodynamic database files are automatically installed in the same directory as the AquaChem installation directory. If you have installed AquaChem in a directory other than the default installation directory, you will need to manually set up the link between AquaChem and the PHREEQC thermodynamic database as follows:

- Start AquaChem.
- Select **Main Menu\File\Preferences**.
- Under the **Start-up Defaults** tab, select the path and filename of the PHREEQC thermodynamic database field (select either phreeqc.dat, wateq4f.dat or mint-eq.dat). If the default path and filename are incorrect, you can browse the directory by clicking on the **[...]** button to the right of the filename.
- Click **[Save]**

NOTE: If you are running Windows NT, you must ensure that the PHREEQC executable file and the PHREEQC thermodynamic database files are located in a directory that follow the DOS naming conventions (e.g. no periods, no spaces and no long filenames).

7.2.1 The PHREEQC Therrmodynamic Database Link

One of the big advantages of the AquaChem PHREEQC interface is the direct link between the two databases of these programs. The link allows you to use records from the AquaChem database and read them into the PHREEQC input data file. Alternatively, you can also import modeled parameters from the PHREEQC simulation results.

In order to let AquaChem know which database parameter corresponds to which PHREEQC element, some minor modifications have been made to each of the thermodynamic databases included with AquaChem. The link between AquaChem and the thermodynamic databases is established by adding the AquaChem parameter name as a comment for each matching parameter in the Masterspecies section of the database file. Each comment is preceeded by a '#' character to flag the AquaChem parameter descriptor.

For example, the following lines are taken from the Masterspecies section of the **phreeqc.dat** file:

Ca	Ca+2	0.0	Ca	40.08	#CA
Mg	Mg+2	0.0	Mg	24.312	#MG
Na	Na+	0.0	Na	22.9898	#NA
K	K+	0.0	K	39.102	#K
Fe	Fe+2	0.0	Fe	55.847	#FE
Fe(+2)	Fe+2	0.0	Fe		
Fe(+3)	Fe+3	-2.0	Fe		
Mn	Mn+2	0.0	Mn	54.938	#MN

These modifications have already been defined for each of the thermodynamic database files provided with AquaChem. You have to redefine this only if you change the thermodynamic database or if you create a more complete AquaChem database.

7.3 Creating PHREEQC Input Files from AquaChem

To create an input file for the PHREEQC program select **PHREEQC\Create PHREEQC Input File** from the **Main Menu**. The **PHREEQC Input** window will be displayed as shown in the following figure.

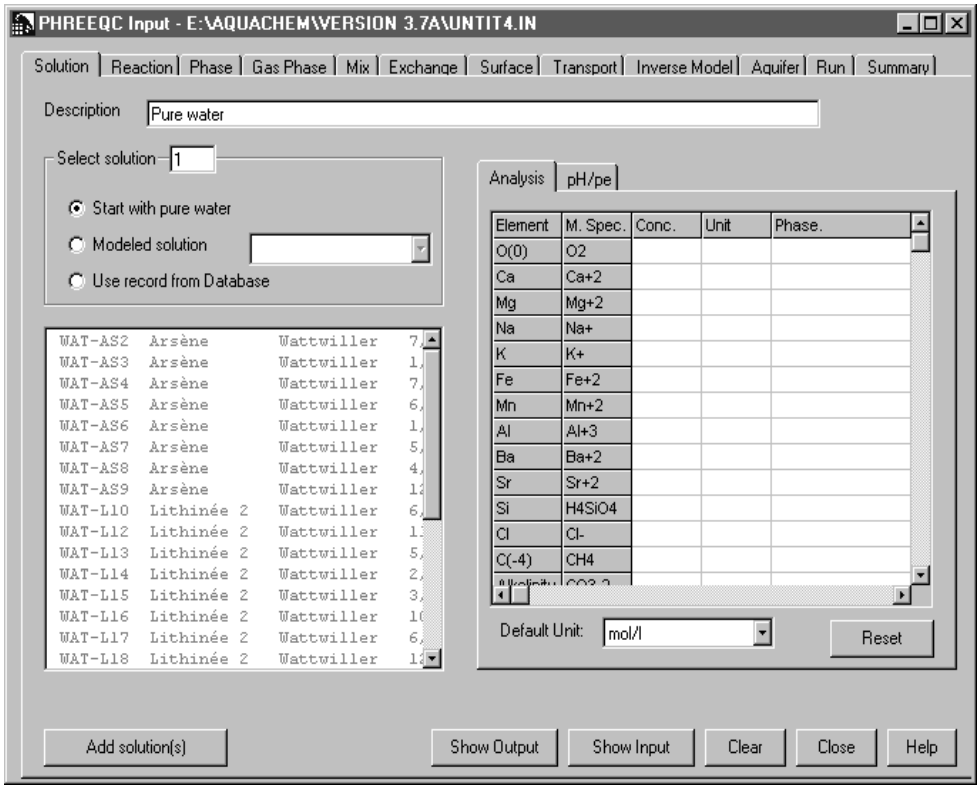

Figure 7.1: PHREEQC Input window

The **PHREEQC Input** window consists on the following elements

A tab strip lets you define most PHREEQC simulation options such as Solutions, Reactions, Mineral Phases, Gas Phases, Mixtures, Exchange assemblages, Surface reactions, Transport, Inverse Models, Aquifer properties and Run settings. After defining each simulation entity you must press the **[Add...]** button at the lower left of the **PHREEQC Input** window in order to write this simulation to the input file.

A summary of the selected PHREEQC simulations is provided in the **Summary** tab on the far right of the tab bar.

The buttons located along the lower part of the **PHREEQC Input** window are common to each of the tabs:

The **[Show Output]** button shows the current output file of the completed simulation.

The **[Show Input]** shows the current input file.

The **[Clear]** button removes all simulation steps from the current input file.

The **[Close]** button ends the current simulation.

The **[Help]** shows the help for the current tab.

The remaining sections describe the functionality of each of the simulation option tabs.

7.3.1 Run Settings

The **Run settings** tab (see Figure 7.2) is used to execute the PHREEQC simulation and to customize the PHREEQC simulation results that are generated.

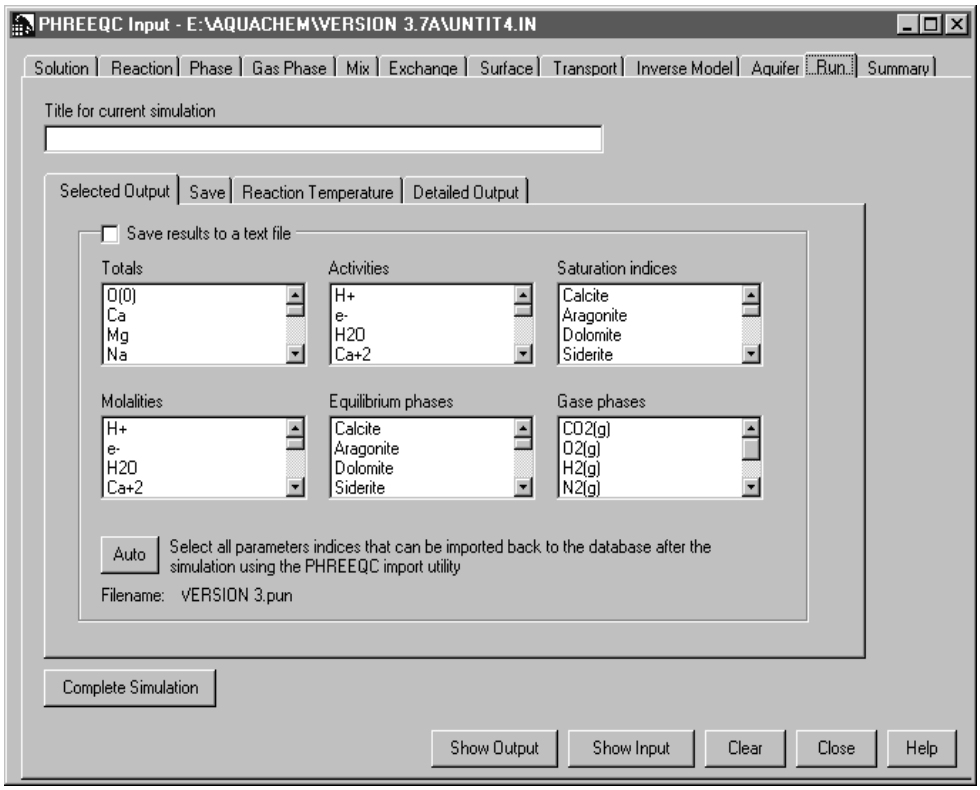

Figure 7.2: PHREEQC Run Settings

The **Title** field is used to provide a unique description for each PHREEQC simulation.

The **[Complete Simulation]** button writes all of the current **Run settings** to the PHREEQC input file and activates the **[Run PHREEQC]** button. The **[Complete Simulation]** button should only be used when you have specified all of the required run options and you are ready to start the PHREEQC simulation.

The **[Run PHREEQC]** button loads the PHREEQC input file and executes the PHREEQC simulation. This button is hidden until the **[Complete Simulation]** button is pressed.

The PHREEQC simulation will run as a DOS application inside a DOS window (look on your Windows task bar and you will see an MS-DOS application indicator). Once the PHREEQC simulation is completed a popup message will appear saying “PHREEQC simulation complete”. Press **[OK]** to close this message and return to the AquaChem PHREEQC interface.

> **NOTE:** The appearance of the popup message does NOT necessarily indicate that the PHREEQC simulation was successfully completed. It only indicates that PHREEQC has finished running. To ensure a successful completion of the PHREEQC simulation, open the MS-DOS window and check the status messages.

The remaining part of the **Run settings** tab is divided into four separate sub-sections:

- Selected Output options
- Save options
- Reaction Temperature options
- Detailed Output option

Selected Output options

PHREEQC will generate an output file (***filename.out***) every time you run a simulation. However, this file is very complete and may contain more information than you need to resove a particular problem. The **Selected Output** tab (see Figure 7.2) lets you create a customized simulation results file (***filename.pun***) containing simulation data for only the parameters you are interested in.

To create a .PUN file for your simulation, choose the **Save Results to a Text File** option and then select the parameters you want to include in the .PUN file. The parameters pH, pe, temperature and ionic strength are included by default in the table output.

The **[Auto]** button will automatically select only the modeled parameters which you have defined in your database template (maskfile).

If you have successfully run the simulation, AquaChem allows you to import the results of your PHREEQC simulation back into the AquaChem database if the results are saved in a .PUN file. Refer to See Importing PHREEQC Results into AquaChem before running your simulation for instructions on how to prepare your database for importing.

Save Options

The **Save** tab (see Figure 7.3) allows you to save the composition of a simulation by creating a new solution, phase, exchange, gas phase or surface assemblage. These new ‘elements’ can then be used as input data for subsequent PHREEQC simulations. Each of these new elements must be indentified by a unique number that is not already in use. If you specify a number that is currently in use, the new element with overwrite the old element.

Reaction Temperature Options

Normally the temperature stays constant during a reaction and is defined as the temperature of the given sample. However, PHREEQC also gives you the option to change the temperature linearly or in steps during the course of a simulation. The **Reaction Temperature** tab provides an easy to use interface for specifying the desired temperature settings.

The **Constant** temperature option is the default setting. It will use the solution temperature described in the **Solutions** tab under the **Ph/pe** sub-section.

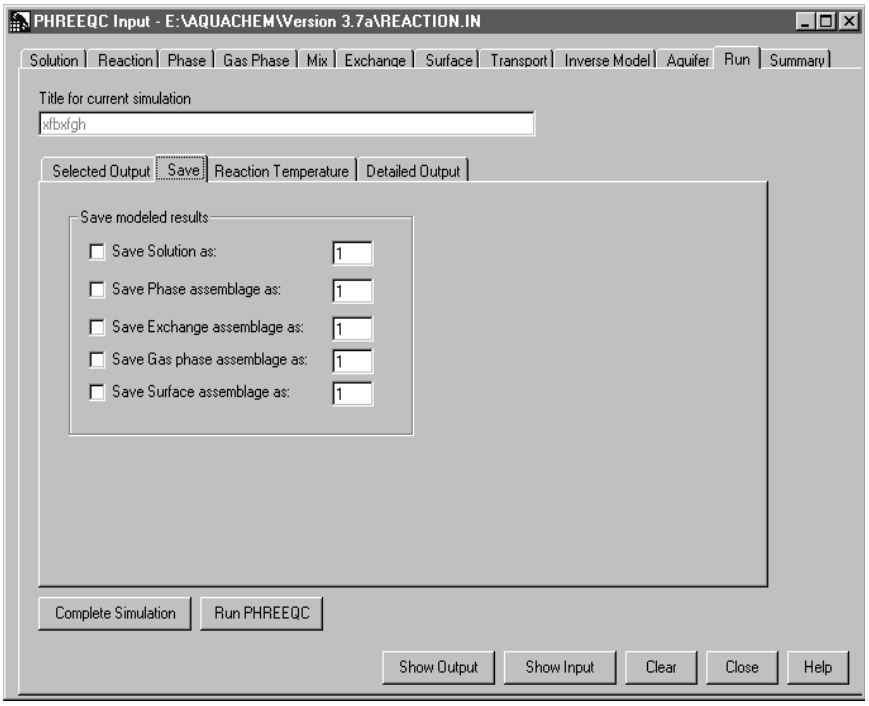

Figure 7.3: Run Settings - Save options

The **Linear Change** option allows you to change the temperature linearly from a starting temperature to an ending temperature in a specified number of steps.

The **List of Steps** option allows you to specify the exact temperature at specific steps during the reaction. The temperatures will be applied in the order they are listed.

Detailed Output Options

The Detailed Output tab (see) allows you to select the various output details to include in the standard PHREEQC results ouput file (.OUT file extension).

7.3.2 Solution Options

The **Solution** tab is shown in Figure 7.4. You must specify at least one solution for every PHREEQC simulation file. AquaChem allows you to select from three types of solutions;

(1) Pure Water,

(2) Previously saved model solutions, or

(3) Samples from your AquaChem database.

The **Select solution** field is used to assign a unique number to each solution used in the PHREEQC simulation. If you choose a sample from your database, AquaChem automatically assigns a solution number equal to the sample's database index number. If you assign the same solution number to two solutions, the second solution will overwrite the first, and you will not be able to recover or use the information of the first solution in subsequent simulations. Be sure to use unique solution numbers for all of your solutions.

The **Description** field is used to identify the solutions. The solution description will appear in the **Summary tab** and also in the PHREEQC input file.

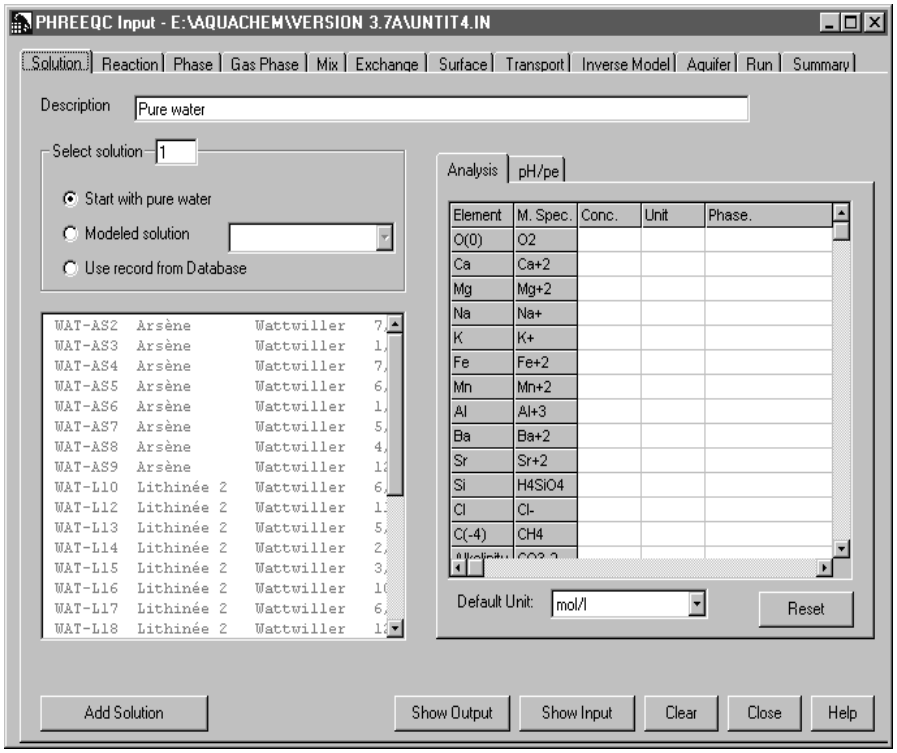

Figure 7.4: Solutions tab

The concentrations of the dissolved elements in solution are displayed in the grid on the right-hand side of the Solutions tab. The first column of the grid contains the element name, while the second column describes the PHREEQC Masterspecies name.

Start with Pure Water

If you enter an analysis starting with pure water you may choose a default unit from the **Default Unit** listbox located below the Concentrations grid. Once you started entering element values for the pure water solution, the default unit may not be changed. However, you can change the unit individually for each entered value by double-clicking in the appropriate grid box in the **Units** column. Please note that it is not possible to freely mix units (i.e. you may not enter some values as mg/l and others as mmol/l). You may only mix units within a "unit family" such as g/l, mg/l ug/l. If the sample information is read from the AquaChem database the default unit is automatically set to mmol/l. The reason for this is that elements may be expressed with different formula weights in the PHREEQC database than in the AquaChem database (e.g. Si may be expressed as SiO2 in one and as H2SiO3 in the other database). If silica concentrations would be imported in mg/l the weight would be falsified.

If you wish to import the simulation results from the pure water solutions into your AquaChem database, you must first ‘prepare’ the database by creating an empty database record for each pure water solution in your simulation.

IMPORTANT: Make note of the database index number for each new database record you create because you will need to assign these numbers to the Solution number for each pure water solution. If you assign a Solution number equivalent to the index number of an existing database sample, you will overwrite the modelled parameters of the existing database sample.

Modeled Solution

A modeled solution is a solution that has been previously added to the PHREEQC simulation. To use a modeled solution, select the desired solution from the drop-down list of available modeled solutions. The concentrations for these solutions will be predefined, but they can still be modified before adding them to the simulation.

Use Record From Database

To use a sample from your AquaChem database:

- Choose the **Use Record from Database** option.
- Select the sample record to use as a solution.
- Click-on the **[Add Solution(s)]** button.

To add multiple samples from your database, use the **<Shift>** and **<Ctrl>** keys with the mouse to select the samples you need, then click the **[Add Solution(s)]** button. This is useful if you want to speciate a large number of samples simultaneously. However, when you add one sample at a time, you have the ability to view and edit or complete the properties of each sample under the **Analysis** tab. Do not add incomplete samples to your simulation. Each complete sample should have pH, alkalinity, and temperature values specified.

To view the contents of the PHREEQC input file, click the **[Show Input]** button at the base of the screen or use the **File/View PHREEQC Input** menu option.

You are now ready to specify the type of simulation(s) that you will run.

Example

To add the WAT-LITH-3 record from the DEMO.HC3 database to a PHREEQC input file, proceed as follows:

- Select **PHREEQC\Create PHREEQC Input File** from the **Main Menu**.
- Select **File/Save As** and enter the name LITHINEE.IN.
- Click the radio button **Use Record from Database** in the **Solutions** tab.
- Select the WAT-LITH-3 record from the list and click the **[Add Solution(s)]** button.

The following text will be saved to the PHREEQC input file LITHINEE.IN and can be viewed by selecting **File\View PHREEQC Input** or by clicking the **[Show Input]** button.

```
SOLUTION 22  Wat-Lith-3  LithinÈe 2   Trias-Kp     Ca-SO4   0022
       units       mmol/l
       pH          7.35
       pe          4
       density     1
       temp        14.6
       redox       pe
       O(0)        3.438574E-02
```

```
Ca          6.327345
Mg          0.847388
Na          0.1348412
K           3.324808E-02
Si          0.1920959
Cl          0.0789778
Alkalinity  2.380016  as HCO3
S           5.829933
```

7.3.3 Reactions Tab

The Reactions simulation options are used to dissolve or precipitate a specified amount of a mineral or to perform another chemical reaction. The **Reactions tab** (see Figure 7.5) allows you to specify multiple reactions for the simulation by giving each reaction a unique identification number and a text description. AquaChem also provides a comprehensive list of available reactant species and phases to choose from.

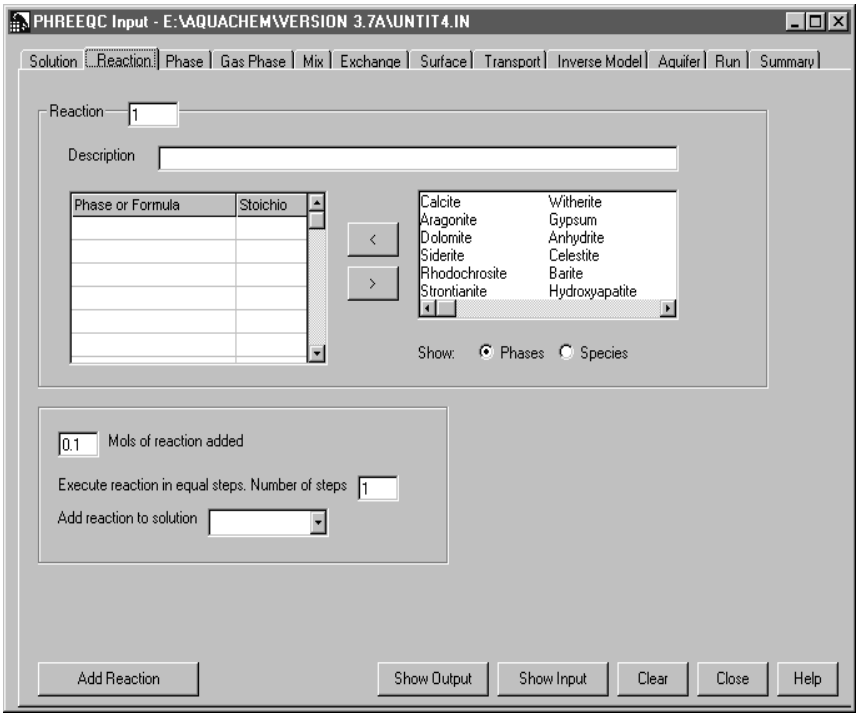

Figure 7.5: Reactions frame

To select from the list of available reactants,

- Click the radio button **Phase** or click **Formula**,
- Choose the reactant you need, and click the left arrow button **[<]**. The reactant will appear in the grid.
- Click the reactant in the grid, and type the stoichiometric factor in the text field above the grid. The stoichiometric factor defines whether the reactants are added (SF>0) or removed (SF<0) from the solution. The stoichometric factor is the

amount of a reactant relative to the other reactants.

- Type the number of moles of the reactant, number of steps for the reaction, and select the reaction solution. The reaction path is revealed when you simulate the reaction in multiple steps. By default the reaction is added to the first solution in the simulation. Note that you are not required to add the reaction immediately to a solution if you only wish to use the reaction in a later simulation step(s).
- Click the **[Add Reaction]** button to save the stoichiometric reaction to your PHREEQC input file.

Example

Follow the steps listed below to specify the following reaction: dissolve 0.01 moles calcite and 2 moles halite (NaCl) in pure water.

- Select **Tools\PHREEQC\Create PHREEQC Input File** from the **Main Menu**.
- The **PHREEQC Input** window will appear, and the **Solutions** tab will be active.
- Select **File/Save As** and enter the simulation name REACTION.INP
- In the **Solutions** tab, specify the solution as pure water.
- Select the **Reactions tab** and click-on the **Phase** button to list the reactant phases.
- Select **Calcite** from the list of phases, and click the left arrow **[<]** button (Calcite will appear in the grid with a default Stoichiometric factor of 1.0).
- Click-on **Calcite** in the grid, and type **0.1** in the **Mols of Reaction added** field (located below the grid).
- Select the pure water solution (**Solution 1**) from the field labeled **Add reaction to solution**.
- Click the **[Add Reaction]** button to add this reaction to the PHREEQC input file (notice that the Reaction number has automatically incremented to '2').

NaCl is not included in the PHREEQC thermodynamic database. However PHREEQC is capable of recognizing the chemical composition of a given formula for reactions. Follow the steps listed below to create a reaction using NaCl.

- Click **Calcite** in the grid.
- Type **NaCl** in the **Species or Phase** field (replacing the word Calcite).
- Click-on **NaCl** in the grid, and type **2.0** in the **Mols of Reactant** field.
- Click the **[Add Reaction]** button.

The following text will appear in the input file:

```
SOLUTION 1 Pure water
units mmol/l
pH 7
pe 0
density 1.0
temp 25
USE solution  1
REACTION 1
Calcite 1
0.1 moles
USE solution  1
REACTION 2
NaCl 1
2 moles
```

7.3.4 Mineral Phases Frame

Adding mineral phases is similar to adding reactions (as described in the previous section). With the Reactions options you add a specified amount of a phase, but with the Mineral Phase options the amount of mineral phase added is limited by a specified saturation indice.

To specify an equilibration of your solution with mineral phases, select the **Phase tab** in the **PHREEQC Input** window (see Figure Figure 7.6).

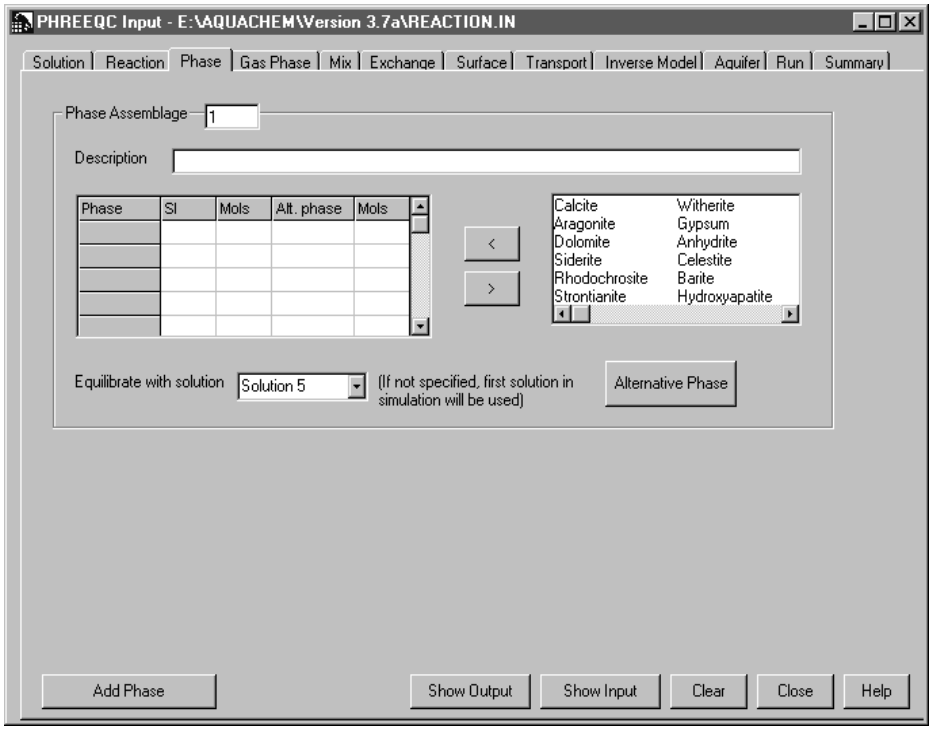

Figure 7.6: Mineral Phases tab

Each mineral phase assemblage is identified by a unique **Phase Assemblage** number and a description. For each mineral phase you choose, you can specify the following properties:

SI (saturation index): SI is the Saturation Index of the selected mineral phase (degree of saturation, default value 0).

SI = log(IAP/KT)

where IAP is the ion activity product for the given material and KT is the reactioin constant at the given temperature.

SI > 0 means the solution is super-saturated with respect to the mineral phase;

SI < 0 means the solution solution is below saturation of the specified mineral phase.

For gas phases the SI corresponds to the log of the partial pressure.

Mols: Mols describes the maximum amount of mineral phase that can be added or dissolved to reach the specified saturation. The default value is 10 mols. This value is typically used for transport problems in order to define a pure phase assemblage.

Alternative Phase: The alternative phase is added or removed until the first mineral is in equilibrium with specified saturation index. In figure 6.4, gypsum is added or removed to the solution until the equilibrium with calcite is reached. An amount must be specified for the alternative mineral phase (default amount of the alternative phase is 10 moles as specified by PHREEQC). The solutions equilibration with calcite will be terminated if the amount specified for the alternative mineral phase is consumed prior to equilibration with calcite. It should be noted that if the alternative phase is specified, the amount of the mineral phase must be equal to zero (i.e. it is not possible to have both an excess of the specified mineral phase and the alternative phase).

Select the solution to equilibrate the mineral phases with from the drop down menu below the grid. If you do not choose a solution from the drop down menu. The specified assemblage is equilibrated with the first solution defined in the current simulation.

Example

In this exercise you will simulate the equilibration of pure water with calcite and dolomite at a partial CO_2 pressure of 0.01 atm.

- Select **PHREEQC\Create PHREEQC Input File** from the **Main Menu**.
- The **PHREEQC Input** window will appear, and the **Solutions** tab will be active.
- Specify the solution as pure water.
- Click-on the **Phases** tab to activate the Mineral Phases options
- Choose **Calcite** from the list, and click the left arrow **[<]** button (**Calcite** will appear in the grid under the Phase column).
- Next transfer **Dolomite** and **CO_2(g)** to the grid using the same procedure.
- The default saturation index (SI) for each mineral phase is 0, which is suitable for calcite and dolomite.
- Select **CO2(g)** in the grid, and type **-2** for the SI value.
- Select the pure water solution (**Solution 1**) from the **Equilibrate with solution** field.
- Click the **[Add Phases]** button.

The following text will appear in your input file:

```
TITLE
SOLUTION 1 Pure water
units mmol/l
pH 7
pe 0
density 1.0
temp 25
USE solution  1
EQUILIBRIUM_PHASES 1
Calcite  0.0
Dolomite  0.0
CO2(g)  -2
```

7.3.5 Gas Phase Options

The **Gas Phase** tab (see Figure 7.7) is used to equilibrate a solution with a finite volume of gas. This simulation is not applicable if fixed partial pressures of the gas components are desired (in this case use the Mineral Phase option instead and fix a gas with a partial pressure that has an infinite volume of gas phase).

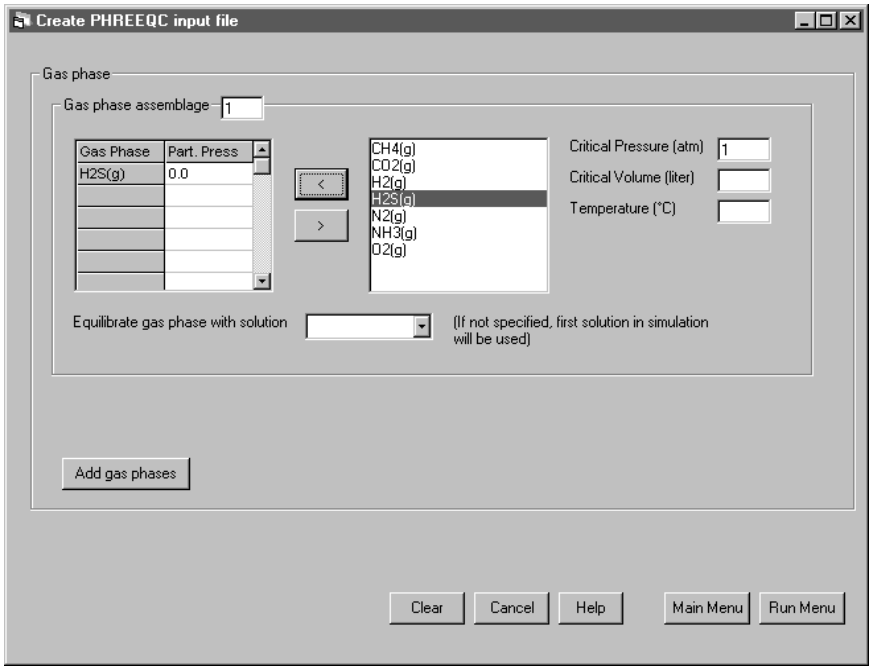

Figure 7.7: Gas Phase frame

The **Gas Phase** option will equlibrate the solution with only those gases which are defined in the simulation. However, gases may be specified with a partial pressure equal to zero at the start of the simulation. In this case, no moles of that component will be present initially, but some gases may evolve during a reaction simulation such as oxidation of organic material. As a result, the partial pressure of all gases included in the gas phase stays constant and the excess gas is removed from the solution as the gas bubbles.

Pressure calculations are computed using the ideal gas law,

$PV=nRT$

where P = defined pressure,
V = volume,
n = number of moles of the gas,
R = universal gas constant, and
T = temperature.

As shown in Figure 7.7, AquaChem provides a list of available gases to choose from and allows you to easily add multiple gases to the Gas Phase Assemblage. To select a gas to equilibrate a solution with, click on the gas(es) you would like to use and then press the left arrow **[<]** button to transfer the selected gas(es) to the Gas Phase Assemblage table. Once

you have selected the gases, enter a partial pressure value for each gas in the Gas Phase Assemblage. If you wish to add air to the solution, click on the **[Air]** button and the major components of air are automatically added to the list at their partial pressures at 1 bar.

To remove a gas from the Gas Phase Assemblage table, select the gas to remove and then press the right arrow **[>]** button.

The Partial Pressure, Initial Volume and Temperature information is required for each Gas Phase Assemblage in order to calculate the weights of each gas component. The default values are:

- Critical Pressure: 1.1 atm
- Initial Volume: 1.0 litres
- Temperature: 25°C

Finally, you can select the solution you wish to equilibrate the gas phase assemblage with. If you do not select a solution from the list, you can save the gas phase to equilibrate in a later simulation step (e.g. during a transport problem).

Each Gas Phase Assemblage is identified by a unique number and can be reused in later simulations.

Example

In this exercise, you will specify the following equilibration reaction in your PHREEQC input file: a gas phase consisting of CO_2, CH_4, N_2, and NH_3 is equilibrated with pure water. The gas phase has a critical pressure of 1.1 bar. Initially 0 mols of this gas phase are present in the solution.

- Select **PHREEQC\Create PHREEQC Input File** from the **Main Menu**.
- The **PHREEQC Input** window will appear.
- Select **File/Save As** and type the name GASPHASE.INP.
- Specify a pure water solution.
- In the pH/pe tab, enter a solution temperature of **10°C** the Temperature tab, choose **Constant Temperature**, and type **10**°C.
- Select the **Gas Phase** tab .
- Choose **CO_2** in the list of gas phases, and click the left arrow button **[<]** (CO_2 will appear in the grid)
- Enter a **CO_2** partial pressure of **0.1**.
- Repeat for **CH_4** with a partial pressure of **0.04**, **NH_3** with a partial pressure of **0.06**, and **N_2** with a partial pressure of **0.8**.
- Enter a Critical Pressure of **1.1** bar, an Initial Volume of **1.0** litres, and a Temperature of **10**°C .
- Select **Solution 1** from the drop down menu below the grid.
- Click **[Add Gas Phases]** to save the gas phase to your PHREEQC input file.

The following text will be saved in your input file:

```
TITLE
SOLUTION 1 Pure water
units mmol/l
pH 7
pe 0
density 1.0
temp 10
```

```
USE solution  1
GAS_PHASE 1
-pressure 1.1
-temperature 10
-volume 1
CH4(g) 0.04
CO2(g) 0.1
N2(g) 0.8
NH3(g) 0.06
```

7.3.6 Mix Options

The **Mix** tab (see Figure 7.8) allows you to simulate the mixing of multiple solutions together with different proportions of each solution added to the mixture.

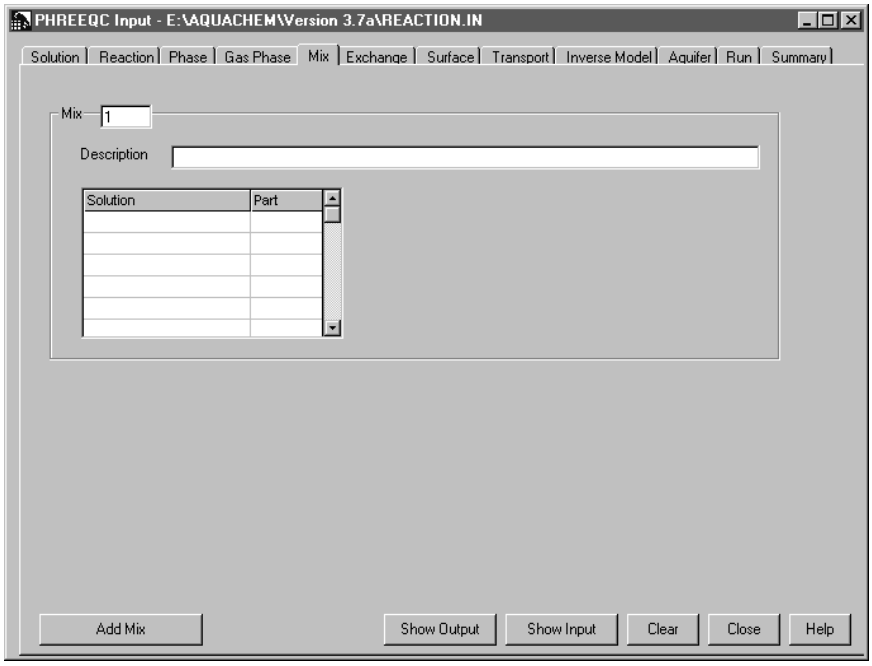

Figure 7.8: Mix frame

To simulate mixing multiple samples together, you must first specify at least two solutions for the PHREEQC simulation.

To add a solution to the mixture:

- Double-click-on the first line in the grid under the **Solution** header.
- Select a solution from the drop down menu that appears in the same cell.
- Click-on the firs line in the grid under the **Part** header and type the proportion of the solution you would like to add to the mixture (e.g. 3 parts of Solution 1 and 4 parts of Solution 2)

When you have added all the necessary solutions to the mixture, click **[Add Mix]**. The specified mixture will be added to your PHREEQC input file.

Each mixed solution has a unique **Mix number** and a **Description** and can be used in a later simulation.

Example

Using the DEMO.HC3 database, perform the steps below to calculate the saturation index of a mixture of two groundwater samples.

- Select **PHREEQC\Create PHREEQC Input File** from the **Main Menu**.
- The **PHREEQC Input** window will appear.
- Select **File/Save As** and type the name MIXTURE.INP.
- Select samples WAT-AS5 and WAT-AS8 from your AquaChem database and add them to the Solutions file.
- Select the **Mix** tab.
- Double-click-on the first line in the grid under the **Solution** header and choose **Solution 1** and then type **0.1** in the Parts field.
- Double-click-on the first line in the grid under the **Solution** header and choose **Solution 2** and then type **0.9** in the Parts field.
- Click **[Add Mix]** at the bottom of the window.

The following text will be added to your PHREEQC input file:

```
SOLUTION 1  WAT-AS5  Arsène       Wattwiller
units mmol/l
pH 7.3
pe 4
density 1
temp 14.8
Ca 3.068862
Mg 0.7486632
Na 1.957373
K 6.393862E-02
Fe 8.237822E-04
Mn 4.368402E-03
Sr 6.847752E-03
Si 0.1920959
Cl 0.9026034
Alkalinity 3.032389
S 2.613059
F 9.474682E-02
Li 0.076
SOLUTION 2 WAT-AS8 Arsène    Wattwiller  93/04/07  Ca-SO4-HCO3
0002 (01)
unitsmmol/l
pH7.55
pe4
density1
temp13
Ca 2.894211
```

```
Mg 0.5141917
Na 1.69639
K 4.347826E-02
Fe 6.088825E-04
Mn 5.460503E-04
Al 3.706449E-04
Si 0.1847963
Cl 0.8461908
Alkalinity 2.507868
S 2.581827
F 9.579957E-02
MIX 1
 10.1
 10.9
```

7.3.7 Exchange Options

Ion exchange involves the replacement of one chemical in the solution for another on a solid surface. Intrusion of fresh water into marine sediments or seawater into coastal fresh water aquifers are probably the most obvious examples for this mechanism. Fresh water typically is dominated by Ca^{2+} and HCO_3- ions due to the presence of dissolved calcite, whereas in seawater, Na^+ and Cl^- are the dominant ions. Sediment in contact with sea water will often have large concentrations of Na^+. When seawater intrudes in a coastal fresh water aquifer an exchange of cations takes place:

$2Na^+ + Ca\text{-}X2 \rightarrow (2Na\text{-}X + Ca^{2+})$

where X indicates the soil exchanger.

Sodium is taken up by the exchanger and Ca^{2+} is then released. The composition of the solution and the exchanger is modified by this reaction.

PHREEQC lets you define the initial composition of an Exchange Assemblage in two ways:

(1) Explicitly by selecting the composition of the Exchange Assemblage, or

(2) Implicitly by specifying that the Exchange Assemblage is in equilibrium with a solution of a fixed composition.

Option 1

AquaChem provides a comprehensive list of available exchanger ions to choose from and allows you to easily add several ions to the Exchange Assemblage (see Figure 7.9). To add an ion(s) to the Exchange Assemblage:

- Click on the ion(s) you would like to use
- Press the left arrow **[<]** button to transfer the selected ion(s) to the table of Exchanger Ions.
- Enter the Amount (in mols) for each ion in the Exchange Assemblage.

To remove an ion from the Exchange Assemblage, click-on the ion you would like to remove, and then press the right arrow **[>]** button.

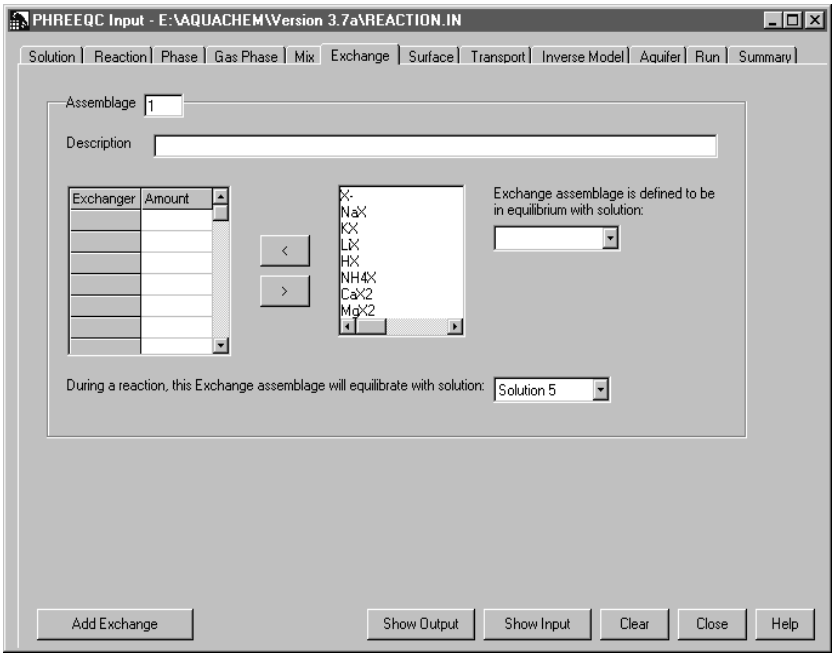

Figure 7.9: Exchange options tab

Option 2

AquaChem provides a dropdown list of available solutions to choose from.

Once you have defined the Exchange Assemblage, you must select the solution you wish to equilibrate with. If you do not select a solution from the list, you can save the Exchange Assemblage to equilibrate in a later simulation step (e.g. during a transport problem).

Each Exchange Assemblage is identified by a unique **Number** and a **Description** so they can be easily recognized in the **Summary** tab and reused in later simulations.

An example how to use the exchange assemblage is given in the PHREEQC transport, section 7.3.9 on page 157.

7.3.8 Surface Options

While ions are exchanged during an exchange process, surface processes involve only the absorption of material on mineral surfaces. This process typically can be observed on hydroxides and is driven by electrostatic processes.

PHREEQC lets you define the initial composition of a Surface Assemblage in two ways:

(1) Explicitly by specifying the parameter values for Surface Assemblage, or

(2) Implicitly by specifying that the Surface Assemblage is in equilibrium with a solution of a fixed composition.

Option 1

To define a Surface Assemblage:

- Double-click in the first column of the table and select a binding site
- Press the <Enter> key to accept this selection and fill in default values for Specific Area (600 m2/g) and Weight (0 g).
- Then specify the total number of sites (in mols) for each binding site in moles and make any appropriate changes to the default values for Specific Area and Weight.
- Choose the appropriate diffuse layer model for the surface reaction (please see the PHREEQC manual for information on selecting the appropriate Diffuse Layer Option for your surface reactions).

To remove a binding site from the Surface Assemblage, select the binding site you would like to remove and then press the **[Remove]** button.

Option 2

AquaChem provides a dropdown list of available solutions to choose from.

Once you have defined the Surface Assemblage, you must select the solution you wish to equilibrate with. If you do not select a solution from the list, you can save the Surface Assemblage to equilibrate in a later simulation step (e.g. during a transport problem).

Each Surface Assemblage is identified by a unique **Number** and a **Description** so they can be easily recognized in the **Summary** tab and reused in later simulations.

7.3.9 Transport Frame

The transport capabilities of PHREEQC are derived from a more complete formulation of one-dimensional, advective, dispersive transport presented by Appelo and Postma (1993). Most of the data for the transport simulation must be specified prior to activating the **Transport frame** itself. This is done in the various other **PHREEQC Input** file tabs.

The way the PHREEQC transport simulation works is to represent your aquifer with a column that is partitioned into cells which are saturated with an initial solution. A cell is defined as the volume of porous media containing 1 litre of solution.

PHREEQC allows you to define an individual pure phase assemblage, an exchange assemblage, a gas phase assemblage or an initial solution for every cell. However, you will often find it useful to assign the same aquifer properties to multiple cells. For example cells 1-5 might contain calcite, whereas cells 6-10 might contain dolomite and an exchanger. The specified system is then flushed once, or several times, with another solution. The changes to the aquifer (the pure phase, the exchanger, and the gas phase) and the flushing solution are calculated by PHREEQC for every shift from one cell to the next cell. In a 10 cell column the entore set of the solution and the aquifer parameter will be written 10 times to the output file for every flush. Since you are usually interested in the behaviour of a very limited number of parameters, it is a good idea to disable the generic output file and instead write the results to a customized spreadsheet format (see section 7.3.1 on page 142).

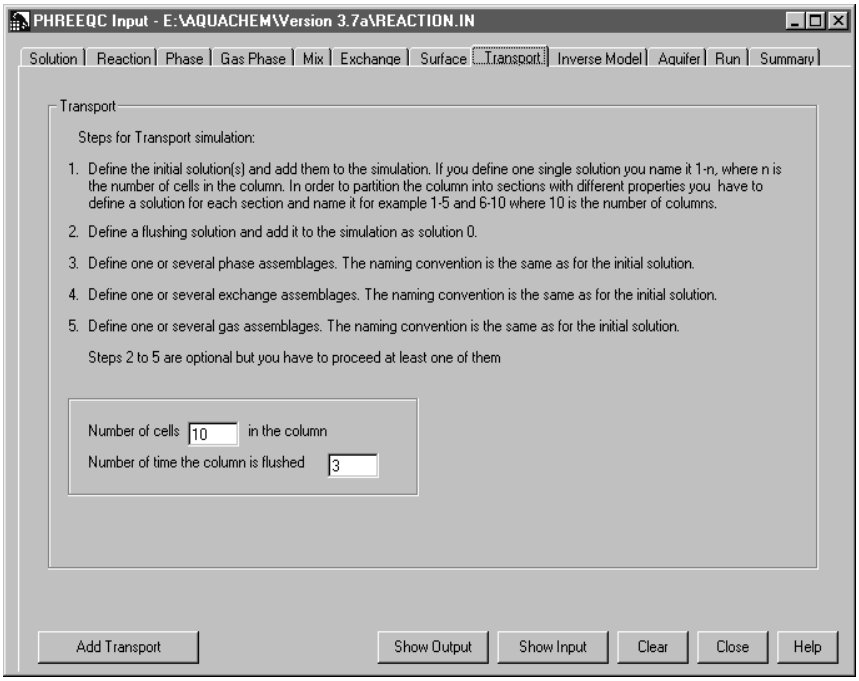

Figure 7.10: Transport frame

Example (Ex. 9 from the PHREEQC manual)

The chemical composition of the effluent from a column containing a cation exchanger is simulated. Initially, the column contains a sodium-potassium nitrate solution in equilibrium with the cation exchanger. The column is then flushed with three pore volumes of a calcium chloride solution. Calcium, potassium, and sodium react to equilibrium with the exchanger.

First define the flushing solution.

- Select a pure water solution and add **0.6** mols of **Ca** and **1.2** mols of **Cl**.
- Set the pe equal to **8**.
- Click the **[Add solution(s)]** button.

Next define the initial filling solution for cells 1-40

- Select a pure water solution and add **1.0** mols of **sodium**, **0.2** mols of **potassium**, and **1.2** mols of **nitrate**.
- Set the pe equal to **8**.
- Assign the number **1-40** to the solution to indicate that all the cells (1-40) are initially filled with this solution.
- Click the **[Add solution(s)]** button.

Finally, define the exchange assemblage which is in equilibrium with the filling solution.

- Select the **Exchange tab**
- Click on "**-X**" from the list of available exchange ions and then click the left arrow [<] button to move it to the selected Exchanger table
- Enter an Amount of **0.0011** mols
- Do not choose a solution to equilibrate with. This is used to eliminate an implic-

itly defined reaction, after the initial solution and initial exchange composition have been calculated. **0.0011** mol is the number of exchange sites per cell.
- Click the **[Add Exchange]** button.
- Select the **Transport tab**.
- Enter the number of cells in the column (**40**) and number of times the column is flushed (**3**).
- Click the **[Add Transport]** button.
- Select the **Run tab**.
- Under **Selected Output** tab, choose the option to **Save results to a text file**.
- Select **Na**, **Cl**, **K**, and **Ca** from the Totals list (to select multiple records from this list keep the **<Ctrl>** key depressed while selecting elements with the mouse).
- Click the **[Complete Simulation]** button and then click **[Run PHREEQC]**.

If you would like to view the PHREEQC input file, choose **File/View PHREEQC Input** from the drop down menu or press the **[Show Input]** button.

The PHREEQC input data file should look similar to the one shown below:

```
SOLUTION 0 CaCl2
units mmol/l
pH 7  charge
pe 8
temp 25
Ca 0.6
Cl 1.2
SOLUTION 1-40 Initial solution for column
units mmol/L
pH 7   charge
pe 8
density 1.0
temp 25
Na 1
K 0.2
N(5) 1.2
EXCHANGE 1-40
-equilibrate  1
X 0.0011
USE exchange none
TRANSPORT
-cells 40
-shifts 120
SELECTED_OUTPUT
-file  ex9.pun
-totals  Ca   Na   K   Cl
-molalities
-activities
-equilibrium_phases
-saturation_indices
-gases
END
```

7.3.10 Inverse Modeling Options

The majority of PHREEQC simulation capabilities deal with so-called forward modelling: You start form a given initial solution, add some reactions such as exchanges, mineral solutions, etc., and it calculates the chemistry of the initial solution after the reaction processes. Inverse modeling starts from a known target solution and tries to quantify the processes that led to the observed chemistry.

With inverse modeling you must define the composition of the final solution and you must specify one more initial solutions where you assume the process starts. This initial solution(s) may be known or just estimated. For example, if you want to quantify the processes along a flowline you must have a water analysis from the recharge area and from the discharge area. On the other hand if you want to model the processes that tranform rainwater to seawater, you can choose any rainwater sample as the initial sample.

Unfortunately you cannot simply enter a initial solution and a final solution and let PHREEQC calculate the geochemical processes that may explain the observed changes between the two sampling points. You must first define the processes that may be occurring and PHREEQC calculates if these processes can create the final solution, and the quantities of each reaction that are required to do this.

Very often you will start with a very simple model. In the first results you search for those elements in the modeled target solution that show a large difference from the observed final solution. Then you add new phases and reactions that would help to reduce this error. You will continue this until there is a close match between the observed and the calculated final solution. Sometimes several models may explain the target solution chemistry. It is up to the user to decide which one is the most probable in the given hydrogeological context.

As shown in Figure 7.11, the **Inverse Modeling** tab allows you to select the Initial Solution(s) and the Final Solution from a list of pre-defined solutions. Only solutions you have already specified in the Solution tab will be listed in the menus.

Under the **Phase constraints** section you can specify the phases you consider responsible for the evolution of the waters. Select the phases you need from the list and click the left arrow **[<]** to transfer them to the Phase table. For each phase in the grid, you may type **dis** or **prec** to indicate whether the phase is dissolving or precipitating in the solutions. Specifying **dis** or **prec** can improve the accuracy of your output.

Under the **Element Constraints** section you can select all of the elements which should be included in the calculations, and specify the analysis uncertainty (the default is 0.02) for each element in each solution.

Refer to the USGS PHREEQC manual for a detailed explanation of the inverse modeling options.

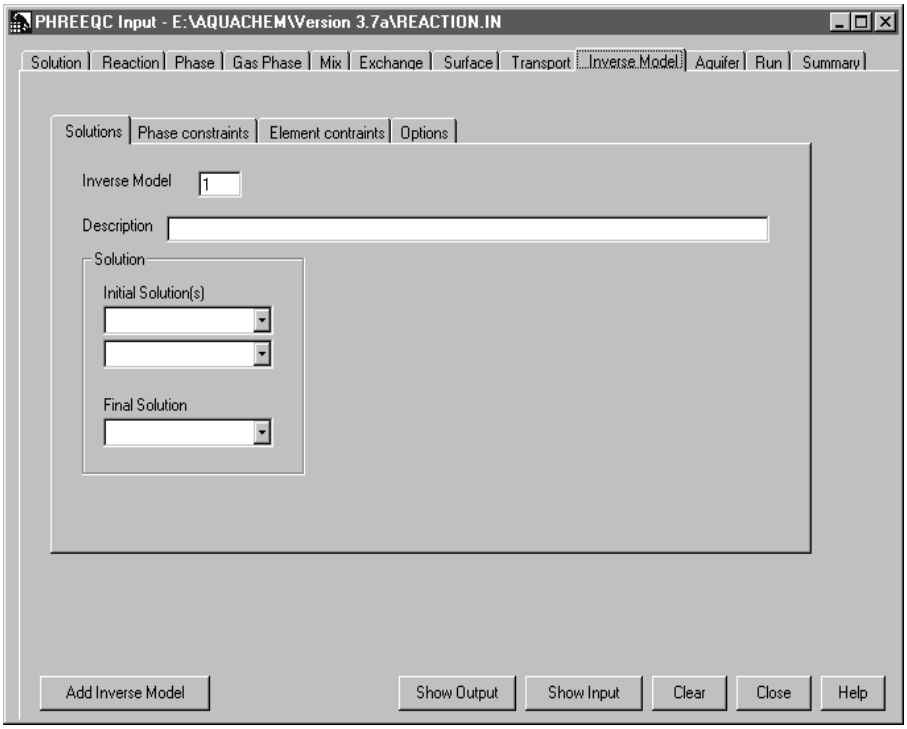

Figure 7.11: Inverse Modeling options

Example

In this exercise you will simulate a forward model and an inverse model. First you will equilibrate pure water with a set of minerals, in a forward tracking simulation. Then you will select the pure water solution and the equilibrated solution for an inverse model simulation, and compare the PHREEQC results with the original forward model.

- Select **PHREEQC\Create PHREEQC Input File** from the Main Menu.
- Select **File/Save As** and enter the name INVERSE.INP.
- Select pure water as **Solution 1**.
- Click the **[Add Solution]** button.
- Select the **Phase** tab.
- Specify the equilibration of the pure water solution (**Solution 1**) with **calcite** (SI = **0.0**), and **gypsum** (SI = **-0.5**).
- Select the **Run** tab and then select the **Save** options.
- Click-on the **Save as Solution** option, and type **2** in the text field.
- Click-on the **[Complete Simulation]** button.
- Select the **Inverse Model** tab.
- Select **Solution 1** from the Initial Solution drop down menu, and **Solution 2 (saved)** from the Final Solution drop down menu.
- Under the **Phase constraints** options, choose **Calcite** and **Gypsum** from the list, and click the left arrow **[<]** button to transfer them to the Phase table.
- Click the **[Add Inverse Model]** button.
- Click the **[Complete Simulation]** button, then click **[Run PHREEQC]**.

To view the input file choose **File\View PHREEQC Input File**. The PHREEQC input data file should look like the following:

```
TITLE
SOLUTION 1 Pure water
units mmol/l
pH 7
pe 0
density 1.0
temp 25
USE solution  1
EQUILIBRIUM_PHASES 1
Calcite  0.0
Gypsum  -0.5
SAVE SOLUTION 2
END
INVERSE_MODELING 1 Tutorial
-solutions 1   2
-uncertainty  0.02  0.02  0.02
-phases
Calcite
Gypsum
END
```

The output file, INVERSE.OUT, should contain the following information:

```
Solution 1: Pure water
             pH      7.000e+00  +   0.000e+00  =   7.000e+00
     Alkalinity      1.082e-10  +  -1.082e-10  =   0.000e+00
          C(-4)      0.000e+00  +   0.000e+00  =   0.000e+00
           C(4)      0.000e+00  +   0.000e+00  =   0.000e+00
             Ca      0.000e+00  +   0.000e+00  =   0.000e+00
           H(0)      0.000e+00  +   0.000e+00  =   0.000e+00
           O(0)      0.000e+00  +   0.000e+00  =   0.000e+00
          S(-2)      0.000e+00  +   0.000e+00  =   0.000e+00
           S(6)      0.000e+00  +   0.000e+00  =   0.000e+00
Solution 2: Solution after simulation 1.
             pH      9.189e+00  +  -1.253e-06  =   9.189e+00
     Alkalinity      5.230e-05  +   0.000e+00  =   5.230e-05
          C(-4)      0.000e+00  +   0.000e+00  =   0.000e+00
           C(4)      2.615e-05  +   5.409e-11  =   2.615e-05
             Ca      6.580e-03  +   4.537e-11  =   6.580e-03
           H(0)      0.000e+00  +   0.000e+00  =   0.000e+00
           O(0)      0.000e+00  +   0.000e+00  =   0.000e+00
          S(-2)      0.000e+00  +   0.000e+00  =   0.000e+00
           S(6)      6.554e-03  +   0.000e+00  =   6.554e-03
```

The inverse modeling section of the output file should contain the following results:

```
Phase mole transfers:                  Minimum        Maximum
  Calcite     2.615e-05      0.000e+00      0.000e+00   CaCO3
  Gypsum      6.554e-03      0.000e+00      0.000e+00   CaSO4:2H2O
```

In this example, it was very easy to select the phases, because they were already known. You did not need to take into account any uncertainties or ranges. Real problems may quickly become much more complex becasue you will normally need to adjust the parameters of your inverse model several times until a satisfactory solution is found.

7.3.11 Aquifer Options

The Aquifer options is used to calculate the various aquifer properties you need for some of the PHREEQC simulations.

General Parameters

Since PHREEQC always assumes a solution volume of 1.0 litres, the General parameters calculator allow you to easily calculate the Volume of rock (litres) and mass of grains (kg) for the aquifer based on a solution containing 1.0 litres of porewater

Surface Complexations

The moles of surface places depends on the content of ferric hydrous oxides in the aquifer. Fe is generally a measured parameter but you must estimate the percentage of iron that is in the form hydrous iron. Since PHREEQC always asks for mols, you also need a formula weight value for your iron minerals. Hydrous iron is a mixture of several minerals, so a suggested value of 89 g is used as a default value.

Exchange Capacity

The **Exchange Capacity** (CEC) is normally expressed as meq/100g. If you know this value you may directly enter it and calculate the exchange places within the given aquifer volume. Otherwise you need to estimate the CEC. The first option lets you select a clay mineral from a list and will use a average CEC value. Choose this option if know the dominant clay mineral of your aquifer. If you know only the percentage but not the mineralogy of your clay minerals you may use a formula given Appelo (1993) to estimate the CEC: CEC=0.7 * clay% +3.5 * org material%.

Mineral assemblage

The **Mineral Assemblage** option lets you convert an analysis expressed as weight percent to mmol/l porewater. You must also know the formula weight for the mineral.

7.4 Importing PHREEQC Results into AquaChem

As mentioned at the beginning of this section, one of the key advantages of the AquaChem interface to PHREEQC is the direct link to the database. This direct link makes it easy to build the PHREEQC data input file using sample information from the database, and it allows you to easily import the simulation results into the database.

When you run a PHREEQC simulation, PHREEQC automatically produces a detailed output file (.OUT extension) describing each simulation step, including all of the minerals and chemical species involved. This file can often be quite large, making it difficult to

extract the information you are interested in. However, AquaChem also allows you to create a customized PHREEQC simulation output file (.PUN extension) containing only the selected output parameters you require for your database.

To create a .PUN file for the PHREEQC simulation:

- Select the **Run** tab.
- Click on the **Save Results to a Text File** option under the **Selected Output** tab.
- Select the parameters you are interested see results for, or click the **[Auto]** button to automatically select the parameters from your AquaChem database.

To import your .PUN file into an AquaChem spreadsheet:

- Select **PHREEQC\Import PHREEQC Results** from the **Main Menu**.
- Click the **[...]** button and choose the .PUN file you wish to import.

These results can be copied and pasted to other Windows applications, or directly imported into your AquaChem database.

For the purpose of importing the simulation results into the AquaChem database, you may consider that there are three types of modeled solutions:

(1) The calculation of a existing database record

(2) The calculation of a pure water sample or a modeled solution

(3) The calculation of 'Virtual' solutions (a result of a simulation involving mixing of two samples, reactions with minerals, incremental temperature increases, etc.)

7.4.1 Importing Simulation Results for Database Solutions

If your PHREEQC simulation involves only calculations performed on existing database records, then the simulation results will be immediately displayed in the spreadsheet and can be easily imported into the AquaChem database by pressing the **[Save]** button. This will read back only the modelled values such as mineral indices and activities and will replace any existing values from previous simulations. If you changed any of the measured parameter values during the preparation of the simulation solution, these changes will not be read back to the database.

7.4.2 Importing Simulation Results for Pure Water Solutions

If your PHREEQC simulation involves calculations performed on pure water solutions, you must first 'prepare' the database to import these results by creating an empty database record for each pure water solution in your simulation.

> **IMPORTANT:** Make note of the database index number for each new database record you create because you will need to assign these numbers to the Solution number for each pure water solution. If you assign a Solution number equivalent to the index number of an existing database sample, you will overwrite the modelled parameters of the existing database sample.

When you import the simulation results for pure water solutions, the simulated solution number should correspond to the daabase index number of the sample record you wish to import the information to. If the information is correct, press the **[Save]** button to read the modelled parameter values for the simulated solutions to the database records. Note that none of the measured parameter values are read from the solution into the database.

7.4.3 Importing Simulation Results for Virtual Samples

A Virtual solution is a solution that is created due to processes such as mixing of two solutions to create a new solution, step-wise reactions with minerals, and incremental temperature changes. Virtual solutions cannot simply be read back to the database since it does not correspond to one single database record. If your simulation contains virtual solutions, AquaChem will create new records in the database corresponding to the virtual solutions and will read in all of the solution information (including both measured and modelled parameters). In the **Import PHREEQC Results** window, these samples are identified by a "Y" value in the **sim** column. While reading them back to the database you are prompted for descriptor text to help identify these samples in the database.

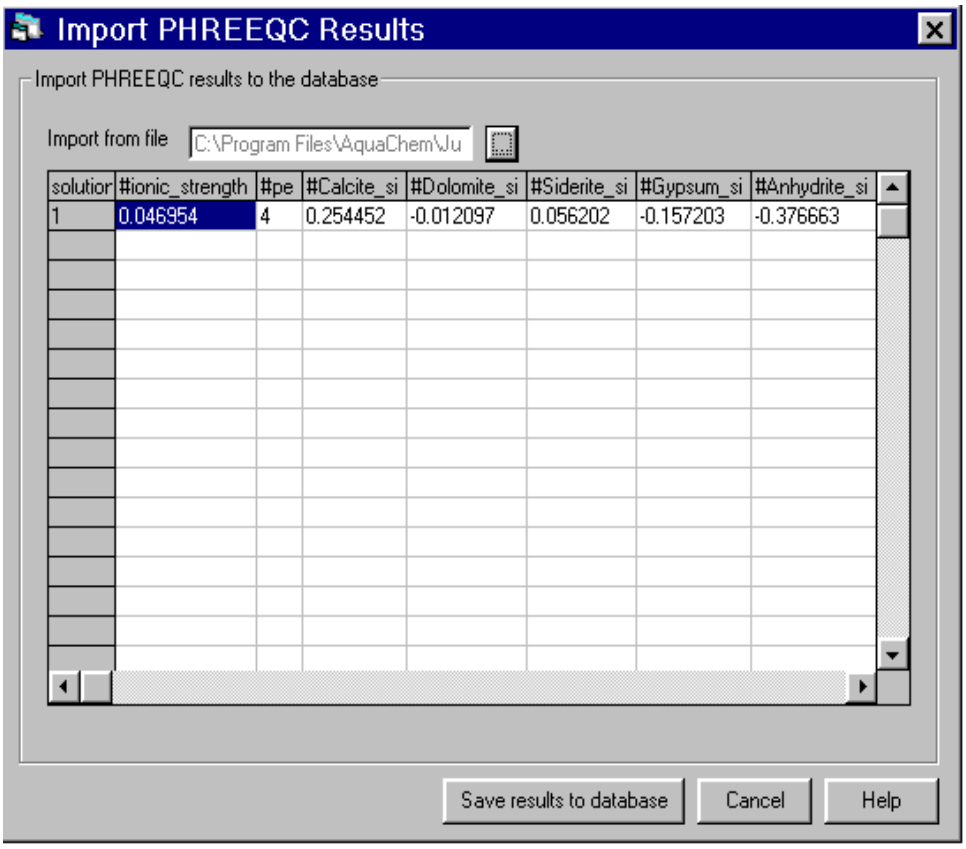

Figure 7.12: Import PHREEQC Results window

8

Creating a Database

8.1 Introduction

Database files (***filename*.HC3**) have a binary format. Each record has a fixed length, depending on the number of elements defined in the maskfile (***filename*.MSK**). Every record is composed of a string header holding text information (e.g. Location, Site, Date etc.), and a user-defined number of parameters (e.g. Na, Mg, Ca, Cl, NO_3, SO_4), each of which occupies 4 bytes.

The maskfile defines the database structure for each record in the database. It contains information of the number and type of database parameters. Before creating a new database file you must fully specify the maskfile. You may either re-use an existing maskfile, or create a new one.

A database can contain an unlimited number of sample records, depending on the number of parameters it uses and the amount of memory on your PC. Working with too many samples can slow some operations even though you are only working with a portion of the database. Working with several databases containing less than 1,000 samples is more efficient than using one large database. Samples can easily be copied from one database to another. Databases should be stored separately from the working directory, and it is recommended that one directory should be created for each AquaChem database project.

8.2 Creating A New Database

To create a new AquaChem database file,

- Close the open database by selecting **File\Close** from the **Main Menu**
- Select **File\New** from the **Main Menu**
- Type the name of the new database, and click **[Save]**
- A pop-up **Database Template** window will appear prompting you to either **Use an existing database template**, or **Create a new database template**

NOTE: When you first start using AquaChem it is highly recommended that you use the existing database template provided in the **DEMO.MSK** maskfile until you become familiar with the steps involved with creating your own database structure.

The **Parameter Group** field contains a list of each AquaChem Parameter Group as described in Section 2.6. By default, the first Parameter Group displayed is the Header Info.

The empty box on the left-hand side of the window labeled **Destination (maskfile)** displays a list of parameters that will be included in the selected Parameter Group. By default, each **Destination maskfile** (parameter list) is empty to start with.

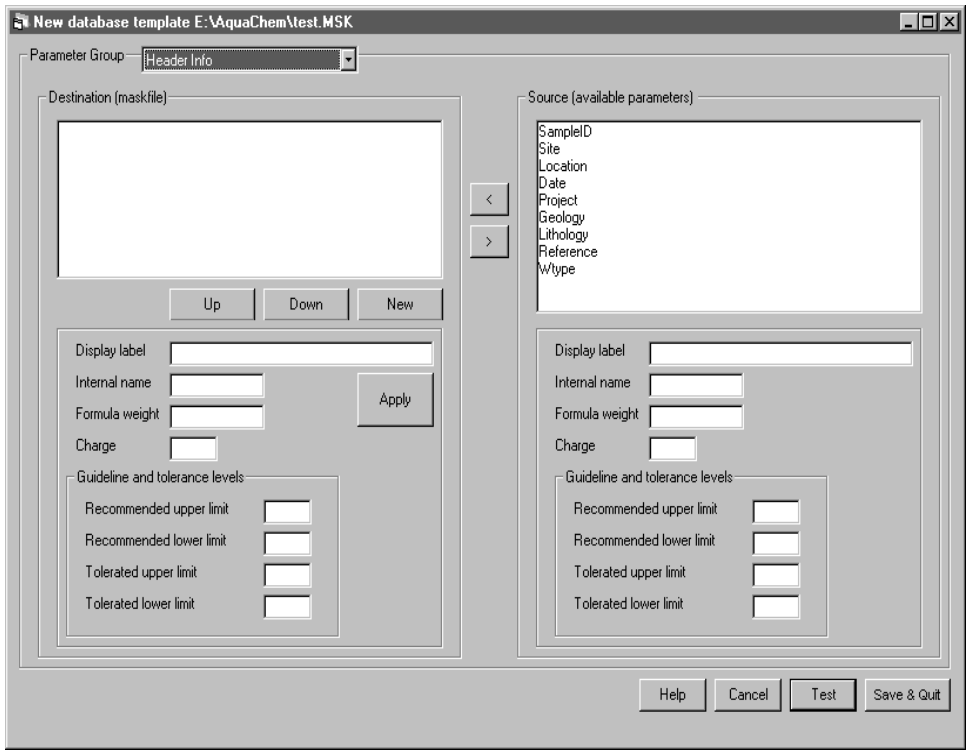

Figure 8.1: New database template window

The box on the right-hand side of the window labelled **Source (available parameters)** lists the default selection of parameters that can be added to the **Destination maskfile** from the selected Parameter Group. Each available parameter has an associated **Display label** that is used to identify the parameter in the data input form, and an **Internal name** that is used to identify the parameter for internal calculations (the **Internal name** is also used as the default axes labels for graphs). All chemical parameters should have a formula weight specified and all ions must be accompanied by their valence number which is always a positive value. **Guideline and Tolerance Levels** should be specified for substances that are involved with health issues.

> **NOTE:** If you choose to edit the **Internal name** of a parameter, it should have less than eight characters and should be unique. However, if possible, you should always use the proposed default name since certain parameters are used for internal calculations (e.g. ion ratios, geothermometers, isotope reports, etc.). If you refer to a parameter by a different name, AquaChem will not recognize it and some calculated parameters will be incorrect.

To set up the database template for your new AquaChem project you must choose the parameters that you want to include for each of the nine Parameter Groups. The number of Parameter Groups and the names of the Parameter Groups cannot be changed.

To add one of the available parameters from the **Source** list to the **Destination** list, simply click-on the parameter in the **Source** list, and then click the left arrow **[<]** button. To add

several parameters press the **<Ctrl>** button while you select multiple parameters from the **Source** list.

Use the **[Up]** and **[Down]** buttons to arrange the order of the parameters in the **Destination** maskfile.

To add a new parameter that is not included in the **Source** list, click the **[New]** button, enter the appropriate information (Display label, Internal Name, etc.) and click the **[Apply]** button to add the new parameter to the **Destination** list.

To remove a parameter from the **Destination** list, select the parameter from the **Destination** list and then click the right arrow **[>]** button.

The order of parameters in the list determines the order they will appear in the AquaChem input screen. To change this order, select an element and click [**Up**] or [**Down**] to move the parameter up and down, respectively, in the list.

Once you have finished selecting the parameters for each Parameter Group you can test the database template by clicking the **[Test]** button on the bottom left-hand corner of the **New database template** window. This will load a sample **Input** Window showing the layout of the database template that you have selected. If this is suitable click **[OK]** and then **[Save and exit]**.

AquaChem will then automatically create an Aquachem database file (*filename.hc3*) and the associated maskfile (*filename.msk*) containing the specified data structure for each record in the database.

When creating a new maskfile, you should take care to make the database structure as comprehensive as possible, so that you can use the same database structure for many types of analyses, rather than creating a new database structure for each project that you work on.

8.3 Editing an Existing Maskfile

If you need to add new sample parameters to your database that are not included in the maskfile, you will need to edit the existing maskfile.

Edit an existing maskfile as follows:

- Start AquaChem
- Load the database
- From the **Main Menu**, select **File\Preferences**
- Choose the **Data Structure** tab

You can add new parameters to the maskfile, from the extensive list of available parameters in AquaChem, or create your own new parameters. You can delete parameters from your maskfile, or change the order in which they appear in AquaChem.

To add new parameters from the list of available parameters in AquaChem, click **[Available Parameters]** under the **Data Structure** tab. The **Available Parameters** window will appear listing all of the parameters that are built in to AquaChem. Choose the Parameter Group from the drop down menu at the top of the window to display the related parameters in the **Parameters** list box.

Choose the Parameter Group you wish to expand from the **Parameter Group** drop down menu near the top of the **Data Structure** tab. Click the Parameters window and then drag the new parameter(s) into the **Parameters** list box. Click **[Up]** to change the order of the

parameters in the list. Edit the properties in the text fields to the right. Click **[Apply]** to save the changes.

To change the attributes (e.g. Display label, Tolerance level) of an existing parameter, make the necessary changes and then click the **[Apply]** button to the right of the **Internal name** field to apply the changes. If you do not click this **[Apply]** button, then the changes will not be accepted.

To add a new parameter to the maskfile, which is not listed in the **Available Parameters** window, click the **[New]** button. This will create a NEW parameter in the **Parameters** list box. Type the **Display label**, **Internal name**, **Formula Weight** and **Charge** in the text fields and then click the **[Apply]** button beside the **Display label** field.

To delete parameters from the maskfile, select the parameter you wish to delete and then click the **[Remove]** button.

Click **[Test]** at the bottom of the **Preferences** window at any time to display a mock up of the database template. Be certain that all the parameters you require are included, and that they appear in the correct order.

Do not forget to click **[Save]** at the bottom of the **Preferences** window when you wish to save the new template and close the **Preferences** window.

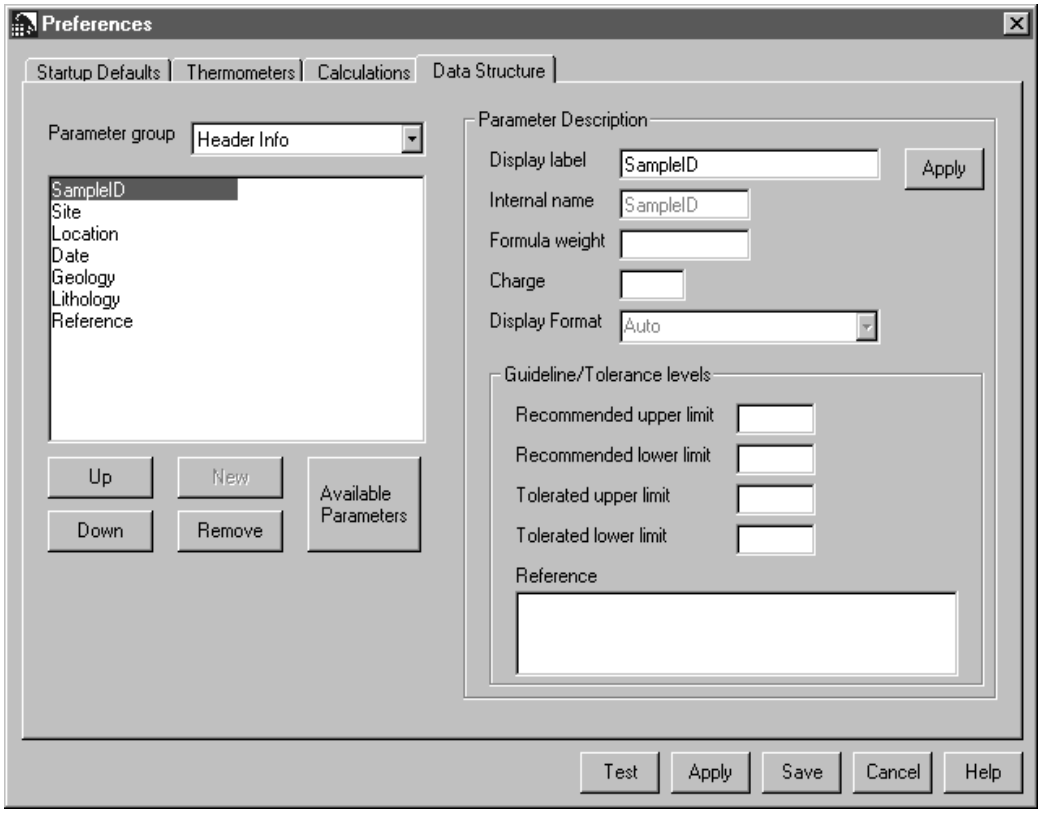

Figure 8.2: Editing an Existing Maskfile

8.4 Adding Data to a Database

Once you have created your AquaChem project database, the next step is to begin entering the sample information. Data can be imported from a tab delimited text file, or manually entered directly into AquaChem using either the **Input** window or the **Spreadsheet** view.

NOTE: AquaChem requires you to use a point "." decimal for all numeric data!

8.4.1 The Input Window

To type in new records, select **Records\New** from the **Main Menu**. The **Input** window will appear with blank cells for each parameter. Click the mouse in the upper cell of the Header Group and then enter the appropriate information. Use the **<Enter>** key to accept the value and advance to the cell below. Select **Record\Save** to add the new record to your database.

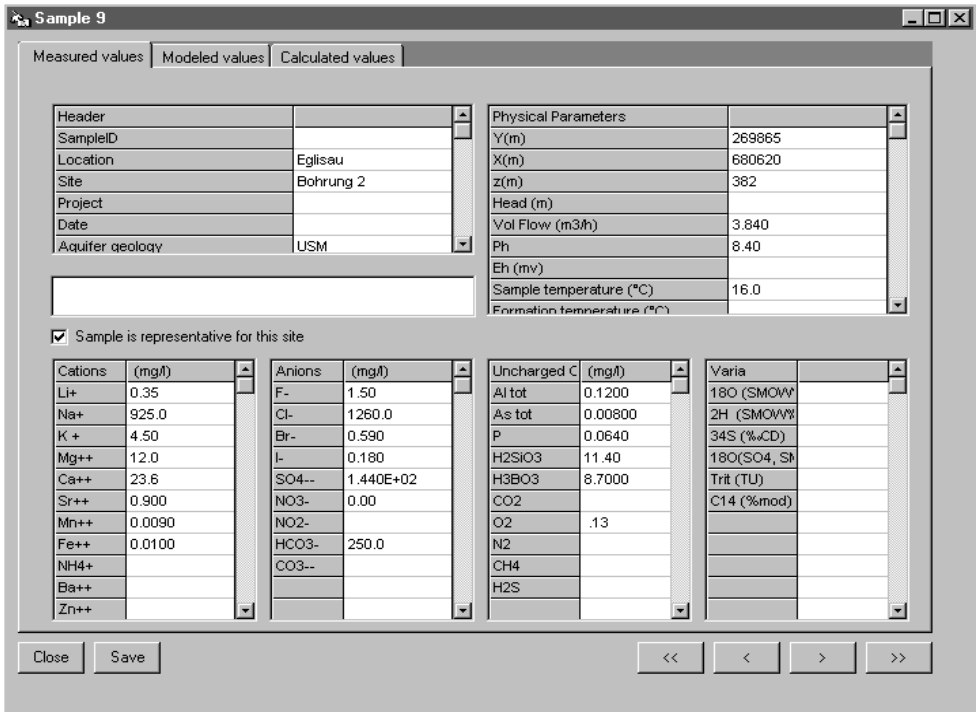

Figure 8.3: Input Window

Records can be created, edited, or viewed in the **Input** window. To display this window for a record in your database you can either:

- double click the sample in the **Record List**
- click a record in the **Record List** and select **Records\Edit** from the **Main Menu**, or
- Right-click a record in the **Record List** and select **Edit**.

You can view the **Input** window for other records by selecting the **Record\Previous** or **Record\Next** menu option. This can also be done by clicking on the push buttons at the bottom of the text window or by using the **<F8>** and **<F9>** keys.

To edit a parameter on the **Measured values** tab in the **Input** window, click on the cell that you want to edit and type the changes. Save the changes to the record by pushing the **[Save]** button at the bottom of the form or by advancing to the next **[>]** or previous **[>]** record. The values in the **Calculated values** tab are internally calculated by AquaChem and cannot be edited.

8.4.2 The Spreadsheet View

To create a spreadsheet, select **Records\View as Spreadsheet** from the **Main Menu**. The **Spreadsheet Settings** dialogue box will appear listing all of the database parameters in the maskfile. Select **[OK]** to accept the default settings or customize the spreadsheet by adding or removing parameters from the list (see Section 4.2.2 for details).

The **Spreadsheet** view lists all of the sample records in the database, one record per row in the spreadsheet, with one column per sample parameter.

Click the mouse in the target cell and then begin entering the sample information. Use the **<Enter>** key to accept the values and advance to the cell below. Changes to the spreadsheet are automatically saved to the database upon closing the **Spreadsheet** view.

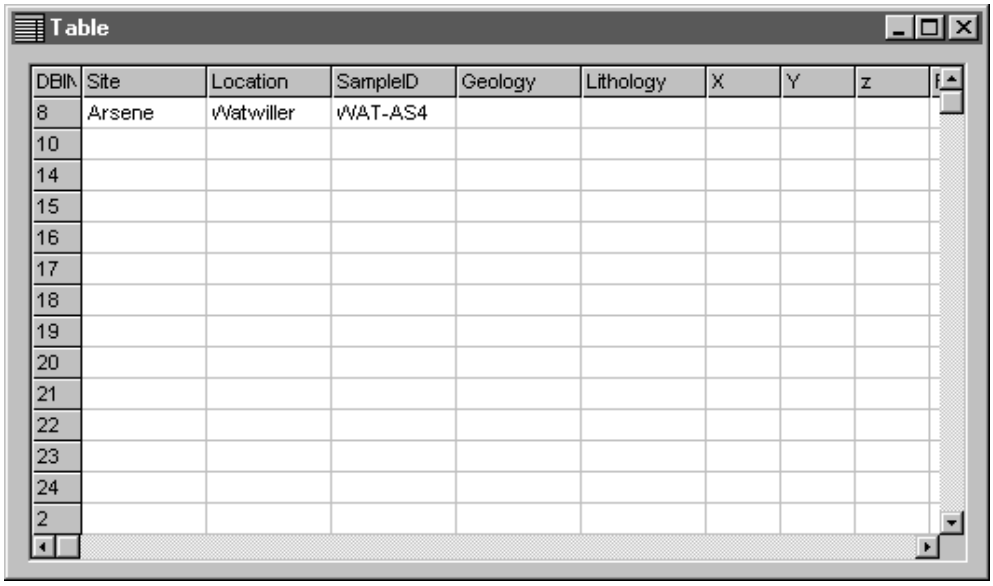

Figure 8.4: Spreadsheet view

8.4.3 Importing Data

If you already have a database or spreadsheet of your sample data and you just want to use AquaChem to analyze and plot the data, you can easily import your data from a tab-delimited ASCII text file. The data file that you import must have the following file structure: sample records as rows, parameters as columns. The first row of the tab-delimited ASCII text file must contain the parameter labels for each column of data.

To import your data file select **File/Import from ASCII** from the **Main Menu**. An Import ASCII dialogue box will display the header for the data file and the corresponding parameter

in AquaChem. To change the AquaChem parameter, double-click in the cell and choose the appropriate parameter from the list of available parameters (see Section 4.1.1 for details). Select **[OK]** to begin importing the data.

Before importing your data file, make sure that you carefully check it for the following:

- Correct date format (see **File/Preferences/Startup Defaults**),
- Consistent units throughout,
- Use decimal points "." and not commas "," for numeric parameters, and
- Don't use text values such as "N.A." or "N.D." for numeric parameters (these will be assigned a value of zero). Instead, use less than "<" or greater than ">" signs (e.g. <0.01).

9

Files

9.1 Introduction

Many AquaChem program and database parameters are configured in external files which can be modified using the tools provided in the AquaChem graphical environment. Each AquaChem database has three essential files:

- The Database File (.HC3 extension)
- The Mask File (.MSK extension)
- The Database Configuration File (.CFG extension)

The Database File and the Mask File are essentially required to open the database. If an associated Database Configuration file does not exist, AquaChem will create one with default database configuration settings.

In order to run a PHREEQC simulation you will need the following files:

- A PHREEQC Thermodynamic Database File (PHREEQC.DAT, WATEQ4F.DAT or MINTEQ.DAT)
- The PHREEQC executable file (PHREEQC.EXE)

The remaining files created and used by AquaChem include:

- Spreadsheet Report File (.RPT extension)
- Graph Configuration File (.GRF extension)
- Print Template File (TEMPLATE.TXT)

This chapter presents information about eac of the AquaChem files and their formats. You should only attempt to edit files directly if you feel confident that you understand the file structure.

9.2 Database File

Database files (***filename*.HC3**) have a binary format. Each record has a fixed length, depending on the number of elements defined in the maskfile (***filename*.MSK**). Every record is composed of a string header holding text information (Location, Site, Date etc.), and a user-defined number of parameters, each of which occupies 4 bytes.

The database structure is defined in a maskfile. A database can contain an unlimited number of samples, depending on the number of parameters it uses and the amount of memory on your PC. Working with too many samples can slow some operations even though you are only working with a portion of the database. Working with several databases containing less than 1,000 samples is more efficient than using one large database. Samples can easily be copied from one database to another. Databases should be stored separately from the working directory, and it is recommended that one directory should be created for each AquaChem database project.

9.3 Mask File

The maskfile (***filename*.MSK**) contains a list of parameters that are included in the database. For each parameter, the following values are specified:

- Display label
- Internal name
- Formula weight
- Charge
- Recommended Upper Limit
- Recommended Lower Limit
- Tolerated Upper Limit
- Tolerated Lower Limit

The AquaChem parameters are grouped into nine categories:

1	HEADER	alphanumeric parameters (Location, Site, Date…)
2	GENERAL	general numeric parameters such as pH, temperature, turbidity
3	CATIONS	positively charged ions
4	ANIONS	negatively charged ions
5	UNCHARGED	uncharged chemical elements
6	VARIA	various physical or chemical parameters such as bacteria, pesticides, isotopes, etc.
7	PHREEQC DESCRIPTION	parameters from the description section of a PHREEQC output file: Ion strength, total alkalinity, etc.
8	PHREEQC MINERALS	saturation index of the specified minerals
9	PHREEQC ACTIVITIES	activities in mol/l for specified chemical compounds

Parameters are separated by a hard return, and properties of each parameter are space delimited. There are nine blocks of parameters in the maskfile. Each block represents one of the nine categories listed above, and begins with the line "#SECTION_NAME,,,,," and ends with the line "#END SECTION_NAME,,,,,". For example, the Header block begins with "#HEADER,,,,," and ends with "#END HEADER,,,,,".

Format of Section Block

#SECTION_NAME,,,,,

"Display label", Internal name, Formula weight, Charge, Recommended upper limit, Recommended lower limit, Tolerated upper limit, Tolerated lower limit

"Display label", Internal name, Formula weight, Charge, Recommended upper limit, Recommended lower limit, Tolerated upper limit, Tolerated lower limit

“Display label”, Internal name, Formula weight, Charge, Recommended upper limit, Recommended lower limit, Tolerated upper limit, Tolerated lower limit

#END SECTION_NAME,,,,,

Example for **DEMO.MSK**

```
CATIONS
"Li+" "Li"  1    1   -999 -999 -999 -999 "EEC, 1980""Auto" 0
"Na+" "Na"  22.99 1  20  -999  200 -999 "EEC, 1980""Auto" 0
"K +" "K"   39.1 1   10  -999  12  -999 ""       "Auto" 0
"Mg++""Mg"  24.31 2  30  -999 -999 -999 ""       "Auto" 0
"Ca++""Ca"  40.08 2  100 -999 -999 -999 "EEC, 1980""Auto" 0
"Sr++""Sr"  87.62 2 -999 -999 -999 -999 "EEC, 1980""Auto" 0
"Mn++""Mn"  54.94 2  .02 -999  .05 -999 "EEC, 1980""Auto" 0
"Fe++""Fe"  55.84 2  .05 -999  .2  -999 "EEC, 1980""Auto" 0
"NH4+""NH4" 18.02 1  .5  -999 -999 -999 ""       "Auto" 0
"Ba++""Ba"  137.34 2 .1  -999 -999 -999 "EEC, 1980""Auto" 0
"Zn++""Zn"  65.37 2  .1  -999 -999 -999 "EEC, 1980""Auto" 0
"Cu++""Cu"  63.546 2 .1  -999  3   -999 "EEC, 1980""Auto" 0
"Ni++""Ni"  58.71 2 -999 -999  .05 -999 "EEC, 1980""Auto" 0
"ZR+4""Zr"  91.22 1 -999 -999 -999 -999 "EEC, 1980""Auto" 0
#END CATIONS
```

9.4 Database Configuration File

The project configuration file (***filename*.CFG)** contains the start-up conditions and the coefficients for most calculations. These calculations are performed in the AquaChem code in the following order:

Name and path of the thermodynamic database of PHREEQC

Default map file

Coefficients for meteoric waterline

Coefficients for ^{18}O-average recharge height relation

Coefficients for ^{2}H-average recharge height relation

Coefficients for ^{18}O-average annual temperature relation

Coefficients for ^{2}H-average annual temperature relation

Number of geothermometers. For each geothermometer:

- Thermometer name
- Author and year: Reference for published thermometers
- Reliability range.
- a, b: index of chemical elements used by the thermometer
- Parameter 1 Label
- Parameter 2 Label
- Parameter 1 Exponent.

Parameter 2, Exponent

Thermometer type index

Average annual temperature and geothermal gradient (° C/km)

Number of columns (attributes) in record list. For each record list parameter:

Database index and column width

Default parameters for binary graphs

Default parameters for the statistics and matrix correlation procedure

Default parameters for Schoeller plots

Maximum number of Schoeller parameters

9.5 Spreadsheet Report File

The spreadsheet report file (.RPT extension) is a binary formatted file containing indexed references to the database parameters which will be displayed in the spreadsheet view. The default spreadsheet report file (DEFAULT.RPT) is set to display every parameter in the database. However, you can customize the spreadsheet settings by deleting parameters you are not interested in and then you can save this spreadsheet setting for easy recall during another AquaChem session.

9.6 Graph Configuration File

Graph files (extension ***.GRF**) contain the entire configuration of graphs. They are created by choosing **File\Save Configuration** from the **Graphics Menu**. Only the graph configuration is saved and not the actual graphics file. Every change to the data, or to a record will automatically be updated next time you load the respective graph file. The graph files hold the following information:

- Index numbers of the selected records,
- Active symbol groups, symbol style settings and connecting line style,
- Parameters to be plotted (Na, Cl...),
- All plot titles and font settings,
- Linear regression information, and
- Symbol label settings

9.7 Print Template File

The print template file (TEMPLATE.TXT) is an ASCII formatted text file containing the settings for the various print templates available. The print template file settings include:

- Template name
- Page size
- Page orientation
- Page Margins
- Page border setting (true/false)
- Bitmap image attributes such as location, domain, and filename
- Line attributes such as start and end coordinates and line thickness
- Fixed Text attributes such as location, font, size and style
- Textbox attributes such as location, font, size and style

The print template file can be customized using the graphical tools provided in the Print Options, or you can edit the TEMPLATE.TXT file. However, manual modifications to the TEMPLATE.TXT file are not recommended unless you are very familiar with the format.

The default print template file provided by AquaChem looks like the following:

```
#NONE
PageSize 1
Orientation 0
MarginLeft 1
MarginRight 1
MarginTop 1
MarginBottom 1
Border 1
#END
#DEFAULT A4 PORTRAIT
PageSize 9
Orientation 0
MarginLeft 2.5
MarginRight 1.5
MarginTop 1.5
MarginBottom 1.5
Border 1
Bitmap 0  2  6.3  2 E:\AQUACHEM\VERSION 3.7A\LOGO.BMP
Line 0  2  17  2  0.2  0
Line 0  3.5  17  3.5  0.2  0
Line 8  0  8  2  0.2  0
Line 8  1.3333  17  1.3333  0.2  0
Line 8  0.6666667  17  0.6666667  0.2  0
Line 13  0  13  0.6666667  0.2  0
Text 8.2  0.2 PROJECT NO.:ARIAL 9 FalseFalse 0
Text 8.2  0.8666667 PROJECT:ARIAL 9 FalseFalse 0
Text 0.2  3 DESCRIPTION:ARIAL 9.75 FalseFalse 0
Text 8.2  1.5 CLIENT:ARIAL 9 FalseFalse 0
Text 13.2  0.2 DATE:ARIAL 9 FalseFalse 0
Textbox 0.2  2.5 DESCRIPTIONARIAL 9.75 FalseFalse 0
Textbox 9.8  0.8666667 PROJECTARIAL 9 FalseFalse 0
Textbox 10.3  0.2 PROJECT NO.ARIAL 9 FalseFalse 0
Textbox 9.4  1.5 CLIENTARIAL 9 FalseFalse 0
Textbox 14.2  0.2 DATE:ARIAL 9 FalseFalse 0
HeaderAPPENDIXARIAL 12 FalseFalse 0  2  0
HeaderPAGEARIAL 10 FalseFalse 0  2  1
#END
```

9.8 PHREEQC Thermodynamic Data File

The PHREEQC thermodynamic data file (**PHREEQC.DAT**) provided with AquaChem is essentially the same as a standard PHREEQC thermodynamic data file with the exception that it contains some necessary links to the AquaChem database. These links allow you to read concentrations of measured parameters from the AquaChem database records for PHREEQC input data, and to import PHREEQC simulation results back into the AquaChem database. The format for the PHREEQC thermodynamic data file is described in the following sections.

9.8.1 Input Parameters

The PHREEQC Master Species section of the PHREEQC thermodynamic datafile describes the parameters that are available for the PHREEQC input data file. The AquaChem database parameters that correspond to PHREEQC master species parameters are identified under the **#AQUACHEM** column heading as shown below. The corresponding AquaChem database parameter is identified using a '**#**' symbol in front of the **Display label** of the parameter.

```
SOLUTION_MASTER_SPECIES
#
#element species  alk   gfw_formula element_gfw   #AQUACHEM
#
H        H+       -1.   H           1.008
H(0)     H2       0.0   H
H(1)     H+       -1.   0.0
E        e-       0.0   0.0          0.0
O        H2O      0.0   O           16.00
O(0)     O2       0.0   O                        #O2
O(-2)    H2O      0.0   0.0
Ca       Ca+2     0.0   Ca          40.08        #CA
Mg       Mg+2     0.0   Mg          24.312       #MG
Na       Na+      0.0   Na          22.9898      #NA
K        K+       0.0   K           39.102       #K
Fe       Fe+2     0.0   Fe          55.847       #FE
```

It is important to note that the spelling of the parameters in the PHREEQC.DAT file (e.g. **#Na**) must be consistent with the spelling of the parameter **Display label** in the AquaChem database file (e.g. **Na**). If you create or edit an AquaChem database and you add some of the Master Species parameters that are not currently included, then you will need to modify the PHREEQC.DAT file accordingly, including the links between the Aquachem parameters and the Master species.

9.8.2 Calculated Parameters

The link between the modeled parameters which are calculated by PHREEQC (activities, saturation indices) is different than with the Master Species. The AquaChem database must use the same names as in the PHREEQC thermodynamic data file.

In the AquaChem database, the PHREEQC Minerals must be spelled exactly the same as in the PHREEQC.DAT file and preceeded by "**#**" (e.g. **#CALCITE**).

In the AquaChem database, the PHREEQC Activities must be spelled exactly the same as in the PHREEQC.DAT file and preceeded by a "#" and followed by a "_la" where "la" stands for "log activity" (e.g. for Sr which is spelled SR+2 in PHREEQC.DAT, the AquaChem PHREEQC Activities parameter would be #SR+2_la). This has been done in order to dinstinguish the measured parameters in the database from the modelled ones.

The minerals and activites are directly read from the PHREEQC thermodynamic data file in the **Preferences/Startup Defaults** screen.

It is important to note that you should not change the default name of the modeled parameters in the maskfile. The necessary labels (e.g. #Sr+2_la) are automatically built into the database maskfile as shown below.

PHREEQC MINERALS,,,,,

"Calcite" #Calcite_si -999 -999 -999 -999 -999 -999

"Dolomite" #Dolomite_si -999 -999 -999 -999 -999 -999

"Siderite" #Siderite_si -999 -999 -999 -999 -999 -999

"Gypsum" #Gypsum_si -999 -999 -999 -999 -999 -999

"Anhydrite" #Anhydrite_si -999 -999 -999 -999 -999 -999

"Celestite" #Celestite_si -999 -999 -999 -999 -999 -999

"Barite" #Barite_si -999 -999 -999 -999 -999 -999

"Fluorite" #Fluorite_si -999 -999 -999 -999 -999 -999

"Chalcedony" #Chalcedony_si -999 -999 -999 -999 -999 -999

"Quartz" #Quartz_si -999 -999 -999 -999 -999 -999

"CO2(g)" #CO2(g)_si -999 -999 -999 -999 -999 -999

"O2(g)" #O2(g)_si -999 -999 -999 -999 -999 -999

#END PHREEQC MINERALS,,,,,

PHREEQC ACTIVITIES,,,,,

"BA+2" #BA+2_la -999 -999 -999 -999 -999 -999

"CA+2" #CA+2_la -999 -999 -999 -999 -999 -999

"FE+2" #FE+2_la -999 -999 -999 -999 -999 -999

"K+" #K+_la -999 -999 -999 -999 -999 -999

"MG+2" #MG+2_la -999 -999 -999 -999 -999 -999

"SR+2" #SR+2_la -999 -999 -999 -999 -999 -999

"F-" #F- -999 -999 -999 -999 -999 -999

"HCO3-" #HCO3-_la -999 -999 -999 -999 -999 -999

"SO4-2" #SO4-2_la -999 -999 -999 -999 -999 -999

#END PHREEQC ACTIVITIES,,,,,

10

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