M3 User's Manual

Version 3.0

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SKB

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Abstract

Hydrochemical evaluation is a complex type of work, carried out by specialists. The outcome of this work is generally presented as qualitative models and process descriptions of a site. To support and help quantify the processes in an objective way a multivariate mathematical tool named M3 (Multivariate Mixing and Mass balance calculations) has been constructed. The computer code can be used to trace the origin of the groundwater and calculate the mixing portions and mass balances even from ambiguous groundwater data. The groundwater composition used traditionally to describe the reactions taking place in the bedrock can now be used to trace the present and past groundwater flow with increased accuracy.

The M3 code is a groundwater response model, which means that the changes in the groundwater chemistry in terms of sources and sinks are traced in relation to an ideal mixing model. The complexity of the measured groundwater data determines the configuration of the ideal mixing model. Deviations or similarities with the ideal mixing model are interpreted as due to mixing or reactions. Assumptions concerning important mineral phases altering the groundwater or uncertainties associated with thermodynamic constants do not affect the modelling because the calculations are solely based on the measured groundwater composition.

M3 uses the opposite approach to that of many standard hydrochemical models. In M3 the mixing processes are evaluated and calculated first. The constituents that cannot be described by mixing are described by reactions. The M3 model consists of three steps: the first step is a standard principal component analysis, followed by mixing and finally mass balance calculations. The measured groundwater composition can be described in terms of mixing portions in % and the sink/sources of an element associated with reactions are reported in mg/l.

Sammanfattning

Hydrokemiska utvärderingar är vanligtvis ett komplext arbete som utförs av specialister. Resultatet av detta arbete presenteras ofta i form av kvantitativa modeller och processbeskrivningar. För att underlätta kvantifieringen och objektiviteten i utvärderingen av grundvattenkemin har ett multivariat matematiskt verktyg konstruerats. Datorprogrammet och konceptet kallas M3 (Multivariate Mixing and Mass balance calculations). Verktyget kan användas för att spåra grundvattnets ursprung, beräkna blandningsproportioner samt för att utföra massbalansberäkningar även i sådana fall där grundvattendata annars är svårtolkade. Grundvattensammansättningen, som traditionellt använts för att beskriva reaktioner som sker i berggrunden, kan nu med ökad noggranhet användas för att spåra moderna eller forntida grundvattenflödens effekter på grundvattenkemin.

M3 programmet är en så kallad grundvattenresponsmodell, vilket betyder att förändringarna i grundvattenkemin undersöks i förhållande till en idealisk blandningsmodell, som konstrueras för det aktuella området. Komplexiteten i uppmätta data bestämmer den idealiska blandningsmodellens konfiguration. Avvikelserna eller likheterna med den idealiska blandningsmodellen antas vara ett resultat av blandning eller reaktioner. Antaganden gällande sammansättningen av sprickmineral eller osäkerheter i termodynamiska konstanter påverkar inte modelleringen, eftersom beräkningarna endast utgår från den uppmätta grundvattensammansättningen.

I M3 använder man sig av ett omvänt angreppssätt jämfört med många andra hydrokemiska modeller av standardtyp. Först beräknas och utvärderas blandningsprocesserna. De förändringar i grundvattenkemin som inte kan beskrivas med blandning förklaras med reaktioner. M3 består av tre steg: det första steget är en vanlig principalkomponentanalys, följt av blandnings- och slutligen massbalansberäkningar. Den uppmätta grundvattensammansättningen kan beskrivas i termer såsom blandningsproportioner i % eller som tillskott eller förluster i mg/l av elementhalter som är asocierade med reaktioner i berget.

Summary

This report describes the **M**ultivariate **M**ixing and **M**ass balance calculations (M3). This new method and computer code is developed to trace the mixing and reaction processes in the groundwater. The aim of the M3 concept is to decode the often hidden and complex information gathered in the groundwater analytical data. The manual presents shortly the theory and practice behind the M3 method. The M3 computer code is also presented and emphasis is put on the reference manual. This includes detailed reference to the M3 program's abilities and limitations, installation procedures and all functions and operations that the program can perform. It also describes sample cases of how the program is used to analyse a test data set. This guide is part of the Help Files distributed together with M3.

Two accompanying reports cover other aspects:

- Concepts, Methods, and Mathematical Formulation, /Gómez et al. 2006/ gives a complete description of the mathematical framework of M3 and introduces concepts and methods useful for the end user.

- M3 version 3.0: Verification and Validation, /Gómez et al. 2009/, gathers a collection of validation and verification exercises, designed to test each part of M3 code and to build confidence in its methodology.

The M3 method has been tested and modified over several years. The development work has been supported by the Swedish Nuclear Fuel and Waste Management Company (SKB). The main test site for the model was the underground Äspö **H**ard **R**ock **L**aboratory (HRL). The examples used in this manual are from a Äspö international groundwater modelling co-operation project where one of the tools used was M3. The M3 concept has been applied on the data from SKB's site investigation programme and in data from Canada, Japan, Jordan, Gabon and Finland.

The groundwater composition is a result of mixing processes and water-rock interaction. Standard groundwater models based on thermodynamic laws may not be applicable in a normal temperature groundwater system where equilibrium with many of the bedrock minerals is not reached and where biological processes seem to play a central role in the groundwater altering process. The major purpose of standard groundwater chemical codes is to describe the measured groundwater composition in terms of reactions. The constituents that cannot be described by reactions are described by mixing using one or several conservative tracer. The M3 model uses an opposite approach compared to the standard methods. In M3 the mixing processes are evaluated and calculated first. This is possible due to the use of multivariate techniques to construct an ideal mixing model of a site. Many variables employed in multivariate analysis are needed to trace and describe the complex mixing processes taking place in the groundwater. The information is used to construct an ideal mixing model of a site. The complexity of the measured groundwater data determines the configuration of this ideal mixing model. The constituents that cannot be described by mixing are described by reactions.

The M3 model consists of three steps; the first step is a standard Principal Component Analysis (PCA), followed by mixing and finally mass balance calculations. In order to take as many relevant elements as possible into consideration PCA is used to summarise and simplify the groundwater information. The M3 model compares the measured groundwater composition of each sample to known well-sampled waters named reference waters by using the results of the PCA. All the measured groundwater compositions at a site are compared to these reference waters. The mixing calculations (ie, mixing portions as a percentage of a selected reference water) determine how much of the observed groundwater composition is due to mixing from the selected reference water. The mass balance calculations (reported in terms of sinks/sources of groundwater constituents in mg/l or moles) determine how much of the measured groundwater constituents is a result from water-rock interaction. Since the calculations are relative to the selected reference waters, modelling can only describe changes in terms of mixing and reactions taking place between the reference waters. The results can be used to describe both mathematically and quantitatively the groundwater characteristics, rather than qualitatively as is often the case in a site description of the groundwater chemistry.

The M3 method can be used for tracing the evolution, past-present dispersion and water-rock interactions. The outcome from the modelling can be reported in non-hydrochemical terms such as changes in mixing portions or in gain/losses due to mass balance reactions. The comparison with hydrogeological models is easier since the results from the M3 model can be compared to the results from the hydrodynamic models. The effect on the groundwater composition observed from biological reactions such as organic decomposition or sulphate reduction can be traced. In groundwater chemical response modelling such as M3 information concerning fracture mineralogy, thermodynamic data bases or groundwater flow directions are not included. The model concentrates solely on tracing changes in the measured groundwater composition which can be interpreted as a result of mixing and reactions.

The validity of the modelling has to be examined carefully using expert knowledge in the areas of hydrochemistry, hydrogeology and alternative modelling together with mathematical validations and verification exercises.

The M3 computer program is a standalone program developed in the MATLAB 7.1 computation environment /MATLAB 2005/. The M3 toolbox calculates and displays the results both as graphs and numerical data. In addition, it offers the user several ways of examining and interpreting data.

Included with the M3 program is an online version of the reference manual, as well as MATLAB libraries required to run the program. The M3 program has been tested on Windows 2000 and XP.

Contents

1 The M3 method

This M3 (**M**ultivariate **M**ixing and **M**ass balance calculations) manual starts with an introduction to the M3 concept /Laaksoharju et al. 1999c/. A detailed account is given of how M3 traces the origin and evolution of groundwater compositions by first calculating the mixing processes and then the contributions from reactions. This is a different approach to other standard methods, which use the reactions as a starting point, rather than the mixing, when describing the groundwater evolution. The next chapter includes the M3 reference manual, showing all the features of the toolbox. The M3 computer program is a standalone program developed in the MATLAB 7.1 computation environment /MATLAB 2005/. The M3 toolbox calculates and displays the results both as graphs and numerical data. In addition, it offers the user several ways of examining and interpreting data. Included with M3 is an online version of the reference manual, as well as MATLAB libraries required to run the program. The M3 program has been tested on Windows 2000 and XP. In the last section of the chapter two step by step examples of M3 modelling using the M3 toolbox is shown. The appendix gives an example of modelling performed at the Äspö Hard Rock Laboratory.

1.1 Background to the development of the M3 method

As already stated, the underlying hypothesis behind M3 is that *the origin and evolution of the groundwater can be described if the effects of mixing and reactions can be examined separately*. Starting with the mixing and letting those constituents that cannot be explained by mixing be described by reactions, rather than approaching reactions first and allowing mixing to explain the constituents, makes modelling simpler since less prerequisite information is needed. A simple two component mixing mass balance model was described by /Laaksoharju et al. 1999d, Smellie and Laaksoharju 1992/. The main aim of the model was to differentiate in the groundwater between what is due to mixing and what is due to water-rock reactions by using one variable e.g. Cl as a conservative tracer. A basic feature of this method is the identification of the original source water types that all others are mixed from. These original types of waters are called end-members. However, the model seemed to have limitations when tracing a more complex system involving several end-members. The real dynamics of the system may thus remain undetected and the processes behind the measured groundwater composition could be misinterpreted. Many variables are important for the understanding of the transport, mixing processes and reactions taking place in the groundwater system, such as Cl, $\delta^{18}O$ and $\delta^{2}H$. The information gathered in many variables can best be handled by using multivariate techniques.

A new method named M3 (Multivariate Mixing and Mass balance calculations) was developed in order to identify with a higher resolution the contribution of the observed groundwater composition from mixing and reactions /Laaksoharju et al. 1999d/. The method is based on a Principal Component Analysis followed by a mixing and mass balance calculation once proper end-members have been identified and defined. The novel feature of this method is to use the result from the principal component analysis as a basis for calculating the effects of mixing and reactions.

The M3 method has been tested and modified over several years on contract from the Swedish Nuclear Fuel and Waste Management Company (SKB).

*   The main test site for the model has been the underground Äspö Hard Rock Research Laboratory /Smellie and Laaksoharju 1992, Laaksoharju et al. 1995a, b, Laaksoharju and Wallin 1997, Laaksoharju et al. 1999a, b, c, d.

*   M3 has also been used in several natural analogs as Cigar Lake, Canada /Smellie and Karlsson, 1996, Laaksoharju et al. 2000/; Maqarin, Jordan /Waber et al. 1998, Smellie (ed) 2000/; Oklo, Gabon /Gurban et al. 1998, 1999, 2003/; Palmottu, Finland /Laaksoharju et al. 1999a/; and Tono Mine, Japan /Yamamoto et al. 2005/.

*   More recently M3 has been used for SKB's Site Characterisation Programme in Forsmark, Sweden /Laaksoharju and Gurban 2003, Laaksoharju et al. 2004b, Laaksoharju 2005,

Laaksoharju et al. 2008/ and Laxemar, Sweden /Laaksoharju et al. 1995b, Laaksoharju 2004, Laaksoharju et al. 2004d, Laaksoharju 2006, Laaksoharju et al. 2009/.

- M3 was also used for SKB's Performance Assessment SR-97 /SKB 1999a, b/.

- M3 has also been used in inter-comparison exercises together with other multivariate statistical methods /Rhén and Smellie 2003/.

- /Olofsson et al. 2005/ have used M3 to trace the movement of leachates at waste sites.

- Papers and reports where M3 is documented include: /Laaksoharju 1999, Laaksoharju et al. 1999b, c, 2004a, c, 2008a, b/, and /Gómez et al. 2006, 2008, 2009/.

The latest version of M3 (v3.0) has enough new features to deserve a thorough update of the 1999 manual. The added functionality of M3 v3.0 tries also to overcome some criticisms raised by specific methodological steps in previous versions, mainly those regarding the use of only two principal components to compute mixing proportions and those regarding the selection of end-members.

Besides the added capabilities, an extra reason to update the documentation is to comply with recent QA regulation to be imposed on all codes used in SKB's Site Investigation programme /SKB 2003, SKB 2004, Hicks 2005/.

/Hicks 2005/ points out that "the results [of the review process of several codes] show that there are varying standard of code documentation and testing with some room for improvement in certain areas". Specifically, Hicks' conclusions for M3 state that "/Laaksoharju et al. 1999b/ provide a comprehensive description of how to run M3. However, no details of the implementation of Principal Component Analysis (PCA) theory and the mass balance calculation method have been identified in any of the references reviewed under this project." To overcome these shortcomings in the documentation and testing of M3 /Gomez et al. 2006/, provided a new report "Concepts, Methods, and Mathematical Formulation, 2006" and a verification and validation report /Gomez et al. 2009/.

What can M3 do

M3 is able to:

- Perform a principal component analysis on a dataset (each row a sample, each column a compositional variable). The benefits of using M3 increase when the size of the dataset increases.

- Plot the results in two and three dimensions using the first two or first three principal components as coordinate axes, respectively (PC-plots).

- Perform a mixing calculation using two or all the principal components once a set of end-members have been defined. This mixing calculation step gives the percentage of each end-member in every sample in the dataset.

- Colour-code each sample in a PC-plot with respect to the contribution of each end-member to the mixing.

- Calculate, for each sample in the dataset, a "theoretical" composition from the above mixing proportions. This "theoretical" composition is that which the sample would have if mixing were the only process affecting its composition *and* if the end-members had been properly selected.

- Perform a mass balance calculation by subtracting the real composition of a sample from the computed ("theoretical") composition. Because the computed composition reflects pure mixing, the difference between the real and the computed compositions is interpreted by M3 as a mass balance, i.e. elements that have been enriched or depleted with respect to pure mixing.

- Via the End-member Selection Module, select the best combination of end-members for a given dataset. This selection procedure is semi-automatic but the user has first to produce a number of end-members (this number could be high) that are believed to have been involved in the genesis of every water sample in the dataset.

- Via the End-member Variability Module, give mixing proportion ranges for a given sample from ranges in the chemical composition of the selected end-members. The ranges in the chemical composition of the end-members are supplied by the user.

All these possibilities are explained in detail in the Concepts, Methods, and Mathematical Formulation, by /Gomez et al. 2006/.

What M3 cannot do

M3 is not able to:

- Interpret in terms of reactions the mass balance calculation step. This is left to the user after taking into account a wide range of background information on the system being studied.

- Separate the effect of a chemical reaction from a pure mixing if the final result of both is identical. In other words, if a chemical reaction has the same effect on the composition of a water sample (considering only the compositional variables that have been used in M3) as a pure mixture of specific end-members, M3 would say that the mass balance is zero and therefore, that the sample can be "constructed" only by the mixing of the selected end-members. It is up to the users to assess the likelihood of one or the other outcome (again, after a careful geochemical and hydrological study of the system).

- Guarantee that the selected set of end-members is the best set in *absolute* terms. It can only assure that it is the best out of all the possibilities covered by the extended set of end-members included in the End-member Selection Module.

- Perform reaction path calculations as many geochemical codes like PHREEQC /Parkhurst and Appelo 1999/ or WATEQ4F /Ball and Nordstrom 2001/.

- Perform reactive transport calculations.

1.2 M3 calculations

1.2.1 Introduction to M3

All the measured groundwater composition is compared to some well-sampled and analysed groundwater of the site, known as a *reference* water. The M3 method compares the measured groundwater composition of each sample to the selected reference water composition. The modelling is therefore always relative to the selected reference water composition just as a measured altitude is relative to a chosen fixed point. A reference water can be a modelled or sampled (extreme) groundwater e.g. glacial melt water, ancient sea water, brine water or rain water, dilute shallow groundwater or sea water.

The number and type of reference waters to be selected in the modelling depend on the aim of the modelling and the complexity of the site. The groundwater data used in the modelling determines the minimum number of reference waters needed to describe the observed groundwater composition. The mixing calculations (reported as mixing portions of the reference water) determine how much of the observed groundwater composition is due to transport and mixing. The mass balance calculations (reported in terms of sinks/sources of groundwater constituents in mg/l) determine how much is a result from water-rock interaction. Since the calculations are relative to the selected reference waters, modelling can only describe changes in terms of mixing and reactions taking place between the reference waters. The results can be used to describe both mathematically and quantitatively the groundwater characteristics rather than qualitatively as is often the case in traditional description of the groundwater chemistry.

1.2.2 Calculation steps in M3

M3 was constructed to explain **how** and **why** we obtain the measured groundwater composition. The M3 method consists of 3 steps:

1 A standard **M**ultivariate technique, called **P**rincipal **C**omponent **A**nalysis (PCA) is used for cluster analyses of the data by using the major components Cl, Ca, Na, Mg, K, SO_4 and HCO_3 in combination with the isotopes ^2H, ^{18}O and ^3H. The chosen variables are generally relatively easy to analyse with a high analytical accuracy and they are known to describe the major groundwater features. Generally, dependent on the analytical program, there may be other variables than those suggested which can also contain important information concerning the evolution of the

groundwater at a site. Such variables should then be included in the PCA analyses. In other cases, where isotopes are not analysed, this may cause lower resolution in M3 modelling. The PCA aims to describe as much as possible of the information from the variables in the first principal component. The rest of the information is described by the second, third, etc principal components, each one explaining less and less variance. The principal components are equations of linear combinations used to summarise most of the information in the data. The weights of the different variables in the equations are calculated automatically by the PCA. For the first two principal components a x, y scatter plot can be drawn. The x is the equation for the first principal component and y the equation for the second principal component. The plot is named the PC-plot and is used to visualise the clustering of the data as well as to identify reference waters. Careful examination of the PCA can provide additional information as to the origin, complexity and relationship of the groundwater system. Lines are drawn between the chosen reference waters so a polygon is formed (see Figure 1-1a and b). By definition the selected reference waters can only describe the samples inside the polyhedron whose vertices are the reference waters. The number of selected reference waters should be the minimum required to describe the observations.

2   Mixing calculations are used to calculate the mixing contribution of the reference waters to the observed groundwater composition. The calculated mixing portion can be used to evaluate, the origin of the groundwater and possible flow paths. The mixing portions are relative to the linear distance to the selected reference waters in the PCA space (see Figure 1-1c).

3   Mass balance calculations (deviation calculations) are used to define the sources and sinks for different elements which deviate from the ideal mixing model based on the mixing of reference waters (see Figure 1-1d). No deviation from the measured value indicates that mixing can explain the element behaviour, whereas source or sink is due to net reactions. The evolution caused by water-rock interactions can thus be described.

Five reference waters were chosen at the Äspö site: brine, glacial, Baltic Sea, altered marine and meteoric (Figure 1-1b). The M3 model describes the origin and evolution of the groundwater chemistry as a result of mixing and mass balance reactions which can be either biogenic or inorganic[1]. If soil processes are of particular interest, rain composition rather than shallow water composition should be used as a reference water in the modelling. If the reference water is changed then all the calculations have to be redone since all the observations are now relative to the new reference water composition and a different system is described.

The above calculations can be performed by using the current M3 toolbox. In the following sections the principal component analysis, mixing and mass balance calculations are described in more detail.

Principal component analysis

Since the groundwater is complex (several variables are needed to understand the system) a multivariate technique helps to trace and thus increase our understanding of the system. The use of multivariate techniques to search for structure in geological data has been described by /Joreskog et al. 1976, Davis 1986, Howard 1991/. Factor analysis has been used together with geochemical reasoning to identify groundwater end-members and their contributions to the measured groundwater composition /Kimball 1992/.

The technique used in M3 is a nearly one-hundred-year-old standard multivariate technique named **P**rincipal **C**omponent **A**nalysis (PCA) described by /Pearson 1901/. The method is generally used for classification, simplification of the data and finding the most important variables in a data set /Chatfield and Collins 1989, Kimball 1992/. The equations used in PCA are described in most standard multivariate textbooks, such as /Chatfield and Collins 1989/. Rather than examining two variables at a time in a x, y plot or perhaps three variables in a 3D plot (x, y and z), all the variables in a data set can be examined simultaneously by use of the PCA method. In PCA a set of interrelated variables are mathematically transformed into a new coordinate system in which the axes (principal components) are linear combinations of the original variables and are mutually uncorrelated (i.e. orthogonal). The new transformed variables, called principal components, together account for the

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[1] A calculated portion of eg, meteoric water based on the reference water composition sampled in a shallow borehole may be 20% higher than the same water based on an end-member composition such as rain.
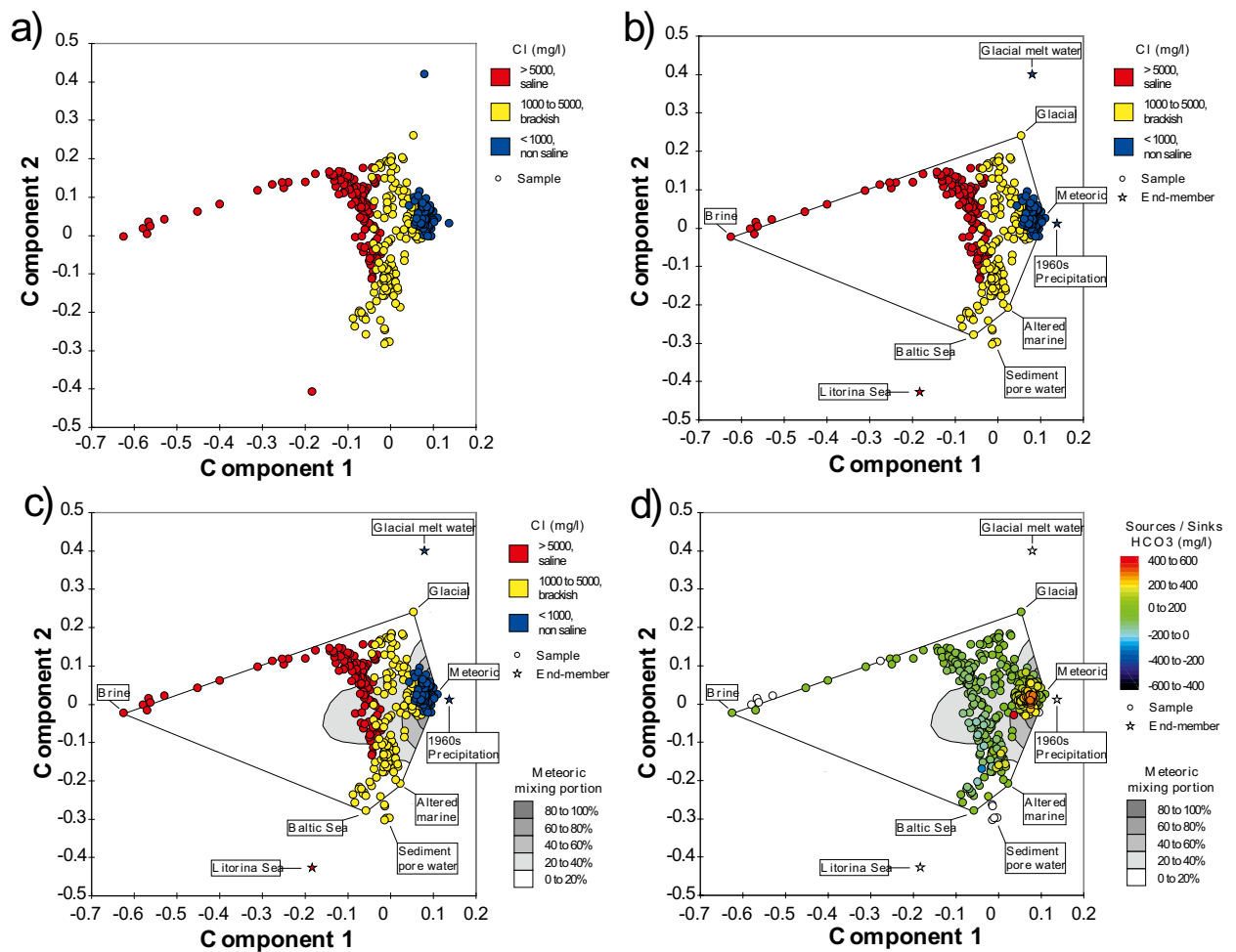
Figure 1-1. *Different steps in the M3 modelling; a) principal component analysis is used to obtain the maximum resolution of the data set, b) selection of reference waters - the other groundwaters are compared to these, c) mixing calculations - the linear distance to the reference waters eg, the portions of meteoric water are shown in the figure, d) mass balance calculations - the sources and sinks of eg, bicarbonate (HCO_3) are shown which cannot be accounted for by mixing. The groundwater samples in Figure a, b and c have been colour coded based on the Cl-content into saline, brackish and non-saline groundwater.*

same information as the original variables. The only difference is that the first principal component accounts for as much of the information as possible. The second principal component accounts for as much of the remaining variance as possible while being uncorrelated with the first component and so forth. The variables and the axes are weighted in proportion to the amount of the total information, or *variance*, that they describe /Alley 1993/. Often the first two principal components describe most of the information in the data set. It is of crucial importance for further modelling that the first and second principal component summarises >60% of the variability or the information in the data set. The outcome of the analyses can then be visualised in an x-y plot where x is the first and y the second principal component.

The strength of this approach is that several or all variables in a data matrix can be examined simultaneously. Greater resolution is obtained and the character of the data in a general data matrix is therefore more easily identified than using univariate analysis, where only one variable is compared at a time. The technique can be used to summarise the groundwater information with an optimum resolution which minimises the loss of information and hence the risk for misinterpretation[2].

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[2] This method does not replace a univariate approach which is necessary for explorative analyses of the data. However, PCA is useful when simplification, classification, systematisation and model building is needed i.e. when the groundwater system as a whole is examined at a site.

PCA is used as a basis for identification of processes coupled to mixing and mass balance reactions /Laaksoharju et al. 1995b, Laaksoharju and Skårman paper #4 in Laaksoharju and Wallin 1997/ in the M3 calculations. It is important to note that both conservative and non-conservative elements were used in the PCA. This is possible since conservative or non-conservative behaviour in one or several of the variables that are tracked by the consequent mixing and mass balance calculations.

2D Mixing calculations

M3 can calculate mixing proportions with two different algorithms: one uses only the information retained in the first two principal components (2D mixing) and the other uses all the principal components (hyperspace mixing). What follows is a summary of the key ingredient of each algorithm, starting with the 2D mixing algorithm. For a detailed explanation of both algorithms, the reader is referred to /Gómez et al. 2006/.

The mixing calculations are used to define the mixing portions from reference waters in samples, forming a mixture of the reference waters in each sample. Lines are drawn between the selected reference waters in the PCA plot (Figure 1-2) to form a polygon. The basic requirement for the
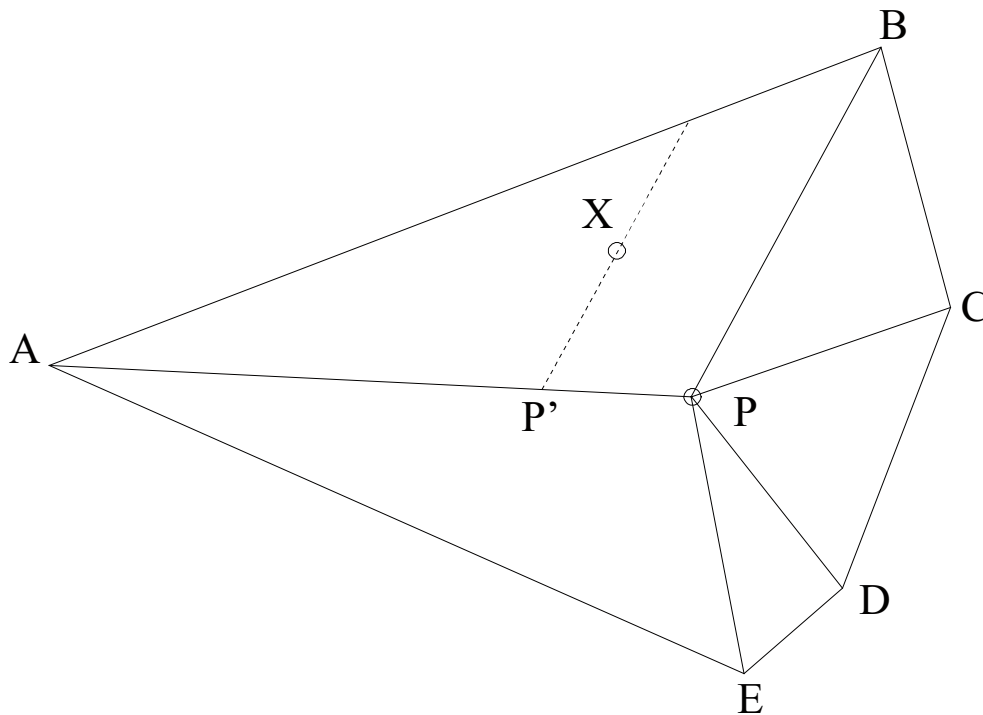

Figure 1-2. *For any point in the PCA surface, the mixing proportions are calculated from the two closest reference points and the centre point P, assumed to be a mixture of equal portions of all reference waters A to E (in the above case 20% from each reference water). For the observation X, located in the triangle ABP, the primary mixing portions from reference waters A and B as well as centre point P are calculated. The equations used to calculate the primary mixing portion of reference water A are:*

$$\frac{PP'}{AP} = R_A \qquad \text{and} \qquad \frac{R_A}{\sum\limits_{A}^{E} R_i} = \text{PrimMix}_A$$

Corresponding equations are used to calculate the primary mixing portions of reference water B and centre point P. *Since the centre point P is assumed to be a mixture of equal portions of the reference waters, the primary mixing portion of centre point P is divided between the number of reference waters, giving the secondary mixing portions of reference waters A to E. In the above case, where the observation is in the ABP triangle, the secondary mixing portions of A and B are added to the primary mixing portions of A and B to achieve the total mixing portion of reference waters A and B. The total mixing portions of reference waters C, D and E are equal to their secondary mixing portions.*

mixing calculations is that the samples are located inside the polygon. The observations within the polygon can by definition be described by the selected reference waters /Laaksoharju et al. 1995b/. The relative distance from any observation to the reference waters can be calculated by using distance calculations within the polygon as shown below in Figure 1-2. It is important to note that these calculations are performed after accomplishing the principal component analysis and are performed in 2D directly on the surface of the M3 plot. A unique mathematical solution can be obtained from a 2D surface with a maximum of three reference waters. In many cases more than three reference waters are needed to describe the observed groundwater. In order to be able to calculate, in a mathematically unique way, systems that include more than three reference waters a centre point P was introduced.

Hyperspace mixing

This new addition to M3 capabilities has a very simple rationale: instead of using only two of the principal components to calculate the mixing proportions, as with previous versions of M3, it calculates them by using all principal components. This is equivalent to saying that the mixing proportions are computed in a space with n-1 dimensions, where n is the number of end-members. Working in hyperspace has the advantage of avoiding the uncertainties derived from the projection of the coordinates onto a plane before calculating the mixing ratios. This uncertainty grows with the number of end-members and can be high when working with end-members which plot close together on the plane defined by the first two principal components (the plane used by the two-principal component mixing routine to perform the calculations). The mixing proportions are calculated from the principal component coordinates. The whole procedure is a simple coordinate transformation, from a n-1 Cartesian coordinate system (principal component coordinates) to a hyper-tetrahedral coordinate system (mixing proportion coordinates).

Figure 1-3 shows how to compute the mixing proportions from the principal component coordinates for a 2D example (three end-members). The mixing proportions are denoted (ξ_1, ξ_2, ξ_3), and the PCA coordinates as (x,y). In Figure 1-3 the X marks the location of the sample whose mixing proportions we want to compute (the red dot in this graph). From this circle we draw straight lines to the three vertices of the triangle. This operation subdivides the total triangle into three sub-triangles (one coloured in blue) whose areas are A_1, A_2, A_3

Mass balance calculations

The results from the above mixing calculations are used to predict, using reference water composition, groundwater concentrations for the following species: Ca, Na, Mg, K, SO_4 and HCO_3. The predicted values are compared with the measured ones for each groundwater sample. A deviation indicates sinks or sources due to reactions. The mass balance calculations describe the mass transfer resulting from reactions altering the groundwater and not accounted for by mixing.
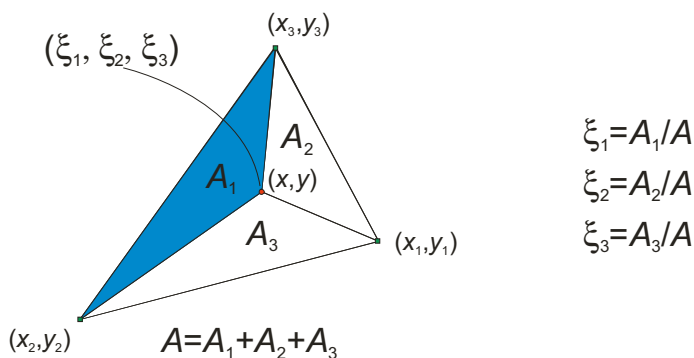

Figure 1-3. Calculation of the mixing proportion coordinates from the Principal Component Analysis (PCA) coordinates.

Conceptual modelling and mixing

The hydrogeochemical evolution of fracture groundwater results from advective mixing and water-rock interactions driven by past and present changes in the climate as evidenced by the extensive site investigations in, among other countries, Sweden and Finland (e.g. /Laaksoharju and Wallin 1997, Laaksoharju et al. 1999, Pitkänen et al. 1999/). Many of the evaluation and modelling steps used in site descriptive modelling are focused on differentiating these effects by using different modelling approaches such as mixing, reactive and transport modelling /Laaksoharju et al. 2009/.

For modelling purposes, different approaches can be used leading to quite different descriptions of the system. For example, when applying end-member mixing models, the choices of end members are crucial for the description of both mixing and reactions. This does not necessarily mean that some models are correct and some models are not. It is more a question of choosing the most suitable model available for describing the part of the system that is to be addressed, and also to focus on the time period of interest. All epochs and all parts of the system can never be described with high resolution using the same model; usually several models are required as well as different sets of end members and starting prerequisites.

Figure 1-4a–d illustrates the different approaches to model groundwater mixing and reactions, using sodium versus chloride as an example. The sodium content in groundwater can be altered by, for example, feldspar weathering or cation exchange, but chloride is regarded as a water conservative tracer not affected by reactions. The task is to model the reactions that have caused the measured sodium content. In Model 1 (Figure 1-4b), the water composition is the result of reactions, for example, the sample with about 0.85 mol/kg Cl, indicated with the arrow, has gained about 0.28 mol/kg Na due to reactions. There is no flux or mixing in the system since the system is closed. In Model
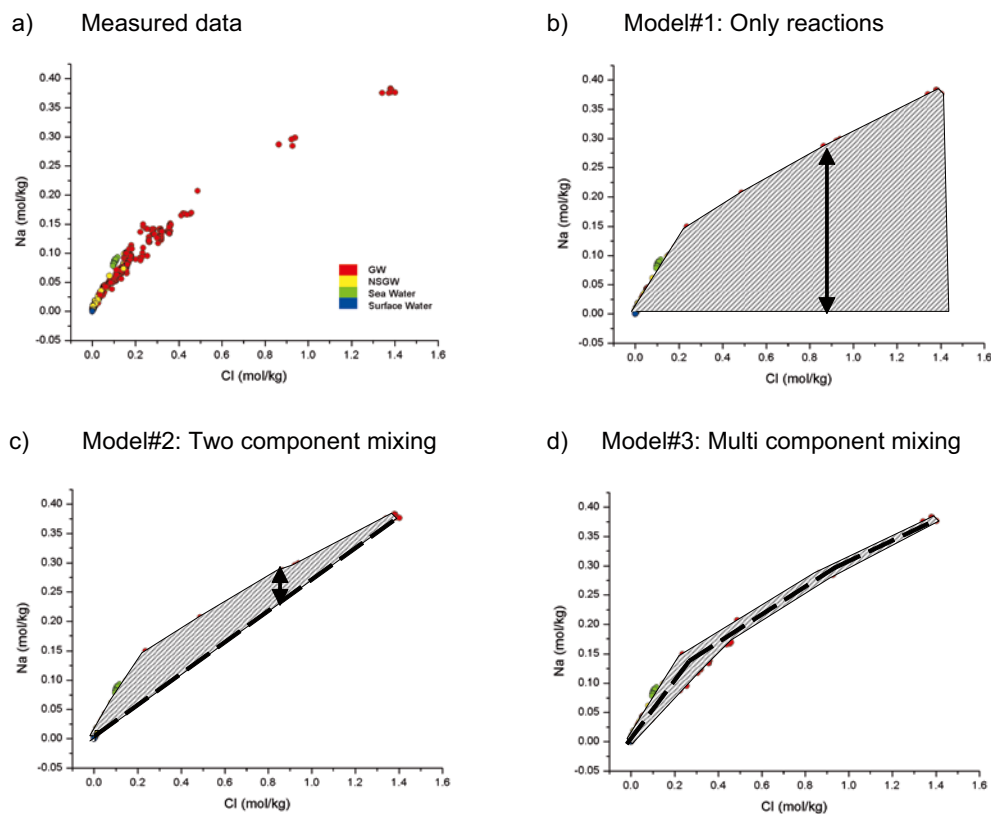

Figure 1-4. *Schematic presentation of how different models are used to describe the processes behind the measured Na content. The arrows indicate the amount of reactions taking place for a particular sample, the grey dashed area indicates samples affected by reactions and the black dashed line indicates the mixing line: a) Measured Na versus Cl, b) Model based on reactions, c) Model based on a mixture of two end members and, d) model based on several end members /Laaksoharju et al. 2009/.*

2 (Figure 1-4c) the water composition is the result of mixing of two end members (indicated with the dashed black line); here the sample has gained about 0.07 mol/kg Na. The water composition is described mainly as a result of two-component mixing with some gain of sodium by reactions. In Model 3 (Figure 1-4d) the water composition is described almost exclusively as the result of mixing of several end members. Here the sample has not gained any sodium, since it plots on, or close to, the mixing line (black dashed line). The water composition is described as the result of multi-component mixing and the sodium content is the result of pure mixing/transport. Plots above the mixing line indicate a gain of sodium, whereas plots below the mixing line indicate a loss of sodium.

The example given above clearly shows that the description of the groundwater system depends on the model selected. Model 1 describes the total amount of reactions taking place to obtain the sodium content measured in the sample. However, it does not describe where and when the reactions took place. Models 2 and 3 describe the water composition in relation to the end-member composition. Hence, these models can be used to calculate the mixing proportions of the end members. This, in turn, can be used not only to indicate the origin, but also to indicate the range of possible residence time in the bedrock. This is useful information when, for example, integrating the results with the hydrogeological modelling. Models 2 and 3 do not describe the evolution of the end-member composition, but assume that the processes responsible for this composition are implicitly considered (including all the reactions that ever took place).

It is generally a relatively easy task to construct Model 2, but with the risk that the system is oversimplified such that the effects from reactions are overestimated and the effects from transport underestimated. Model 3 can provide realistic descriptions of conservative and non-conservative compounds, but model uncertainties (such as uncertain end-member compositions and mathematical uncertainties in the model applied) can still lead to an erroneous conclusion concerning the gain/losses of element concentrations. The accuracy of Models 2 and 3 can be tested by, for example, plotting the model-predicted Cl and $\delta^{18}O$ contents versus the measured ones. The deviation from a perfect correlation will then indicate the model uncertainties /Laaksoharju 1999/.

The importance of mixing becomes apparent under the following circumstances:

1. The palaeo- and present climate has a huge impact on the hydrogeology and, hence, on hydrochemistry in Fennoscandia /Laaksoharju et al. 2009/. This facilitates different water types (i.e. glacial, sea water and meteoric water) to enter or to be flushed out from the bedrock.

2. The temperature in the rock is relatively low (at –200 m = 11°C; the gradient is 1.6°C per 100 m) and therefore most water-rock interaction processes are slow.

3. Where groundwater flow is faster and more dominating than reaction times (i.e. for highly transmissive conditions), the origin of the water may still be distinguished.

The significance of reactions becomes apparent, particularly with respect to: a) redox conditions where microbiologically mediated reactions are rapid, and b) pH and alkalinity values buffered by kinetically fast calcite precipitation/dissolution reactions /Smellie et al. 2008, Gimeno et al. 2008, 2009, Laaksoharju et al. 2009/.

The exact quantification of the contribution from reactions versus mixing is complex, and at best semi-quantitative at the site scale. This requires different modelling approaches ranging from explorative analyses, mass-balance calculations, mixing calculations and coupled reactive transport modelling (e.g. /Gimeno et al. 2009/). The extensive testing of optimum models for mixing calculations /Gimeno et al. 2009/ has shown that indications of mixing contra reactions can be achieved by simplifying the system by using less end members and hence being able to use water conservative elements as tracers in the M3 model quantitatively.

1.2.3 Accuracy of the M3 calculations

The accuracy of the M3 calculations has been tested by predicting the behaviour of conservative elements, using back propagation tests and sensitivity tests. Exhaustive tests were prepared by /Gómez et al. 2009/ in the report M3 version 3.0: Verification and Validation.

The following tests were performed and analysed:

1) Verification tests

- Test Case A1: Eigenvectors, eigenvalues and PC loadings
- Test Case B1: Mixing proportions when end-members are fully known: two-principal component mixing routine
- Test Case B2: Mixing proportions when end-members are fully known: hyper-space mixing routine
- Test Case C1: Absolute and relative deviations using synthetic samples
- Test Case D1: Test of the combinations generating routine
- Test Case D2: Test of ESM using as end-members the same used to create the samples
- Test Case E1: Test of random number generator
- Test Case E2: Construction of input probability distributions: Identical lower and upper ranges
- Test Case E3: Construction of input probability distributions: different lower and upper ranges
- Test Case F1: Linear mixing (no redundancy)
- Test Case F2: Linear least squares (redundancy)
- Test Case F3: PHREEQC in pure-mixing mode

2) Validation tests

- Test Case VA1: Dependence of mixing proportions on the number of samples in the dataset
- Test Case VA2: Dependence of mixing proportions on the number of input variables
- Test Case VA3: Dependence of mixing proportions on the inclusion/exclusion of end-members from the PCA
- Test Case VB1: Propagation of end-member composition uncertainties into mixing proportions (validation of the End-member Variability Module, part 1)
- Test Case VB2: Propagation of end-member composition uncertainties into mass balance deviations (validation of the End-member Variability Module, part 2)
- Test Case VC1: Stability of mixing proportions against changes in the number or type of end-members
- Test Case VD1: Validation of mass balance and analysis of reactions
- Test Case VE1: Cross-check against PHREEQC
- Test Case VF1: Cross-check against /Carrera et al. 2004/ maximum likelihood method
- Test Case VF2: Cross-check against /Douglas et al. 2000/ linear mixing method
- Test Case VG1: Mineral solid solutions (garnets)

3) Sensitivity test of M3

An extensive sensitivity test of the M3 model has been performed (see /Gómez et al. 2008/). The number, type and composition of the end-members and the reference waters were changed and varied systematically in order to find the model that gave the lowest possible deviation for the conservative water constituents. The tests show that the M3 model is surprisingly robust and that an altered or even excluded reference water affects the results of the mass balance calculations more quantitatively than qualitatively.

1.2.4 Important rules concerning M3 modelling

Important rules to follow when interpreting the results from the M3 calculations as follows:

- The waters described by the reference waters are believed to be hydrogeologically connected and gradually mixed (this should be supported by the PCA analysis, where the observations should not form isolated clusters).

- The results are always relative to the chosen reference waters. The influence of unknown reference waters, or isolated reference waters, as well as samples from totally isolated groundwater systems and other model errors bias the calculations. The precision is also diminished if the selected reference water is an end-member with seasonal variation in the composition (e.g. precipitation, where in the winter and summer can occur). A reference water that has existed in the system for a long time also is more likely to have changed during this period. This means that the composition of glacial meltwater is more uncertain than that of modern precipitation.

- The outcome of the modelling is sensitive to the data distribution and the chosen variables included in the model. The chosen observations and variables determine what kind of processes can be described.

- The PCA plot is always oriented so that the maximum resolution is achieved. If an extreme water is removed from the data set the orientation of the plot may change. The internal relations between the observations may still be largely unchanged.

- The outcome of the modelling has to be critically reviewed by means of independent geochemical or hydrological modelling or reasoning.

2 Reference manual

2.1 About the reference manual

In the reference manual the following text formats are used to refer to different types of information. Different formats can be combined.

Bold text	Refers to other sections of the reference manual
`Courier text`	Refers to file names, directory names, commands to be typed by the user or text that appears in the Command window
Italic text	Refers to menus and menu items in the M3 figure window
<Brackets>	Refers to user-defined text or text that may vary

The appearance of the actual M3 figures and menus on the screen may vary slightly from the illustrations in the reference manual due to late changes in the program files. These figures are all based on a set of data from about 450 groundwater samples. This data set is included in M3 as training material and is stored in the Excel file Aspo1.xls.

Included in the M3 package is also a help file. It is essentially an online version of this reference manual. Changes made after this report was printed may be included in the help file, so in the case of inconsistencies, the help file is more likely to be correct.

Apparent inconsistencies in British and American spelling, especially in the cases of "colour" vs. "colormap" and "colorbar", are due to the fact that MATLAB uses American spelling and the reference manual is written in British English. Specific objects and concepts in MATLAB, eg colormaps and colorbars, are therefore spelled the American way when referred to in this manual. The same "inconsistency" is present in M3 itself.

2.1.1 Installing M3 on your computer

1. Run the setup.exe file from the M3 CD-ROM or downloaded from the Projectplace.com (requires an invitation from SKB). Make sure to install the MATLAB Component Runtime.

2. After M3 has been installed the copy protection guide will start. Follow the instructions to complete the activation of the software. You will be required to supply SKB with an unlocking code to get the license code required to use the program.

3. Start M3 from the Programs menu under the Start button.

NOTE: The copy protection mechanism is based in part on your computer's hardware. Changes to the hardware may require a renewed activation.

WARNING: Select "English" in: Start*/Control Panel/Regional And Language Option/Regional Options/Standard And Format* when M3 is used on Windows.

2.2 Using M3

2.2.1 Getting started

The M3 method follows a series of consecutive steps. In short they are:

1. Import element concentrations for the samples in the data set. The element concentrations must include the concentration for possible end-members.

2. Calculate principal components for the imported element concentrations.

3. Select end-members. This can be done with the aid of the PCA plot or from expert knowledge of the imported data. Several combinations of end-members can be analysed using the coverage test tool. Further investigation of the end-members' impact on mixing calculations can be analysed using the End-member Variability Module (EVM).

4. Calculate mixing in samples from end-members. Normally this is done automatically after selecting end-members, but can also be done manually.

5. Calculate mass balance deviation. Normally this is done automatically after selecting end-members, but can also be done manually.

6. Export calculated variables.

2.2.2 Program particulars

- Almost all of M3's functionality is reached through the menu system, which can be accessed in any plot window. Even though the easiest way to control the program is by using the mouse, most functions can be accessed by using the keyboard.

- M3 creates a new window for (almost) every new plot. The advantage of this is that it is possible to compare different plots without saving them and viewing them in a separate image viewer. The disadvantage is that you'll have a lot of windows after working with the program for a while. Make it a habit to close the windows when you do not need them. Closing the last window will cause the program to exit.

- M3 has a main console window that is the "parent" of all other M3 windows. **Closing the console window will cause the program to exit.**

2.2.3 Example data sets

M3 comes with four example data sets for testing: Aspo1, Aspo2, Oklo and Synthetic. They can be found in the corresponding CSV files in the examples directory in the M3 installation directory, typically c:\program files\M3\examples.

- The Aspo1 data set is based on samples from a real site (Äspo in Sweden) and contains 450 samples. This set has been used when producing the plots used in this manual. Since it contains measured concentrations from real samples, it displays the complexity of a site that is not entirely the result of mixing. There are several possible end-members in the data set.

- The Aspo2 data set is from the same site and is used in Äspö calculations example. See the Äspö example section for more information.

- The Oklo data set is used in the Oklo calculations example. See the Oklo example section for more information.

- The Synthetic data set contains of 3,000 synthetic samples and is designed to emulate a situation that is primarily the result of mixing. There are four distinct end-members in this data set.
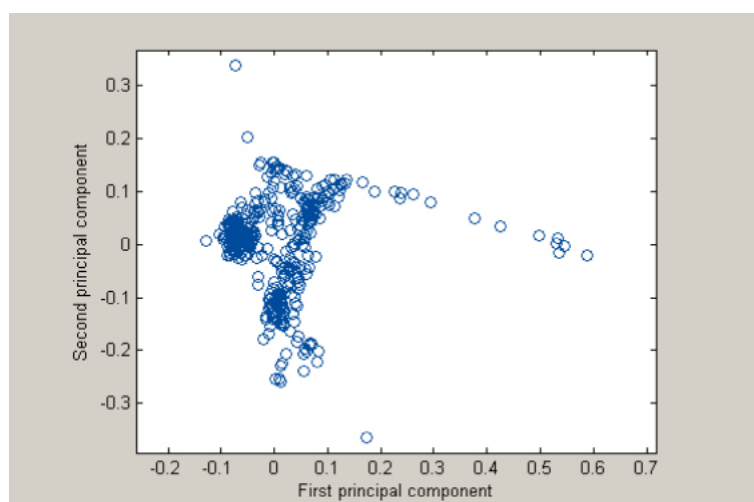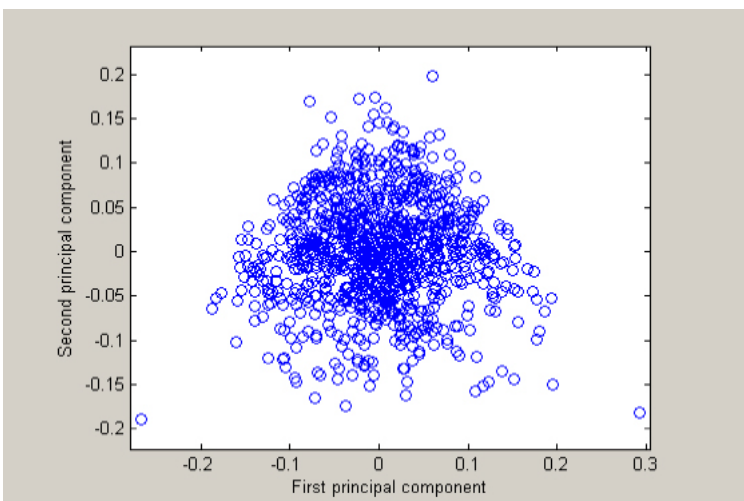

PCA plot of the Aspo1 data set
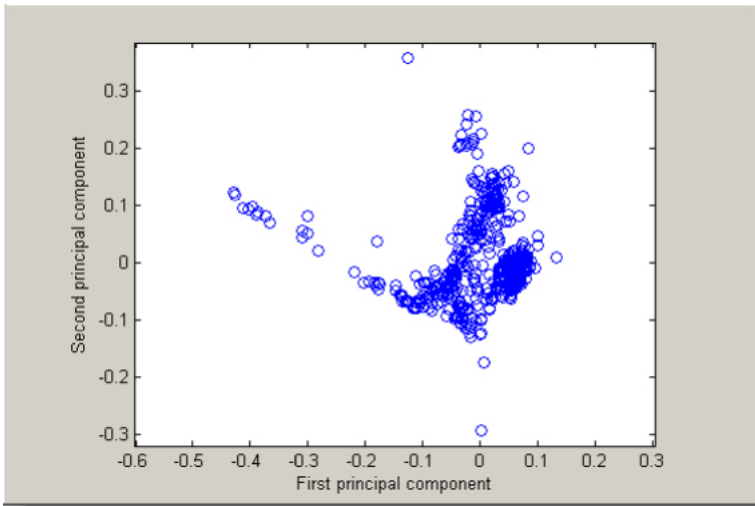
PCA plot of the Aspo2 data set
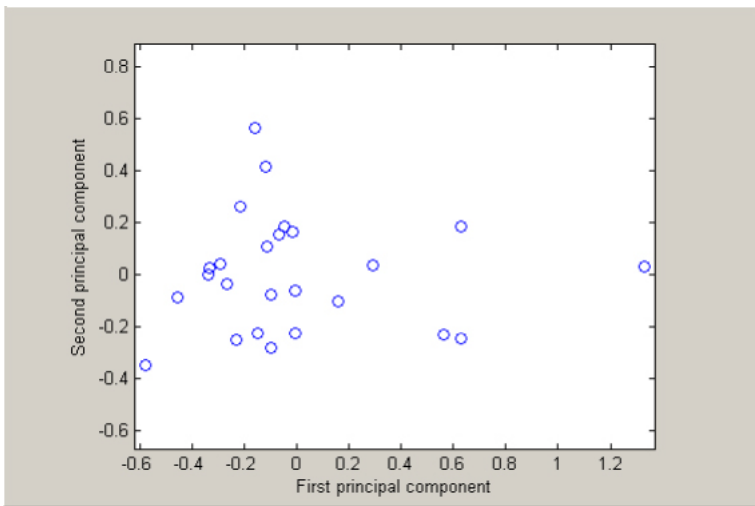
PCA plot of the Oklo data set

PCA plot of the Synthetic data set

2.2.4   Menus

The user controls M3 through its menu system. The top-level menus are organised as follows:

Menu	Functionality
Data	Functions relating to import and export of data, elements' labels etc.
Calculations	Functions relating to calculation and visualisation of PCA, end-members, mixing and deviation.
EVM	Functions relating to the End-member Variability Module.
Tools	Functions for editing plots and changing preferences.
Help	Help system and version information.
Exit	Quit the program.

Menus are enabled as the necessary variables are calculated or imported, e.g. PCA can only be calculated when element concentrations have been imported, mixing can only be calculated when end-members have been selected etc.

2.2.5   Data

Data menu contains functions relating to import and export of data from the program. A new M3 session for a specific data set typically begins with an import of elements that are the raw material for the calculations and ends with the export of the variables calculated in M3. Plots generated in the program can be saved in several image formats.

Load saved variables

All relevant variables are automatically saved in the current working directory. To resume or inspect previous calculations, these saved variables can be loaded into M3.

Selecting Data/Load saved variables will load the variables saved in the current working directory. Variables not available in the current working directory are disabled in the import dialogue. To load data from another directory, change your working directory. Disabled menus will be enabled as the necessary variables are loaded.

NOTE: Saved EVM data is not affected when loading saved variables. See Analyze saved EVM data.

Clear all variables from memory

This option clears all variables from memory and resets M3 to startup conditions. It also deletes any automatically saved variables in your current working directory. The selected working directory is not changed.

Import elements from CSV-file

Before starting M3 calculations on a new data set, the element concentrations for all samples must be imported. This is done by importing a character-separated value file (a CSV-file).

To import elements from a CSV-file, select Data/Import elements from CSV-file and specify the relevant CSV-file. A dialog will let the user specify if element and/or sample labels are present in the file. All existing plots and variables, except for those related to the EVM, are cleared from memory. The elements will then be imported to M3. Most spreadsheet software, such as MS Excel and OpenOffice Calc, are able to export worksheets to CSV format.

CSV-file format

The data in the CSV-file must be organised with one row per sample and one column per element. The decimal separator must be a period (".") character. The default column delimiter in the CSV-file

is a semi colon ("·"). The column delimiter for CSV import and export can be set by selecting Tools/ Preferences. Apart from the first row, the data set must only contain numerical values and NOT other characters, as letters etc. There must be no empty cells in the data set imported. The user should check that this is true as M3 interprets empty cells as numerical value zero.

Sample and element labels

Depending on import options selected by the user, element and sample labels will be set. If the first row contains element labels, these strings will be used as default when setting element labels.
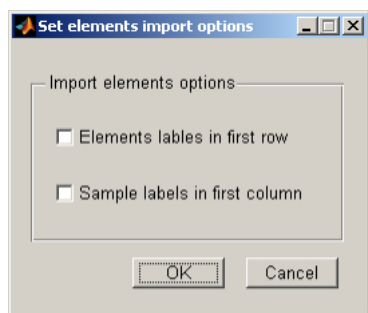
When both element and sample labels are used, the first column in the element labels row must be empty (see CSV example below). If sample labels are used, these are used to refer to individual samples through out the program. If no sample labels are specified, the sample's row number in the imported matrix will be used to identify the sample. Sample labels must be unique numerical, integer values. If M3 encounters repeated sample labels it will issue the warning message 'Duplicates in sample's labels' and elements will not be imported.

CSV example

A CSV file with the following contents

```
;Na;K;Ca;Mg;HCO3;Cl;SO4;Tr;D;O18
1;8500;45.5;19300;2.12;14.1;47200;906;4.2;-44.9;-8.9
2;613;2.4;162;21;61;1220;31.1;0.1;-124.8;-15.8
3;1960;95;93.7;234;90;3760;325;42;-53.3;-5.9
```

will be interpreted by M3 as

	Na	K	Ca	Mg	HCO3	Cl	SO4	Tr	D	O18
Sample 1	8,500	45.5	19,300	2.12	14.1	47,200	906	4.2	–44.9	–8.9
Sample 2	613	2.4	162	21	61	1,220	31.1	0.1	–124.8	–15.8
Sample 3	1,960	95	93.7	234	90	3,760	325	42	–53.3	–5.9

NOTE: There must be no empty cells in the matrix containing the elements, as the PCA method requires numerical values in all cells.

Edit element labels

Every element must have a label to distinguish it from other elements. When importing elements, a dialogue for entering element labels is opened. To edit labels after import, select Data/Edit element labels to access the dialogue again.

NOTE: Special characters and font settings can be used in labels, see Special Characters.

Export variables to CSV-file

Values for a calculated variable can be exported to a CSV-file.

Selecting Data/Export variables to CSV-file will produce a dialog box for selection of which variable to export. Variables that have not yet been calculated are disabled. Select the desired variable and click on "Export". Enter the CSV-file name and click on "Save". To save all variables at once, see Export all variables to CSV-files.

Exportable variables

Name	Description
Elements	The elements concentrations imported at the beginning of an M3 session, one row per sample, one column per element.
Principal components	The principal components calculated when selecting Calculate principal components, one row per sample, first principal component in first column, second principal component in second column, etc.
PCA eigenvectors	Eigenvectors of the covariance matrix calculated when selecting Calculate principal components.
PCA eigenvalues	Eigenvalues of the covariance matrix calculated when selecting Calculate principal components.
End-member indices	Sample indices for the selected end-members, referring to their corresponding row numbers in the elements matrix.
Coverage	Coverage calculated when selecting Test sample coverage. The first column is 2-PC coverage, second is n-PC coverage and the third column is the end-member combination. Coverage is expressed as percent number of samples inside the mixing polyhedron. A negative value means that the mixing model is not applicable with the end-member combination in question.
Mixing portions of samples	Mixing portions, one row per sample, one column per element. Mixing is expressed as a percentage, the sum of which is 100% for each sample. Samples that are outside the mixing volume have a value of NaN ("Not a Number").
Deviation	The calculated elements deviation from the imported elements, one row per sample, one column per element. Deviation is expressed as a difference in concentrations. Samples that are outside the mixing area have a value of NaN ("Not a Number").
Calculated elements	The element concentrations calculated from the mixing portions, one row per sample, one column per element. Samples that are outside the mixing area have a value of NaN ("Not a Number").

M3 does not export labels for elements and end-members in the CSV-files.

NOTE: For more information on the CSV-file format, see Import elements from CSV-file.

Export all variables to CSV-files

All exportable variables can be saved at once by selecting Export all variables to CSV-files. The user selects an output directory where all variables are saved to CSV-files with default file names. The (self-explanatory) filenames are:

- Elements.csv
- PCA.csv
- EndMembers.csv
- Mixing.csv
- Eigenvalues.csv
- Eigenvectors.csv
- CalcElements.csv
- Deviation.csv

Save figure

Figures can be saved in the following formats:

- Tagged Image File Format (TIFF)
- Joint Photographers Expert Group (JPEG)
- 256-Colour PCX
- 24-bit Colour PCX
- Encapsulated PostScript
- Encapsulated Colour PostScript
- Encapsulated Lvl 2 PostScript
- Encapsulated Lvl 2 Colour PostScript
- Adobe Illustrator 88

Select the desired format, click on "Export" and enter the name of the file to save to.

2.2.6   Calculations

Functions relating to calculation and visualisation of PCA, end-members, mixing and deviation are accessible under the Calculations menu.

PCA

The Principal Component Analysis (PCA) is the first step in the M3 method. The PCA, a standard multivariate technique, is used for finding privileged orientations to view datasets at maximum spreading. For that purpose several numerical variables that characterise the samples are selected. For groundwater systems, variables comonly used are the major elements (e.g. Cl, Ca, Na, Mg, K, SO_4, HCO_3, etc) in combination with stable isotopes (^2H, ^{18}O) and radiogenic isotopes (^3H). The chosen variables are generally relatively easy to analyse with a high analytical accuracy and they are known to describe the major groundwater features. Generally, depending on the analytical program, there may be other variables than those suggested which can also contain important information concerning the evolution of the groundwater at a site. Such variables should then be included in the PCA.

A principal component is simply a linear combination of the original variables. The PCA aims to describe as much of the information as possible from the linear combination that defines the first principal component. The rest of the information is described by the second, third, etc principal components. The weights of the different variables in the linear equations are calculated automatically by the PCA. For the first two principal components an x-y scatter plot can be drawn. This is the type of plot used most frequently in the M3 user interface to provide graphical representations of the data. There, x is the equation for the first principal component and y is the equation for the second principal component. The plot is called a PC-plot and is used to visualise the clustering and trends in the data as well as to identify end-members. Careful examination of the PC-plot can provide additional information as to the origin, complexity and relationship of the groundwater system. The number of selected end-members should be the minimum required to describe the observations.

Refer to the 'Concepts, Methods, and Mathematical Formulation' report /Gomez et al. 2006/ for a more thorough discussion of PCA

Calculate principal components

Selecting Calculations/PCA/Calculate principal components will calculate the principal components and produce a 2D graph in the current figure window, displaying the samples as blue circles. The value of the first principal component is shown on the x-axis and the second component on the y-axis.
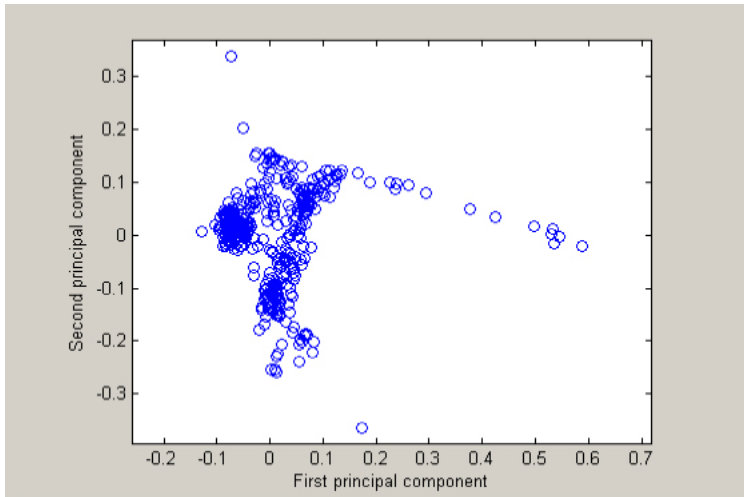
A message box will appear and show the percent accumulated variance in the first three principal components. For example:
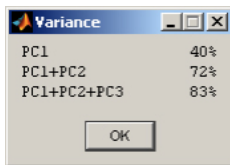

This means that the first principal component represent 40% of the variation of the original data, principal component one and two together represent 72% of the variation and principal components one, two and three represent 83% of the variation in the original set of data. The variance is automatically displayed when the PCA calculation starts. The amount of variance explained by the retained principal components should always be indicated.

NOTE: There must be no empty cells in the matrix containing the elements, as the PCA method requires numerical values in all cells. See Import elements from CSV-file.

Display principal components

Selecting Calculations/PCA/Display principal components will produce a 2D plot of the first two principal components, identical to the plot displayed after the principal components calculation. There's a button in the lower right corner of the window that allow the user to toggle between a 2D and 3D plot of the principal components. In the 3D plot the value of component one is shown on the x-axis and component two on the y-axis. The third principal component is on the z-axis. When in 3D view the mouse can be used to rotate the plot in three dimensions to to better appreciate the relative position of the samples with respect to the three principal components.
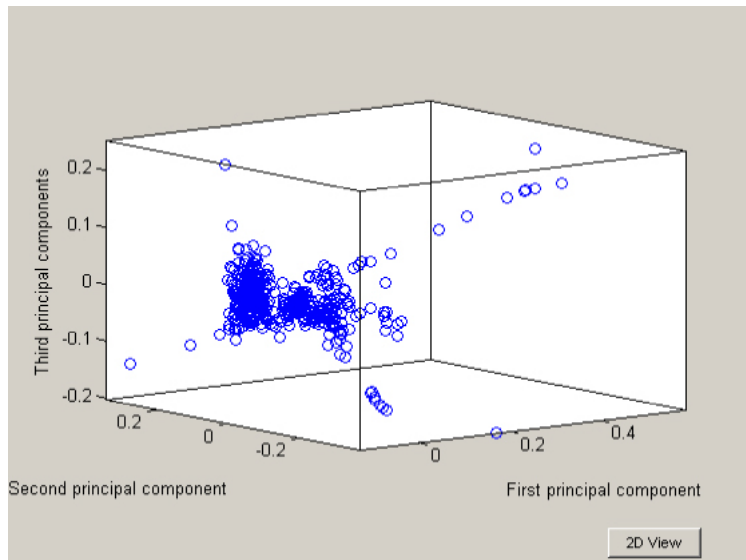
Reload imported elements

When using the coverage test tool the number of samples is reduced due to the removal of unwanted "candidate" end-members that were present in the imported element concentrations. The Reload imported elements is a fast way to revert to the element concentrations originally imported without re-importing them.

End-members

The concept of end-members is a cornerstone in M3 methodology. How many end-members are to be used and their particular chemical and isotopic composition is something that in principle lies outside M3 methodology and should be decided (also in principle) by expert judgment after a careful geochemical and hydrological study of the system. However, this version of M3 includes a pseudo-automatic procedure to select the proper set of end-members for a given dataset. A end-member can be a modelled or sampled (extreme) groundwater e.g. glacial melt water, ancient sea water, brine water or rain water, dilute shallow groundwater or sea water. As a general rule, the number and type of end-members to be selected in the modelling depend on the aim of the modelling and the complexity of the site. The groundwater data used in the modelling determines the minimum number of end-members needed to describe the observed groundwater composition. The chosen end-members must be included in the imported elements dataset.

The inclusion of the end-members in the PC analysis could introduce a bias if

1. the end-members have a chemical composition radically different from the waters in the dataset;

2. there are very few water samples in the dataset;

3. the statistical uncertainties affecting the samples of the dataset and of the end-members are different.

Case (1) should never occur in a system dominated by mixing (if it were the case, it would mean that the end-members had been incorrectly selected); case (2) is not compatible with M3 philosophy, whose purpose is always use the joint analysis of a large dataset (for very small datasets, other methods not based on multivariate statistics are more suitable); finally, case (3) is not realistic when both the end-members and the dataset belong to the same category (in this case, ground waters).

Refer to the 'Concepts, Methods, and Mathematical Formulation' report /Gomez et al. 2006/ for a more thorough discussion of end-members.

Select end-members

Selection of end-members can be done either graphically, by clicking on selected samples in a 2D PCA plot, or with the keyboard by entering the id label of the samples in the text box in the lower left corner of the figure window and pressing the enter key. When a sample is selected it will change colour to red in the plot and its id label will be added to the plot next to the sample, as well as to the text box. To remove a sample from the selection, simply delete its id label in the text box and press enter.
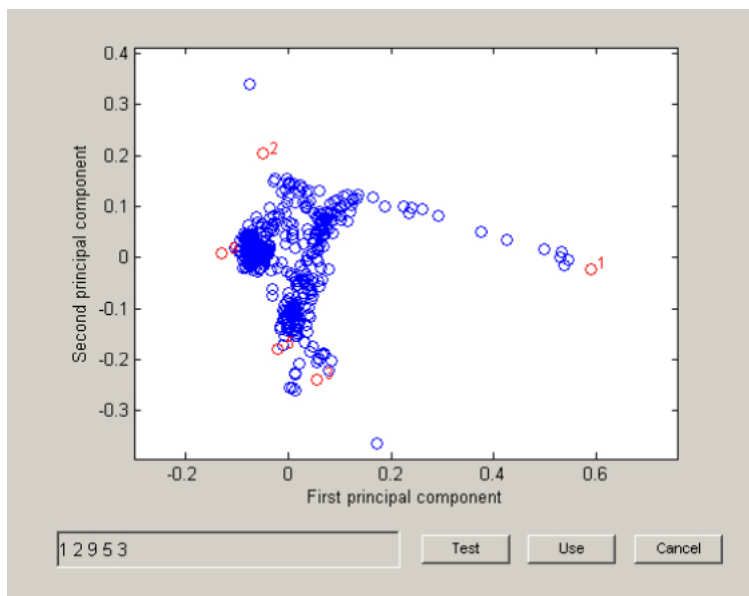
If you are confident with your selection of end-members, click on the "Use" button to continue with the mixing and deviation calculations. If a mixing model is not available given the selected end-members, a window will open and state the reason. Then a window will open to let the user set the end-member labels. After that the mixing and deviation calculations will follow.

If you are not confident about the proper selection of end-members, the program can test all the combinations of the selected end-members and calculate what percentage of all samples are covered by each combination. To do that select the potential end-members and click on the "Test" button. The sample coverage test is described in detail in the "Test sample coverage" section.

Inspect end-members

Selecting Calculations/End-members/Inspect end-members will produce a plot very similar to the Display principal components plot. The only difference is that the end-members are coloured red and has the end-member label and sample id label next to it.

Test sample coverage

In order to analyze possible combinations of end-members and mixing models, M3 can test all possible combinations of the selected end-members and calculate what percentage of all samples would be included in the mixing polyhedron for each case. A high coverage is desirable. By including several potential end-members ("candidates") in the input file, the user can test and compare several possible end-member combinations at once. The candidate end-members that are not included in the selected combination will be removed from all subsequent calculations.

Selecting Calculations/End-members/Test sample coverage will produce a dialog box asking for an allowance factor for the n-PC mixing calculations. Enter the appropriate allowance factor and click the "OK" button. The sample coverage calculation will take place and the results presented in a new figure window. If several end-member candidates have been selected this may take several minutes. The coverage analysis window has three areas: the sample coverage plot, the list of coverage percentages and the current end-member combination. In addition to this there are two radio buttons to select a mixing model.
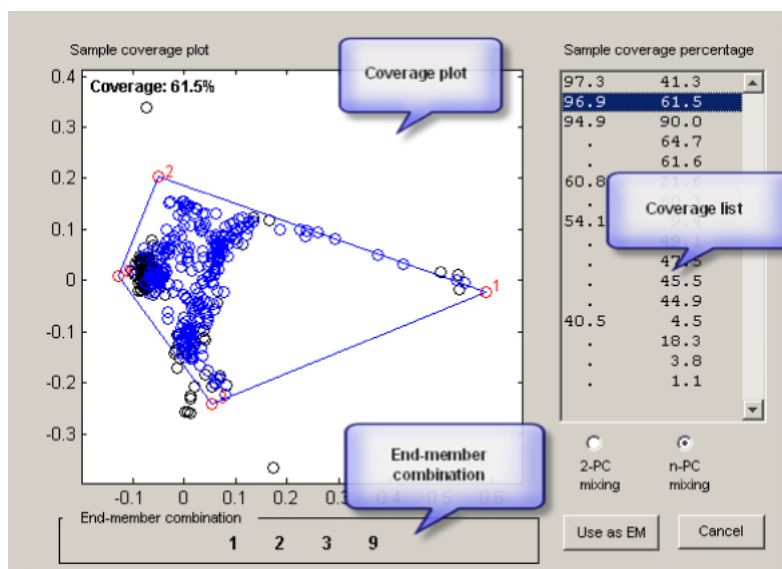
The coverage percentage list is ordered in descending coverage and has two columns, the left for 2-PC mixing and the right for n-PC mixing. Each row in the list represents a combination of the end-member candidates from the end-members' selection. A period instead of a percentage indicates that the mixing model isn't applicable to the end-member combination in question. When clicking on a row in the coverage list, the corresponding end-member combination appears in the end-member combination text box below the plot and the coverage plot displays the end-members as red circles, samples inside the mixing polyhedron as blue circles and the rest of the samples as black circles. The mixing model is selected by clicking on the 2-PC / n-PC radio buttons below the coverage list.

The end-member candidates that are not part of a given end-member combination are omitted from the coverage calculations. Because of that, the shape of the PCA in the coverage plot vary with different end-member combinations.

Click on the "Use as EM" button to set the selected combination as end-members for the calculations. If the combination consists of fewer than all candidates, a warning message will tell the user that that the dataset will be resized. This means that all end-member candidates that are not part of the selected combination will be deleted deleted from the imported elements and PCA will be recalculated. To later revert to the original imported dataset, either select Calculations/PCA/Reload imported elements or clear all variables and re-import data.

NOTE: Due to the nature of principal component analysis, very small changes in the input data can easily "flip" the PCA plot left/right or up/down. Although this may look like big variations, only the samples' positions relative to each other are relevant, not their nominal values by themselves, and a "flip" has no impact in itself. To make the coverage plots easier to follow, M3 tries to keep all plots in the same up/down – right/left orientation. If a plot has been re-oriented, this will be indicated in the lower left corner of the coverage plot. This re-orientation has no impact on calculations and is only used when comparing different coverage plots. In all other plots in the program the PCA orientation is untouched.

Edit end-member labels

Every end-member must have a label to distinguish it from other end-members. When selecting end-members, a dialogue for entering end-member labels is opened. To edit labels later, select PCA/ end-members/ Edit end-member labels to access the dialogue again. The end-member labels are also used as identifiers in the End-member Variability Module (EVM).

NOTE: Special characters and font settings can be used in labels, see Special Characters.

Calculate mixing and deviation

Selecting Calculations/Calculate mixing and deviation will calculate mixing in samples and deviation in one sequence. First a dialog will let the user set the mixing model, including the allowance factor if using the n-PC mixing model.
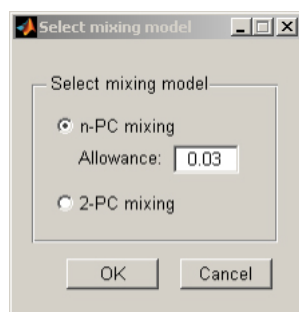
After clicking OK, a message box displays the current process. It is not necessary to click on "OK" on the process message box. It is also possible to carry out these calculations separately under the Calculations sub-menus Mixing/(Re-)calculate mixing in samples, and Deviation/(Re-)calculate deviation. The results from the calculations are saved in the current working directory.

Mixing

M3 provides two models for calculating mixing, both based on geometrical calculations on the PCA results: 2-PC mixing and n-PC mixing. Which model to use requires expert judgment and depends on the characteristics of the data set in question. M3 has several functions, such as the End-member Variability Module and the samples' coverage test, to assist the user in analyzing the data set to determine the suitable mixing model. Please refer to the 'Concepts, Methods, and Mathematical Formulation' report /Gomez et al. 2006/ for a more thorough discussion of mixing models.

2-PC mixing model

The 2-PC mixing model uses the first two principal components from the PCA as the basis for the mixing calculations (hence the name). The number of end-members can be three or more. There's no mathematical upper limit to the possible number of end-members.

Since it uses only two principal components there is no allowance factor for this mixing model, as the two-dimensional projection can disguise samples that are actually outside the mixing polyhedron. Using an allowance factor would only add more uncertainty to the mixing calculations.

n-PC mixing model

The n-PC mixing model uses as many principal components from the PCA as there are end-members minus one, e.g. if there are five end-members, the mixing calculations will be based on the first four principal components from the PCA. The number of end-members can be between three and the number of elements (input variables) plus one.

n-PC allowance factor

Samples outside of the end-member hyper-polyhedron are excluded from the mixing calculations in both the 2-PC and the n-PC models. However, samples that are outside but very close to the edges of the polyhedron may be there due to rounding errors or because one (or more) of the end-members are not contributing to the mixing for that sample. To accommodate for these factors and enable the user to include such samples as well in the calculations, an allowance factor has been introduced to the n-PC mixing model. The allowance factor is expressed as a fraction of the mixing proportion, allowing samples with a "negative" mixing portion not superseding the allowance level to be included in

the mixing calculations. By testing the coverage at different allowance levels, the user can determine if there are many samples belonging to this category. If the coverage remains stable when going step-by-step from a 0.00 allowance factor to a 0.05 level, this indicates that most samples are well inside the polyhedron. On the other hand, if the coverage increases abruptly, then there are many samples close to the edges and that including them should improve the calculation results.

Typically, the allowance should be in the range of 0.01 to 0.05.
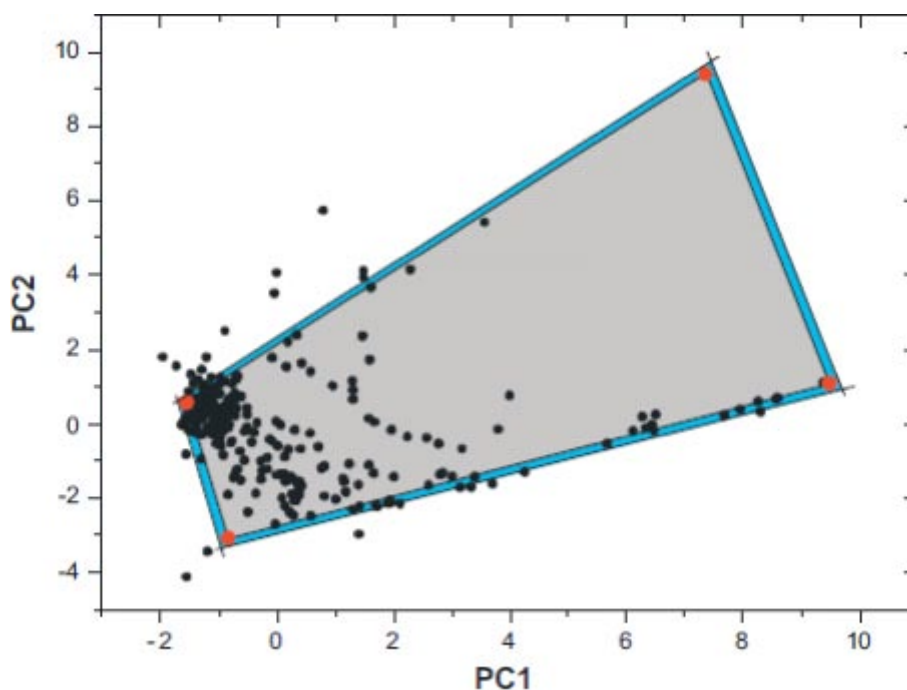
A fictive dataset with four end-members projected onto the PC1-PC2 plane is shown in the figure above. The red circles are the end-members and define a polygon (shaded area), which includes all the samples which can be explained by the mixing of the four end-members. The blue extension of the polygon includes the samples that will be moved to the edges of the polygon if an allowance parameter different from zero is set in M3 (after /Gomez et al. 2006/).

(Re-)calculate mixing in samples

In order to carry out the M3 calculations step by step, it is possible to calculate mixing in samples, as well as deviation, separately. This can be useful for instance when testing different allowance factors.

Selecting (Re-)calculate mixing in samples will calculate the mixing portions of each end-member in the samples. A message box will appear and indicate that the calculation is in progress. It is not necessary to click on "OK" in this message box.

Display mixing in samples

The mixing portions from a end-member in the individual samples can be displayed as coloured circles, with the colour of each sample representing the mixing portion from the selected end-member. This option lets the user examine the mixing portions of the individual samples carefully.

Select Calculations/Mixing/Display mixing in samples. Select the end-member whose mixing portion you want to display and click on "OK". A new figure window with the samples as coloured circles will be opened. The colour of the samples represents the mixing portion from the selected end-member.
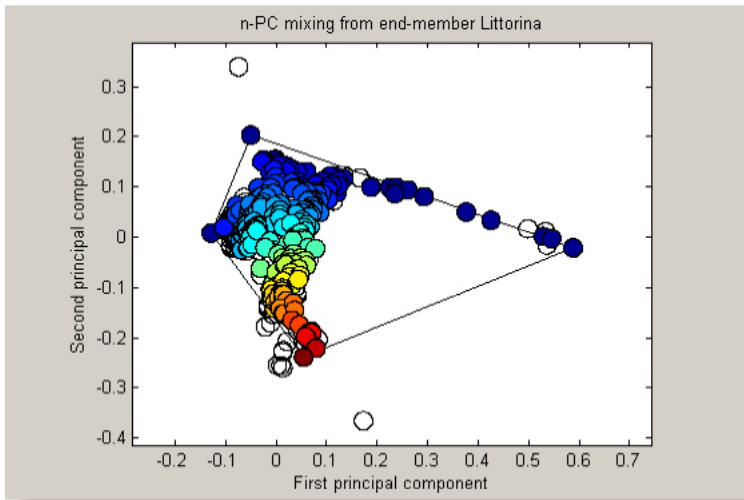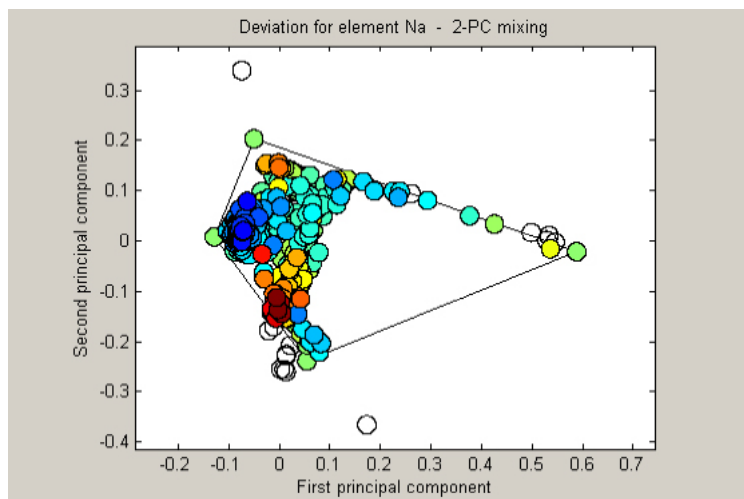
NOTE: To add a colorbar for interpretation of the colours, select Add/update colorbar from the Tools menu.

To change the size of the circles, select Tools/Preferences and set circle size.

Calculate 2-PC mixing at any point in polygon

The Calculate 2-PC mixing at any point of polygon option lets the user calculate the 2-PC mixing portions from the different end-members at any point in the polygon that may contain observations.

Selecting Calculations/Mixing/Calculate 2-PC mixing at any point of polygon will produce a graph in a new figure window, displaying a polygon whose corners are the end-members. The samples are plotted as blue circles. Place the hair-cross pointer in the polygon and click on the left mouse button. A red circle will be plotted in the graph to indicate the selected position. The mixing portions for that point will be calculated and displayed in the upper left corner of the figure window. Clicking outside the polygon will give a mixing of NaN ("Not-a-Number") for all end-members, as 2-PC mixing only applies to samples within the polygon.
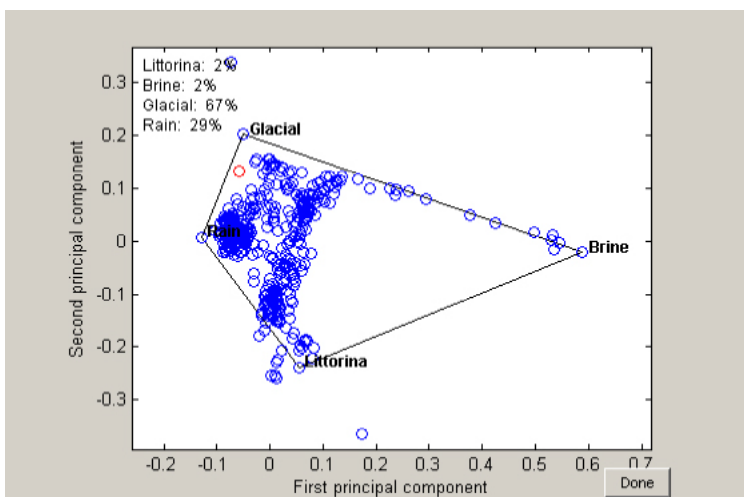
When no more positions need to be checked, click on "DONE".

Deviation

Mass balance calculations (deviation calculations) are used to define the sources and sinks for different elements which deviate from the ideal mixing model based on the mixing of end-members. No deviation from the measured value indicates that mixing can explain the element behaviour, whereas source or sink is due to net reactions. The evolution caused by water-rock interactions can thus be described.

(Re-)calculate deviation

In order to carry out the M3 calculations step by step, it is possible to calculate mixing in samples, as well as mixing in polygon and deviation, separately. This can be useful for instance when testing different allowance factors.

Selecting (Re-)calculate deviation will calculate the absolute deviation between the calculated and actual composition of the samples. A message box will appear and indicate that the calculation is in progress. It is not necessary to click on "OK" in this message box.

Display deviation in 2D

When displaying deviation in 2D, colours are used to describe the magnitude of the deviation. This gives the user a good overview of all samples and is useful both for initial examination of the observations and for displaying the final result of M3 calculations. The values of the deviation are measured in the same unit that was used for the elements' compositions in the original CSV-file (e.g. mg/l).

Selecting Calculations/Deviation/Display deviation in 2D will produce a dialog box to let the user select the element whose deviation to display. A new figure window will be opened and a 2D graph will display the samples as coloured circles. The colour of the samples represents the deviation of the calculated values from the actual values for the selected element. That is, a positive value of the deviation means that M3 has overestimated the amount of the element, and a negative value that M3 has underestimated it.

NOTE: To add a colorbar for interpretation of the colours, select Add/update colorbar from the Tools menu.

To change the size of the circles, select Tools/Preferences and adjust the values for deviation.

Display deviation in 3D

Displaying the deviation in three dimensions enables the user to examine more carefully the characteristics of the sources and sinks of an element. The 3D-rotation feature enables the user to select different viewpoints from where specific patterns can be identified. The method of display is, however, not so well suited for use in publications, since it can be confusing when the graph cannot be rotated. The values of the deviation are measured in the same unit that was used for the elements' compositions in the original CSV-file (eg, mg/l).

Selecting Calculations/Deviation/Display deviation in 3D will produce a dialog box to let the user select the element whose deviation to display. A new figure window will be opened and a 3D graph will display the samples as circles. The samples' values on the z-axis represent the deviation of the calculations from the actual values for the selected element. Samples where M3 has overestimated the amount of the plotted element are located in the positive side of the z-axis.
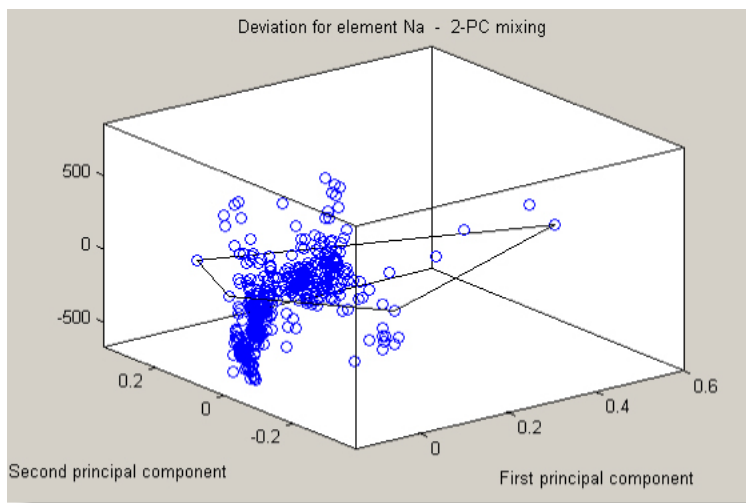
NOTE: The Rotate 3D function (Tools/Graphics- Rotate 3D) gives the user easy control of the view of the figure.

2.2.7   EVM

The End-member Variability Module (EVM) accepts as an input a range of compositions for each end-member (the end-members have been already selected, either by expert judgment or with the help of the end-member coverage test tool) and construct from every range an input probability distribution (in terms of compositions), which is propagated through the PCA and converted into an output probability for the mixing proportions and the deviation, respectively.

The EVM takes into account the intrinsic compositional variability of the end-members. The procedure starts from a pre-selected number of end members, i.e. no attempt is made here to define which end members to be use in the analysis, and has the following steps:

1. Define the compositional variability of the end-member waters. This can be done by defining compositional ranges for each input compositional variable.

2. Construct a probability density function for each compositional variable. This probability density functions are called input probabilities.

3. Generate, according to the chosen input probabilities, a large number of end member compositions.

4. For each run one of the calculated end-member composition is used to compute the mixing proportions and the deviation of selected samples.

5. After all runs have been finished, mixing proportions and deviation for each sample are binned to construct the output and deviation probability distributions.

EVM calculations

When selecting EVM calculations, several tests are made to ensure that the EVM input data is consistent with the EVM settings. If no inconsistencies are found, a dialog lets the user set the mixing model and number of calculation runs. Depending on the number of runs and the size of the dataset this may take several minutes. When the calculations are completed the EVM analysis window is opened. Any previously calculated EVM data in the current working directory will be overwritten.

EVM analysis window

The EVM analysis window has five distinctive parts:

- The Plot panel, where plots corresponding to the selected type and entities is displayed
- The Type panel, where the user selects the type of probability to investigate
- The Entities panel, where the user selects which entities to investigate
- The Statistics panel, where statistics for the selected entities is displayed
- Save buttons for statistics and plots
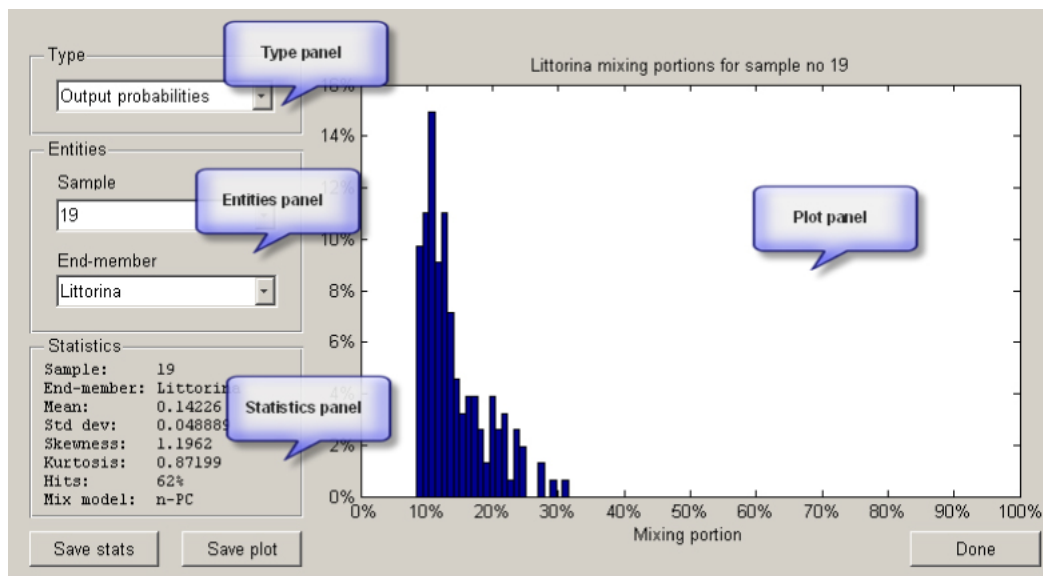
EVM analysis window

Probability types

There are four probability types:

- PCA probabilities
- Input probabilities
- Output probabilities
- Deviation probabilities

PCA probabilities

The initial probability type displayed is the PCA probabilities. The plot shows the accumulated PCA results for the runs. The end-members are plotted in colours and the samples are plotted in black. The shape of the distribution of a end-member is a result of the probability density function for that end-member. The title of the plot panel indicates how many samples there are in the data set and how many calculation runs were successful. Unsuccessful runs occur when the calculated end-members' principal components generate a shape that cannot be described by the selected mixing model.
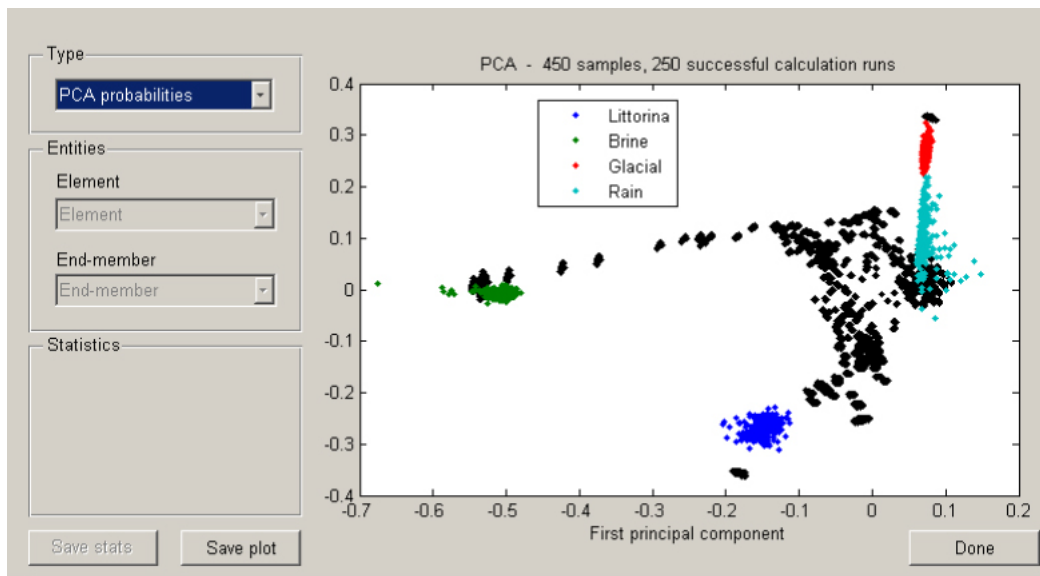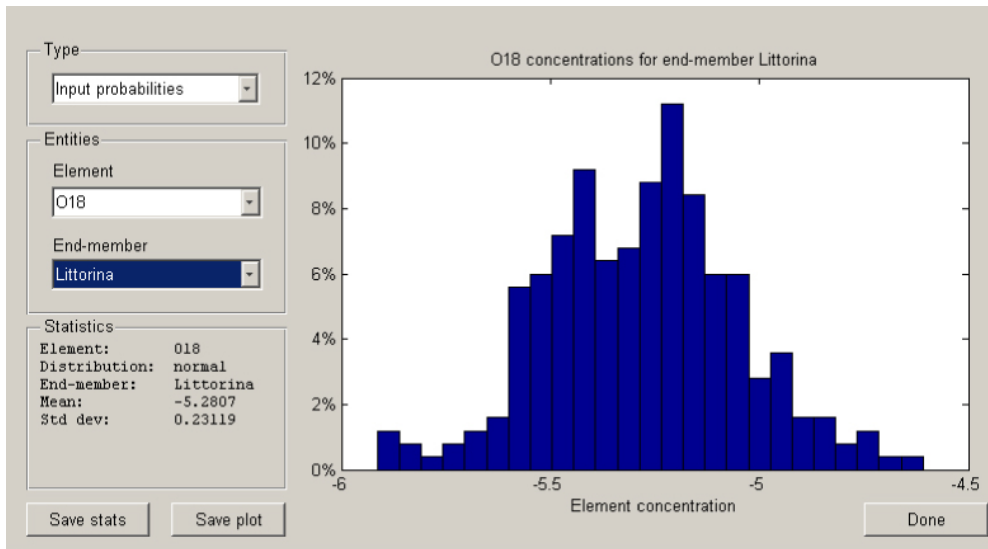
PCA probabilities

Input probabilities

The input probabilities show the concentrations of input elements for the different end-members. The plot panel shows a histogram for the end-members distributions. When selecting all end-members, the plot shows the histograms for all end-members together and the statistics for all samples can be saved using the "Save stats" button. By selecting individual end-members, the user can investigate statistics about the element concentrations for the given element/end-member combination. The statistics panel display the following data:

- Element label
- Probability distribution type for the element
- end-member label
- Concentration mean
- Standard deviation
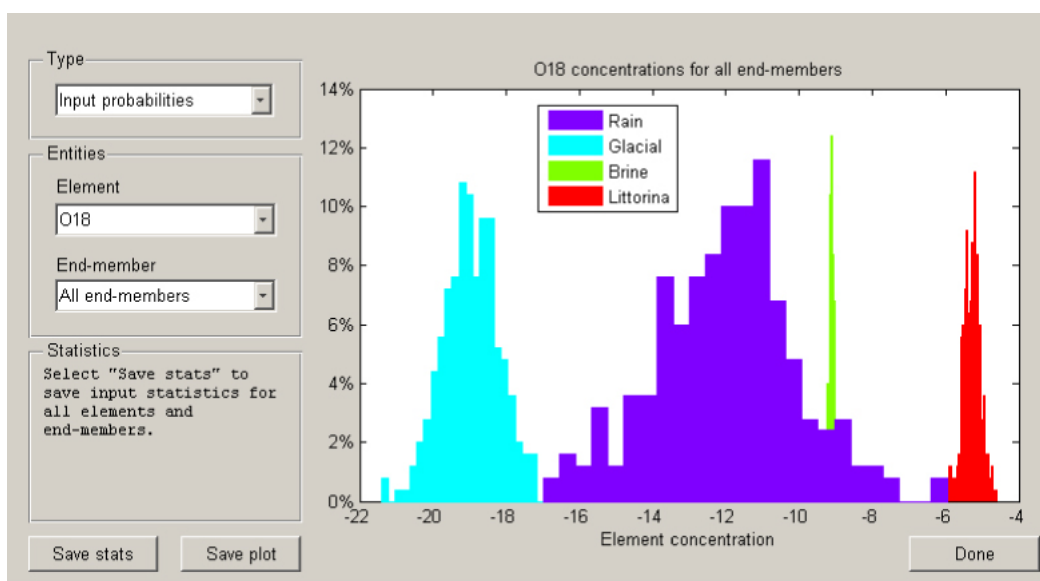
Input probabilities for all end-members

Input probabilities for one end-member

Output probabilities

The output probabilities show the mixing portions for the different end-members. The plot panel shows a histogram for the mixing distributions for a given sample/end-member combination. When selecting all samples, no plot is shown but the statistics for all samples can be saved using the "Save stats" button. When selecting one sample and all end-members, the plot shows the histograms for all end-members together for the selected sample. However, pressing the "Save stats" button at this point saves the statistics for all samples. By selecting individual samples/end-member combinations, the user can investigate statistics about the mixing portions. The statistics panel display the following data:

- Sample label
- end-member label
- Mixing mean
- Standard deviation
- Skewness
- Kurtosis
- Hits, i.e. in how many of the runs the sample was part of the mixing calculations
- Mixing model used
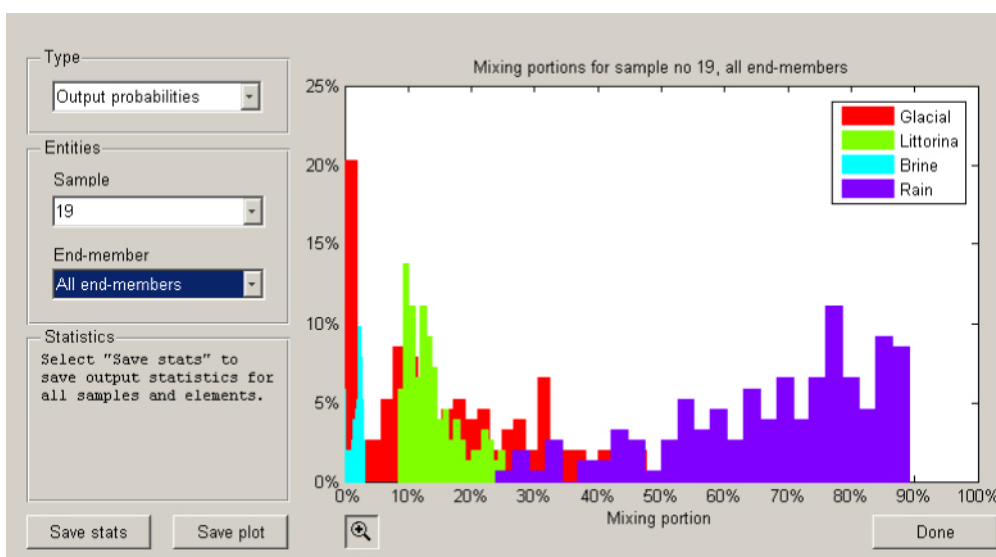
Output probabilities for one sample, all end-members
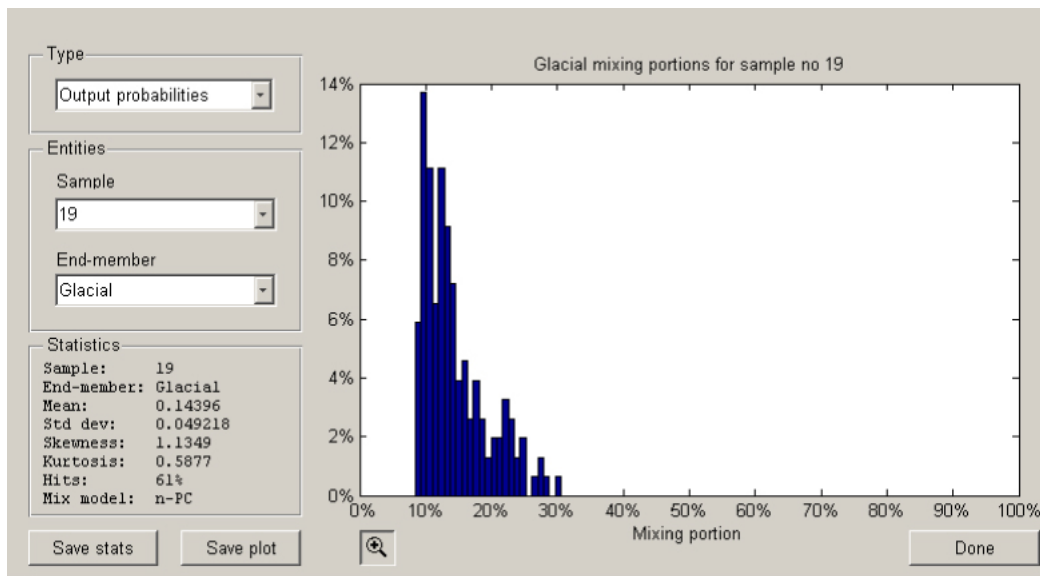
Output probabilities for one sample, one end-member

Deviation probabilities

The deviation probabilities show the deviation of concentrations based on mixing calculations from the imported elements concentrations for the different end-members. The plot panel shows a histogram for the deviation for a given sample/element combination. When selecting all samples, no plot is shown but the statistics for all samples can be saved using the "Save stats" button. By selecting individual samples, the user can investigate statistics about the deviation. The statistics panel display the following data:

- Sample label
- Element label
- Mixing mean
- Standard deviation
- Skewness
- Kurtosis
- Hits, i.e. in how many of the runs the sample was part of the mixing calculations
- Mixing model used
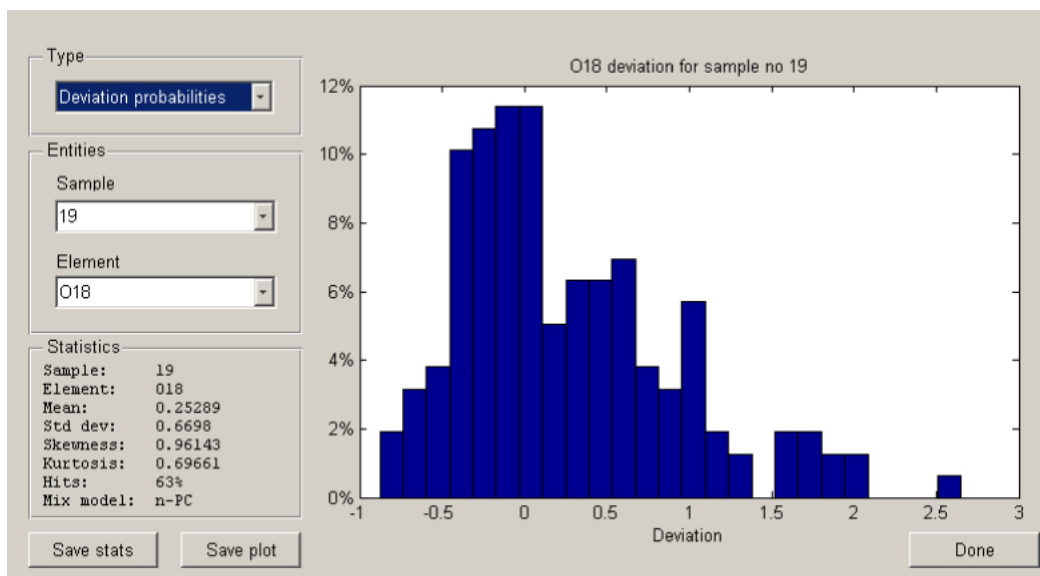
Deviation probabilities for one sample

EVM input data

In many aspects the EVM is a module separated from the rest of M3. In order to perform the EVM calculations, the EVM "imports" certain values from the previous calculations and selections made by the user in the "normal" flow of the program. These values are:

- Element concentrations, used as basis for PCA for all samples except for the selected end-members, which are calculated.

- Element labels, for plotting.

- end-member labels, to find the correct probability density function ("range file") and for plotting.

- end-member sample identities, to be able to replace the original element concentrations with the calculated ones.

Since the end-member labels are used to find the corresponding settings for probability density functions, it's important that they are identically spelled. See EVM settings for further information.

Analyze saved EVM data

Since EVM calculations can take a significant amount of time, it is possible to open previous EVM calculations for examination by selecting Analyze saved EVM data. The program will load previously calculated EVM data from the current working directory into the EVM analysis window.

EVM settings

All settings for the EVM (except for the variables described as EVM import data) are kept in CSV-files in a special directory on the hard drive. In order to change the settings the user must manually edit these files and in some cases create new files. Since the EVM settings must be based on expert knowledge of geochemistry to give correct and relevant results, great care should be exercised when modifying the settings files. As a security measure, it is possible to restore the default installation settings. Refer to the 'Concepts, Methods, and Mathematical Formulation' report before modifying the EVM settings.

Basic concepts

The EVM relies on the column order of the elements for identification of the elements. Therefore, it's important that the elements column order in the EVM settings files is the same as that of the imported elements. All elements have a Probability Density Function (PDF), that can either be normal or log-normal. This is set in the prob_labels.csv file. Also, the impact of chloride, deuterium and oxygen 18 is taken into account in the calculations. Rather than requiring the user to use fixed element labels for these elements, the column numbers are saved in separate files loaded by the EVM. Each end-member has a defined compositional range for each element used in in the PDF calculations. The range files are named by end-member label and must be identical to the labels set by the user in the program. In the range files the first row contains minimum values and the second row maximum values. The elements (columns) in the range files must be in the same order as in the imported elements.

Element related files

- **prob_lables.csv**

  PDF distribution type (normal or lognormal) corresponding to element columns. Used to determine PDF calculation type for element.

- **cl_col.csv**

  Column number of Cl concentrations. Used in PDF calculations to identify correct element.

- **d_col.csv**

  Column number of Deuterium concentrations. Used in PDF calculations to identify correct element.

- **o18_col.csv**

  Column number of Oxygen 18 concentrations. Used in PDF calculations to identify correct element.

- **elem_labels.csv**

  Element labels for the EVM settings. If the labels in this file doesn't match the element labels "imported" from the program, a warning will be issued when starting EVM calculations.

- **element.csv**

Array with the column numbers or the elements. If the number of elements in this file doesn't match the number of elements "imported" from the program, a warning will be issued when starting EVM calculations.

End-member related files

- **<reference_water_label>_ranges.csv**

  Concentration ranges for a end-member. The label in the file name must correlate exactly to the end-member label set by the user. The ranges files installed with the program are:

  Brine_ranges.csv
  DGW_ranges.csv
  Glacial_ranges.csv
  Littorina_ranges.csv
  Rain_ranges.csv

Mixing model related

- **evm_allwnc.csv**

  Allowance for EVM when using the n-PC mixing model.

Editing EVM settings files

The EVM settings files are plain text CSV-files and can be edited in any text editor, such as MS Notepad or IDM UltraEdit. The EVM requires that the settings files use semi-colon (";") as column delimiter. The EVM settings files' column delimiter is not affected by settings under Tools/Preferences. The effects of changes can be checked by selecting View saved EVM ranges and View EVM element properties.

EVM settings menus

View saved EVM ranges

All saved ranges for elements compositions used by the EVM can be inspected by selecting View saved EVM ranges. The minimum and maximum values of element concentrations for end-members are displayed in a matrix with end-members as rows and elements as columns. To edit the compositional ranges, select Open EVM settings directory and follow procedures described in the EVM settings section.

```
         Na       K      Ca      Mg     HC03      Cl     S04      Tr       D     018
Brine
       8500    45.5   19300    2.12    14.1   47200     906     0.1   -44.9    -8.9
       9540      28   18000     130     8.2   45200     8.4     0.1   -49.5    -9.3

DGW
       19.2       3    38.5     3.8     162      12    21.5    11.9   -68.4    -9.9
        237       4      25       6     370     119     118     0.8   -73.8    -9.9

Glacial
       0.17     0.4    0.18     0.1    0.12     0.5     0.5     0.1    -158     -21
       0.17     0.4    0.18     0.1    0.12     0.5     0.5     0.1    -125     -17

Littorina
       3674     134     151     448      93    6500     890     0.1     -38    -4.7
       1960      95    93.7     234      90    3760     325     0.1   -53.3    -5.9

Rain
        0.1     0.1     0.1     0.1     0.1     0.1     0.1     0.1    -125     -17
        0.1     0.1     0.1     0.1     0.1     0.1     0.1     168     -44    -6.9

                                 [  OK  ]
```

EVM ranges in default installation

View EVM element properties

The saved settings that are used to define the elements properties for the EVM can be inspected by selecting View EVM element properties. Column numbers, element labels and distribution type is displayed , as well indicators to which, if any, elements the EVM has marked as deuterium, oxygen-18 and chloride. To edit the element properties, select Open EVM settings directory and follow procedures described in the EVM settings section.

```
Column     Label   Distribution    D   O18   Cl

   1         Na      lognormal
   2          K      lognormal
   3         Ca      lognormal
   4         Mg      lognormal
   5        HC03     lognormal
   6         Cl      lognormal                  x
   7        S04      lognormal
   8         Tr      lognormal
   9          D        normal      x
  10        O18        normal            x

                 [  OK  ]
```

EVM elements' properties in default installation

Open EVM settings directory

Use this menu option to open the EVM settings directory. Manually edit the settings files as described in the EVM settings section.

Restore default EVM settings

Selecting Restore default EVM settings will reset EVM settings to the installation defaults. All files affected are described in the EVM settings section, including the default installed end-member range files. Range files created by the user will not be affected.

2.2.8 Tools

Show/hide end-member labels

The labels of the end-members can be displayed in any plot.

Selecting Tools/Show end-member labels will display the end-members labels in the plot to the upper right of the coordinates of the end-members. Zooming in a plot where the end-member labels are visible will leave the labels in the same position as before the zooming. To adjust the positions to fit the zoomed view, select Show end-memberlabels once again.
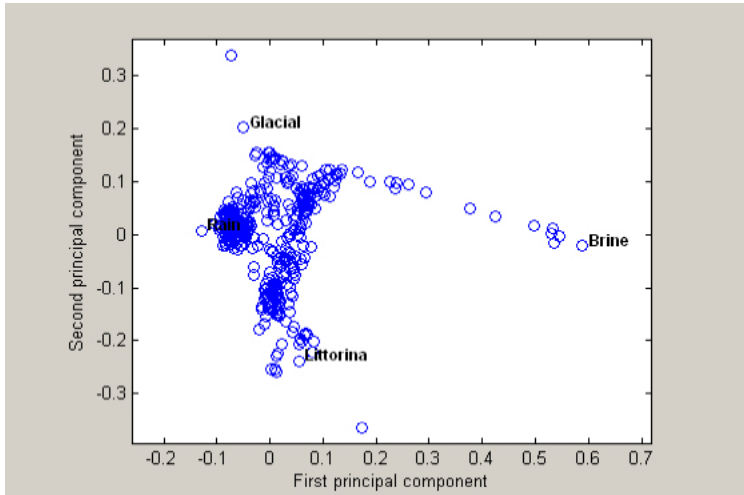
Identify samples from screen

When the location of a specific observation in the PCA plot is known but its sample id label in the original matrix is not, the label can be identified from the screen. When the label has been identified, it can be used to check the information about the observation that has not been transferred to M3.

Selecting Tools/Identify sample from screen will produce a figure window with the samples plotted as blue circles. If end-members have been selected, lines will be drawn between the end-members, forming a polygon. Click with the cross hair pointer on a sample to display its index number, i.e. the sample's label . The selected sample will turn red and the text "Sample index no:", followed by the sample label, will be displayed in the upper left corner of the figure window. When no more samples need to be checked, click on "Done".
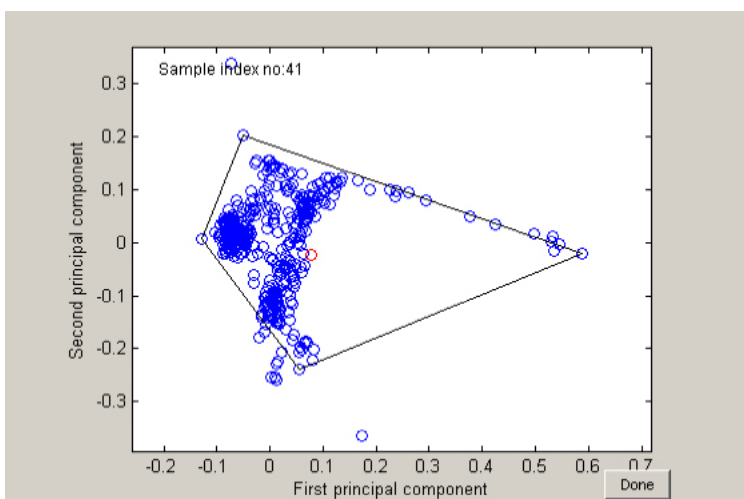
Identify samples from sample id labels

Identify selected samples

Selected samples can be displayed with a symbol in a specified colour. There are eight symbols and seven colours that can be combined.

Selecting Tools/Identify selected samples will cause a dialog box to appear, prompting the user to enter the id labels of the samples that are to be displayed as coloured symbols. Enter the samples that should be displayed, choose the appropriate colour and symbol for each selection and click on "OK". The sample id labels must be separated by a space if more than one sample is to be displayed. By default, a new figure window will be opened and all samples will be plotted as black circles. Checking or unchecking the two check boxes in the dialogue box ("Plot selection in new figure" and "Do not plot unselected samples") can change this behaviour.

The selected samples will be plotted with the chosen symbol/colour combination on top of the black circles. If end-members have been selected for mixing calculations, the 2-PC end-member polygon is also drawn.

NOTE: Unchecking "Plot selection in new figure" will cause M3 to plot the selection in the current window only if the current window is the result of a previous selection, i.e. the window appeared after the user selected Identify selected samples or Identify ranges of samples. The selection can not be plotted in figure window showing, for example, mixing in polygon.

Identify ranges of samples

Ranges of samples can be displayed with a symbol in a specified colour. There are eight symbols and seven colours that can be combined.

Selecting Tools/Identify ranges of samples will cause a dialog box to appear, prompting the user to enter the first and last sample id label of the ranges of samples that are to be displayed as coloured symbols. Enter the row indices that should be displayed, choose the appropriate colour and symbol for each selection and click on "OK". By default, a new figure window will be opened and all samples will be plotted as black circles. Checking or unchecking the two check boxes in the dialogue box ("Plot selection in new figure" and "Do not plot unselected samples") can change this behaviour.

The selected samples will be plotted with the chosen symbol/colour combination on top of the black circles. If end-members have been selected for mixing calculations, the end-member polygon is also drawn.

NOTE: Unchecking "Plot selection in new figure" will cause M3 to plot the selection in the current window only if the current window is the result of a previous selection, i.e. the window appeared after the user selected Identify selected samples or Identify ranges of samples. The selection can not be plotted in figure window showing, for example, mixing in polygon.

Show sample id labels

The id labels of the samples can be displayed in any plot.

Selecting Tools/Show sample id labels will display the sample labels of the visible samples to the right of each sample in the current figure window. Zooming in a plot where the id labels are visible will leave the labels in the same position as before the zooming. To adjust the positions to fit the zoomed view, select Show sample id labels once again.
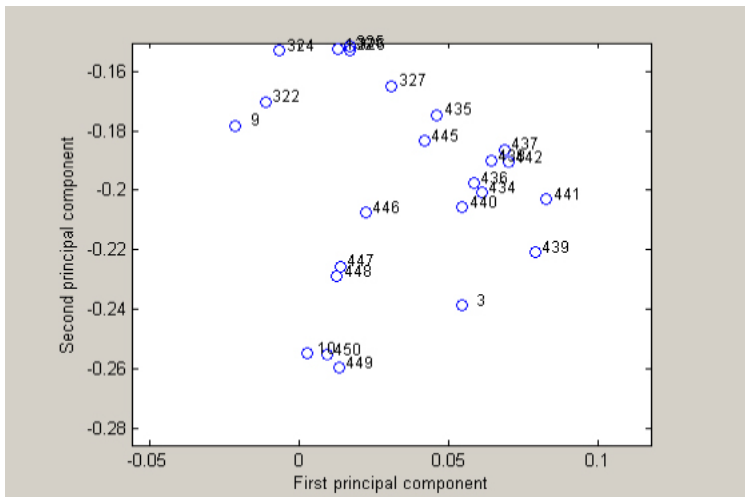
Hide sample id labels

The sample id labels displayed in a plot can be deleted.

Selecting Tools/Hide sample id labels will delete all displayed sample id labels in a plot.

Graphics

Zoom

The zoom function is used when examining observations in more detail than the default figures allow for.

The Zoom menu contains the following menu items: Zoom on and Zoom off. The zooming functions can also be controlled by using the zoom buttons in the plot window.

Selecting Zoom on will make a click on the left mouse button zoom in the figure at the point where the arrow pointer is positioned. Pressing the left mouse button and dragging the cursor in the axis area defines the area to zoom. Clicking the right mouse button will zoom out in the figure.

To turn the zooming function off, select Zoom off.

Colorbars can be zoomed separately from the axis area.

Rotate 3D

When examining 3D figures it is sometimes necessary to rotate the figures to be able to examine all aspects of the information displayed. The 3D-rotation function is used to control this rotation.

The Rotate 3D menu contains the following menu items: Rotate on and Rotate off. Rotation can also be controlled by using the rotate 3D button in the plot window.

When Rotate on is selected, clicking on an axis draws an animated box, which rotates as the mouse is dragged, showing the view that will result when the mouse button is released. A numeric readout appears in the lower-left corner of the figure during this time, showing the current Azimuth and Elevation of the animated box. Releasing the mouse button removes the animated box and the readout, and changes the view of the axes to correspond to the last orientation of the animated box.

To turn the Rotate 3D function off, select Rotate off.

Clear axis

Selecting Tools/Graphics- Clear axis will clear the area within the x and y (and z) axes in the current figure window from any plot or graph it may contain.

Add text to plot

Text can be added to a plot to explain or highlight the information displayed.

Selecting Tools/Add text to plot will cause a dialog box to appear, prompting for a text string to add to the plot. Enter the text and click on "OK". When you move the pointer over the current figure window it becomes a cross hair, indicating the location of pointer. Pressing a mouse button or keyboard key while the pointer is within a figure window will add the text with its lower left corner at the position of the cross hair.

NOTE: Special characters and font settings can be used in text added to the plot, see Special Characters.

Title/axis label

The Tools/Title/Axis label menu contains the following four menu items: Title, X-axis, Y-axis and Z-axis.

Selecting one of these items will cause a dialog box to appear, prompting for the new title or axis label.

It is possible to enter two lines, one in each text box. By default the boxes contain a space, which can be erased or substituted with text. Enter the new text string and click on "OK". The figure will then be updated with the new title or axis label.

NOTE: The figure window does not automatically adjust to make space for two lines of title or axis label text. If the title or axis label does not fit, resize or maximise the figure window.

NOTE: Special characters and font settings can be used in axis labels, see Special Characters.

Add/update colorbar

A colorbar works as a legend to the colours in a plot. What colours are assigned to what values can be read on the colorbar.

Selecting Tools/Add/update colorbar will update the colorbar in the current figure window or add a colorbar if there is none. The colorbar can also be turned on and off using the colorbar button ⬛ in the plot window.
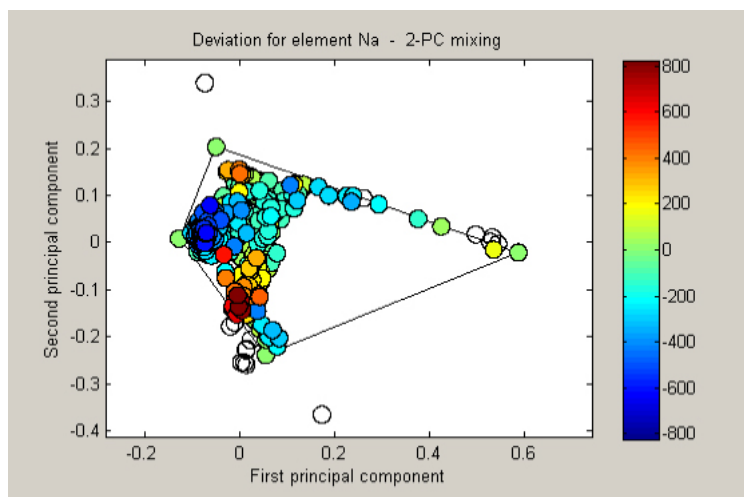
Change working directory

Variables are loaded from and automatically saved to the working directory selected when M3 starts. The working directory can be changed without restarting M3. Clearing all variables from memory, changing working directory and loading previously saved variables enables the user to start working with a different data set without restarting the program.

NOTE: Press "Save" to change to the selected directory.

Preferences

CSV-file delimiter and graphics preferences are set under the Tools/Preferences menu. Values that control the size of circles for mixing and deviation can be adjusted.

The default circle size for mixing and deviation is 5. Read more about CSV files in the Import elements section.

2.2.9   Help

Selecting Help/M3 Help topics will open this help file.

Selecting Help/About M3 will display version information about M3.

Exit

Selecting Exit will exit the program.

2.3   Special characters

It is possible to enter labels and text strings that contain special characters, such as mathematical symbols and Greek letters, using TeX syntax. The full syntax is extensive and well beyond the scope of this help, but some basic operations are:

Subscript and superscript

Type	Syntax	Example	Result
subscript	_{string}	H_{2}CO_{3}	H_2CO_3
superscript	^{string}	^{3}H	^3H

Font control

Type	Syntax	Example	Result
Italic font	\it{string}	\it{This is italic}	*this is italic*
Bold font	\bf{string}	\bf{Bold}	**Bold**
Normal font	\rm{string}	\rm{normally}	normally
Font name	\fontname{fontname}	\fontname{Script}TEST	$\mathcal{TEST}$
Font size	\fontsize{fontsize}	\fontsize{16}Hello	Hello
Font colour	\color(colorSpec)-	\color{red}Roses	Roses

Special characters

Type	Syntax	Example	Result
Lower-case Greek letters	\letter-name	\delta	δ
Lower-case Greek letters	\Letter-name	\Delta	Δ
Mathematical symbols	\symbol-name	\int	∫

Expressions can be nested to create complex text strings:

My friend, _{\it{this \color{red}is \color{black} ^{a}\bf{bold}} example} of T_{E}X

is displayed as

My friend, *this is a **bold** example* of T$_E$X

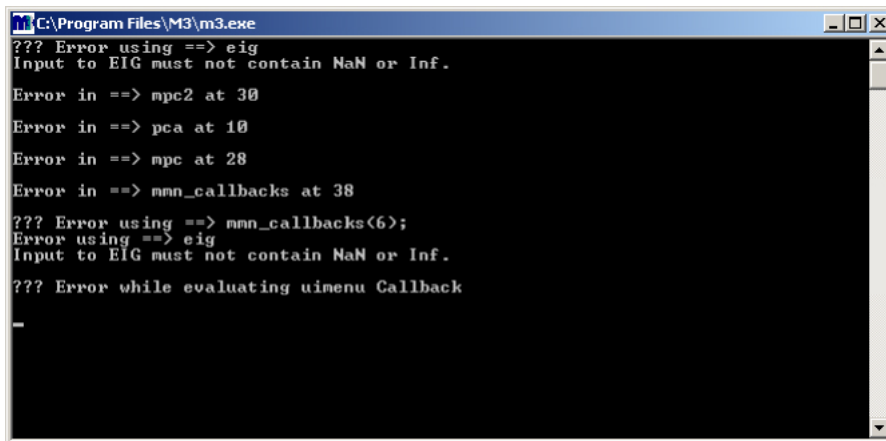Full documentation of TeX can be found on the TeX Users Group web site http://www.tug.org.

NOTE: The TeX characters will only be interpreted as such when displayed in a plot, i.e. an element label for tritium will be displayed as 3H when plotted to the screen but will appear in dialogues and other components in the program as ^{3}H.

NOTE: Using special characters in end-member labels may cause problems when using the EVM if the file system doesn't allow the used syntax characters in file names. Most notably, the backslash ("\") character can't be used.

2.4 M3 console window

The M3 console window is the "parent" of all other M3 windows. Closing the console window will cause M3 to exit. If M3 is started from a command promt, STDOUT and STDERR is used as the console window.

Although M3 tries to check for probable errors and give the user explanatory error messages, sometimes unforseen situations cause internal errors in the program. In case of such errors, error or warning messages are printed to this window in order to help the user find the cause of the error. E.g. when trying to calculate PCA on elements that contain the special "NaN" ("Not-a-Number") value, the following error message is printed to the console window:

Error messages in M3's console window

Although these error messages can be very hard to decrypt, they are very useful when reporting trouble to the software support. The error messages may also be an indication of a software bug. Reporting the errors displayed in the console window may help improve future versions of M3.

To record error messages in the console window to a text file called "m3output.txt", start M3 from a command promt in the following fashion:

m3.exe > m3output.txt 2>&1

2.5 Examples

2.5.1 Oklo Natural Nuclear Analogue

Working with M3

SKB is conducting and participating in Natural Analogue activities as part of various studies regarding the final disposal of high level nuclear waste (HLW). The Bangombé site at Oklo (Gabon) provides the unique opportunity to study the behavior of products from natural nuclear reaction in the vicinity of reactor zones which were active around 2 billion years ago. One of the principal aims was to study indications of present time migration of elements from the reactor zones under ambient conditions, as an analogue of spent nuclear fuel behavior. This provides the opportunity to assess the necessary tools for future performance assessment of the prospective real waste repository sites.

Bangombé is a shallow site with a homogeneous layering situated in a area of meteoric alteration. Many compositional and physicochemical variables obtained during different sampling campaigns are important for the understanding of the natural system. The information gathered can be handled using multivariate techniques.

M3 code is such a tool used to characterize the groundwater system based on existing data. The origin and evolution of the groundwater can be described if the effect from mixing and reactions can be described separately. M3 consists of 3 steps where the first step is a standard principal component analysis, followed by mixing, and finally by mass-balance calculations. Mass balance calculations are used to define the sources and sinks for different elements, which deviate from the ideal mixing model used in the mixing calculations. The mixing portions are used to predict the recalculated values for the elements. No deviation from the measured values indicates that mixing can explain the element behavior. A source or sink is due to mass-balance reactions. M3 uses the opposite approach to that of other standard methodologies. In M3 the mixing processes are evaluated and calculated first. The constituents that can not be described by mixing are described by reactions. M3 determines the origin of the water, the mixing proportions and the most important mass balance reactions that take place in the groundwater.

The field studies and the conceptualization provide information for the modeling. M3 was used to model the Bangombé data set and the different steps of the M3 modeling. A total of 23 groundwater samples from 15 boreholes have been investigated.

As an example of the use of the M3 code, the Bangombé data is presented below.

Preparing data

Bangombé data was stored as an MS Excel workbook and is presented at the end of this document. The user can step by step follow the M3 code use and check the data. In the table, the measured data from the site are marked in red and represent the columns from 1 to 8. The M3 results are presented in columns 9 to 19. If the user employs an XLS-file, this shall be converted into a comma delimited CSV- file and saved in the working folder. Bangombé data set is formed by 23 samples. Three end-members are identified: "Deep water", "Rain water" and "Intermediate water". The working file for M3 shall contain only the data, with an optional first row containing the elements' labels and, equally optional, a first column with numeric sample labels. For the present example, a CSV file is built from the excel file (Figure 1, upper) columns 1 to 8 and rows 3 to 27. This will give the CSV file (Figure 1, lower) with 8 columns and 25 rows.

	A	B	C	D	E	F	G	H
1	1	2	3	4	5	6	7	8
2	Alk mole/l.	Cl mole/l.	SO4 mole/l.	Na mole/l.	K mole/l.	Ca mole/l.	Mg mole/l.	U mole/l.
3	2.18E-05	8.40E-06	5.50E-06	1.09E-05	3.60E-06	2.49E-06	1.60E-06	9.32E-09
4	4.96E-04	9.90E-06	4.50E-06	4.35E-05	1.46E-05	8.70E-06	1.52E-05	1.13E-09
5	1.60E-03	5.90E-06	1.47E-05	3.83E-04	2.56E-05	4.60E-04	1.83E-04	5.63E-08
6	1.68E-03	7.10E-06	1.51E-05	3.83E-04	2.60E-05	4.80E-04	1.88E-04	7.94E-08
7	1.64E-04	6.80E-06	1.34E-05	7.60E-05	7.20E-06	1.62E-05	2.10E-05	1.27E-08
8	7.87E-04	1.02E-05	3.00E-05	1.60E-05	2.07E-05	1.37E-05	3.58E-05	2.33E-09
9	5.01E-04	9.30E-06	1.45E-05	2.80E-05	3.48E-05	1.37E-05	4.77E-05	8.85E-09
10	2.09E-04	8.74E-06	1.25E-05	1.78E-05	7.93E-06	2.25E-05	4.94E-05	4.62E-09
11	2.51E-03	2.17E-05	1.35E-05	5.22E-04	5.37E-05	7.98E-04	2.10E-04	8.82E-08
12	7.31E-04	4.23E-06	1.35E-05	3.48E-04	1.71E-05	8.98E-05	4.53E-05	1.76E-09
13	1.00E-03	1.30E-05	1.07E-05	5.22E-05	1.76E-05	9.98E-05	3.33E-04	1.34E-09
14	5.70E-04	8.74E-06	1.35E-05	3.65E-05	1.41E-05	4.74E-05	1.32E-04	4.62E-08
15	1.08E-03	1.75E-05	1.25E-05	1.83E-04	2.56E-05	1.12E-04	1.60E-04	6.89E-08
16	4.41E-04	2.25E-06	2.03E-05	3.17E-05	1.13E-05	6.75E-05	2.48E-05	9.12E-09
17	4.04E-04	3.66E-06	1.78E-05	1.35E-05	9.49E-06	3.53E-05	1.85E-04	1.11E-07
18	8.47E-04	1.72E-05	1.06E-05	1.61E-05	6.92E-06	4.13E-05	1.37E-04	1.18E-09
19	6.96E-04	6.98E-06	6.98E-06	1.14E-04	1.41E-05	1.85E-04	1.67E-04	1.48E-08
20	2.36E-03	1.69E-05	1.77E-05	2.39E-04	2.95E-05	4.08E-04	1.65E-04	1.13E-08
21	5.74E-04	8.17E-06	2.29E-05	2.65E-04	1.41E-05	9.25E-05	5.00E-05	2.31E-10
22	4.44E-04	1.30E-05	2.29E-05	1.52E-05	8.21E-06	2.10E-05	7.29E-05	1.30E-08
23	4.92E-04	2.68E-06	2.19E-05	1.48E-05	6.15E-06	2.50E-05	9.17E-05	1.41E-07
24	7.70E-04	1.35E-05	1.88E-05	1.35E-04	1.36E-05	4.75E-05	1.04E-04	2.18E-08
25	1.84E-04	7.61E-06	2.92E-06	1.87E-05	1.10E-05	4.25E-05	1.88E-04	1.00E-09
26	1.33E-05	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.00E-12
27	6.30E-05	2.28E-05	2.46E-05	2.98E-05	1.58E-05	2.30E-05	2.60E-05	7.73E-09

	A	B	C	D	E	F
1	2.18E-05;8.40E-06;5.50E-06;1.09E-05;3.60E-06;2.49E-06;1.60E-06;9.32E-09					
2	4.96E-04;9.90E-06;4.50E-06;4.35E-05;1.46E-05;8.70E-06;1.52E-05;1.13E-09					
3	1.60E-03;5.90E-06;1.47E-05;3.83E-04;2.56E-05;4.60E-04;1.83E-04;5.63E-08					
4	1.68E-03;7.10E-06;1.51E-05;3.83E-04;2.60E-05;4.80E-04;1.88E-04;7.94E-08					
5	1.64E-04;6.80E-06;1.34E-05;7.60E-05;7.20E-06;1.62E-05;2.10E-05;1.27E-08					
6	7.87E-04;1.02E-05;3.00E-05;1.60E-05;2.07E-05;1.37E-05;3.58E-05;2.33E-09					
7	5.01E-04;9.30E-06;1.45E-05;2.80E-05;3.48E-05;1.37E-05;4.77E-05;8.85E-09					
8	2.09E-04;8.74E-06;1.25E-05;1.78E-05;7.93E-06;2.25E-05;4.94E-05;4.62E-09					
9	2.51E-03;2.17E-05;1.35E-05;5.22E-04;5.37E-05;7.98E-04;2.10E-04;8.82E-08					
10	7.31E-04;4.23E-06;1.35E-05;3.48E-04;1.71E-05;8.98E-05;4.53E-05;1.76E-09					
11	1.00E-03;1.30E-05;1.07E-05;5.22E-05;1.76E-05;9.98E-05;3.33E-04;1.34E-09					
12	5.70E-04;8.74E-06;1.35E-05;3.65E-05;1.41E-05;4.74E-05;1.32E-04;4.62E-08					
13	1.08E-03;1.75E-05;1.25E-05;1.83E-04;2.56E-05;1.12E-04;1.60E-04;6.89E-08					
14	4.41E-04;2.25E-06;2.03E-05;3.17E-05;1.13E-05;6.75E-05;2.48E-05;9.12E-09					
15	4.04E-04;3.66E-06;1.78E-05;1.35E-05;9.49E-06;3.53E-05;1.85E-04;1.11E-07					
16	8.47E-04;1.72E-05;1.06E-05;1.61E-05;6.92E-06;4.13E-05;1.37E-04;1.18E-09					
17	6.96E-04;6.98E-06;6.98E-06;1.14E-04;1.41E-05;1.85E-04;1.67E-04;1.48E-08					
18	2.36E-03;1.69E-05;1.77E-05;2.39E-04;2.95E-05;4.08E-04;1.65E-04;1.13E-08					
19	5.74E-04;8.17E-06;2.29E-05;2.65E-04;1.41E-05;9.25E-05;5.00E-05;2.31E-10					
20	4.44E-04;1.30E-05;2.29E-05;1.52E-05;8.21E-06;2.10E-05;7.29E-05;1.30E-08					
21	4.92E-04;2.68E-06;2.19E-05;1.48E-05;6.15E-06;2.50E-05;9.17E-05;1.41E-07					
22	7.70E-04;1.35E-05;1.88E-05;1.35E-04;1.36E-05;4.75E-05;1.04E-04;2.18E-08					
23	1.84E-04;7.61E-06;2.92E-06;1.87E-05;1.10E-05;4.25E-05;1.88E-04;1.00E-09					
24	1.33E-05;1.00E-12;1.00E-12;1.00E-12;1.00E-12;1.00E-12;1.00E-12;1.00E-12					
25	6.30E-05;2.28E-05;2.46E-05;2.98E-05;1.58E-05;2.30E-05;2.60E-05;7.73E-09					

Figure 1. Bangombé data set and conversion in CSV file.

Starting M3

Click on the M3 icon ![icon]. The M3 start-up image appears for a few seconds, and then an M3 figure window will be opened. Select your working directory. The CSV-file shall be previously saved in the selected working directory. Click "OK".
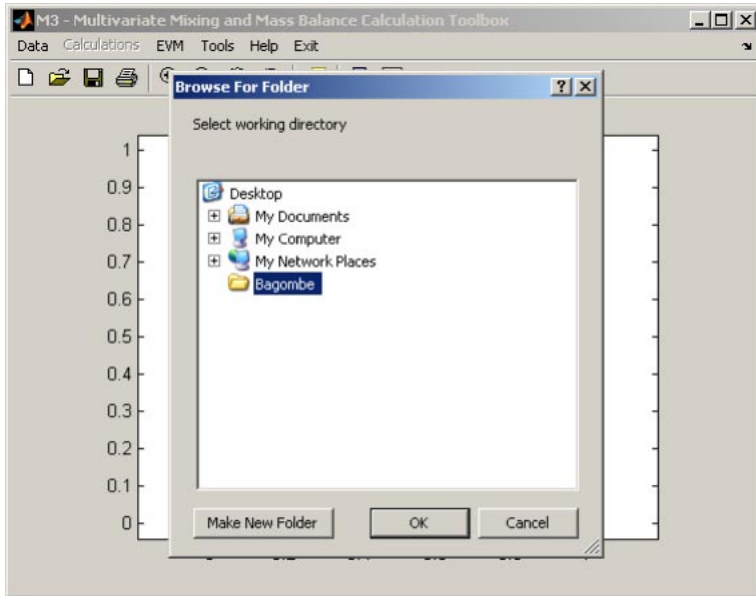

Figure 2. *Browse for Folder.*

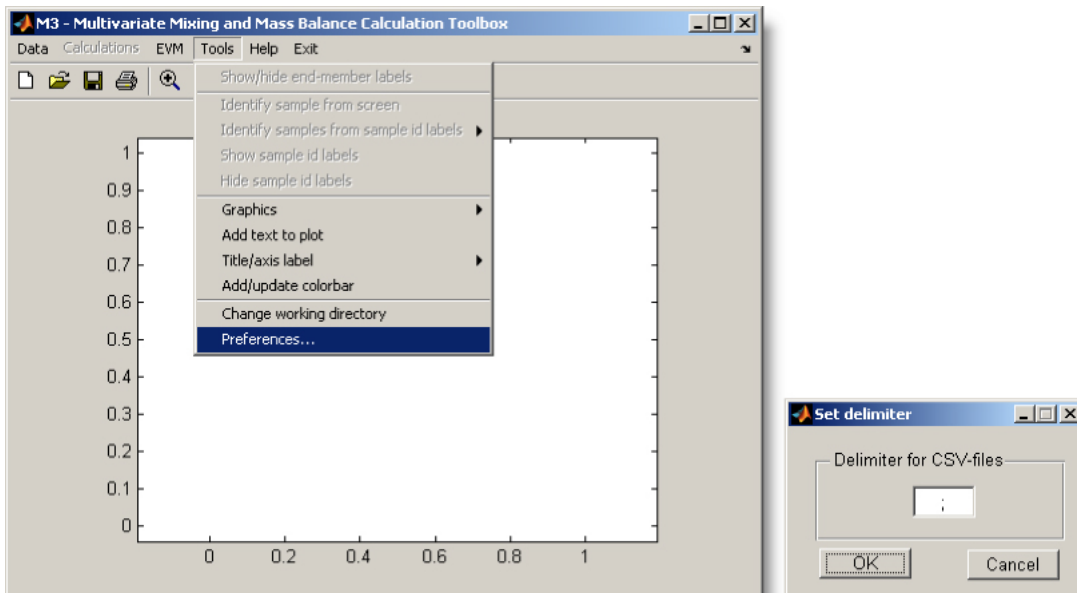From the Tools menu, choose under "Preferences" the type of input file data (for example, comma or semicolon).

Figure 3. *Delimiter for CSV-files.*

Click "OK".

From the "Data" menu choose "Import elements from CSV-file". A window with the CSV-file will appear. Select the CSV-file and click "Open" on the Import window.
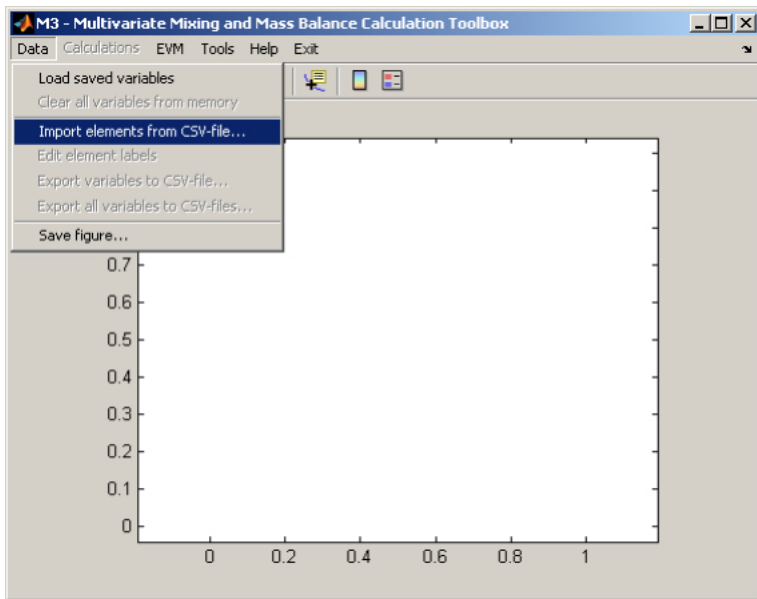
Figure 4. *Import elements from CSV-file.*

The program will display:
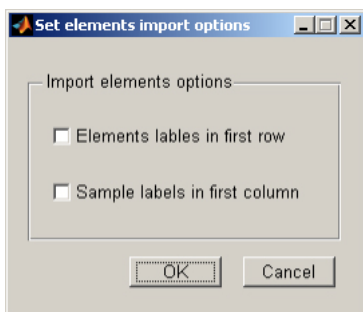
Figure 5. *Set element import options.*

Since our CSV-file only contains the element concentrations values (not element labels or sample labels) we leave the check boxes unmarked and click "OK".

The window "Enter element labels" will open. If the input CSV file had contained the labels in the first row, they would have appeared in this window. For Bangombé the elements are: Al, Cl, SO4, Na, K, Ca, Mg, U.
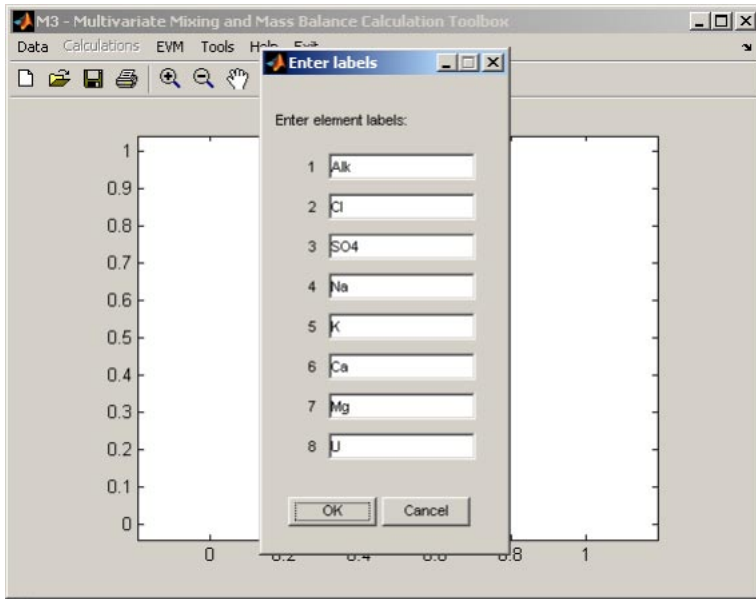
Figure 6. Enter element labels.

Click "OK".

Calculate principal components

Selecting "Calculations/PCA/Calculate principal components" will calculate the principal components and produce a graph in the current figure window, displaying the samples as blue circles. The program will display the variance of the first three principal components PC1, PC2 and PC3.

The first principal component is shown on the x-axis and the second principal component on the y-axis.
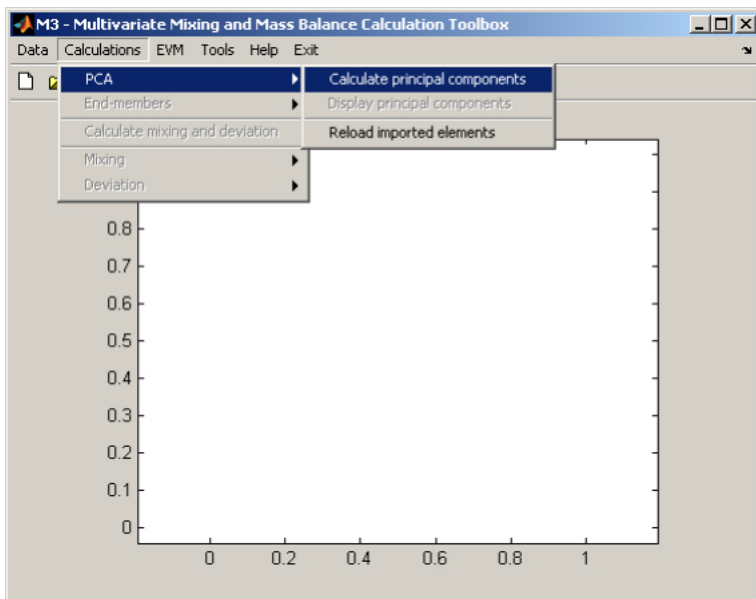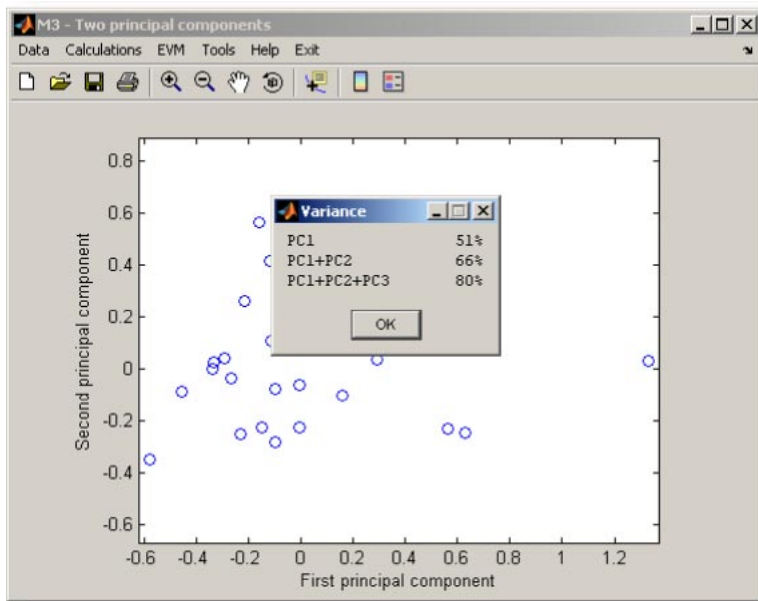
Figure 7. *Calculate principal components and variance on the two principal component plot.*

Click "OK":
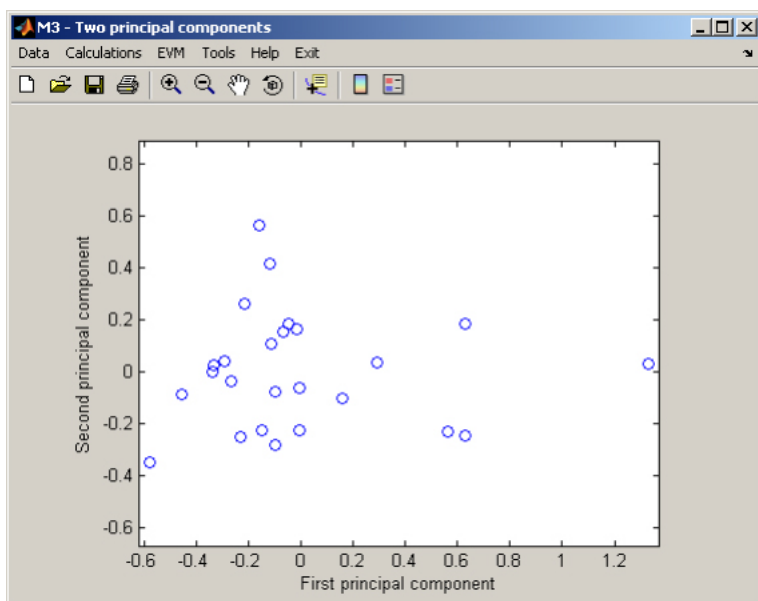
Figure 8. *Two principal component plot.*

Select end-members

The M3 mixing method generally uses end-member waters to calculate and describe mixing. These end-members are considered to be the original waters that have been mixed to form the other observations. End-members are usually the most extreme waters in the PCA plot and are selected by the user from the menu Calculations/End-members/Select end-members. The end-members are selected by clicking on the selected values or directly entering the row number in the data windows below the PC graph. When clicking on a sample, the sample turns in red and the numbered value is displayed on the bottom of the window. This number is the sample's row index in the imported matrix, i.e. the sample's row number in the CSV file.

Note: The mixing model requires that the corners of the polygon are convex, i.e. do not point inwards in the polygon. M3 requires that the end-members are selected in sequence and the program cannot handle crossed lines in the polygon.

For Bangombé the end-members are: Sample no. 9, Sample no. 24, and Sample no. 25.
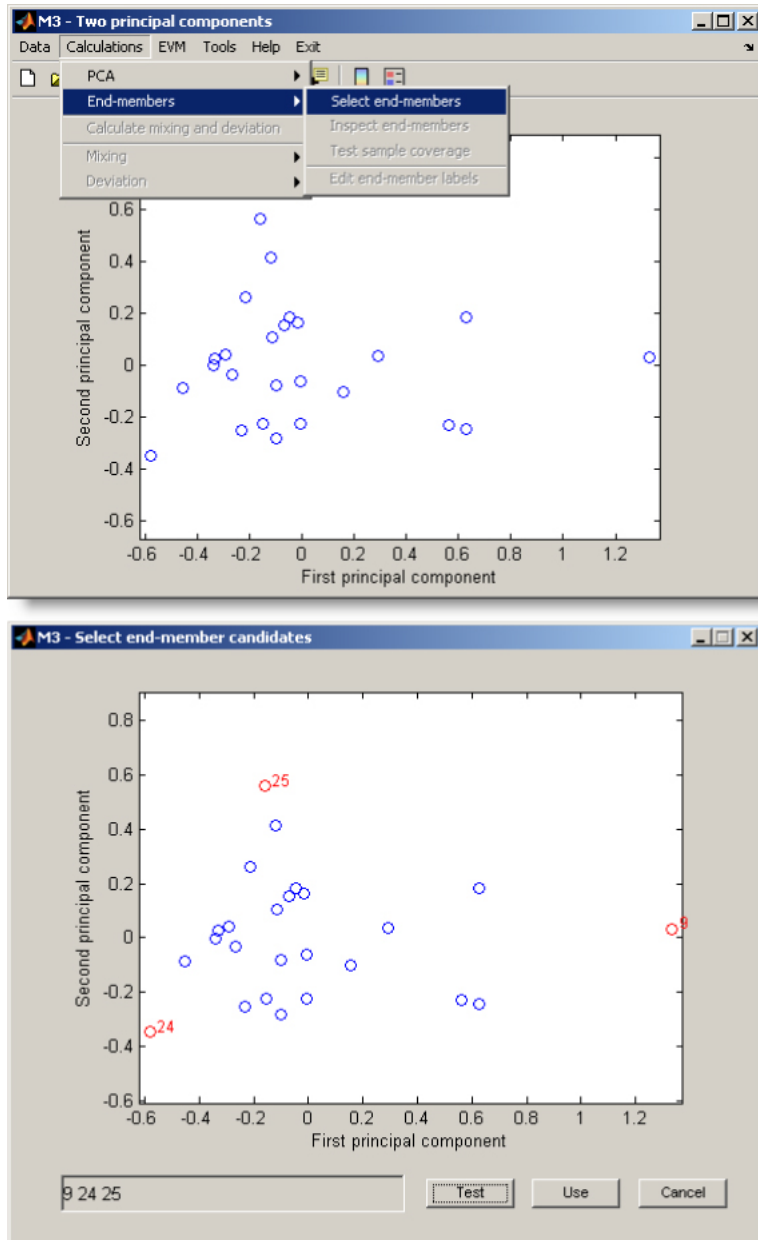
Figure 9. *Select end-members.*

Select "Test".

The window with "Select allowance for n-PC mixing" will appear. The allowance factor determines how samples near an edge of the mixing polygon but outside it are dealt with, and affects the coverage (number of samples explained by mixing). We change the default value 0.03 to 0.07. This increases the coverage on our data set from 88% to 92% (one more sample is included in the calculations). Click "OK".
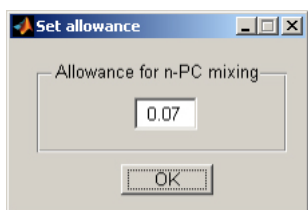
Figure 10. *Allowance for n-PC mixing.*

The program will display a window for few seconds "Please wait while calculating sample coverage".

Select end-member combination

M3 can calculate mixing in two coordinates with "2-PC mixing" or in n-coordinates using "n-PC mixing". In this case, where there are only 3 end-members, the 2-PC and n-PC are identical. In the right side of the window M3 will display the sample coverage percentage for the model with 0.07 allowance factor. For Bangombé model the coverage is 92%. A polyhedron will be drawn on the graph showing the selected configuration of end-members. Those inside the mixing polygon are shown in blue and those outside it are shown in black.
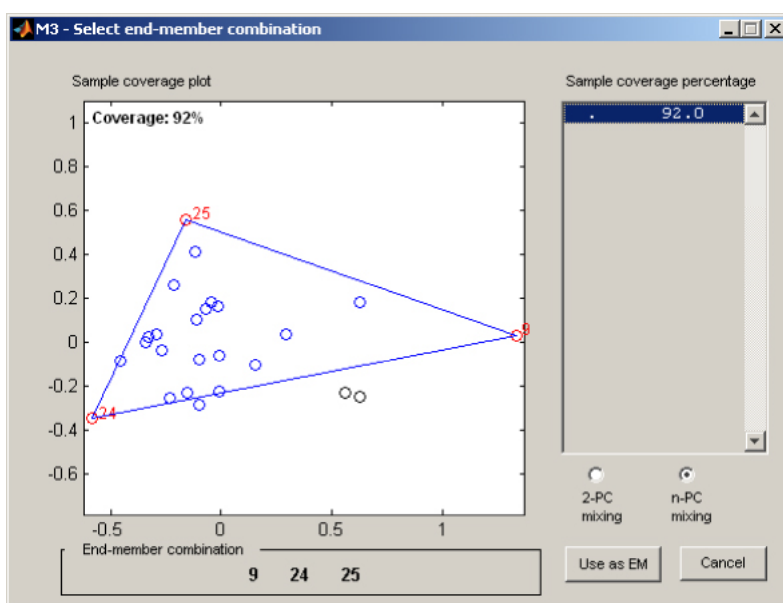
Figure 11. *Select end-member combinations.*

Click "Use as EM" to use as end-members. A new window will be displayed asking for the end-members names.
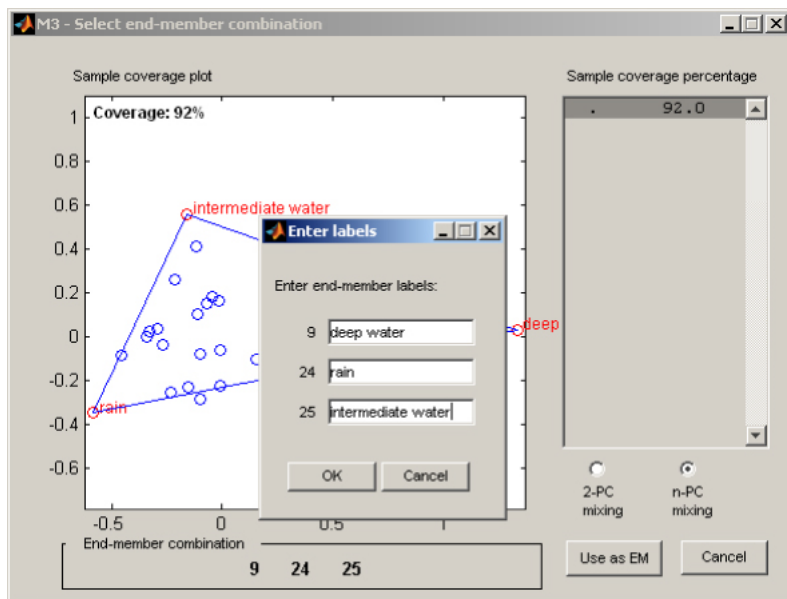
Figure 12. *Enter end-member labels.*

For the Bangombé model the end-members are:

*   Sample 9 corresponding to "Deep water".
*   Sample 24 corresponding to "Rain".
*   Sample 25 corresponding to "Intermediate water".

Click "OK".

Calculate n-PC mixing and deviation

From the window "Select mixing model" select n-PC mixing (allowance value shall correspond with the previous select one). In Bangombé model the allowance was chosen by default at 0.07. Click "OK".
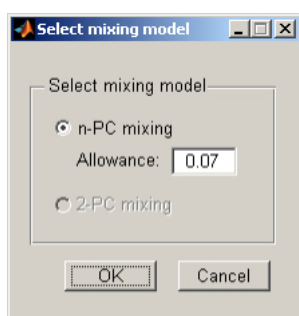

Figure 13

M3 will calculate mixing proportions and the deviation from the measured values. As the calculations proceed a message box display the current process. The results from the calculations are automatically saved.
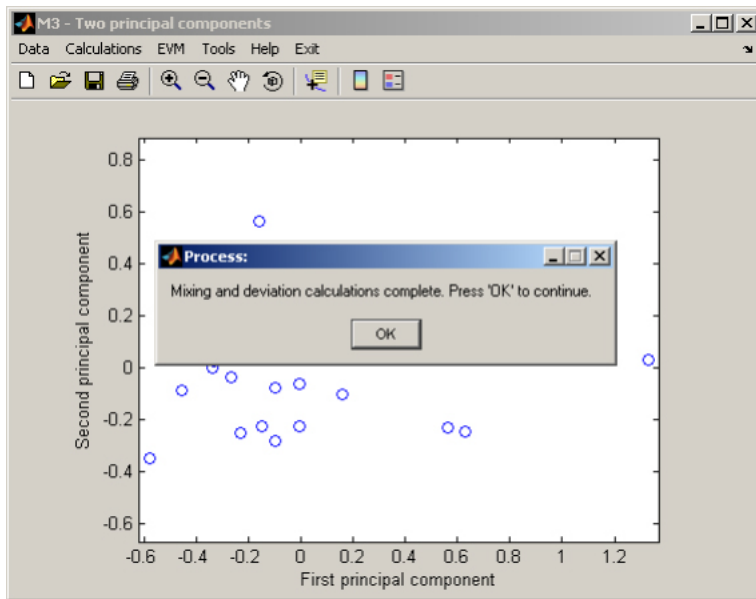
Figure 14

When calculations are completed a message box will appear indicating "Mixing calculation complete". Click "OK".

Export variables

Exporting mixing

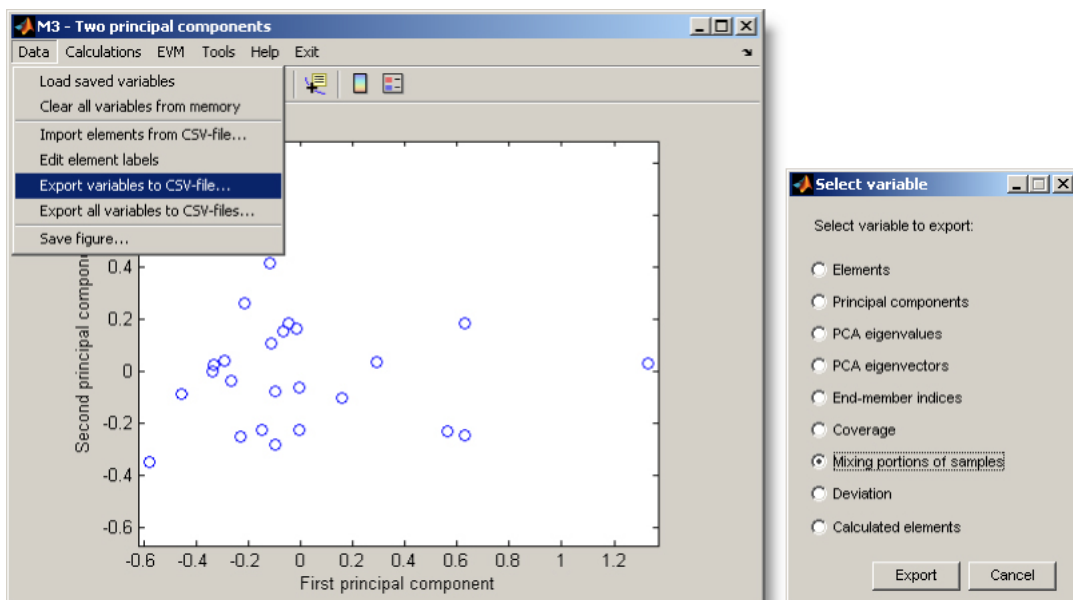From "Data" menu select "Export variables to a CSV-file". A new window will open.

Figure 15. *Exporting variables to a CSV-file.*

Select "Mixing proportions of samples (mix)" and click "Export". The program will display a new window asking to choose the file name and the folder where CSV-file shall be saved.
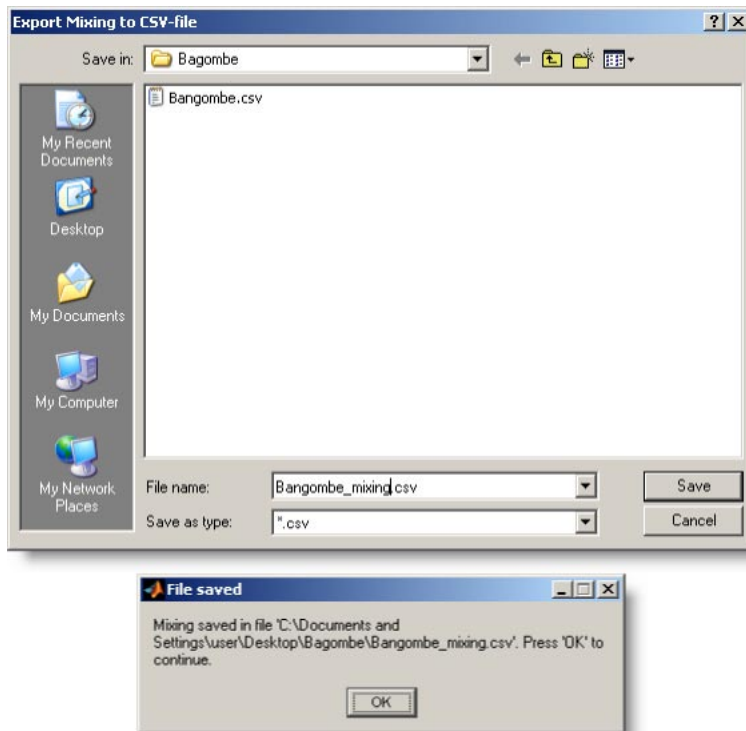
Figure 16

Name the file in the "Export Mixing to CSV-file". Click "Save". Click "OK".

Exporting deviation (dev)

From Data menu select Export variables to a CSV-file. Select "Deviation (dev)" and click "Export".

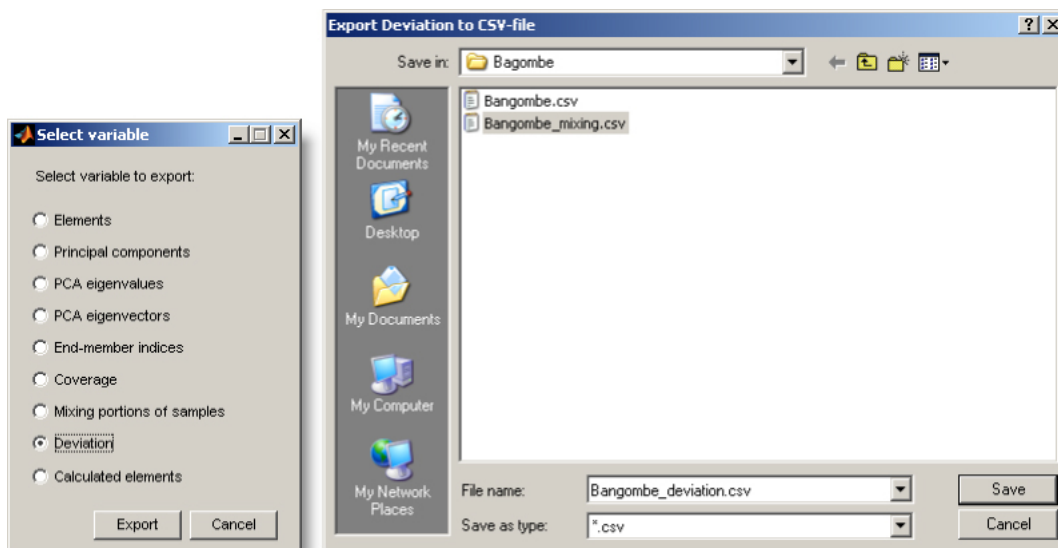Name the file in the "Export Deviation to CSV-file". Click "Save". Click "OK".

Figure 17

Save figure

From Data menu select "Save figure" and select the picture format. Click "Export".
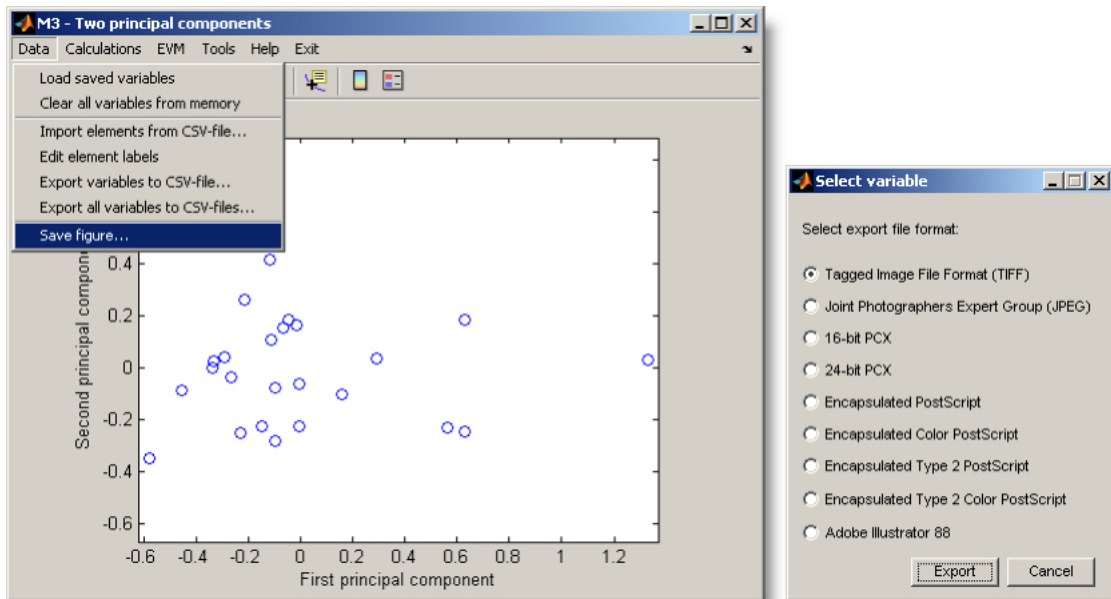
Figure 18

Name the file in the "Export figure" window and click "Save". Figure will be saved in the chosen directory.

Exit M3

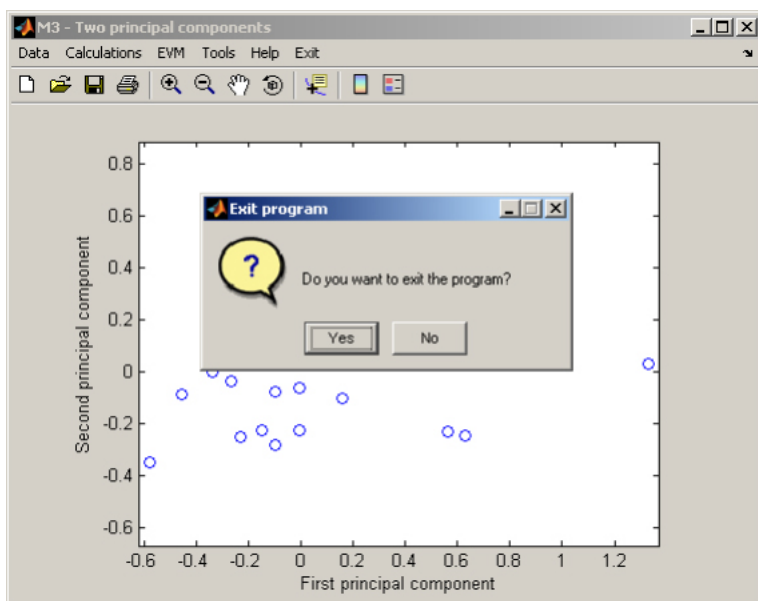To exit M3 select the Exit menu item.

Figure 19

Click "Yes" and the program will close.

Conversion of data

The results of the M3 modelling of Bangombé data are obtained as comma delimited CSV-file and shall be converted to a Microsoft Excel workbook XLS-file and saved in working folder. The results can be expressed in terms of mixing proportions and/or deviations (see Table 1).

Table 1. Measured data and M3 modeling results for Bangombé data set.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Sample	Alk mole/l.	Cl mole/l.	SO4 mole/l.	Na mole/l.	K mole/l.	Ca mole/l.	Mg mole/l.	U mole/l.	Deep water mixing prop.	Rain mixing prop.	Interm. water mix prop.	devAlk mole/l.	devCl mole/l.	devSO4 mole/l.	devNa mole/l.	devK mole/l.	devCa mole/l.	devMg mole/l.	devU mole/l.
Sample 1	2.18E-05	8.40E-06	5.50E-06	1.09E-05	3.60E-06	2.49E-06	1.60E-06	9.32E-09	0.0036631	0.71042	0.28592	-1.49E-05	1.80E-06	-1.58E-06	4.67E-07	-1.11E-06	-7.01E-06	-6.60E-06	6.79E-09
Sample 2	4.96E-04	9.90E-06	4.50E-06	4.35E-05	1.46E-05	8.70E-06	1.52E-05	1.13E-09	0.09688	0.59934	0.30378	0.0002257	8.72E-07	-4.28E-06	-1.61E-05	4.60E-06	-7.56E-05	-1.30E-05	-9.76E-09
Sample 3	1.60E-03	5.90E-06	1.47E-05	3.83E-04	2.56E-05	4.60E-04	1.83E-04	5.63E-08	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
Sample 4	1.68E-03	7.10E-06	1.51E-05	3.83E-04	2.60E-05	4.80E-04	1.88E-04	7.94E-08	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
Sample 5	1.64E-04	6.80E-06	1.34E-05	7.60E-05	7.20E-06	1.62E-05	2.10E-05	1.27E-08	0.046792	0.59283	0.36037	1.60E-05	-2.43E-06	3.90E-06	4.08E-05	-1.01E-06	-2.94E-05	1.80E-06	5.79E-09
Sample 6	7.87E-04	1.02E-05	3.00E-06	1.60E-05	2.07E-05	1.37E-05	3.58E-05	2.33E-09	0.062218	0.12462	0.81317	0.00057795	-9.69E-06	9.16E-06	-4.07E-05	4.51E-06	-5.47E-05	1.59E-06	-9.44E-09
Sample 7	5.01E-04	9.30E-06	1.45E-05	2.80E-05	3.48E-05	1.37E-05	4.77E-05	8.85E-09	0.16117	0.35508	0.48375	6.13E-05	-5.23E-06	4.24E-07	-7.05E-05	1.85E-05	-0.000126	1.28E-06	-9.10E-09
Sample 8	2.09E-04	8.74E-06	1.25E-05	1.78E-05	7.93E-06	2.25E-05	4.94E-05	4.62E-09	0.044293	0.5642	0.39151	6.57E-05	-1.15E-06	2.27E-06	-1.70E-05	-6.34E-07	-2.19E-05	2.99E-05	-2.31E-09
Deep water	**2.51E-03**	**2.17E-05**	**1.35E-05**	**5.22E-04**	**5.37E-05**	**7.98E-04**	**2.10E-04**	**8.82E-08**	**1**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Sample 10	7.31E-04	4.23E-06	1.35E-05	3.48E-04	1.71E-05	8.98E-05	4.53E-05	1.76E-09	0.25464	0.53609	0.20926	7.15E-05	-6.07E-06	4.91E-06	0.00020884	1.19E-07	-0.0001182	-1.36E-05	-2.23E-08
Sample 11	1.00E-03	1.30E-05	1.07E-05	5.22E-05	1.76E-05	9.98E-05	3.33E-04	1.34E-09	0.35891	0.52235	0.11874	8.47E-05	2.50E-06	2.93E-06	-0.0001387	-3.55E-06	-0.0001893	0.00025454	-3.12E-08
Sample 12	5.70E-04	8.74E-06	1.35E-05	3.65E-05	1.41E-05	4.74E-05	1.32E-04	4.62E-08	0.20635	0.58574	0.20791	3.12E-05	-4.78E-07	5.60E-06	-7.74E-05	-2.66E-07	-0.0001221	8.33E-05	2.64E-08
Sample 13	1.08E-03	1.75E-05	1.25E-05	1.83E-04	2.56E-05	1.12E-04	1.60E-04	6.89E-08	0.40099	0.34522	0.25379	5.29E-05	3.01E-06	8.43E-07	-3.39E-05	5.69E-08	-0.0002138	6.92E-05	3.16E-08
Sample 14	4.41E-04	2.25E-06	2.03E-05	3.17E-05	1.13E-05	6.75E-05	2.48E-05	9.12E-09	0.063216	0.53902	0.39777	0.0002501	-8.19E-06	9.66E-06	-1.32E-05	1.62E-06	7.91E-06	1.18E-06	4.69E-10
Sample 15	4.04E-04	3.66E-06	1.78E-05	1.35E-05	9.49E-06	3.53E-05	1.85E-04	1.11E-07	0.25162	0.74838	0	-0.0002375	-1.80E-06	1.44E-05	-0.0001179	-4.02E-06	-0.0001655	0.00013216	8.88E-08
Sample 16	8.47E-04	1.72E-05	1.06E-05	1.61E-05	6.92E-06	4.13E-05	1.37E-04	1.18E-09	0.14905	0.41428	0.43668	0.00043987	4.01E-06	-2.15E-06	-7.47E-05	-7.98E-06	-8.77E-05	9.43E-05	-1.53E-08
Sample 17	6.96E-04	6.98E-06	6.98E-06	1.14E-04	1.41E-05	1.85E-04	1.67E-04	1.48E-08	0.29781	0.69103	0.01116	-6.14E-05	2.63E-07	2.69E-06	-4.18E-05	-2.07E-06	-5.29E-05	0.00010417	-1.16E-08
Sample 18	2.36E-03	1.69E-05	1.77E-05	2.39E-04	2.95E-05	4.08E-04	1.65E-04	1.13E-08	0.55339	0.091659	0.35495	0.00094741	-3.20E-06	1.50E-06	-6.04E-05	-5.83E-06	-4.18E-05	3.96E-05	-4.03E-08
Sample 19	5.74E-04	8.17E-06	2.29E-05	2.65E-04	1.41E-05	9.25E-05	5.00E-05	2.31E-10	0.16799	0.32012	0.51189	0.00011584	-7.15E-06	8.04E-06	0.00016206	-3.01E-06	-5.33E-05	1.41E-06	-1.85E-08
Sample 20	4.44E-04	1.30E-05	2.29E-05	1.52E-05	8.21E-06	2.10E-05	7.29E-05	1.30E-08	0.048684	0.30153	0.64979	0.00027686	-2.87E-06	6.26E-06	-2.96E-05	-4.67E-06	-3.28E-05	4.58E-05	3.68E-09
Sample 21	4.92E-04	2.68E-06	2.19E-05	1.48E-05	6.15E-06	2.50E-05	9.17E-05	1.41E-07	0.21517	0.74234	0.042498	-6.06E-05	-2.96E-06	1.80E-05	-9.88E-05	-6.08E-06	-0.0001477	4.54E-05	1.22E-07
Sample 22	7.70E-04	1.35E-05	1.88E-05	1.35E-04	1.36E-05	4.75E-05	1.04E-04	2.18E-08	0.18916	0.32841	0.48242	0.00026044	-1.60E-06	4.38E-06	2.19E-05	-4.18E-06	-0.0001146	5.17E-05	1.39E-09
Sample 23	1.84E-04	7.61E-06	2.92E-06	1.87E-05	1.10E-05	4.25E-05	1.88E-04	1.00E-09	0.17703	0.79245	0.030515	-0.0002728	3.07E-06	-2.21E-07	-7.46E-05	1.01E-06	-9.95E-05	0.00015003	-1.49E-08
Rain water	**1.33E-05**	**1.00E-12**	**1.00E-12**	**1.00E-12**	**1.00E-12**	**1.00E-12**	**1.00E-12**	**1.00E-12**	**0**	**1**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Intermediate	**6.30E-05**	**2.28E-05**	**2.46E-05**	**2.98E-05**	**1.58E-05**	**2.30E-05**	**2.60E-05**	**7.73E-09**	**0**	**0**	**1**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

Conclusions of the modelling

In Bangombé case, where there are only 3 end-members, the 2-PC and n-PC models are identical, giving the same results. The n-PC option was used here for the calculations, with the allowance factor 0.07.

Figure 20 shows the interpolated mixing proportions obtained for the Bangombé site. Boxes labeled 1 to 7 in the figure represent the location of the sampling for Bangombé. The measured and calculated data are interpolated along the vertical profile in Bangombé.

Figure 21 shows the interpolation of the measured values for Alkalinity and for the deviation from the measured values calculated by M3. M3 shows an increase of the Alkalinity, indicating the existence of a chemical buffer around the natural nuclear reactor which may hinder the uranium transport. M3 traced the effects from organic matter and iron reducing bacteria. This process was suggested to play an important role in regulating the redox conditions around the reactor. This was identified by M3 relatively easy. After this founding, the HYTEC-2D reactive transport code was employed and confirmed the M3 results.

Thus, M3 can relatively easily be used to calculate the mixing proportions and to identify the sinks or the sources that may exist in a geochemical system. This can help to address the reactions in a standard code, thermodynamic or coupled transport and reactive code, to identify the system and reduce the computation time.
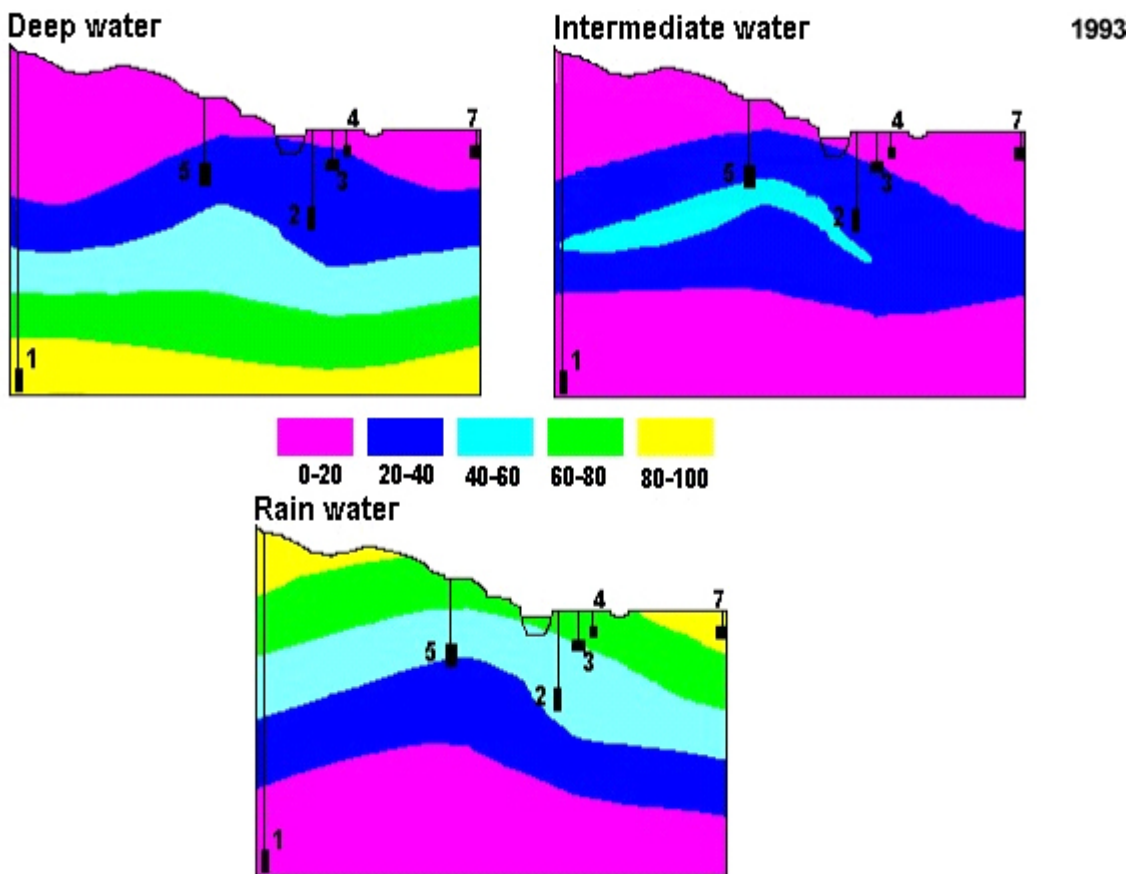
Figure 20. *Mixing proportions of Deep water, Intermediate water and Rain water calculated with M3 for Bangombé data set.*

1993
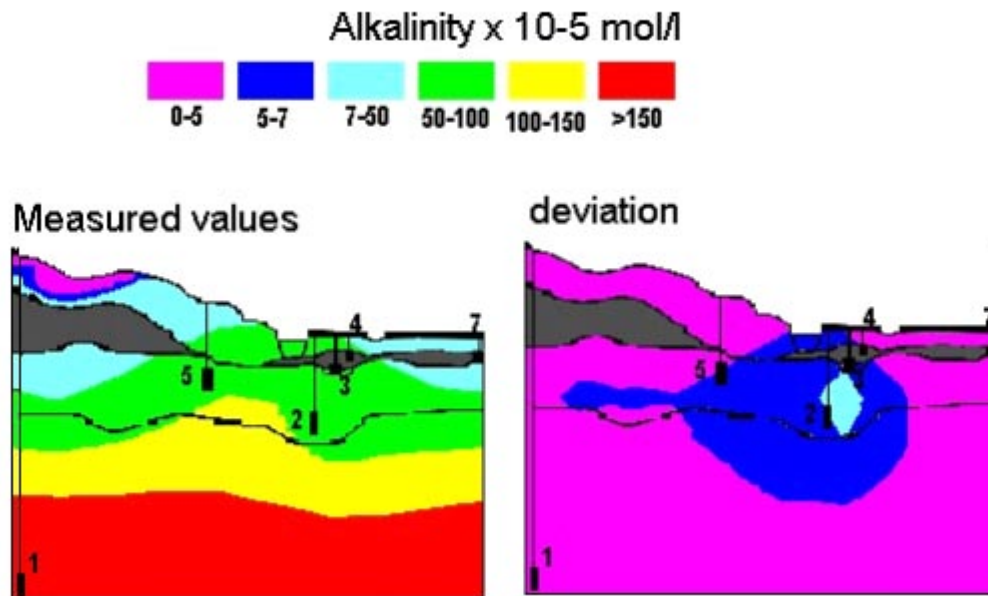
Figure 21. *Alkalinity measured (left) and deviation from the measured data calculated with M3 model (right).*

References

- **Gurban I, Laaksoharju M, Ledoux E, Madé B, Salignac A L, 1998.** Indications of Uranium transport around the reactor zone at Bangombé (Oklo), SKB Technical Report, 98–06.

- **Gurban I, Laaksoharju M, Ledoux E, Madé B, 2003.** Uranium transport around the reactor zone at Bangombé and Okélobondo (Oklo): Examples of hydrogeological and geochemical model integration and data evaluation, Journal of Contaminant Hydrogeology 61 (2003), pp. 247–264.

2.5.2   Äspö data set

Working with M3

The example below shows how M3 code was employed for the Äspö dataset. In order to understand the results of the modelling better, a short introduction to the Äspö site is given bellow. The Äspö laboratory is located in the island of Äspö in crystalline rock of the Baltic coast approximately 450km south of Stockholm. The access tunnel to the HRL proceeds from the mainland, under the Baltic sea bed for a distance of 3.6 km, to a depth a 450 m below the island of Äspö. A total of 438 groundwater samples from 110 boreholes have been investigated. The data set contains boreholes that have been drilled down from ground level during the tunnel pre-investigation phase and from inside the tunnel during the tunnel construction phase. The boreholes have been used for geological, hydrogeological and hydrogeochemical measurements of the Äspö site.

The following paragraphs show how to operate the M3 code step by step for modeling the Äspö site.

Preparing data

Äspö data are as MS Excel workbook and is presented at the end of this document. The user can step by step follow the M3 code use and check the data. Äspö data set is formed by 604 samples and 4 end-members: Glacial, Rain, Littorina and Brine. If the user employs a XLS-file, this shall be converted in a comma delimited CSV- file and saved in working folder.

The CSV file shall contain only the data, with an optional first row containing the elements' labels and, equally optional, a first column with numeric sample id labels. In this case both element labels and sample id labels are included in the CSV-file.

Starting M3

Click on the M3 icon [icon]. The M3 start-up image appears for a few seconds, and then an M3 figure window will be opened.

The following window will open. Select the working directory. The CSV-file shall be previously saved in selected working directory.
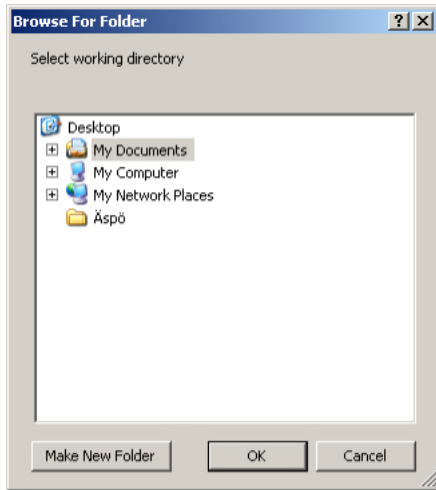

Figure 1. *Browse for Folder.*

From the "Tools" menu, choose under "Preferences" the type of input file data (for example, *comma or semicolon).*
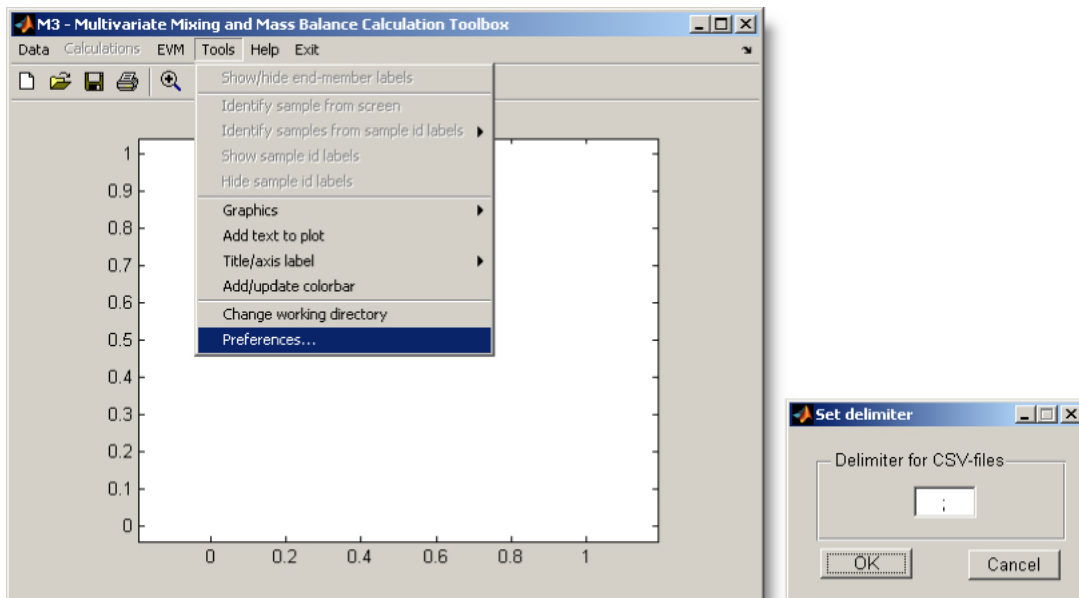

Figure 2. *Delimiter for CSV-files.*

Click "OK".

From the "Data" menu choose "Import elements from CSV-file". A window with the CSV-file will appear. Select the CSV-file and click on the "Import" window.
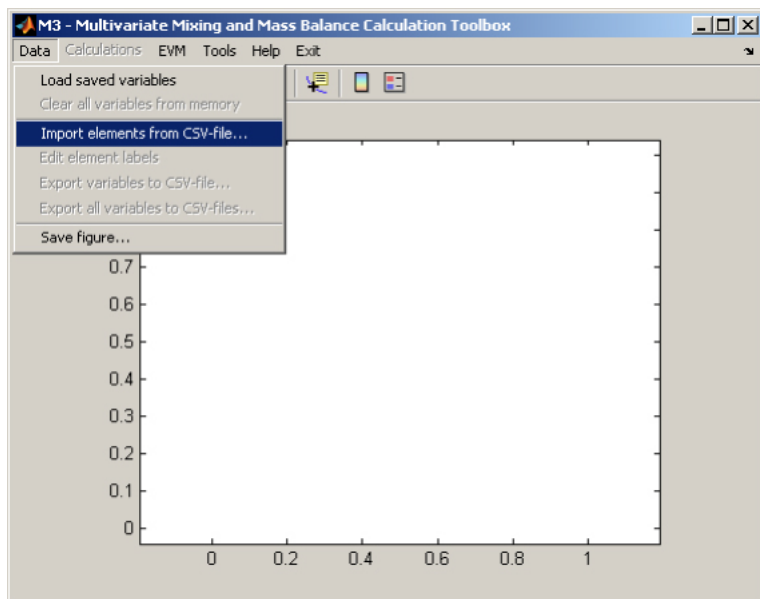
Figure 3. *Import elements from CSV-file.*

The program will display:
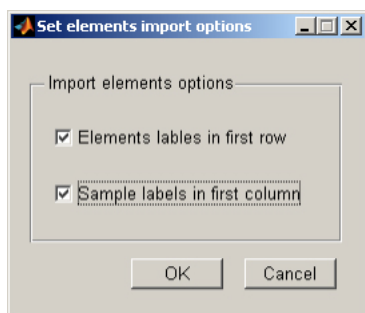
Figure 4. *Set element import options.*

Since our CSV-file contains both element labels and sample labels we mark both check boxes and click "OK".

The window "Enter element labels" will open. If the input CSV file has the labels in the first row, they will appear in this window.

For Äspö the elements are: Na, K, Ca, Mg, HCO_3, Cl, SO_4, D (^2H), Tr (^3H) and O18 (^{18}O). Click "OK".
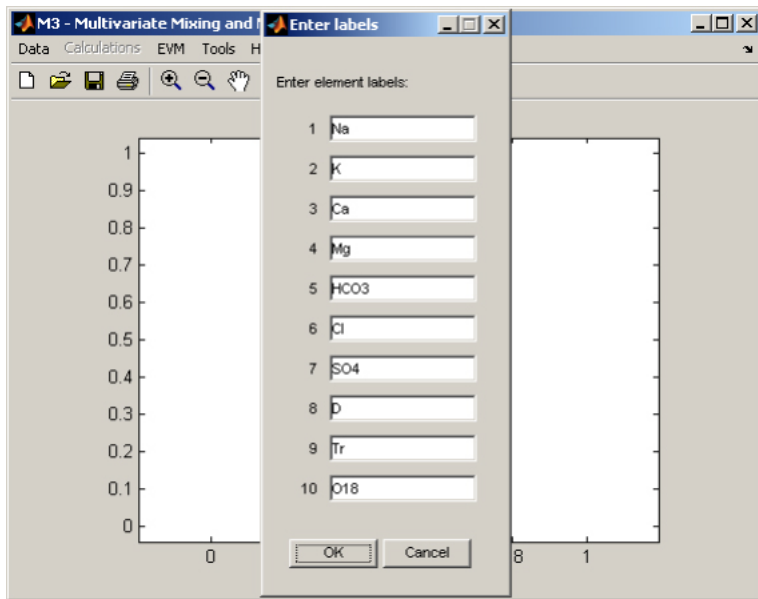
Figure 5. *Enter element labels.*

Calculate principal components

Selecting the menu option "Calculations/PCA/Calculate principal components" will calculate the principal components and produce a graph in the current figure window, displaying the samples as blue circles. The program will display the amount of variance accounted for by the first three principal components PC1, PC2 and PC3.

The first principal component is shown on the x-axis and the second principal component on the y-axis.
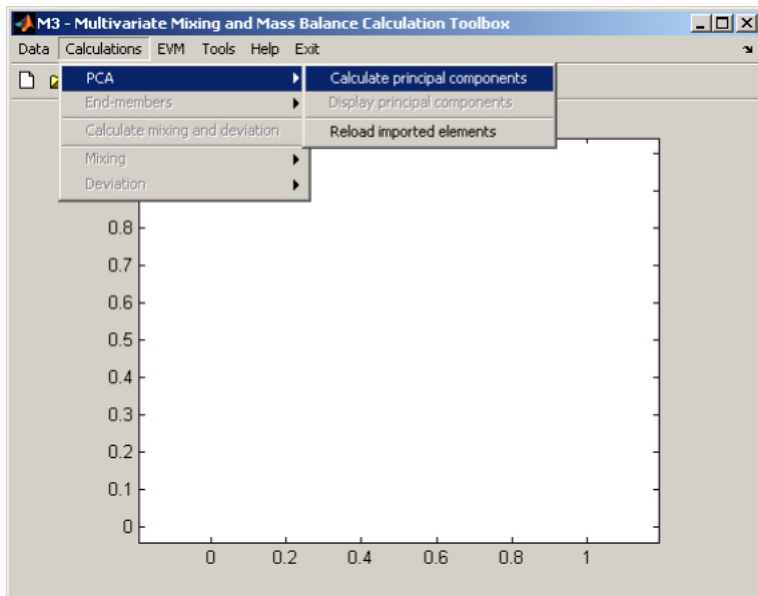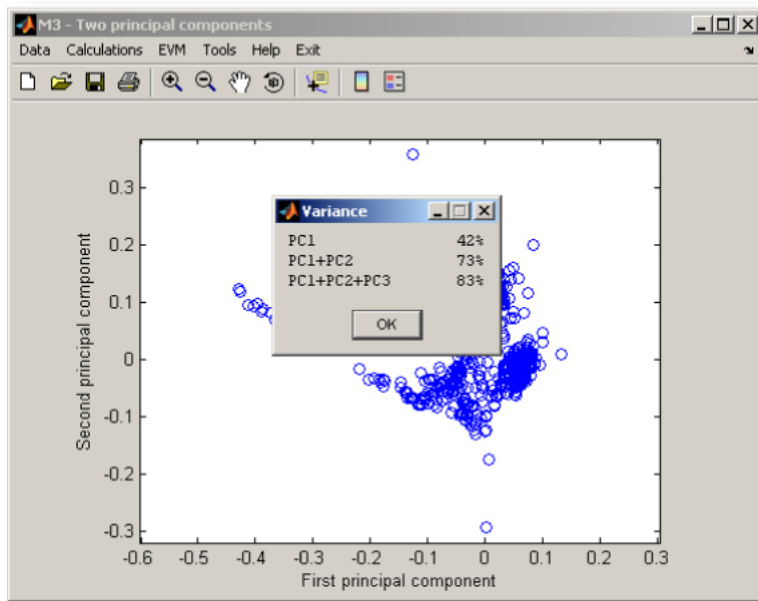
Figure 6. *Calculate principal components and variance on the two principal component plot.*

Click "OK".
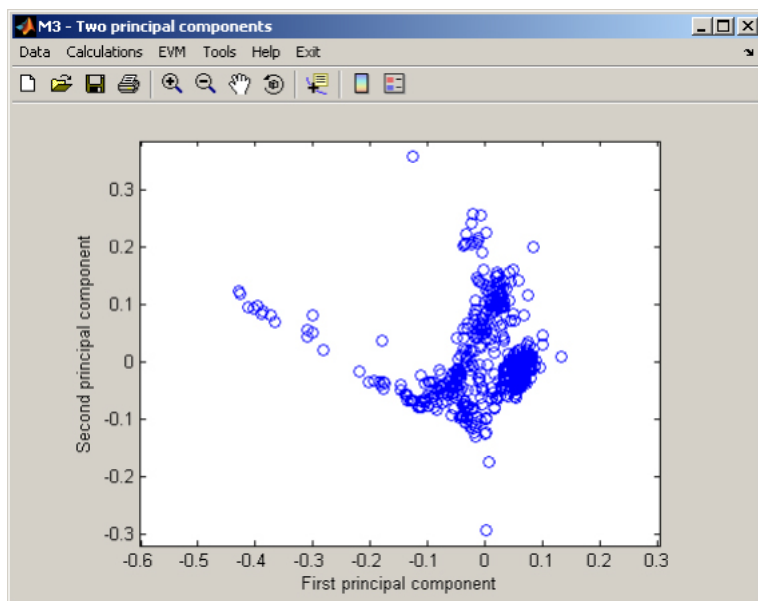
Figure 7. *Two principal component plot.*

Select end-members

The M3 mixing method generally uses end-member waters to calculate and describe the mixing. These end-members are considered to be the original waters that have been mixed to form the other observations. End-members are usually the most extreme waters in the PCA plot and are selected by the user from the menu Calculations/End-members/Select end-members. The end-members are selected by clicking on the selected values or directly entering the row number in the data windows below the PC graph. When clicking on a sample, the sample turns red and the numbered value is displayed on the bottom of the window. This number is the sample's row index in the imported matrix, i.e. the sample's row number in the CSV-file.

Note: The mixing model requires that the corners of the polygon are convex, i.e. do not point inwards in the polygon. M3 requires that the end-members are selected in sequence and the program cannot handle crossed lines in the polygon.

For Äspö the end-members are:

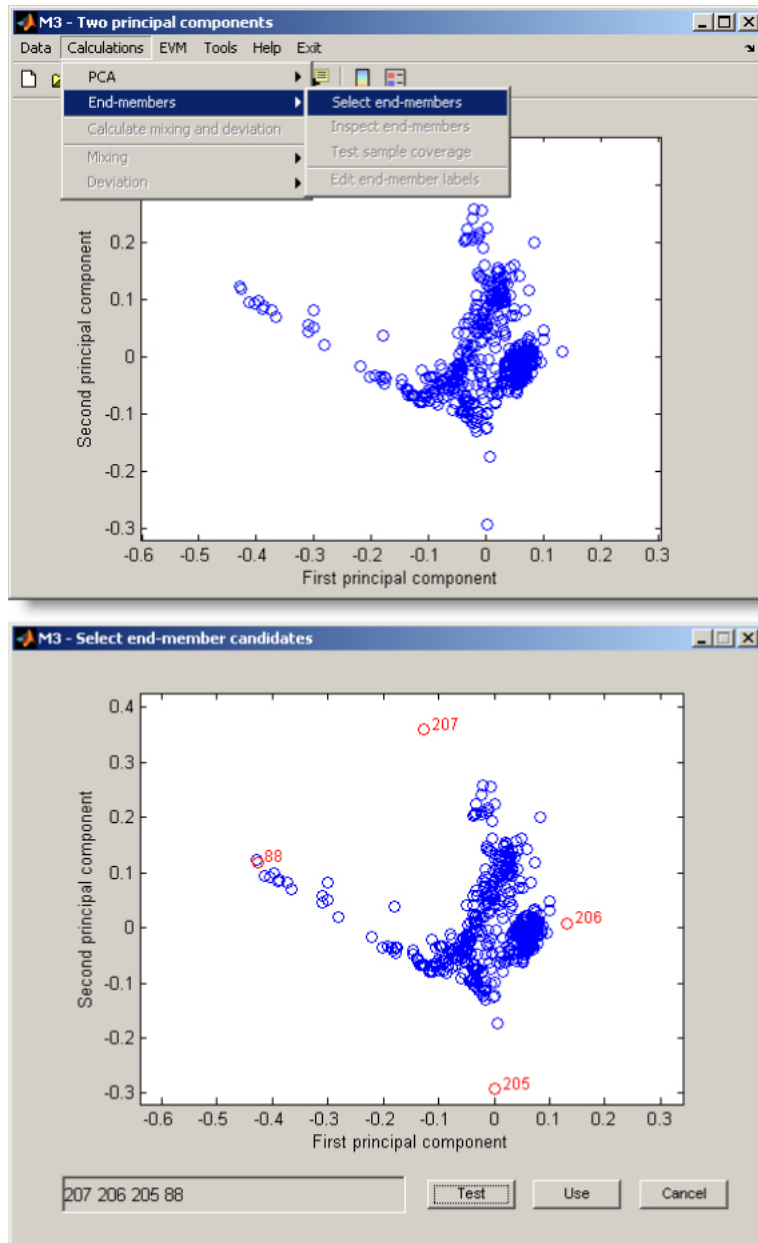Sample no. 207, Sample no. 206, Sample no. 205 and Sample no. 88.

Figure 8 Select end-members

Select "Test". The window with "Select allowance for n-PC mixing" will appear. The allowance factor determines how samples near an edge of the mixing polygon but outside it are dealt with, and affects the coverage (number of samples explained by mixing). Setting the allowance to 0.07 will in this case obtain a coverage of 97.7%. Click "OK".
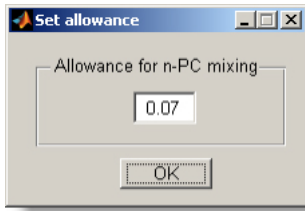
Figure 9

The program will display a window for few seconds "Please wait while calculating sample coverage".

Select end-member combination

M3 can calculate mixing in two coordinates with "2-PC mixing" or in n-coordinates using "n-PC mixing". In the right side of the window M3 will display the sample coverage percentage available for the model. For Äspö model, by selecting the 4 end-members and the allowance factor 0.07, the coverage is 97.7% for n-PC mixing. For another allowance factor, the coverage is different. The allowance factor should be chose to meet the needs of the modelling. A polyhedron will be drawn on the graph showing the configuration selected.
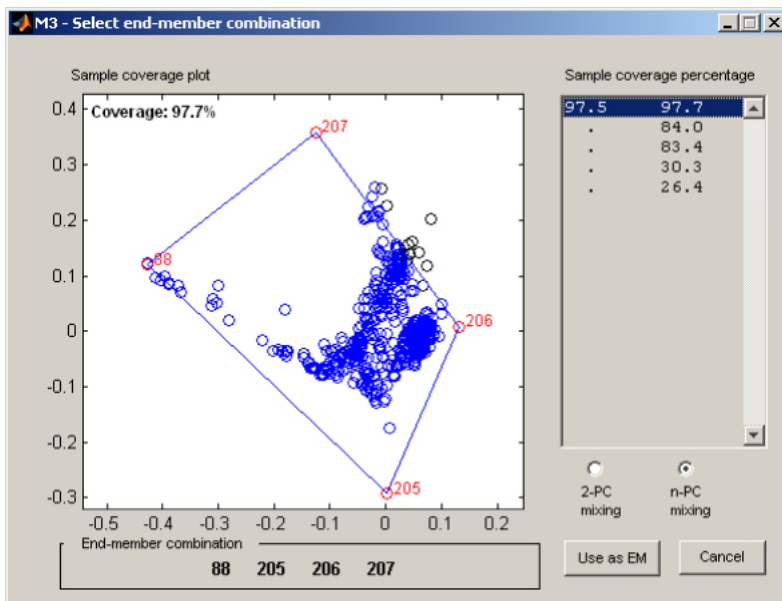

Figure 10. Select end-member combinations.

Once the best combination of end-members has been selected, click "Use as EM". A new window will be displayed asking for the end-members names.
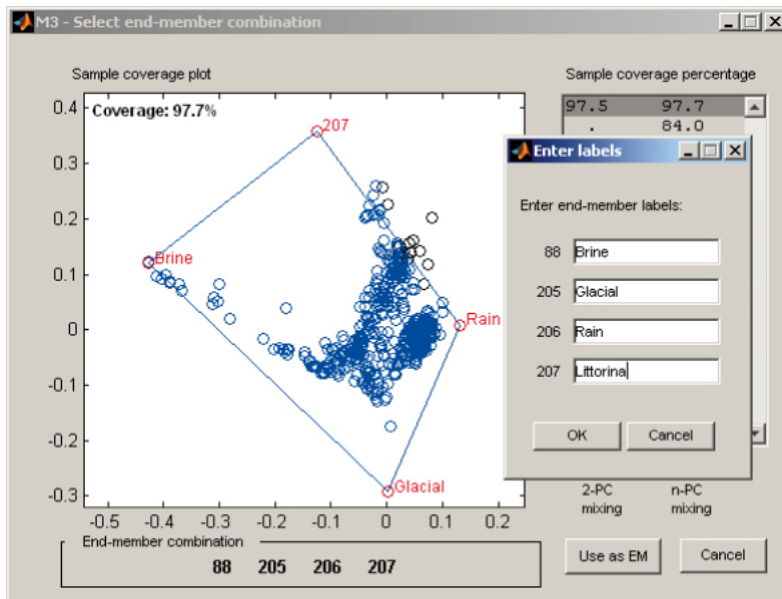
Figure 11. Enter end-members.

For the Äspö model the end-members are:

- Sample 205 corresponding to Glacial
- Sample 206 corresponding to Rain
- Sample 207 corresponding to Littorina
- Sample 88 corresponding to Brine

Click "OK".

Calculate n-PC mixing and deviation

From the window "Select mixing model" select n-PC mixing. In Äspö model the allowance was choosen by default at 0.07.
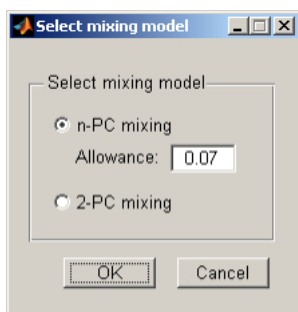

Figure 12

Click "OK". The program will calculate the n-PC mixing and the deviation.

M3 will calculate mixing and deviation. As the calculations proceed a message box display the current process. The results from the calculations are automatically saved. When calculations are completed a message box will appear indicating "Mixing calculation complete".
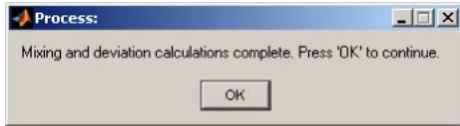

Figure 13

Exporting variables

Exporting mixing

From "Data" menu select "Export variables to a CSV-file". A new window will open.
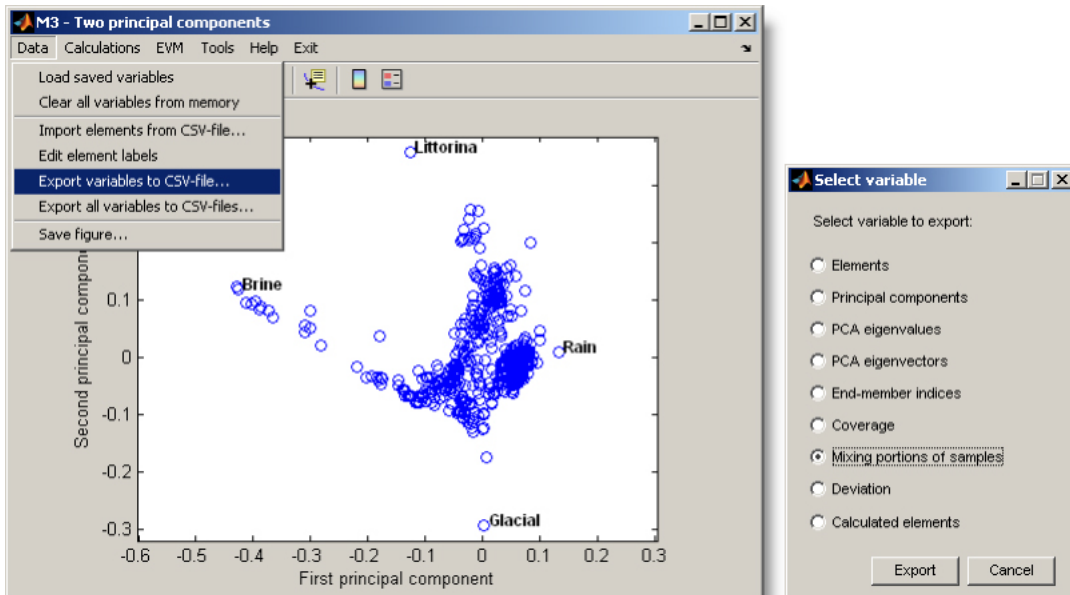

Figure 14. *Exporting variables to a CSV-file.*

Select "Mixing proportions of samples" and click "Export". The program will display a new window asking to choose the file name and the folder where CSV-file shall be saved.
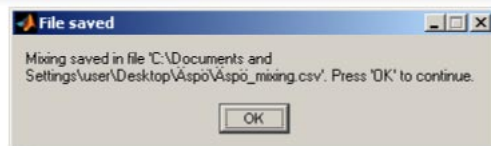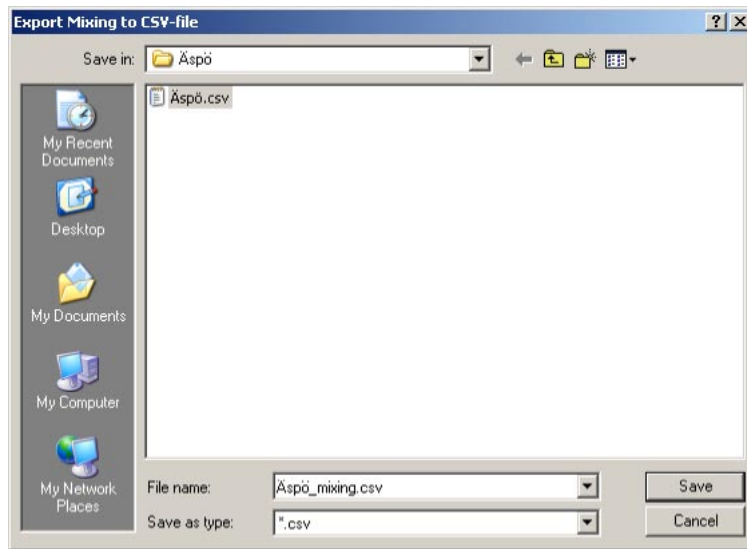
Figure 15

Name the file in the "Export Mixing to CSV-file". Click "Save". Click "OK".

Save figure

From Data menu select "Save figure" and select the picture format. Click "Export".
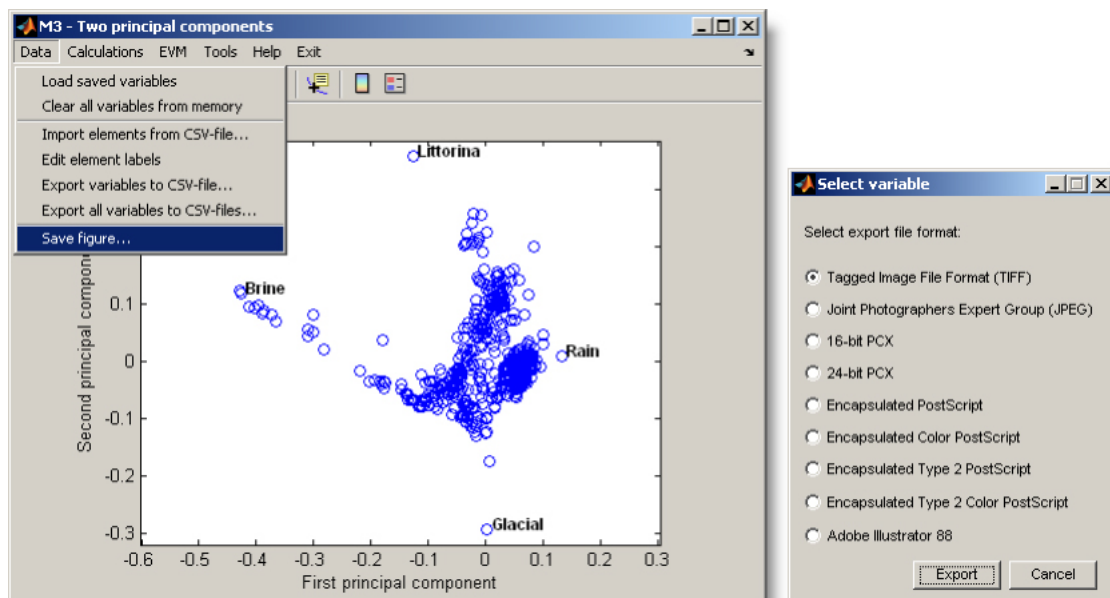

Figure 16

Name the file in the "Export figure" window and click "Save".

The figure will be saved in the chosen directory.

Calculate 2-PC mixing and deviation

In order to calculate 2-PC mixing repeat steps 3 and 4. When the "Select end-member combination" is displayed, choose "2-PC mixing".
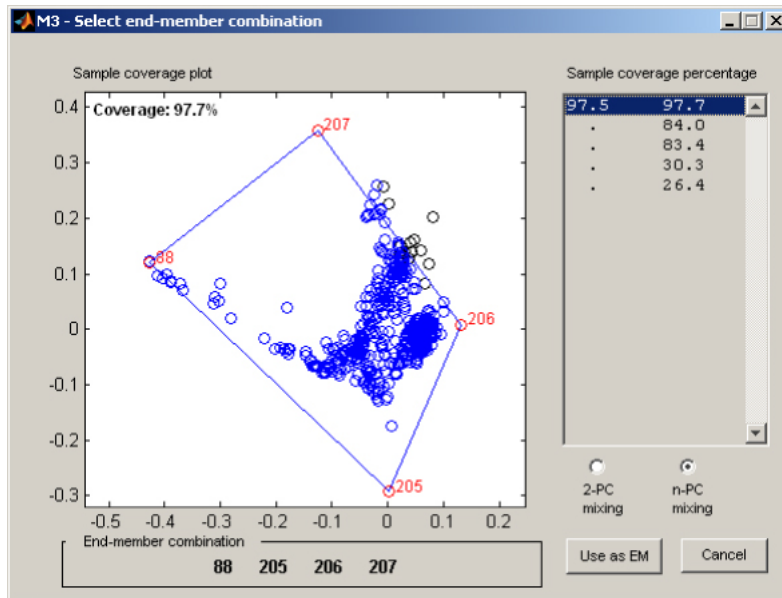

Figure 17. *Select end-member combination.*

Click "Use as EM". The program will display the window with end-members previously entered (i.e. Glacial, Rain, Littorina and Brine).
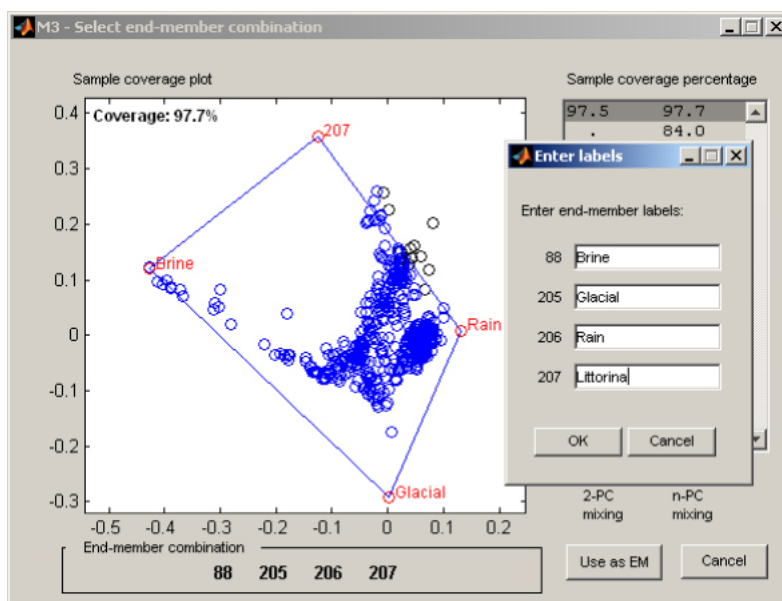
Figure 18

Click "OK". The window "Select mixing model" will display the option 2-PC selected. Choose "OK" to validate.

Figure 19

As the calculations proceeds a message box display the current process. The results from the calculations are automatically saved. When calculations are completed a message box will appear indicating "Mixing calculation complete".

Figure 20

Click "OK".

Follow the step 6 to export variables.

Exit M3

To exit M3 select the Exit menu item.

Figure 21. Exit M3.

Click "Yes" and the program will close.

Conclusions of the modelling

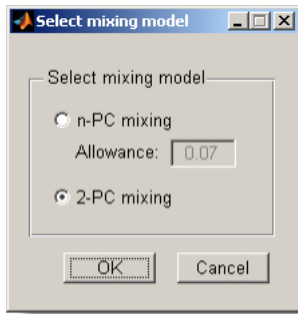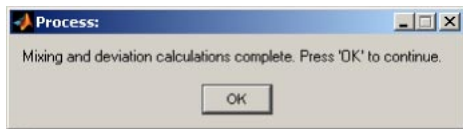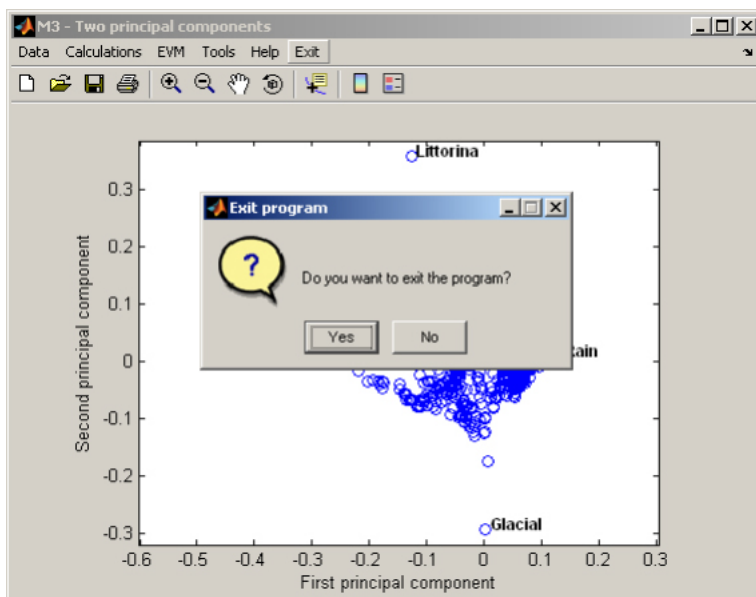The results in terms of mixing and deviation are presented in the Table 1 for the M3 2-PC and M3 n-PC. By statistical evaluations (for example standard deviation or root mean square error) applied to the measured data versus the calculated values, the user can chose which model is more accurate.

The findings and experiences from the M3 modelling at the Äspö site can be summarized accordingly:

- By calculating the mixing proportions of the different water types, the groundwater origin and evolution were described by means of mathematical models rather than by means of quantitative descriptions. Fundamental information for understanding the groundwater system was obtained after decoding the measured groundwater element concentration in terms of contributions from mixing and reactions.

- Mixing is the dominating process affecting the groundwater composition.

- A simple model e.g. using one conservative tracer cannot be used to describe a complex natural system at the Äspö and Oklo sites without significant loss of information.

- Different elements and isotopes from the same water sample may contain different information concerning the groundwater evolution history. Conservative natural ground waters tracers Cl, ^{18}O and ^{2}H have several sources and origins.

- Groundwater evolution models based on thermodynamic laws alone may not be applicable to a low temperature groundwater system such as Äspö where the equilibrium is not reached and where most of the reactions are biogenic.

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Example of M3 modelling at the the Äspö site

A.1 Introduction to the Äspö site

A.1.1 The Äspö HRL

The results from the M3 calculations used in the following example are from the international ground-water modelling cooperation project at the Äspö site /Laaksoharju and Wallin (eds) 1997/. In order to understand the result of the modelling better a short introduction to the Äspö site is given below.

The laboratory is located on the island of Äspö in crystalline bedrock off the Baltic coast approximately 450km south of Stockholm. The access tunnel to the HRL proceeds from the mainland, under the Baltic Sea bed for a distance of 3.6km, to a depth of 450 m below the island of Äspö (Figure A-1).

A total of 438 groundwater samples from 110 boreholes have been investigated. The data set contains boreholes that have been drilled down from ground level during the tunnel pre-investigation phase and from inside the tunnel during the tunnel construction phase. The boreholes have been used for geological, hydrogeological and hydrogeochemical measurements of the Äspö site. The site comprises the following sampling areas: Äspö and the surrounding locations such as Ävrö, Laxemar, the HRL tunnel, Redox Zone, Baltic Sea and extracted pore water from the sea bed sediments.

A.1.2 Geology

The Äspö site comprises a slightly undulating topography (10 m above sea level) of well-exposed rock. The geology is characterised by a red to grey coloured Småland-type medium grained porphyritic
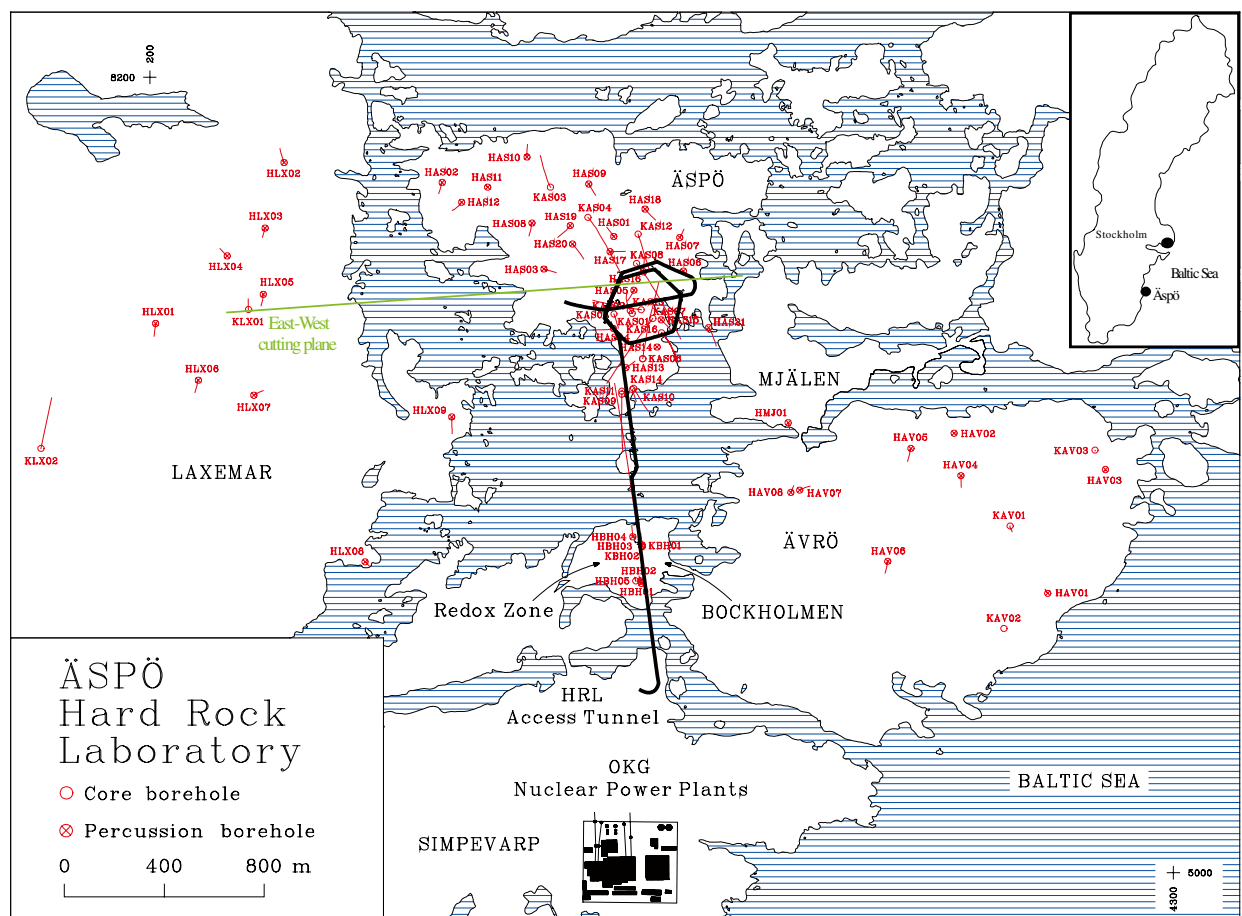

Figure A-1. *Location of the Äspö site and the sampled boreholes at Äspö island, Laxemar, Redox Zone (Bockholmen) in relation to the layout of the Hard Rock Laboratory (HRL).*

granite to quartz monzodiorite. The rock type belongs to the vast Trans Scandinavian Igneous Belt /Gaal and Gorbatschev 1987, Johansson 1988/ with intrusion ages of the rock at Äspö of 1,805 Ma based on U-Pb dating technique i.e. late to post orogenic in relation to the Svecofennian deformation (1,800–1,850 Ma). To the south of the island a more reddish granite variety, the Ävrö "true" granite, outcrops. The granitoids are intersected by fine-grained alkali granites present as lenses and dikes and by east-west trending lenses of fine-grained strongly altered greenstone (metabasalt). Subordinate lenses of fine-grained grey metavolcanites (of dacitic composition) also occur. Both of these rock types predate the Småland granitoids. Finally, pegmatite commonly occurs as very narrow dykes. These geological features are found in the HRL tunnel. The main fracture filling mineral phases in the area (in decreasing order of frequency) consist of: chlorite, calcite, epidote, fluorite, guartz, hematite/FeOOH, pyrite and clay minerals /Tullborg 1997/.

A.1.3   Hydrogeology

The aerial distribution of hydraulic conductivity at Äspö on the site scale is heterogeneous. Generally, the fine-grained granite/aplite tends to be the most conductive lithological unit, probably because it is the most competent rock type and is therefore inclined to fracture easily in response to tectonic movement. The increased fracture frequency in the northern block of Äspö reflects a correspondingly higher hydraulic conductivity. Furthermore, there is a general decrease in the variability of hydraulic conductivity with depth. A significant increase in conductivity at depths between 100–200 m and 400–500 m is observed, which may correspond to the vertical distances separating gently dipping subhorizontal fracture zones. The geohydrology of the recharge/discharge and groundwater flow through Äspö is controlled by the major tectonic fractures and discontinuities. A general groundwater flow trend, at least in the upper 500 m or so, from south to north, is facilitated by the NNW-trending vertical to subvertical fractures. The major E-W trending shear zone is a strong recharge feature. Before the HRL tunnel was constructed the groundwater flow was small due to the small gradients caused by natural water levels and the hydraulic head distribution at deeper levels. When the tunnel was constructed the hydraulic gradients increased considerably in the vicinity of the tunnel causing a different flow pattern to that of the previously undisturbed conditions /Rhén and Smellie 2003/.

A.1.4   Historical events affecting the groundwater at Äspö

Different pre- and postglacial events have affected the groundwater composition at Äspö. However the effects from the last glaciation and the consequent land uplift are the most recent important events which are likely to affect the measured groundwater composition the most. A conceptual model showing these events at the Äspö site is shown in Figure A-2. The following major events have been identified /Laaksoharju and Wallin (eds) 1997/:

1. The continental ice melted and retreated and glacial melt water was injected into the bedrock (>13,000BP). The exact penetration depth is still unknown but a depth of several hundred meters is possible according to cold climate signatures ($\delta^{18}O$) and groundwater flow modelling. Glacial melt water was mixed with brine water in the bedrock. A saline groundwater with a glacial signature was formed. A non-saline glacial water was present in the upper part of the bedrock.

2. Different non-saline and brackish lake/sea stages covered the Äspö site (13,000 BP– 4000 BP). Only a dense brackish sea water such as Yoldia and Littorina sea water could penetrate and affect the groundwater. The density of the intruding sea water in relation to the density of the groundwater determined the final penetration depth of the sea water. The Littorina sea stage (8000 BP to 2000 BP) contained the most saline groundwater and this water was supposed to have the deepest penetration depth. The result was that the glacial and brine groundwaters were mixed with intruding brackish marine water.

3. When the Äspö island rose above sea level (4000 BP) a freshwater pillow was developed. The continuous land rise increased the hydraulic driving force and the groundwaters in the upper part of the bedrock could then be flushed out. The flushing out on the mainland started directly after deglaciation and since this part of the bedrock was elevated above sea level the postglacial marine water did not affect the groundwater composition.

As a result of the above mentioned sequence of events a mixture of meteoric, glacial, marine and brine groundwater was formed.
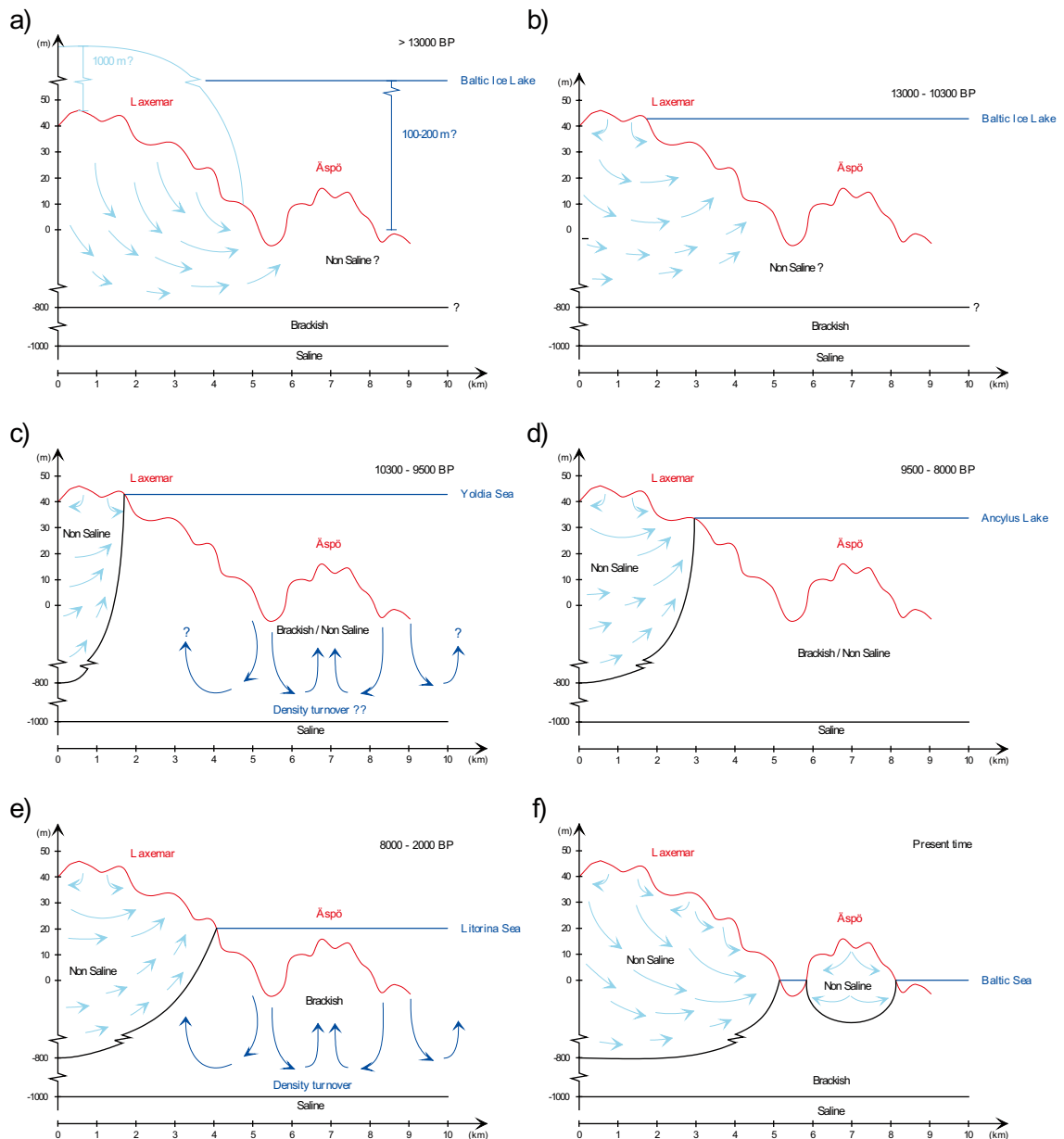
Figure A-2. A conceptual postglacial scenario at the Äspö site and the mainland of Laxemar. Possible flow lines, density driven turnover, non-saline, brackish and saline water interfaces are shown a) Injection of Glacial melt water into the basement. b) Baltic Ice Lake, c) Yoldia Sea, d) Ancylus Lake, e) Littorina Sea and f) present day situation. The orientation of the cutting plane is E-W (see Figure A-1).

The complex groundwater history has resulted in complicated groundwater mixtures. It should be possible to detect traces of the different events in the bedrock. They may be present in varying amounts in the different groundwater types. Groundwaters at large depths, in discharge areas, in fractures with a low hydraulic driving force or groundwaters with a high density can preserve their historical signatures better than other waters which may be more affected by the present groundwater mixing.

The conclusion from the conceptual model is that a freshwater aquifer was formed when the Äspö island rose above sea level. The fresh water flushes out the older water types. The depth to which the waters are flushed out is determined by the prevailing hydraulic driving forces. The hydraulic forces were highest during deglaciation. The land rise gradually increased the penetration depth of meteoric water until a certain depth was reached where the hydraulic force could not remove the dense saline groundwater. The overlying sea water affect the groundwater in the bedrock by density turnover. The higher the salinity of the sea water the deeper the penetration depth.

A.2   Major groundwater characteristics

A.2.1   Data and quality

The groundwater analytical data used in the modelling is from the Äspö site which comprises data from Äspö, Laxemar, Ävrö and the HRL tunnel extracted from Sicada (formerly GEOTAB), the SKB database, and reported by /Smellie and Laaksoharju 1992, Laaksoharju et al. 1995a, b/. Many of these reports have addressed the representativeness of the samples. A representative groundwater sample reflects the existing hydrogeological and groundwater geochemistry in-situ conditions. An unrepresentative sample has been affected by in-situ, on-line or on-site errors such as excessively high or low extraction pump-rates, contamination from borehole activities, complex hydrological situations, contamination from tubes of varying compositions, air contamination, losses or uptake of CO_2, long storage times prior to analyses, analytical errors etc /Laaksoharju et al. 1993/. The representativeness of the groundwater samples from 14 sites in Sweden and Finland was compared, using 18 quality related variables. The Äspö site scored highest among the investigated sites /Laaksoharju et al. 1993/. We therefore think that the samples from the Äspö site are generally representative although on a site like Äspö with high permeability and low gradients water extraction procedures can cause significant disturbance of the natural distribution of water types. Only the most representative groundwater samples have been used for the modelling.

A.2.2   Groundwater classification

A widely used classification of waters is based on Total Dissolved Solids (TDS). Salinity means essentially the same as TDS, which is based on summing up the dissolved constituents. According to this classification *fresh* water is dilute potable water with a TDS content of ~1,000 mg/l (~600 Cl, mg/l), *brackish* water is non potable with a TDS content of ~1,000–20,000 mg/l (~600–12,000 Cl, mg/l) and *saline* waters are waters with a salinity similar or greater to ocean sea water with a TDS content of ~35,000 mg/l (~21,000 Cl, mg/l). *Brine* is a water with significantly more salinity than ocean sea water /Drever 1988/.

To apply a widely used classification system such as TDS content to a site specific groundwater aquifer is not always the most efficient way to simplify the information, since the data distribution may be such that a poor separation is obtained. The Äspö site groundwater was therefore classified into three different groups: *non-saline, brackish* and *saline* groundwaters, on the basis of the site specific chloride distribution. The chloride concentration for the groups is as follows:

• Non-saline groundwater   <1,000 (Cl, mg/l)
• Brackish groundwater   1,000–5,000 (Cl, mg/l)
• Saline groundwater   >5,000 (Cl, mg/l)

The Brine groundwater (>40,000 Cl, mg/l) at the Äspö site belongs to the saline groundwater group. The above classification is used throughout the report.

Piper plots /Piper 1953/ are widely used to present and classify major ion groundwater data. To show the distribution of the Äspö site groundwater data, standard trilinear Piper Plots were used based on modifications suggested by /Davis and De Wiest 1967/. The major variables used were Cl, Na, Ca, HCO_3, Mg, K and SO_4. The samples were divided into the following three groups: non-saline, brackish and saline groundwaters. In addition, a classification system developed by /Morgan and Winner 1962, Back 1966/ was included in the plot. The water types were designated according to the domain in which they occur on the diagram segments (Figure A-3).

The Piper Plot clearly demonstrates the large spread of groundwater composition with two distinct groupings: where the non-saline and brackish groundwaters represent a sodium alternatively a calcium bicarbonate type; and the other, a calcium-chloride type of brine origin. Similarities to these general groundwater patterns from Äspö have been described from two locations in Finland; from Hästholmen /Nordstrom 1989/ and more recently from Olkiluoto /Pitkänen et al. 1999/. The plot indicates that there is an evolutionary trend from non-saline water through brackish water to the saline water. The disadvantage with Piper plots is the higher resolution for the more shallow waters than for the intermediate and the deep groundwaters with the latter usually forming tight clusters. Important changes in some variables such as SO_4 may be masked by larger changes in other variables such as Cl.
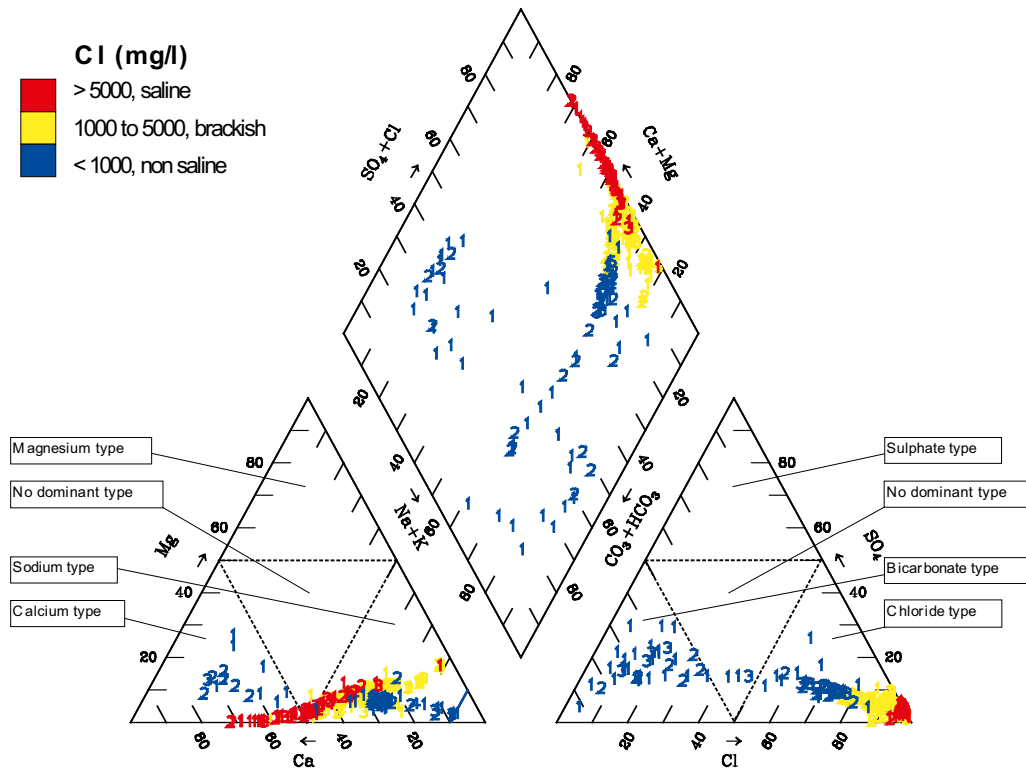
Figure A-3. *Standard Piper Plot showing the main groundwater types for the Äspö site groundwaters. The samples were divided into three groups: non-saline, brackish and saline groundwaters. The waters are classified according to the domain or field in which they occur on the diagram segments.*

A.2.3   Scatter plots

In order to examine the general trends of the analytical groundwater data in more detail, x and y scatter plots for the Äspö site data (Äspö, Ävrö, Laxemar, Redox Zone, HRL tunnel, Baltic Sea, precipitation, pore water extracted from the sea bed sediments, including identified end-members) are shown in Figure A-4a,b, A-5a, A-5b and A-5c for the variables; Cl, Na, Ca, HCO_3, Mg, K, SO_4, tritium, δ^2H and $\delta^{18}O$ plotted against Cl and depth.

For visualisation purposes an interpolation of the Cl distribution was performed in 3D using INTERGRAPH's Voxel Analyst computer code. The 2D cutting plane of that modelling is shown prior to and 3.8 years after the start of the tunnel construction (Figure A-6). The cutting plane shows the conditions under the Äspö island in a N-S direction (for orientation see Figure A-1). The result of the interpolation shows similarities with earlier conceptual models of Äspö based on salinity distribution presented by /Smellie and Laaksoharju 1992, Smellie et al. 1995/.
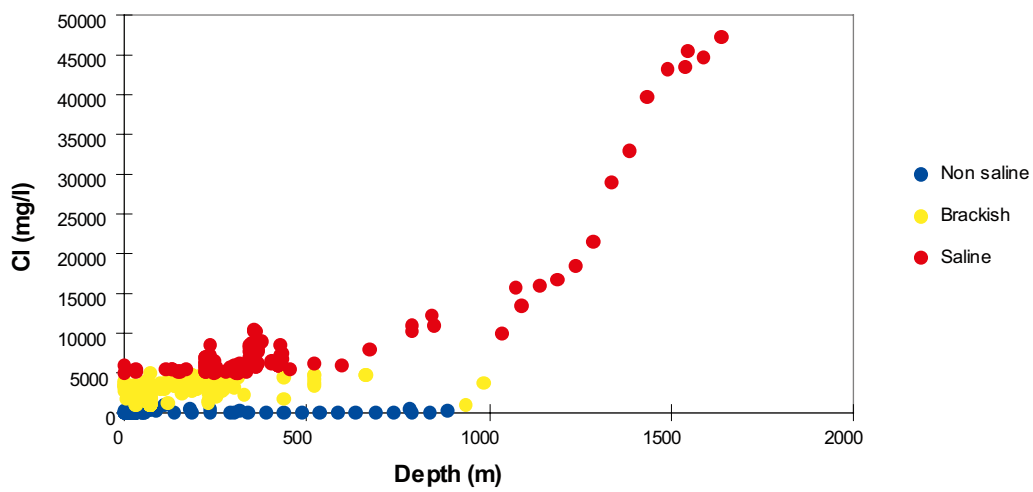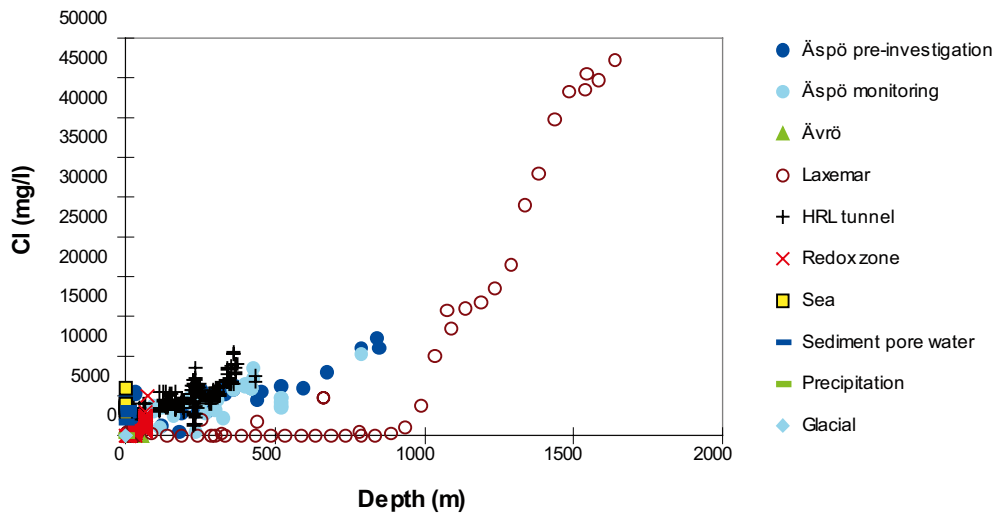
Figure A-4a,b. *Scatter plots for the Äspö site data shown for Cl versus depth. a) The samples from: Äspö (during the pre-investigation and monitoring phase of the HRL tunnel), Ävrö, Laxemar, Redox Zone, HRL tunnel, Baltic Sea, precipitation and sea bed sediments. b) The observations have been divided according to the groundwater classification: non-saline, brackish and saline.*
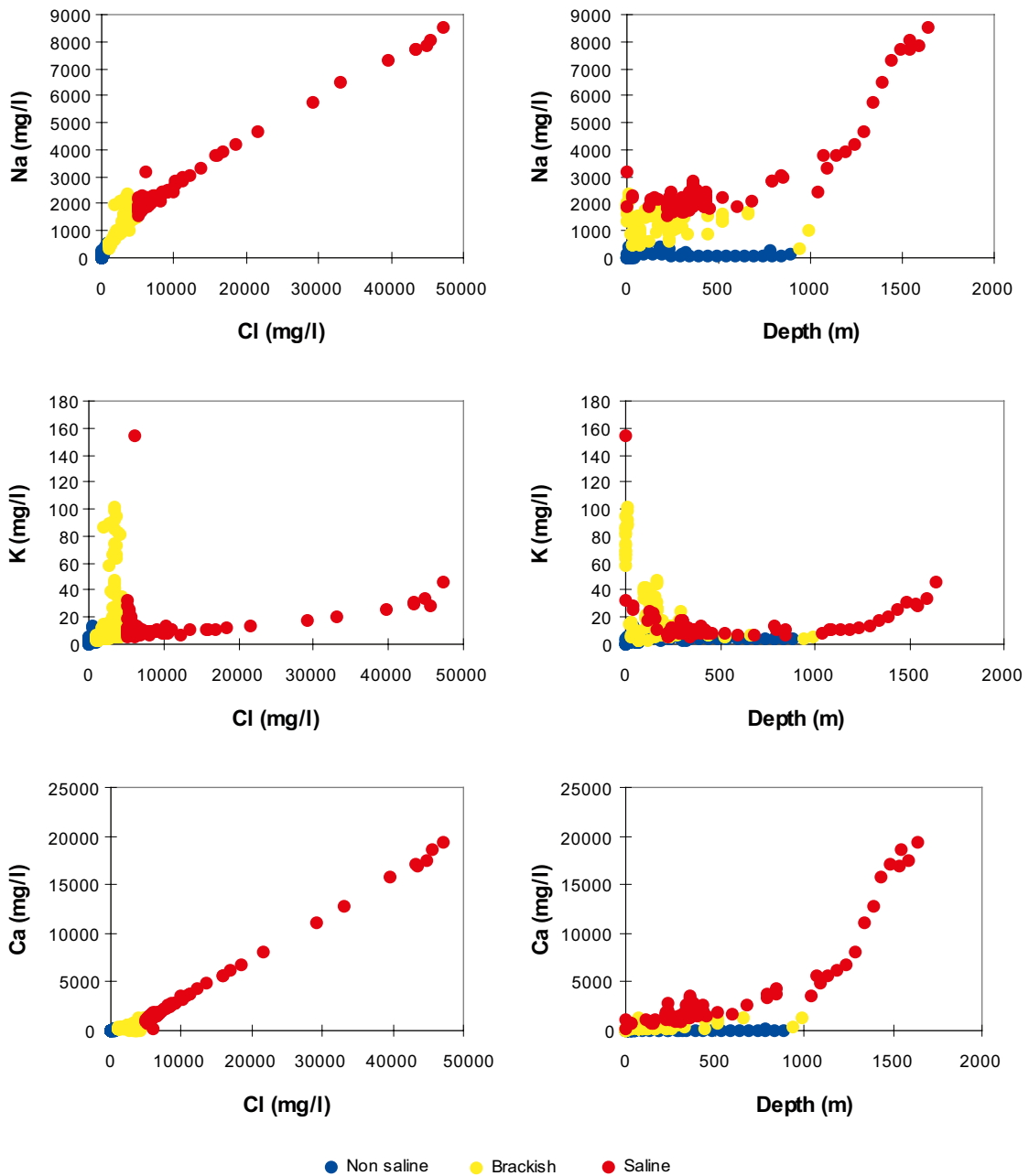
Figure A-5a. *Scatter plots for the Äspö site data shown for Na, K and Ca versus the Cl concentration and depth. The observations have been divided according to the groundwater classification: non-saline, brackish and saline.*

Figure A-5b. *Scatter plots for the Äspö site data shown for Mg, HCO₃ and SO₄ versus the Cl concentration and depth. The observations have been divided according to the groundwater classification: non-saline, brackish and saline.*

Figure A-5c. *Scatter plots for the Äspö site data shown for tritium, δ²H and δ¹⁸O versus the Cl concentration and depth. The observations have been divided according to the groundwater classification: non-saline, brackish and saline.*

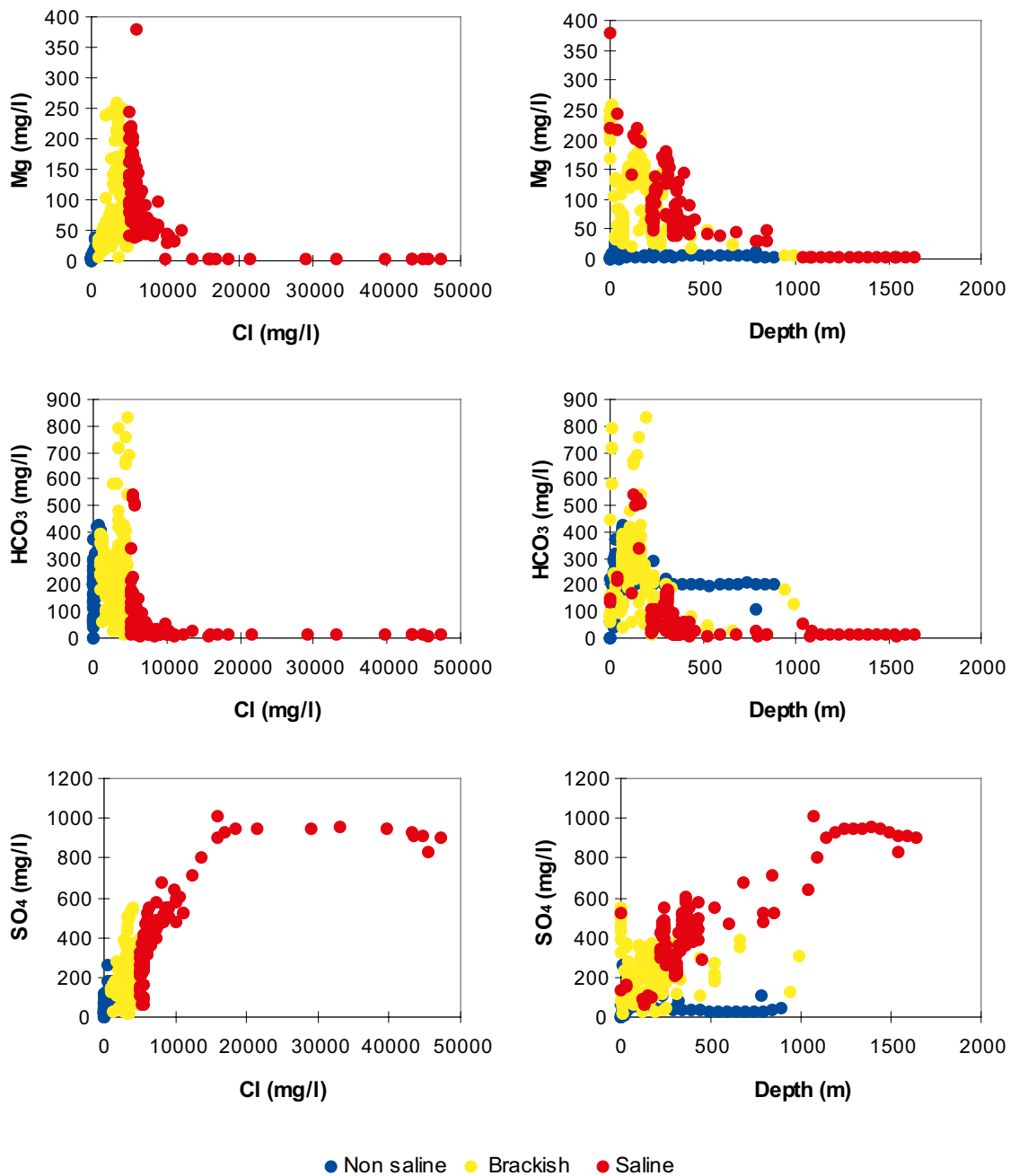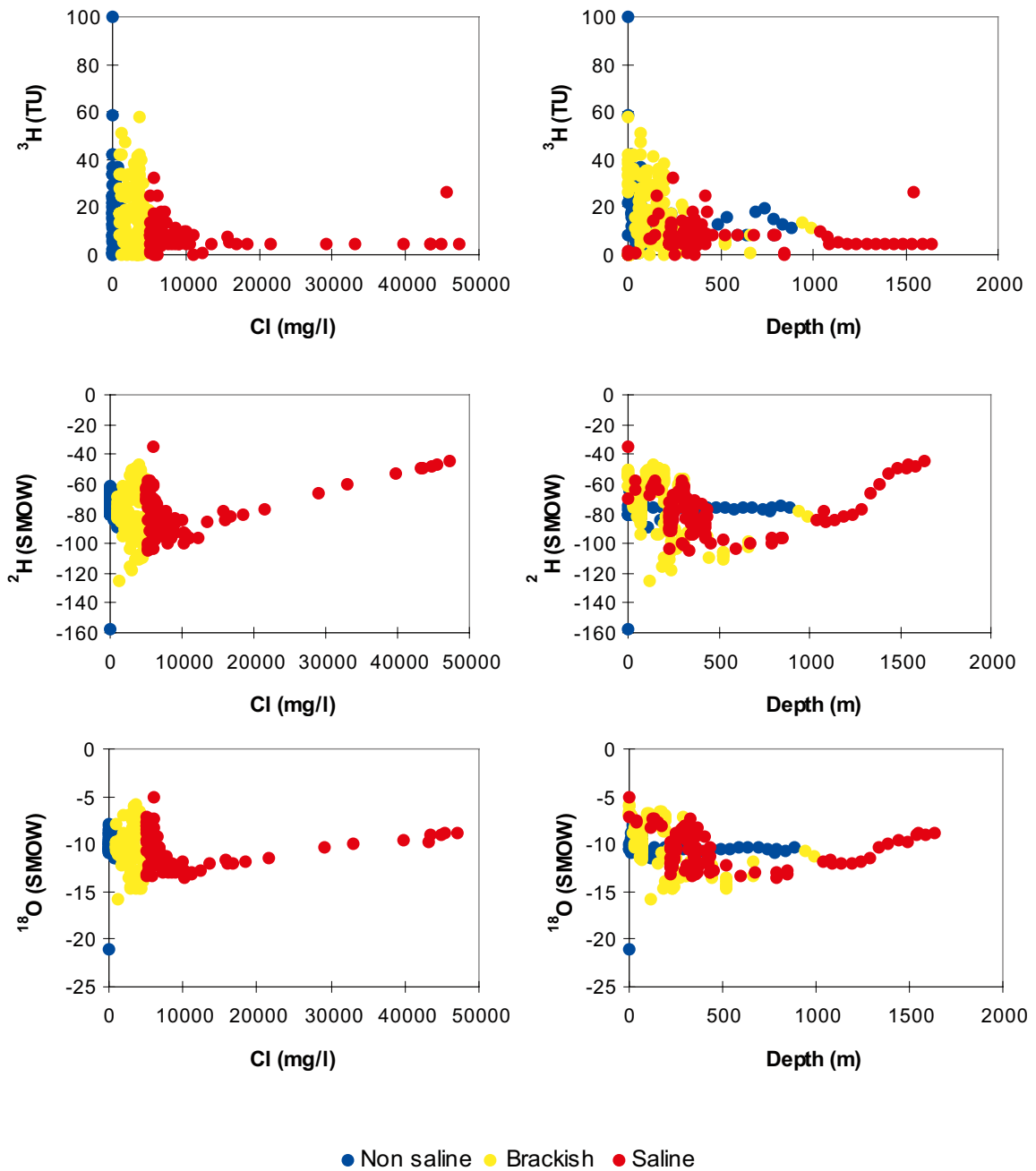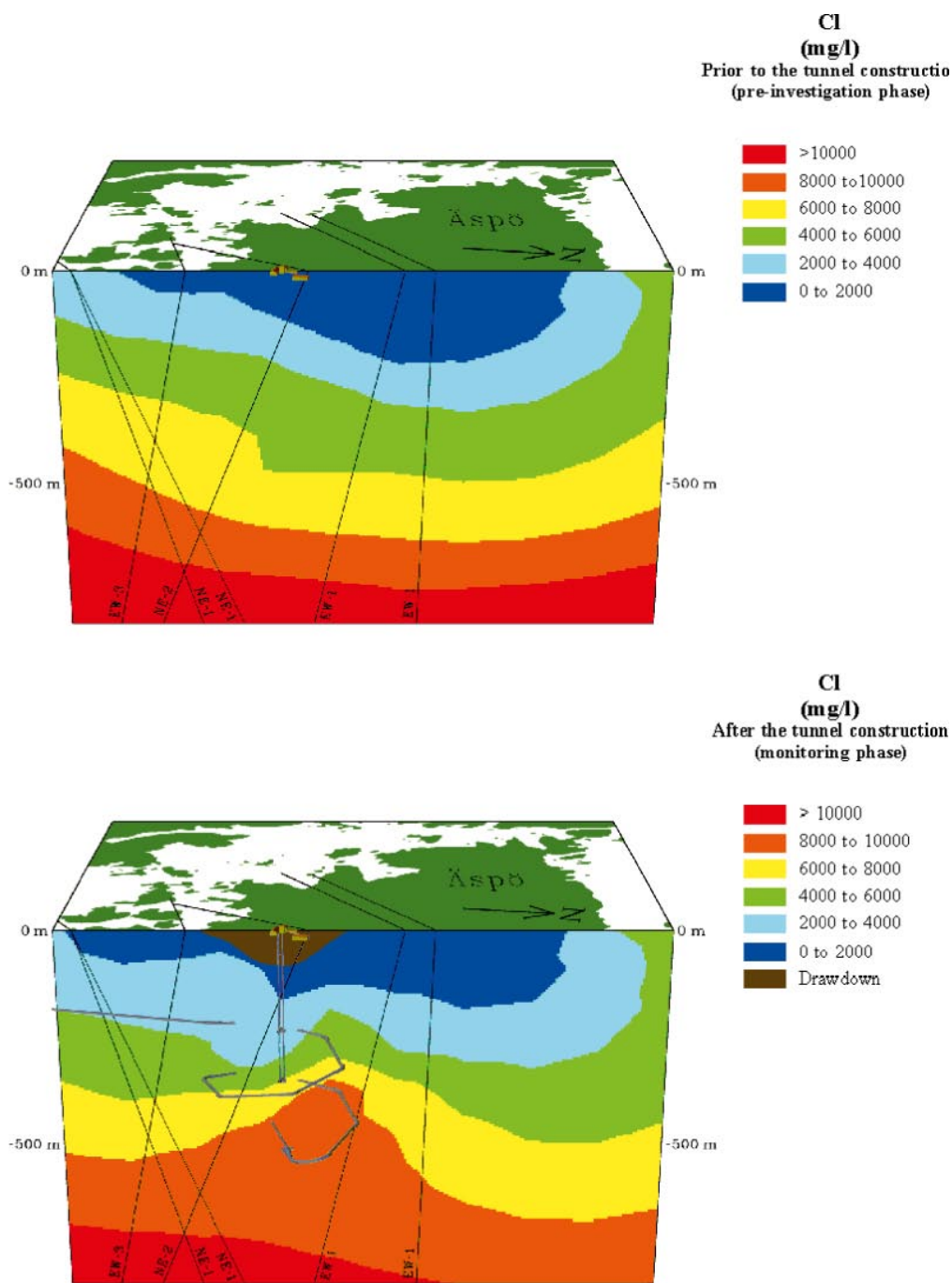**Figure A-6.** *Cl distribution at the Äspö site prior to (pre-investigation) and after the tunnel construction (monitoring). The major features of the non-saline, brackish and saline groundwaters are listed in the table above. The drawdown (80 m) of the groundwater surface, above the tunnel, is shown in the lower picture. The orientation of the cutting plane is N-S (see Figure A-1).*

Depth (m)	Water type	Major ions	Cl (mg/l)	pH (units)	Eh (mV)
0–100	Non-saline	Na–Ca–K:HCO$_3$–SO$_4$–Cl	<1,000	~ 6.5	~ –100
100–350	Brackish	Na–Ca–K: Cl–SO$_4$–HCO$_3$	1,000–5,000	~ 7.5	~ –200
350–1,700	Saline	Ca–Na–K:Cl– SO$_4$–HCO$_3$	>5,000	~ 8.5	~ –300

When studying the major component chemistry the first working hypothesis was that: a) The groundwater evolution is fairly simple and can be described as following a two component evolution path between non-saline and saline groundwaters; b) The system is stable and the HRL tunnel construction does not induce mixing between the non-saline and saline groundwaters to any large extent since the Cl stratification is almost unchanged; c) The stability of the groundwater system and a long term contact with the rock are generally regarded to result in water-rock interaction which is the major groundwater altering process. The working hypothesis had to be modified after a more careful examination of the groundwater data.

The depth stratification of groundwaters at the Äspö site is a result of the prevailing hydraulic forces, and this can be depicted when the Cl, Na, K, Ca, Mg, HCO_3 and SO_4 are plotted versus depth. Highly saline groundwaters characterised by a high Cl, Na, K, Ca, Mg and SO_4 content and a low HCO_3 and tritium content can be found within 50 m from the bedrock surface down to 1,700 m depth. In contrast, waters with a recognisable near-surface component such as a low Cl, Na, K, Ca, Mg and SO_4 content but a high HCO_3 and tritium content can be detected at 900 m depth.

A more detailed evaluation of the known groundwater conservative tracers such as $\delta^{18}O$ or δD showed a low correlation with Cl (when Cl < 10,000 mg/l) which indicates a more complex system than first assumed (see Figure A-5c). The complexity increases further when considering that fast reactions such as bacteria mediated, ion-exchange, carbonate system and redox reactions can change the groundwater character relatively fast. Marine water may have undergone reactions such as ion-exchange with sea bed clay minerals outside the bedrock prior to entering the bedrock rather than reacting with the fracture clay minerals. Glacial water may have reacted eg, with pyrite in glacial sediments outside the bedrock. The slow reactions such as water-rock interaction with aluminium silicates may be a less important water modification. The relative low temperature of the groundwater in the bedrock, (at -200 m = $11°C$ at $-1,600$ m = $33°C$, the gradient is $1.6°C$ per 100 m) may lead to the fact that many of the reactions need more time than the residence time of the groundwater /Laaksoharju and Wallin (eds) 1997/. If transport processes and reactions taking place *outside* the bedrock are not compensated for, the mass balance calculations applied to groundwaters *in* the bedrock aquifer may be overestimated. The overestimation and the ambiguous groundwater data may lead to wrong assumptions concerning the residence time and, in the end, the stability and history of the groundwater.

A.3 Results of the M3 groundwater modelling

A.3.1 Identified reference waters and end-members

Groundwaters used in the M3 modelling as a comparison to other groundwaters are by definition called *reference waters*. An *end-member* is a modelled water composition that is believed to be the original groundwater composition. It is important to note that all the available information such as $\delta^{14}C$ dating $\delta^{34}S$ and ^{36}Cl (where available) have been used to correctly name the reference waters and end-members. The end-member composition varies over time i.e. the meteoric water composition has changed along an evolutionary line between the glacial end-member and modern precipitation during the last 10,000 years. A common feature for the end-members is that the composition is uncertain due to assumed composition i.e. glacial melt water composition. In reality an end-member is not a fixed composition but only an extreme water which can change over time. The end-member water composition is important for understanding the origin of the water. The reference waters should be regarded as fixed points to which the observed groundwater composition is compared. The selected reference waters and the identified end-members are shown in the results from the principal component analysis in Figure A-7. If the main purpose is to model the evolution and to minimise uncertainty the reference water composition sampled in the rock rather than modelled end-member compositions should be utilised. The result of the modelling thus reflects mixing and reactions taking place in the bedrock which can explain the measured groundwater composition.
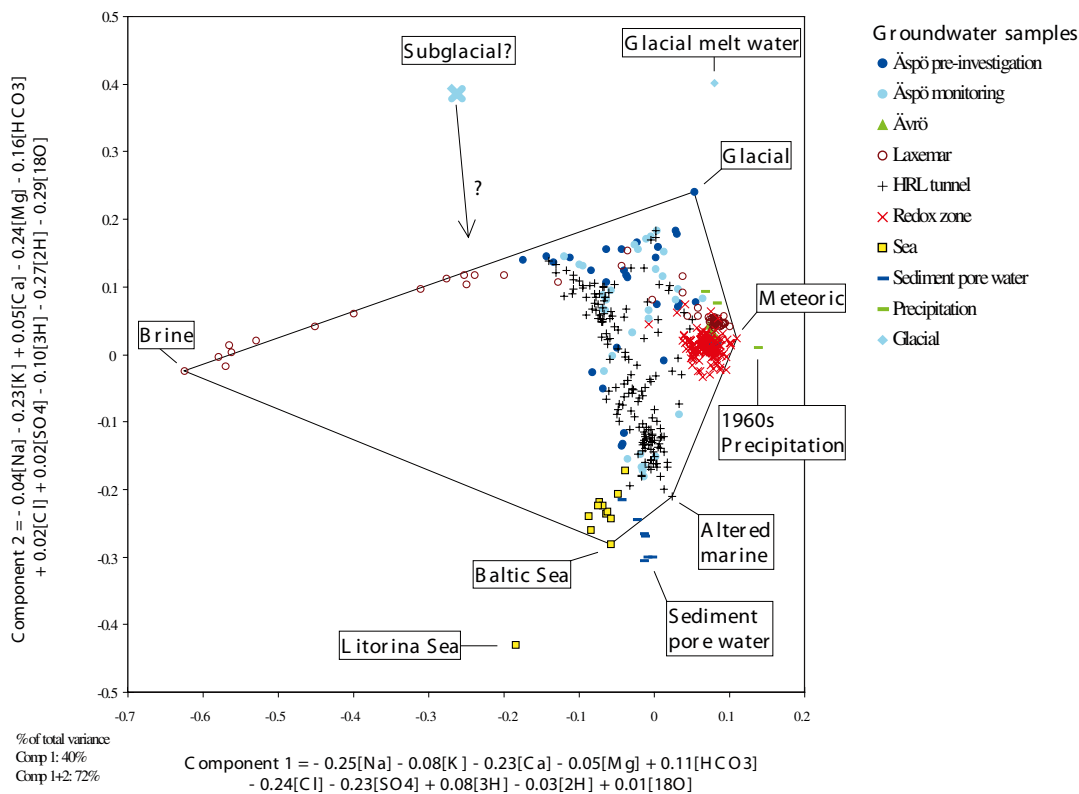
Figure A-7. *The M3 code was used to make a principal component plot based on the major components, stable isotopes and tritium values from the Äspö site. The selected reference waters to which all the other groundwater samples are compared are labelled. An end-member is a modelled water composition that is believed to be the original groundwater. A line is drawn between the reference waters so a polygon is formed. The polygon is used to define the observations for further modelling. The mixing ratios and the mass balances for the different observations are calculated. The weight for the different elements is shown in the equations for the first and second principal component respectively. These two principal components together account for 72% of the variability, or the information in the data.*

The reference waters for the current modelling shown in Figure A-7 were selected so that most of the sampled Äspö site data can be described. In order to minimise the uncertainty only analysed samples of high quality were used. Too few or incorrect reference waters may lead to errors in the mixing and mass balance calculations and result in a misunderstanding of the processes. Most of the reference waters were samples taken in the rock except for the Baltic reference water. The selected reference waters and end-members are:

- **Brine reference water** which represents the brine type of water found in KLX02: 1,631–1,681 m with a measured Cl of 47,200 mg/l /Laaksoharju et al. 1995b/. Brines are waters with significantly higher salinity than Ocean sea water. At the Äspö site the limit for Brine was set to > 40,000 Cl, mg/l. The initial approach was to assume that the deep brine groundwater in Laxemar was a totally closed two component system where diffusion was the dominating process. The Laxemar deepwaters were treated as a stagnant system in contact with the brackish groundwater systems rather than as a totally closed system. This contact may have taken place during the melting of the continental ice, natural influx or enhanced influx during drilling, hydrotesting or sampling. However, the samples at large depths have traces of tritium, indicating contact with the upper part of the aquifer /Laaksoharju et al. 1995b/. This may be attributed to a contamination of significantly younger waters in connection with the drilling operations.

- **Glacial reference water** which has been determined as a glacial water based on stable isotope values which indicate cold climate recharge ($\delta^{18}O = -15.8$ SMOW and $\delta^{2}H = -124.8$ SMOW) in combination with an apparent ^{14}C age of 31,365 years /Smellie and Laaksoharju 1992/. This type of water is found in Äspö KAS03:129–134 m. The glacial water is believed to have been injected into the basement during the melting and retreating of the continental ice sheet. These

melt waters have most likely been mixed with saline groundwaters resulting in negative $\delta^{18}O$ signatures of the water obtained. Glacial melt water can be observed at Äspö today at various depths in the basement /Smellie and Laaksoharju 1992, Wallin and Peterman 1994/. The *Glacial melt water end-member* is a modelled glacial melt water composition where the stable isotope values ($\delta^{18}O$ = –21 SMOW and $\delta^{2}H$ = –158 SMOW) were based on measured values ($\delta^{18}O$) in the calcite surface deposits, and interpreted as sub-glacial precipitates, collected from different geological formations in Sweden. Some of the fracture fillings were assumed to be subglacial formations /Tullborg and Larson 1984/. Tests were made using many possible water compositions for the glacial water in order to select the composition that gave the best fit with the measured $\delta^{18}O$ content in the groundwater. In order to sample glacial melt water a sampling campaign was performed on one of the largest glaciers in Europe called the Josterdalsbreen in Norway. The glacier is situated in crystalline granitic bedrock and the main core of this glacier is up to 20,000 years old. Samples from the glacier ice were taken and the melt water stream was sampled for 36 km downstream /Laaksoharju 1997/.

A modelled *Subglacial water,* in this case related to a possible water type formed below the continental ice as a result of element concentration due to repeated freezing, is shown in the PCA (Figure A-7). In order to demonstrate the effect of freezing a laboratory test was conducted on the groundwater sample from KAS03: 129–134 m. The original water had a chloride concentration of 1,220 mg/l. A 250 ml sample was frozen and then, when 50% of the ice fraction had melted, the chloride concentration in the melt water was 2,318 mg/l. The remaining ice fraction was melted separately and the chloride concentration in this melted water was 219 mg/l. The freezing had concentrated the first fraction of the original water by a factor of 1.9 (2,118/1,220 mg/l). The second fraction was diluted (compared to the original water) by a factor of 5.6 (1,220/219 mg/l) /Laaksoharju 1997/. The assumed composition of the subglacial groundwater was calculated from the difference between predicted and measured groundwater composition. This water composition could explain important deviations in constituents such as SO_4 and Ca. But since this water composition is uncertain, further tests and investigations are needed before this water composition can be included as an end-member. In addition, the subglacial water composition most probably changed with time during repeated freezing and melting of the continental ice sheet.

- **Baltic Sea reference water** which represents modern Baltic Sea water. The end-member is *Littorina Sea* with a Cl concentration of 6,100 mg/l based on analyses of microfossils from the marine sediments in southern Finland /Kankainen 1986/. Based on microfossil determination in the southern part of the Baltic Sea, concentrations up to 14,000 mg/l Cl have been suggested /Winn et al. 1988/. Mixing portion tests were performed where various possible Littorina Sea water concentrations were tested. The former concentration of 6,100 mg/l gave the best fit with the measured Cl and $\delta^{18}O$ content in the groundwater. The Littorina sea had a higher salinity (of almost a factor of two) compared to the selected reference water composition which was sample Baltic Sea water outside Äspö. Further investigations of the microfossils in the marine sediments around Äspö could give new information concerning the local situation during the Littorina stage. The saline component in Littorina Sea water is ocean water.

- **Altered marine reference water** which represents Baltic sea water altered by bacterial sulphate reduction /Laaksoharju et al. 1995a/. This water type is obtained in the HRL tunnel below the marine sediments. The end-member is the composition of the extracted marine *sediment pore water*. The stable isotopes were not measured for the pore water and a test was performed where the samples were given Littorina as well as modern values. The position of the samples in Figure A-7 did not change considerably. The pore water composition resembled a more modern Baltic Sea water composition than a Littorina sea water composition. In addition the hydrogeological modelling indicated that the modern sea could affect the sediments. Based on this knowledge the modern isotope values were kept in the modelling. The origin and the isotopical composition of microfossils of the sediments need further investigation. This information can be of great importance for the total postglacial scenario of the Äspö site.

- **Meteoric reference water** which represents a dilute (Cl = 5 mg/l) non-saline water found in HBH02: 7.5 m. The end-member is an average *1960 precipitation* composition with a high tritium (100 TU) content. This value is an estimate based on the modern tritium values measured at Äspö and taking into account the 12.43 years of half-life for tritium. The precipitation of 1960 could contain up to 3,000 tritium units /Alley 1993/.

A.3.2 Result of the mixing and mass balance modelling

The results of the M3 modelling concerning the behaviour of the carbonate system in association with meteoric water at the Äspö site is described below. The complete modelling results are reported in /Laaksoharju and Wallin (eds) 1997/.

Major element hydrochemistry as well as carbon and oxygen stable isotope data indicated large inputs of HCO_3 and biogenic $CO_2(g)$ in the shallow non-saline groundwaters at Äspö. Elevated CO_2 concentrations in the groundwater (6,050 to 15,037 ppm) exceeded atmospheric concentrations by one or two orders of magnitude. High TOC values (up to 20 mg/l) and the $\delta^{13}C$ isotope values of the HCO_3 (–16 to –14 per mille PDB) confirmed a large uniform organic carbon source as one end-member for the carbon system. Methane (1,030 to 4,070 ppm) in the Redox fracture zone and the shallow boreholes with $\delta^{13}C$ values between –39.8 and –50.8 o/oo strongly supported a biogenic source for this gas. The build-up of the bicarbonate reservoir most probably took place in the lower saturated part of the shallow groundwater (below 30 m). The effect of this process as a source of HCO_3 can be seen in Figure A-8. Input of organic carbon with shallow groundwater provides a possible energy and carbon source for anaerobic respiration. The accelerated input of organic carbon added net reducing capacity to the groundwater that in turn prevented oxygen penetration. Reduction of iron(III) minerals to iron(II) in solution is an anaerobic process similar to sulphate reduction. This process was found to be the successor to the aerobic respiration of organic matter that was observed in the block scale Redox experiment. The process takes place when the amount of organic matter is larger than the amount of dissolved oxygen. This is roughly the case at >10 mg/l total organic content. A detailed description of the iron reduction is given in the reporting of the Redox project. Inorganic oxygen reduction was expected, but biological consumption was found. Other processes that can be a source for HCO_3 are calcite solution, iron and manganese and sulphate reduction. The $\delta^{14}C$ data from April 1995 indicated that calcite dissolution is more important in waters with short residence times while the biogenic input (slower process) completely dominates boreholes which
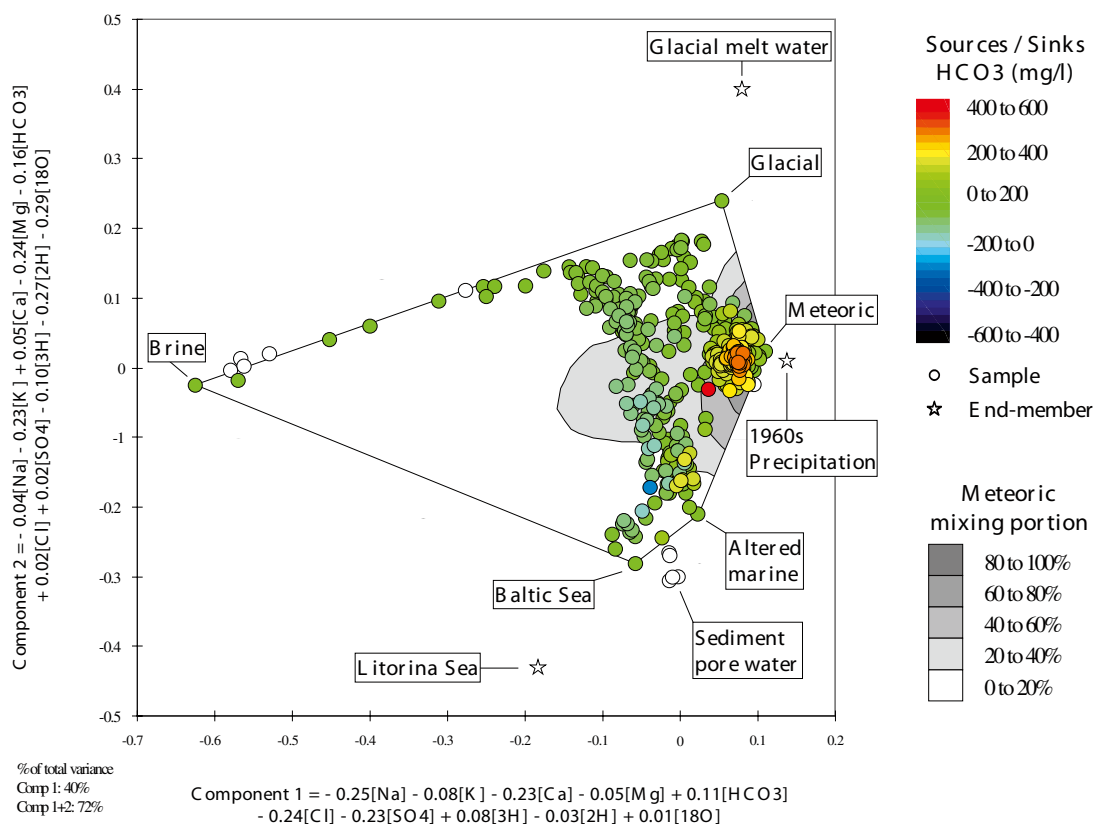

Figure A-8. *Anaerobic respiration linked with organic decomposition is believed to be the major source for HCO₃. The effect from the mixing portion of Meteoric water is shown in the background. The mixing portion is shown progressively: 0-20%, 20-40%, 40-60%, 60-80% and 80-100%. The weight for the different elements is shown in the equations for the first and second principal component respectively.*

themselves are dominated by lateral flow. The calculations and the isotope data indicate that three carbon sources contribute to the dissolved bicarbonate /Tullborg and Gustafsson in Laaksoharju and Wallin (eds) 1997/. These are inorganic CO_2, anaerobic respiration and dissolution of calcite. Sinks for HCO_3 are often associated with calcite precipitation. Evidence from carbon isotope geochemistry /Wallin 1993, Wallin 1995, Tullborg and Gustafsson in Laaksoharju and Wallin (eds) 1997/ as well as the modelling of the $\delta^{18}O$ and tritium data from the groundwater in the fracture zone suggest that an extensive lateral flow of the water takes place. This, together with the decreasing chloride content over time, rules out the possibility of a large saline water component being mixed into the system.

3D visualisation of M3 calculations

The result of the modelling can be used to visualise the origin and mixing behaviour of the groundwater at the site. The major reactions taking place in the bedrock were identified by means of M3 modelling in combination with standard geochemical modelling. The 3D interpolation of the M3 mixing calculations were performed by using INERGRAPH's Voxel Analyst computer code. The results of the modelling are shown using a 2D cutting plane. The location of the cutting plane is N-S, for orientation see Figure A-1. The observations used in Figure A-9 are common for the model used in Figure A-6. The hydraulic transmissivity /Rhén (ed) 1997/ of the major fracture zones is shown based on the calculations before drawdown. The tunnel construction created a –80 m drawdown of the groundwater table around the elevator shaft. This drawdown is shown in Figure A-9. The drawdown resulted in changing inflow patterns and increased the mixing of different groundwater types. The short-term reactions listed in the Figures are believed to increase in intensity because of the increased flow associated with the drawdown.

The non-saline groundwater is characterised by a Na–HCO_3 or a Ca–HCO_3 signature. The water is a result of infiltrated meteoric water that may have been mixed to some degree with brackish groundwater at different depths. Identified short-term fast reactions are redox reactions that hinder deep oxygen penetration into the bedrock. Oxygen consumption and carbonate production linked to organic decomposition and iron reduction is the dominating redox reaction. Solution of calcite in the upper part of the bedrock and the resulting precipitation of calcite in the lower part of the bedrock can change the groundwater flow paths in fractured bedrock. Sinks and sources of anions and cations due to sorption/desorption (due to surface complexation and ion exchange) alter the water composition of the non-saline groundwater.

Figure A-9 shows a different picture than expected from the Cl distribution in Figure A-6. This is due to the fact that Cl is not always a good tracer when it comes to finding out the evolution; neither is it always a good indicator of the dynamics of a groundwater system. For example, the Cl concentration in Figure A-6 shows minor changes during the tunnel construction around NE-1, the most conductive fracture zone. The mixing proportions in Figure A-9 show more dynamic changes around this fracture zone. The Cl concentration is not affected by a replacement of water with a similar Cl content but the change may be detected by integrating the information from several elements and isotopes that may have undergone modifications. The older brine and glacial water in NE-1 is replaced by modern Baltic sea water and modified marine water. The increased mixing portion of meteoric water in the deeper part of this fracture zone remains undetected when examining the Cl distribution.

A.3.3 Conclusions of the modelling

The findings and experiences from the M3 modelling at the Äspö site can be summarised accordingly:

The groundwater origin and evolution were described by means of mathematical models rather than by means of qualitative descriptions. Fundamental information for understanding the groundwater system was obtained after decoding the measured groundwater element concentration in terms of contributions from mixing and reactions.

Mixing is the dominating process affecting the groundwater composition.

A simple model eg, using one conservative tracer cannot be used to describe a complex natural system at the Äspö site without significant loss of information.
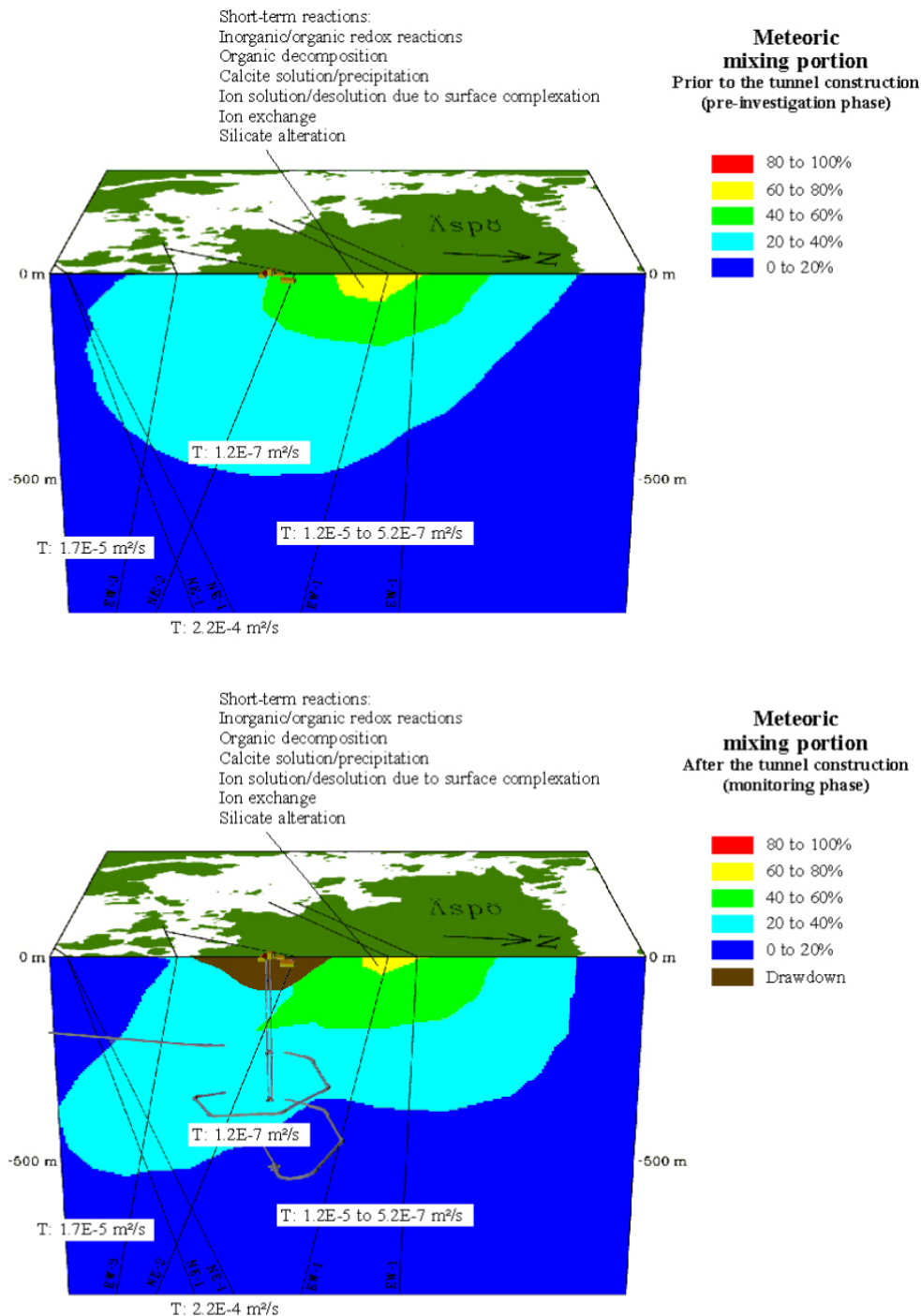
Figure A-9. *Proportion (%) of meteoric water at the Äspö island prior to and after tunnel construction calculated by using M3. The major reactions altering the groundwater are listed and the hydraulic trans-missivity of the major fracture zones are shown. The mixing proportions are always relative to the selected reference water composition. The orientation of the cutting plane is N-S (see Figure A-1).*

Different elements and isotopes from the same water sample may contain different information concerning the groundwater evolution history. Conservative natural groundwater tracers Cl, $\delta^{18}O$ and δ^2H have several sources and origins.

Groundwater evolution models based on thermodynamic laws alone may not be applicable to a low temperature granitic groundwater system such as Äspö where equilibrium is not reached and where most of the reactions are biogenic.