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Applied Geochemistry 23 (2008) 1921–1940

Applied Geochemistry

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Understanding groundwater chemistry using mixing models

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Abstract

For the last 15 a, SKB (the Swedish Nuclear Fuel and Waste Management Company) has been using the Äspö Hard Rock Laboratory (HRL) as the main test site for the development of suitable tools and methods for the final disposal of spent nuclear fuel. Major achievements have been made in the development of a new groundwater modelling technique. The technique described in this paper is used within the ongoing site investigations of Forsmark and Simpevarp in Sweden.

The limitations of existing geochemical models used at many sites and the need to decode complex groundwater information in terms of origin, mixing (transport) and reactions at site scale, necessitated the development of a new modelling tool, M3, (multivariate mixing and mass-balance calculations). In M3 modelling, the assumption is made that the groundwater chemistry is a result of mixing as well as water/rock interactions. The M3 model compares groundwater compositions (measured in terms of major ionic components, stable isotopes and ^{3}H) at a site. The model differs from many other standard geochemical models which primarily use water–rock interactions, rather than mixing, to determine groundwater chemical evolution. The tool is not dependent on thermodynamic databases, potentially uncertain redox and pH data, and can deal with the effects of biological reactions. The results of mixing calculations can be compared or integrated with hydrodynamic models.

In this paper, the M3 method has been applied to two large hydrogeochemical databases, for the Äspö Hard Rock Laboratory in Sweden, the Underground Research Laboratory in Canada (URL) together with data from the ongoing site investigations of Forsmark and Simpevarp in Sweden. Decreasing amounts of precipitation and increasing proportions of saline and brine waters are seen with increasing depth in both areas. Biogenic waters, caused by uptake of CO_2 from organics causing additional formation of HCO_3 by water–rock interaction, occur at intermediate depths in both areas but more glacial water is detected in the URL area. The origin and evolution of the groundwater at the Äspö and URL sites have been quantified with the aid of M3. In addition, the conceptual present/post-glacial hydrogeological model has been verified.

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1. Introduction

The main objective of all graphical and statistical techniques for evaluating groundwater chemistry in a rock formation is to obtain information that is not readily apparent from the analytical results. The specific technique used depends largely on the type of information required and the size of the database. Techniques range from simple, but informative, *x–y* plots where variations in concentration of one species are compared with those of another, to complex

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0883-2927/$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.apgeochem.2008.02.018

diagrammatic or statistical methods depicting the data so that sources of dissolved salts, groundwater residence time, water–rock interactions and mixing of different water types, can be identified.

One approach to this type of analysis is to assume that groundwater composition evolves to its present state by reaction path modelling using speciation and solubility constraints as the controlling mechanisms. This approach is used in most geochemical modelling codes (e.g. PHREEQC, EQ3/6). However, because it relies primarily on water–rock interactions, it is difficult to account for high concentrations of soluble species such as Cl^- and corresponding cations (Na, Ca) that make up the large part of groundwater composition, since these ions are generally not considered to be part of the minerals reacting with the groundwater in an igneous rock environment. In addition, geochemical modelling does not consider the hydrogeological characteristics and processes, especially the possibility of mixing between groundwater types or uptake of soluble salts from the rock matrix (e.g. as fluid inclusions) which may be an important source of these soluble ions.

To account for the high salinities of deep groundwaters in a silicate rock environment it is useful to consider all groundwater compositions to be primarily a result of mixing of water types and derive specific water–rock interactions from the residual composition that cannot be accounted for by mixing. The origin of complex groundwaters can be determined by statistical analysis. The method applied in this paper is multivariate analysis, in particular, principal component analysis (PCA), to determine the types and quantities of groundwaters that mix to create the groundwater found at a particular depth in a rock formation.

2. Principles of modelling by mixing

The composition of groundwater can be considered to be based on the fact that

Measured composition = mixing + reactions

A simple two-component model can be used to describe the portion due to mixing and transport (i.e. non-reactive) and that due to water–rock interactions (i.e. reactive) (Laaksoharju, 1990) in the above equation. Two end-members can be postulated as mixing components. Frequently, Cl concentration in each is a useful conservative tracer that helps in determining the composition of the end-members. The model is used to predict concentrations for other groundwaters in the area and any deviation between the predicted and measured values can be interpreted as a sink or source, due to chemical reactions.

2.1. Mixing processes

At any given site, standard groundwater chemical models can be difficult to apply due to the complexity of the groundwater flow system. The role of reactions may be over-emphasised since transport of groundwater may not be correctly described. For instance, the constituents of a saline groundwater may be described as a result of water–rock interaction rather than as a result of the influx of ancient seawater. The challenge in groundwater modelling is to reveal the origin, mixing and maturity of a groundwater sample and to eliminate alternative explanations (see the mixing example in Fig. 1).

In most cases, a groundwater may have more than two end-members and multivariate statistical methods can be used to identify the contributions from each of the postulated end-members. With large databases and many analytical determinations per sample, relatively complex statistical methods are required to evaluate the analyses and distinguish the individual contributions.

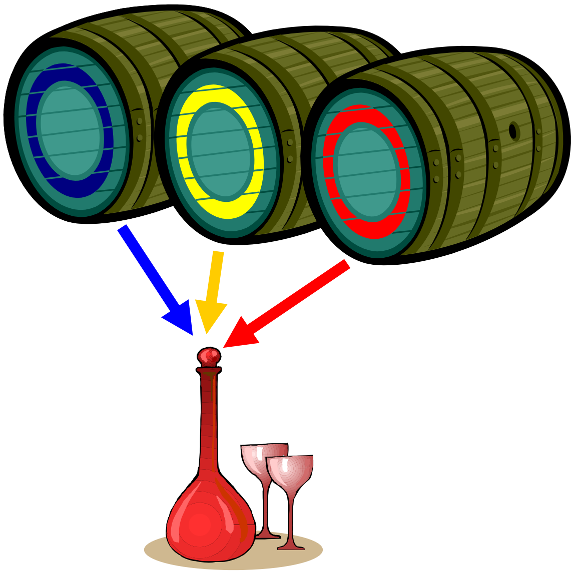


Fig. 1. Groundwater samples are almost like a mixture of different wines in a carafe. The challenge is to trace the origin, calculate the mixing processes and determine the reactions.

The concept of “mixing” of groundwaters is not a simple one to visualise, however. Unlike the analogy in Fig. 1, different groundwater types are not able to ‘mix’ in the normal sense by discharging into an underground cavity from where they emerge as a fully mixed water. This process might be feasible in karstic terrain, for instance, where several streams from different directions, carried by separate fractures, enter a large cavity and mix by turbulence before flowing onwards as a single large stream. It is difficult to envisage that thorough mixing would occur in a saturated, fractured rock where cavity sizes are orders of magnitude smaller. Nevertheless, mixing with more saline waters must occur in some manner because Cl concentration increases along the flow path in recharging waters and the Cl may not be available from host rock minerals, especially in igneous rocks in the amounts needed to account for large increases in Cl concentration with depth. Land uplift and changing climate can also cause water types to mix.

In some cases, mixing can be thought of as the uptake of salts from leaking fluid inclusions whose composition represents one end-member of the mixing fluids. Mixing of fracture groundwaters may occur by ionic diffusion within the fracture if groundwaters are essentially stagnant, as often found at depth in rock formations. In the case of advective flows that commonly occur in fractures at shallower depths, flow into and out of microcrack dead-end spaces adjoining the fracture probably account for the mixing.

3. Principles of M3 modelling

Multivariate analysis has been used for decades in analyses of geochemical data (e.g. Hitchon et al., 1971; Shaw, 1974; Joreskog and Klovan Reyment, 1976; Davis, 1986; Kimball, 1992). One application of multivariate analysis in understanding the origins of groundwater compositions is the application of PCA and the development of the Multivariate Mixing and Mass-balance model, designated as M3, (Laaksoharju and Skårman, 1995; Laaksoharju et al., 1999a). In M3 modelling, the assumption is that the groundwater composition is primarily a result of mixing and secondarily, of reactions. Initially, the method evaluates the contribution from the flow system (i.e. from mixing). Subsequently, contributions from reactions are considered. The aim is to classify and quantify the amounts of, for instance, rain water, glacial melt-water and sea water contributing to the final groundwater, and to trace possible reactions. As noted above, the model is an opposite approach to other standard geochemical models, which use reactions rather than mixing to determine the evolution of groundwater composition.

3.1. The M3 modelling method

M3 modelling uses the PCA method to analyse variations in groundwater compositions so that the mixing components, their proportions, and chemical reactions are revealed. The method quantifies the contribution to hydrochemical variations by mixing of groundwater masses in a flow system by comparing groundwater compositions with identified reference waters. Subsequently, contributions to variations in non-conservative solutes from reactions are calculated. The modelling assumes that the compositions of groundwaters being studied are predominantly determined by mixing of a number of chemically-distinct water types or ‘reference waters’ and that the chemical composition is a good tracer for the evolution by mixing and reactions of a groundwater; deviations from this mixing model are assigned to chemical/microbial reactions.

The features of the M3 model are:

- It is a mathematical tool which can be used to evaluate groundwater field data, to help construct a conceptual model for the site and to support expert judgement for site characterisation.
- It uses the entire hydrochemical data set to construct a model of geochemical evolution, in contrast to a thermodynamic model that simulates reactions or predicts reaction potential for a single water composition.
- It can account for the high Cl-salinities that are seen in the deeper waters. No chemical reaction model does this for igneous rocks because soluble evaporite salts such as NaCl and $CaCl_2$ are not regarded as part of a igneous silicate rock matrix and are, therefore, not normally used in calculating the geochemical evolution of the groundwater.
- The results of mixing calculations can be integrated with hydrodynamic models, either as a calibration tool or to define boundary conditions.
- Experience has shown that to construct a mixing model based on physical understanding often requires more information than available espe-

cially at site scale. M3 results can provide additional information on the major flow paths, flow directions and residence times of the different groundwater types, which can be valuable in transport modelling.

- The numerical results of the modelling can be visualised and presented for non-expert use.

3.2. Calculation steps in M3

The M3 model consists of four steps: standard principal component analysis (PCA), selection of reference waters, calculations of mixing proportions, and mass-balance calculations. The steps are described in detail by Laaksoharju et al. (1999a,d) and can be summarised as:

(1) *Principal component analysis* PCA is used for clustering the data in order to summarise the information and to construct an ideal mixing model for the site. The starting point is the measurement of various chemical variables for a number of groundwater samples (variables 1, 2, 3…*n*). Generally the major solutes, Cl, Ca, Na, Mg, K, SO_4 and HCO_3, in combination with the isotopes, δ^2H, $\delta^{18}O$ and ^3H, are the chemical variables. Using PCA, the samples can be visualised as corresponding to points in multi-dimensional space where the number of dimensions equals the number of chemical constituents. PCA rotates the co-ordinate system in this space to find the optimum orientation that gives the largest possible resolution of the different clusters of points. The shape and orientation of the PCA will change dependent on the number of samples included in the analysis because the first two principal components are always orientated to give maximum resolution. The mixing calculations are therefore always relative to all the samples included in the plot. This means that the results cannot directly be compared between two PCA-plots containing different data. In the case where the same set of end-members are used the mixing proportions will be similar regardless of the number of samples included or the orientation of the principal components.

(2) *Selection of reference waters* The PC-plot (principal component plot) is used to identify reference waters. Reference waters are compositions that are selected as the component waters from which the sampled groundwaters can be derived by mixing. A reference groundwater can be any composition but generally extreme water compositions or, in some cases, end-members (modelled waters which are believed to be the original composition of the water type, such as rainwater or deep groundwaters) are assigned. There are no limitations on the number of reference waters that can be selected in the modelling, but the general rule is to use as few as possible to describe the observed variations. The number of reference waters can also be guided by the type of modelling to be performed or by a conceptual model of the site. Lines are drawn in the PC-plot between the reference waters so that a polygon is formed. The polygon defines the observations that can be described by the selected reference waters. By definition, samples inside the polygon can be described by the selected reference waters.

(3) Calculations of mixing proportions The mixing proportions describe the contributions of each reference water composition to the observed water. They are inversely proportional to the distance of a sample to the selected reference waters in the plot. On a two-dimensional surface, a mathematically unique solution is only obtained from mixing proportions containing a maximum of three reference waters. If there are more than three reference waters, a centre point P is automatically created at the weight point of the polygon. By using this centre point, mixing proportions can be assigned when there are more than three reference waters in a two-dimensional plot (Laaksoharju et al., 1999a). For a polygon containing, say, four reference waters, M3 would suggest that a sample plotting at the centre point consists of 25% of each reference water. The updated version of M3 contains an option to calculate the mixing proportions in the multivariate space (see, Gómez et al., 2008) which is reducing the uncertainties in the mixing calculations. The validity of the mixing model for the site is always tested by comparing how well the model predicts the measured Cl and $\delta^{18}O$ content (c.f. Fig. 12).

(4) *Mass-balance calculations to estimate non-conservative behaviour* The mixing proportions estimated from M3 are used to recalculate concentrations of the individual variables, assuming conservative mixing between reference waters. Deviation between calculated and measured values indicates that there is a source or sink due to reaction. Mass-balance calculations are then used to quantify gains or losses due to these reactions. Only reactions or mixing not contained in the reference water composition are modelled.

4. Data sources

The M3 method has been tested, evaluated, compared with standard geochemical methods and modified over several years within domestic and international research programmes for nuclear waste disposal. This work has been supported by the Swedish Nuclear Fuel and Waste Management Company (SKB). The main test and application site for the model described here was the Hard Rock Laboratory (HRL) constructed on the island of Äspö on the SE coast of Sweden (Laaksoharju and Wallin, 1997; Laaksoharju et al., 1999b). A second test site used data from the Whiteshell Research Area and the Underground Research Laboratory (URL), in SE Manitoba, Canada, operated by Atomic Energy of Canada Limited (Gascoyne, 2004). The use of the model within the ongoing site investigations in Sweden is discussed in Section 4.3. These studies were performed using large hydrogeochemical databases obtained as part of the characterisation of igneous rock bodies at these sites. The studies aimed to improve the understanding of the geochemical processes important in the disposal of spent nuclear fuel in metal canisters at a depth of about 500–1000 m in granitic bedrock.

M3 calculations have also been applied at other sites where databases are smaller, for instance, at various sites in Sweden (Laaksoharju et al., 1998), at the Cigar Lake U ore deposit in Canada (Smellie and Karlsson, 1996), at the Oklo natural analogue site in Gabon (Gurban et al., 1998, 2003), at a U ore deposit at Palmottu in Finland (Laaksoharju et al., 1999c) and have been recently applied to groundwater data from Honorobe and Tono in Japan.

Hydrogeochemical characterisation of the potential disposal site is required to establish the composition, origin, evolution, major flow paths and reactive processes in the natural groundwaters of the site. The results from the groundwater characterisation and modelling can be used to examine whether the groundwater (1) can be corrosive to the canisters, (2) is capable of weakening the surrounding barrier of bentonite clay, (3) can act as a transport medium for radionuclides, (4) reflects the flow dynamics/stability of a site, and (5) to judge whether the site is appropriate from a chemical point of view, for final disposal.

4.1. Äspö, Sweden

The HRL at Äspö has been excavated by SKB to provide geoscientific data to a depth of 450 m below the surface (Fig. 2a). The groundwater data set consists of analyses of 438 water samples collected from 110 boreholes. The depth stratification of the samples, at and in the near vicinity of the Äspö site, ranges from 0 to 1700 m with the majority of the samples collected over the depth interval 0–600 m. The hydrogeochemical data set contains mainly downhole groundwater samples mostly collected from packed-off fracture zones in boreholes; however, some samples from open boreholes are also

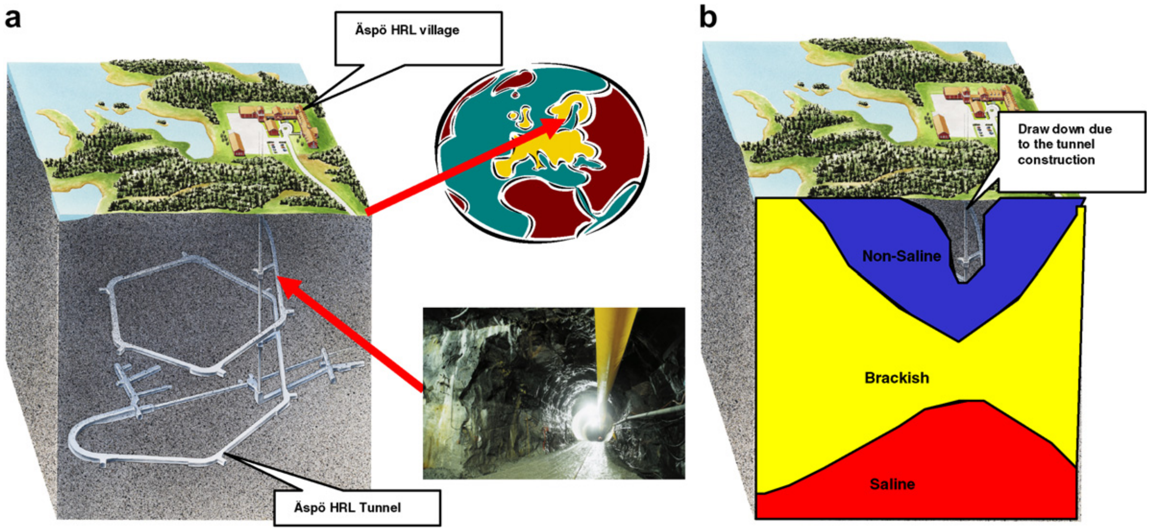


Fig. 2. (a) The Äspö HRL location and layout. (b) Schematic distribution of the water types non-saline (<1000 mg/L, Cl), brackish (1000–5000 mg/L, Cl) and saline (>5000 mg/L, Cl) (after Laaksoharju et al., 1999c).

included. In addition, environmental samples such as sea bed sediments, sea water and meteoric precipitation have also been included in the evaluation. The groundwater analytical data is stored in the SKB database SICADA. A schematic distribution of the water types, non-saline (<1000 mg/L, Cl), brackish (1000-5000 mg/L, Cl) and saline (>5000 mg/L, Cl) is shown in Fig. 2b.

The complex groundwater evolution and patterns at Äspö are a result of many factors, including (1) the relatively flat topography and the proximity to the Baltic Sea results in small hydrogeological driving forces which can prevent old water types from being flushed out, (2) the changes in hydrogeology related to glaciation/deglaciation, (3) repeated sea/lake water regressions and transgressions and (4) organic or inorganic alteration of the groundwater caused by microbial processes or in situ water/rock interactions. In various degrees, the sampled groundwater reflects modern or ancient water/rock interactions and mixing processes. This means that in order to understand the origin and evolution of the groundwater, the geology, as well as past and present hydrogeology, has to be understood. The detailed glacial/post-glacial events are compiled from Björck (1995) and Laaksoharju et al. (1999b) and are summarised as

1. concentration of salts in groundwaters due to permafrost formation to a depth of 300–600 m during continental ice formation (100–20 ka BP) (Bein and Arad, 1992); residual waters had a higher density and could sink,
2. meltwater injection into the bedrock as ice melted (~13 ka BP) possibly to depths exceeding several 100 m (Svensson, 1996),
3. ingress of different non-saline and brackish lake/sea stages (13–4 ka BP) such as the Yoldia and Litorina; the Litorina Sea stage (8–2 ka BP) contained the most saline groundwater (twice the salinity of modern Baltic Sea water) and is believed to have the deepest penetration depth,
4. development of a freshwater lens as Äspö island rose above sea level (starting in 4 ka BP); groundwaters in the upper bedrock were flushed out gradually, and
5. change in direction of the original groundwater flow due to drilling, pumping and testing of boreholes and excavation of the HRL resulting in new mixtures and water compositions when sampling the groundwater.

The effects from the last glacial and de-glacial event should be easier to detect than from previous glacial events which probably have been flushed from the groundwater system. In order to visualise some important origins of groundwater and events which may have affected the present groundwater at Äspö, a schematic groundwater conceptual model for the post-glacial phase has been constructed (Fig. 3). As a result of the sequence of events, brine, glacial, marine and meteoric groundwaters are expected to be mixed in a complex manner at various levels in the bedrock, depending on the hydraulic character of the fracture zones, groundwater density variations and borehole activities prior to groundwater sampling.

Four reference waters were chosen at the Äspö site using the M3 method: brine, glacial, marine and meteoric. The existence of these reference waters is also supported by the conceptual post-glacial scenario model of the site. The selected reference waters for the current modelling are (for analytical data see Table 1):

- *Brine reference water* which represents the sampled deep brine type (Cl = 47000 mg/L) of water found in KLX02: 1631–1681 m (Laaksoharju et al., 1995).
- *Glacial reference water* represents a possible meltwater composition from the last glaciation >13 ka BP. Modern sampled glacial melt water

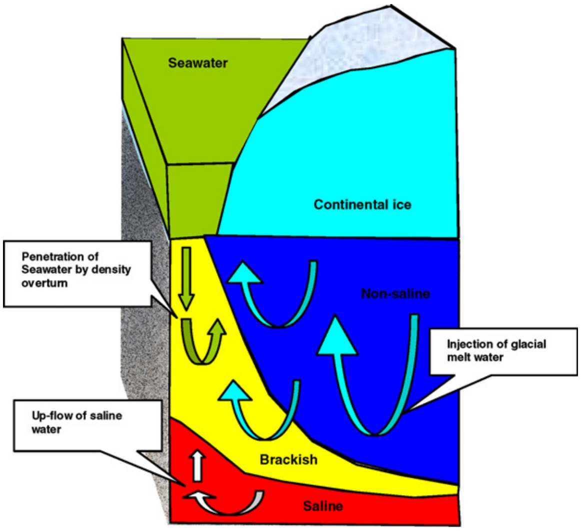


Fig. 3. Conceptual post-glacial scenario at the Äspö site showing some important events (meltdown of continental ice sheet, density overturn of sea water) that may have affected the water types.

Table 1
Analytical or modelled data (indicated with *) for the selected reference waters used for Äspö site modelling

	Cl (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	^3H (TU)	δ^2H (‰)	$\delta^{18}O$ (‰)
Brine	47200	8500	45.5	19300	2.12	14.1	906	4.2	−44.9	−8.9
Glacial	0.5	0.17	0.4	0.18	0.1	0.12	0.5	0	−158*	−21*
Marine	3760	1960	95	93.7	234	90	325	42	−53.3	−5.9
Meteoric	0.23	0.4	0.29	0.24	0.1	12.2	1.4	100*	−80	−10.5

from Norway was used for the major elements and the $\delta^{18}O$ isotope value (21‰ SMOW) was based on measured values of $\delta^{18}O$ in calcite surface deposits (Tullborg and Larson, 1984). The δ^2H value (158‰ SMOW) is a modelled value based on the equation ($\delta H = 8 \times \delta^{18}O + 10$) for the meteoric water line.

- *Marine reference water* which represents sampled modern Baltic Sea water.
- *Meteoric reference water* corresponding to the precipitation and infiltration of meteoric water from 1960. Sampled modern meteoric water with a modelled high ^3H (100 TU) content was used to represent precipitation from that period.

4.2. URL, Canada

One of the concepts for disposal of Canada's nuclear fuel waste is disposal of used fuel packaged in corrosion-resistant containers emplaced in an excavated vault at a nominal depth of 500–1000 m in a crystalline rock formation of the Canadian Shield (AECL, 1994). Several studies have been conducted in order to understand and characterise the long term effects of the influences on the groundwater geochemical environment of the vault (e.g. Gascoyne, 1997; Gascoyne et al., 1991,1997; Kotzer et al., 1998). Because the principal mechanism for transport of radionuclides from the waste disposal vault to the biosphere is expected to be via groundwater advection and diffusion within pores and fractures in the rock, considerable attention has been given to both the hydrogeological and hydrogeochemical properties of groundwater in the rock.

The URL (Underground Rock Laboratory) was constructed by Atomic Energy of Canada Limited (AECL) in a previously undisturbed portion of the granitic Lac du Bonnet batholith in southeastern Manitoba, Canada. A number of experiments have been conducted in the URL and the surrounding area to assess aspects of the disposal concept. The compositions of groundwaters sampled at the URL (Fig. 4) represent the principal part of the data set used in this work (Gascoyne, 1997). A more recent data set has been published (Gascoyne, 2004) but, for the area of the URL, the data sets are essentially the same.

In order to select reference waters for URL data in M3 modelling, the variables Na, K, Ca, Mg, Cl, SO_4 HCO_3, δ^2H, ^3H and $\delta^{18}O$ were used in a principal component analysis.

The selected reference waters for the current modelling are (see Table 2)

- *Brine reference water* representing the brine type of water found in the rock matrix (Cl = 53,300 mg/L).
- *Saline reference water* representing saline (Cl = 30,200 mg/L) groundwater found at depths of about 1000 m at the URL site.
- *Glacial reference water* determined as a glacial water with an assumed stable isotope value ($\delta^{18}O = -25$‰ SMOW) indicating cold-climate recharge.
- *Biogenic reference water* representing water altered by bacterial decomposition of organic material.
- *Precipitation reference water* representing a dilute infiltrating surface water affected by the precipitation from the 1960s and containing more ^3H (90 TU) than modern rain (~20 TU).

4.3. Site investigations, Sweden

The main objectives of the hydrogeochemical modelling within the ongoing site investigations of the Forsmark and Simpevarp sites in Sweden (see Ström et al., 2008; SKB, 2005a,b) are to describe the chemistry and distribution of the groundwater in the bedrock and overburden and the processes involved in its origin and evolution. Details of the SKB hydrogeochemistry programme are described by Laaksoharju et al. (2008). M3 is used in this modelling to determine the origin, mixing and major reactions influencing groundwater samples. The results

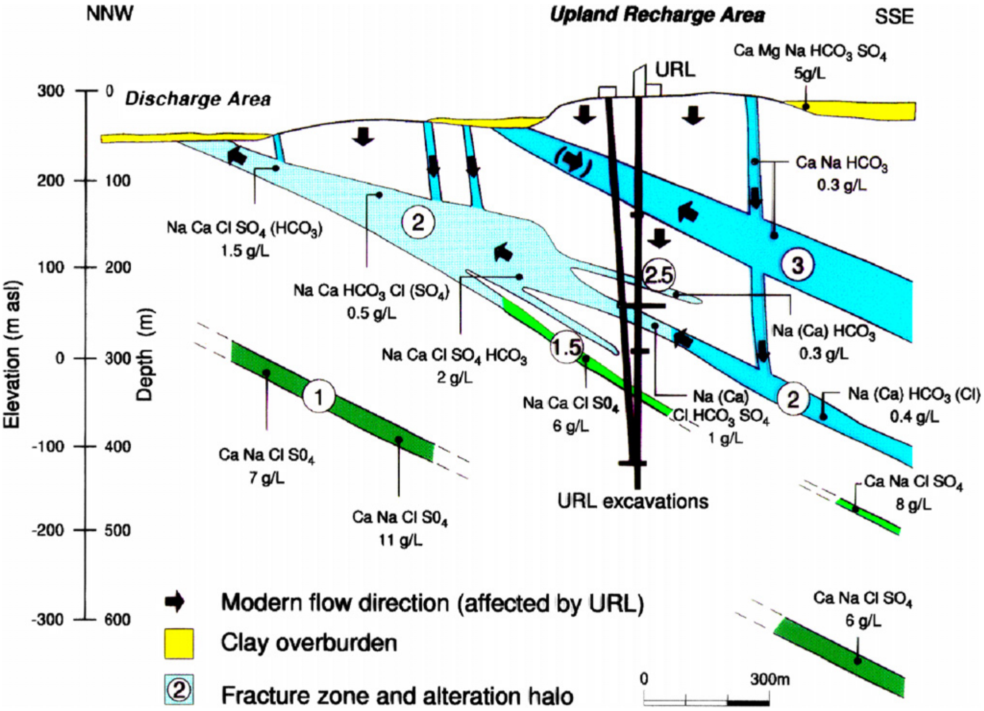


Fig. 4. Hydrogeological section through the URL area. Groundwater compositions and salinities (TDS) are based on pumping and sampling numerous boreholes in the URL area. The flow directions are based on pre- and post-excavation head distributions (Gascoyne, 1997).

Table 2
Analytical or modelled data (indicated with *) for the selected reference waters used for URL site modelling

	Cl (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	^3H (TU)	δ^2H (‰)	$\delta^{18}O$ (‰)
Brine	53300	1410	22.8	31270	0.118	28	284	0.8	−17	−17
Precip.	0.44	0.29	0.31	0.55	0.085	1.85	1.09	90	−80	−11.3
Glacial	2	20	2	35	10	180	15	0	−200*	−25*
Biogen	6.71	98	0.87	6.7	0.72	255	7.2	18	−105	−13.4
Saline	30200	11000	24	8410	51.1	9.9	1040	2.1	−94.35	−12.96

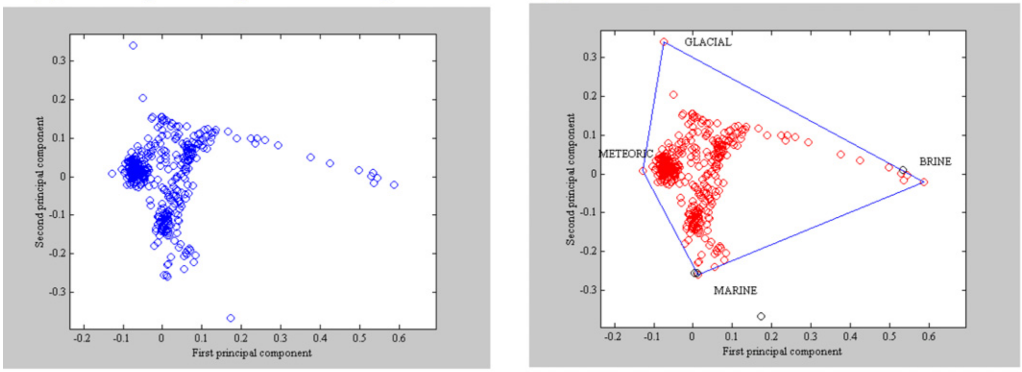
of the modelling are used for site understanding and conceptualisation of the site. The conceptual understanding of the origin of the groundwater and the mixing proportions is used in the hydrogeological modelling to set boundary conditions of the models and as a calibration tool (see Hunter et al., 2008; Follin et al., 2008).

The reference waters used in the M3 modelling have been identified from (a) previous site investigations (e.g. Äspö, see Section 4.1, and during the main site investigation, SKB, 2004, 2006), (b) evaluation of the Forsmark and Simpevarp primary data set, and (c) selecting possible compositions of end-members which, according to the post-glacial conceptual model (see, Fig. 3), may have affected the site. The selected reference waters are more extreme than actually present at Forsmark and Simpevarp (e.g. Rain from 1960 containing high ^3H, 2000 TU, or ancient Littorina Sea water). Their function is (a) to be able to compare differences/similarities of the Forsmark and Simpevarp groundwaters with possible end-members, (b) to be available to describe all data used in the local and regional model, and (c) to facilitate comparison with the results from the hydrogeological modelling.

5. Results of M3 modelling

5.1. Äspö HRL

The process used in M3 modelling of the Äspö data is shown in Fig. 5. Mixing calculations are



(a) Principal component analysis

(b) Identification of Reference waters

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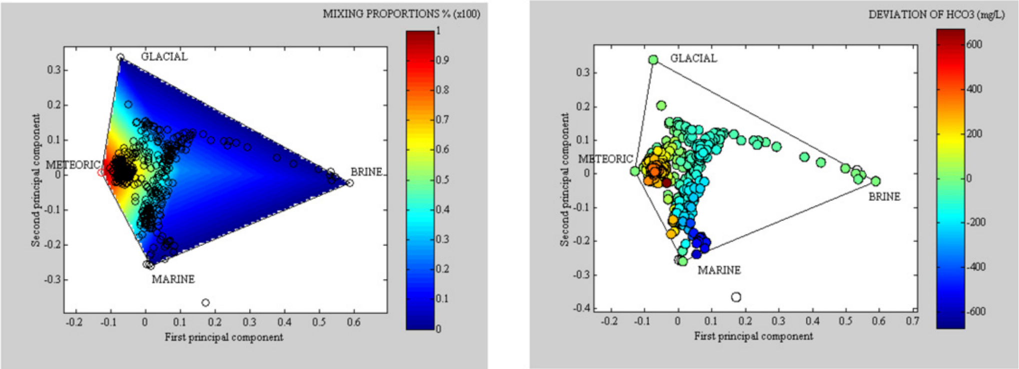

(c) Mixing calculations

(d) Mass-balance calculations

Fig. 5. M3 modelling of hydrogeochemical data at the Äspö site: (a) principal component analysis obtains the maximum resolution of the data set in order to summarise the information. (b) Reference water compositions are selected and shown for comparison with other groundwaters. The polygon defines the observations described by the selected reference waters. (c) Mixing calculations are made using the linear distance of a sample to the reference waters (the portions of meteoric water (%) are shown). (d) Mass-balance calculations are made – the sources and sinks (mg/L) of carbonate (HCO_3) are shown which cannot be accounted for by using the ideal mixing model.

made using the linear distance of a sample to the reference waters (the portions of meteoric water (%) are shown in Fig. 5c). Mass-balance calculations (Fig. 5d) show that the sources and sinks (mg/L) of carbonate (HCO_3) cannot be accounted for using the ideal mixing model.

The mixing portions of the groundwaters are shown in Fig. 6 along with the identified major reactions. Fig. 6 shows a somewhat different picture than expected from the salinity distribution in Fig. 2. The salinity distribution describes the behaviour of one variable whilst the figure showing the mixing is based on the behaviour of 10 groundwater constituents and the interpretation of the origin of the groundwater. The HRL tunnel construction caused groundwater withdrawal and increased the mixing portions of meteoric, marine and brine waters. The glacial water portion decreased since this water is a relict water and is not re-supplied. The location, depth and hydraulic properties of the rock determine the degree of groundwater mixing. The major characteristics of the dominating waters (meteoric, marine marine, glacial and brine) are described below.

5.1.1. Meteoric

As seen in Fig. 6, in the area in the middle of Äspö island, the dominating water component is meteoric water to a depth of approximately 250 m. After the tunnel construction this depth increased to 350 m. This water type is dominated by fast short-term reactions such as redox reactions that prevent deep O_2 penetration into the bedrock. Oxygen consumption and carbonate production linked to organic decomposition, Fe reduction and CH_4 production (Pedersen and Karlsson, 1995) are the dominating redox reactions (Banwart et al., 1996). Dissolution of calcite in the upper recharge part of

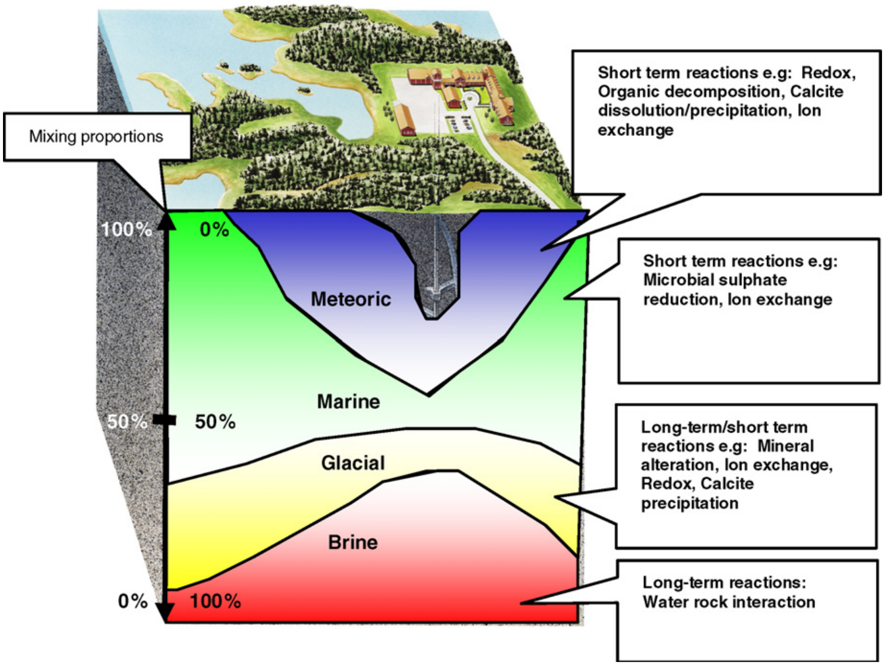

Fig. 6. Mixing proportions (%) and dominating mass-balance reactions associated with brine, glacial, marine and meteoric water. The groundwater is modelled to be a mixture of several water types and is only close to the source where the groundwater is less mixed with other water types. The mixing proportions add up to 100% at all measuring points.

the bedrock and the resulting precipitation of calcite in the lower part of the bedrock can alter the direction of the groundwater flow paths in fractured bedrock. Sinks and sources of anions and cations due to sorption/desorption (i.e. surface complexation and ion exchange) alter the water composition of the meteoric groundwater (Viani and Bruton, 1994 in Laaksoharju and Wallin, 1997).

5.1.2. Marine

The construction of the tunnel increased the inflow of marine waters from the sea. The Baltic Sea water is characterised by fast, short-term reactions that modify the waters when they enter the bedrock, this has been identified as a sink of K and Na, and a source of Ca, due to ion exchange with clays (Laaksoharju and Wallin, 1997). The marine water can undergo decomposition of organic material due to microbiological SO_4 reduction which has been detected by M3 modelling as a sink for SO_4 and a source for HCO_3 (Laaksoharju, 1995). The calculations correlate well with the measured content of SO_4-reducing bacteria. The source of Mg is shown to be associated with an influx of marine water, present Baltic Sea or possibly Litorina Sea water. Identified fast short-term reactions that have modified the sea water are a loss of Na and a gain of Ca, due to ion exchange with clays.

5.1.3. Glacial

An important water type found at Äspö contains a component of cold-climate recharge (Tullborg, 1997). The low δ^{18}O value indicates a climate which corresponds to a mean annual temperature of −3 °C using Dansgaard's formula (Dansgaard, 1964). Such a low-temperature has not prevailed during post-glacial times at Äspö. Cold climate signatures are found in many groundwaters from various depths at the Äspö site and on the mainland of Laxemar (Laaksoharju et al., 1995). The interpretation from the conceptual model (see Section 2) and the M3 calculations are that this water type has been formed by melting of the continental ice sheet and the water has been injected into the saline water. The amount, oxidation state, penetration depth and velocity of glacial meltwater are not completely known. Despite the many indications of glacial meltwater at great depth, there is no clear evidence from the fracture mineral distribution that this water was oxygenated to more than 50-100 m in the upper part of the bedrock (Tullborg, 1997). The calculated sink for Ca may be due to calcite precipitation during injection of glacial groundwater and consequent mixing with calcite-saturated saline groundwater which caused supersaturation of calcite (Laaksoharju and Wallin, 1997).

5.1.3. Brine

At depths below 800 m the brine groundwater mixing portion starts to play an important role. The origin of the brine component at the Äspö site is unknown. Alternatives such as ancient metamorphic fluids, water/rock interaction, fluid inclusions, leaching of Permian evaporites or early Paleozoic sediments, and localised freezing, have been discussed as a source for the brine water component (Laaksoharju and Wallin, 1997). The stable isotope data ($\delta^{18}O = -10.4‰$ to $-8.9‰$; $\delta^{2}H = -60.2‰$ to $-44.9‰$) of the deep saline groundwaters show significant deviation from the meteoric water line (MWL). Characteristics similar to these low-temperature Precambrian granitic shield areas are found in the deep Canadian brines (Frape et al., 1984; Frape and Fritz, 1987). The deviation from the MWL is ascribed to water/rock interaction over long periods of time. Considerable age for the brine is also suggested by the measured ^{36}Cl values indicating a minimum residence time of 1.5 Ma for the Cl component (Laaksoharju and Wallin, 1997). The origin may be unclear but the mean residence time for the groundwater is considerable.

5.2. URL

Results of M3 modelling of the URL data are shown on Fig. 7. The locations of the URL data generally indicate a greater contribution of shallow water and cold-recharge water. Also, at depth, the saline water and brine (a pore fluid) component increase. The interpolated distribution of measured Cl is shown in cross-section in Fig. 8. The Cl content can be seen to increase with depth and towards the NNW. The Cl distribution may give the impression that the groundwater system is fairly simple and can be described mostly as following a two component evolutionary path between non-saline and saline groundwater. However, the $\delta^{18}O^{18}O$ content decreases in the NNW part of the model which indicates presence of cold recharge in this part of the bedrock. A more detailed evaluation of these conservative groundwater tracers shows that their correlation is not always high, which may indicate a more complex groundwater system than can be assumed from the Cl distribution.

The reason for the low correlation between Cl and $\delta^{18}O$ is that waters with the same Cl content may have different origins. For example, a water containing the same Cl content could have been affected by waters with different recharge temperatures and therefore a different origin. An example of the M3 mixing calculations is shown as a 2D

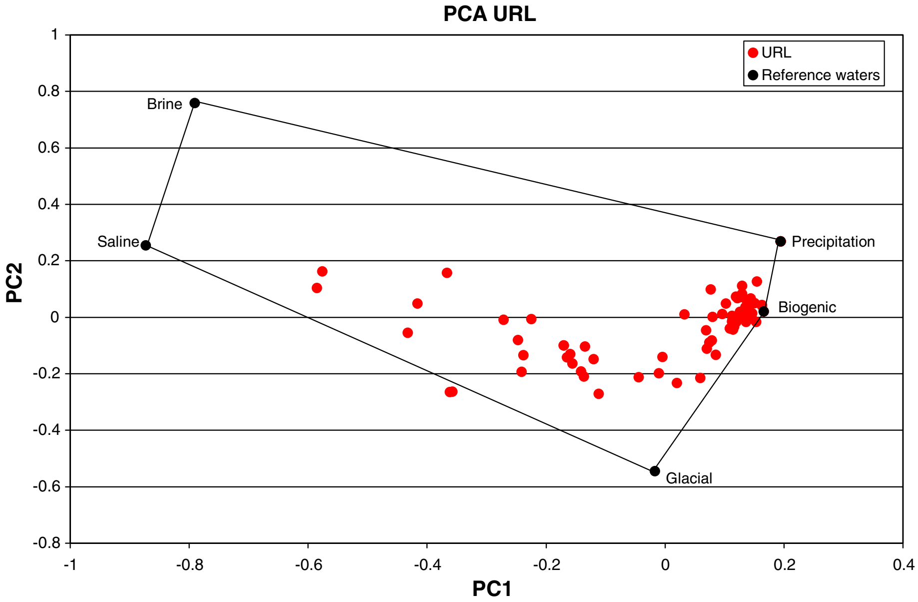

Fig. 7. M3 modelling of hydrogeochemical data at the URL site.

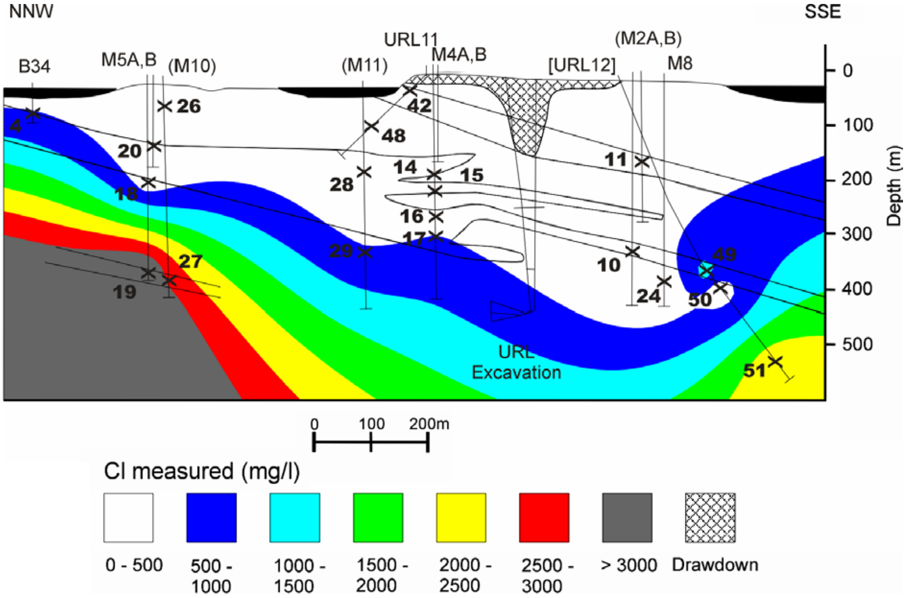

Fig. 8. Visualisation of the measured Cl distribution at the URL site. The Cl content seems to be increasing with depth and towards NNW. The shaft construction, the major fracture zones, boreholes and sampling locations are shown (Laaksoharju et al., 2000). The numbers refer to observation numbers used in the M3 analysis.

cross-section in Fig. 9 for the glacial water type (Laaksoharju et al., 2000). The conclusion from the M3 modelling is that the modelled present-day groundwater conditions at the URL site consist of a mixture in varying degrees of the following water types: precipitation, biogenic, glacial, saline and brine (Laaksoharju et al., 2000). The results of the M3 mixing calculations indicate that the upper part

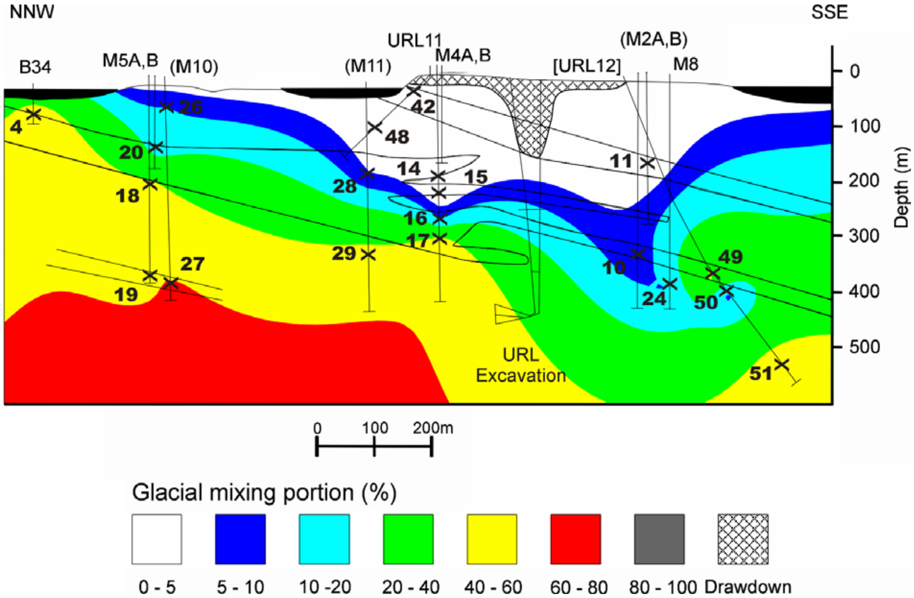

Fig. 9. Visualisation of the M3 calculated proportion (%) of glacial water in the bedrock at the URL site. The glacial water content is high in the NNW part of the bedrock at greater depths than 400 m. The glacial signature in the saline waters may be due to mixing between a small amount of a very saline, warm-climate groundwater and a high glacial-content shallow water (Laaksoharju et al., 2000). The numbers refer to observation numbers used in the M3 analysis.

of the bedrock (0–100 m) is dominated by precipitation type water (100–40%). At greater depths (100–400 m) the precipitation water is replaced by biogenic water (40–100%) which gradually consumes the O_2 of the groundwater and becomes reducing. At depths 300–600 m and in the NNW part of the bedrock glacial water (40–80%) from the last deglaciation dominates. In the NNW and SSE part and at the same depth interval as the glacial water (300-600 m) the influences from saline (5–20%) and brine (5–20%) type of waters are detected. The glacial water is a relatively thin lens and is underlain by the saline, warm-climate water typical of WB 1–7 at ~1000 m depth. The M3 modelling indicated further, that the draw-down from the shaft increased the portions of precipitation and biogenic water but seemed to have flushed out historical waters such as glacial, saline and brine from the near vicinity of the shaft. The M3 mass-balance modelling indicated that there is a gain of HCO_3 not accounted for by mixing probably associated with organic decomposition and CO_2 uptake in the biogenic water type. At greater depths and in the NNW part of the bedrock, the modelling indicates a loss which may be due to calcite precipitation. The occurrence and the distribution of water types and the mass-balance calculations for carbonate are in general agreement with earlier groundwater modelling of the site (e.g. Gascoyne, 1997).

5.3. Forsmark and Simpevarp

The results of the PCA modelling are shown at a regional scale for the Forsmark and Simpevarp sites and compared with groundwater data from other sites in Sweden and Finland (Nordic sites) in Fig. 10. The M3 modelling shown in Fig. 10 indicates that the Forsmark samples are affected by the reference waters: meteoric, marine and glacial. The surface meteoric water types show seasonal variations and, closer to the coast, the influence of marine water (Baltic Sea) is detected in the shallow samples. Several samples from Forsmark show a possible Littorina Sea water influence which is much stronger at Forsmark compared with data from the Simpevarp area. Only a few samples at depth from Forsmark indicate a glacial–brine component while many more samples from Simpevarp show this influence. The deviation calculations in the M3 mixing calculations show potential for organic decom-

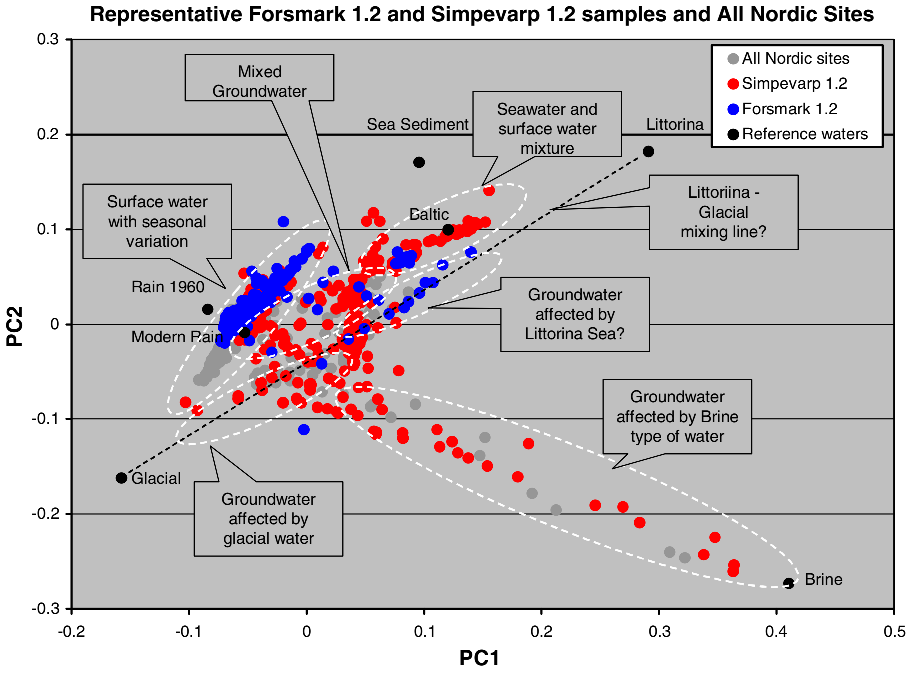

Fig. 10. PCA modelling of the representative Forsmark (blue dots), Simpevarp area (red dots) and Nordic sites data (grey dots). The reference waters used in the modelling are shown and the possible influences from different end-members on the samples are indicated (SKB, 2005b). The dashed mixing line indicates samples possibly affected by infiltrating Littorina sea water when the rock contained glacial water 8 ka BP (c.f. Fig. 3).

position/calcite dissolution in the shallow waters. Indications of ion exchange and SO_4 reduction have been identified and modelled. These M3 results support the initial site evaluation of primary data and general modelling results as described in Laaksoharju et al., 2008.

Measured Cl, ^3H, and $\delta^{18}O$ content and the calculated M3 mixing proportions based on representative samples are shown for one cored borehole within the Forsmark modelling domain in Fig. 11 (SKB, 2005b). The purpose of the plots is to show the water type, changes with depth, and to facilitate comparison of the hydrochemical results with the hydrogeological results. Due to the fact that the hydrogeologists use only four reference waters, the marine components (Littorina and Sea sediment reference waters) were combined and referred to as marine water.

An example of a M3 validation test which is routinely made is to test how well the mixing model can predict the measured water conservative parameters Cl and $\delta^{18}O$ for Simpevarp and Forsmark sites (See Fig. 12a and b). This test can indicate the model error and the correctness of the number of end-members and the composition used. In this particular case the Cl prediction is fairly accurate but there is a systematic error in the prediction of $\delta^{18}O$. The reason is believed to be due to a too low $\delta^{18}O$ value used for the glacial end-member. The M3 program reports automatically the deviation from the measured values of Cl and $\delta^{18}O$.

6. Discussion

6.1. Comparison of sites

The M3 model can be used for explorative data analysis where large data sets are examined. Groundwater samples from different sites can be combined in the same PCA-plot for comparison and modelling as long as the sites have been affected by a similar palaeo climate and contain the same type of bedrock.

For instance, in this paper, the URL area data set may be compared with the data set obtained for the Äspö groundwaters (Fig. 13). The modelling is based on the major dissolved components, stable isotopes and ^3H values for over 1000 samples. Groundwater samples which plot close to each other have a similar groundwater composition. Waters with extreme compositional values (end-members) are plotted (e.g. marine water, precipita-

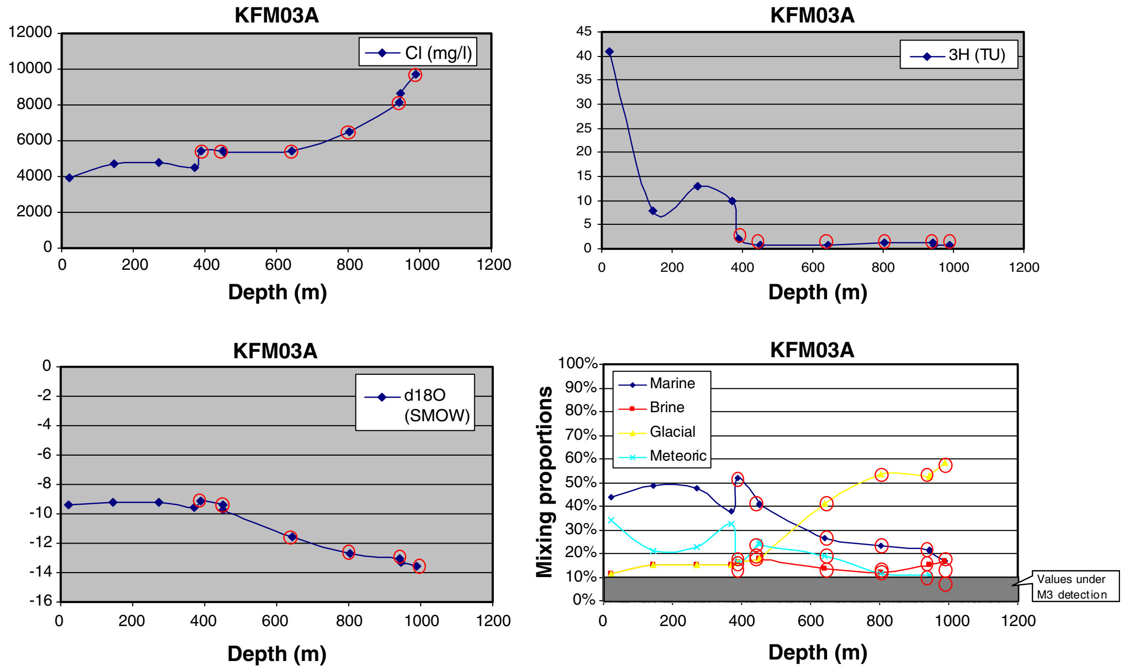

Fig. 11. Cl, ^3H and $\delta^{18}O$ content and mixing proportions with depth for borehole KFM03A. The samples with red circles indicate representative samples. A mixing proportion of less than 10% is regarded as being under the detection limit of the M3 method and is therefore shaded. The mixing proportions have an uncertainty range of ±0.1 mixing units (SKB, 2005b).

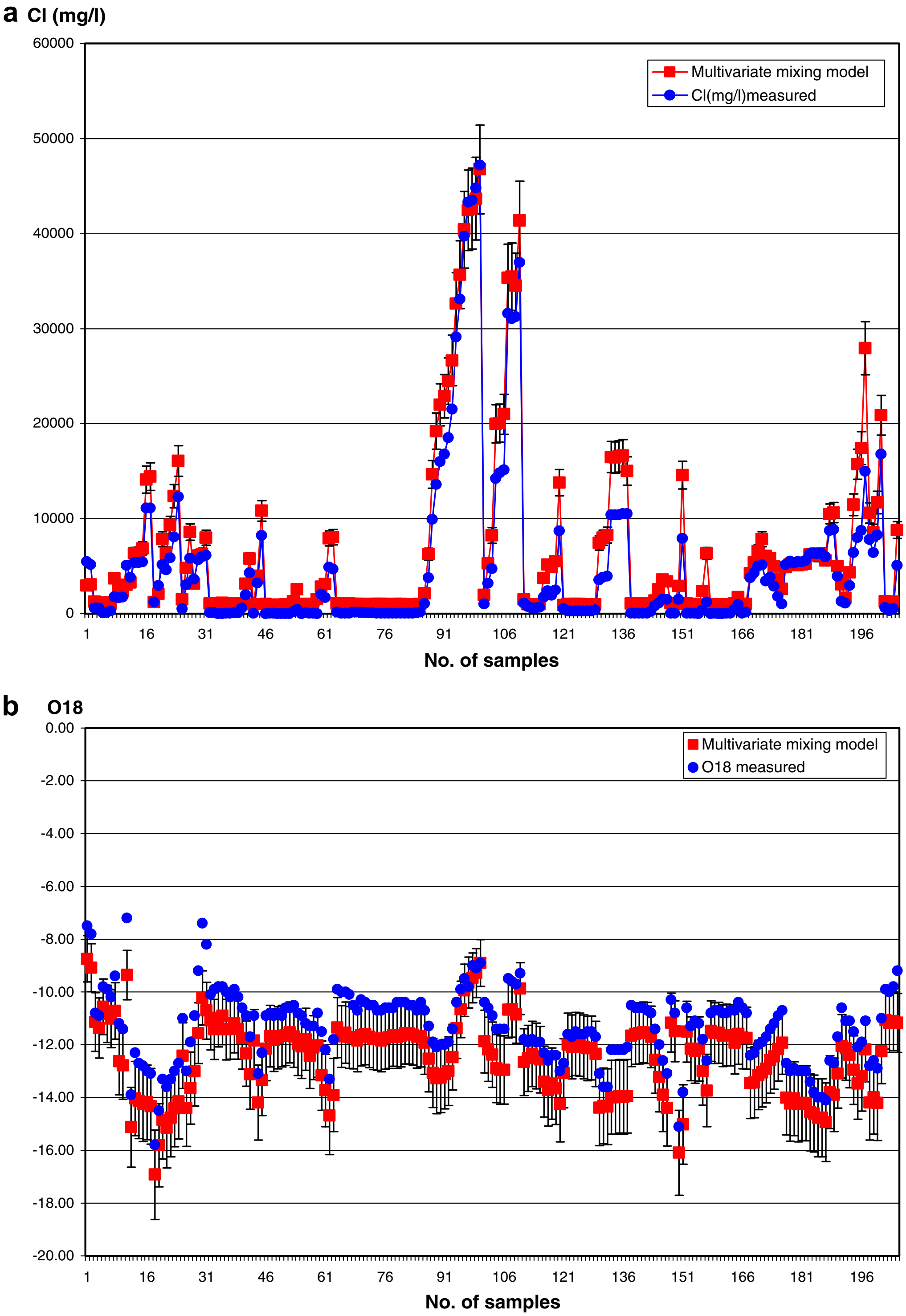

Fig. 12. Measured (a) Cl and (b) $\delta^{18}O$ (blue dots) is predicted using the M3 model (red dots) for groundwater samples from the Simpevarp and Forsmark areas. The error bar indicates the model uncertainty in M3 (±10%).

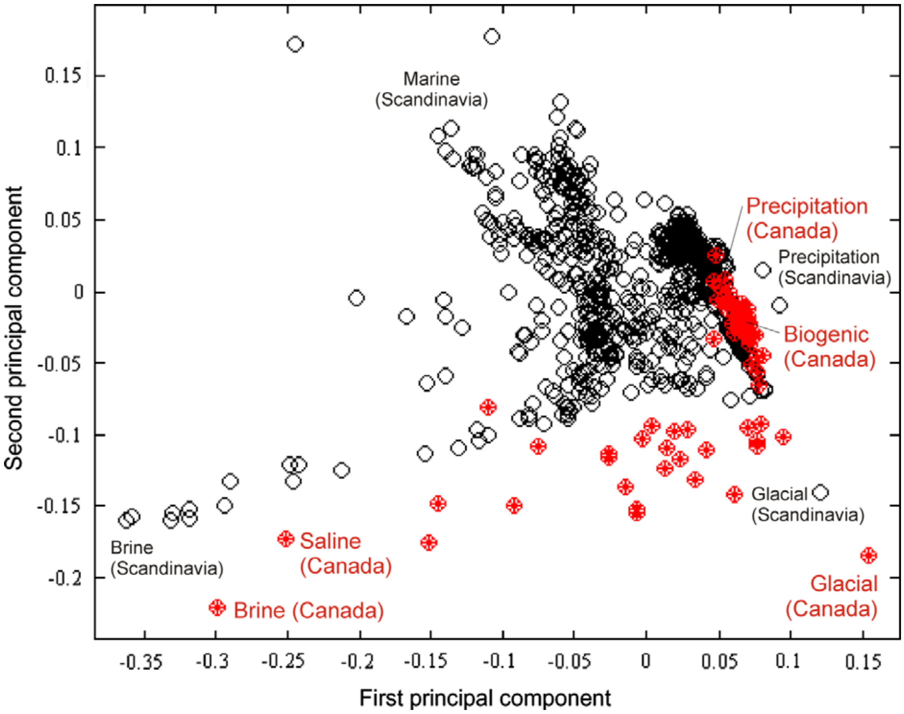

Fig. 13. Principal component analysis in M3 has been used to compare groundwater samples from Scandinavia (Sweden and Finland) with Canadian URL data. The modelling is based on the major components, stable isotopes and ^{3}H values in more than 1000 samples. Samples with a similar groundwater composition tend to form clusters in the plot. In order to help the comparison some extreme waters (end-members) such as marine water (sea water), precipitation (rain water), biogenic (water affected by e.g. organic decomposition), glacial water (cold-recharge water from the last de-glaciation) and brine water (old saline water affected by long term water–rock interactions with the rock matrix) are shown. The two principal components together account for 65% of the variability, or the information in the data set.

tion, biogenic water (water that is affected by decomposition of organics), glacial water (cold-climate recharge) and brine water. The two principal components together account for 65% of the variability of the information in the two data sets.

The results show that the URL data are similar to the shallow waters (precipitation, biogenic water) but are more affected by cold-climate recharge water (glacial water) than seen in the Scandinavian data. Furthermore, the brine waters differ from the Scandinavian brine sample (from one borehole, KLX02) and, not surprisingly, marine water has not affected the URL data set to any large extent.

6.2. Geochemical reactions

In theory, any effect of an inorganic or organic reaction can be traced using M3 modelling. In practice, selection of reference waters, validity of the ideal mixing model, model errors and the fact that the gain or loss of an element can be due to several different reactions, constrain the kind of reactions that can be traced with any accuracy. M3 modelling is always performed relative to the selected reference water and, therefore, describes only the *net* reactions which have to take place if these waters are mixed. The *total* reactions are the net reactions plus the chemical interactions which have to occur to form the reference water.

Other codes have been developed that, in part, use mixing models to supplement geochemical reactions when accounting for observed groundwater compositions. For instance, the standard code NETPATH (Plummer et al., 1991) examines all possible gas–water–rock reactions between components in the system and then, to satisfy mass- balance requirements, introduces elements or species that are not present in any of the selected phases, by mixing calculations. In the M3 approach, mixing is regarded as the dominant process by which groundwater composition is changed. In NETPATH and similar codes, reactions are generally the dominant process. NETPATH works in a numerical mode whereas M3 works in a graphical mode. Modelling with NETPATH requires hydrologic, geologic and chemical data, as well as knowledge of the system and intuition when selecting end-members, phases and constraints. Modelling with M3 requires only chemical data; knowledge and intuition are needed only when interpreting the results. Thus, modelling with M3 is simpler because less information is needed as a prerequisite and the risk of making erroneous assumptions is less.

The M3 concept should be applied to identify end-members and important mixing and mass-balance calculations at a site scale. A more detailed process of identification and hypothesis testing can be applied to a specific water volume by NETPATH modelling (as used in Pitkänen et al., 1999). Tests have shown that NETPATH and M3 models give similar results for the same data set (Banwart et al., 1996).

At Äspö, most of the groundwater chemistry is described by mixing; some redox, ion exchange and carbonate equilibrium play a role in the upper part of the bedrock. In deeper bedrock, mixing dominates because the slow kinetics of many inorganic reactions hinder water–rock interaction. Much of the groundwater compositions used in modelling the URL data in this study aimed at describing the groundwater situation as affected by the presence of the shaft and ventilation raise. This adds an important constraint to the modelling, to focus on fast reactions that occur over the short-term because the low groundwater temperatures hinder attainment of equilibrium between groundwater and fracture minerals. Stroes-Gascoyne and Gascoyne (1998) have shown that microbes mediate in many reactions occurring at the URL that would otherwise not take place. The processes that are of major influence on groundwater composition at the URL site are biological, redox reactions, calcite dissolution or precipitation, and ion exchange.

6.3. Uncertainties in M3 calculations

The following uncertainties can affect the M3 calculations:

1. Input hydrochemical data errors originating as sampling errors caused by the effects from drilling, borehole activities, extensive pumping, hydraulic short-circuiting of the borehole and uplifting of water which changes the in situ pH and Eh conditions of the sample, or as analytical errors.
2. Conceptual errors such as incorrect general assumptions, selecting the wrong type or number of end-members, and mixing samples that are not mixed.
3. Methodological errors such as oversimplification, bias or non-linearity in the model, and the systematic uncertainty which is attributable to use of the centre point to create a solution for the mixing model. A recent development of the M3 code, where the mixing proportions are calculated in the multivariate space rather than in 2D, improves the accuracy of the mixing calculations (Gómez et al., 2008).

Most of these uncertainties are common to many types of modelling. The effects of sampling errors are difficult to estimate as there is generally no in situ sample from undisturbed conditions. By labelling drilling water, the effects from drilling can be estimated. The borehole activities and short-circuiting effects of an open borehole may cause unnatural mixing of the different groundwaters. In the URL, the water flow is towards the shaft, which reduces this type of contamination. De-pressurisation of the water cause supersaturation of calcite which may change the Ca and HCO_3 content of the sample. The uncertainty due to sampling errors has been estimated/modelled to be of the order of 10% in most of the cases. Analytical errors for different elements vary but extensive comparison between different laboratories generally indicates a deviation of 1–5% in the values.

An example of conceptual error is the assumption that the groundwater composition is a good tracer for the flow system. While this is generally the case, the water composition is not necessarily a unique tracer of mixing since there is not a point source as occurs when labelled water is used in a tracer test. The accuracy is, therefore, much lower in M3 modelling than in a tracer test. On the other hand, the temporal space is much greater and so the information is of greater value. A further conceptual error is that all reference waters are mixed. While this is necessary for constructing an ideal mixing model and sample comparison, physical hindrances such as depth or geological structures may prevent mixing from occurring and so not every end-member necessarily contributes to every water sample taken. Generally, three reference waters dominate in M3 calculations and the others are close to or less than the detection limit. Uncertainty can also result from selecting the wrong number and type of end-members.

Methodological errors in M3 that cause uncertainty include the loss of information when using only the first two principal components. The third principal component generally gathers around 10% of the groundwater information compared with the first and second principal components which contain around 70% of the information. A sample could appear to be closer to a reference water in the 2D surface than in a 3D surface involving the third principal component. This can affect the accuracy of the mixing portion calculations. Uncertainty in mixing calculations is smaller near the boundary of the PCA polygon and larger near the centre. The uncertainties have been handled in M3 by calculating an uncertainty of 0.1 mixing units (with a confidence interval of 90%) and stating that a mixing portion <10% is under the detection limit of the method. The errors in the model can be tested by calculating the deviation of water conservative constituents such as Cl and $\delta^{18}O$, this is done automatically in the M3 computer program.

7. Conclusions

Limitations of existing geochemical models and the need to decode the complex hydrochemical characteristics of groundwater at a site has resulted in the development of the modelling tool, M3 (multivariate mixing and mass-balance). M3 can be used to decode measured groundwater compositions in terms of mixing proportions of end-member types and indicate the effects of water–rock interactions. The model differs from many other geochemical models, which primarily use reactions rather than mixing, to determine groundwater chemical evolution.

The M3 method has been applied to two large hydrogeochemical databases, for the URL area in Canada and the Äspö HRL, in Sweden. Decreasing amounts of precipitation and increasing proportions of saline and brine waters are seen in with increasing depth in both areas. Biogenic waters, caused by uptake of CO_2 from organics and formation of HCO_3, occur at intermediate depths in both areas but more glacial water is detected in the URL area.

The mixing proportions, sinks and sources of the elements due to chemical mass-balance reactions, and information concerning the origin and evolution of the groundwater at the Äspö and URL sites have been quantified with the aid of M3. In addition, the conceptual present/post-glacial hydrogeological model has been verified.

In summary, the major advantages of the M3 model are:

1. It is a mathematical tool that can be used to evaluate groundwater chemical data and develop an understanding of a site.
2. The tool is not dependent on thermodynamic databases, uncertain redox and pH data, and can deal with the effects of biological reactions.
3. The results of mixing calculations can be compared or integrated with hydrodynamic models.
4. Numerical results of M3 modelling can be visualised and understood by non-experts.

Acknowledgements

This study forms part of the Äspö Hard Rock Laboratory (HRL) research programme, managed and supported by Swedish Nuclear Fuel and Waste Management Company (SKB), Stockholm. Dr. Ignasi Puigdomenech and Dr. Peter Wikberg, SKB are acknowledged for all the support and constructive discussions. The review comments by Dr. Zell Peterman, USGS and Dr. Catherine Beaucaire, CEA improved the paper.

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