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Groundwater characterisation and modelling: problems, facts and possibilities

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Abstract

For the last 10 years, the Äspö Hard Rock Laboratory (HRL) in Sweden has been the main test site for the development of suitable methods for the final disposal of spent nuclear fuel. Major achievements have been made in the development of new groundwater sampling and modelling techniques.

The natural condition of the groundwater is easily disturbed by drilling and sampling. The effects from borehole activities which may bias the real character of the groundwater have been identified. The development of new sampling techniques has improved the representativeness of the groundwater samples. In addition, methods to judge the representativeness better have been developed.

For modelling of the Äspö site, standard groundwater modelling codes based on thermodynamic laws have been applied. The many limitations of existing geochemical models used at the Äspö site and the need to decode the complex groundwater information in terms of origin, mixing and reactions at site scale necessitated the development of a new modelling tool. This new modelling concept was named M3. In M3 modelling the assumption is that the groundwater chemistry is a result of mixing as well as water/rock reactions. The M3 model compares the groundwater compositions from a site. The similarities and differences of the groundwater compositions are used to quantify the contribution from mixing and reactions on the measured data. In order to construct a reliable model the major components, stable isotopes and tritium are used. Initially, the method quantifies the contribution from the flow system. Subsequently, contributions from reactions are calculated. The model differs from many other standard models which primarily use reactions rather than mixing to determine the groundwater evolution. The M3 code has been used for the following type of modelling: calculate the mixing portions at Äspö, quantify the contribution from inorganic and organic reactions such as biogenic decomposition and sulphate reduction, comparison of groundwaters at different sites in Sweden and natural analogue modelling in Africa. The groundwaters at the Äspö site have been calculated to consist of a complex mixture of meteoric water, Baltic Sea water, glacial meltwater and brine water. This reflects present and known historical groundwater flow situations which have affected the site.

The major conclusions are that the groundwaters record the present and paleo effects but this signal can be easily weakened by borehole activities such as drilling, borehole testing and sampling. The complex groundwater information has been decoded and quantified by means of new modelling techniques.

Sammanfattning

Äspö berglaboratorium utanför Oskarshamn har under de senaste tio åren utgjort det viktigaste testområdet för utvecklingen av lämpliga metoder vid slutförvar av använt kärnbränsle. I samband med grundvattenundersökningsprogrammet har viktiga framsteg gjorts gällande provtagningsmetodik och grundvattenmodellering.

Grundvattensammansättningen är känslig för all typ av störning i samband med borrning, mätning och provtagning. Möjliga störningskällor som kan maskera den verkliga grundvattenkaraktären har identifierats. Utvecklingen av ny provtagningsteknik har förbättrat provens representativitet men även metoder för att bättre kunna bedöma representativitet har utvecklats.

Vid modelleringen av Äspö grundvattendata har standard termodynamiska modeller använts. De många begränsningar som dessa modeller har och nödvändigheten av att bättre kunna avkoda de komplexa samband gällande grundvattnens ursprung, blandningsförhållanden och reaktioner på Äspö, gjorde det nödvändigt att utveckla en ny modelleringsteknik som kallas M3. Inom M3 konceptet antas grundvattnet alltid vara ett resultat av blandningar och reaktioner. Modellen summerar och jämför grundvatteninformationen genom användningen av huvudkomponenter, stabila isotoper och tritium. Likheter eller olikheter i vattensammansättningen används för att först kvantifiera tillskottet från blandning och reaktioner. Modellen skiljer sig från standard modeller som fokuserar på reaktioner mera än blandningsprocesser. M3 datorprogrammet har använts vid följande typ av modellering: beräkning av blandningsproportioner för grundvattnen i Äspö området, identifiering och kvantifiering av oorganiska och organiska reaktioner som tex. biogen nedbrytning av organiskt material och sulfat reduktion, jämförande av olika ursprung på grundvattentyper i Sverige och vid modellering av s.k. naturliga analogier i Afrika. Äspö grundvattnen har beräknats bestå av en komplicerad blandning av nederbördsvatten, havsvatten från Östersjön, glacial smältvatten och saltlake. Beräkningarna återspeglar moderna och den kända historiska grundvattenflödes situationen för området.

Huvudslutsatsen är att grundvattnen reflekterar väl effekter allt från paleo till moderna blandnings och reaktionsprocesser. Men denna signatur kan lätt störas av borrhålsaktiviteter som borrning, borrhålstester och provtagning. Med hjälp av ny modelleringsteknik har grundvattnets komplexa information avkodats och kvantifierats.

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1 Introduction to the work

The aim of this work is to describe problems, facts and possibilities associated with groundwater characterisation and modelling of deep groundwaters. The experiences were gathered during a decade of work associated with site investigation programmes for spent nuclear fuel. The work has mainly been supported and performed for the Swedish Nuclear Fuel and Waste Management Company (SKB)which is responsible for the safe handling and disposal of nuclear waste in Sweden.

Various issues are of importance for the safety of the final disposal of spent nuclear fuel with time and safety aspects up to and beyond 100,000 years. The concept used by SKB is to store the spent nuclear fuel in copper/steel canisters surrounded by bentonite clay at a depth of 500m in the granitic bedrock. In this programme the aim of the hydrogeochemical characterisation programme is to establish the composition, origin, evolution, major flow paths, dominant reactions and reactive processes in the natural groundwater. The results from the groundwater characterisation and modelling can be used in different ways: to examine whether the groundwater can be a corrosion risk for the canisters, to weaken the barriers of bentonite clay, to act as a transport medium for radionuclides if the canister is faulty, to reflect the dynamics/stability of a site and finally to judge whether the site is appropriate from a chemical point of view for final disposal.

The work described here has been performed in an international scientific environment with scientists from around the world (Sweden, Finland, France, Switzerland, USA, Canada, and Japan). Most of the work has been performed in Sweden at the SKB test site named the Äspö Hard Rock Laboratory (HRL), located on the island of Äspö on the Baltic Sea, approximately 350 km south of Stockholm in south-east Sweden (Figure 1-1). However, examples of work performed in Finland and Gabon are included.

The Äspö HRL has been excavated in order to provide opportunities for research, development and demonstration of e.g. sampling methods and modelling techniques in a realistic and undisturbed underground crystalline rock environment down to the depth planned for the future deep repository. The HRL project at Äspö was launched in 1986 with an extensive site characterisation programme from the surface and boreholes up to 1990, when excavation of the laboratory started. In 1995, the 3600m long tunnel reached its target depth of 450m below the island of Äspö. During and after the excavation, detailed investigations of the geological, hydrogeological and hydrogeochemical conditions continued to gain new knowledge of the properties that are important in the safety and performance assessment of a nuclear waste repository.

The HRL layout, orientation of the cross-sections used in this document for visualisation of the modelling results and the location of boreholes at the Äspö site are shown in Figure 1-1. The sampling locations are: Äspö, Ävrö, Laxemar, the HRL tunnel, Redox Zone, Baltic Sea and extracted pore water from sea-bed sediments. The groundwater analytical data used in this study have been extracted from SICADA, the SKB database.

The geological history of the Äspö site dates back to 1.85Ga and is dominated by granitoids belonging to the Trans-Scandinavian Igneous Belt but also includes basic xenoliths as well as lenses and dikes of fine-grained granite. Seven tectonic episodes, giving rise to fracture mineralisation and major discontinuities and fracture zones (see Figure 1-1). Sets of open fractures in the NNW-NW and N-S directions and the brittle fine-grained granite are important water conductors. Groundwater flow modelling shows that the location of Äspö island close to the Baltic Sea has a major impact on the current distribution of groundwater salinity due to varying hydraulic conditions in the late and post glacial period (Stanfors et al., 1999, Svensson 1996). Models for geology, hydrogeology and hydrochemistry were constructed based on the field data (Rhén et al., 1997) see Figure 1-2.

The Äspö site groundwater data set used in this study comprises a total of 438 groundwater samples collected from 110 boreholes. The depth stratification of the samples, at and in the near vicinity of the Äspö site, ranges from 0-1700m with the majority of the samples collected at the depth interval 0-600m. The hydrogeochemical data set contains mainly downhole groundwater samples collected from packed off fracture zones in boreholes; however, some samples from open boreholes are also included. The boreholes at the site have been sampled during different stages of the HRL tunnel construction. An overview of the groundwater sampling points prior to and after the HRL tunnel construction is shown in Figures 1-3a,b.

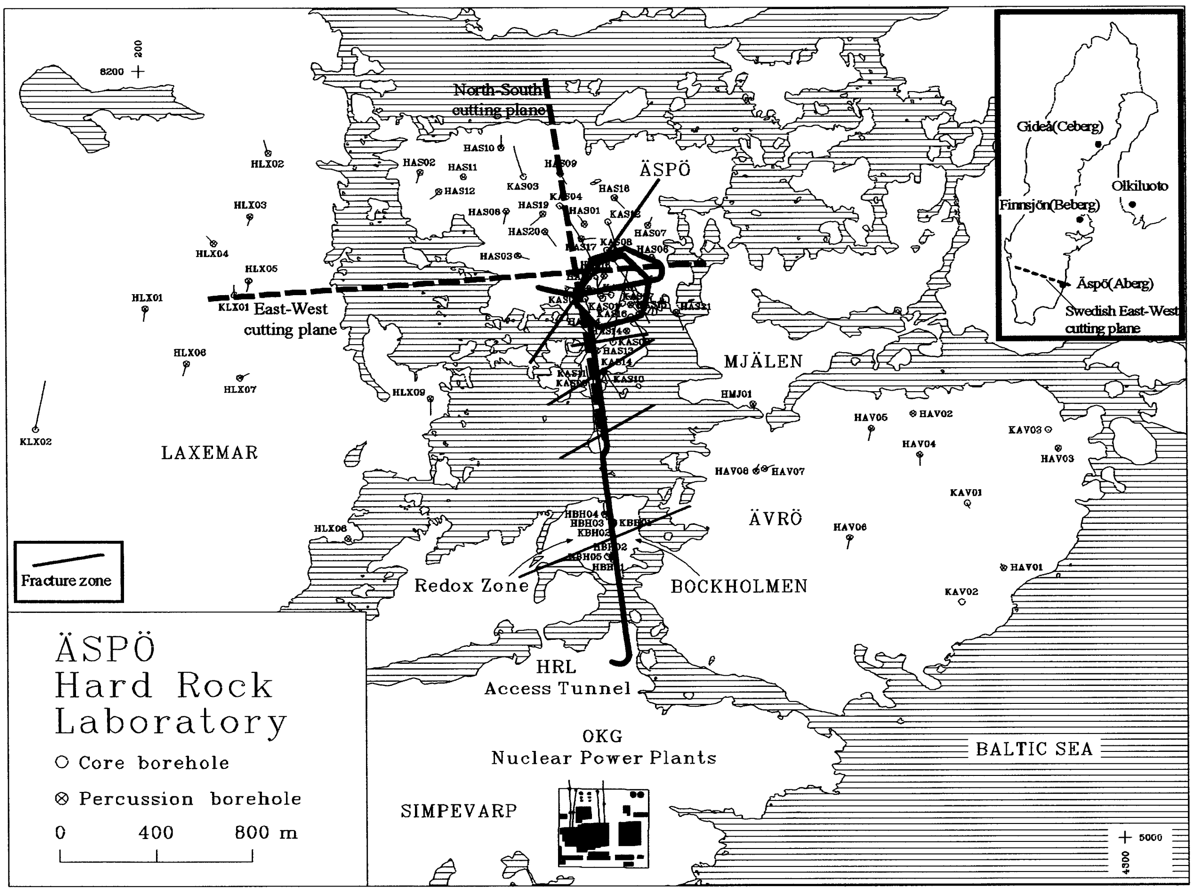


Figure 1-1. HRL layout showing orientation of the cross-sections used for the visualisation of the modelling results and boreholes at the Äspö site. The sampling locations are: Äspö, Ävrö, Laxemar, the HRL tunnel, Redox Zone, Baltic Sea and extracted pore water from sea-bed sediments. The inserted map shows the location of different sites described or referred to in this work: Äspö (Aberg), Finnsjön (Beberg), Gideå (Ceberg) and Olkiluoto in Finland.

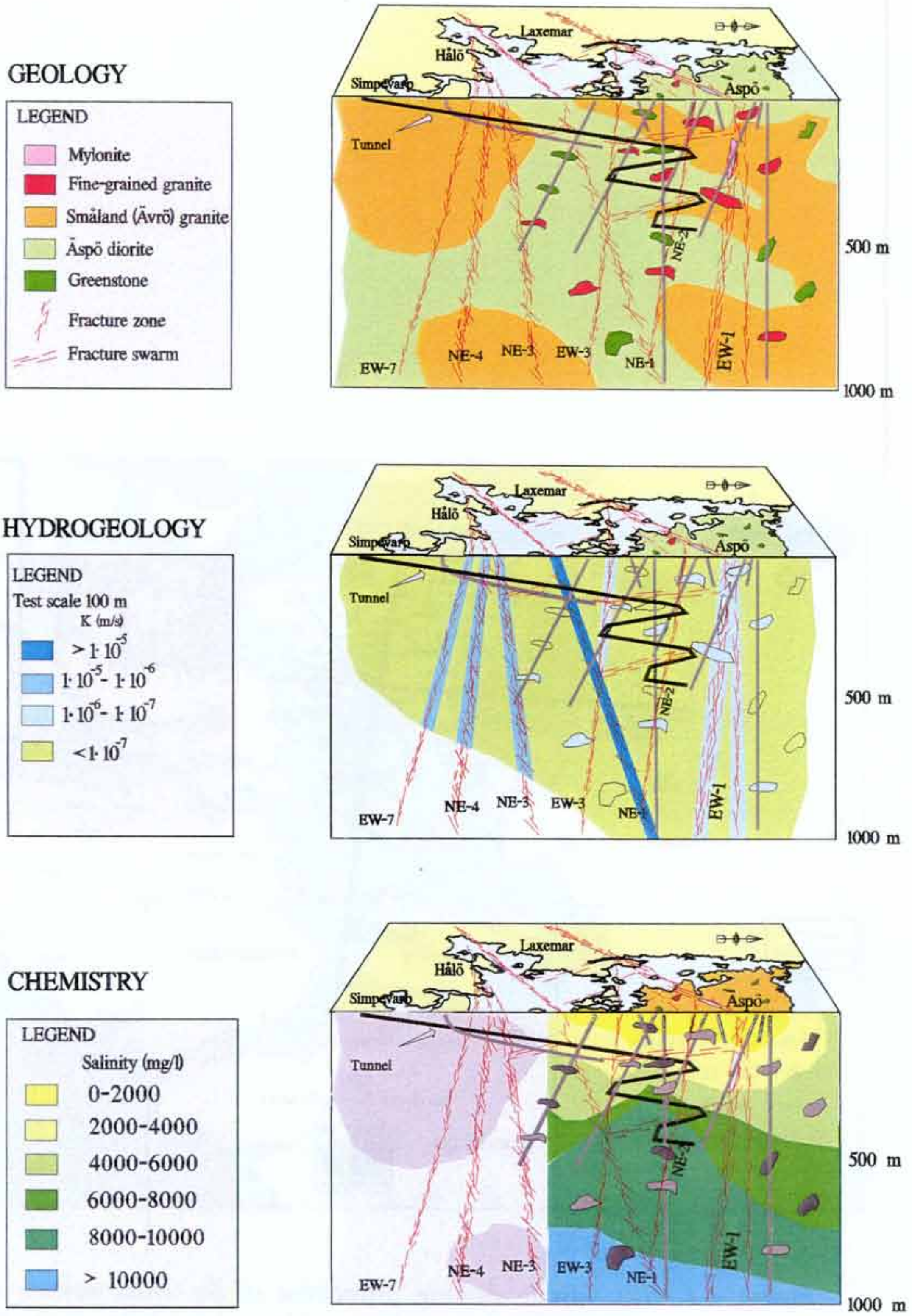


Figure 1-2. *Models for geology, hydrogeology and hydrochemistry were constructed based on the field data (Rhén et al., 1997). The orientation of the East-West cutting plane is shown in Figure 1-1.*

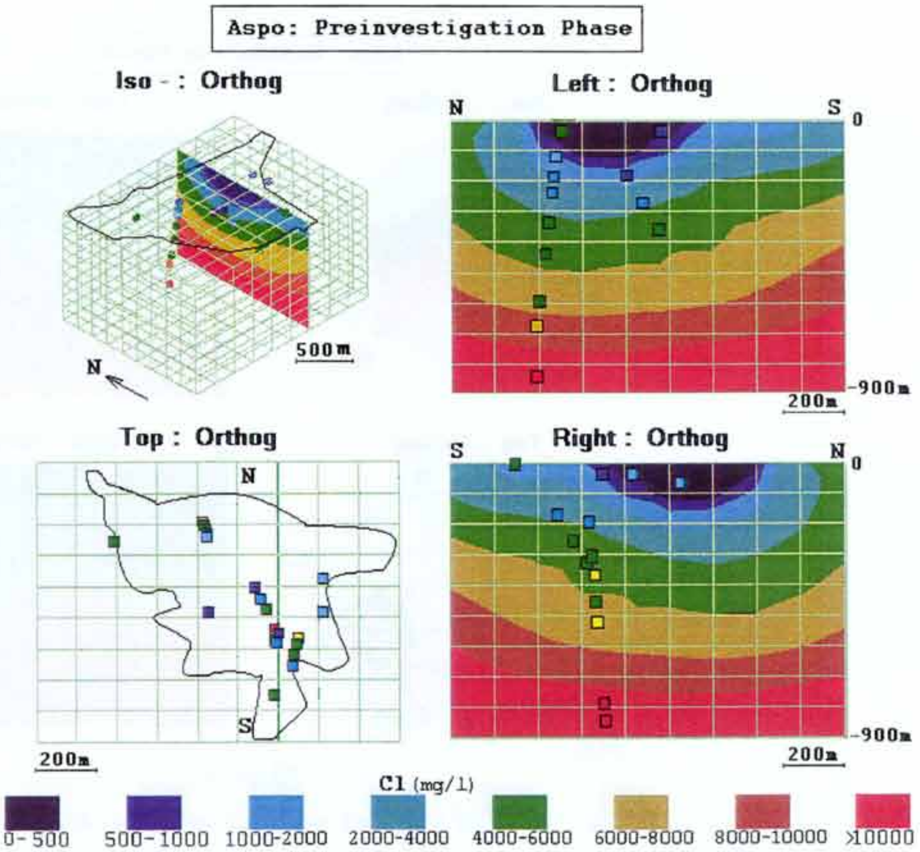


Figure 1-3a. *Location of the sampling points prior to the construction of the HRL, shown in this figure with the Cl concentration (Laaksoharju and Wallin (eds.), 1997). The orientation of the North-South cutting plane is shown in Figure 1-1.*

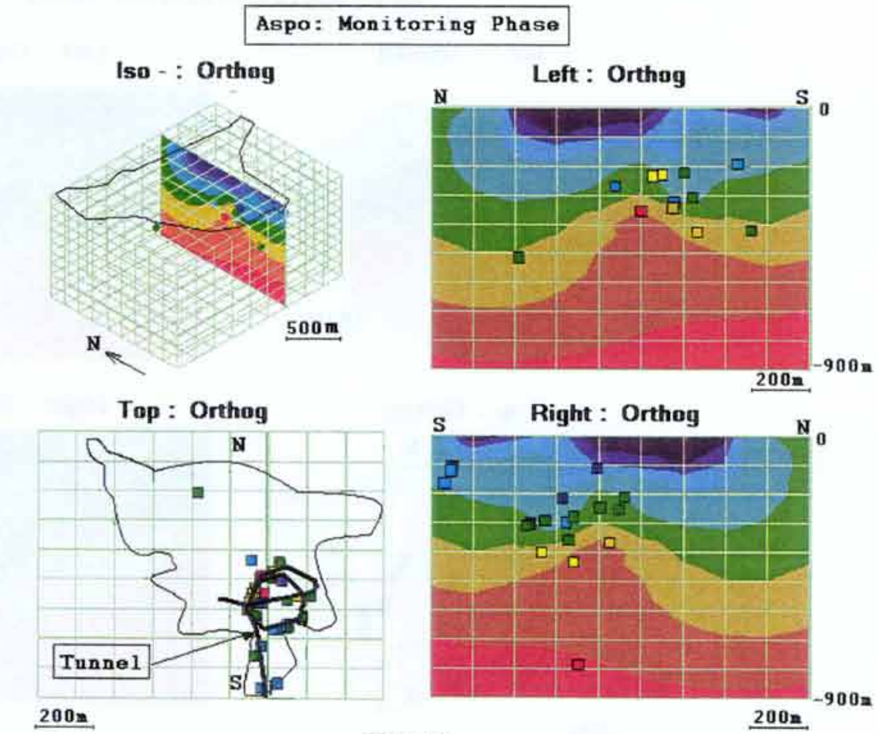


Figure 1-3b. *Location of the sampling points after the construction of the HRL, shown in this figure with the Cl concentration (Laaksoharju and Wallin (eds.), 1997). The orientation of the North-South cutting plane is shown in Figure 1-1*

The results from borehole and surface measurements have been reported in numerous reports and scientific papers, for example concerning hydrogeochemistry (Smellie and Laaksoharju, 1992; Banwart et al., 1994; Banwart (ed.), 1995; Nilsson, 1995; Laaksoharju et al., 1995a; Laaksoharju and Skårman, 1995; Smellie et al., 1995; Laaksoharju and Wallin (eds.), 1997; Rhén (ed.), 1997; Laaksoharju et al., 1999c , hydrogeology (Rhén et al., 1993; 1994; Rhén and Stanfors, 1993; Rhén (ed.), 1997 and geology (Stanfors et al., 1992; 1993 a,b; 1999; 1994; Rhén (ed.), 1997).

The first task within this work was to develop simple and suitable sampling equipment for sampling fracture water in deep boreholes. Simple equipment for open hole sampling to sophisticated state of the art downhole equipment developed by SKB for in-situ measurements of Eh and pH have been used. The sampling is difficult since a water at say 1000m depth is in equilibrium with the prevailing downhole pressure and chemical conditions. When drilling and investigating the borehole the natural conditions can be disturbed and mix the groundwater, thus changing the original composition. The often long transport time from the sampled section up to the surface and the gassing or degassing of atmospheric gases may further change the groundwater composition. The transportation of the sample to a laboratory and inaccuracy in the analytical methods may change the original water composition and hence the impression when examining the analytical data.

It can be difficult to interpret or model analytical groundwater data. This is because the data set may contain many groundwater samples with up to 30 analysed variables. The present groundwater chemical models require knowledge of chemistry, geology, fracture mineralogy and hydrogeology. The difficulty occurs when a solution is not unique, meaning that solutions other than those in the presented model can exist. Present or past reactions or transport patterns may give a similar groundwater composition to the suggested one based on water/rock interactions. The second major task within this work was therefore to develop a modelling technique which could be used to better describe the complex mixing and reaction behaviour of natural groundwaters. This document has the following structure; following the introductory chapter, a conceptual model of the groundwater evolution at Äspö is presented. Chapters 3, 4 and 5 describe field experiences and chapters 6, 7 and 8 describe modelling experiences.

2 Conceptualisation of the post-glacial groundwater evolution at the Äspö site

The complex groundwater evolution and patterns at Äspö are a result of many factors such as: a) the relative flat topography and the closeness to Baltic Sea resulting in small hydrogeological driving forces which can preserve old water types from being flushed out, b) the changes in hydrogeology related to glaciation/deglaciation, c) repeated Sea/lake water regressions/transgressions and d) organic or inorganic alteration of the groundwater caused by microbial processes or in situ water/rock interactions. The sampled groundwater reflects in various degrees 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. In order to visualise the different possible origins of groundwater and events which may have affected the present groundwater at Äspö, a groundwater conceptual model for the last 100,000 years (information compiled from Björck, 1995) was constructed (Figure 2-1):

- When the continental ice was formed >100,000BP permafrost formation could take place at a depth of 300m – 600m which concentrated the existing groundwater by freezing (Bein and Arad, 1992). The water formed had a higher density and could sink to the depth containing a water with the same salinity and density.

- When the continental ice melted and retreated, glacial meltwater was hydraulically injected under considerable head pressure into the bedrock (>13,000BP). The exact penetration depth is still unknown, but a depth exceeding several hundred metres is possible according to hydrogeological models (Svensson, 1996).

- Different non-saline and brackish lake/sea stages then covered the Äspö site (13,000BP – 4,000BP). Of these only a dense brackish sea water such as Yoldia and Litorina Sea water could penetrate by density overturn and affect the groundwater in the more conductive parts of the bedrock. 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 Litorina Sea stage (8,000 to 2,000BP) contained the most saline groundwater (twice the salinity of modern Baltic Sea water) 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.

- When Äspö island subsequently rose above sea level (starting in 4,000BP) a freshwater pillow of meteoric recharge water developed. The continuous land rise increased the hydraulic driving force so that the groundwaters in the upper part of the bedrock were flushed out gradually. On the mainland this flushing started directly after deglaciation and, since this part of the bedrock had already risen above sea level, the postglacial marine water at these locations did not affect the groundwater composition.

- When conducting drilling, pumping and measurements of boreholes and even more so when excavating the HRL at Äspö the direction of the original groundwater flow may be affected resulting in new mixtures and water compositions when sampling the groundwater. The data may become less representative for the downhole undisturbed conditions.

Many of the natural events shown in figure 2-1 are repeated during a repository lifespan of 100,000 years. The effects from the last glacial and de-glaciation event should therefore be easier to detect than from any previous glacial events which probably have been flushed out from the groundwater system.. As a result of the described 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.

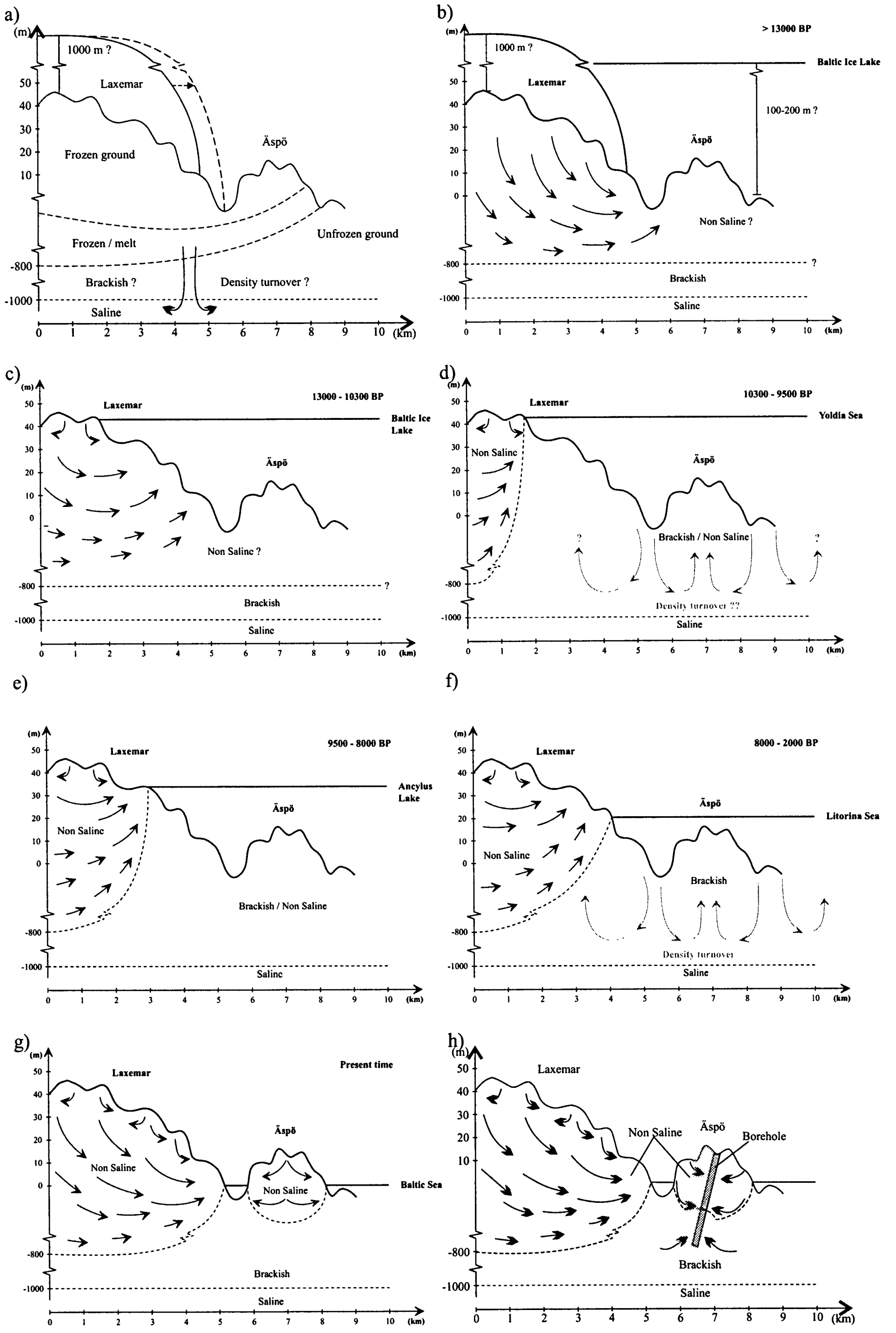


Figure 2-1. Conceptual post-glacial scenario at the Äspö site and the adjacent Laxemar mainland (after Laaksoharju et al., 1999c,). Possible flow lines, density driven turnover, non-saline (<1000 mg/l, Cl), brackish (1000-5000 mg/l, Cl) and saline (>5000 mg/l, Cl) water interfaces are shown: a) Concentration of groundwater due to freezing associated with permafrost formation, b) Injection of Glacial melt water into the basement, c) Baltic Ice Lake, d) Yoldia Sea, e) Ancylus Lake, f) Litorina Sea, and g) present-day undisturbed situation, h) present-day disturbed situation due to drilling and borehole activities. The orientation of the E-W cutting plane is shown in Figure1-1.

3 Groundwater sampling techniques

The sections below describe the type of equipment that has been developed and used within the SKB programme to extract groundwater samples from deep boreholes.

3.1 Tube sampler

The so-called *Tube sampler* is a simple yet innovative sampler equipment which has been described by Nurmi and Kukkonen (1986). This equipment has been used at the Äspö site on two sampling occasions - in 1993 (Laaksoharju et al., 1995a) and in 1997 (Laaksoharju et al., 1995b). The sampled borehole was KLX02 which was drilled in 1992 to a depth of 1705m, some 2.5km WSW of Äspö HRL on the Laxemar mainland (Figure 1-1). This borehole represents the deepest borehole drilled in the Äspö site area.

The Tube sampler consists of 50m sections of polyamide tubes (10mm outer diameter; maximum length 1700m) with a hand-operated valve and connector fastened at both ends of each tube. The first string placed in the borehole contains a check-valve; the following tube is connected to the upper part of the tube in the borehole and the hand-operated valves are opened. Several tube strings are connected until the desired measuring depth is achieved (Figure 3-1). It is important to note that only the water column in the open borehole is sampled; no pumping is involved. When the tube string is filled with borehole water the individual lengths are isolated by closing the valves and subsequently removing the sampler; water contained in the 50m tube lengths (1 litre) is collected for analysis.

The advantage of this technique is that the equipment is convenient, easy and rapid to operate even down to considerable depths. The results can be used to reflect the major chemical changes with depth in the sampled borehole. The disadvantage is that the water column collected represents open-hole conditions, i.e. the chemical distribution in the groundwater is controlled by the hydraulic properties of the borehole, which may not always conform to adjacent bedrock conditions. Furthermore, lowering the tube into the open borehole may cause perturbation and mixing of groundwater types around and inside the tube which affects the sampled groundwater.

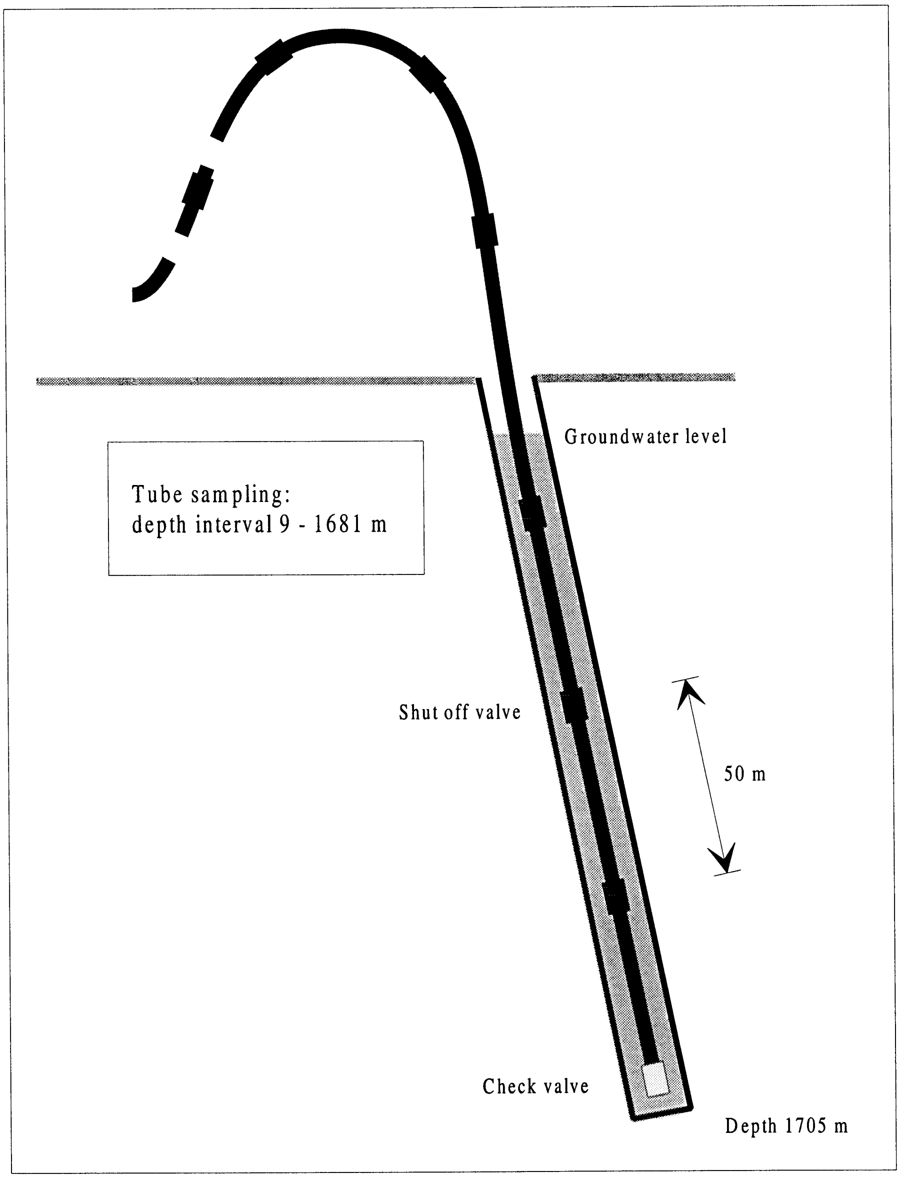


Figure 3-1: *Diagrammatic representation of the Tube sampler (from Laaksoharju et al., 1995a).*

3.2 Light pump packer sampler

The need to characterise deep and shallow bedrock hydrogeological conditions in remote terrain encouraged the development of an inexpensive, fast and easily transportable double packer sampler named *LPP sampler* (Light Pump Packer sampler) (Laaksoharju et al., 1995b,). Three main objectives were met: 1) inexpensive equipment, 2) ease of transportation and 3) combination of groundwater chemical sampling with hydraulic measurements from sealed-off borehole fractures. One of the main objectives was to keep the construction as simple as possible in order to minimise expenses for construction and maintenance. To meet these requirements any large pressure differences in the equipment when sampling had to be avoided so that commercially available parts and components could be used. Chemically inert materials were used to minimise contamination when sampling for groundwaters.

The hand held double packer equipment can be divided into four operational parts: the downhole packer unit, the connecting tubes, the pressure unit, and the control unit at the surface. A schematic description of the equipment is shown in Figure 3-2.

The inflation and deflation of the packers is controlled by a single tube, through which the water sample is also withdrawn. The uppermost part of the tube branches into two tubes; the pumping action is generated by cyclic pressure pulses applied to one of these tubes. The pumping does not create any under-pressure which hinders the risk of withdrawal of foreign water types to the sampling section. The groundwater pH and Eh properties can be measured on-line while sampling and the water recovery during pumping can be used to determine hydraulic properties of the sampled section. The equipment can be used to characterise the hydraulic properties of the bedrock. The collected data can, through comparison to K-values and chemical constituents be used to estimate transport pathways, aquifer yield, travel times, groundwater evolution etc. The range of hydraulic conductivity measured with the equipment was 10^{-10} to 10^{-7} m/s (Laaksoharju et al, 1995b).

The equipment has mainly been used in narrow 46mm diameter boreholes down to a depth of about 1000m; versions capable of operating in large diameter (110mm) boreholes and with higher pump capacity have been used for sampling at the Äspö site (Laaksoharju, 1988). At one sampling site, the chemical composition of water from an isolated fracture zone was compared with open hole water sampled with the Tube sampler at the same depth. The water from the fracture had a different chemical composition compared with the mixed water sample from the open hole (Figure 3-3).

The significant differences resulting from the two sampling methods demonstrate the importance of the packer sampling technique. Observations elsewhere earlier had pointed out the need for packer equipment in combination with optimisation of the pump rate and pumping time for representative groundwater sampling (e.g. Smellie 1983; Wikberg 1987; 1995; Laaksoharju et al. 1994; Smellie et al. 1995).

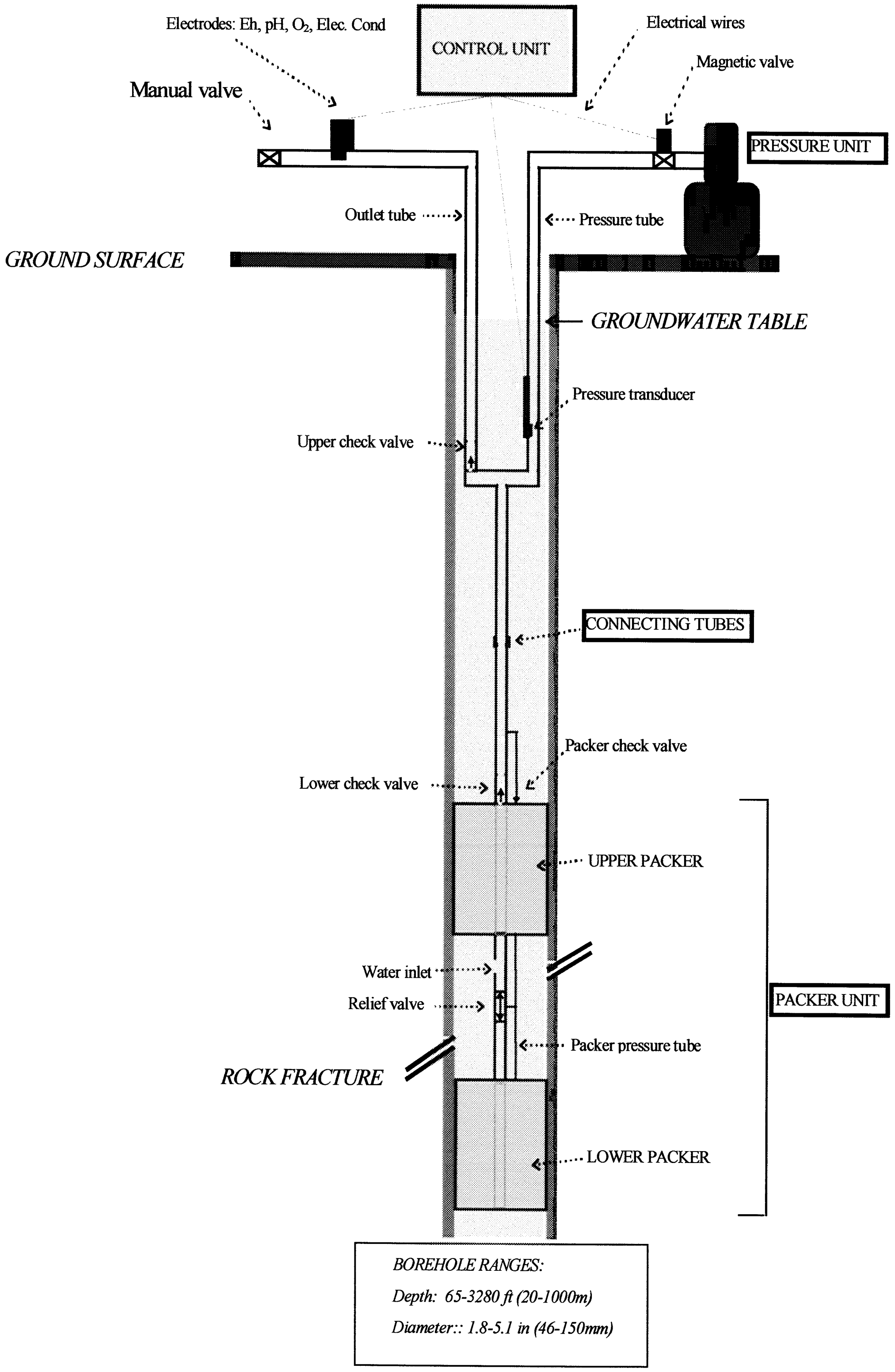


Figure 3-2: *Schematic description of the double packer pump equipment and its components (Laaksoharju et al., 1995b).*

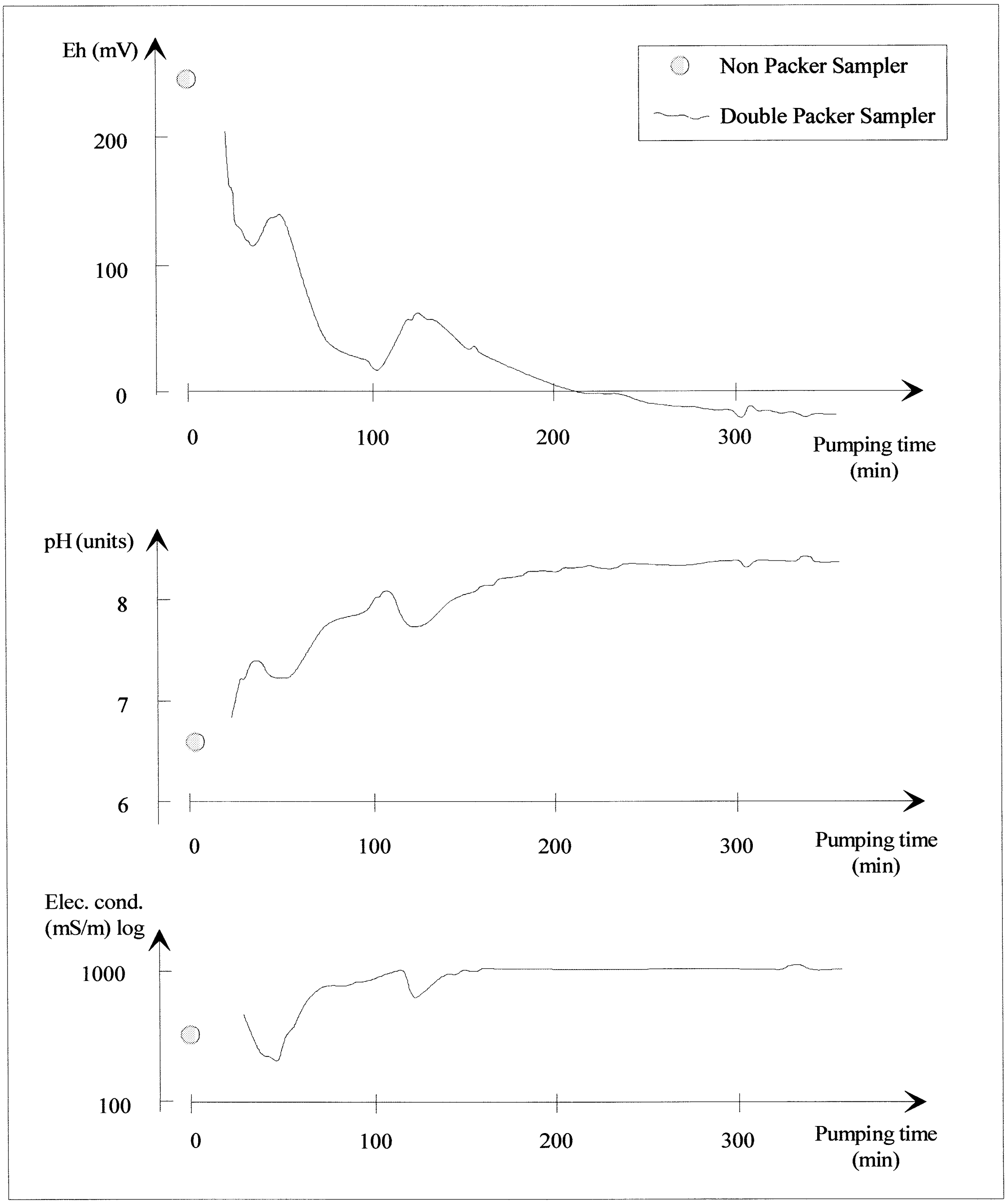
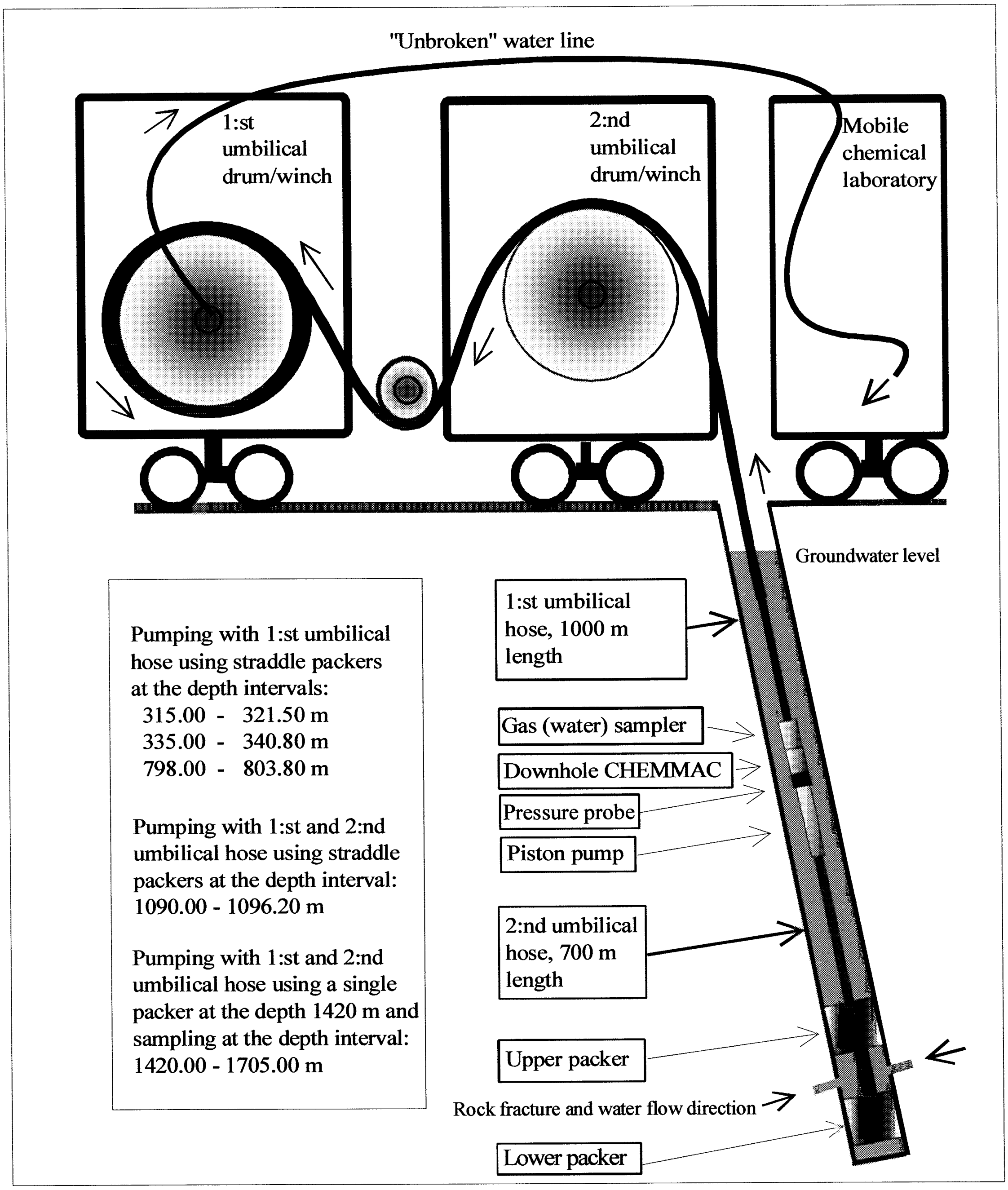


Figure 3-3: *Comparison of the results when measuring parameters with a double packer equipment (LPP sampler) which seals off the fractures versus non-packer equipment (Tube sampler) which reflects open hole conditions. Eh, pH and electrical conductivity of groundwater versus pumping time (indicated with solid curves) were sampled with the packer equipment. Filled circles give recorded values for open hole water sampled with non-packer equipment. Borehole (OKU-740) at Outokumpu, eastern Finland, was sampled at a depth interval of 435 - 460m (Laaksoharju et al., 1995b).*

3.3 SKB packer pump equipment and mobile field laboratory

The *SKB-MFL* (Mobile Field Laboratory) represents the state of the art for sampling and in-situ characterisation of deep groundwaters. The SKB-MFL unit has been used at several sites in Sweden and Finland although most of the data has been gathered at the Äspö site. The basic equipment has been described in detail by Almén et al. (1986) Axelsen et al. (1986) and Wikberg (1987). The equipment can be modified depending on the depth or type of groundwater sampling to be performed. One example of a sampling configuration is the sampler built for the 1705m deep borehole KLX02 at Laxemar shown in Figure 3-4. The SKB-MFL includes a chemical laboratory unit, hose unit, borehole equipment, packer units and the in-situ measuring system (CHEMMAC). The unique feature of CHEMMAC is to facilitate in-situ pH and Eh measurements, values which represent the major chemical parameters and which otherwise are difficult to measure with high accuracy. The Eh and pH values can be monitored both downhole and at the bedrock surface, where the water is pumped through a flow-through cell located in the mobile laboratory. Another unique feature is that many of the elements dissolved in the groundwater can be analysed in the chemical laboratory unit see Figure 3-5.



Pumping with 1:st umbilical hose using straddle packers at the depth intervals:
315.00 - 321.50 m
335.00 - 340.80 m
798.00 - 803.80 m

Pumping with 1:st and 2:nd umbilical hose using straddle packers at the depth interval:
1090.00 - 1096.20 m

Pumping with 1:st and 2:nd umbilical hose using a single packer at the depth 1420 m and sampling at the depth interval:
1420.00 - 1705.00 m

Figure 3-4: *One configuration of the SKB-MFL groundwater sampling equipment including a chemical laboratory unit, hose unit, borehole equipment, packer units and the in-situ measuring system (CHEMMAC). The downhole CHEMMAC probe houses the Eh and pH electrodes.*

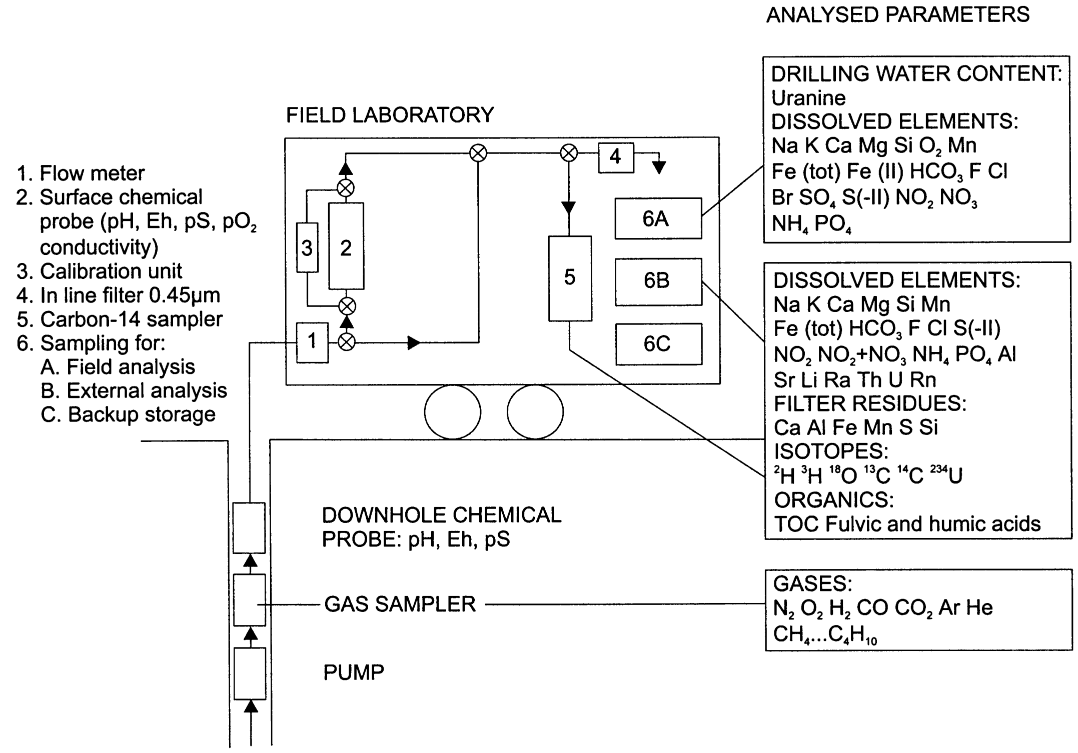


Figure 3-5: *Detailed picture of the chemical laboratory unit belonging to the SKB-MFL unit. The in-situ probes and the analysed parameters are listed (Wikberg, 1987).*

4 Borehole activities affecting the groundwater quality

This chapter describes the borehole activities necessary to extract downhole information but also how these activities can affect the aim to obtain representative groundwater samples.

4.1 Natural conditions and disturbances

The groundwaters are in natural conditions when the natural hydraulic forces determine the flow paths and the prevailing pressure. In a normal site-specific investigation programme, where boreholes are drilled from the surface to depths close to several hundred and even several thousand metres to determine the geology, hydrogeology and ultimately the groundwater chemistry, several potential sources of disturbance and contamination are encountered in the natural groundwater conditions. It is well known that small changes in pressure, temperature or flow directions can induce reactions and mixing processes which can create new water compositions which do not reflect the natural conditions. The importance of planning to avoid borehole disturbances prior to groundwater sampling cannot be overemphasised (Laaksoharju et al., 1995a). Possible borehole activities which may affect the sampled groundwater composition are shown in Figure 4-1.

Drilling, open hole effects, borehole logging and testing, and downhole changes and changes when uplifting the groundwater to the surface are the major sources of contamination and mixing which may be reflected in the groundwaters sampled for hydrochemical characterisation. These borehole events are discussed in more detail in the following chapters.

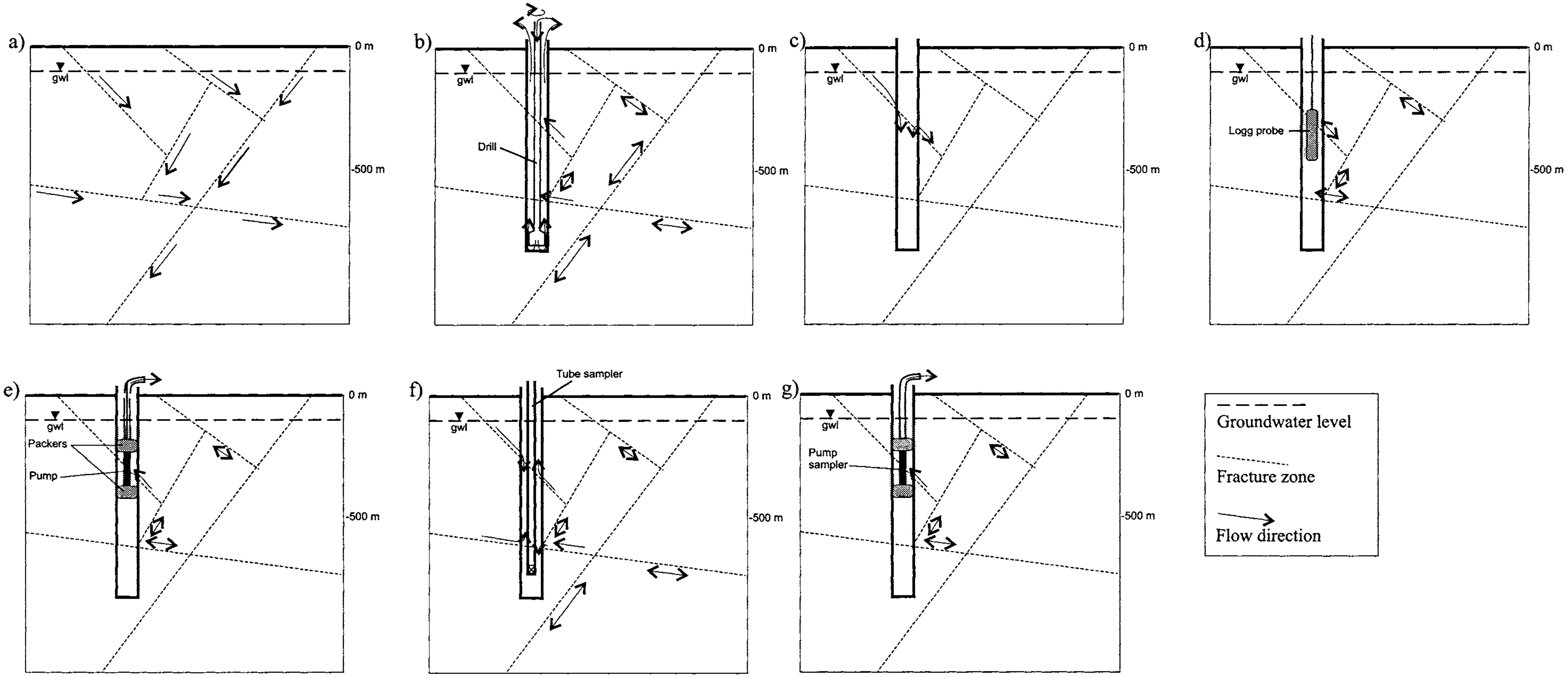


Figure 4-1: *Borehole activities affecting the groundwater composition: a) initial conditions, b) drilling, c) open hole effects, d) borehole logging, e) hydrotest, f) open hole groundwater sampling, g) groundwater sampling of fracture water.*

4.2 Drilling

The borehole activity which most affects the natural groundwater conditions and hence the quality of the groundwater is the drilling activity as described e.g. by Smellie et al., 1985; Smellie et al., 1987; Smellie and Wikberg, 1991; Graham and Johnson, 1991; Almén and Zellman, 1991; Smellie et al., 1999. In Sweden, percussion drilling techniques have been used for shallow boreholes down to 100m. In this technique the rock is crushed and water or air removes the drilling debris. At larger depth down to about 1700m, water-flush rotary-cored diamond drilling techniques are used. Here the water serves to cool the drill bit and also to remove the accumulating rock debris. Field tests showed that 5kg of rock debris was recovered from a calculated total of 1000kg for a borehole 376m long with a diameter of 56mm (Albom and Tirén., 1991). The presence of rock debris can seal fractures and very fine particles may influence subsequent colloidal studies and increase the reactive surface (Laaksoharju et al., 1995c).

The flushing water used during drilling is always tagged with a suitable tracer (e.g. uranine) which provides a sensitive indication of contamination (i.e. ~ 1% is acceptable). The aim is to limit flushing water to formation groundwaters. Generally, groundwater pumped from the upper 100-150m in a nearby borehole is used for flushing water. If this is not possible, surface waters from nearby lakes and streams are used. The selection of flushing water which is very different from the in-situ groundwater increases the risk for contamination.

During and following drilling, the boreholes are cleared from the accumulation of rock chips/flour and drilling water by gas-lift pumping techniques. This is carried out several times (normally 4) with sufficient time between each flushing pulse for the groundwater level in the borehole to recover. This action, although necessary, increases the risk for unnatural mixing.

4.3 Open-hole effects

After drilling and prior to sampling the borehole may be open for a considerable time (months to years). The borehole acts as a “super conductor” short-circuiting fracture zone which may induce mixing of groundwaters. This effect is referred to as the *open hole effect*. Under certain conditions, short-circuiting will operate for a long time affecting the natural flow and hence the groundwater chemistry (Smellie et al., 1985). Even when the groundwater level has equilibrated following borehole activities, the groundwater will continue to circulate in the borehole, flowing from zones of higher hydraulic conductivity and head to zones of lower hydraulic head.

4.4 Borehole logging and testing

To gather information from the borehole used, i.e. to guide the groundwater sampling, a testing and logging activity is started after the drilling. Unfortunately these necessary actions can disturb the groundwater chemistry.

Downhole probes (including the spinner and flowmeter probes) were used to measure physical and geophysical parameters, include calliper, temperature, electrical conductivity, single point resistance, radar, sonic, TV-imaging etc. Raising and lowering these probes causes disturbances to the open borehole system (e.g. mixing of different groundwater sources and increasing particle concentrations) which may be reflected in the sampled groundwater parameters. The most suitable methods, chosen to give the maximum resolution of borehole fractures and their hydraulic properties, whilst causing minimal perturbation to the borehole and the borehole groundwaters, include geology (drillcore lithology; fractures), calliper, radar measurements (fracture orientation), hydraulic head, spinner/flowmeter and difference flow measurements (to determine direction and amount of natural flow, Rouhiainen and Pöllänen, 1998), as well as electrical conductivity (salinity) (Smellie et al., 1999). Traditionally after drilling hydraulic pumping, injection and cross-hole tests are conducted. From a hydrochemical contamination viewpoint this should be avoided. These can be conducted after the hydrochemistry has been well characterised.

As an example, Figure 4-2 outlines the chronological sequence of borehole activities carried out in borehole KLX02 at Laxemar prior to, during and subsequent to the chemical sampling campaign performed with two different sampling methods (Tube sampler and SKB-MFL). This allows some indications of possible causes of contamination in the sampled groundwaters. Figure 4-2 shows that drilling and borehole cleaning by airlift pumping were completed by December 1992. Maintenance pumping (pump set at 100m in casing) was conducted periodically over a period of 181 days between December 1992 and June 1993 at an extraction rate of 2.95 l/sec. During July 1993 downhole activities included radar measurements and geophysical logging, both of which are known to perturb the borehole groundwater environment. These activities were immediately followed by open-hole hydrochemical sampling using the tube sampling method in August 1993, followed by downhole TV characterisation of the borehole. Complete hydrochemical sampling from isolated borehole sections was conducted using the SKB-MFL four months later in November 1993 (Laaksoharju et al., 1995a). The results from drilling and logging activities in KLX02 at Laxemar are shown in Figure 4-3.

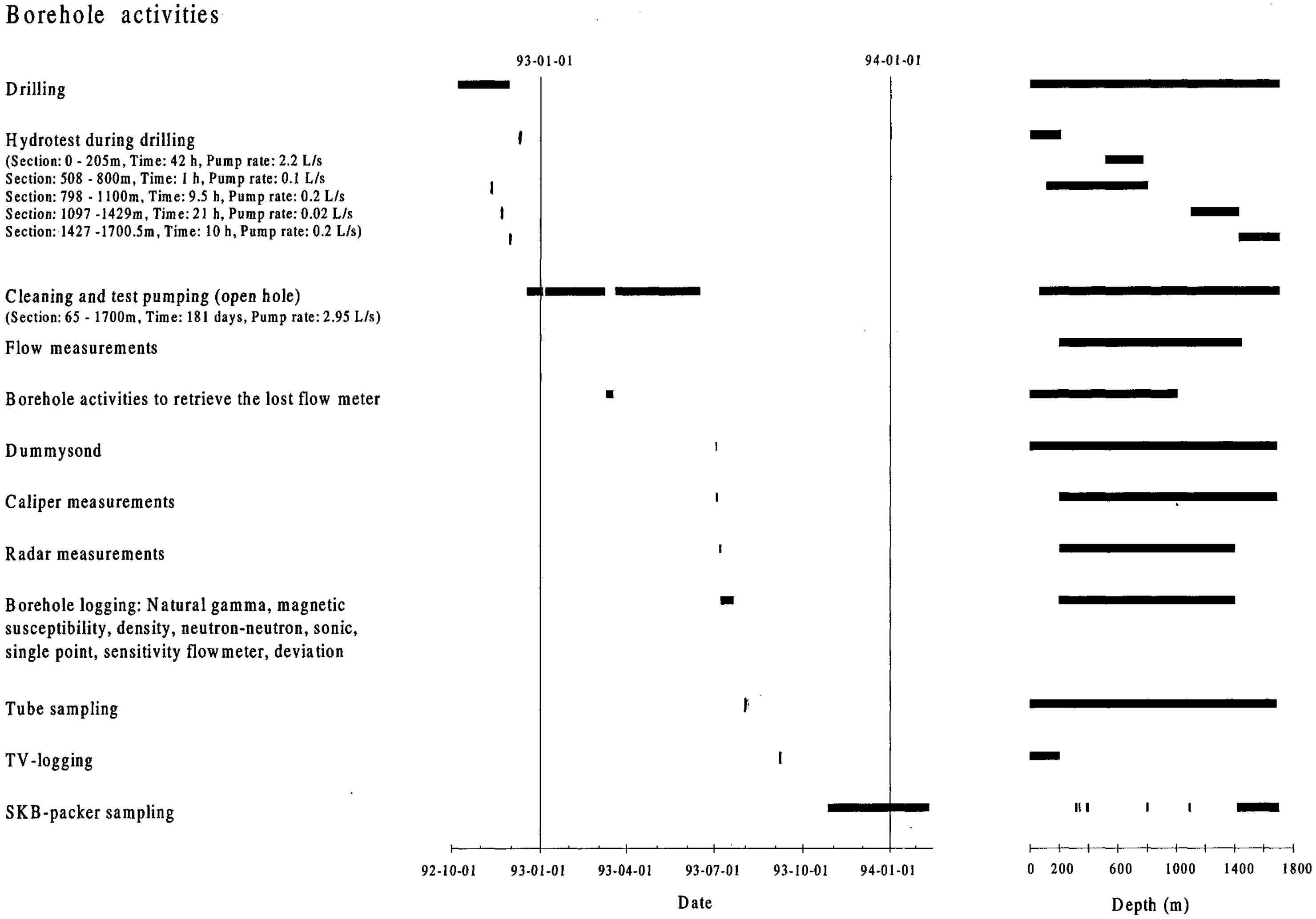


***Figure 4-2:** Chronological sequence of activities carried out in borehole KLX02.*

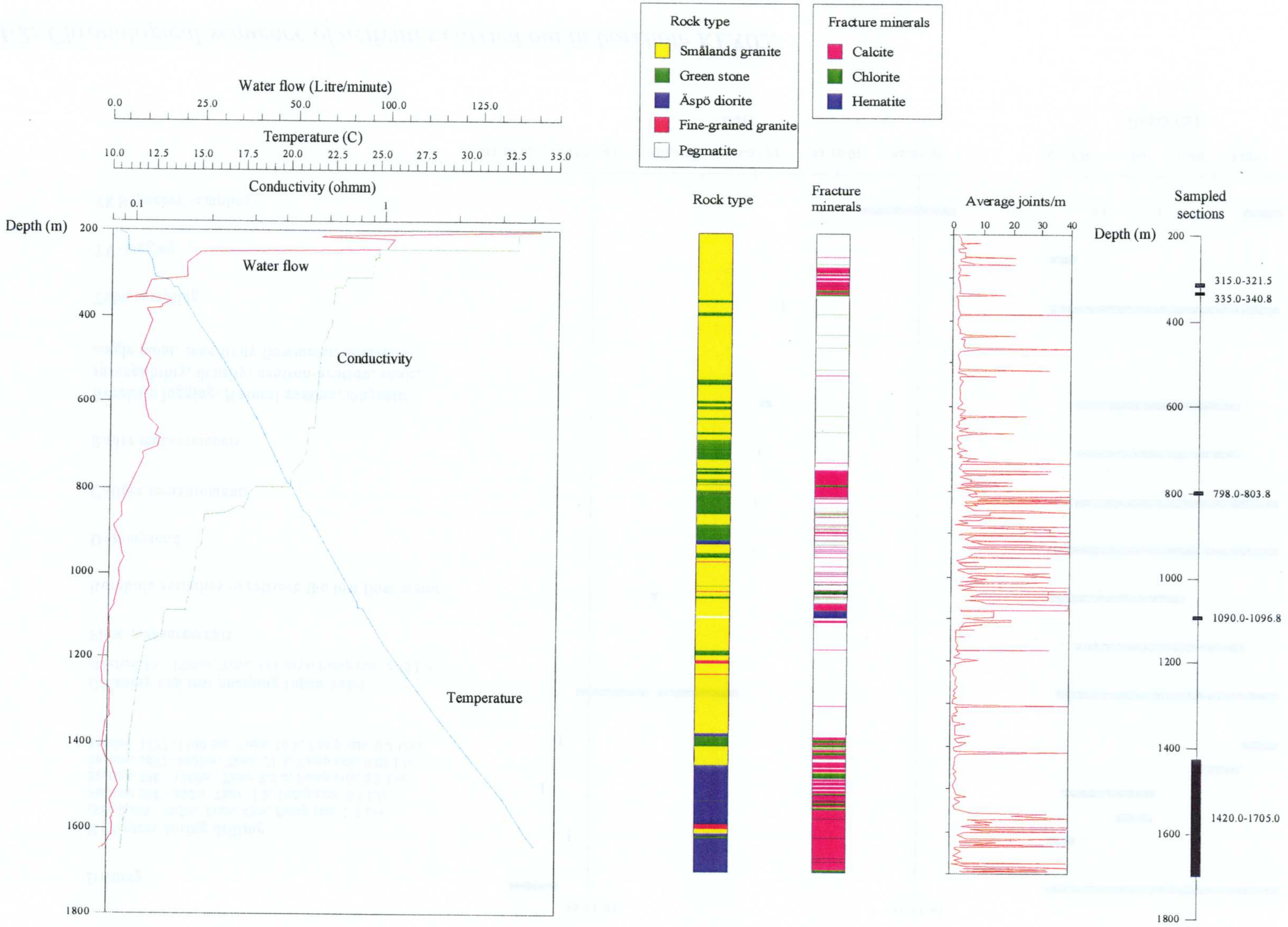


***Figure 4-3**: Example of the results from drilling and logging of borehole KLX02 prior to groundwater sampling (water flow, temperature, electrical conductivity), and core mapping (rock type, fracture minerals and average fracture frequency). Based on the above information the appropriate borehole sections were selected and packer groundwater sampling was conducted. The depth scale is common for all the plots (Laaksoharju et al., 1995a).*

Using the conservative ion chloride, Figure 4-4 compares the variations of salinity represented by Cl measurements during drilling, open hole and fracture water in borehole KLX02. A strong dilution of the borehole water had taken place during drilling which may have introduced mixing of foreign water types. In this specific case there is a close correlation of chloride variation between the open hole and fracture water, even though a greater difference is generally detected. It is anyhow obvious that higher salinity is obtained from sealed-off fractures especially at the 1100m and 1600m levels (Laaksoharju et al., 1995a). These data provide an interesting insight into sensitivity of the groundwater system where the borehole activities and type of sampling can affect the measured groundwater composition.

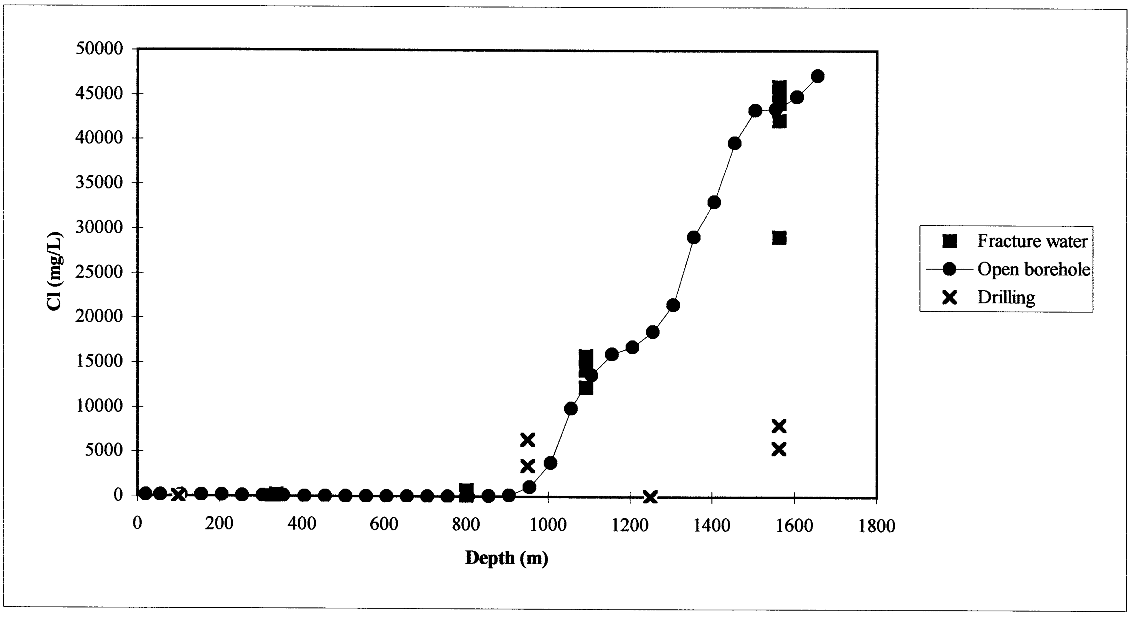


Figure 4-4: *Variations of Cl concentrations in groundwaters sampled in KLX02 during drilling, open borehole and sampled fracture water (Laaksoharju et al., 1995a).*

4.5 Downhole changes when sampling groundwaters

In order to obtain undisturbed groundwater samples from sealed-off fractures, pumping takes place for a considerable time, generally 1-4 weeks. Several thousand litres of water are removed, and the reason for this is the long time required to remove tracers from the drilling and other borehole activities and to obtain reliable in-situ Eh and pH readings. The drawback is that the samples will represent groundwater from a large rock volume. With a flow porosity in the bedrock of one promille, 1000 litres of groundwater will represent a bedrock volume of 10x10x10m. During sampling, when the water composition is unchanged the water may reflect the bedrock water alternatively a constant mixing situation where waters with different origins are mixed along flow paths.

An example of downhole changes when sampling groundwater is the sampling of borehole KLX02 at Laxemar. During the KLX02 sampling campaign the groundwater was pumped up from chosen water-conducting sections in the bedrock sealed off by packers using the SKB-MFL equipment. The hydraulic conductivity of these sections averaged between 10^{-8} ms^{-1} and 10^{-6} ms^{-1}. The hydraulically operated piston pump, which gave a maximum flow of about 250 ml/min from the isolated borehole section, has the capacity to reduce the pressure within the sampled section by more than 10 bars (100 metre water column). At Laxemar 1 bar of under-pressure was generally used to avoid the risk of withdrawing water from sections other than those sampled. For practical reasons a minimum flow rate of 5 ml/min is needed for sample collection.

The Eh, pH and temperature values were monitored both in-situ and at the bedrock surface where the water was pumped through the flow-through cell located at the surface. In addition, electrical conductivity and dissolved oxygen was measured in the flow-through cell at the surface (for equipment configuration see Figures 3-4 and 3-5). Measurements of the on-line and in-situ temperature, pH, electrical conductivity and Eh are presented as plotted curves for two sampled borehole sections (KLX02:798-804m and 1420-1705m) in Figures 4-5 and 4-6. Important borehole activities and technical problems which have affected the sensitive measurements of Eh and pH are also shown. At section 798-804m (Figure 4-5) the electrical conductivity values are still changing and this section should have been sampled for a longer period of time. Technical packer problems are relatively common resulting in maintenance uplifting of the equipment and perturbation of the groundwater. Possible leakage around the packers may have caused unrepresentative sampling. The sensitivity to disturbance illustrates the problems encountered when sampling deep groundwaters.

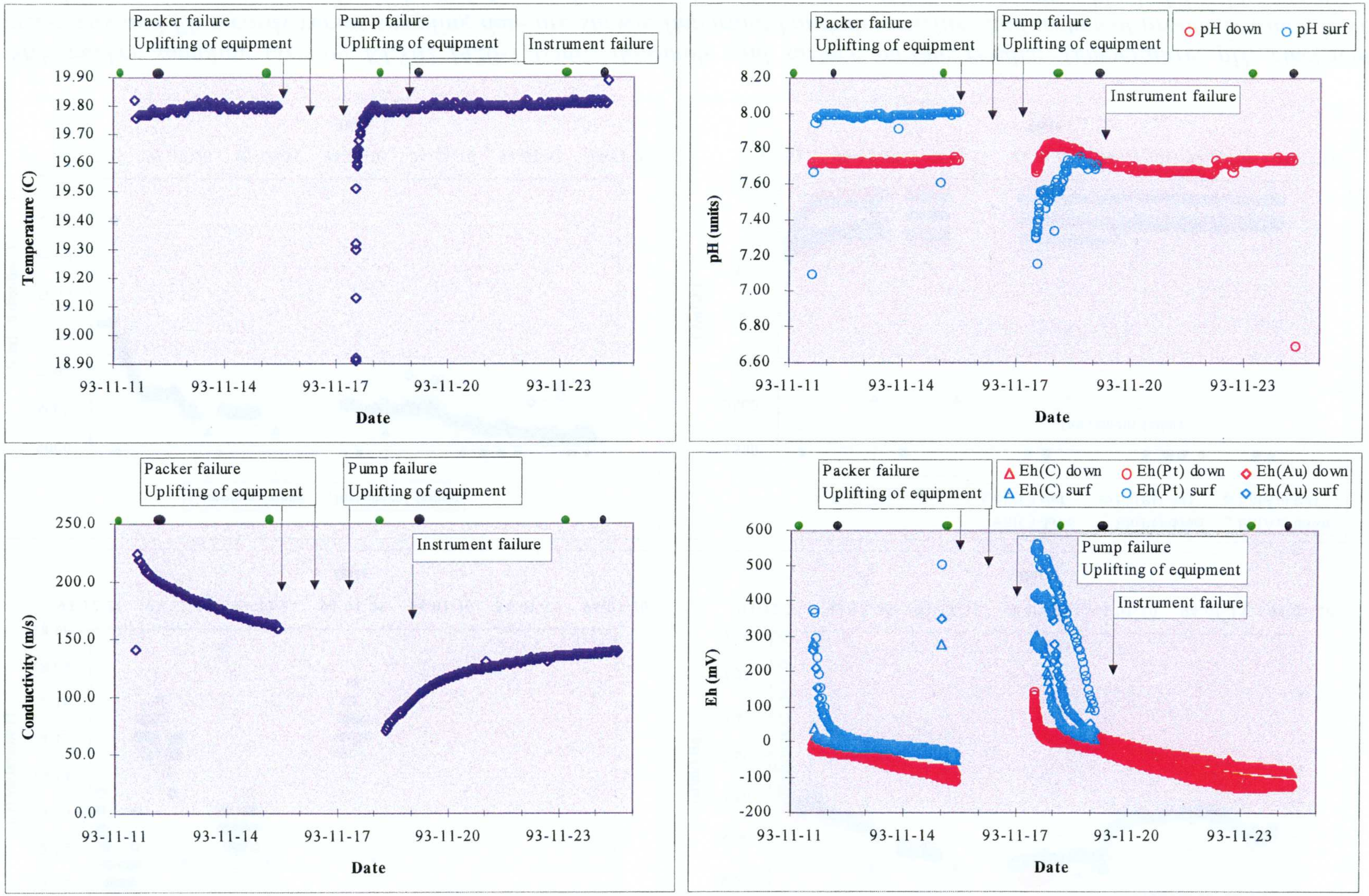


Figure 4-5: *SKB packer sampling (section KLX02:798-804m); downhole and surface on-line results: Temperature, pH, electrical conductivity and Eh records versus sampling date are shown. Important borehole activities and technical problems which have affected the measurements are also indicated. Green dot = complete chemical sampling programme; black dot = less extensive chemical sampling programme.*

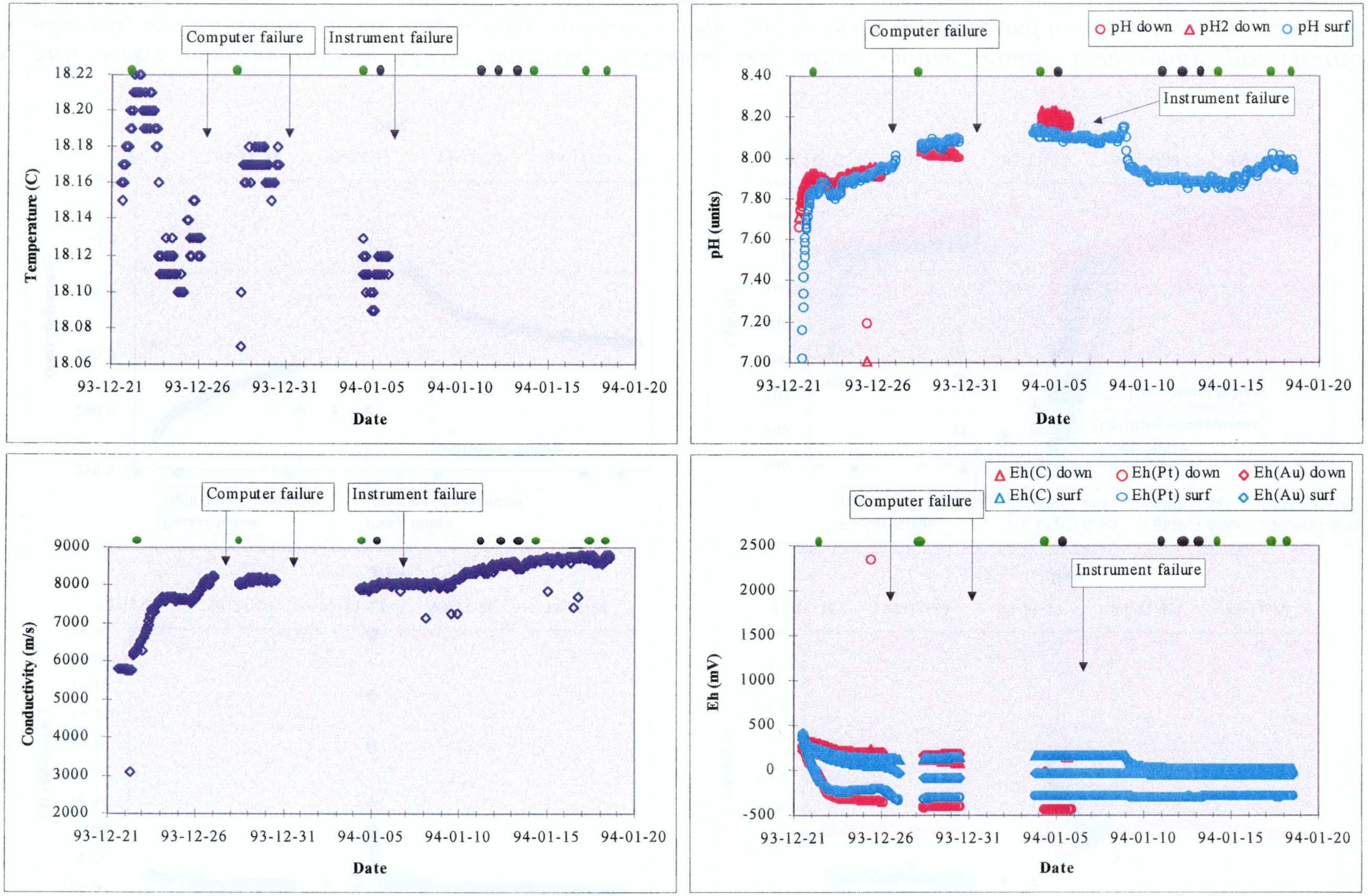


Figure 4-6: *SKB packer sampling (section KLX02:1420-1705m); downhole and surface on-line results: Temperature, pH, electrical conductivity and Eh records versus sampling date are shown. Important borehole activities and technical problems which have affected the measurements are also indicated. Green dot = complete chemical sampling programme; black dot = less extensive chemical sampling programme.*

The on-line surface Eh values are generally 100mV higher and the pH values one unit higher or lower (because of in-gassing or out-gassing of atmospheric gases such as CO_2). Pumping was continued until the “dead” water volume between the packer and tubes was removed and a stable groundwater composition was achieved, on average after at least two days. Stable conditions are often determined by unchanging electrical conductivity of the groundwater. When stability is achieved, it is often the continuous change in composition of the main constituents that determines the length of the ensuing sampling and pumping period. Depending on earlier drilling activities and borehole hydraulics, chemical stability of the groundwaters being monitored may be achieved after a few hours, but equally it may take days or even weeks. This stage of the programme is critical in order to ensure representative sampling. In general the 1-4 weeks allocated to each section proved to be adequate in most cases (Laaksoharju et al. 1995a). Unstable constituents such as bicarbonate iron (II) and sulphide concentrations were measured before reactions with the atmosphere which can change the composition. Other constituents were sent for analysis at external laboratories.

When sampling groundwaters in addition to induced mixing there is a risk of contamination from foreign materials such as metal and plastics used in the borehole equipment. The low trace element concentrations in the groundwater are sensitive to this kind of contamination. Erroneous results for e.g. aluminium, copper, zinc, chrome, zirconium and molybdenum have been detected within the SKB programme (Peter Wikberg, 1999 pers. comm.). These elements are therefore not used in the geochemical modelling resulting in the absence of saturation index calculations for aluminium silicates. Enhanced TOC contents may also occur from excessive water/PVC tube contact (Andrews et al., 1988; Holm et al., 1988; Lampén and Snellman, 1993), and bacterial activity (particularly iron oxidation) may be encouraged.

4.6 Downhole changes when sampling colloids

Colloids are small particles in the size range 10^{-3} to 10^{-6} mm (Freeze and Cherry, 1979). These colloidal particles are of interest for the safety of spent nuclear fuel because of their potential for transporting radionuclides from a faulty repository canister to the biosphere. One important limiting factor for the transport is their concentration, generally at ppb level. It is therefore of paramount importance to make representative sampling since minor disturbances in the chemistry can create colloids and may lead to overestimating their transport capacity (Laaksoharju et al., 1995c).

Wikberg (1987) demonstrated how borehole activities can affect the colloid concentration. Native groundwater was pumped from a depth of 468m to the surface where it was oxidised, tagged with uranine and re-injected. Groundwater sampling was then conducted using a constant pump rate. The amount of tagged groundwater decreased rapidly in the studied section from 4% down to 0.2% within a few days. However, the measured Eh in the section rapidly levelled out at a value of -250mV, indicating reducing conditions. The intrusion of oxygen had a dramatic effect on the concentration of colloids in the groundwater. Si and the Fe increased more than 6 times during the first day and then decreased to "initial" values after an additional two days.

The sulphur content increased more than 20 times and was still 7 times higher than the initial value after four days. Al was constant and unaffected by the experiment.

Another example of how the downhole changes affect the measurements was demonstrated when sampling colloids in Olkiluoto, Finland (for location see inserted map in Figure 1-1) (Laaksoharju et al., 1994). The most important sequences in colloid sampling is to avoid withdrawal of groundwater from other borehole sections or fractures with different groundwater compositions. Figure 4-7 illustrates the structural complexity around the borehole. Several intersecting fracture planes are present which enhance the possibility of groundwater mixing from different sources.

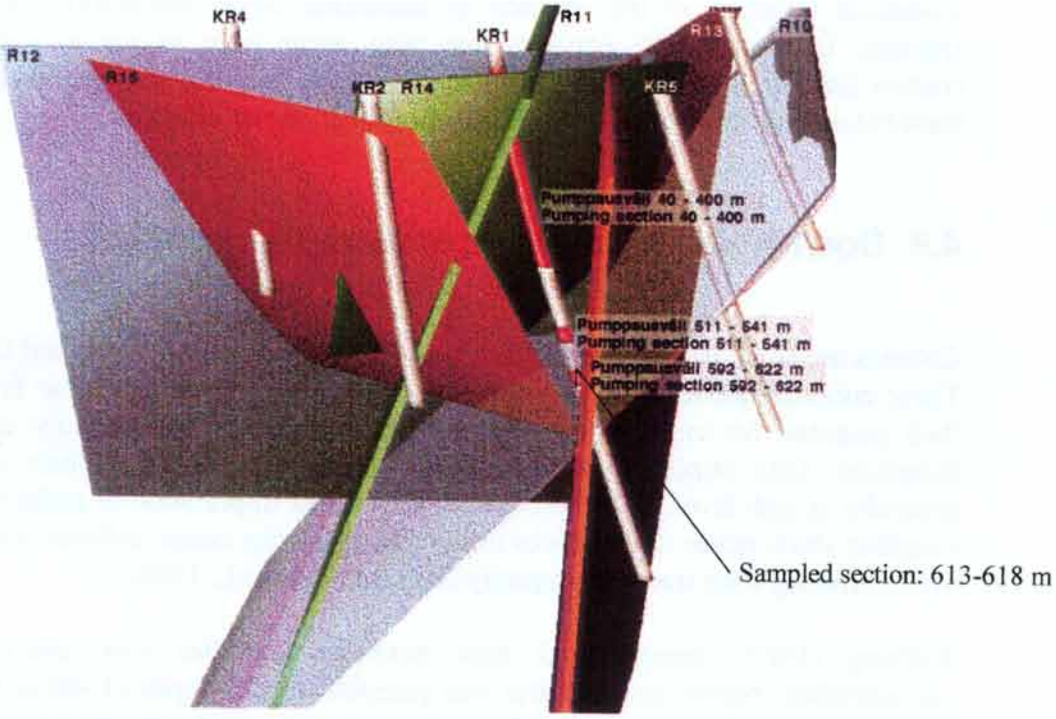


Figure 4-7: *The many intersecting fractures and fracture systems may result in complex mixing of the sampled groundwater in the Olkiluoto borehole OL-KR1(Laaksoharju et al., 1994).*

Different pump rates were used to test the effect on the colloid concentration and water composition due to groundwater mixing and erosion in the sampling section. The test was conducted in section 591-621m in borehole OL-KR1. The pump rate was fixed at three levels; 0.5 l/min for 9 days, 1.5 l/min. for 12 days and 3.3 l/min. for 9 days. The colloid filtering was performed at the beginning (when the dead water volume of the tube was removed) and at the end of all the different rates of pumping (totally 6 samples). The results of the Al and Si values on the 400nm filter during the test are shown in Figure 4-8a. The change in the Cl- content of the groundwater during the same period is shown in Figure 4-8b.

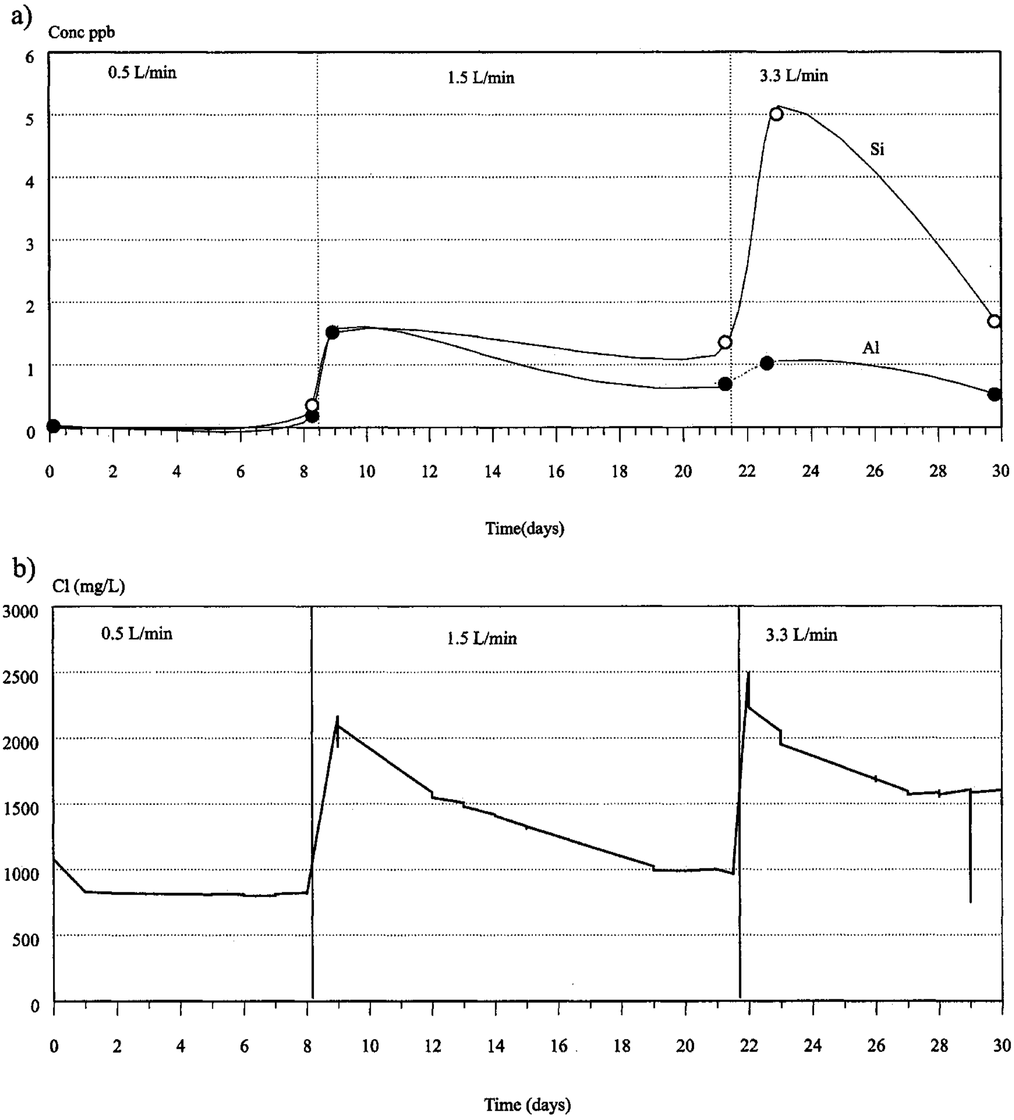


Figure 4-8: *a) Al and Si content measured on the 400nm filters; pump rate changes are indicated for the respective period. b) The Cl content change of the groundwater is calculated from on-line continuous measurements of the electrical conductivity; pump rate changes are indicated for the respective period (Laaksoharju et al., 1994).*

The Al and Si contents (from clay and silica particles i.e. drilling debris) increased, especially at the beginning of each pumping period. The largest Si content corresponded to the highest pump rate, while Al was greatest at the beginning of the second period. The other measured elements (S, Ca and Mn) were not affected by changes in the pump rate. The Fe content increased towards the end of the second period, which may indicate an inflow of shallow groundwater due to a proven hydraulic connection to a higher level in a nearby borehole. The complex mixing situation is indicated by a sudden increase of the Cl- content in the beginning of each period followed by a decrease. Interestingly, a strong pulse of diluted groundwater was detected on day 29 (Figure 4-8b). This pulse was monitored with extra care using repeated off-line measurements to rule out possible instrument errors.

The test indicates the importance of knowing the hydraulic properties in the borehole. A general recommendation in this particular case was to use < 15% of the maximum pump capacity in order to try to minimise contamination from drilling debris, erosion and foreign water types. Fast and accurate sampling was performed at low flow in combination with a relatively long pumping period (weeks). However, this caused increased uplift time of the groundwater to the surface and caused increased risk of precipitation/dissolution reactions in combination with air contamination prior to analysis (Laaksoharju et al., 1994) as described in detail in the next chapter.

4.7 Changes when uplifting the groundwater

Another common contamination is air contamination when pumping the groundwater to the surface for sampling and analysis. The redox sensitive elements as well as the carbonate system are affected. The reactions taking place in the groundwater sample change the original groundwater element concentration. The most efficient method of measurement is to make on-line measurements. If on-line measurements are not possible to perform it is critical that the time be short between sampling and analysis. Short term effects from air contamination affects iron (FeII), manganese and sulphide concentrations. These elements, together with uranium, are the most important redox indicators in the groundwater which can be used to calculate an operational Eh in case of missing or unreliable Eh values (Grenthe et al., 1992). Together with Eh the pH is the most important indicator of the state of the groundwater. The values are affected by the elements dissolved in the groundwater as well as by the pressure and the amount of dissolved gases. The chemical equilibrium state of the groundwater is different 1000m down in the bedrock than when the groundwater is on the surface. It is therefore of paramount importance to measure pH and Eh in-situ (Wikberg, 1987). As mentioned the differences between the downhole and surface Eh values can vary by 100mV and the pH values by 1 pH unit. Similar pH discrepancies were noted within the Canadian programme by Gascoyne et al. (1988). How a delay between sampling and chemical analysis can affect the pH measurements was tested at Äspö HRL. The pH of the sample SA0813A was measured during a period of 5 hours. The initial value was 7.1 and after one hour the pH value had decreased by 0.8 units to 6.3 due to the in-gassing of CO_2.

A geochemical modelling exercise was performed (Laaksoharju et al., 1994) to demonstrate the changes from in-situ conditions of groundwater to conditions where the groundwater is uplifted. The computer code PHREEQE (Parkhurst et al. 1980) using the CHEMVAL2 database was used to simulate the different chemical systems obtained during in-situ, at-line, on-site and off-site conditions during groundwater and colloid sampling. The indicated changes of iron hydroxide- and calcite-saturation indexes as well as the partial pressure of carbon dioxide are modelled in Figure 4-9.

In the sampling procedure the chemical master variables Eh and pH change and hence affect the overall chemical system causing precipitation (positive saturation indexes) or dissolution (negative saturation indexes) for different phases. The calculations indicate a risk of calcite precipitation as well as iron precipitation in ordinary and inert filtration of colloids. In ultra-filtration the risk is lower. The calculations are in good agreement with the observed results from that sampling (Laaksoharju et al., 1995c). The risk of calcite precipitation in the inert- and ultrafiltration methods could be minimised if a mixture of CO_2 and N_2 is used to simulate the prevailing in-situ partial pressure of carbon dioxide. The calculations demonstrate once again the difficulties in groundwater sampling since small changes in the chemical system strongly affect the groundwater composition.

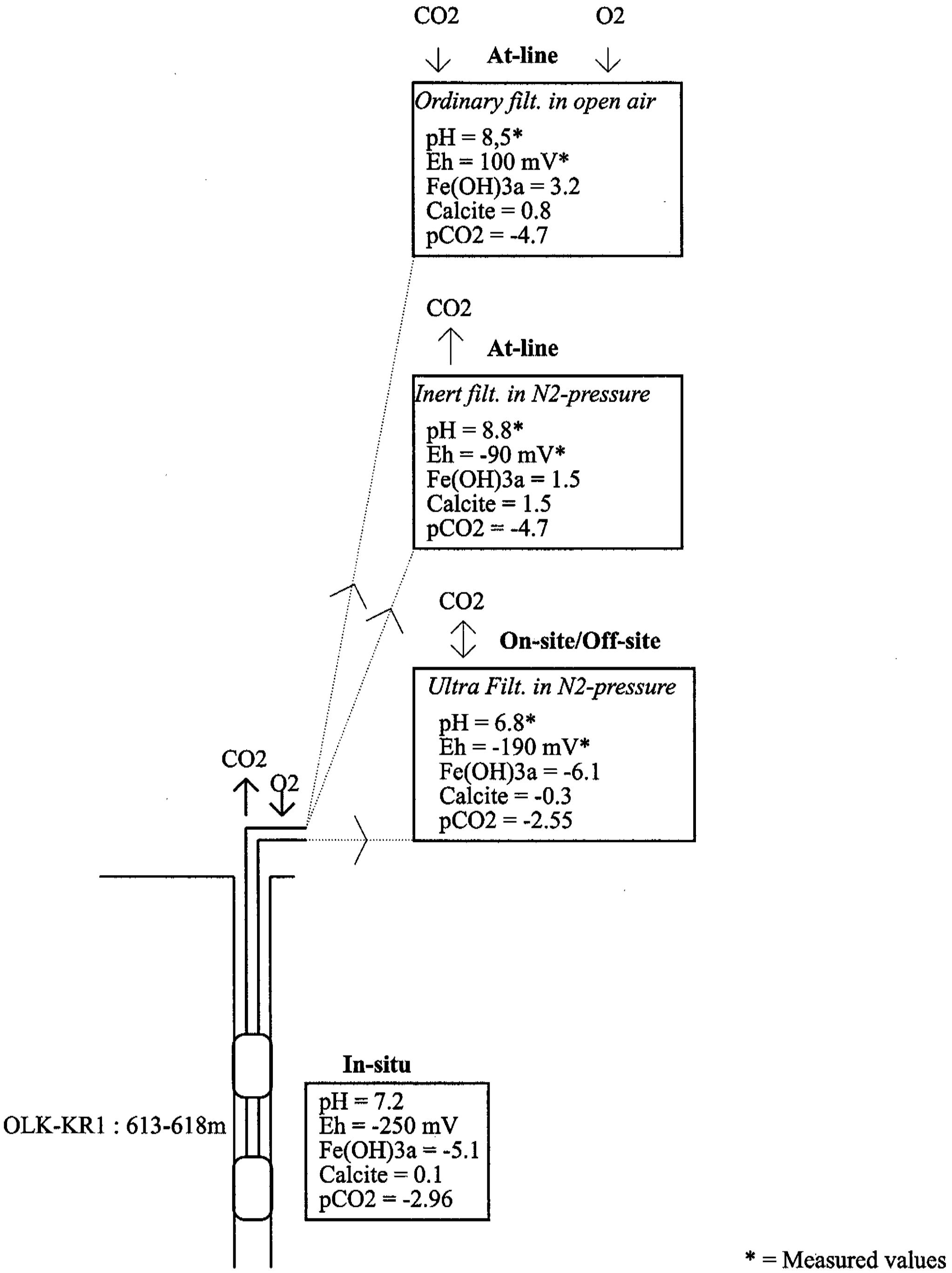


Figure 4-9: *Modelling simulations (PHREEQE) of the different chemical systems obtained when pumping the groundwater up to the surface; in-situ, at-line, on-site and off-site conditions for the water samples. The chemical system is constantly changing, depending on de-compression, loss or uptake of carbon dioxide and oxygen contamination. The assumed in-situ conditions are; Eh = -200mV and saturation index for calcite = 0. The measured on-line conditions (flow trough cell) are; Eh = -90...-65mV and pH = 8.4...8.6. Positive values for the saturation indexes (SI) indicate risk for precipitation, negative values indicate possible dissolution. Fe(OH)₃a = amorphous iron hydroxide, pCO₂ = partial pressure of carbon dioxide (log bar) (Laaksoharju et al., 1994).*

5 The concept: Representativeness of the groundwater samples

Groundwater hydrogeochemical data often comprises a large number of variables, all of which are informative in themselves. The history, reactions, mixing situations and flow paths of the groundwater may be coded in these variables. In order to make the best use of these variables the quality of the field and laboratory data must be ensured as an understanding of natural groundwater systems is no better than the data on which they are based. By definition *a representative sample is considered to be one which best reflects the undisturbed hydrological and geochemical in situ conditions for the sampled section.* A sample which reflects in situ, on-line, at-line, on-site or off-site errors such as contamination from tubes of varying compositions, air contamination, losses or uptake of CO_2, long storage times prior to analysis, analytical errors etc. has a low representativeness. The representativeness may also be influenced by the rationale in locating the borehole and selecting the sampling points. Some errors are easily avoided; others are difficult or impossible to avoid. Furthermore, chemical responses to these influences are sometimes, but not always, apparent (Laaksoharju et al. 1993). The representativeness of the groundwater is discussed below in terms of sampling and analytical representativeness.

5.1 Representativeness of the sampling

The representativeness of the downhole sampling is often dependent and sometimes hindered by lack of downhole information as well as practical and economical restrictions. Often the problem with unrepresentativeness is detected several months or even years after the sampling campaign. Until now there have been general suggestions on how to avoid contamination sources. The ideal strategy when sampling is still under debate and partly unresolved. The success of a sampling can only be compared with expert knowledge based on expected groundwater compositions at the sampling depth. The representativeness of the samples has been addressed in previous reports concerning the Äspö site (Smellie and Laaksoharju, 1992; Laaksoharju et al. 1995a; Laaksoharju and Skårman, 1995). In order to lower the risk of known contamination sources the following recommendations (after Smellie et al., 1999) have been suggested:

1. Integration of fracture geochemistry and hydrogeology with the hydrogeochemical sampling programme for the same borehole sections sampled for groundwater. This ensures that the information can be integrated with the measured groundwater parameters.

2. A step-wise drilling/sampling protocol to sample "first-strike" groundwater samples - the aim is to supply important source-term hydrochemical and isotopic information regarding the formation groundwaters. Although tests have shown that the high amount of drilling debris and drilling fluids can make this kind of sampling difficult

(John Smellie, pers comm. 1998), there is still a need for further tests to better understand the changes in the groundwater chemistry during drilling.

3. To determine the extent of fracturing along the borehole and to distinguish between open fractures (water conducting) and sealed fractures. This is best carried out by integrating core mapping with downhole TV-imaging. Once the fracture type and frequency are known, then the nature of the hydraulic testing programme can be planned. The best approach is to conduct spinner or flowmeter tests, and difference flow measurements and at this stage to avoid traditional injection and cross-hole tests.

4. Sections of the boreholes selected for sampling should be based on the hydraulic data. It may be that one or more ranges of hydraulic conductivity will be of interest, e.g. representing high, medium or low conducting bedrock sections.

5. When sampling an optimum pump rate should be chosen which provides a balance between minimising the risk of contamination through short-circuiting, and avoiding excessively long groundwater transport times from the borehole section to the bedrock surface. Successful sampling will depend on planning and the time available for sampling.

6. During groundwater sampling of the boreholes, regular monitoring of the uranine content in the pumped water is important. Cleaning of the boreholes should continue until the uranine content is below 1%.

7. The packed-off sampling sections should entail the measurement of Eh (Pt), pH, electrical conductivity, temperature and uranine; Eh and pH should be measured downhole. Monitoring of the key parameters should continue throughout the sampling period to ensure that any change in groundwater composition is recorded.

8. The analytical programme for the groundwater samples should focus on not analysing as many samples as possible but rather a few samples as well as possible. No “holes” in the table should occur since this lack of information generally means that the whole observation has to be disregarded in modelling. Normally major elements, stable isotopes and tritium should always be determined.

5.2 Representativeness of the chemical analysis

The foundation of the representativeness of the chemical analysis within the SKB programme is based on sampling protocols and quality controls of the analysed groundwater samples (Nilsson, 1995).

5.2.1 Sampling protocols

A sampling and analytical protocol is established prior to a sampling campaign. This protocol is based on established sampling routines or special requirements associated with the sampling campaign. As an example, two types of samples were collected in the HRL tunnel - *documentation samples* and *chemistry samples* (Nilsson 1995). The documentation samples were collected from new boreholes with a water flow rate of over 5 litres per minute. Only a few parameters were determined i.e. electrical conductivity, pH, chloride and alkalinity. The chemistry samples were repeated follow-up sampling of selected boreholes. The chemistry samples were subjected to a complete analytical programme covering all the major components, some minor components and special analysis i.e. isotopes and in some cases trace elements. Ferrous and ferric iron and minor anions were determined in the SKB-MFL. The redox sensitive components were determined as soon as possible without atmospheric contamination. Water for iron determination in the field and for ICP-AES analysis was collected in acidified and acid-washed bottles. Extra precautions were taken to avoid contamination of the acidified samples collected for trace element analysis by ICP-MS. Sample bottles for sulphide determination were preserved using sodium hydroxide and zinc acetate.

5.2.2 Quality control

To ensure data quality, control analysis by independent laboratories was carried out on one sample at each sampled section. This sample was taken at the end of the pumping period using the SKB-MFL. Generally the concentration of each controlled component agreed to within 10% between the various laboratories, although this was to a large extent dependent on the element in question and its concentration. If a large disparity was noted, the analysis was repeated. When the analytical sets from different laboratories were considered to be in good agreement, the data were compiled and further evaluated to produce the final data set for each sample. A schematic presentation of the data flow from the field to SKB geodatabase SICADA is shown in Figure 5-1. Detailed information of the data handling routines is given in a comprehensive report by Laurent et al. (1992).

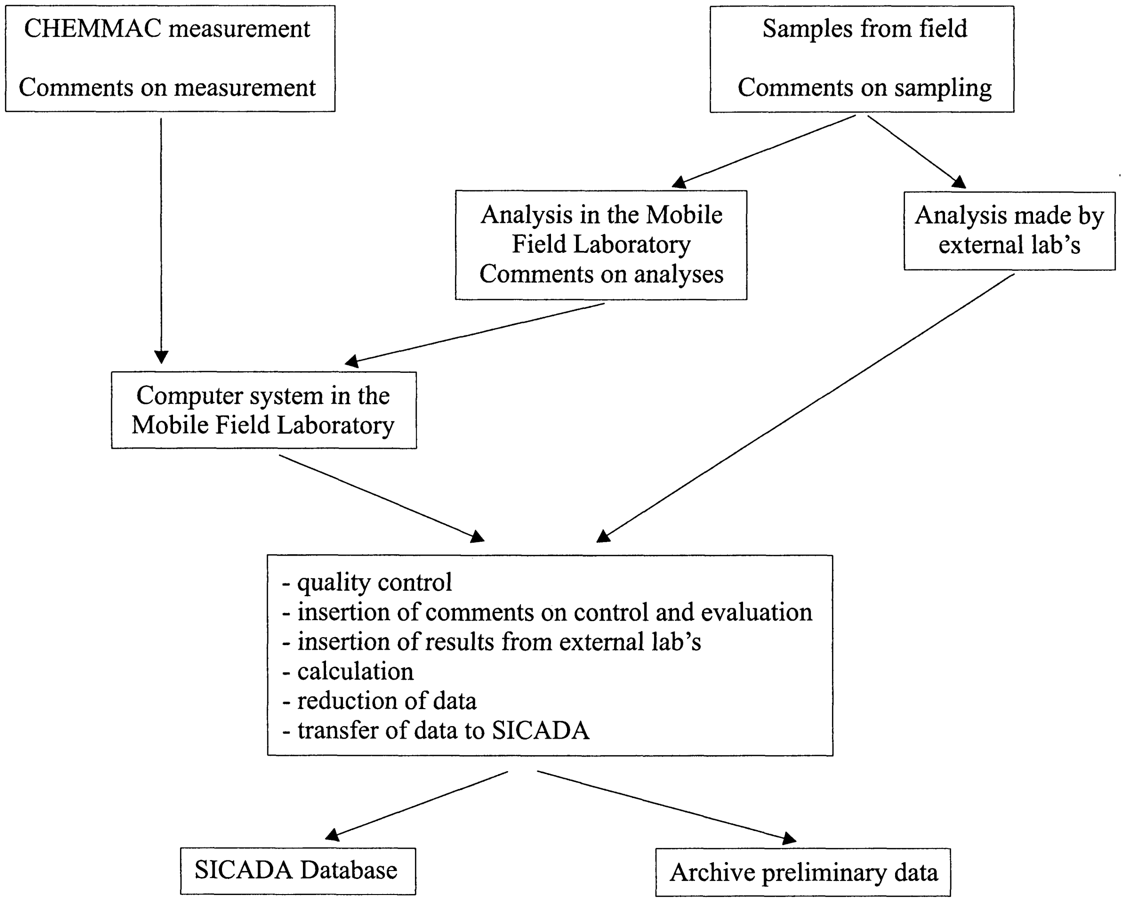


Figure 5-1: *Schematic presentation of the data flow from the field to the SKB database SICADA (modified after Laurent et al. 1992; Nilsson 1995).*

The analytical accuracy for the major components: sodium, potassium, calcium, magnesium, bicarbonate, chloride and sulphate were checked by ion-balance calculation, where the difference between the anions and cations was calculated. The difference was given in percentages and generally within the SKB programme the range was within 1-5%. A very saline groundwater can cause analytical problems for some methods and some of the components. Analytical problems because of high salinity or analytical limitations have been recorded concerning potassium, silica, sulphate, bromide, phosphate, nitrite, ammonium (Laaksoharju et al., 1995a).

For trace elements the analytical uncertainties were larger although elements such as iron, manganese, silica, lithium, strontium and fluoride had almost the same accuracy as the major components. For bromide and iodide the uncertainty was in the range of 20%. For sulphide the accuracy was high but the concentrations were generally under the detection limit. The analytical inaccuracy for nitrate, nitrite, ammonium, and phosphate has been estimated at 50-100%. For trace elements the sampling contamination masked the true element concentrations.

The isotopical analysis has its unique uncertainties, tritium, deuterium and oxygen-18 were reported to be 0.5Bq/l, 1% and 0.2% respectively. The uncertainty for the other isotopes varied from one measurement to another but they were generally around a factor of one higher or lower than the given value. The precision for the pH and Eh measurements with the SKB field laboratory was generally in the order of 0.1 pH and 25mV for the Eh measurements (Wikberg, 1987).

5.3 Methods to judge representativeness

5.3.1 Methods based on expert judgement

The quantification of uncertainties caused by drilling, sampling activities, analytical and modelling uncertainties are in some cases straightforward (analytical uncertainties). In other cases one has to rely on estimates and expert judgements (e.g. the total effect from drilling activities). It can also be difficult to quantify the total effect from a disturbance since there is nothing to compare it with since no groundwater samples are available from totally undisturbed conditions prior to drilling.

Within the SKB site characterisation programmes, groundwater quality has been mainly addressed manually based on expert knowledge (e.g. Smellie and Laaksoharju, 1992). In some cases geochemical equilibrium modelling has been used to correct field data and model the in situ conditions. This essentially means that a synthesis of water quality is based on establishing and understanding the interplay between the many variables which can influence the quality of a sampled groundwater. This is achieved by being familiar with the analytical data and systematically approaching, for example, each borehole and borehole section etc., in order to address the variables which can contribute to (and also identify) all the potential sources which can influence the quality of the groundwater. A certain amount of subjectivity is sometimes necessary to judge how important certain variables are and to predict their consequences. However, for the geochemist closely linked with the site investigations, this should not pose a major problem as he or she should be aware of, and probably have helped to plan, the programme of investigations with all the accompanying pitfalls and difficulties.

As an example, for the safety assessment modelling of spent nuclear fuel the following priorities and representativeness criteria based on expert knowledge have been established (Rhén & Bäckblom (eds.) 1997):

- Reliable measurements of pH, Eh, redox and pH sensitive constituents like bicarbonate, iron and sulphide are of importance for safety assessment.
- Major constituents, sodium, potassium, calcium, magnesium, bicarbonate, chloride and sulphate are unaffected by disturbances from drilling or contamination from other investigation methods, as long as the proportion of drilling or testing water can be analysed and corrected for.
- Trace elements and stable oxygen-18 and deuterium isotopes are reliable even with a content of up to 5% of drill flushing water.
- pH sensitive trace elements, tritium and carbon-14 data are reliable only when contamination by drilling water or meteoric water entering through the borehole is less than 0.1%.
- Eh and redox-sensitive elements are reliable when the electrode readings have stabilised and the Eh value can be interpreted. Normally several days of continuous pumping is needed with measurements of on-line flow through cells, and preferably downhole measurements of Eh and pH.

Another example is representativeness modelling of groundwaters made for SR-97 a safety assessment study (Laaksoharju et al., 1998). The sites studied were three sites arbitrarily named Aberg (Äspö), Beberg (Finnsjön) and Ceberg (Gideå) (see Figure 1-1). The starting point was that the annual variation of the groundwater level at Aberg was ±1m. By applying the Ghyben-Herzberg relation (Freeze and Cherry, 1979) on the salinity (10000 mg/l, Cl) at Aberg this annual fluctuation of the groundwater level of ±1m corresponded to a theoretical fluctuation of the non-saline/saline interface of ±80m. This meant that during undisturbed conditions there was a potential force to move the water ±80m from the actual sampling depth. In reality the movement was much lower since the hydraulic properties of the rock generally hindered fast changes deep in the bedrock. The mixing processes in the fracture network generally also hindered the occurrence of a sharp non/saline interface in the bedrock. In any case, the Ghyben-Herzberg relation can be used to indicate the maximum potential for natural changes in the groundwater system. If the sampling activities cause a larger fluctuation this would result in less representative samples. This was used as a comparison base and the disturbances from e.g. drilling, sampling activities and analytical error were compared with the effects of changing the water column in the borehole.

To demonstrate the sensitivity of the groundwater system when sampling, the Ghyben-Herzberg relation was transformed to groundwater chemical mixing portions (Laaksoharju et al., 1998), which means that in the Aberg case a ±1m annual fluctuation of the water has a potential to change the mixing portion of e.g. meteoric water by ±7%. If the maximum uncertainty allowed (from drilling, sampling, analysis and modelling) should be within this annual fluctuation, the proportion of meteoric water can change by maximum ±7% (or ±80m water column). The uncertainty was estimated to be ±2% from drilling water contamination or from uncertainty in analyses. Both errors caused the same uncertainty concerning the representativeness of the sampled water. In this case the error was equal to a change in the fluctuation of the water column of ±23m. A drilling water content of 7% was equal to a fluctuation of the water column of ±82m which is more than the annual fluctuation and this made the groundwater sample less representative of the sampled depth.

The calculations indicate that the sensitivity to disturbances is determined in many cases by the prevailing hydrogeological conditions and the sampling depth. The risk is that the deeper the water and the lower the hydraulic conductivity, the larger the risk for disturbances. The calculations seem to indicate that the positive effect from a low extraction rate can be lost if there is a long transport time up to the surface, or through storage of the samples prior to analysis but it can be compensated for by in-situ measurements of Eh and pH. The uncertainties in the measured Eh and pH values will dramatically affect the outcome of groundwater equilibrium calculations e.g. one unit error in the pH calculation will give one unit error in the saturation index calculations of calcite. The under-saturated phase may appear over-saturated in the calculations which may affect the interpretation of the overall stability of the groundwater system. There is a risk that a relatively small uncertainty in one step of the sampling procedure may lead to a large uncertainty in the next step.

The conclusion is that in most cases the SKB groundwaters reflect the sampled depth and the disturbances are generally lower than the natural annual variation. In the Safety Assessment analysis an uncertainty range of ±10% should be used for the groundwater composition. The uncertainty range covers most of the natural annual variation and in-situ, at site, off-site and modelling errors affecting the original groundwater composition. The availability, sampling and analytical accuracy of the groundwaters sampled at Aberg, Beberg and Ceberg have been qualitatively estimated in Table 5-1.

Table 5-1: Availability, sampling accuracy and analytical accuracy of the groundwater analysis qualitatively estimated for Aberg (Äspö), Beberg (Finnsjön) and Ceberg (Gideå).

	Availability			Sampling accuracy			Analysis accuracy		
	+ = low; ++ = medium; +++ = high			+ = low; ++ = medium; +++ = high			+ = low; ++ = medium; +++ = high		
Groundwater chemistry	Aberg	Beberg	Ceberg	Aberg	Beberg	Ceberg	Aberg	Beberg	Ceberg
Eh	+++	++	++	+++	++	+	+++	+++	+++
pH	+++	+++	+++	+++	++	+	+++	+++	+++
Na	+++	+++	+++	+++	++	+	+++	+++	+++
K	+++	+++	+++	+++	++	+	+++	+++	+++
Ca	+++	+++	+++	+++	++	+	+++	+++	+++
Mg	+++	+++	+++	+++	++	+	+++	+++	+++
HCO3	+++	+++	+++	+++	++	+	+++	+++	+++
SO4	+++	+++	+++	+++	++	+	+++	+++	+++
Cl	+++	+++	+++	+++	++	+	+++	+++	+++
Fe	+++	++	++	+++	++	+	+++	+++	+++
Mn	+++	+++	+++	+++	++	+	+++	+++	+++
U	+++	++	+	+++	++	+	++	++	++
Th	+++	++	++	+++	++	+	++	++	++
Ra	+++	++	++	+++	++	+	++	++	++
Si	+++	+++	+++	+++	++	+	+++	+++	+++
Al	+	+	+	+++	++	+	+	+	+
Li	+++	++	+	+++	++	+	+++	+++	+++
Cs									
Sr	+++	++	+	+++	++	+	+++	+++	+++
Ba									
HS	+++	++	+	+++	++	+	+	+	+
I	++	++	++	+++	++	+	++	++	++
Br	+++	++	+	+++	++	+	++	++	++
F	+++	+++	+++	+++	++	+	+++	+++	+++
DOC	+++	++	++	+++	++	+	+	+	+
TDS	+++	+++	+++	+++	++	+	+++	+++	+++
O-18 (in H2O)	+++	+++	+++	+++	++	+	+++	+++	+++
H-2 (in H2O)	+++	+++	+++	+++	++	+	+++	+++	+++
C-13 (in DOC)	++	++	+	+++	++	+	++	++	++
S-34 (in SO4)	+			+++			+++		
O-18 (in SO4)	+			+++			+++		
S-34 (in HS)	+			+++			+++		
Sr-87 / Sr-86	++			+++			+++		
Tritium	+++	+++	+++	+++	++	+	++	++	++
C-14 (in DiC)	+++	++	+	+++	++	+			
C-14 (in DOC)	+++	++	+	+++	++	+			
U234/U238	+	+	+	+++	++	+	++	++	++
HA/FA									
NO3	+++	+++	+++	+++	++	+	+	+	+
NO2	+++	+++	+++	+++	++	+	+	+	+
NH4	+++	+++	+++	+++	++	+	+	+	+
HPO4	+++	+++	+++	+++	++	+	+	+	+
N2									
H2									
CH4									
CO2									
Ar	+			+++			++		
He	+			+++			++		
Radon	+			+++			++		
Bacteria	++			+++			+++		
Colloids	++			++			++		
O2									
XE isotopes									
Kr isotopes									
Cl-36									
He-3									
He-4									
Trace metals, others	+			+			+		

5.3.2 Mathematical tool to help judge representativeness

A mathematical tool to evaluate representativeness of groundwaters and to support expert judgement was developed (Laaksoharju et al., 1993). The aim was to create a powerful, reproducible yet simple and flexible quality scoring system to classify groundwater data. A standard spreadsheet program was used for this purpose. The objective was to formalise the often-used variables and assumptions that form the basis of the manual representativeness judgements in a more mathematical way. The system is based on a simple quoting and scoring system.

The starting point was to focus on the variables which may reflect disturbance of the downhole in situ conditions. The following 18 quality indicating variables were used; drilling water, pump rate, oxygen content, charge balance, time-lag of analysis, pH errors, Eh errors, distance between packers, tritium content, partial pressure of carbon dioxide, ammonium, phosphate, total organic carbon, manganese, deuterium, oxygen-18, ferrous versus total iron ratio and sulphide.

Models were constructed to reflect the known or assumed general natural behaviour of these elements in the groundwater. The degree of deviation from the model was then calculated; the higher the deviation the lower the quality for that variable. The models were checked for possible known or assumed in situ, on-line, on-site or off-site errors. The relevance of the selected model for any specific data set was generally easily checked using x,y plots. The models are often simple quotients which are easy to replace or modify based on later experience, special hydraulic conditions, or the number of special requirements for the data (Laaksoharju et al., 1993).

The models used were generally simple and straightforward, for example: the lower the drilling water content of the sample the higher the value and hence the quality. The error between measured and calculated pH was based on the assumption that saturation index calculations of calcite should be close to zero. If not, the error was assumed to be dependent on the measured pH. It should be noted that no importance was given to whether the field value was an in-situ, on-line or off-site value. Instead this was represented by the time lag of analysis; the quicker the analysis following sampling, the higher the scores. The error in the Eh measurements was based on a comparison between a modelled value and the measured value. The calculated Eh value was based on the measured pH and the Fe^{2+} content in the groundwater according to the method suggested by Grenthe et al., (1992). An increase of the packer distance results in lower scores; this assumes that the risk to remove foreign water increases with increasing sampling borehole lengths. High tritium levels found in deep bedrock sections give lower quality scores than the same amount of tritium in shallow sections.

These models used were simplifications that aimed to describe the "undisturbed" in situ groundwater conditions. Therefore, as an example, the pH error calculations were valid in low conductive and moderate mixing situations. However, in fractures where different water types meet or in natural high mixing ratio zones, where supersaturation is obtained under natural conditions (Puidomènech and Nordstrom, 1987;

Laaksoharju, 1990), the selected model would no longer be valid. In such a case the situation may instead be accounted for by the pump-rate quotient which may then reduce the scores.

In order to test the method, groundwater data from all the Swedish and Finnish sites (a total of 14 sites) at depths greater than 100m, and containing isotopes δ^2H and δ^{18}O, were selected. From Sweden 75 observations from 23 deep (> 500m) boreholes at 8 sites were considered; the Finnish data set contained 69 observations from 17 deep boreholes at 6 sites. The locations of the sites are shown in Figure 5-2 as well as the quality scores for the 14 evaluated sites in Finland and Sweden. The samples from the Äspö site scored highest amongst the investigated sites and the samples from the Äspö site are generally representative.

5.4 Conclusions on representativeness

The major conclusions are that the real groundwater character can be easily biased during borehole activities such as drilling, borehole testing and sampling. There is no well-tested or fixed strategy which can be applied when sampling groundwater, each borehole is unique and only general recommendations can be used. The reason is that the representativeness of groundwater samples are a function of many interacting variables such as borehole location, sampling depth, in-situ groundwater composition, pump rate, economical and time constraints. In addition the success of a sampling can only be compared with expert knowledge based on expected groundwater compositions at the sampling depth. There are no samples from totally undisturbed downhole conditions which could be used as a reference sample for the actual sampling.

Despite the difficulties when sampling for groundwaters it is important to note that the groundwater sampling conducted within the Swedish site investigation programmes are of such quality that they reflect well-known paleo or present events such as deglaciation, different marine signatures, land uplift, tunnel constructions, organic/inorganic reactions and effects from microbiological processes (see section 8). The groundwaters in the bedrock have been accurately sampled starting from modern rainwater to brine water with an age of more than 1.5Ma. This information may be biased in the order of ±10% (Laaksoharju et al., 1998) but the original character of the groundwater would have been lost if vigorous groundwater disturbances from sampling activities had taken place. Improvements in sampling techniques and understanding of the sources of disturbances have increased the representativeness. However, in the future, a better monitoring of downhole pressure and groundwater changes associated with various borehole activities is suggested.

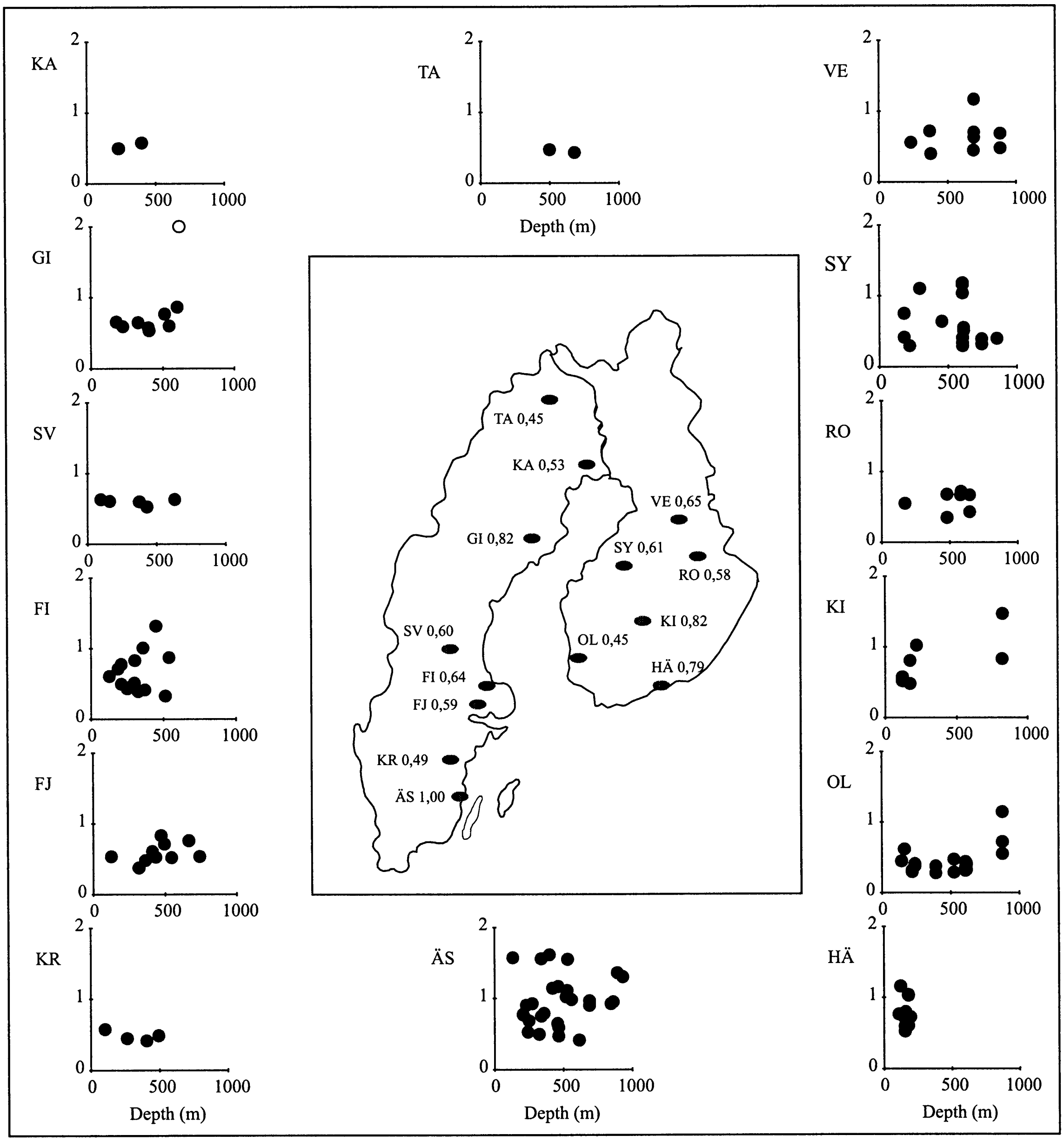


Figure 5-2: *Map showing the average quality scores (%) from different sites in Sweden and Finland. The x,y plots show the scores (%) versus depth (m) for the observations at each site. The higher the scores the better the quality of the sampled water at the site. (Sweden: TA=Taavinunnanen, KA=Kamlunge, GI=Gideå, SV=Svartboberget, FI=Finnsjön, FJ=Fjällveden, KR=Kråkemåla, ÄS=Äspö+Ävrö+Laxemar. Finland: OL=Olkiluoto, HÄ=Hästholmen, KI=Kivetty, SY=Syyry, RO=Romuvaara, VE=Veitsivaara) (Laaksoharju et al., 1993).*

6 Classical hydrogeochemical modelling

The geochemical models are used e.g. to describe the composition, origin, age, chemical properties and stability of the groundwater system. These results can be used to judge the suitability of the groundwater as a media surrounding the final repository. The word modelling is used in the sense "description" where mathematical or non-mathematical tools can be used. A commonly used approach in groundwater modelling is to start the evaluation by explorative analysis of different groundwater variables using scatter plots. The next phase often includes a groundwater classification based on the salinity or major constituents of the groundwater. The effects from the major water rock interactions are modelled using some of the standard mass-balance codes. The origin of the groundwater, perhaps described in relation to the present or paleo events, is discussed. The often-complex groundwater information is summarised in a qualitative conceptual model based on expert knowledge.

The following sections give an example of how classical geochemical evaluation and modelling were applied to the Äspö data set (Laaksoharju et al., 1999c). The starting point is grouping of data based on salinity, explorative analysis where the data set is examined, followed by classification, visualisation of the distribution of water conservative elements (Cl and $\delta^{18}O$) in the bedrock and finally, a short description of the standard type of groundwater modelling tools with some modelling examples.

6.1 Scatter plots

To simplify the information the groundwaters at the Äspö site were divided into three different groups: *non-saline, brackish* and *saline* groundwaters, based on chloride concentration. The chloride concentration for the groups is as follows:

• Non-saline groundwater	<1000 (Cl, mg/l)
• Brackish groundwater	1000-5000 (Cl, mg/l)
• Saline groundwater	>5000 (Cl, mg/l)

At the Äspö site a water sample with twice the salinity of Ocean water is named Brine (>40000 mg/l, Cl). This follows the classification suggested by Drever (1988) where a sample with a similar or considerably greater salinity than seawater can be named Brine. This classification is used throughout this document.

In order to show the general trends and complexity of the analytical groundwater data some examples are shown in Figure 6-1 for the variables Cl, $\delta^{18}O$ and HCO_3 all plotted against depth. The complete data set is shown in Laaksoharju et al., 1999c. Cl and $\delta^{18}O$ are water conservative elements which can be used to trace the origin of the groundwater: Cl for tracing e.g. meteoric/brine water and $\delta^{18}O$ for tracing influences from e.g. cold recharge water such as from the last glaciation. The variable HCO_3 can be used to trace shallow water undergoing calcite dissolution or organic decomposition (Banwart et al., 1996).

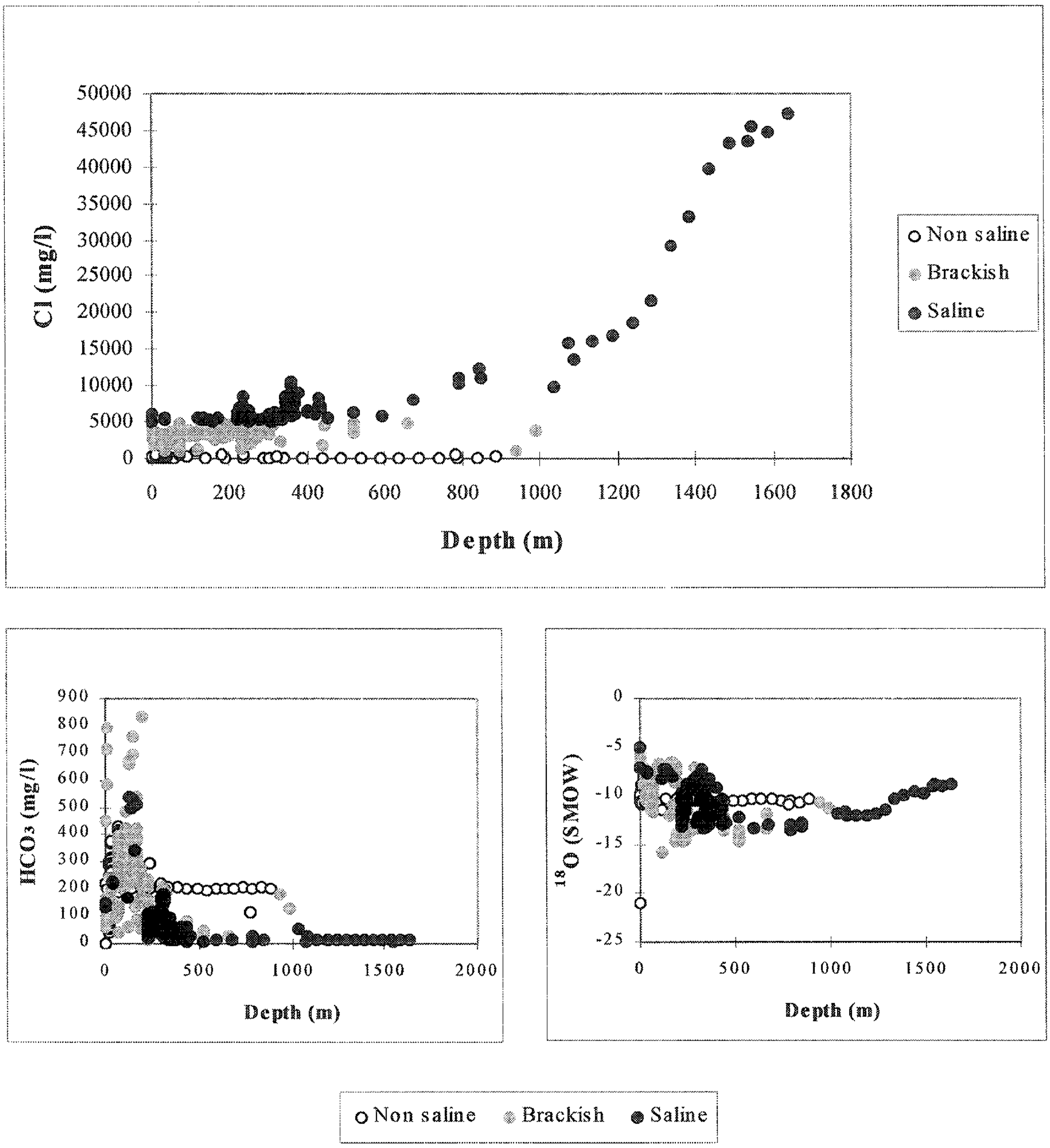


Figure 6-1: *Scatter plots for the Äspö site data shown for Cl, $\delta^{18}O$ and HCO_3 versus depth. The groundwater observations have been divided into: non-saline, brackish and saline groundwaters.*

The complex depth distribution of groundwater chemistry at the Äspö site is reflected by the variations in Cl, $\delta^{18}O$ and HCO_3 as shown in Figure 6-1. Saline groundwaters are characterised by a high Cl, Na, K, Ca, Mg and SO_4 content and a low HCO_3 and tritium content and they occur at various depths between 50 to 1700m. 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 content can be detected at 900m depth.

6.2 Groundwater classification

Piper plots (Piper, 1953) are widely used to simplify and classify major ion groundwater data. To show the distribution of the Äspö site groundwater data, a standard trilinear Piper plot was 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. A classification system developed by Morgan and Winner (1962) and 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 6-2).

The Piper plot clearly demonstrates the large spread of groundwater composition with two distinct groupings. One represents non-saline and brackish groundwaters characterised by a sodium, alternatively a calcium, bicarbonate-type water. The other is characterised as a calcium-chloride type of water. An evolutional trend from non-saline water through brackish water to the saline water was observed in the Piper plot. Similar general groundwater patterns, like those at Äspö, have been described in other locations close to the Baltic Sea in Finland; in Hästholmen (Nordstrom, 1989) and in Olkiluoto (Pitkänen et al., 1994).

The disadvantage of Piper plots is the higher resolution for the non-saline waters than for the intermediate and saline groundwaters, with the latter usually forming tight clusters. For example, important changes in some variables such as SO_4 may be masked by larger changes in other variables such as Cl. The often crucial isotopic information is not included in the Piper plot. The Piper plot is based on the assumption that reactions with the bedrock minerals determine the measured water composition.

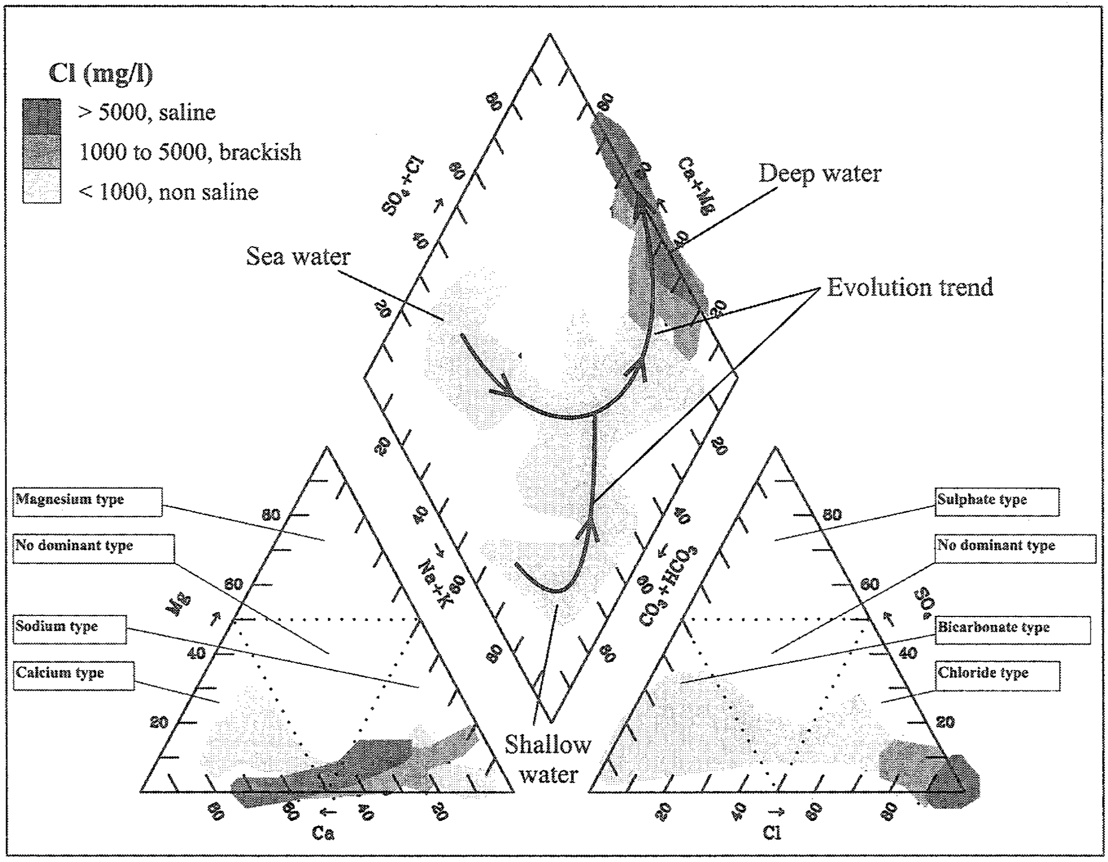
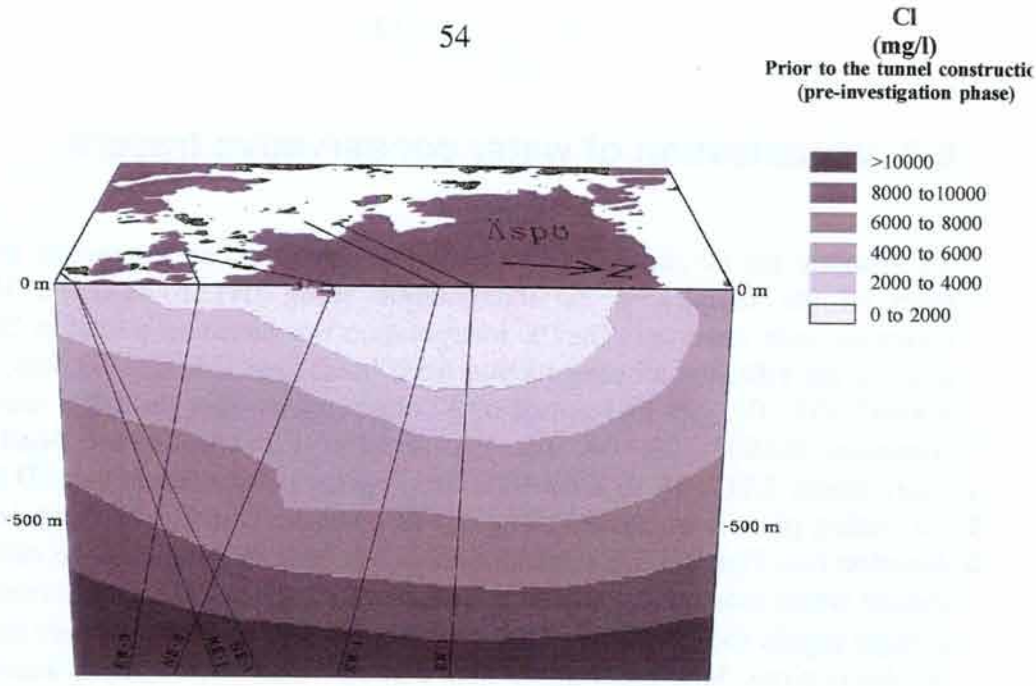


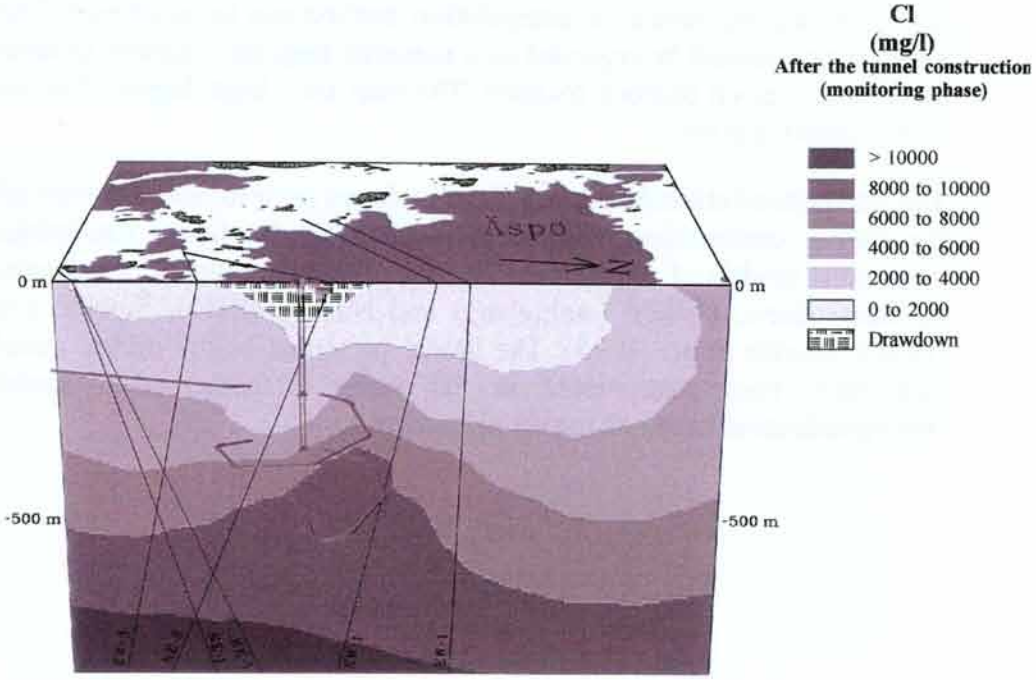
Figure 6-2: *Standard Piper plot showing the main groundwater types for the Äspö site groundwaters. The samples were divided into three groups: non-saline, brackish and saline groundwaters. The waters are classified according to the domain or field in which they occur on the diagram (Laaksoharju et al., 1999c).*

6.3 Visualisation of water conservative tracers

To visualise the Cl and $\delta^{18}O$ distribution at Äspö, and to summarise the information from all the samples, a 3D interpolation using INTERGRAPH's Voxel Analyst computer code was used. The 3D interpolation was based on a total of 28 observations prior to the HRL tunnel construction from boreholes: HAS02, -03, -05, -06, -07, -13, KAS02, -03, -04, -06, and a total of 37 observations after the HRL construction from boreholes: KAS02, -03, -04, -06, -07, -08, -09, -12, -13, -14, and finally HRL tunnel observations SA1210A to KA3191F (see Figures 1-3a,b). From this 3D interpolation a 2D cutting plane was chosen showing the conditions under the Äspö island in a N-S direction (see Figure 1-1 for orientation). To reduce uncertainties the cutting plane was chosen where most of the sampling points were located. The interpolation is uncertain at large depths (>500m) and in the corners of the cutting plane where there are few or no observations. It is important to note that the water is flowing in fractures, but since the fracture network at Äspö is rather dense at large scale the site can be regarded as a porous media and hence an interpolation method can be employed. The results of the interpolation should be regarded as a potential map for a certain groundwater property to occur at a given bedrock location. The map has a high degree of accuracy only close to the sampling points.

The interpolated chloride-cutting plane is shown prior to, and 3.8 years after, the start of the tunnel construction (Figure 6-3). The result shows similarities with earlier conceptual models of Äspö based on data prior to the tunnel construction as presented by Laaksoharju, (1988); Laaksoharju and Nilsson (1989); Smellie and Laaksoharju, (1992); Smellie et al. (1995). The model presented below differs mainly because the data have been interpolated in 3D using a mathematical model rather than conceptualisation based on expert judgement.





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	<1000	~ 6.5	~ -100
100-350	Brackish	Na-Ca-K: Cl-SO_4-HCO_3	1000-5000	~ 7.5	~ -200
350-1700	Saline	Ca-Na-K:Cl- SO_4-HCO_3	>5000	~ 8.5	~ -300

Figure 6-3: *Visualisation of the Cl distribution at the Äspö site prior to (pre-investigation) and after the tunnel construction (monitoring). The drawdown (80m) of the groundwater surface, above the tunnel, is shown in the lower diagram. The major features of the non-saline, brackish and saline groundwaters are listed in the table above. The orientation of the cutting plane is N-S (see Figure 1-1) (Laaksoharju et al, 1999c).*

The non-saline groundwater in Figure 6-3 is characterised by a Na-HCO_3 or a Ca-HCO_3 signature as a result of mixed meteoric water. Brackish groundwater (1000-5000 Cl, mg/l) is characterised by a Na-Cl-SO_4 or Na-Cl-HCO_3 water and is generally present at a depth of 100-350m at Äspö and in the HRL tunnel. On the mainland of Laxemar the brackish water is found down to a depth of 1000m. Here the penetration depth of brackish groundwater is governed by the prevailing hydraulic conditions. The saline groundwater is characterised by a Na-Cl rich variety at depths of 100-600m and a Ca-Cl variety at depths greater than 600m.

The Cl distribution in Figure 6-3 may give the impression that the groundwater system is fairly simple and can be described mostly as following a two component evolutional path between non-saline and saline groundwaters. Many of the major components (Figure 6-1) and the Piper plot (Figure 6-2) seem also to support this assumption. The HRL tunnel construction does not seem to affect mixing between the non-saline and saline groundwaters to any large extent since the Cl stratification is almost unchanged. This is in contrast to the hydrogeological description of the site which shows relatively large flow dynamics because of the HRL tunnel construction (Rhén (ed) et al, 1997).

An evaluation of the known groundwater conservative tracers such as $\delta^{18}O$ or δD nonetheless showed a low correlation with Cl (when Cl < 10000 mg/l, Figure 6-1) which may indicate a more complex groundwater system than can be assumed from the Cl distribution. The $\delta^{18}O$ distribution prior to and following the tunnel construction is shown in Figure 6-4. The interpolation method and data used in Figure 6-4 is identical to the approach used in Figure 6-3.

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. The groundwater mixing results in ambiguous groundwater signatures and difficulties in understanding and modelling the site if only one variable is used as a tracer for the transport of constituents. A simple test to detect the possible ambiguity and complexity of the groundwaters is a correlation analysis between Cl and $\delta^{18}O$. The scatter between Cl and $\delta^{18}O$ as shown in Figure 7-5c supports the premise that the Äspö site groundwaters are of complex origin.

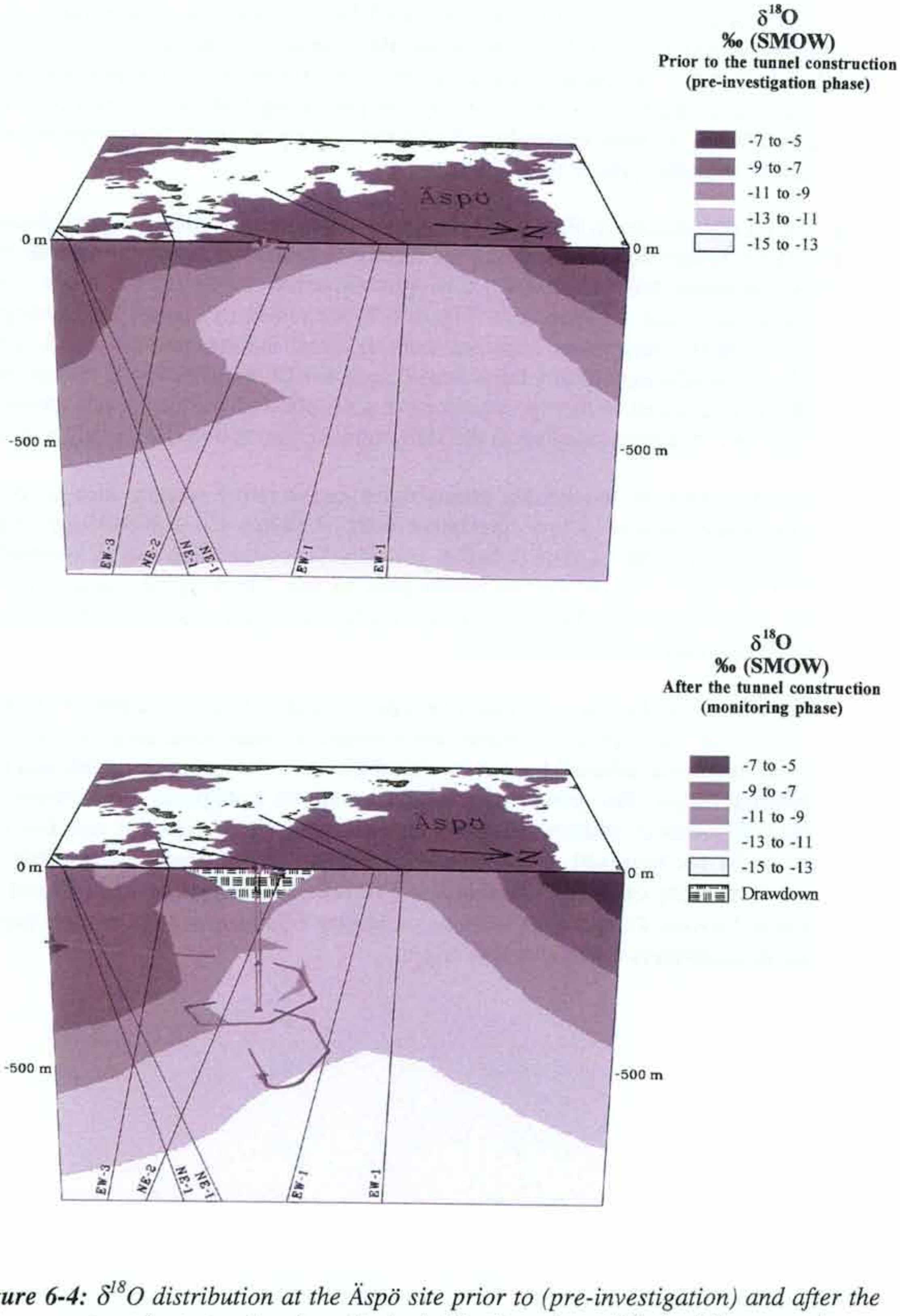


Figure 6-4: *$\delta^{18}O$ distribution at the Äspö site prior to (pre-investigation) and after the tunnel construction (monitoring). The drawdown (80m) of the groundwater surface, above the tunnel, is shown in the lower diagram.*

6.4 Modelling tools

Standard geochemical models are used in the interpretation of geochemical reactions. In regional groundwater systems the models can be used to determine the prevailing conditions and the extent of geochemical reactions as well as estimating the direction of groundwater flow. Within the SKB groundwater modelling programme *speciation* modelling with the codes PHREEQE (Parkhurst et al., 1980), WATEQF (Plummer et al., 1976) and EQ3/6 (Wolerey, 1979) has been used. For *mass-balance* modelling Netpath (Plummer et al, 1991) has been employed and for *reaction-transport* modelling HYTEC-2D (Salignac, 1997, 1998) was tested. In the following chapters the advantages and disadvantages of the models are briefly described.

6.4.1 Speciation modelling

The main purpose of speciation modelling is to calculate, based on thermodynamic properties, the mineral saturation indices. The indices are indicators of the saturation state of a mineral with respect to a given water composition. A positive value indicates that thermodynamically a mineral can precipitate a negative value that it can dissolve. A value close to zero indicates that the mineral is not reacting. The saturation index indicates the potential not the rate at which the process will proceed. From this information conclusions concerning possible major reactions taking place and indirect indications of the dynamics of the system can be drawn. The advantage is that it is relatively easy to modify the model to include new species and elements and there is extensive literature on test cases and on complexation reactions and estimates of the stability constants.

The following difficulties can occur (after Parkhurst and Plummer in Alley, (ed.), 1993): 1) The theory used (Debye-Hückel) or its modification can be applied only on dilute water or on sodium chloride groundwater of maximum seawater concentration. 2) Insufficient laboratory work has been performed to reproduce mineral solubilities. 3) The thermodynamic data is based on high temperatures because of slow equilibrium in low temperatures (~25°C). 4) Minerals can have a range of stability due to their composition and structure. 5) Lack of mechanisms to account for repulsive forces in mixed electrolytes. 6) Sensitive to accuracy of chemical analyses especially for pH and Eh. 7) Many of the reactions such as redox reactions are biologically mediated or kinetically slow and therefore not in equilibrium.

For low-temperature calculations, the number of minerals for which meaningful saturation indices can be calculated is relatively small. Reliable indications can be obtained for fast reactions such as: carbonate, sulphate and chloride minerals. For kaolinite, clays, feldspars and other aluminium silicates qualitative results can be obtained due to uncertainties in the thermodynamic data and the aluminium measurements.

6.4.2 Mass-balance modelling

The aim of mass-balance modelling is to determine the *type* and *amount* of geochemical reactions that are occurring in a groundwater system. This is done by identifying the minerals that are reacting and determining the amounts of the minerals that dissolve or precipitate. The basic conceptual model for this kind of mass-balance modelling is that two waters (A and B) are on a single flow line, where water A is the initial water and B is the final water. The final water composition is modelled from the occurrence of geochemical reactions along the flow path. There are variations of the conceptual model where two initial waters A and B of different compositions mix as geochemical reactions occur to produce the final water C. The assumption is that there is a steady state concerning flow and the chemical composition in the aquifer. If the water has been affected by transient chemical conditions or is not within the same flow system the conceptual model is not applicable and erroneous results may occur (Parkhurst and Plummer in Alley, (ed.), 1993). Interpretation of groundwater mixtures often requires additional data to that used in the model.

The stoichiometry of many minerals is relatively well defined except for phases forming solid solutions or minerals containing trace elements. When modelling, several mass-balance models can account for the observed groundwater chemistry. To narrow the number of possibilities one has to rely on expert knowledge in combination with additional information from saturation index calculations, microscopic mineralogical studies and isotopes such as $\delta^{13}C$, ^{14}C and $\delta^{34}S$ which can be used to support or reject a mass-balance model. Correctly used the model can be used to indicate the valid geochemical reactions that quantitatively account for the chemical evolution of waters along a flow path.

6.4.3 Reaction-transport modelling

Reaction-transport modelling can be used to solve geochemical reactions and processes of advection, dispersion and diffusion. The aqueous model used is based on thermodynamic speciation modelling and the uncertainties are therefore the same as those discussed above. The model has to calculate the flow field for a steady state or possibly transient aquifer that is under study and hence the hydraulic properties of the aquifer must be known and moreover, in greater detail than for groundwater flow modelling. This is the case if transport of a particular source of an element (e.g. uranium mineralisation) is to be modelled (Salignac, 1997, 1998).

The following is needed when modelling reaction-transport: a qualitative assessment of the distribution and composition of reactive minerals, the initial composition of the groundwater estimates of the rates of inversible reactions, a conceptual model of the groundwater flow history if transient conditions are modelled (Parkhurst and Plummer in Alley, (ed.), 1993). A large amount of information is needed for applying this kind of modelling in a site investigation programme. If successfully applied, the model has the capability to model chemical reactions in time and space.

6.5 Examples of performed groundwater modelling

The aim of the geochemical modelling can vary, in some cases the redox system is modelled (Grenthe et al., 1992). In other cases, organic carbon oxidation (Banwart et al., 1996), shallow water intrusion (Banwart et al., 1994), general water rock interaction or the origin of the groundwater and mixing processes (Smellie et al., 1995; Laaksoharju et al, 1999c) are modelled. Since the purpose differs so do the tools used. In some cases, the groundwater modelling is based on laboratory studies (Grenthe et al., 1992) and in other cases large scale field measurements including geological, hydrogeological and hydrochemical information are evaluated in the modelling (Banwart et al., 1996; Smellie et al., 1995; Laaksoharju et al., 1999c). Sometimes geochemical reasoning and expert judgement are used; in other cases standard or new computer codes (see section 7) have been used to decode the often complex and ambiguous field data. The aim is to describe the processes affecting or that have affected the groundwater system. Some examples of traditional groundwater modelling such as Eh modelling, influx of shallow water modelling and site modelling performed on data from the Äspö site are briefly presented in the following chapters.

6.5.1 Eh modelling

There has been much discussion within the scientific community concerning the possibility of obtaining reliable in-situ Eh measurements in deep groundwaters. It was shown both in laboratory investigations and field studies of deep groundwater systems that stable and reproducible redox potentials can be measured with a precision of +25mV. The measured potentials are consistent with redox reactions involving dissolved Fe (II) and hydrous Fe (III) oxide phases (Wikberg 1987). This work led to modelling where the laboratory and field data were used to evaluate the main processes behind the redox reactions (Grenthe et al., 1992).

The Eh data measured in the field was in good agreement with the half cell reaction: $Fe(OH)_{3(s)} + 3H^+ + e^- = Fe^{2+} + 3H_2O$ involving hydrous ferric oxide and Fe^{2+} in solution, as indicated both by the slope of a plot of Eh vs. ($3pH + \log [Fe^{2+}]$), and the value of the solubility product for $Fe(OH)_{3(S)}$ calculated from these data. The solubility product: $pK_s = -\log[Fe^{3+}] [OH^-]_3 = 40.9 \pm 1.1$ falls in the range $37.3 < pK_s < 44.1$, as given for amorphous ferric hydroxide and crystalline goethite, respectively. The measured Eh values could therefore be modelled fairly well using the measured pH and the Fe^{2+} content in the groundwater according to: Calculated $Eh = E_0 - (RT/F)(3pH + \log[Fe2+])$; where $E_0 = 707mV$ and $RT/F = 56mV$ (Grenthe et al., 1992).

6.5.2 Modelling of influx of shallow water

On March 13, 1991, construction of the entrance tunnel to the Äspö HRL opened a vertical fracture zone at a depth of 70m. The zone was called the “Redox Zone”, see Figure 1-1. This provided an opportunity to study geochemical changes resulting from shallow water inflow into a crystalline bedrock aquifer as anticipated during construction and operation of a deep repository for spent nuclear fuel. Three weeks after the fracture zone opening a sharp dilution front corresponding to 80% shallow water inflow to the originally saline fracture zone arrived at the entrance tunnel depth. In spite of this large inflow of shallow water, the fracture zone has remained persistently anoxic.

Input of organic carbon into shallow groundwater provides a possible energy and carbon source for anaerobic respiration (Banwart et al., 1996; Banwart et al., 1994). The effect of this process is a source of HCO_3 in combination with the calculated mixing portion of meteoric water. 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 meteoric groundwaters. The CO_2 concentrations in the groundwater exceeded atmospheric concentrations by one or two orders of magnitude. High organic content (up to 20 mg/l) and the $\delta^{13}C$ isotope values of the HCO_3 confirmed a large uniform organic carbon source as one of the end-members for the carbon system in this zone (Banwart (ed.), 1994). Methane in the redox fracture zone with $\delta^{13}C$ values between -39.8 and -50.8 o/oo strongly supported a biogenic source for this gas.

This modelling result, together with other studies, implies that any sources of organic carbon, such as the soil layer, may provide important protection against penetration of an oxygen front from the surface. This is of paramount importance for the safety of the repository since reducing conditions hinder transport of radionuclides in the case of capsule failure. Measurements show that there is generally organic material present in the upper part of the groundwater (Jacks 1990). The only situation when this is absent is at deglaciation where the inorganic redox reactions are believed to be able to reduce the groundwaters when the flow situation has been stabilised. The results and conclusions are also of importance when considering the disturbed aquifer conditions anticipated during construction and operation of an open repository at a depth of several hundred metres (Banwart et al., 1996, Banwart et al., 1994).

6.5.3 Äspö site modelling

Descriptive groundwater modelling is often combined with the use of standard groundwater modelling tools e.g. NETPATH (Plummer et al., 1991). In this respect, Äspö is no exception. The effect from mixing and the state of equilibrium between fracture minerals and the groundwater in specific fracture zones have been calculated, and the net geochemical reactions taking place in the groundwater formation at Äspö have been described (e.g. Laaksoharju 1990, Smellie and Laaksoharju, 1992; Smellie et al. 1995; Pitkänen et al. 1994). In addition, mixing models have been constructed where components such as Cl, S, Mg, ^{3}H, $\delta^{2}H$ and ^{14}C were used as tracers for modelling the flow in fracture zones (Laaksoharju and Nilsson, 1989; Laaksoharju and Wallin (eds), 1997). The Äspö site data have been used to describe the chemistry and origin of the Äspö groundwaters. Hydrogeochemical observations have been integrated with known geological and hydrogeological parameters to construct a conceptual groundwater flow model for the Äspö island (Smellie et al, 1995). Integrated hydrochemical modelling with fracture geology was tested. The outcome of the work was that the groundwater reflected the fracture geology of the site rather than specific geology at the sampling point. This was taken as an indication of the groundwater being a result of mixing and reactions along different flowpaths rather than being stagnant and in equilibrium with the sampled fracture section (Smellie et al, 1995).

7 M3 method for geochemical modelling

7.1 Introduction

The advantage of standard geochemical modelling is that there are many models and numerous examples of its use in scientific literature. Sometimes it can be difficult to repeat this type of modelling since site-specific expert knowledge is required. The focus is on the reactions; the flow is generally dependent on a separate hydrodynamic model. The modelling approach is generally such that rainwater is supposed to slowly infiltrate and evolve through reactions with the bedrock fractures to a more concentrated fluid. Influences from e.g. ancient sea water or glacial water are seldom quantified. The result of the modelling is presented as descriptive conceptual models which can be difficult to integrate with hydrodynamic modelling and even to understand.

On a site scale, some standard models can be difficult to apply. Sometimes the reason may be the lack of special isotope data, in other cases the complexity of the groundwater flow at a site cannot be described using one or several variables individually as tracers. The role of reactions will therefore be overamplified since the transport of groundwater may not be correctly described. The groundwater constituents in a saline groundwater may be described as a result of water/rock interaction rather than as a result of the influx of an ancient sea water.

When modelling the groundwater chemistry at site scale the following difficulties may occur:

- When using a mixing model the end-member composition has to be identified. This can be a difficult task if many end-members exist.

- If the mixing calculations employ only one variable, such as Cl, and if $\delta^{18}O$ is incorporated, a new modelling result is obtained. A complex and ambiguous system cannot be easily modelled where different events (e.g. glaciation, sea water intrusion, land up-lift) have affected the groundwater composition.

- Some models require the minerals and gases in contact with the groundwater to be identified or assumed. This is a difficult task especially at site scale.

- Standard mass-balance models require water analyses unaffected by transient chemical conditions or samples that are sampled within the same flow system. Otherwise the modelling may produce erroneous results.

- Some models are applicable strictly to the chemical equilibrium along a flow path. Short contact time combined with the relatively low temperature at depth (at -200m = 11C°; the gradient is 1.6 C° per 100m at the Äspö site) may lead to a situation where equilibrium is never reached.

- Few models can describe the effects from biogenic processes where microbes mediate in many reactions that otherwise would not take place (e.g. Pedersen and Karlsson, 1995). These processes seem to have a major influence on the obtained groundwater chemistry at the Äspö site.

The limitations of existing models and the need for a tool to visualise and summarise the complex groundwater information at site scale necessitated the development of a new modelling tool. The aim was to make a model based on the fact that:

measured groundwater composition = mixing + reactions

The first attempt was to construct a simple two end-member mixing mass-balance model described by Laaksoharju (1990) and used in Smellie and Laaksoharju (1992), Banwart et al. (1992; 1994) and Banwart (ed) (1995). The main aim of the model was to differentiate in the groundwater between what is due to mixing/transport and what is due to water/rock reactions by using one variable such as Cl as a conservative tracer to create an ideal mixing model between two extreme waters. The model was used to predict concentrations for the other groundwater elements. A deviation between the predicted and measured value was interpreted as sink or source associated with reactions. No deviation for an element was taken to be an indication that transport and mixing determine that particular element concentration. However, the model seemed to have limitations when tracing a more complex system involving several end-members.

The subsequent groundwater modelling concept was named M3 (Multivariate Mixing and Mass-balance calculations) Laaksoharju and Skårman, (1995); Laaksoharju et al., (1999b,). In M3 modelling the assumption is that the groundwater is always a result of mixing and reactions. Initially, the method evaluates the contribution from the flow system i.e. mixing. Subsequently, contributions from reactions are considered. The model is an opposite approach to many other standard models, which use the reactions rather than the mixing, to determine the groundwater evolution.

The M3 method has been tested, evaluated, compared with standard methods and modified over several years within domestic and international research programmes supported by the Swedish Nuclear Fuel and Waste Management Company (SKB). The main test and application site for the model has been the Äspö HRL. Many of the examples used in this document are from an Äspö international groundwater modelling co-operation project report where one of the tools used was M3 (Laaksoharju and Wallin (eds.) 1997; Laaksoharju et al., 1999c). Mixing seems to play an important role at many crystalline and sedimentary rock sites where M3 calculations have been applied such as in different Swedish sites (Laaksoharju et al., 1998), Canada (Smellie and Karlsson, 1996), Oklo in Gabon (Gurban et al., 1998) and Palmottu in Finland (Laaksoharju et al, 1999a).

7.2 Principles of M3

The aim of M3 modelling is to calculate how *mixing* and *reactions* affect the obtained groundwater. The M3 modelling starts by comparing groundwater compositions. The assumption is that waters with similar compositions have a similar origin and have undergone similar mixing and reaction processes. To make this comparison with the highest possible accuracy several groundwater constituents have to be compared. This is performed in an optimum way using multivariate techniques. The result of the comparison is used to construct an *ideal mixing model* between the groundwater samples which seem to participate in the groundwater system studied. The ideal mixing model can employ different *reference waters* (selected waters that the other waters are compared with) depending on how the modeller prefers to describe the groundwater system in terms of origin, mixing and reactions. The calculations are therefore generally repeated several times to test different models where measured and even prescribed end-members (e.g. glacial meltwater) are tested for an optimum description of the measured groundwaters. These tests require knowledge of the paleo and present groundwater flow situation and moreover, specific isotopic data is required e.g. ^{14}C, ^{36}Cl, $\delta^{34}S$ before a end-member or reference water is correctly identified. The number of reference waters to be used is guided by the ideal mixing model which is dependent on the complexity of the groundwater signatures. The relevance of the chosen ideal mixing model is then tested by predicting the water conservative elements such as Cl and $\delta^{18}O$. If this test shows that the model can predict the conservative elements fairly well, the non-conservative elements are calculated and a deviation from the ideal mixing model can be used to show the effects from reactions. A source (gain) with respect to the ideal mixing model can indicate dissolution of a mineral; a sink (loss) can indicate precipitation of a mineral phase. The uncertainty of the model varies from case to case depending on the quality and geometrical distribution of the collected samples but in the Äspö case the resolution has been determined at ±10%.

7.3 Calculation steps in M3

The M3 method consists of 3 steps - *multivariate analysis*, followed by *mixing*, and finally by *mass-balance* calculations. The M3 calculations contain the following steps (the data used in this example is from the Äspö Hard Rock Laboratory (Laaksoharju et al., 1999c):

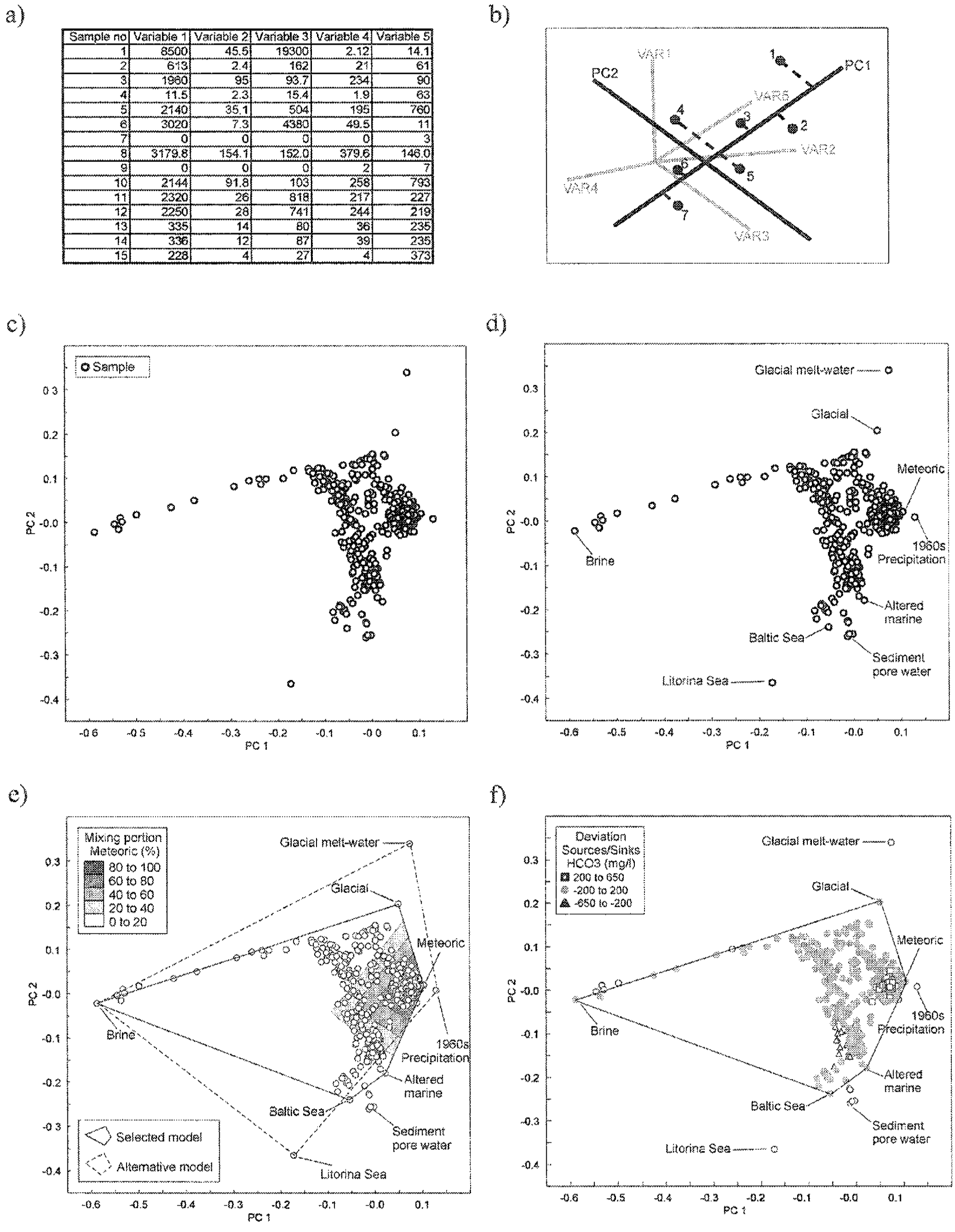
1. A data table containing groundwater compositions is compiled (Figure 7-1a). The table contains the groundwaters that will be compared with each other. The data set will determine the type of modelling that will be performed. Generally, the M3 modelling has to be run several times to test different options and build confidence in the selected model. This testing can include insertion

of modelled groundwater compositions such as glacial meltwater or ancient sea water compositions.

2. A standard multivariate technique, called Principal Component Analysis (PCA) is used for summarising the information in the data by using the major components Cl, Ca, Na, Mg, K, SO_4 and HCO_3 in combination with the isotopes δ^2H, $\delta^{18}O$ and ^3H. If other variables are used in the modelling the resolution and hence the type of modelling that can be performed may be different. If $\delta^{18}O$ is not included the effect from influx glacial meltwater cannot be modelled. These groundwater components and isotopes were chosen since: a) they are routinely analysed in most of the samples, b) the analytical accuracy is high, c) they contain most of the groundwater information. The principal components are equations of linear combinations which describe most of the information in the data (see figure 7-1b). PCA aims to describe as much of the information from the ten variables in the first equation (called the first principal component) as possible. As much as possible of the remaining information is described by the second principal component. The weights for the different variables in the equations are calculated automatically by the PCA. Generally, for groundwaters sampled at different depths at a site the first two principal components can be used to describe ~70% of the information in the data set. The third or fourth principal components do not usually contain useful information but this depends on the complexity of the examined data and the chosen variables. If the first two principal components contain most of the information, an x, y scatter plot can be drawn (see figure 7-1c). The x is the equation for the first principal component and y the equation for the second principal component. The plot is named the M3 plot and is used to visualise the clustering of the data as well as to identify extreme waters and useful *reference waters* for constructing the ideal mixing model. A reference water is a well-sampled or modelled groundwater composition which is useful for comparing the other samples to and helpful in understanding the groundwater origin and evolution. Some possible reference waters at the Äspö HRL are shown in Figure 7-1d.

3. Mixing calculations are used to calculate the contribution of mixing from the reference waters to the samples. Lines are drawn between the reference waters so a polygon is formed. By definition the selected reference waters can describe the observations inside the polygon. This polygon represents the ideal mixing model for the site where the assumption is that all the selected reference waters contribute in various degrees to the groundwater composition. The mixing portions are equal to the trigonometrical distance to the selected reference waters in the M3 plot (see 7-1e). The calculated mixing portion (%) can be used to describe the origin and the effects from the flow in the groundwater.

4. Mass-balance calculations are used to define the sources and sinks (mg/l) for different elements which deviate from the ideal mixing model (see Figure 7-1f). The mixing portions are used to calculate new values for the elements. No deviation from the measured value indicates that mixing can explain the element behaviour. The formula used in mass-balance calculation is: *Deviation = measured - calculated*. Deviations of water conservative elements such as Cl and $\delta^{18}O$ reflect model error. For non-conservative elements a source or a sink can be a result of mass-balance reactions. The evolution of the groundwater can thus be indicated and modelled.



Sample no	Variable 1	Variable 2	Variable 3	Variable 4	Variable 5
1	8500	45.5	19300	2.12	14.1
2	613	2.4	162	21	61
3	1960	95	93.7	234	90
4	11.5	2.3	15.4	1.9	63
5	2140	35.1	504	195	760
6	3020	7.3	4380	49.5	11
7	0	0	0	0	3
8	3179.8	154.1	152.0	379.6	146.0
9	0	0	0	2	7
10	2144	91.8	103	258	793
11	2320	26	818	217	227
12	2250	28	741	244	219
13	335	14	80	36	235
14	336	12	87	39	235
15	228	4	27	4	373

Figure 7-1: *Different steps in the M3 modelling; a) Data table containing measured or modelled groundwater compositions. b) The principle for PCA; seven groundwater samples and their locations in the multivariate space (VAR1-VAR5) and their projection on principal component 1 (PC1) are shown. PCA is used to obtain the maximum resolution of the data set. c) The result of the PCA showing principal components 1 and 2. d) Selection of possible reference waters - the other groundwaters are compared to these. e) Mixing calculations – the linear distance of a sample to the reference waters e.g. the portions of meteoric water (%) are shown in the figure for the selected ideal mixing model, the alternative model uses a new set of reference waters. f) Mass-balance calculations – the sources and sinks (mg/l) of carbonate (HCO_3) are shown which cannot be accounted for by using the ideal mixing model. The M3 model is applied to data from the Äspö HRL.*

The new approach in the M3 concept is that the information gathered using PCA can be further quantified in terms of mixing and reactions. Five reference waters were chosen at the Äspö site using the M3 method: Brine, Glacial, Baltic Sea, Altered marine and Meteoric (Figure 7-1e) (Laaksoharju and Wallin, (eds.), 1997; Laaksoharju et al., 1999c).

The existence of these five reference waters - Brine, Glacial, Baltic Sea, Altered marine and Meteoric waters - is also supported by the conceptual post-glacial scenario model in Figure 2-1. The selected reference waters for the current modelling are (the analytical data are listed in Table 7-1):

- **Brine reference water** which represents the deep brine type of water found in KLX02: 1631-1681m (Laaksoharju et al., 1995a).
- **Glacial reference water** which has been determined as a glacial water based on stable isotope values which indicate cold climate recharge in combination with an apparent ^{14}C age of 31,365 years (Smellie and Laaksoharju, 1992). This type of water is found in Äspö KAS03:129-134m.
- **Baltic Sea reference water** (also named **Marine water** in some of the examples in this document) which represents modern Baltic Sea water.
- **Altered marine reference water** (also named **Sea bed** or **Biogenic** water in some of the examples in this document) which represents Baltic Sea water altered by bacterial sulphate reduction (Laaksoharju ed., 1995). The response recorded in M3 was a high HCO_3 and a low SO_4. This water type is obtained in the HRL tunnel below the marine sediments.
- **Meteoric reference water** which represents a dilute non-saline shallow water found in HBH02: 7.5m.

In accordance with the conceptual model (see, Figure 2-1), the following four modelled or measured end-member water compositions were added to the data set (the analytical composition is listed in Table 7-1):

- *Glacial melt water;* represents a possible meltwater composition from the last glaciation >13000BP. Precipitation water composition 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, interpreted as sub-glacial precipitates, and collected from different sites on the west coast of Sweden (Tullborg and Larson, 1984). The $\delta^{2}H$ value (-158 ‰ SMOW) is a modelled value based on the equation ($\delta H=8\times\delta^{18}O+10$) for the meteoric water line.
- *Litorina Sea;* represents a modelled ancient Baltic sea water composition (8000-2000BP) with a Cl concentration of 6100 mg/l and was modelled based on $\delta^{18}O$ analysis of microfossils from the marine sediments in southern Finland (Kankainen, 1986). A similar Cl content was suggested by Sjöberg et al. (1984) based on measurements of interstitial water in postglacial black clays. The other constituents

were calculated based on dilution of ocean water to the appropriate Cl concentration.

- *Sediment pore water;* is an extracted pore water composition from marine sediments adjacent to Äspö (Landström et al., 1994). The major component chemistry in the pores resembled modern Baltic Sea values except for sulphate and bicarbonate. Based on this knowledge the modern isotope values measured from the Baltic Sea water were used since the isotopes were not analysed in the pore water.

- *1960 precipitation;* represents an average precipitation from 1960. Modern precipitation with a calculated high tritium (100 TU) content was used to represent precipitation from that period. This value is based on measured tritium values found in present-day shallow groundwater at Äspö and taking into account a half-life of 12.43 years for tritium.

Table 7-1: Analytical or modelled data for the selected reference waters and end-members used for the Äspö site modelling.

	ID code	Date	SNO	Na	K	Ca	Mg	HCO_3	Cl	SO_4	^3H	^2H	^{18}O
Brine reference water	SGKLX02	93-08-03		8500	45.5	19300	2.12	14.1	47200	906	4.2	-44.9	-8.9
Glacial reference water	KAS03	89-02-21	1569	613	2.4	162	21	61	1220	31.1	0.1	-124.8	-15.8
Sea reference water	SEA01	92-08-28	1994	1960	95	93.7	234	90	3760	325	42	-53.3	-5.9
Altered marine reference water	SA1094A	92-04-23		2140	35.1	504	195	760	4490	111.6	17	-60.3	-7.3
Meteoric reference water	HBH02	91-09-11	1931	11.5	2.3	15.4	1.9	63	5	13.2	59	-77.1	-10.2
Glacial end-member	Glacial			0.17	0.4	0.18	0.1	0.12	0.5	0.5	0	-158	-21
Litorina Sea end-member	Litorina			3180	154	152	380	146	6100	527	0	-35	-5
Sediment pore water end-member	SAS48			2144	91.8	103	258	793	3383	53.1	0	-61	-7
Precipitation end-member	1960s Precipitation			0.4	0.29	0.24	0.1	12.2	0.23	1.4	100	-80	-10.5
Possible Subglacial end-member	Subglacial			3550	0	2985	0	0	10766	1472	0	-158	-21

7.4 Demonstration of how M3 calculates effects from mixing and mass balances

To demonstrate how M3 models the groundwater composition in terms of mixing and mass balances, samples from the KLX02 borehole in Laxemar were used. The measured values for Cl, oxygen-18 ($\delta^{18}O$) and HCO_3 along borehole KLX02 were compared with calculated M3 values (Figure 7-2). Figure 7-2d shows a detailed picture of how M3 calculates the contribution of HCO_3 from the different reference waters and the effects from water/rock interaction.

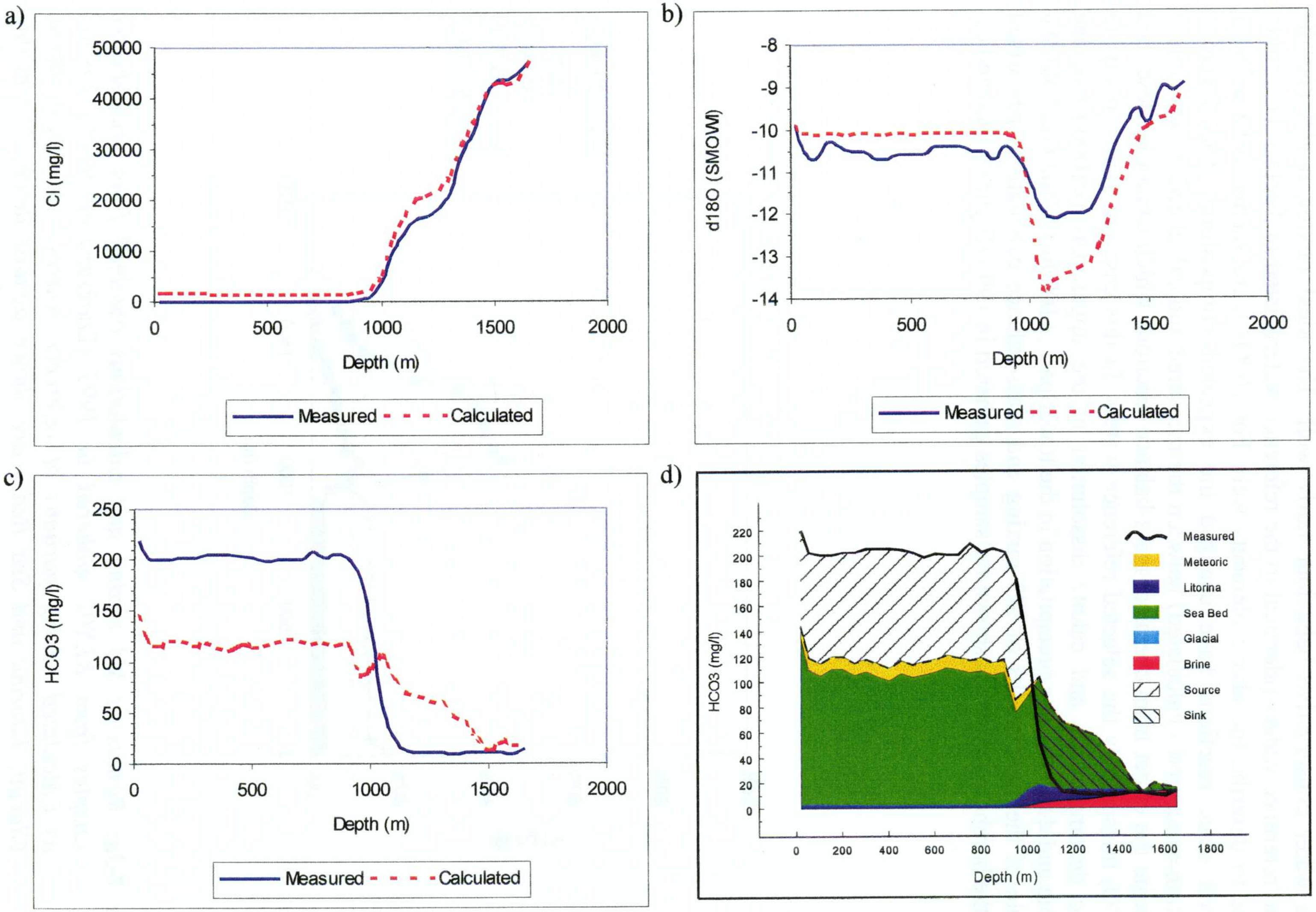


Figure 7-2: *Measured values for a) Cl, b) oxygen-18 ($\delta^{18}O$) and c) HCO_3 along the borehole KLX02 are compared with calculated M3 values. Figure d) shows a detailed picture of how M3 calculates the contribution of HCO_3 from the different reference waters. The deviation=measured - calculated defines the contribution from the reference waters and the source and sink which is due to water/rock interaction. In this case the source is due to organic decomposition and calcite dissolution in the upper part (<1000m) of the borehole and due to calcite precipitation in the lower part (>1000m) of the borehole.*

Figure 7-2 indicates that the M3 model seems to predict Cl and oxygen-18 values which have a water conservative behaviour fairly well. The ideal mixing model and the selected reference waters (identical to the reference waters listed in Table 7-1) seem to be able to describe the above elements well. For HCO_3 there seems to be a larger deviation since reactions have changed the expected composition. The deviation (deviation=measured - calculated) between the measured and calculated values is used to indicate the effect from chemical mass-balance reactions which cannot be described by HCO_3 transport by the selected reference waters. In this case the source is due to organic decomposition and calcite dissolution in the upper part (<1000m) of the borehole and due to calcite precipitation in the lower part (>1000m) of the borehole. An example of the final results of M3 mixing and mass-balance calculations performed along the borehole KLX02 is shown for samples gathered in 1993 (Figure 7-3a,b and c).

a)

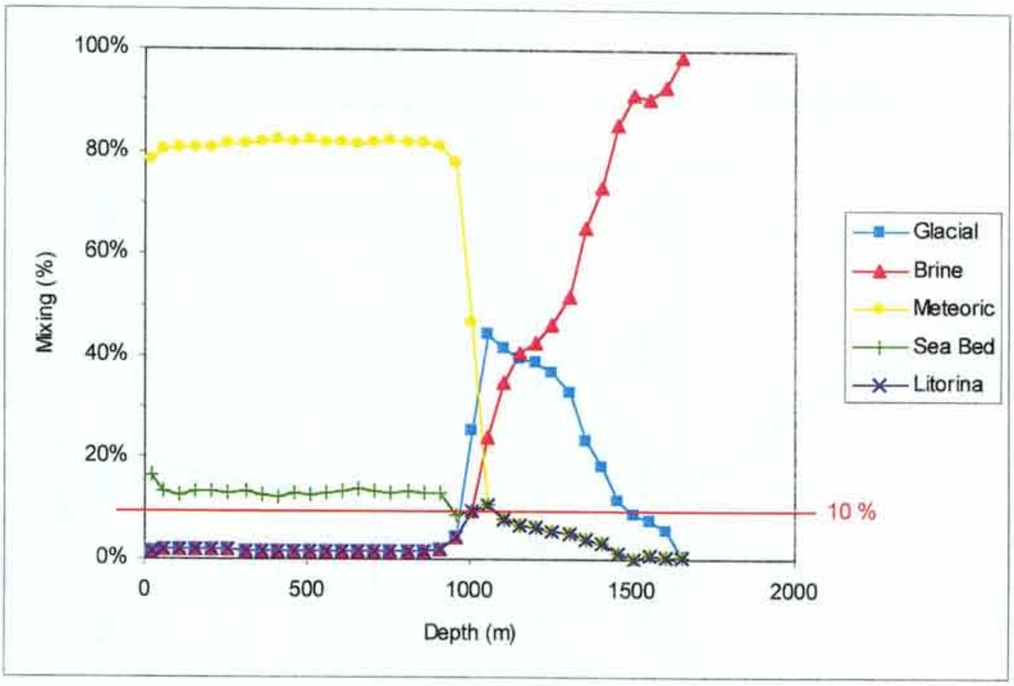
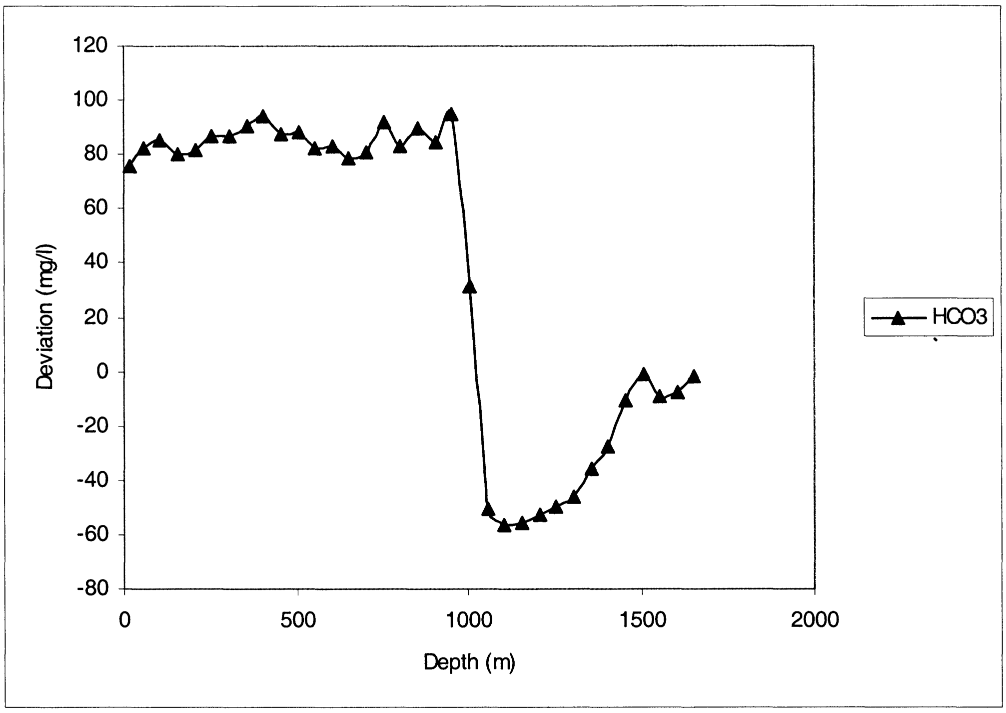


***Figure** 7-3a: Results of M3 mixing and calculations obtained from groundwater samples from KLX02 gathered in 1993 (Laaksoharju et al., 1995a). a) Calculated mixing portions of reference waters - Meteoric, Brine, Glacial, Litorina and Sea Bed - are shown against depth. The mixing portions add up to 100% for all the samples. A mixing portion of less than 10% is regarded as under the detection limit for the M3 method and is therefore uncertain.*

b)



c)

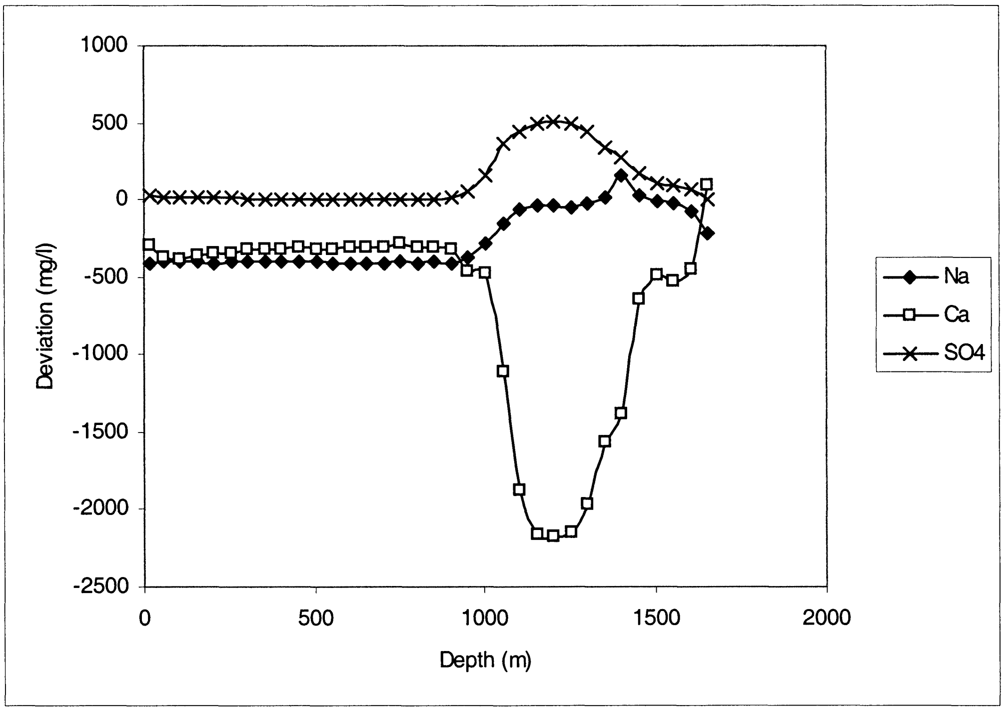


Figure 7-3b and c: *Results of M3 mass-balance calculations obtained from groundwater samples from KLX02 gathered in 1993 (Laaksoharju et al., 1995a).*

b) Deviation of the element HCO_3. c) Deviation of Na, Ca and SO_4. A source (positive value) and a sink (negative value) can be a result of mass-balance reactions.

7.5 M3 computer code

The M3 calculations can be performed using the M3 computer code (Laaksoharju et al., 1999b) which runs as a toolbox under MATLAB® (version 5 or higher) and the platform is Windows® 95/98 and NT 4.0. Figure 7-4 shows a window view from the M3 code.

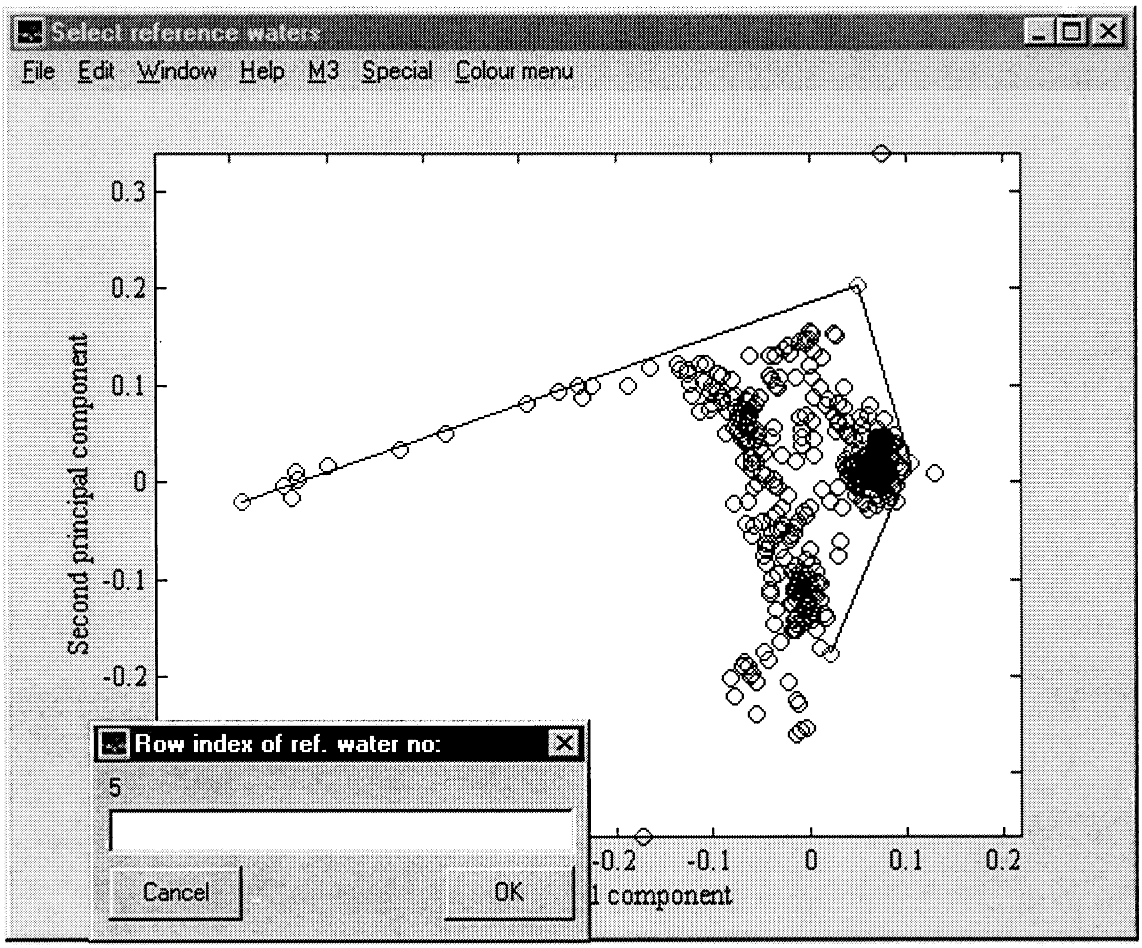


Figure 7-4: *Window view from the M3 code showing the modelling step when selecting reference waters to construct the ideal mixing model for a site.*

7.6 Advantages and disadvantages of M3 and comparison with standard tools

M3 can be regarded as a simple yet powerful reaction-transport model. The model requires measured groundwater data and initial waters (reference waters) affecting the site. The model compares all observations in respect to the initial waters and determines the degree of mixing and the amount of element gain or loss which is interpreted as being associated with reactions. The results of the modelling can be used to determine the origin of the groundwater, flow paths, degree of hydraulic dynamics and type of dominating reactions. No thermodynamic database is used in the M3 model, no geological or hydrogeological information and no space or time is modelled. This type of information can be used to validate the outcome of the modelling. Relatively little site information is therefore required since there is no need for detailed geological or hydrogeological data to be included in the model. The results can be visualised in space by using 3D interpolation techniques (e.g. Figure 8-9). If transient modelling has to be performed this can be done by using groundwater data from a time series. If there is no time series available the modelling can be done by increasing (e.g. meteoric water) or decreasing the mixing portions to simulate a transient groundwater flow situation.

The difficulties with M3 can be: 1) New model with relative few test cases. 2) Complex multivariate mathematics is required. 3) The same equation in PCA is used for all the observations which may lead to low resolution for some of the observation. A low resolution may cause uncertainty in the mixing and mass-balance calculations. 4) Multivariate statistics require quite a few observations before a reliable calculation can be performed. 5) There is no test of what type of reaction is occurring only gain/loss of elements which may be interpreted as a result of a certain reaction.

It is important to note that the modelling is always relative to the selected reference waters. The boundary conditions of the modelling can be changed depending on the selection of reference waters (Figure 7-1e). If, for example, the chosen reference water for Glacial water is changed to the end-member composition (Glacial melt water in Figure 8-7), the average mixing portion of glacial water at the Äspö site changes from 22% to 16%. If only end-member compositions are used as reference waters in the M3 calculation, the average Glacial mixing portion is 19%. When a glacial end-member is used in the modelling, the model describes the proportions of the groundwater that are derived from melting of the continental ice. When a glacial reference water is used which is sampled in the bedrock, the modelling describes what mixing and reactions have to take place inside the bedrock after mixing with the existing groundwater. For modelling purposes such as mass-balance calculations greater accuracy is generally obtained if reference waters sampled in the bedrock are used rather than modelled end-member compositions.

The conceptual uncertainty of the ideal mixing model consists of uncertainties concerning changes in the reference waters over time, and from using several reference waters to describe waters where perhaps only one or two reference waters participate in reality in the groundwater formation. The model compensates by giving less influence to a reference water with distant water composition, although a trace amount of e.g. brine water may bias the calculations. A deviation from the water conservative elements such as Cl and $\delta^{18}O$ can indicate errors in the model and can be used to test optimum selection of reference waters. The sampling errors and analytical uncertainties add bias to the model but these are common for all the groundwater models which are applied to site data.

Tests have shown that the M3 calculations describe the Äspö site data by a factor of 2.9 times better for Cl and $\delta^{18}O$ compared with a standard univariate method where Cl used as a water conservative tracer is used to predict $\delta^{18}O$ behaviour and vice versa. Back-propagation tests where 400 given mixtures of groundwaters were modelled using the M3 concept show that the accuracy of the mixing calculations is generally ±10.5% (Laaksoharju et al., 1999b). Small errors in the prediction of conservative element behaviour may lead to large errors in the mass-balance calculations. A mixing portion of less than 10% is regarded as under the detection limit and is therefore uncertain.

The same reference waters used in M3 modelling can be identified, but with a lower resolution, using other common groundwater evaluation tools (see Figures 7-5a,b,c and d). The possible influence of several end-members on the groundwater and the possible ambiguity can be identified by a simple correlation test between water conservative constituents such as Cl versus $\delta^{18}O$ (Figure 7-5c). If the correlation is low there are two or more end-members involved in the groundwater system and a multivariate approach such as M3 should be employed. Tests have shown that the M3 calculations describe the Äspö site data with a higher accuracy than many univariate methods. Small errors in the prediction of conservative element behaviour may lead to large errors in the mass-balance calculations. A low resolution may lead to difficulties in (c.f. Figures 7-5a and d) identifying the end-members and in correctly modelling the system.

The results from standard groundwater modelling are compared with the approach used in M3 in Figure 7-6. Despite the different approaches used in the groundwater models the results from the modelling can be compared and integrated at fracture scale (Banwart (ed.), 1995). At site scale the comparison is difficult since the standard geochemical models generally use a simplified flow description, consisting of one or two water conservative elements and are therefore generally not applicable at site scale. This can be circumvented by having a step-wise modelling approach following the groundwater flow paths (Pitkänen et al., 1999). In all modelling (including M3) it is important to note that mathematics help to summarise, simplify and model the information but geochemical understanding and additional information e.g. hydrogeological and geological evolution of the site in combination with expert knowledge are needed for the explanation and critical evaluation of the results.

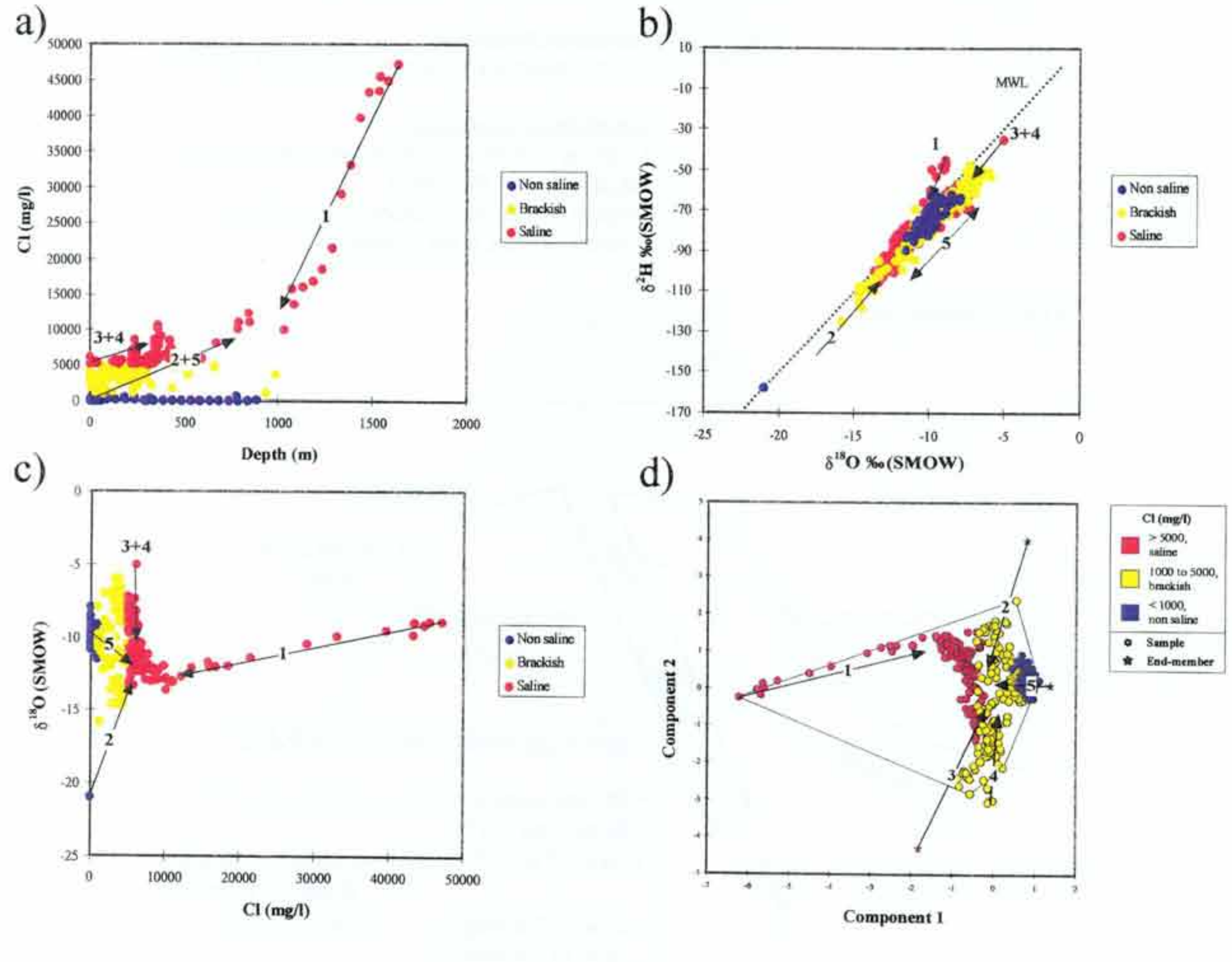
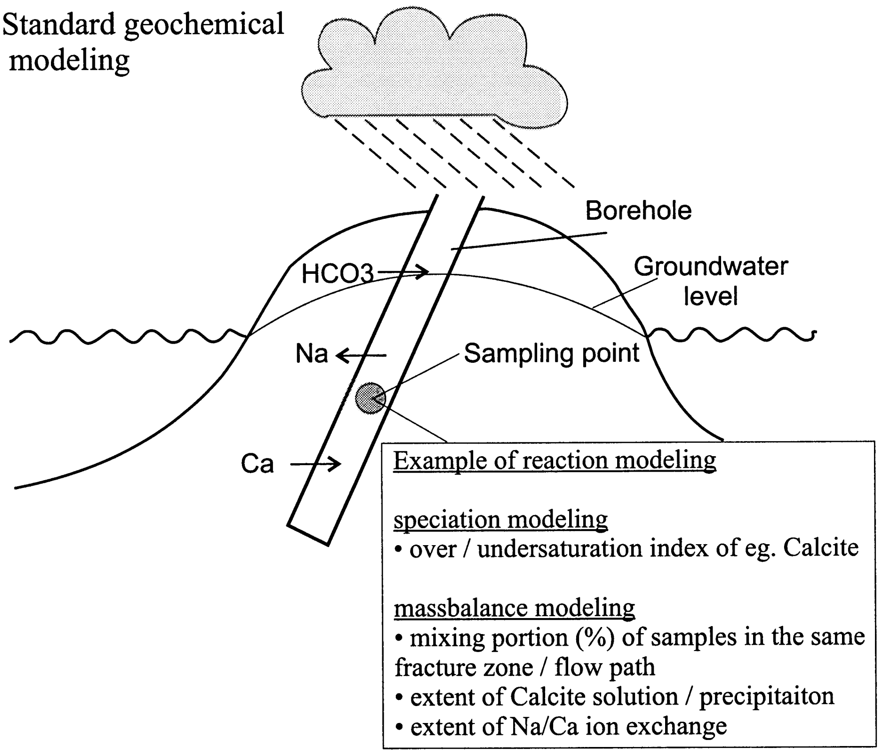


Figure 7-5: Different methods and plots used to trace the origin of the groundwater at the Äspö site; a) Cl versus depth, b) δ^2H versus $\delta^{18}O$, c) $\delta^{18}O$ versus Cl, d) M3 model. Where 1=brine, 2=glacial, 3=marine, 4=altered marine and 5=meteoric groundwater trends. The groundwater samples have been colour coded based on the Cl content into saline, brackish and non-saline groundwaters. The same data set has been used in all the models.

a) Standard geochemical modeling

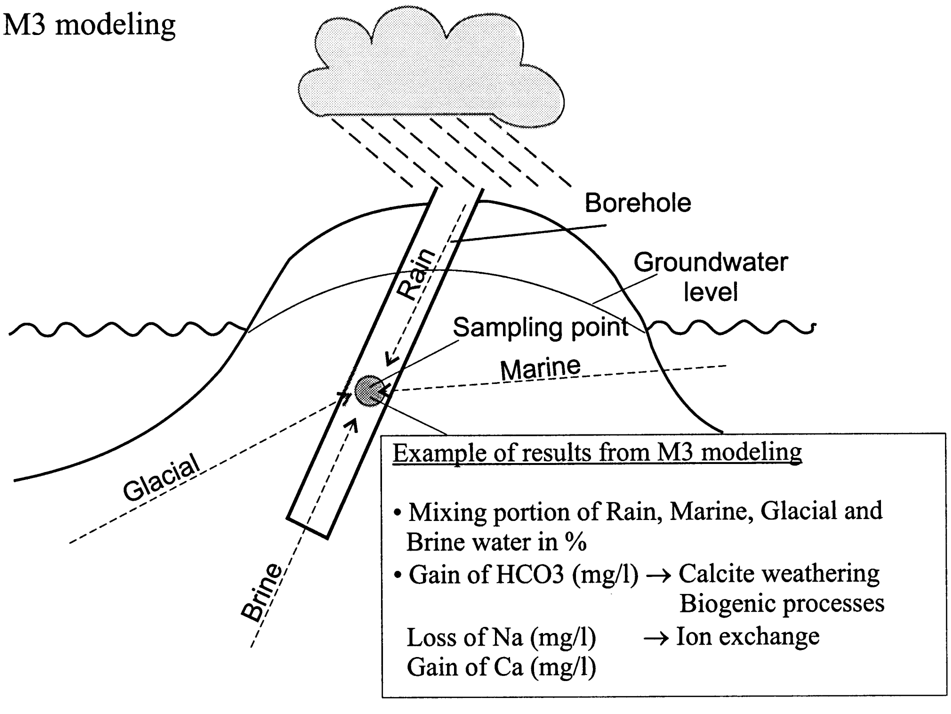


Example of reaction modeling

speciation modeling
- over / undersaturation index of eg. Calcite

massbalance modeling
- mixing portion (%) of samples in the same fracture zone / flow path
- extent of Calcite solution / precipitaiton
- extent of Na/Ca ion exchange

b) M3 modeling



Example of results from M3 modeling

- Mixing portion of Rain, Marine, Glacial and Brine water in %
- Gain of HCO3 (mg/l) → Calcite weathering
  Biogenic processes
  Loss of Na (mg/l) → Ion exchange
  Gain of Ca (mg/l)

Figure 7-6: *Comparison of approaches and results in standard modelling versus M3 modelling: a) The standard way of modelling (speciation and mass-balance modelling) is orientated towards reactions and mixing in fracture scale. b) The M3 way of modelling - first the origin is traced and expressed as mixing portions then the effects of reactions are calculated. Despite the different approaches used in the groundwater models the results from the modelling can be compared at fracture scale.*

8 Results of M3 modelling

In the following sections some examples of M3 modelling are given such as explorative analysis, modelling of Äspö groundwaters, comparison of three Swedish sites and modelling of a natural analogue site in Africa.

8.1 M3 used for explorative analysis

PCA plots are used in order to show how M3 can be used for explorative analysis (to identify and investigate major groundwater characteristics) of the Äspö site. The PCA plot can be used to: a) visualise the groundwater information, b) find the interrelationship among the observations, c) find clusters which are useful for understanding and classifying the data and, d) to identify groundwater end-members and reference waters.

The superimposed PCA plots with results from the M3 modelling are here called *M3 plots*. Examples of M3 plots used for explorative groundwater analysis are: 1) depth distribution (Figure 8-1), 2) water type classification (Figure 8-2), 3) measured pH values (Figure 8-3) and 4) calculated Eh values (Figure 8-4). Groundwater changes in the major fracture zones in the HRL tunnel with time are shown in Figure 8-5. The above plots show the different features in relation to the major groundwater chemistry.

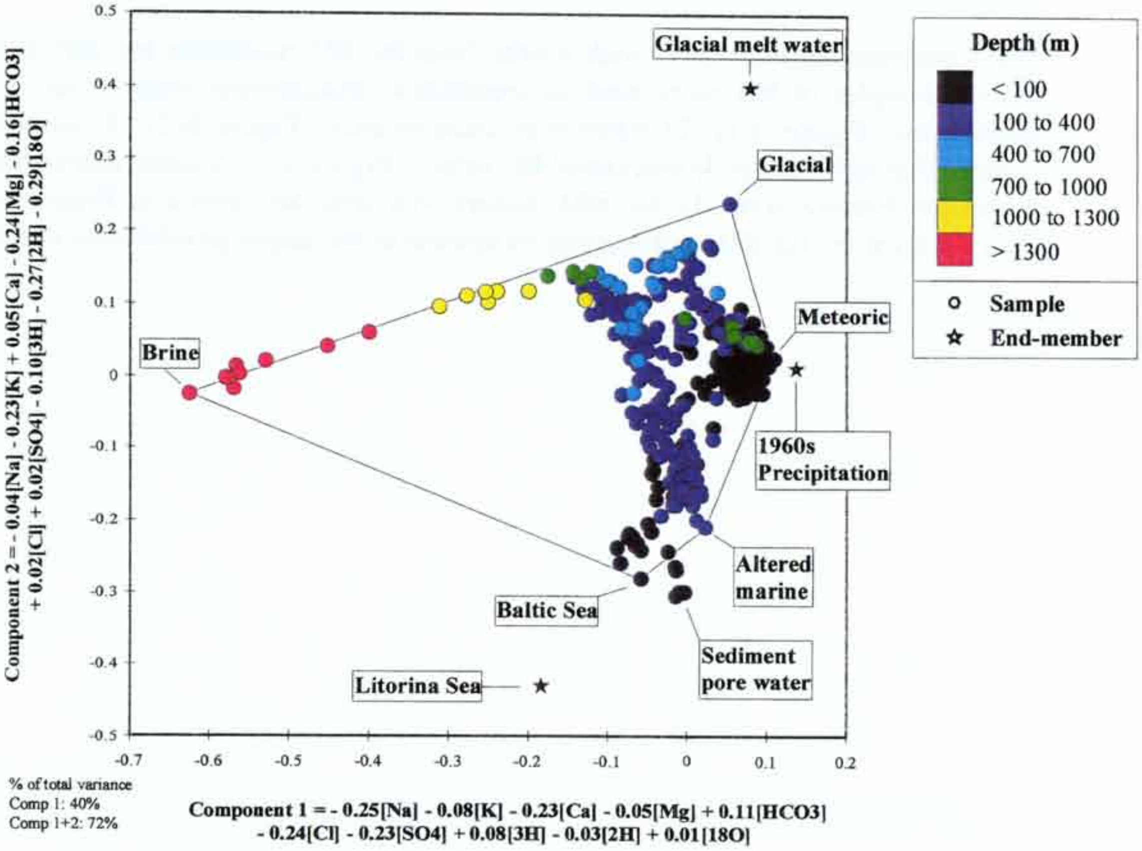


Figure 8-1: *M3 plot showing the depth distribution of the groundwater samples. The superimposed colour coding of the observations i.e. the red colour shows observations collected from a depth larger than 1300m.*

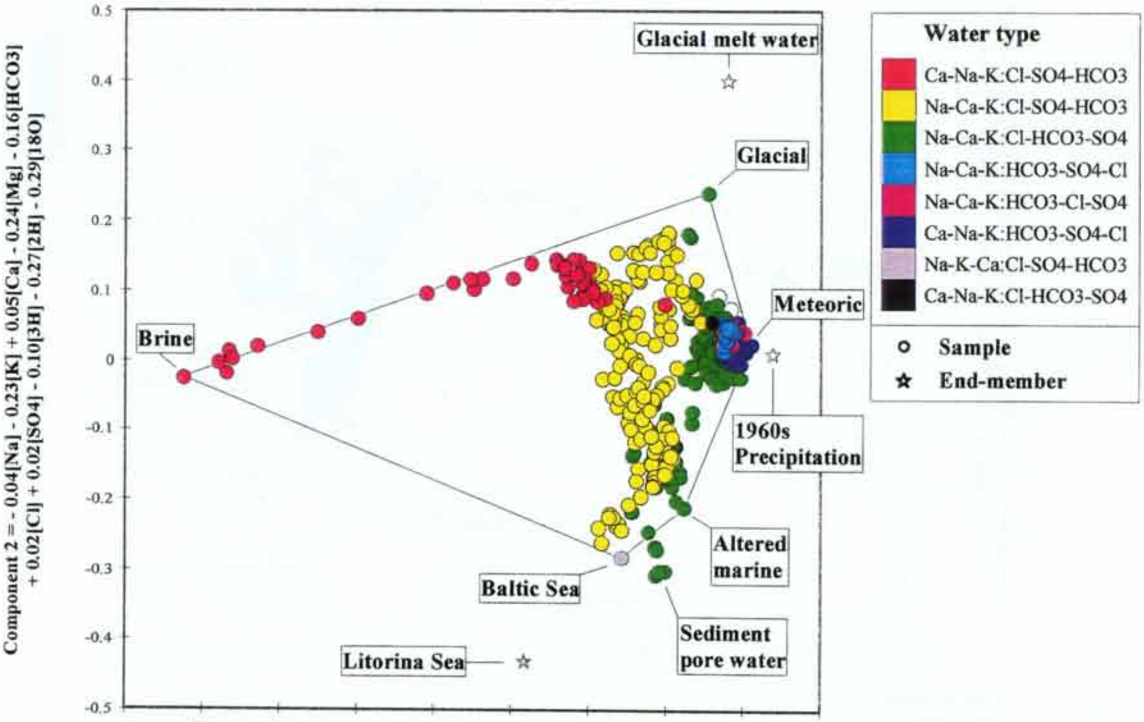


Figure 8-2: *M3 plot showing the distribution of groundwaters classified according to the dominating anions and cations. The superimposed colour coding of the observations i.e. the red colour shows samples consisting of a [Ca-Na-K:Cl-SO_4-HCO_3] type of water.*

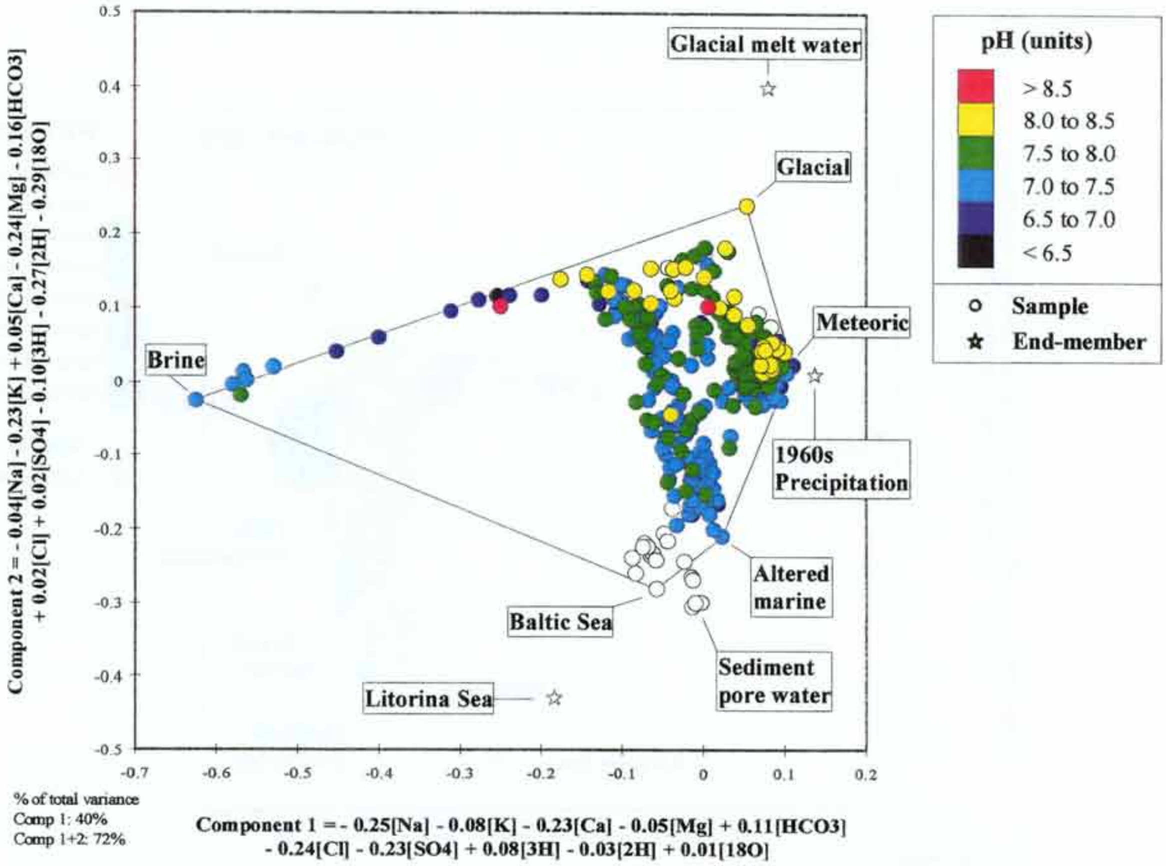


Figure 8-3: *M3 plot showing the distribution of measured pH values in the groundwaters. The superimposed colour coding of the observations i.e. the red colour shows a sample with a pH higher than 8.5. Open circles indicate missing data. The saline samples showing a pH range of 6.5-7.0 are believed to be due to less accurate measurements associated with a test of the Tube sampler (Laaksoharju et al. 1995a).*

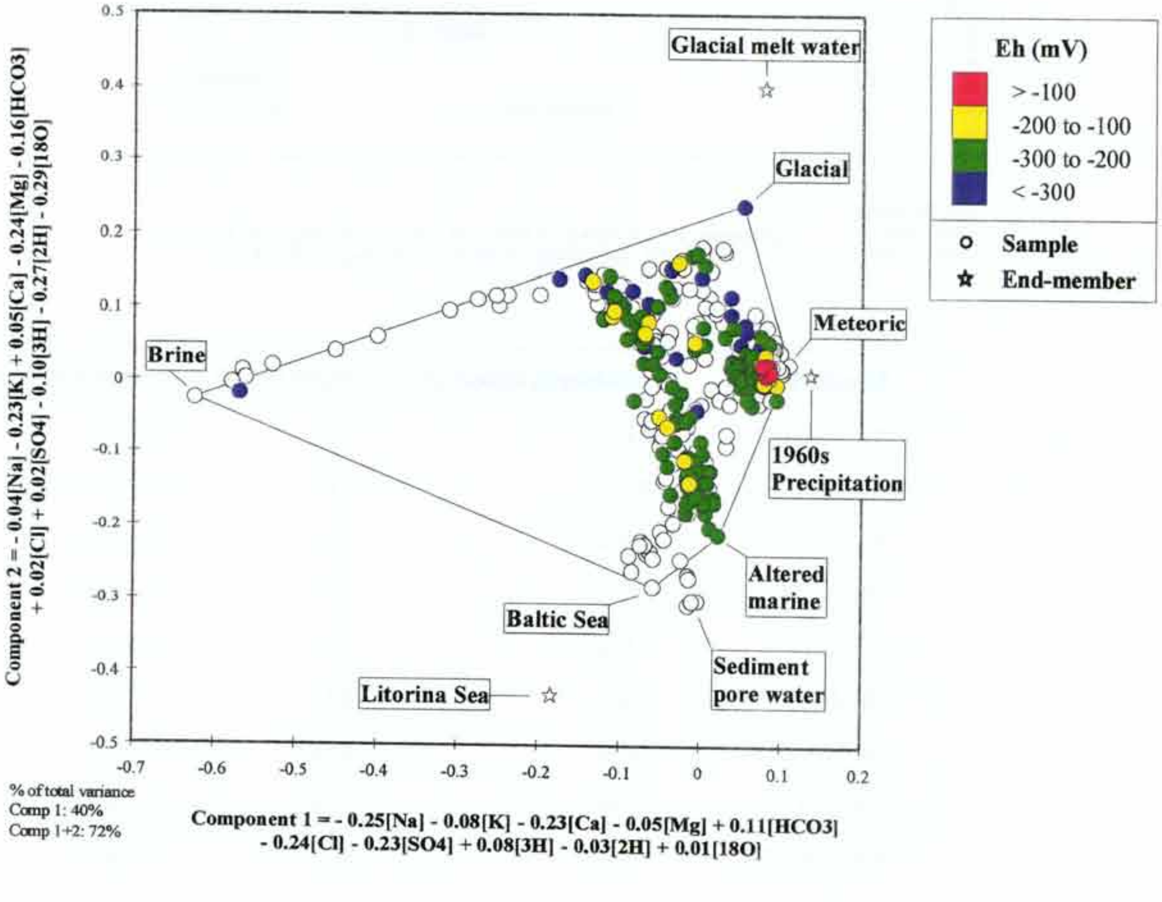
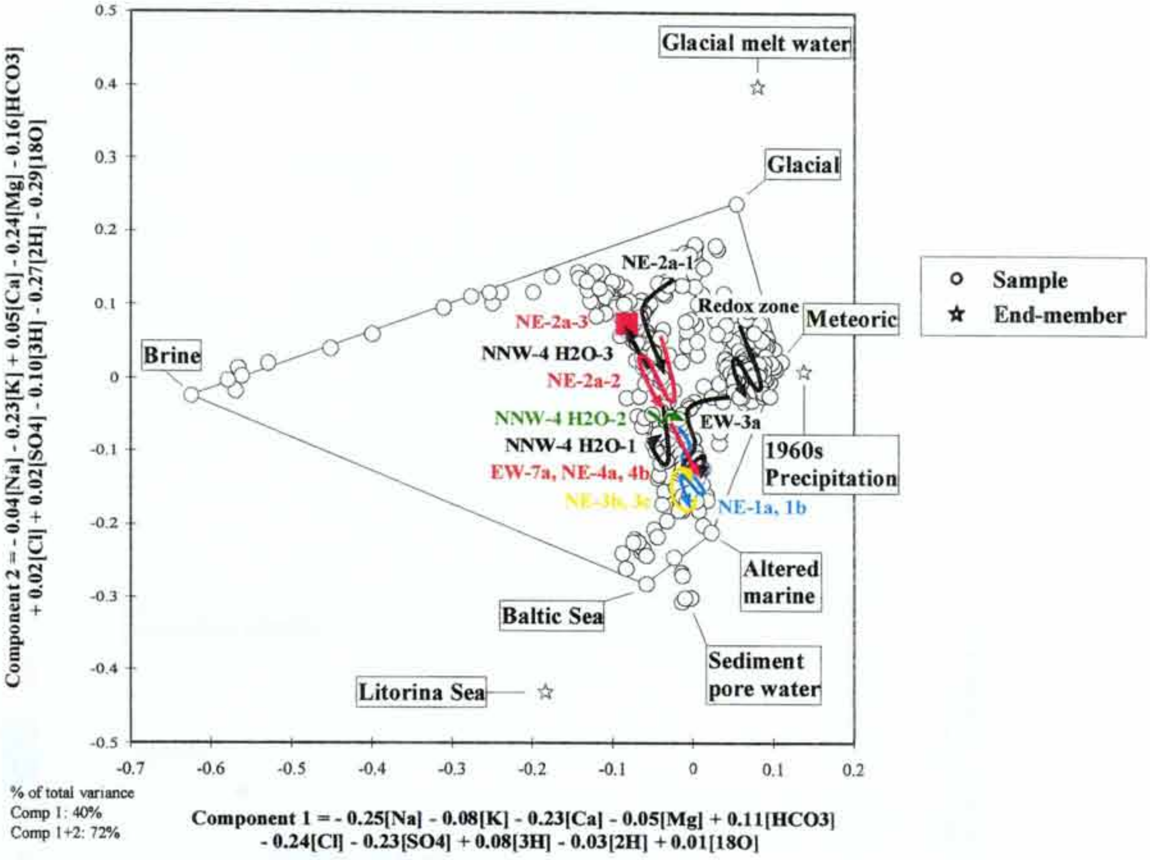


Figure 8-4: *M3 plot showing the distribution of calculated Eh values (according to methodology suggested by Grenthe et al, 1992). The superimposed colour coding of the observations i.e. the red colour shows a sample with an Eh above -100mV. Open circles indicate observations lacking iron data needed for the Eh calculations.*



Fracture zone	Position in tunnel (m)	Depth (masl)	Monitoring time
Redox zone	513	-71	3.4 years
EW-7a, NE-4a, 4b	822	-110	3.1 years
NE-3b, 3c	1002	-135	2.7 years
NE-1a, 1b	1320	-179	2.4 years
EW-3a	1442	-196	2.1 years
NE-2a-1	1628	-221	1.6 year
NE-2a-2	1893	-252	1.6 year
NE-2a-3	2536	-333	2.4 months
NNW-4 H2O-1	2057	-272	1.3 year
NNW-4 H2O-2	2160	-285	1.3 year
NNW-4 H2O-3	3214	-417	1 day

Figure 8-5: *M3 plot showing the groundwater changes with time in the major fracture zones in the HRL tunnel. The groundwater samples are sampled ±100m from the actual fracture zone. The name, position and depth as well as the length of the chemical monitoring of the fracture zones are listed in the table (data from Laaksoharju and Skårman 1995).*

Depth (Figure 8-3) shows a complex dependency on the groundwater chemistry which is in good agreement with the information in Figure 6-1. Figure 8-2 shows that the non-saline waters consist of a [Na-Ca-K:HCO_3-SO_4-Cl] alternatively a [Ca-Na-K:HCO_3-SO_4-Cl] and changing to a [Na-Ca-K:Cl-HCO_3-SO_4] water at the near-surface (0-100m). The brackish groundwater consists of a [Na-Ca-K:SO_4-HCO_3] water at a depth of 100-350m. The saline groundwaters found generally at a depth of 350-1700m consist of a [Na-Ca-K:Cl-SO_4-HCO_3] alternatively of a [Ca-Na-K:Cl-SO_4-HCO_3] type of water. The groundwaters at the Äspö site seem to have pH values in a range of 6.5-9 units (Figure 8-3). The pH buffering is mainly controlled by calcite and feldspar weathering.

The calculated Eh values, using the relationship associated with the iron redox couples according to Grenthe et al., (1992), show that the values decrease with depth in the range of -100 to -300mV (Figure 8-4). The measured Eh values coincide with the calculated ones. Of importance for the safety assessment of spent nuclear fuel is the fact that at these Eh values uranium exists in a reduced hexavalent (+IV) form and is extremely insoluble (Stumm and Morgan, 1981). The ferrous and ferric iron minerals generally govern the redox properties in groundwater (Wikberg 1987; Grenthe et. al., 1992). In some cases, however, other systems are thought to dominate e.g. the uranium or sulphide system (Blomqvist et al., 1995; Pitkänen, 1999). Regardless of which system controls the Eh it has been clearly demonstrated that the deep groundwaters are reducing, and that the dissolved oxygen in the infiltrating surface water is consumed by microbiological processes. The effective oxygen consumption by bacteria increases the general opinion that anoxic (oxygen free) conditions could always be expected in the deep groundwater (Wikberg in Rhén (ed), 1997).

Groundwater composition changes associated with the major fracture zones in the HRL tunnel (Figure 8-5) show a complex pattern. Most of the groundwaters in the major fractures seem to evolve, sometimes with large fluctuations over time, into groundwaters with a marine signature. This is not surprising since the HRL tunnel is covered or surrounded by the Baltic Sea. There are however fractures which show an evolution towards a brine signature or even no evolution at all and this indicates stagnant conditions over the measured time span (2.4 months). The advance of the tunnel construction, location along the tunnel, depth and hydrological properties determine the groundwater evolution of the fracture groundwater with time.

Figure 8-6 shows an extreme case of how the groundwater composition in the borehole can change during drilling, open hole and fracture sampling (the data used is identical with data in Figure 4-4). The mixing evolution to the brine may in many cases be enhanced because of this kind of perturbation. The uncertainty range (±10%) of M3 modelling is also shown in Figure 8-6. The uncertainty range covers the uncertainty of the groundwater composition from drilling, sampling, chemical analysis and modelling. Figure 8-7 shows M3 used for different scenario modelling.

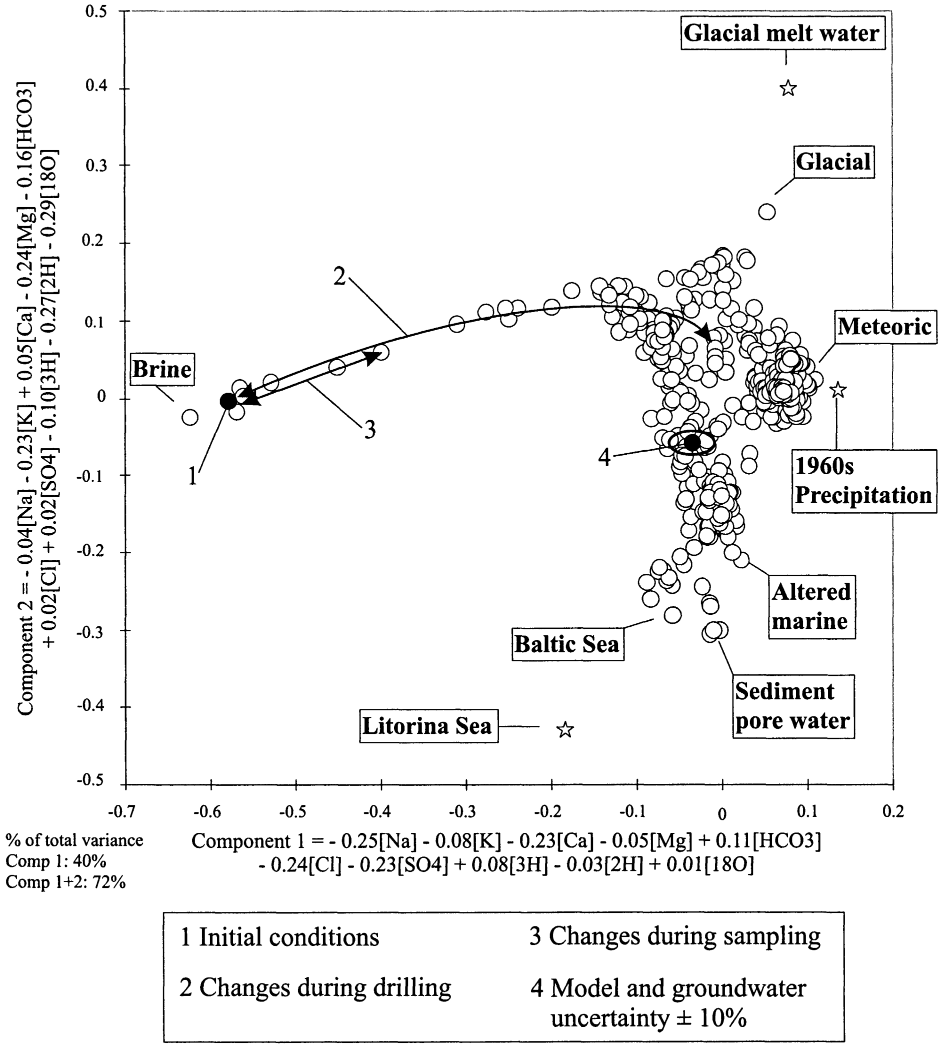


Figure 8-6: *M3 plot used to illustrate the initial groundwater conditions (1), groundwater changes during drilling in the open borehole (2), packer sampling (3) (first strike sample and last sample when sampling a sealed-off section) for the groundwater samples at a depth of 1420m-1705m at KLX02 in Laxemar (Laaksoharju et al., 1995a). The changes are extreme in this particular case due to borehole activities at large depths which increase the potential for disturbances. The plot is also used to illustrate how much the effect from the general uncertainty of ±10% (4) affects the position of a sample in the PCA plot. The uncertainty range covers the uncertainty of the groundwater composition from drilling, sampling, chemical analysis and modelling.*

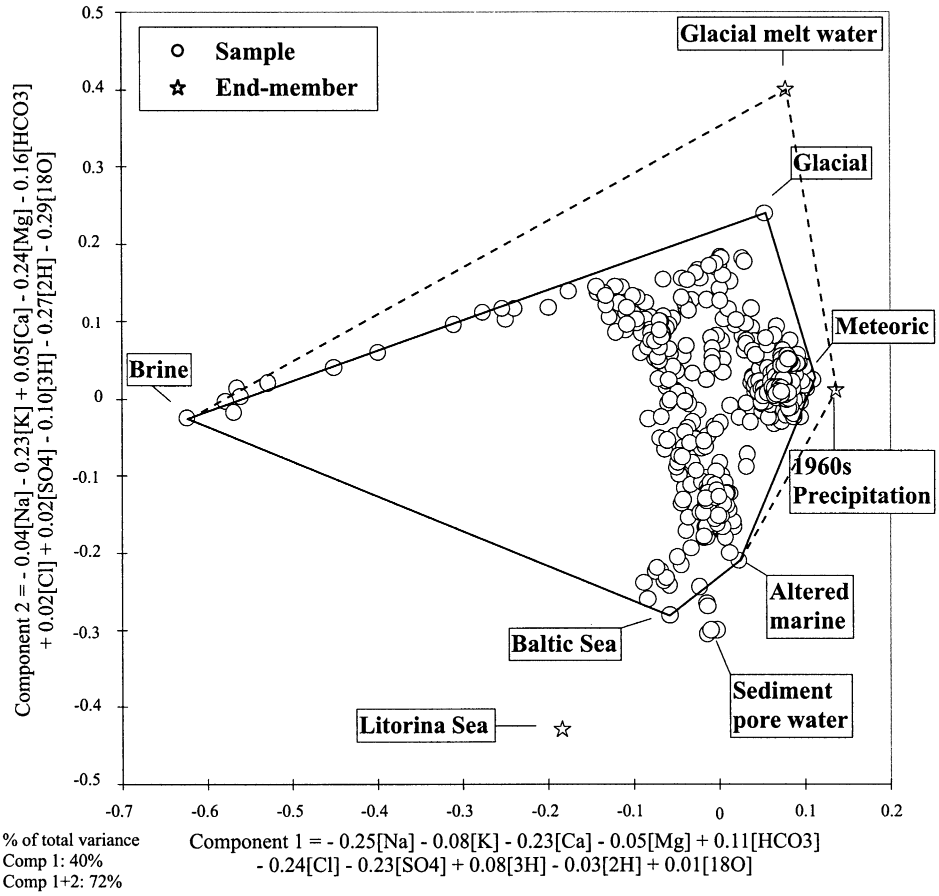


Figure 8-7: *M3 plot used to test the effect on the M3 calculations by changing the reference waters and hence simulating a new groundwater system. The original reference water – Meteoric - is changed to 1960 Precipitation, and Glacial is changed to the reference water Glacial melt water. The change affected the mixing calculations by an average of 8% (Laaksoharju et al., 1998).*

8.2 M3 modelling of Äspö Groundwaters

8.2.1 Reactions considered in M3 modelling

In theory thousands of chemical reactions could be written involving the water, solids and gases in regional aquifers such as those at the Äspö site. There are eight main categories of reactions and processes that control the chemistry of most groundwaters: precipitation-dissolution, acid-base, complexation, substitution-hydrolysis, oxidation-reduction, ion-filtration-osmosis, dissolution and exsolution of gases and sorption - desorption. Worldwide site modelling has revealed that the actual number of reactions that dominate the groundwater chemistry is quite small (Alley, ed., 1993) such as:

1) Introduction of CO_2 gas in the unsaturated zone
2) Dissolution of calcite and dolomite, and precipitation of calcite
3) Cation exchange
4) Oxidation of pyrite and organic matter
5) Reduction of oxygen, nitrate, and sulphate, with production of sulphide
6) Reductive production of methane
7) Dissolution of gypsum, anhydrite and halite
8) Incongruent dissolution of primary silicates with formation of clays

Since much of the Äspö modelling aimed to describe the groundwater changes due to the tunnel construction this added an important constraint in the modelling, namely to focus on the fast short-term reactions in the modelling. The relatively low temperature (at -200m = 11°C; the gradient is 1.6°C per 100m) of the groundwater hinders equilibrium being established between the groundwater and fracture minerals. Instead, recent research (Pedersen and Karlsson, 1995) has shown that microbes mediate in many reactions that otherwise would not take place. Organic material (CH_2O) generally plays an important role in these kinds of biogenic processes. The processes that are of major influence on the obtained groundwater at the Äspö site are biological processes, redox reactions, calcite dissolution/precipitation and ion exchange. The following six major reactions have been modelled in detail within the Äspö HRL research programme:

1) **Organic decomposition:** This reaction is detected in the unsaturated zone associated with Meteoric water. This process consumes oxygen and adds reducing capacity to the groundwater according to the reaction (after Pedersen and Karlsson, 1995): $O_2 + CH_2O \rightarrow CO_2 + H_2O$. M3 reports a gain of HCO_3 as a result of this reaction.

2) **Organic redox reactions:** An important redox reaction is reduction of iron III minerals through oxidation of organic matter: $4Fe(III) + CH_2O + H_2O \rightarrow 4Fe^{2+} + 4H^+ + CO_2$. M3 reports a gain of Fe and HCO_3 as a result of this reaction. This reaction takes place in the shallow part of the bedrock associated with influx of Meteoric water.

3) **Inorganic redox reaction:** An example of an important inorganic redox reaction is sulphide oxidation in the soil and the fracture minerals containing pyrite according to the reaction: $HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$. M3 reports a gain of SO_4 as a result of this reaction. This reaction takes place in the shallow part of the bedrock associated with influx of Meteoric water.

4) **Dissolution and precipitation of calcite:** There is generally a dissolution of calcite in the upper part and precipitation in the lower part of the bedrock according to the reaction: $CO_2 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$. M3 reports a gain or a loss of Ca and HCO_3 as a result of this reaction. This reaction can take place in any groundwater type.

5) **Ion exchange:** Cation exchange with Na/Ca is a common reaction in groundwater according to the reaction: $Na_2X_{(s)} + Ca^{2+} \rightarrow CaX_{(s)} + 2Na^+$, where X is a solid substrate such as a clay mineral. M3 reports a change in the Na/Ca ratios as a result of this reaction. This reaction can take place in any groundwater type.

6) **Sulphate reduction:** Microbes can reduce sulphate to sulphide using organic substances in natural groundwater as reducing agents (Laaksoharju ed., 1995) according to the reaction: $SO_4^{2-} - + 2(CH_2O) + OH^- \rightarrow HS^- + 2HCO_3^- + H_2O$. This reaction is of importance since it may cause corrosion of the copper capsules. Vigorous sulphate reduction is generally detected in association with marine sediments that provide the organic material and the favourable salinity interval for the microbes. M3 reports a loss of SO_4 and a gain of HCO_3 as a result of this reaction. This reaction modifies the seawater composition (the water type is named Altered Marine) by increasing the HCO_3 content and decreasing the SO_4 content. For more details see section 8.2.4.

As an example of results from the mixing and mass-balance calculations in M3 the behaviour of the carbonate system in association with meteoric water at the Äspö site is shown in Figure 8-8. Input of organic carbon into shallow groundwater provides a possible energy and carbon source for anaerobic respiration (Banwart et al., 1996). The effect of this process is a source of HCO_3 which can be seen in Figure 8-8 in combination with high portions of meteoric water. The complete modelling results for all the reference waters and the behaviour of all the elements are reported in Laaksoharju and Wallin (eds.), 1997. In the next two chapters (8.2.2 and 8.2.3) the results from M3 modelling is visualised. The groundwater domains which have been affected by the reactions listed above (1 to 6) are indicated in the Figures 8-9, 8-10 and 8-11.

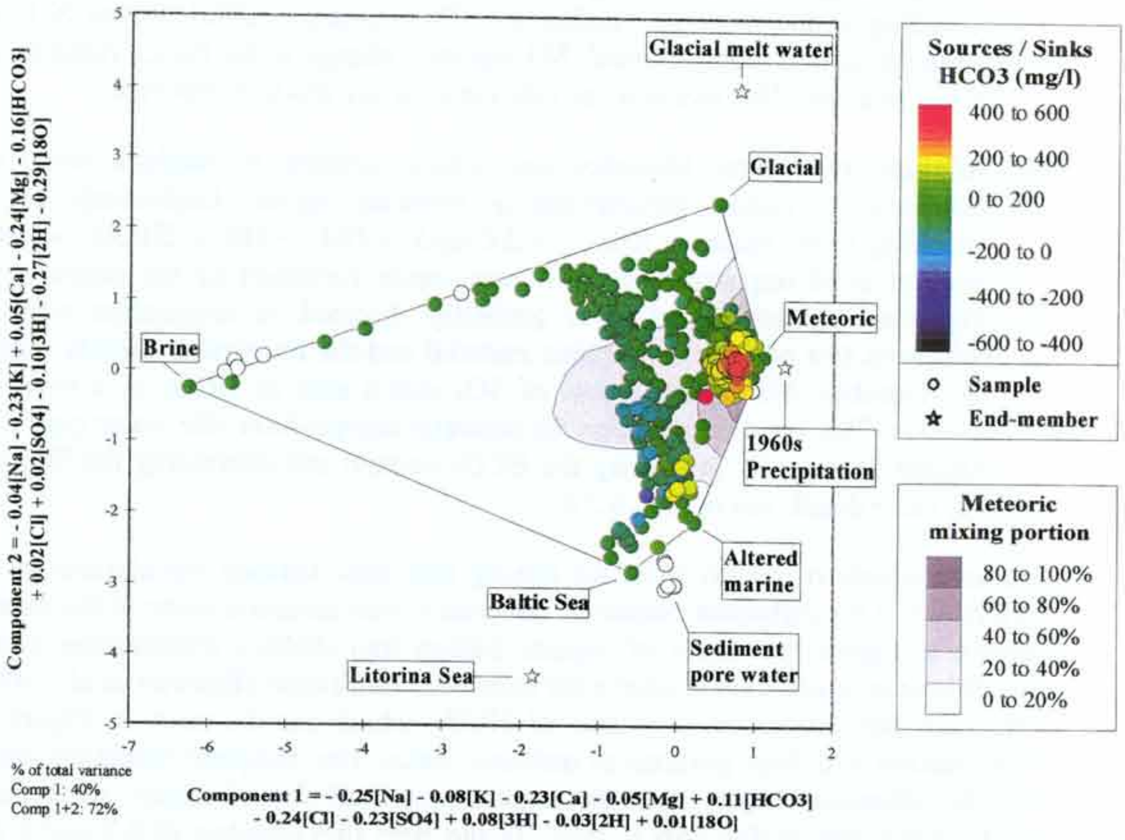


Figure 8-8: *M3 plot showing the results of mixing and mass-balance calculations. The results from the mixing portion calculations of Meteoric water are shown in the background. The mixing portion is shown progressively: 0-20%, 20-40%, 40-60%, 60-80% and 80-100%. The weight (eigen values) of the different elements is shown in the equations for the first and second principal component respectively. The results of mass-balance calculations for* HCO_3 *are shown as sources and sinks in relation to the ideal mixing model. Anaerobic respiration linked with organic decomposition is believed to be the major source of* HCO_3.

8.2.2 Visualisation of M3 results

The results from the above M3 modelling (Figure 8-8) can be shown as contour plots e.g. as the influence of meteoric water prior to or after the tunnel construction. The results of modelling for meteoric water are shown in 2D cutting plane oriented N-S (see Figure 8-9 for orientation see Figure 1-1). The hydraulic transmissivity (Rhén (ed.), 1997) of the major fracture zones is shown, based on the calculations before drawdown. The tunnel construction created a 80m drawdown of the groundwater table around the elevator shaft. The drawdown resulted in changing inflow patterns and increased the mixing of different groundwater types. The short-term reactions listed in Figure 8-9 are believed to increase in intensity and cause more chemical mass transfer because of the increased flow associated with the tunnel construction. Figure 8-10 shows the result of M3 mass-balance calculations for HCO_3. The sources can indicate locations at Äspö where organic decomposition (source), sulphate reduction (source), calcite dissolution (source) or calcite precipitation (sink) can occur.

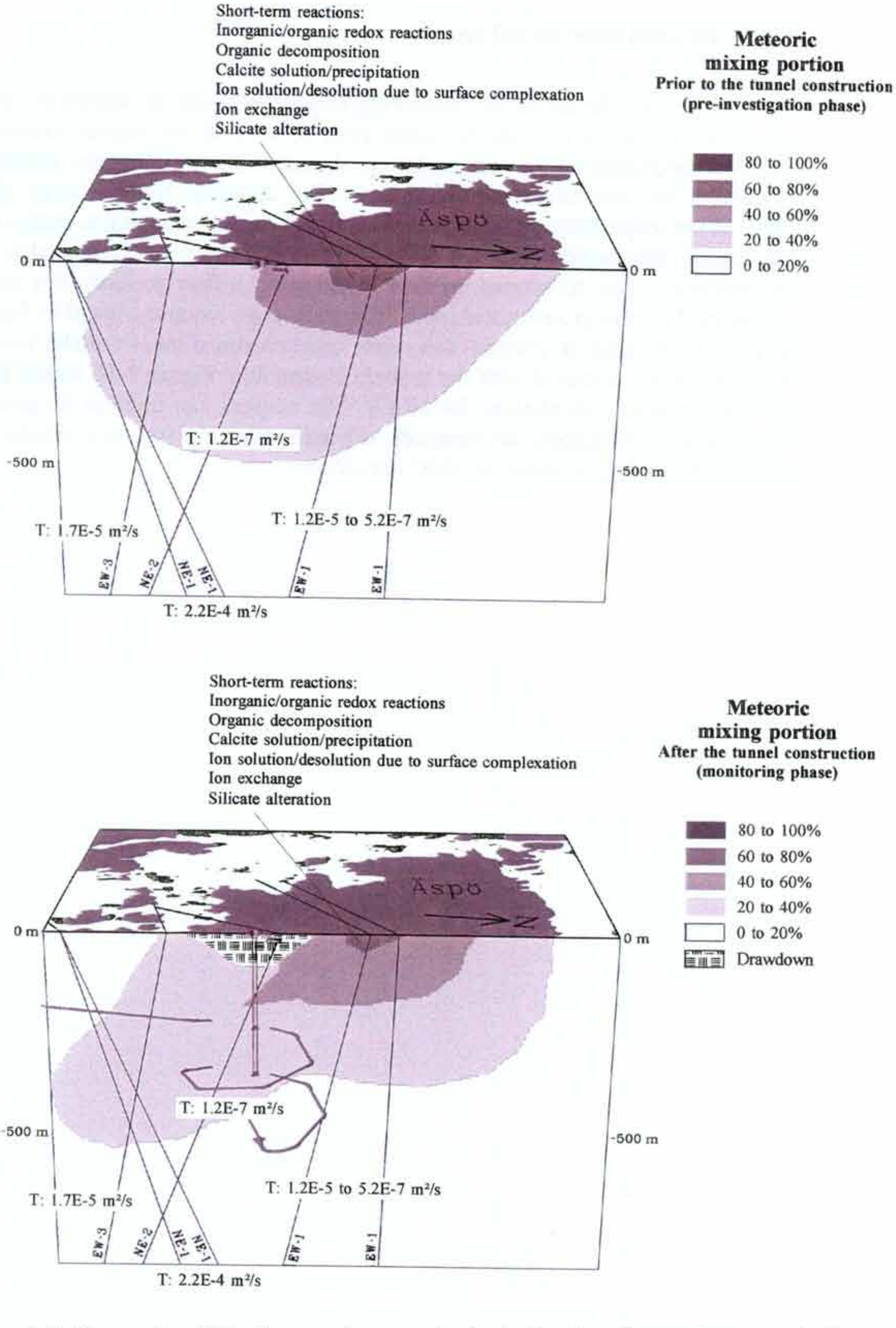


Figure 8-9: *Proportion (%) of meteoric water in the bedrock at Äspö prior to and after tunnel construction calculated using M3. The major water/rock reactions altering the groundwater are listed and the transmissivity of the major fracture zones are shown. The orientation of the cutting plane is N-S (see Figure 1-1).*

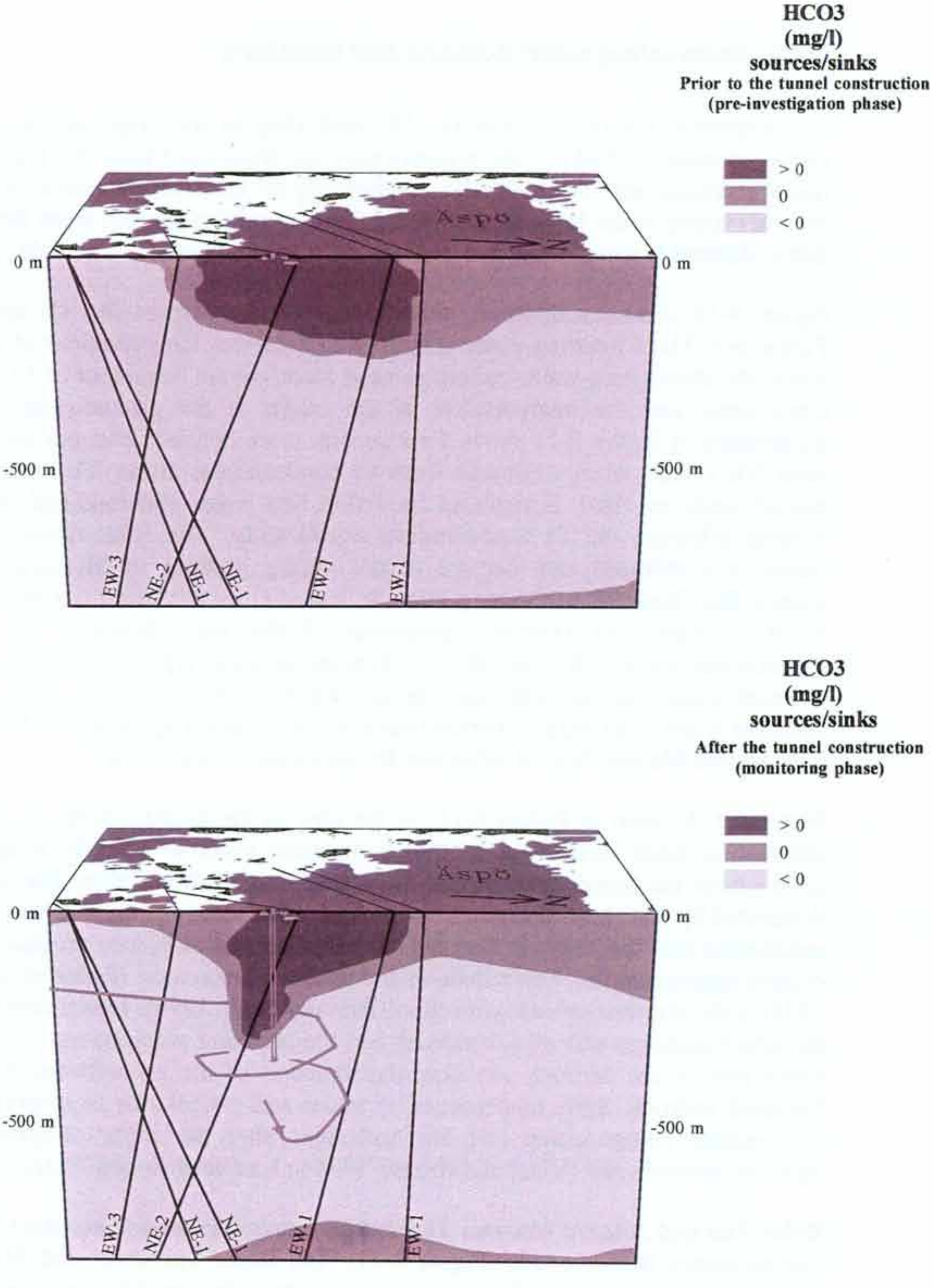


Figure 8-10: *M3 mass-balance calculations of HCO_3 in the bedrock at Äspö prior to and after tunnel construction. A positive value indicates a gain and the area where organic decomposition (resulting in reducing conditions, calcite dissolution or sulphate reduction can occur. A negative value indicates a loss which may indicate Calcite precipitation. The orientation of the cutting plane is N-S (see Figure 1-1).*

8.2.3 Dominating water portions and reactions

To summarise the results from the M3 modelling of the Äspö site the dominating mixing portions (>30%) of the groundwaters are shown in Figure 8-11 along with the major reactions and the hydraulic conductivity of the fracture zones. A dominating mixing portion is the largest calculated individual mixing portion from Brine, Glacial-Brine, Altered Marine, Baltic Sea or Meteoric waters obtained in a sample.

Figure 8-11 shows a different picture than expected from the Cl distribution in Figure 6-3. The Cl-cutting plane (Figure 6-3) describes the behaviour of one variable whilst the dominating-water-cutting plane is based on the behaviour of 10 groundwater constituents and the interpretation of the origin of the groundwater. The mixing proportions in Figure 8-11 show, for example, more dynamic changes around fracture zone NE-1 than when evaluated from Cl concentration alone. The older brine and glacial water in NE-1 is replaced by Baltic Sea water and modified marine water without affecting the Cl concentration significantly. The HRL tunnel construction caused a withdrawal and increase of the mixing portions of Meteoric and Marine waters. The Glacial-Brine water portion decreased since this water is a relict water. The location, depth and hydraulic properties of the rock determine the degree of groundwater mixing. By definition, a dominating water type consists of a mixture of different water types but with one reference water accounting for more than 30% of the obtained water. The major characteristics of the dominating waters (Meteoric, Baltic Sea, Altered Marine, Glacial-brine and Brine) are described below:

Meteoric: As seen in Figure 8-11, in the area in the middle of the Äspö island the dominating water component (>30%) is meteoric water to a depth of approximately 250m. After the tunnel construction the penetration depth is 350m. This water type is dominated by fast short-term reactions such as redox reactions that prevent deep oxygen penetration into the bedrock. Oxygen consumption and carbonate production linked to organic decomposition, iron reduction and methane production (Pedersen and Karlsson, 1995) is the dominating redox reaction (Banwart et al., 1996). Dissolution of calcite in the upper recharge part of 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, 1998 in Laaksoharju and Wallin (eds), 1997).

Baltic Sea and Altered Marine: The construction of the tunnel increased the inflow of marine waters from the side (Figure 8-11). The Baltic Sea water and Altered Marine water are characterised by fast, short-term reactions that modify the waters when they enter the bedrock and have been identified as a sink of K and Na, and a gain of Ca, due to ion-exchange with clays (Laaksoharju and Wallin (eds.) 1997). The Altered Marine groundwater has undergone decomposition of organic material due to microbiological sulphate reduction which has been detected by M3 modelling as a sink for SO_4 and a source for HCO_3 (Laaksoharju (ed.), 1995). The calculations correlate well with the measured content of sulphate-reducing bacteria (see chapter 8.2.4). 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 Altered Marine groundwater are a sink of Na and a gain of Ca, due to ion exchange with clays.

Glacial-Brine: An important water type found at Äspö has been affected by a component of cold climate recharge. The low $\delta^{18}O$ 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 samples from various depths at the Äspö site and on the mainland of Laxemar (Laaksoharju et al., 1995a). The interpretation from the conceptual model (Figure 2-1b) and the M3 calculations (the waters between these reference waters plot almost on a straight line in Figure 8-8) are that this water type has been formed by the continental ice sheet melting and the water has been injected into the Brine water. The resulting water is therefore a mixture of glacial meltwater and Brine and the water type is named Glacial-Brine. The amount, oxidation state, penetration depth and velocity of glacial meltwater are not yet known. This has led to discussions concerning possible penetration of oxygenated water to repository depths. 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 50-100m 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 Brine groundwaters which caused an oversaturation of calcite (Laaksoharju and Wallin (eds.), 1997).

Brine: At depths below 800m 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 as well as early paleozoic sediments, and localised freezing have been discussed (Laaksoharju and Wallin (eds.), 1997) as a source for the brine water component. The stable isotope data ($\delta^{18}O$= -10.4 to -8.9 o/oo; $\delta^{2}H$ -60.2 to -44.9 o/oo) from the deep saline groundwaters show significant deviation from MWL (Meteoric Water Line) (Figure 7-5b). Characteristics similar to these low temperature Precambrian granitic shield areas are shown for the deep Canadian brines (Frape et al., 1984; Frape and Fritz, 1987). The deviation from MWL is ascribed to water/rock interaction during long periods of time. An old age for the Brine is also suggested by the measured ^{36}Cl values indicating a minimum residence time of 1.5Ma for the Cl component (Laaksoharju and Wallin (eds.), 1997). The origin may be unclear but the mean residence time for the groundwater is considerable although modern water portions have also been introduced either naturally or due to borehole activities. Different groundwater events including mixing of different waters and water-rock interactions change the element concentration and isotope ratios in different ways.

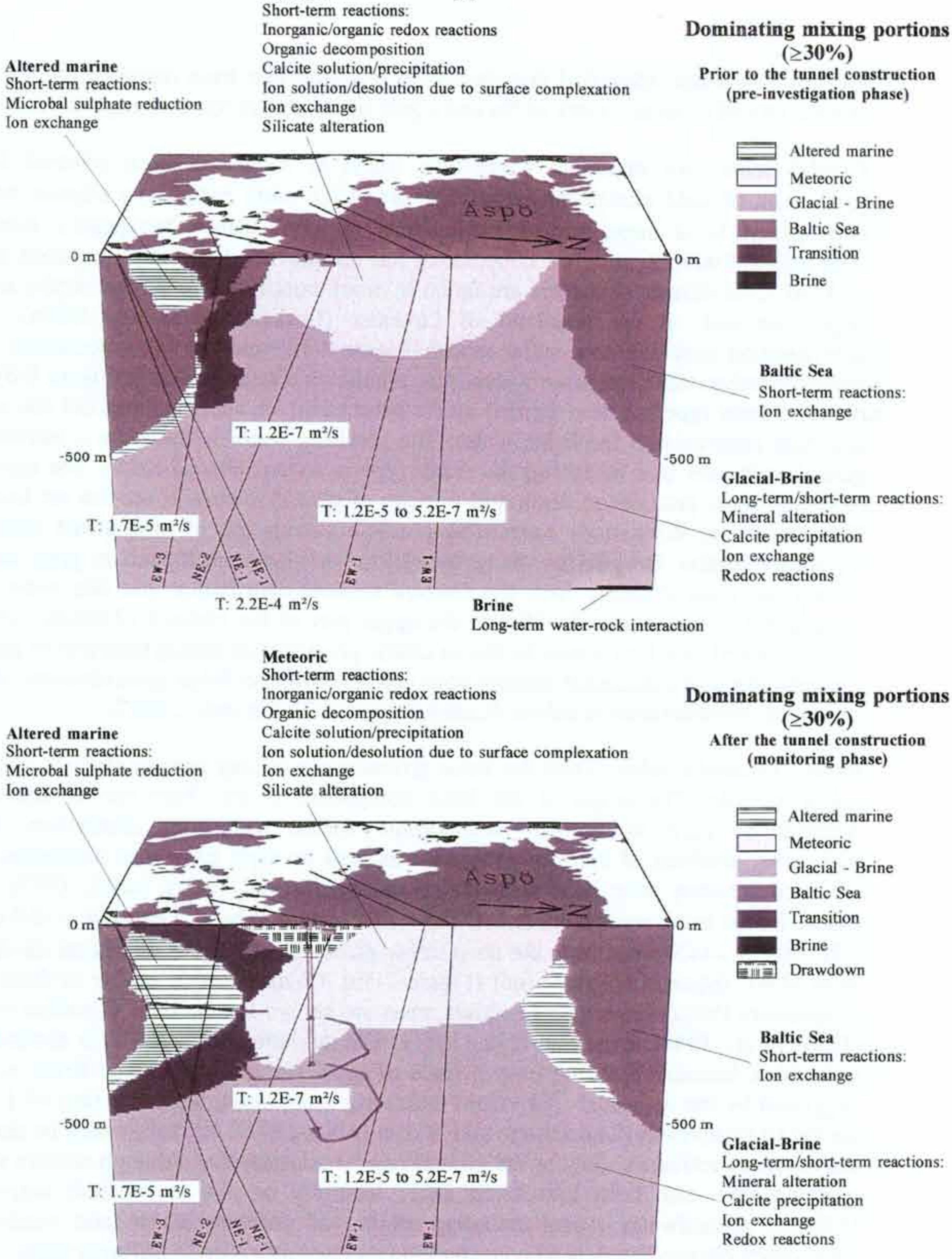


Figure 8-11: *Dominating mixing portions (%) of Brine, Glacial-Brine, Altered Marine, Baltic Sea and Meteoric groundwaters prior to and after tunnel construction. The figure shows the domains where one water type dominates more than 30%. The groundwater is generally a mixture of several water types and is only close to the source where the groundwater is less mixed with other water types. The major water/rock reactions altering the groundwater are listed and the transmissivity of the major fracture zones is shown.*

8.2.4 Identification of sulphate reduction in the Äspö tunnel

Since sulphide can corrode a copper canister placed in a 500m deep reducing environment, the process generating sulphide has to be known in such detail that a repository can be located without the risk of extensive sulphide generation at the copper canister surface. M3 was used to trace the effects from sulphate reduction which produce sulphide at Äspö HRL (Laaksoharju (ed), 1995).

Sulphate reduction is indicated by the presence of Sulphate Reducing Bacteria (SRB) (Figure 8-12) or by analysing the amount of sulphide generated in the groundwater. The sampling and identification of SRB cannot generally be done due to economical and practical restrictions. The reactivity of HS^- leads to special requirements for sampling and analysis. The lack of HS^- data from the boreholes in the Äspö HRL tunnel in combination with relatively few samples of bacteria made it necessary to search for additional signs of bacterial sulphate reduction.

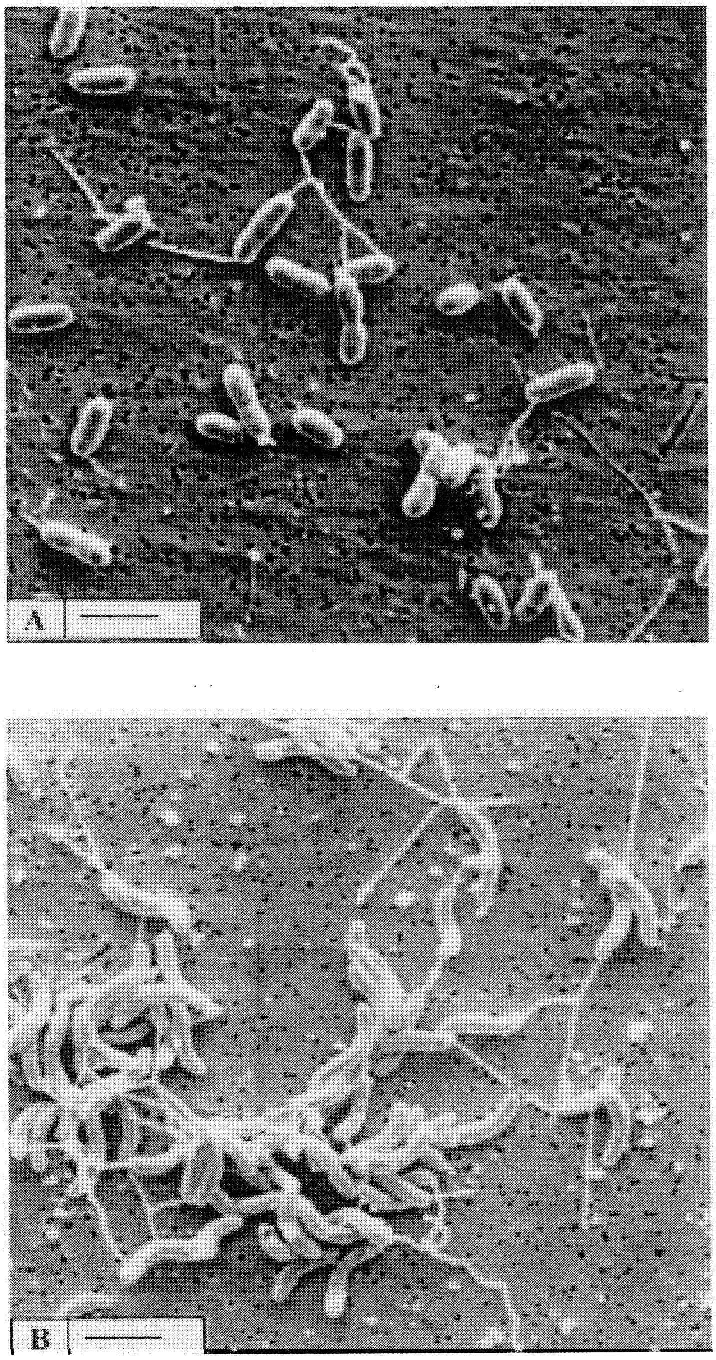


Figure 8-12: *Scanning electron microscopy image of sulphate reducing bacteria that has been enriched and isolated from the Äspö HRL environment. DNA sequences have demonstrated the bacterium in Figure A to be Desulfomicrobium baculatum, while the bacterium in Figure B was found to be related to the genus Desulfovibrio. The bar in the figures denotes 2 µm (Laaksoharju ed., 1995).*

The SRB can reduce sulphate to sulphide using organic substances in natural groundwater as reducing agents (electron donors) according to the reaction:

$$SO_4^{2-} + 2(CH_2O) + OH^- \Rightarrow HS^- + 2HCO_3^- + H_2O$$

This means that sulphate reduction in the groundwater is indicated by an abnormally *low* dissolved SO_4^{2-} content and an abnormally *high* HCO_3^- content. The effect from mass transport mixing on different groundwaters, which can also give a similar SO_4^{2-}/HCO_3^- ratio, was compensated for by the M3 calculations. After this compensation, using mixing calculations, the observations which have undergone or undergo an obvious microbiological sulphate reduction can be identified. According to the formula given above the deviation ratio from the M3 model between bicarbonate and sulphate should be larger than 1.27 expressed as mole ratio ($\Delta[2HCO_3^-]/\Delta[SO_4^{2-}] > 1.27$) and the SO_4^{2-} deviation is negative and the HCO_3 is positive there is a large probability that an *obvious* sulphate reduction has taken place (Laaksoharju ed., 1995).

The M3 plot (Figure 8-13) was used to indicate areas with obvious sulphate reduction in the Äspö groundwaters. The results from the microbial sampling together with M3 modelling are shown and seem to correlate. The mixing portion of the water with obvious sulphate reduction (Altered Marine water) is shown as mixing iso-lines. The mixing calculations show that water affected by sulphate reduction can be transported to other locations in the HRL tunnel especially in the tunnel sections under the Baltic Sea or in the near vicinity.

Sulphate reduction occurs most prominently in the tunnel section passing below the sea (Figure 8-14), but also occasionally at depth in the tunnel spiral. A high content of organic material (>10 mg/l) in combination with a salinity (Cl) interval of 4000-6000 mg/l seemed to favour the biological sulphate reduction. However, it also occurs at a lower organic content where the substrate might be hydrogen gas and in this case excessive HCO_3 production does not occur. Recent research has shown that NH_4 content in the groundwater can increase as a result of sulphate reduction (Luukkonen et al., 1999). The obvious sulphate reduction has in a few cases been seen to give bicarbonate concentrations of above 1000 mg/l with a corresponding decrease of sulphate from above 500 mg/l to less than 100 mg/l (Laaksoharju ed., 1995).

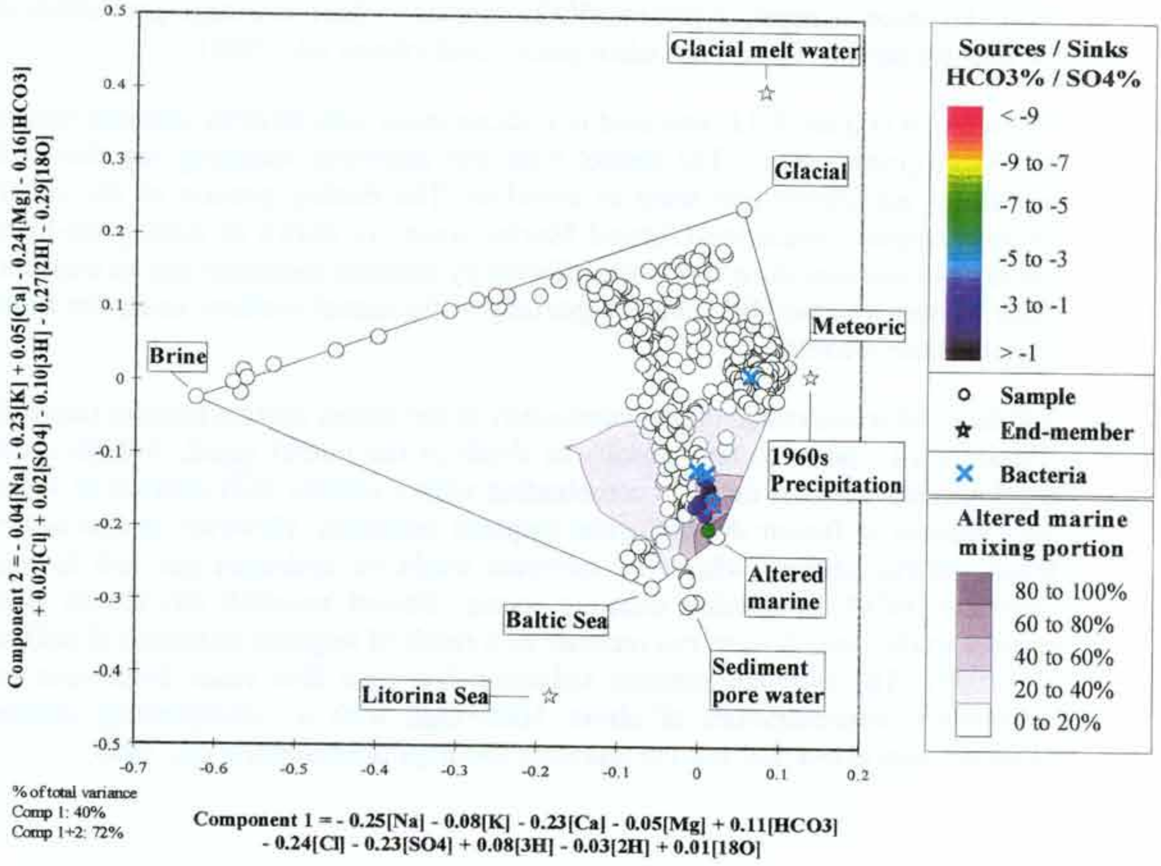


Figure 8-13: *Observations with obvious sulphate reduction (where the ratio HCO_3/SO_4 is >1.27) and the effect of the mixing portion of sulphate reduced water (Altered Marine) in the HRL tunnel. The results from the sampled sulphate reducing bacteria are superimposed and seem to correlate well with the modelling. 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.*

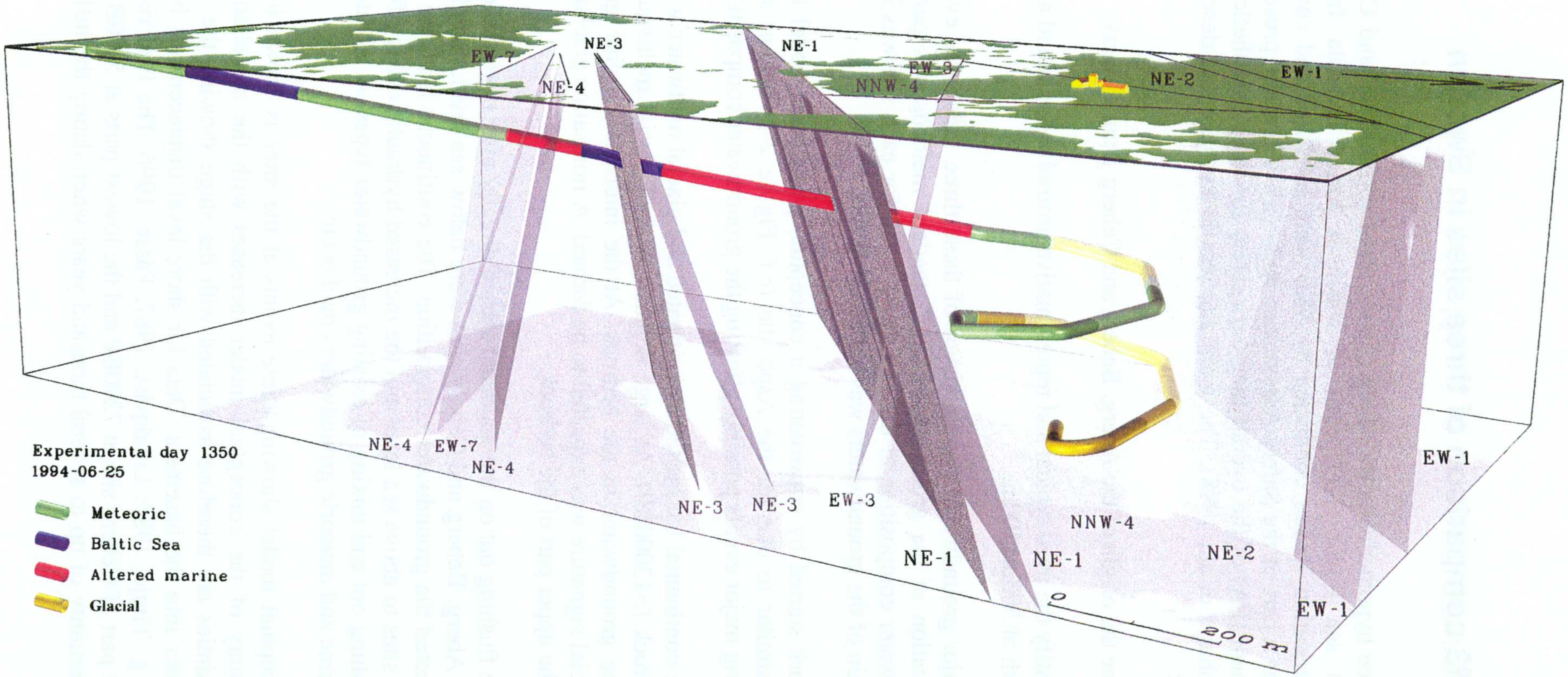


Figure 8-14: *Mixing portion of the dominating water (>30%) in the HRL tunnel on day 1350 (1994-06-25) of the tunnel construction. The Altered marine water is affected by sulphate reduction (Laaksoharju ed., 1995).*

8.3 M3 comparison of three sites in Sweden

The three hypothetical sites Aberg (Äspö), Beberg (Finnsjön) and Ceberg (Gideå) (for location see Figure 1-1), each of which is based on data from previous site characterisation studies conducted by SKB were modelled and compared using M3. This was a part of the Safety Assessment study (SR-97) which presents a performance assessment (PA) of the overall long-term safety for three hypothetical sites in Sweden (Laaksoharju et al., 1998). The main aim was to evaluate and describe the following aspects:

- Trace the origin of the Aberg, Beberg and Ceberg groundwaters.
- Identify the most typical and representative groundwaters found at the repository depth of 500m±100m.

The major groundwater characteristics of these three sites were evaluated. A general classification of the groundwater using standard methods was performed. A typical groundwater composition at the repository depth for each site was identified and then the origin of the groundwaters was traced using M3.

The work started by constructing a conceptual postglacial model for the last 10,000 years, similar to that for the Äspö site (c.f. Figure 2-1) but on a larger scale. The following major events possibly affecting the groundwater composition were identified:

1. The continental ice melted and retreated and glacial meltwater was injected into the bedrock (>13000BP). At large depths (>800m) glacial meltwater was mixed with brine groundwater in the bedrock. At the interface a saline groundwater with a glacial signature was expected to be formed. A non-saline glacial water was present in the upper part of the bedrock.
2. The flushing out on the mainland started directly after deglaciation. However, since the Aberg, Beberg and Ceberg sites were below sea level, postglacial marine water affected the groundwater composition. The continuous land rise gradually elevated the sites to above sea level and the increased hydraulic driving force resulted in the flushing out and mixing of existing groundwater types. A mixture of glacial, brine, marine and meteoric groundwater could occur.

A conceptual model showing these events at the sites is shown in Figure 8-15. The uncertainty of the conceptual model increases with the modelled time. The largest uncertainties are therefore associated with the stage showing the injection of glacial meltwater into the basement. Data for shore level displacements have been extracted from e.g. Timje, 1983; Lundqvist, 1987; Påsse, 1996. The land rise elevated e.g. the highest part of Ceberg site at 7200BP and the lowest parts at 5300BP. There is anyhow an uncertainty of up to several thousand years when dating the influence from marine water.

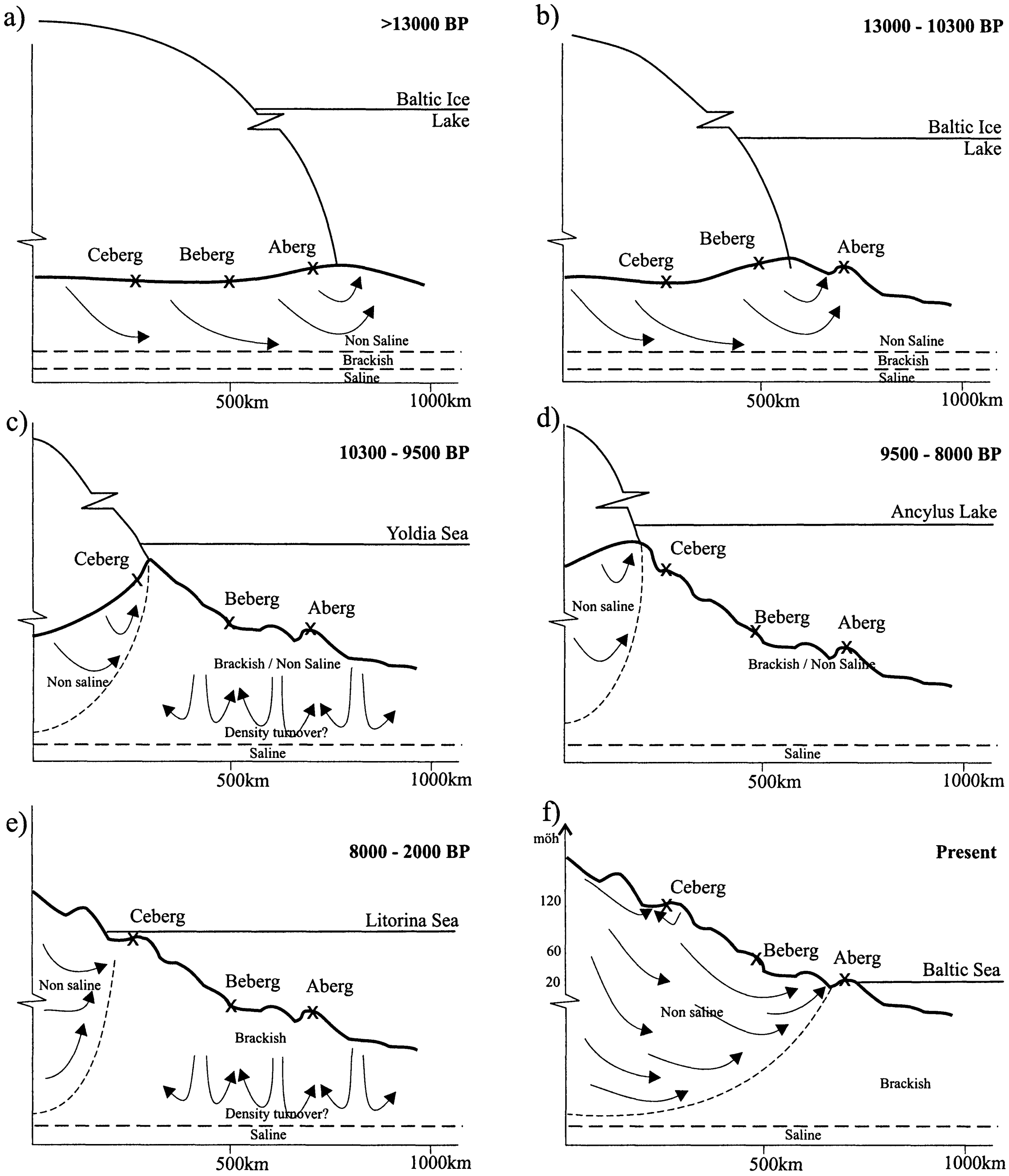


Figure 8-15: *A conceptual postglacial scenario at the Aberg (Äspö), Beberg (Finnsjön) and Ceberg (Gideå) sites (for location see inserted map in Figure 1-1). Possible relation to different known post-glacial stages and land uplift which have affected the hydrochemical evolution of the sites is shown a) Glacial stage. b) Baltic Ice Lake stage, c) Yoldia Sea stage, d) Ancylus Lake stage, e) Litorina Sea stage and f) present day Baltic Sea stage. The orientation and length of the cutting plane is shown in the inserted map in Figure 1-1. The uncertainty of the model increases with the modelled time*

At Aberg, Beberg and Ceberg where the different sea water stages covered the bedrock at some point in time, the salinity of the sea water could have affected the groundwater in the bedrock by density turnover. The higher the salinity of the sea water the deeper the penetration depth. The land rise resulted in the formation of a freshwater aquifer at these sites. The fresh water flushed out the traces of older waters. The depth to which the waters were flushed out was 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 a denser water such as a brackish-saline groundwater.

For the PA modelling the representative waters were chosen from Aberg, Beberg and Ceberg. The following major criterion was used for the selected samples: *The representative water sample should be the best estimate reflecting the natural conditions at the repository depth of 500m±100m.* The depth criteria eliminated most of the samples and the choice was generally between 1-4 possible candidates. The candidate samples were examined in detail and M3 modelling was used to compare the candidate samples in relation to other sampled groundwaters in Sweden (see Figure 8-16). The M3 plot was used for examining the variability and origin of the groundwater at different sites e.g. groundwater samples which plot close to the meteoric water contain more meteoric water (e.g. at Ceberg) compared to samples from another site which plot close to the brine end-member (i.e. deep groundwater samples at Aberg). The mixing portions which can indicate the origin of the groundwaters were calculated.

The complete analytical data for the reference samples, the quality scores are compared in Table 8-1 with the Scandinavian mean values (based on 146 samples) according to Laaksoharju et al. (1993). The reference water (KAS02) from Aberg and one of the Beberg reference waters (BFI01) score higher than the Scandinavian mean quality. The other reference sample (KFI07) from Beberg and the Ceberg reference sample (KGI04) have a lower score than the Scandinavian mean quality. The drill water content is higher in the KGI04 sample. The KAS02 and BFI01 samples reflect the undisturbed conditions at 500m more accurately than samples KFI07 and KGI04. The calculated saturation indexes (by using WATEQF in NETPATH (Plummer et al. 1991) were used to indicate whether a groundwater was under or supersaturated in respect to a mineral or gas phase. M3 was used to calculate mixing portions for the selected samples. This information can reflect the quality of the sampling, effect of major reactions, mixing situations and the residence time of the groundwater (Laaksoharju et al., 1998).

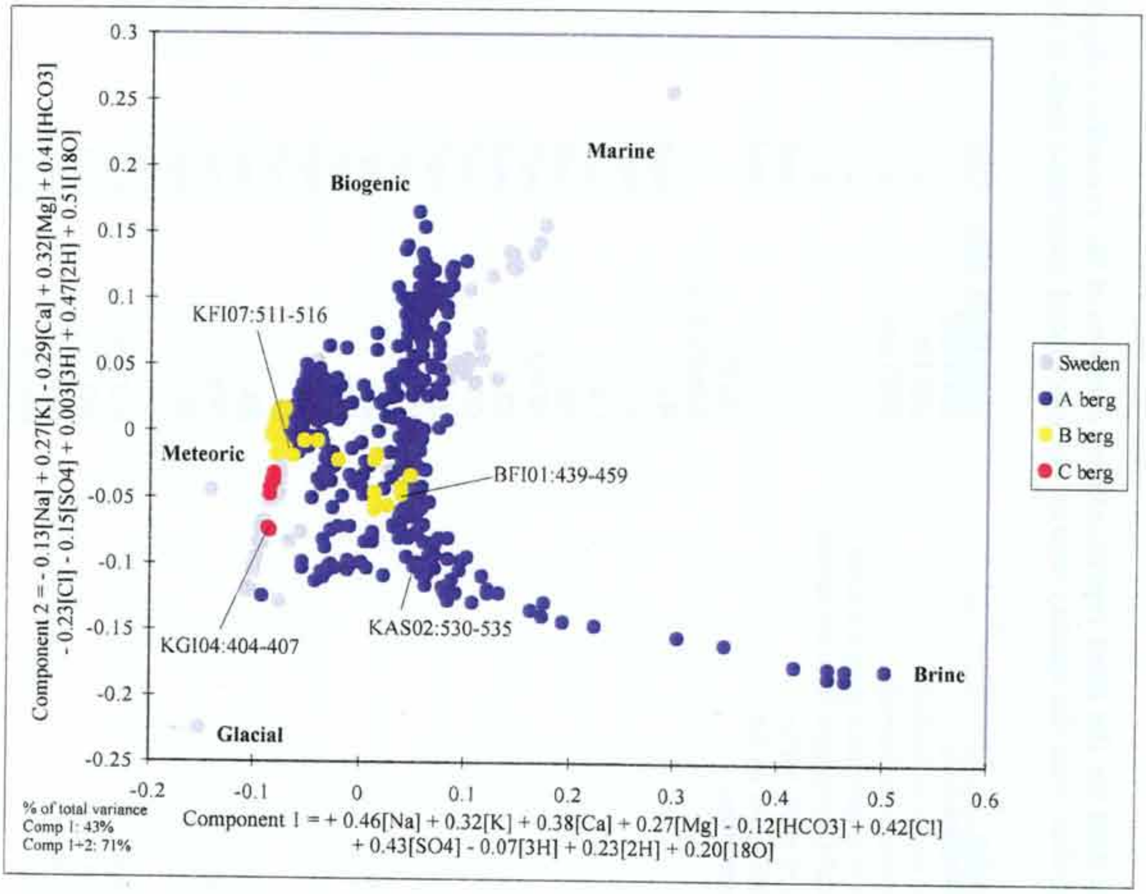


Figure 8-16: *M3 plot based on the major components, stable isotopes and tritium values from the Swedish SKB sites compared to data from Aberg (Äspö), Beberg (Finnsjön) and Ceberg (Gideå). The identified reference water samples at 500m±100m depth are tagged. The weight of the different elements is shown in the equations for the first and second principal component respectively. These two principal components together account for 71% of the variability, or the information in the data.*

Table 8-1: Complete analytical data for the most representative samples at the repository depth of 500m - based on samples from Aberg, Beberg and Ceberg together with the quality scores, the calculated saturation indices and M3 mixing portions.

Description of codes	Code in SICADA	Unit	Aberg	Beberg	Beberg	Ceberg
Borehole identification code	**IDCODE**		**KAS02**	**BFI01**	**KFI07**	**KGI04**
Position of upper packer in borehole	SECUP	m	530	439	511	404
Position of lower packer in borehole	SECLOW	m	535	459.1	516	406.7
Vertical position of upper packer from the surface		m	528.2	435.8	507.8	384.3
Vertical position of lower packer from the surface		m	533.2	455.7	512.8	386.9
Vertical position of upper packer		masl	-520.5	-406.6	-474.9	-268.3
Vertical position of lower packer		masl	-525.5	-426.5	-479.9	-270.9
Date, day of measurement	DATE		880504	861027	801119	820704
Sample number	SAMPLE_NO		1432	1265	-478	194
Na	NA	mg/l	2100	1700	275	105
K	K	mg/l	8.1	13.0	2.0	1.9
Ca	CA	mg/l	1890	1650	142	21
Mg	MG	mg/l	42	110	17	1.1
HCO_3	HCO3	mg/l	10	47	278	18
Cl	CL	mg/l	6410	5500	555	178
SO_4	SO4	mg/l	560	370	49	0.1
Br	BR	mg/l	40	32		
F	F	mg/l	1.5	1.2	1.5	3.2
SiO_2 calculated as Si	SI	mg/l	4.1	5.4	5.6	4.7
Fe(II)	FEII	mg/l	0.24		1.80	0.05
Mn	MN	mg/l	0.29	0.82	0.13	0.01
Li	LI	mg/l	1.0	0.007		
Sr	SR	mg/l	35	21		
Dissolved organic carbon	DOC	mg/l	1.0		5.7	2.0
HS^-	S2	mg/l	0.15	0.01^*		0.01^*
I	I	mg/l		0.12		0.14
NO_2 calculated as N	NO2_N	mg/l	0.001^*	0.005	0.010	0.001^*
NO_3 calculated as N	NO3_N	mg/l	0.010^*	0.005^*	0.002^*	0.009
NH_4 calculated as N	NH4_N	mg/l	0.03	0.35	0.09	0.012
PO_4 calculated as P	PO4_P	mg/l	0.005	0.005	0.040	0.008
^{238}U	U238	mBq/kg	3.19^{**}	195.40		

*= Under the detection limit

**= Measured 950505

***= Oxidation during drilling

****= According toYJT-93-24 pp32-35 and SKB TR 92-10 and compared to the Scandinavian mean

Table 8-1. Continuing.

Description of codes	Code in SICADA	Unit	Aberg	Beberg	Beberg	Ceberg
Borehole identification code	**IDCODE**		**KAS02**	**BFI01**	**KFI07**	**KGI04**
^{235}U	U235	mBq/kg	0.5**	9.1		
^{234}U	U234	mBq/kg	10.4**	365.9		
natural U		µg/l	3.86	19.3***	0.35	0.17
Th	TH	µg/l	0.022**	0.120		0.028
^{226}Ra	RA226	mBq/kg	0.224**	1		0.004
^{222}Rn	RN222	mBq/kg	67.4**	39.5		88.1
^{14}C (percent modern carbon)	PMC	%		34.40		
^{13}C	C13	‰ PDB		-9.9	-14.6	
^{14}C (age before present)	AGE_BP	year		8390	4440	
Age before present based on ^{14}C with correction of ^{13}C	AGE_BP_CORR	year		8640	4610	
D	D	SMOW	-97.2**	-88.7	-89.0	-99.4
Tr	TR	TU	8**	3*	8	8
^{18}O	O18	SMOW	-12.30**	-11.81	-11.90	-13.63
Representative Eh		**mV**	**-308**		**-250**	**-202**
Representative pH		**units**	**7.73**	**7.04**	**7.90**	**9.30**
Representative electrical conductivity		**mS/m**	**1890**	**1610**	**190**	**65.5**
Water flow at measurement	S_W_FLOW	l/min	0.118	0.060		0.098
Drill water content	DRILLW	%	0.19	0.02		11.03
Ionic strength			2.40E-1	2.10E-1	2.52E-2	6.19E-3
Total dissolved solids (TDS)		mg/l	11107	9457	1339	338
Quality Scores****			**0.86**	**0.63**	**-0.36**	**-0.15**
Calcite, saturation index		LOG IAP/K	-0.14	-0.20	0.71	0.11
Aragonite, saturation index		LOG IAP/K	-0.29	-0.36	0.55	-0.05
Dolomite, saturation index		LOG IAP/K	-1.69	-1.41	0.65	-0.91
Siderite, saturation index		LOG IAP/K	-1.80	-3.00	1.54	-0.27
Rhodochrosite, saturation index		LOG IAP/K	-1.51	-1.06	-0.002	-0.93
Strontianite, saturation index		LOG IAP/K	-1.36	-1.57		
Gypsum, saturation index		LOG IAP/K	-0.32	-0.50	-1.78	-4.99
Anhydrite, saturation index		LOG IAP/K	-0.56	-0.75	-2.03	-5.24
Celestite, saturation index		LOG IAP/K	-0.35	-0.69		
Hydroxyapatite, saturation index		LOG IAP/K	0.58	-2.79	0.90	1.44

*= Under the detection limit

**= Measured 950505

***= Oxidation during drilling

****= According toYJT-93-24 pp32-35 and SKB TR 92-10 and compared to the Scandinavian mean

Table 8-1. Continuing.

Description of codes	Code in SICADA	Unit	Aberg	Beberg	Beberg	Ceberg
Borehole identification code	**IDCODE**		**KAS02**	**BFI01**	**KFI07**	**KGI04**
Fluorite, saturation index		LOG IAP/K	0.25	0.06	-0.32	-0.28
SiO_2 amorph, saturation index		LOG IAP/K	-1.01	-0.86	-0.88	-1.03
Chalcedony, saturation index		LOG IAP/K	-0.14	0.02	0.01	-0.15
Quartz, saturation index		LOG IAP/K	0.32	0.50	0.48	0.33
Talc, saturation index		LOG IAP/K	-1.26	-3.97	-0.62	3.96
Chrysotile, saturation index		LOG IAP/K	-4.48	-7.53	-4.15	0.74
Sepiolite, saturation index		LOG IAP/K	-3.06	-4.68	-2.47	0.54
Hematite, saturation index		LOG IAP/K	0.50	0.27	7.71	12.56
Goethite, saturation index		LOG IAP/K	-0.37	-0.34	3.37	5.79
Fe(OH)3 amorphous, saturation index		LOG IAP/K	-6.26	-6.23	-2.52	-0.10
Pyrite, saturation index		LOG IAP/K	5.87	7.88		9.90
FeS ppt, saturation index		LOG IAP/K	-0.10	-3.08		-0.09
Vivianite, saturation index		LOG IAP/K	-6.88	-11.87	1.17	-2.81
Pyrolusite, saturation index		LOG IAP/K	-28.75	-24.94	-25.47	-20.63
Hausmannite, saturation index		LOG IAP/K	-30.14	-28.46	-26.89	-18.53
Manganite, saturation index		LOG IAP/K	-13.42	-11.66	-11.44	-8.14
Pyrochroite, saturation index		LOG IAP/K	-5.62	-6.53	-5.49	-3.73
pCO_2, partial pressure		bar	-3.99	-2.60	-2.59	-5.28
H_2 gas, partial pressure		bar	-4.69	-10.01	-8.38	-11.46
Melanterite, saturation index		LOG IAP/K	-6.63	-7.89	-5.54	-9.96
K-Jarosite, saturation index		LOG IAP/K	-28.80	-27.03	-20.08	-22.01
Mixing portion						
Meteoric		%	31	30	50	43
Biogene		%	15	19	22	17
Marine		%	12	16	10	7
Glacial		%	29	26	15	28
Brine		%	14	10	3	5

*= Under the detection limit

**= Measured 950505

***= Oxidation during drilling

****= According toYJT-93-24 pp32-35 and SKB TR 92-10 and compared to the Scandinavian mean

The results of the M3 modelling show that the selected waters at the repository depth have a different origin and composition which not only reflect the postglacial events but are also due to the prevailing hydrogeological conditions.

At the repository depth at Aberg the water consists of a mixture of 31% meteoric water infiltrated during the past 3,000 years, 29% glacial meltwater and 27% modern and old Baltic Sea water (Marine + Biogenic). 14% of the water is of an old (brine) type of groundwater, which has been isolated from the atmosphere for more than 1.5Ma. Aberg has the highest salinity of the selected sites and the salinity increases with depth.

At the repository depth at Beberg two different representative waters have been identified, one fresh and one saline. The freshwater consists of 50% meteoric water, 15% glacial melt-water, 32% water of marine origin (Marine + Biogenic) and 3% Brine water. The saline reference water consists of 30% meteoric water, 26% glacial water, 35% marine water (Marine + Biogenic) and 10% brine. Beberg's salinity increases with depth but the salinity content is intermediate compared with the other two sites.

At the repository depth at Ceberg the reference water consists of 43% meteoric water, 28% glacial water, 17% water with a high biological activity, 7% water of a marine and 5% of brine origin. Ceberg had the lowest salinity of the selected sites (Laaksoharju et al., 1998).

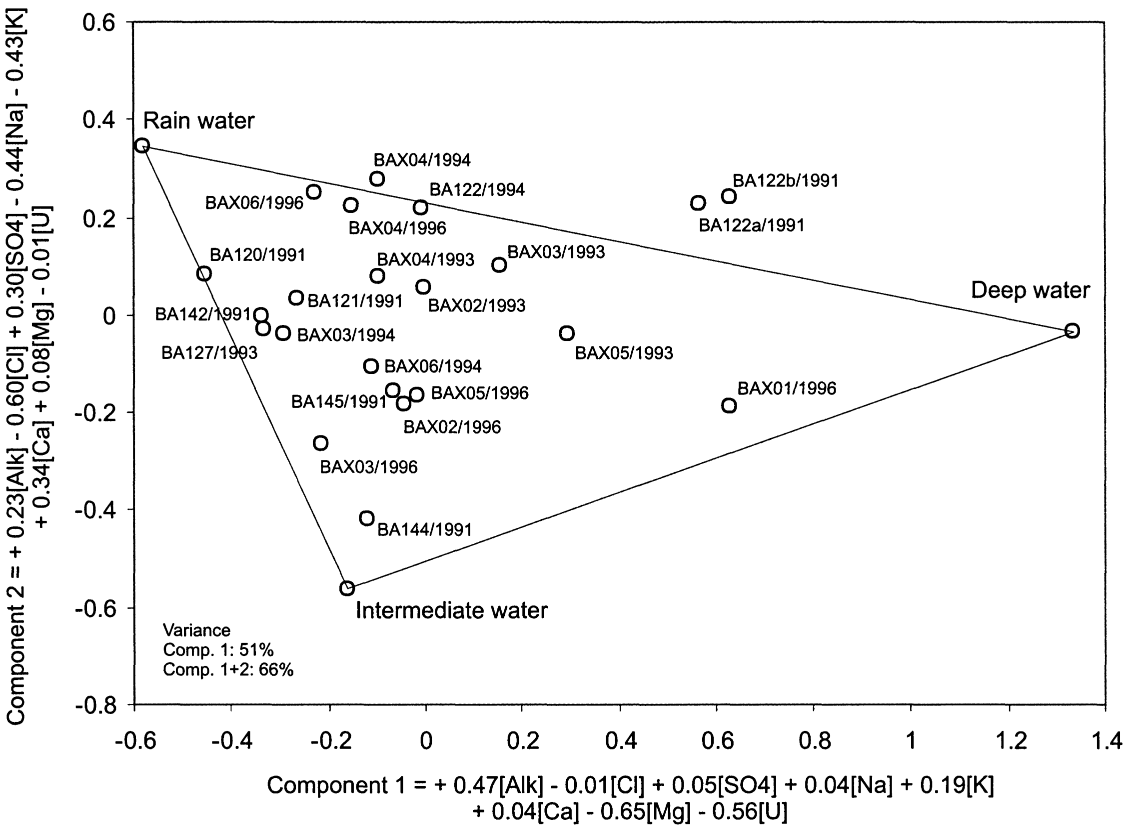
8.4 M3 modelling of a natural analogue site in Africa

SKB is conducting and participating in so-called Natural Analogue studies where the aim is to learn from nature how a repository will perform during a time span of 100,000 years or more. This information can be used to identify chemical processes which can hinder or promote transportation of radionuclides up to the biosphere. The Oklo site in Gabon, Africa underwent a natural fission 2,000 million years ago and is therefore used e.g. to study chemical processes which have hindered dissolution and transport of uraninite from the natural reactors. The geology of the site consists of the following rock types: pelites (which contain the mineralisation) and sandstones, see Figure 8-18.

M3 was used to model flow and chemical transport processes. The outcome of the modelling was compared (Gurban et al., 1998) with an independent coupled transport and reaction code HYTEC-2D (Salignac, 1997; 1998). The approach was to test if the biological processes could regulate the redox conditions around the reactor and by maintaining reducing conditions could hinder transport of uranium. The following biological processes, as suggested by Pedersen and Karlsson (1995), could add reducing capacity and were therefore tested by M3:

- Oxygen consumption through oxidation of organic matter: $O_2 + (CH_2O) \rightarrow CO_2 + H_2O$.
- Reduction of iron(III) minerals through oxidation of organic matter: $4Fe(III) + (CH_2O) + H_2O \rightarrow 4Fe^{2+} + 4H^+ + CO_2$.

The selected reference waters for the Oklo modelling are shown in Figure 8-17.



Reference water	Date	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 (BAX01)	mar-93	2.51E-03	2.17E-05	1.35E-05	5.22E-04	5.37E-05	7.98E-04	2.10E-04	8.82E-08
Rain		1.33E-05	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.00E-12	1.00E-12
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

Figure 8-17: *M3 plot with the identification number for the samples from the different boreholes (BA and BAX) and the identified reference samples: rain, intermediate and deep water (Gurban et al., 1998). The analytical data of the selected reference waters are listed in the table.*

The M3 modelling results of the 1993 sampling campaign for mixing portions and Cl distribution are shown in Figure 8-18; measured and modelled alkalinity in Figure 8-19; and measured and modelled uranium distribution in Figure 8-20.

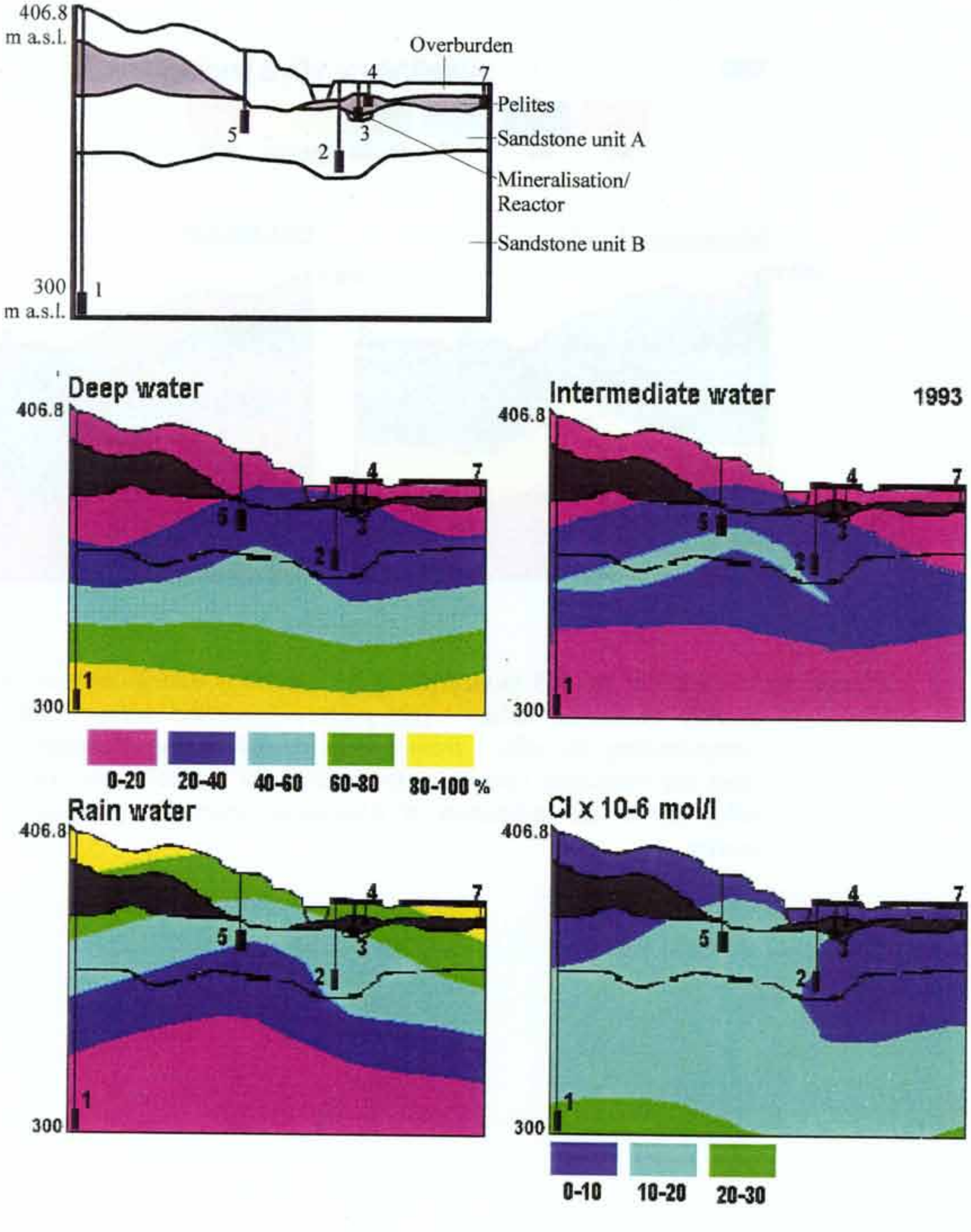


Figure 8-18: Geology and result of the M3 modelling of the Oklo site. The geology of the site consists of the following rock types: pelites (which contain the mineralisation) and sandstone unit A and B. The calculated proportions of deep, intermediate and rain waters (%), and the salinity distribution are shown. A high proportion of rainwater is present at the surface of the model, decreasing towards the bottom. The deep water is present in a very small proportion at the surface, increasing towards the bottom where it is 100% deep water. The salinity distribution shows the same tendency as the deep water distribution. A high proportion of intermediate water is present in the sandstone, which appears to be the highest permeable area of the system. The location of the boreholes BAX01 to BAX07 is shown. The Black pelites represent the mineralised rock type: Boreholes BAX03 and 04 are drilled into the reactor.

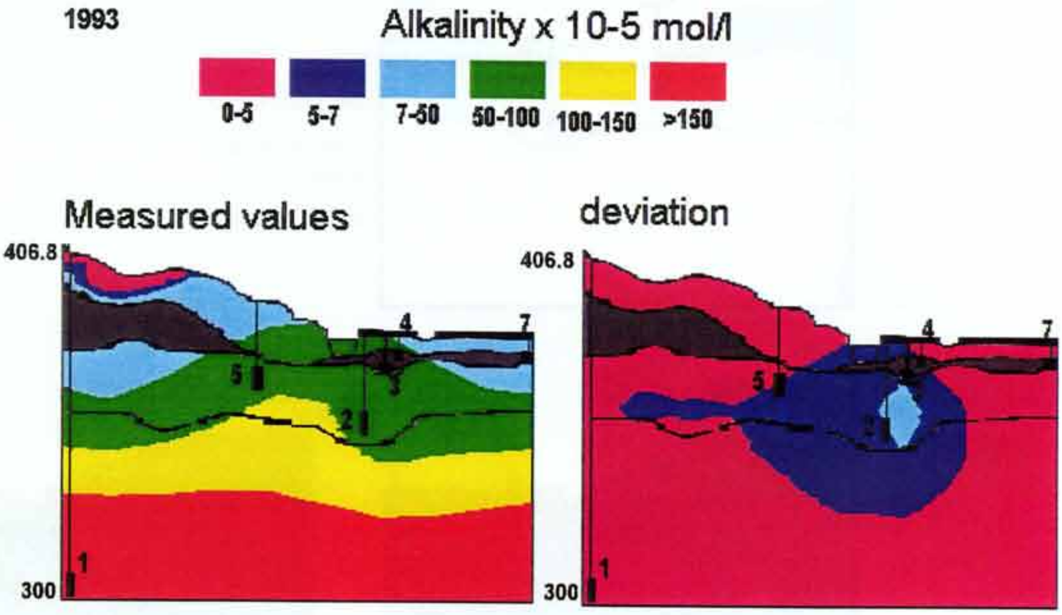


Figure 8-19: *Result of the M3 modelling of the alkalinity distribution in mole/l. Left picture measured values, right picture modelled values with M3 after compensating for effects from transport and mixing. A positive deviation from the measured values is observed in the reactor zone. An increase in alkalinity is an indication of biological process decomposing organic matter.*

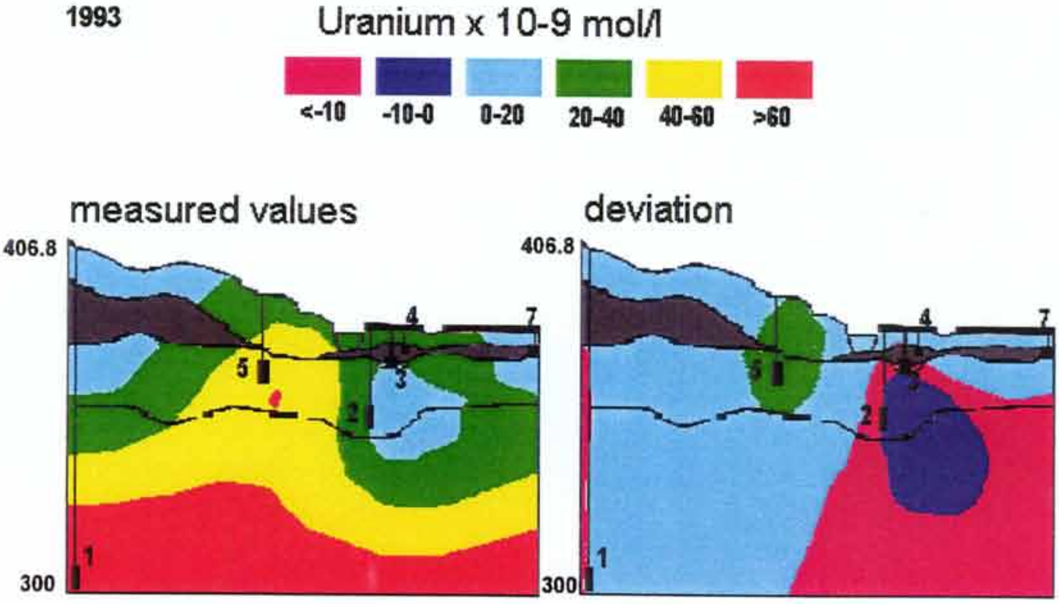


Figure 8-20: *Result of the M3 modelling of the uranium distribution in mole/l. Left picture measured values, right picture modelled values with M3 after compensating for effects from transport and mixing. A negative deviation from the measured uranium values is observed in the reactor zone. The left half of the deviation plot shows an anomaly with high U. A loss of uranium in the reactor zone is observed, showing no transport of uranium downstream the reactor. This result confirmed the HYTEC-2D results of the existence of a buffer around the reactor zone protecting the uranium and hindering uranium transport.*

The conclusion from the modelling is that despite the high content of rainwater around the reactor the gain of alkalinity indicates the presence of biological processes which decompose organic matter. This process acts like a buffer around the reactor and consumes oxygen resulting in a reducing condition which hinders uranium transport. The oxygen consumption process in this case seems to be faster than the influx of rain water.

At a later field campaign microbes were sampled and identified in and around the reactor. Large amounts of iron reducing microbes and organic matter were detected at the site and in-situ measurements of Eh indicated reducing conditions. The field measurements agreed well with the M3 and HYTEC-2D modelling results (Gurban et al. 1998).

9 Summary and Conclusions

The aim of this document is to describe the difficulties and risks but also the findings and improvements in both sampling and modelling of deep groundwaters gathered during 10 years of on-going site investigation programmes.

Äspö HRL (Hard Rock Laboratory) in Sweden has been the main test site for the development of suitable methods for the final disposal of spent nuclear fuel. The postglacial events at this site have to a great extent influenced the hydrochemical evolution since the last glaciation which ended some 13,000 years ago. At that time glacial melt water is believed to have been flushed down into the fracture system to a depth of several hundred metres. The next episodic event took place when the Baltic fresh water lake became the brackish Litorina Sea some 7,000 years ago. Äspö was covered by the sea and the denser sea water partly replaced the glacial water down to a depth where the density equilibrated with the replacement sea water. 3,000-4,000 years ago Äspö started to rise above sea level and meteoric water began to infiltrate the rock. The different events have resulted in complex groundwater compositions.

One major conclusion is that the real groundwater character can be easily biased during borehole activities such as drilling, borehole testing and sampling. There is no well-tested or fixed strategy which can be applied when sampling groundwater, only general recommendations can be used. The reason is that the representativeness of groundwater samples is a function of many interacting variables such as borehole location, sampling depth, in-situ groundwater composition, pump rate, economical and time constraints. In addition the success of a sampling can only be compared with expert knowledge based on expected groundwater compositions at the sampling depth. There are no samples from totally undisturbed downhole conditions which could be used as reference samples for the actual sampling. Improvements in sampling techniques and understanding the sources of disturbances have increased the representativeness.

The complex post-glacial history of the Äspö site made standard modelling codes based on thermodynamic laws often difficult to apply. Multicomponent mixing has occurred and this process may dominate over water/rock interaction processes. The many limitations of existing geochemical models used at the Äspö site, and the need to decode the complex groundwater information in terms of origin, mixing and reactions at site scale, necessitated the development of a new modelling tool. This new modelling concept was named M3 (Multivariate Mixing and Mass-balance calculations).

In M3 modelling the assumption is that the groundwater chemistry is a result of mixing as well as water/rock reactions. The M3 model compares the groundwater compositions from a site. The similarities and differences of the groundwater compositions are used to quantify the contribution from mixing and reactions on the measured data. In order to construct a reliable model, the method is used to summarise the information from the groundwater data set by using the major components Cl, Ca, Na, Mg, K, SO_4 and HCO_3 in combination with the isotopes δ^2H, $\delta^{18}O$ and ^3H. Initially, the method quantifies the contribution from the flow system by comparing the groundwater composition to identified extreme-waters named reference waters. Subsequently, contributions from reactions are calculated. The model differs from many other standard models, which primarily use reactions rather than mixing, to determine the groundwater evolution.

The modelled present-day groundwater conditions of the Äspö site consist of a mixture in varying degrees of the following water types: Brine, Glacial, Baltic Sea, Altered marine and Meteoric waters. The location, depth and hydraulic properties of the rock determine the degree of groundwater mixing. In the upper 250m of the bedrock the dominating mixing portion (>30%) is meteoric water. At greater depths a brackish-saline water consisting of proportions of present and ancient Baltic Sea water and glacial melt water occurs at a depth of 250-600 metres. Below this level the saline water still contains proportions of glacial water which could represent even older glaciations and a brine water of which the major portion has been stagnant for periods of time extending to millions of years.

During the tunnel construction phase there were changes in the composition of the water flowing into the tunnel at different locations. The variation in e.g. salinity was however relatively small, while the variations in the proportions of the different water types varied considerably. Where the HRL-tunnel penetrated shallow bedrock parts under the Baltic Sea modern or ancient sea water portions dominated. Where the tunnel passed shallow parts of the Äspö island meteoric water dominated but was replaced by sea water where the tunnel penetrated fractures in contact with Baltic Sea. At larger depths glacial or brine water composition started to dominate in the collected samples.

The processes considered having a dominating impact on the present Äspö groundwater chemistry are mixing, calcite dissolution and precipitation, redox reactions and biological processes. The mixing of the groundwater can be natural or enforced due to borehole activities or driven by the drawdown caused by the tunnel construction. The mixing of waters of different origins and composition is a continuous process. The mixing portions, sinks and sources of the elements due to chemical mass-balance reactions have been quantified. The important information concerning the origin and evolution of the groundwater at the Äspö site has been quantified, and the conceptual postglacial hydrogeological model has been verified. The M3 code was used for testing and modelling of the various processes and sites such as sulphate reduction, comparison of groundwaters at different sites in Sweden and natural analogue modelling in Africa.

Despite the many challenges when sampling and modelling deep groundwaters an increased understanding of the origin, mixing processes and major reactions taking place in the groundwater systems has been achieved. The groundwaters within the Swedish programme are generally of such quality that they reflect well-known paleo or present events such as de-glaciation, different marine signatures, land uplift, tunnel constructions, organic/inorganic reactions and effects from microbiological processes. The groundwaters in the bedrock have been accurately modelled by means standard and new modelling techniques starting from modern rainwater to brine water with an age of more than 1.5Ma. This information would have been lost in the case of vigorous groundwater disturbances. The major results are: better sampling techniques, higher representativeness of groundwater samples, modern and paleo groundwater effects that have been traced and modelled, the effects from mixing on the groundwater composition that are better understood, the effects from biogenic reactions that are better described and modelled.

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