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Research

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Review of Geochemical Data Utilisation
in SR-Site Safety Assessment

SSM perspective

Background
The Swedish Radiation Safety Authority (SSM) reviews and follows associated research related to the Swedish Nuclear Fuel Company's (SKB) work with establishing a repository for spent nuclear fuel and an encapsulation facility.

Objectives of the project
The objective of this study is to understand how data for groundwater compositions were used in producing the Site Descriptive Model for Forsmark and as input data for the safety assessment, SR-Site. Improving this understanding sheds further light on the significance of data uncertainties, data processing and interpretation on the degree of uniqueness in the descriptive model, parameterisation of processes, and long-term safety assessment.

Results
The first part of the report (Sections 2 to 4) summarizes the geochemical parameters that need to be measured on groundwater samples and their relevance for site characterization and long-term safety assessment. The chemistry parameters that are considered to be most significant for performance of the engineered and geosphere barriers are identified as 'safety functions' with specifications (as requirements or preferences) that need to be assured for the repository system and the associated 'safety function indicator criteria' that are used in scrutiny of data from the site investigation.

There needs to be sufficient understanding of how groundwater compositions might evolve to allow geochemical parameter values that are measured for present-day groundwaters to be modelled forwards in time for the duration of the safety assessment period.

Geochemical measurements have two major uses in the SDM and in safety assessment: (i) interpretations of hydrochemical and isotopic data that test conceptual and numerical models of groundwater movement and solute transport, and (ii) the hydrogeochemical model of the bedrock that describes the evolution of groundwater chemistry around a repository and between repository and biosphere in the long-term future so that the potential influences on the engineered barrier system (EBS) and on radionuclide mobility and retention can be forecast.

Hydrochemical data are processed by statistical analysis to support and calibrate the groundwater model. The analysis quantifies the proportions of end-member or reference waters that represent groundwater sources with distinct compositions and inferred ages. The development and application of this approach to describing the palaeohydrogeology of the system, i.e. how the system evolved from post-glacial conditions to its present state, for the SDM is explained. Some of the aspects that introduce uncertainty into the interpretations are discussed.

The site-scale long-term groundwater flow and solute transport model has been calibrated by comparing palaeohydrogeological simulations using initial and boundary conditions defined in terms of reference waters with proportions of reference waters calculated for sampled groundwaters. This method has been further developed to calibrate matrix diffusion in the transport model by comparing simulated and measured pore water salinities and stable isotopes. Specific comparisons for model calibration have been made using individual borehole depth profiles and could also be done at site-scale in 2D or 3D representations. Heterogeneity and sparse data constrain the rigour of this approach. The reported comparisons for calibration show quite large discordances and it is unclear how these have been used to calibrate model parameters.

The site descriptive model of hydrogeochemistry provides a conceptual model of the processes controlling long-term evolution of groundwater compositions, especially in relation to the repository

volume. It has been tested by showing that the processes account for the observed compositions at the present-day. There are many hydrogeochemical processes that could influence the chemical environment for the EBS to function. The conceptual hydrogeochemical model tends to be rather simplified, for example for pH and redox buffering, sulphide production, water-rock reactions controlling cation concentrations in dilute groundwaters.

The modelling method for describing hydrogeochemical evolution of groundwater compositions over time is based on hydrodynamic transport and mixing of individual reference water or end-member components. Model validity in forecasting how specific solutes evolve over time can be tested by comparing palaeohydrogeological reactive transport simulations with measured data. Results suggest that the hydrogeochemical model requires further development and detailed parameterisation of both transport and geochemical processes. The present model has been used for forecasting evolution of groundwater compositions to 10,000 years in the future. Other approaches have been used for longer timescales and variable boundary conditions that have to be considered in the safety assessment.

Measured analytical data for certain chemical entities, mostly at trace concentrations that have specific significance in safety assessment, have been processed and interpreted in SDM-Site and SR-Site to derive best estimates and ranges of uncertainty for their present-day concentrations in the groundwater system. These data and the resulting interpretations of geochemical (and biogeochemical) processes are the basis for describing initial state and for hydrogeochemical modelling of future evolution of these entities in the safety assessment.

The second part of the report reviews the use and requirements of geochemical data, including many of the trace entities reviewed in the previous section, for assessment of two important processes of the EBS: canister corrosion, and buffer alteration and erosion. It concludes that the processing and evaluation of data against safety function indicator criteria is reasonable. The third part of the report compares the hydrochemical properties of deep groundwaters at the Finnish site at Olkiluoto with those for groundwaters at Forsmark. There are various substantial differences, e.g. in concentrations of dissolved methane, in contrast to many similarities. The reasons for the differences are not yet fully explained and might be relevant to understanding potential future evolution of Forsmark groundwaters.

The final section of the report (Section 8) summarises some recommendations and suggested objectives for future geochemical data acquisition at Forsmark, especially exploiting the opportunities that become available for underground measurements during construction operations.

Future research
The challenge for both processes and their relevant geochemical data is to increase confidence that causes of variability are understood and adequately incorporated into the hydrogeochemical models. This requires further data and research of observed systems, perhaps in future underground investigations at Forsmark or at analogue localities. Results would be used to further develop the coupled reactive transport to a level of complexity that provides adequate simulations of the heterogeneity observed now and that could potentially occur in the future.

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essarily coincide with those of SSM.

Content

1 Introduction

After a site identification program starting in 1992, SKB narrowed the prospective locations for a spent nuclear fuel repository using the KBS-3 method to two sites. These two sites were Simpervarp/Laxemar (in Oskarshamn community) and Forsmark (in Östhammar community). Detailed characterisation of these two sites was carried out from 2002 to 2007. Site Descriptive Models ('SDM') for each of the two siting areas were published in 2008-9 (SKB 2009 and SKB 2008) plus supporting reports including those on hydrogeochemistry by Laaksoharju et al. (2009) and Laaksoharju et al. (2008). In late 2009, SKB announced that Forsmark would be the site of the spent fuel repository, on the basis of it having sound rock with sparse transmissive fracturing in the target repository depth range.

The safety assessment for the proposed spent fuel repository at Forsmark using the KBS-3 design, SR-Site, was published in 2011 (SKB 2011). It formed part of SKB's application in March 2011 for a license to construct and operate a spent fuel repository at Forsmark. SR-Site and its hierarchy of supporting technical reports have been evaluated by SSM and a panel of external experts during 2012-13. An international peer review of SR-Site was also carried out under the auspices of the OECD-NEA in 2011-12 (NEA 2012).

SSM published in 2015 the preliminary results of its review of the data and reasoning on which the selection of Forsmark has been based. SSM's reviews of SKB's methods for defining 'initial state' of the repository system and for consequence analysis were also published in 2015. In June 2016, SSM gave its opinion on SKB's application for a construction license to the Land and Environment Court. On the basis of the Environmental Impact Assessment of a spent fuel repository at Forsmark, SSM's opinion is that SKB's plans and designs have the potential to fulfil the requirements for protection of human health and environment against harmful effects of radiation.

The objective of the present study is to understand how data for groundwater compositions were used in the Site Descriptive Model (SDM) of Forsmark and as input data for the safety assessment, SR-Site. Improving this understanding sheds further light on the significance of data uncertainties, data processing and interpretation for the degree of uniqueness in the descriptive model, parameterisation of processes, and long-term safety assessment.

Some geochemical data have been used by SKB to assess whether indicator criteria for safety functions are met in the present-day system and will be met in the future evolving system. Many geochemical data were processed and interpreted by SKB to constrain quantitative models of long-term processes in the repository system. Both (palaeo-) hydrogeological and hydrogeochemical models have been developed this way. Palaeohydrogeological modelling is a prominent use in SR-

Site of data for groundwater compositions, whilst being a novel and 'in development' methodology for which uncertainties and alternative models need to be fully considered.

This overview of how data have been used in the SDM and SR-Site aims to improve SSM's understanding of the methods of data processing and interpretation, and to clarify and evaluate further the inherent uncertainties by examining the supporting hydrogeological and hydrogeochemical reports.

Having reviewed how data have been used in SR-Site, the study is able to identify some of the areas where additional data and further development of data processing and interpretation methods could improve confidence in the interpretations and models. Opportunities to carry out further data acquisition and to develop interpretation methods may arise in future underground investigations. For some parameters, it may be possible to achieve more reliable and/or more frequent measurements from underground. It may also be possible to carry out experiments underground, supplementing those already done in the Äspö HRL (Hard Rock Laboratory). Such experiments might constrain the potential breadth of concepts for how the hydrogeochemical system will evolve in the long-term future.

Hydrogeochemical site characteristics are significant for the assessment of engineered barrier stability, primarily the corrosion resistance of the copper canister and the stability of the buffer in the context of mineralogical alteration, swelling capacity and erosion. The geochemical variables of interest for corrosion are redox and coupled biogeochemical conditions, and concentrations of redox-affecting groundwater constituents including reactive gases. Site investigations must provide information to understand sufficiently the redox-affecting chemical and microbial processes and how the redox system will evolve in the future. Similarly, site data and processes that influence potential evolution of groundwater salinity and chemical species affecting bentonite performance and potential erosion and alteration must be sufficiently understood. Variations of groundwater compositions, including natural isotopic compositions, also have underpin the conceptual and quantitative understanding of groundwater movements and other aspects of site understanding. Groundwater compositions in the engineered barrier system (EBS) and in the surrounding geosphere influence the chemical speciation, retardation and transport of radionuclides. The suitability of the geochemical measurement campaign from the perspective of gaining as much information as possible regarding site hydrogeology, site understanding, and radionuclide transport is therefore a necessary part of this evaluation.

2 Geochemical Measurements

2.1 Required data for geochemical properties

The objectives of measuring the chemical properties of groundwaters for forecasting in the safety assessment the performance of the engineered barriers and the geosphere are:

- To quantify the likely corrosion of the copper canisters and thus to forecast the period for which groundwater will be excluded from contact with spent fuel;
- To assess the long-term integrity of the bentonite buffer and to model its performance in protecting the canisters for as long as possible and in retarding the release of radionuclides after canister failure;
- To estimate the rate of spent fuel dissolution and to model the processes by which water composition will control the solubility and release of radionuclides, after canister failure and access of water;
- To model the future performance of the far-field rocks in retaining, or slowing the movement of, any radionuclides that might be released from the engineered barriers.

Table 1 is a fairly comprehensive list of the chemical and associated (e.g. microbiological) parameters for groundwater compositions that are significant for characterising chemical properties and quantitatively assessing those aspects of repository system performance. It is based on the list given by SKB (Andersson et al. 1998) but has been modified here by a few additions and deletions to better represent the present consensus on important parameters. 'Essential' indicates those parameters that have direct, and in some cases, quantitative influence on the particular barrier performance, whereas 'limited' indicates those parameters that have an indirect and minor influence that is probably not quantifiable.

The chemistry parameters that are considered to be most significant for performance of the engineered and geosphere barriers are identified as safety functions and are shown in Table 2, along with the specifications (as requirements or preferences) that need to be assured for the repository system and the associated safety function indicator criteria that are used in scrutiny of data from site investigation.

Table 1. Groundwater chemistry parameters of importance for repository performance (modified from Andersson et al. 1998)

	Canister corrosion		Bentonite performance		Spent fuel dissolution and radionuclide solubilties		Radionuclide retention	
	Essential	Limited	Essential	Limited	Essential	Limited	Essential	Limited
TDS[1]		✓	✓			✓		✓
pH		✓	✓		✓		✓	
O_2 (diss)	✓							
Eh	✓				✓		✓	
Na^+			✓					✓
Ca^{2+}			✓					✓
K^+			✓					
Mg^{2+}			✓					
Cl^-	✓					✓	✓	
SO_4^{2-}	✓					✓		✓
HCO_3^-		✓			✓		✓	
Fe^{2+}	✓				✓		✓	
HS^-	✓					✓		✓
SiO_2				✓				
Al^{3+}				✓				
NH_4^+	✓							
HPO_4^{2-}		✓				✓		✓
F^-						✓		✓
Mn^{2+}								✓
H_2 (diss)		✓						
CH_4 (diss)		✓						
DOC		✓						✓
microbes		✓					✓	
colloids							✓	

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[1] TDS Total Dissolved Solids
DOC Dissolved Organic Carbon

Table 2. Suitability indicators for groundwater compositions (from Andersson et al. 2000)

Parameter	Requirement or Preference (Required/Preference)	Criteria in Site Investigation
Dissolved O_2	Req: Absence at repository level (indicated by negative Eh, occurrence of Fe^{2+} and/or HS^-)	At least one of requirements for Eh, Fe^{2+} or HS^- must be satisfied
pH	Pref: Undisturbed groundwater at repository level should have pH between 6-10	Values should be in range 6-10 below -100 m depth
TDS	Req: TDS <100 g/l	Values at repository level must be <100 g/l; occasional higher values are acceptable if located in areas that can be avoided
Others	Pref: DOC <20 mg/l Pref: Colloids <0.5 mg/l Pref: Low NH_4 Pref: $Ca^{2+}+Mg^{2+}$ >4 mg/l at repository depth Pref: Low Rn and Ra	Attention is needed to deviations from preferred maximum/minimum concentrations

SKB included in their site characterisation strategy several geochemical, mineralogical and petrographic analyses and other types of information (Table 3). These data support the interpretations of hydrochemical and isotopic data for groundwaters and the conceptual model for radionuclide transport and retardation in the geosphere.

Table 3. Groups of geochemical, petrographical and mineralogical parameters that are required from drillcore samples of rock

Sample types	Analyses and other information
Bulk rock in drillcore	Bulk rock composition, major and trace elements incl. S, F, P, REEs, U, Th, ore-forming metals (Cu, Zn, V, Cr, Ni, etc.)
Bulk drillcore and thin sections	Visual logging and petrography of rock fabric, filled and open fractures, fracture edge and matrix alteration, micro-porosity
Thin & polished sections, stub mounts	Identity and composition of matrix minerals including trace minerals
Thin sections, 'picked' samples, stub mounts	Identities and petrogenesis of fracture-coating and fracture-filling secondary minerals including sulphides, carbonates and clays; stable O and C and U/Th isotopic analyses of secondary calcites; trace element analyses e.g. U, REEs in secondary minerals

A variety of hydrochemical and isotopic data were used in the SDMs for Forsmark and Laxemar for defining conceptual models of groundwater movement, palaeohydrogeology and solute transport (Table 4). Isotopic data were also used to support interpretation of site geochemistry and of the water-rock reactions that might control the future evolution of groundwater compositions.

Table 4. Hydrochemical and isotopic parameters used to test and support the conceptual and numerical models of groundwater movement and solute transport and to understand other aspects of the geochemical SDM.

Parameters	How data are used in the SDM
Salinity, TDS	Characterisation of volumes and types of groundwater that are distinct in terms of sources
Na, K, Ca, Mg	Characterisation of volumes and types of groundwater that are distinct in terms of sources and water-rock reactions
Cl, SO_4, Br	Characterisation of volumes and types of groundwater that are distinct in terms of sources
$^{18}O/^{16}O$, $^2H/^1H$	Characterisation of volumes and types of groundwater that are distinct in terms of sources
^3H	Indicator of young water that has infiltrated in last 60 years (very low concentrations could also be produced in situ)
$^{13}C/^{12}C$	Distinguishing carbon sources e.g. abiotic or microbial sources; indicator of extent of ^{14}C dilution
^{14}C(TIC), ^{14}C(TOC)	Estimation of groundwater ages in terms of sources and evolution of dissolved inorganic carbon or organic carbon
$^{34}S/^{32}S$ in HS and SO_4, $^{18}O/^{16}O$ in SO_4	Evidence for dissolved sulphur sources and biogeochemical redox transformations
^4He	Indicator of groundwater age, flow heterogeneity and mixing of water from different sources (produced radiogenically from decay of natural U and Th in rocks)
^{36}Cl	Indicator of chloride residence time, groundwater age, and mixing of groundwater masses with differing salinity sources
$^{37}Cl/^{35}Cl$	Identification of groundwater masses with differing salinity sources
Rn, U, Th, Ra	Natural solutes that are analogues of radionuclide behaviours; U is also an indicator of redox conditions
U & Th series nuclides	Evidence for water-rock reactions affecting dissolution, precipitation and migration of uranium and radium (through isotopic disequilibrium in parent-daughter decay series)
I, Cs	Natural solutes that are analogues of radionuclide behaviours
REEs	Analogues for behaviour of trivalent radionuclides and diagnostic of water-rock reactions
Si, Al	Input to hydrogeochemical model for present-day groundwater compositions and evolution of future water compositions (other inputs are pH, major ions, redox-active species)

2.2 Measurements of groundwater compositions

Having summarised the geochemical data requirements for site investigations at Forsmark and Simpevarp/Laxemar, it is interesting to look at what was measured in the site investigations. Table 5 has been compiled by the present author based on SKB's information in 'P' reports. It summarises the preliminary data that were reported from site investigations prior to data processing and quality control. Subsets of these data were approved by SKB for use in interpretation, modelling

and safety assessment, with appropriate caveats and uncertainty ranges related to sampling and analytical reliability.

Significant numbers of analyses for phosphate (as total P), iodide, caesium and rare earth elements (REEs) were also carried out for both Simpevarp/Laxemar and Forsmark, but the data are not easily accessible. Analyses of microbes and colloids in groundwaters, mostly around proposed repository depth at Simpevarp/Laxemar and Forsmark, have been reported in summaries by Hallbeck et al. (2008a,b).

Table 5. Geochemical parameters reported from SKB's investigations of groundwaters at Simpevarp/Laxemar and Forsmark (numbers of data shown here are generally the data for individual samples; total numbers of analyses taking account of replicates and rejected data are higher).

Parameters	Numbers of data reported for Simpevarp/Laxemar	Number of data reported for Forsmark
pH	441 (95 by Chemmac)	207 (31 by Chemmac)
HCO_3	339	180
DO	12	18
Na, K, Ca, Mg	299	179
Cl, Br	337, 337	208, 208
Eh, Fe^{2+}, HS^-, SO_4	45 (all by Chemmac), 158, 104, 310	26 (all by Chemmac), 78, 71, 180
Mn	173	39
CH_4 & H_2	10, 6	14, 7
DOC	110	98
NH_4, NO_3^-, NO_2^-	90, not known	47, 8, 8
U, Rn, Ra	36, 54, 54	66, 45, 45
Si, Al	165, 2	111, 49
F, HPO_4	337, not known	208, 17
I, Cs	not known, 32	not known, 27
REEs	not known	10
$^{18}O/^{16}O$ & $^2H/^1H$	224	145
^{13}C, ^{14}C(TIC), ^{14}C(TOC)	74, 74, 0	45, 45, 3
$^{34}S/^{32}S$ in SO_4	85	57
^3H	267	134
^4He	10	18
^{36}Cl	4	13
$^{37}Cl/^{35}Cl$	46	24
$^{11}B/^{10}B$	22	30
U & Th series nuclides	56	25
colloids	10	10
microbes	14	18

3 Geochemical Data in the Groundwater Model

The Site Descriptive Model (SDM-Site) for Forsmark describes conceptual models and features and processes for geology, hydrogeology, geomechanics and geochemistry. The SDM considers how these models are confirmed and quantified by data and interpretative modelling. Geochemical data have been used to support and test the bedrock hydrogeology model (below), and the bedrock hydrogeochemistry model (in Section 4).

The spatial distribution of groundwater types has been identified and used for three purposes: (a) interpretation of individual groundwater compositions in terms of the origins and mixing of end-members; (b) interpretation of palaeohydrogeological evolution by mixing of reference waters and calibration of a transport model of how the post-glacial groundwater system has evolved to the present day; and (c) the hydrogeochemical description of the evolution of groundwater compositions by hydrodynamic mixing and geochemical reactions.

The integrated hydrogeochemical model of water types, water origins and water-rock reactions is illustrated in Figures 9-22 and 9-23 of SDM-Site (SKB 2008). Cross-sections through Forsmark site show the depth dependence of hydrogeochemistry that is correlated to the major structural features of the site, especially the 'hanging wall' and 'footwall' structural blocks.

3.1 Identification of water types, origins and ages

Compositions of fracture waters in terms of Cl^- concentrations and water $\delta^{18}O$ values are used as a generalised confirmation of the conceptual model for groundwater flow at site scale (Section 4.8, SKB 2011). The origins and distributions of fresh, brackish and saline waters in the Forsmark groundwater system are inferred from Cl^-, $\delta^{18}O$ and Br/Cl data.

Cl^- and $\delta^{18}O$ data for groundwaters sampled from the two main structural systems in the Forsmark site, i.e. the footwall fracture domains and the hanging wall fracture domain are shown as depth profiles and categorised according to water salinities and origins, i.e. fresh, mixed brackish, brackish marine/Littorina, transitional, and brackish-to-saline non-marine waters, in Figure 9-5 in SKB (2008) and in Figure 4-21 in SKB (2011) (see also Figure 1 in this report). The lateral scatter of data, especially of $\delta^{18}O$, in Figure 1 indicates that groundwaters at any particular depth across the site have heterogeneous origins. This heterogeneity is also seen in the interpreted mixing proportions of end member reference waters.
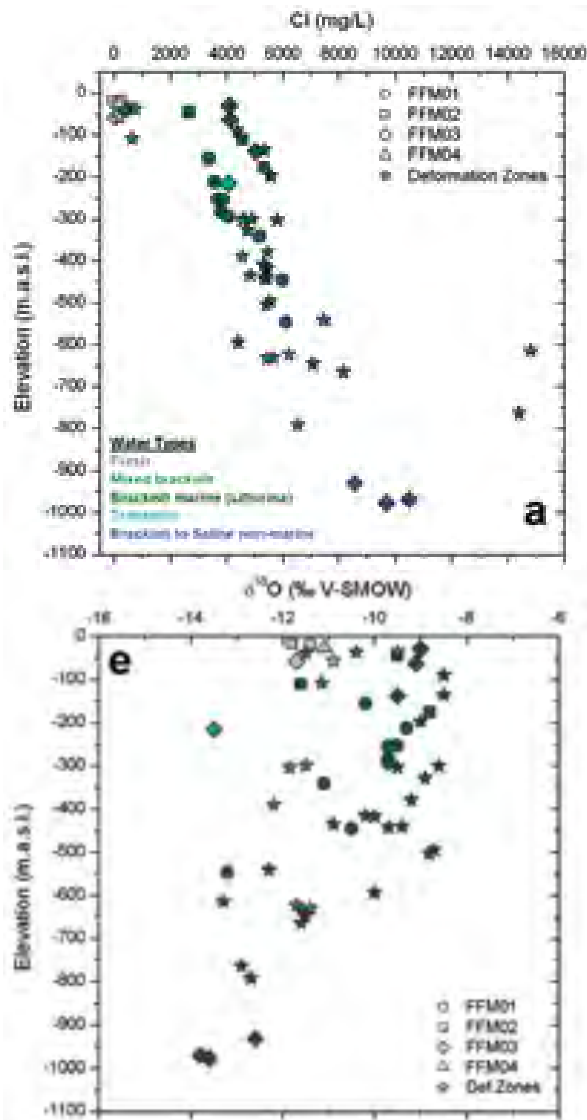
Figure 1. Depth profiles of Cl⁻ and δ¹⁸O in groundwaters in the two main structural systems at Forsmark: footwall fracture domains (FFM01 & FFM02) and hanging wall fracture domain (FFM03); also showing categorisation of groundwaters according to water types (Fig 4-21 in SKB 2011 & Fig 9-5 in SKB 2008).

Schematic representations of how present-day groundwater compositions and water types vary with depth and structural situation at site scale are shown as Figures 4-22 and 4-23 in SR-Site (SKB 2011). These cross sections based on hydrochemical variations illustrate the simplified conceptual model for groundwater flow and palaeohydrogeology in groundwater domains that are delineated by the major faults and fractures. Statistical analysis of major solute and stable isotopic data using SKB's M3 tool (Gomez et al. 2009) to deconvolute the groundwater mixtures into proportions of reference waters will be discussed in Section 3.2. Further indications of the timescales of vertical movements of groundwaters could potentially be interpreted from ages inferred from natural isotopic tracers, primarily ³H (tritium) and ¹⁴C (carbon-14).

12

There is a possibly-significant decrease from moderately high tritium values in shallow groundwater samples to a persistent background of 1-3 TU (Tritium Units) at around 150-200 m depth (Laaksoharju et al. 2008, Section 4.9.3). It suggests that infiltration may circulate to that depth range within about 50 years.

Quantitative age data for meteoric water infiltration, isotopically-light 'older' infiltration, or brackish intrusion would help to estimate the travel times for those groundwater components to move through the system. Travel times interpreted from ^{14}C data have not been used for groundwater model calibration in SDM-Site because of large uncertainties in calculating ^{14}C-decay ages (Smellie et al. 2008). ^{14}C data do not indicate the depth-dependency of ages of the fresh water component that is mixed in with deeper saline groundwaters, though the trend of ^{14}C values with increasing depth, excluding one sample at around 650 m that is thought to be contaminated (Figure 2), indicates that ^{14}C-containing water might exist beyond 500 m depth, but there are no data from groundwater samples deeper than 650 m. The ^{14}C contents of brackish groundwaters down to 500 m (Figure 2) give semi-quantitative support to these waters having a postglacial origin as intrusion of Littorina sea water (Laaksoharju et al. 2008, Section 4.9.3). This is supported by a few analyses of ^{14}C in dissolved organic carbon in similar brackish groundwaters which indicate ages of 5000-6000 years.

Water stable isotope ratios are systematically used to discriminate qualitatively between isotopically-light water that infiltrated during the Pleistocene ice ages and water that has isotopic composition close to modern precipitation.
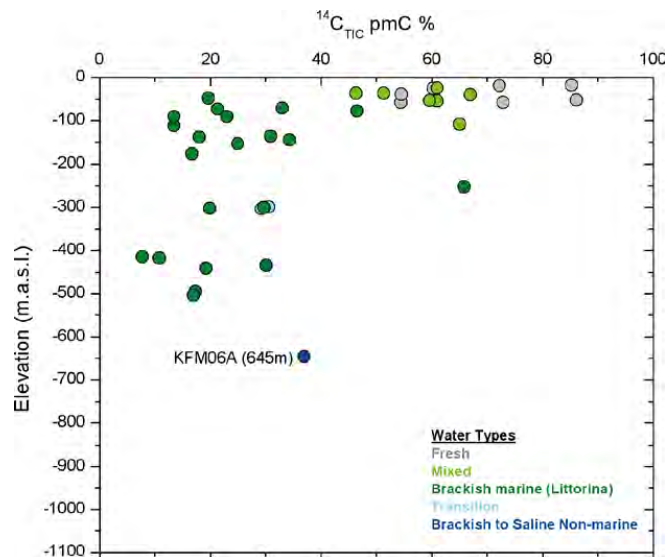

Figure 2. Depth profile of ^{14}C data for groundwaters at Forsmark according to water type; groundwaters analysed were all of fresh, mixed or brackish marine origin (i.e. Littorina seawater) except for one brackish non-marine sample which is believed to have been contaminated during sampling (Fig 4-21 in SKB 2011).

3.2 Statistical analysis of reference water sources and mixtures

Groundwaters are hydrodynamic mixtures of end-member waters with past and present environmental origins. The mixing proportions of end members at each sampled point vary according to present and past groundwater flows. Data for chemical and stable isotopic compositions of groundwater samples were processed with a multivariate statistics tool to estimate the proportions of hypothetical end-member waters in the groundwaters. The tool used for this statistical deconvolution of the groundwater mixtures is the 'M3' (Multivariate Mixing and Mass-balance Calculations) code which uses the principal components analysis method (Gómez et al. 2009).

To be hydrogeologically and hydrochemically meaningful, the statistical deconvolution tool needs compositions of waters to be assumed that represent probable end members. The concept that all sampled groundwaters are composed of mixtures of a small number of end-member waters with fixed compositions for all points in space and time is a simplification of a spatially large groundwater system with a complex palaeohydrogeological evolution over a prolonged period in which environmental and climatic boundary conditions changed. This assumption and simplification underlie the analysis of past groundwater evolution, the palaeo-hydrogeological calibration of the groundwater flow model and the modelled forecasting of groundwater evolution scenarios.

Likely end-member waters for which measured compositions are available are e.g. recently-infiltrated groundwater at shallow depth and modern Baltic seawater. Compositions are not directly measurable for palaeohydrogeological end members i.e. Littorina seawater and cold-climate water of Pleistocene age, and for end members that are speculative e.g. a high salinity or brine groundwater at greater depth than has been sampled. For these end members, hypothetical reference water compositions were based on relevant literature data and expert judgement. Measured or expertly-judged compositions of end-member waters have been adjusted to achieve water-rock reaction equilibria e.g. with respect to carbonate and sulphide minerals. Parameters that are adjusted in this way are pH, total inorganic carbon (TIC) and redox-active solutes such as HS^-. The resulting equilibrated end-members have significance as 'typical' groundwater masses, each with different origins and driving forces that have been active in the evolution of the groundwater system over a long period up to the present. For example, the driving forces might have varied due to changing boundary pressures as a consequence of climatic changes (e.g. glaciation or permafrost) or water density changes.

In the preliminary exploratory numerical analysis of analysed groundwater samples, six end-member waters were assumed (Gurban in Kalinowski, ed, 2008):
- Deep saline water
- Saline water
- Glacial melt water

- Old meteoric-glacial water
- Littorina water
- Recent altered meteoric water.

Of these, compositions of the first two and the last were defined by observed groundwater compositions (although the deep saline water was defined by the most saline water found at Laxemar, whilst the saline water was defined by the most saline water found at Forsmark.

Three variant M3 models were evaluated, using slightly different input data and different end member combinations. The variant with the deep saline, rather than the saline, end member was recommended for use in subsequent hydrogeological transport modelling (see Section 3.3). This selection of end member waters was propagated through into the Bedrock Hydrogeochemistry Model report (Laaksoharju et al. 2008, Section 4.2) and thence into the final SDM-Site report (SKB 2008).

Uncertainties have been assessed in Gimeno et al. (2008a), Section 4.10.1 of Laaksoharju et al. (2008), Section 3.7 of Gimeno et al. (2008b) and by the validation exercise that is reported in Gómez et al. (2009).

The assumption that end-member waters or reference waters have time-invariant compositions is one of several sources of uncertainties that are potentially significant in both calibration of the hydrogeological model and construction of the hydrogeochemical site descriptive model. Three other potential sources of uncertainties are: (i) the saline water component at Forsmark is represented by a groundwater composition from Laxemar that may not be representative, (ii) there are two end-member waters, glacial melt and old meteoric-glacial, that are characterised by light stable isotopic ratios so the resolution of glacial melt water occurrence will not be unique, and (iii) the selection assumes that reactive as well as non-reactive water chemistry parameters are used as input to M3 to obtain a unique solution to mixing proportions. Data for reactive solutes such as HCO_3^- have many different causes of variability, other than mixing, and therefore introduce greater degrees of uncertainty into the statistical analysis despite the apparent uniqueness of the solution.

The spatial distribution of reference waters modelled with M3 is an interpretation of past groundwater movements, i.e. of palaeohydrogeology, and is an indication of the likely future evolution of the groundwater system. Some features of the palaeohydrogeology are of particular interest because they indicate potential temporal and spatial scales of groundwater movement under scenarios for future site evolution:
- Depth of penetration of sub-glacial infiltration, represented by the old meteoric-glacial reference water;
- Depth to which post-Littorina meteoric infiltration has reached in the ~2500 years since Forsmark emerged from the Littorina/Baltic Sea, represented by the Holocene or recent meteoric reference water;

- Depth of penetration of sea water that infiltrated during the post-glacial Littorina period of about 9000 years duration, represented by the Littorina/Baltic reference water;
- Migration of groundwater from repository depth into shallow groundwater, represented by the distribution of the deep saline and saline reference waters.

SKB has noted a caveat that a calculated mixing proportion of <10% for any of the reference waters is probably below the detection limit of the M3 method, i.e. too small a fraction to be confident that it is hydrogeologically significant. Figure 3a shows that 'recent meteoric water' reference water is detectable, i.e. is calculated to be present at >10%, down to at least 700 m. Similarly, Figure 3b shows that Littorina water is detectable to at least 600 m depth. The depth plots show roughly linear decreases in the maximum proportion of infiltration as depth increases. Infiltration of quite large proportions of recent meteoric and Littorina reference waters to at least 500 m, i.e. to the target depth for a repository, is indicated by M3 analyses. The approximate timescales for infiltration to penetrate to these depths are 2500 and 9000 years respectively, based on the palaeoclimatic timing of these water sources at the surface. These timescales compare with travel times of 2500 to 4000 years that were calculated deterministically with a Continuous Porous Medium (CPM) groundwater model of the Forsmark site (Hartley et al. 2006) and median travel time in the order of 10^2 to 10^3 years that were calculated probabilistically with the site-scale transport model (Figure 6-17 in Joyce et al. 2010).

Quantifying the depth to which sub-glacial melt water had penetrated during the Pleistocene glaciations, by attempting M3 analysis with a distinct 'melt water' reference, is problematic because of the dispersion and mixing that has occurred at many hundreds of metres depth and also because of the poorly-defined range of stable isotopic compositions for potential infiltration water during that period. Calculating the proportion of 'old meteoric-glacial' reference water is sensitive to $\delta^{18}O$ value that is assumed to be intermediate between the very low value of glacial melt water and the higher value for temperate climate water (Laaksoharju et al. 2008, Section 4.2). Interglacial infiltration would have mixed with glacial melt water. It means that glacial melt water infiltration *per se* is not discriminated in the M3 analysis. The result of the M3 analysis of depth-dependent proportions is shown in Figure 4; the calculated proportions of the old meteoric-glacial end member increase progressively with depth and reach 75% at the greatest investigated depth of around 1000 m. This does not give unequivocal information about the maximum penetration of sub-glacial melt water but indicates that pre-Holocene fresh water of varied origins forms a component of deep groundwater and has circulated to 1000 m or more.

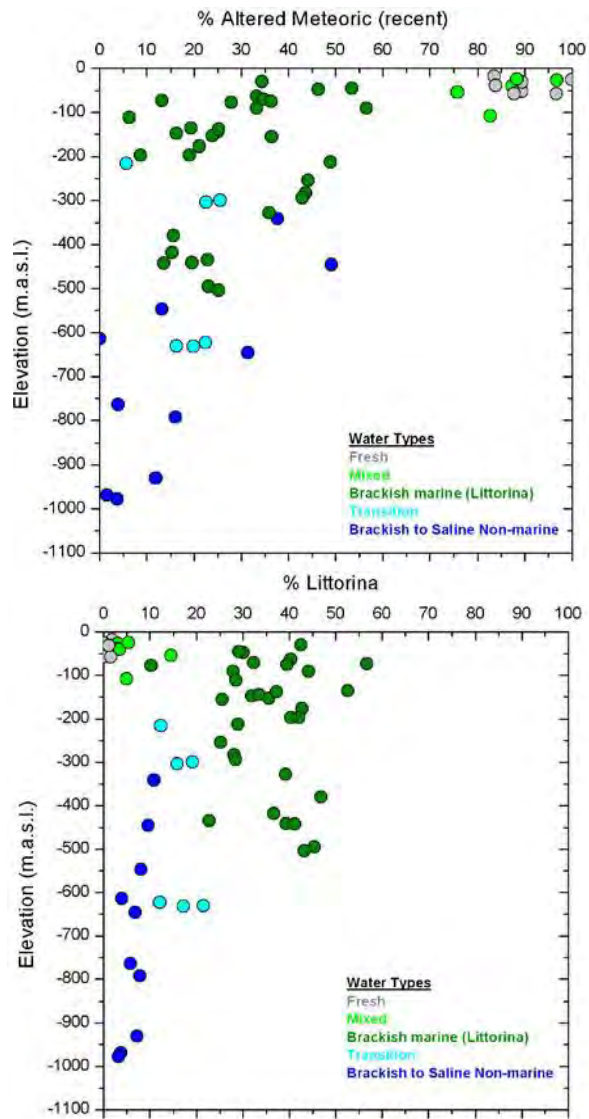**Figure 3.** Mixing proportions versus depth of (a) recent Altered Meteoric end member and (b) Littorina sea water end member in current groundwaters at Forsmark (Fig 9-11 in SKB 2008).
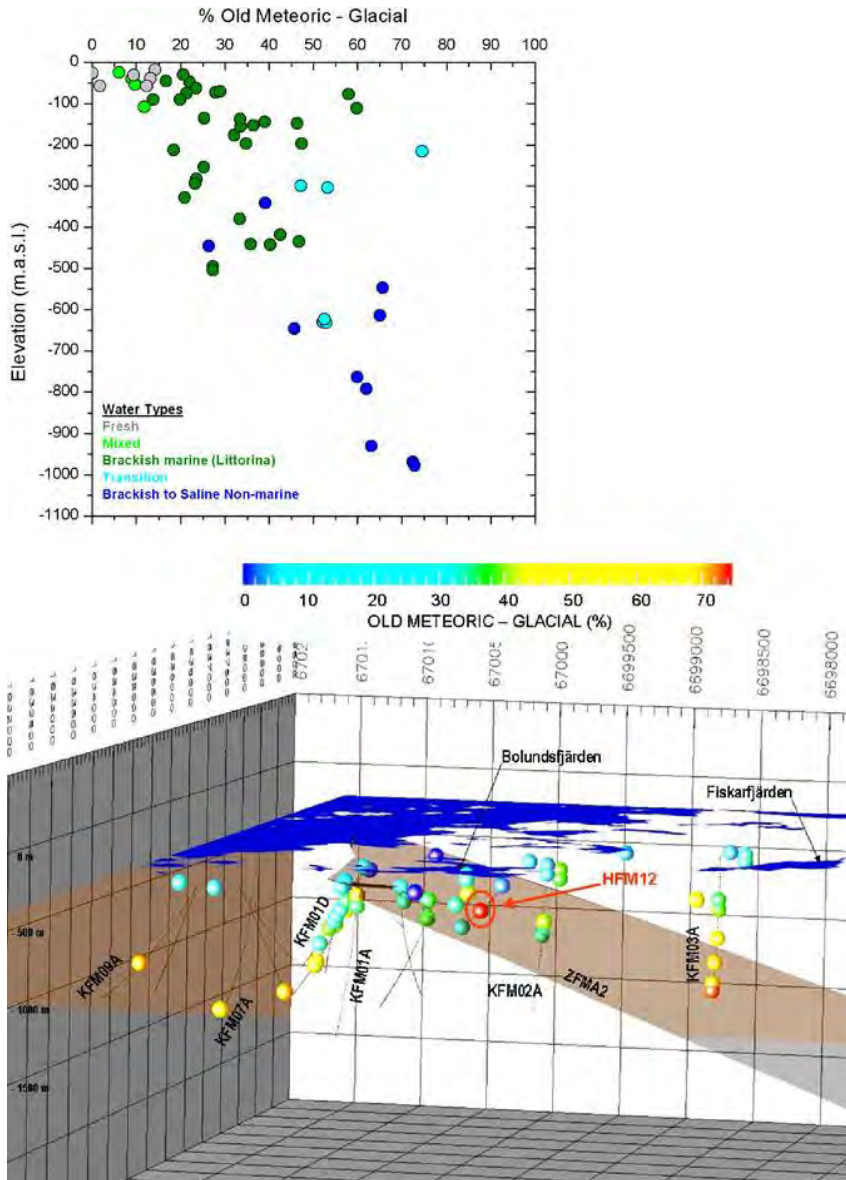
Figure 4. Mixing proportions calculated with M3 of the Old Meteoric-Glacial end member in groundwater samples versus depth and salinities at Forsmark (upper figure) and in 3D borehole trajectories (lower) (Figure 4-13 in Laaksoharju et al. 2008).

Choosing a water composition that has been observed at Laxemar, but not at Forsmark, to be the 'deep saline' end member adds further uncertainty to the M3 analysis of deep groundwaters at Forsmark. In other words, carrying out an M3 analysis with an end member that has higher salinity than is observed forces M3 to 'create' higher proportions of dilute water end member, i.e. the 'old meteoric – glacial' end member, than are probably present. In qualitative terms, the steadily decreasing salinity with decreasing depth does however imply that dilution of a saline water has occurred due to deep circulation of meteoric water or glacial melt water. It does not indicate the timing of the dilution, except that it can be inferred to have involved water with 'temperate climate' as well as 'cold climate' stable isotopic compositions. Therefore, it could have occurred through the interglacial and pre-glacial periods through which the groundwater system has evolved. Proportions of the 'deep saline' end member that are calculated by M3 to be in groundwaters are shown in Figure 5. SKB notes that calculated mixing proportions of a deep saline water component at shallow depths are within the detection uncertainty of 10% in proportions calculated with the M3 tool (Laaksoharju et al. 2008). The calculated proportions of deep saline water at proposed repository depth and below are >10% and therefore significant. It is not known whether this indicates upwards movement at the present time of deep saline water from below repository depth towards the surface, or whether this distribution is relict from past hydrogeological conditions. The former case would be significant for better understanding of upwards solute transport paths. It is suggested that an aim of future site characterisation could be to understand better the movement and palaeohydrogeology of deep saline water, as distinct from Littorina salinity, in pathways between repository depth and surface. Data from porewaters in the rock matrix contribute to understanding this issue (Waber et al. 2008).

The general conclusion drawn concerning the statistical analysis of data from sampled groundwaters and depth distribution of reference waters is that the approach has many uncertainties that tend to give erroneous indications of the 'tails' of reference water occurrences in the depth profiles of M3 output. In general, caution is necessary in equating calculated proportions of reference waters with hydrogeologically-distinct water masses. The converse is that palaeohydrogeological calibration of the groundwater flow and transport model with outputs from the statistical analysis of reference water proportions in groundwater compositions also has poorly-quantified uncertainties. Support for the parameterisation of the long-term flow and transport model, particularly for origins, flow directions and dispersive mixing of groundwaters at repository depth, would potentially be improved by more data and interpretation for the deep saline end member and for groundwater ages and travel times. Realistic ranges of variation for reference water compositions that cannot be sampled because they are palaeohydrogeological (or in the future, in the case of the hydrogeochemical evolution model) will remain uncertain.
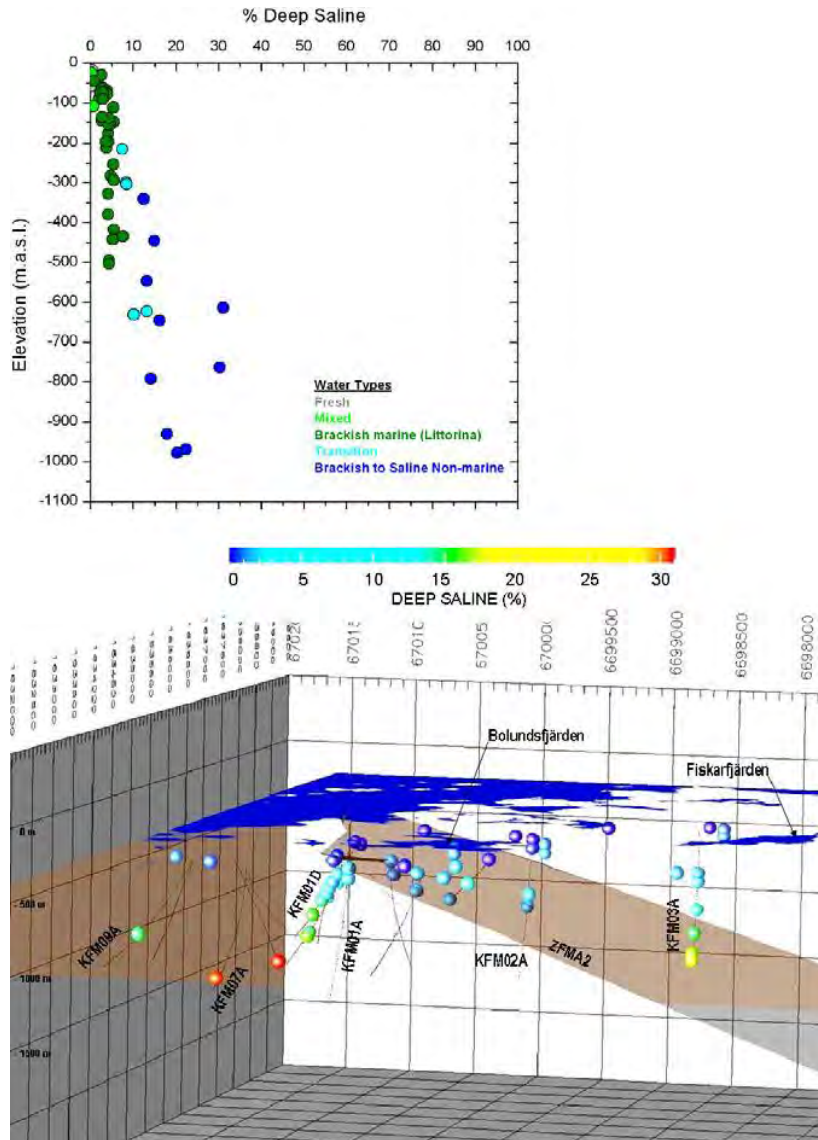
Figure 5. Mixing proportions calculated with M3 of the Deep Saline end member in groundwater samples versus depth at Forsmark (upper figure) and in 3D borehole trajectories (lower) (Figure 4-12 in Laaksoharju et al. 2008).

3.3 Palaeohydrogeological calibration of the groundwater flow and transport model

The aim of calibration is to adjust the parameters of the flow and transport model so that it provides an improved simulation of groundwater evolution and solute transport over a timescale that is comparable with that of the scenarios in safety analysis. Environmental and climatic processes and boundary conditions driving groundwater evolution in the post-glacial calibration timescale of around 10,000 years probably have not been the same as the processes that will influence groundwater conditions through the temperate climate and other climate scenarios

analysed in SR-Site. So palaeohydrogeological calibration is one of several approaches for developing the long-term safety assessment transport model.
The site-scale groundwater flow and solute transport model has been calibrated by means of a palaeohydrogeological reconstruction of the flow and transport of natural solutes. The flow and transport model is run forwards from a starting point in the past at which there is some justification for hypothesising what the initial groundwater condition was in terms of spatial variation of proportions of reference waters. The transient model is run forwards from a starting point 10,000 years ago, i.e. at the end of glaciation and prior to Littorina Sea inundation and infiltration, to the present. Model calibration is achieved in principle by comparing modelled distribution of reference water proportions to proportions indicated by M3 analysis of compositions of sampled groundwaters. A further calibration has subsequently been made using concentrations for specific entities, e.g. Cl$^-$ and δ^{18}O, in borehole-specific depth profiles rather than reference water distributions at site scale (see below).

Palaeohydrogeological modelling is done with the ConnectFlow model using the most appropriate reference waters, that best describe the water compositions in terms of distinct water sources, ages and initial compositions, as the transported entities (Joyce et al. 2010). It assumes two reference waters that constitute pre-Holocene groundwater at Forsmark, i.e. prior to the end of the Weichselian glaciation, and three more reference waters that entered the system during the Holocene (SKB 2008, Section 8.6.3). The five reference waters are slightly different from the six reference waters used in the preliminary statistical deconvolution of groundwater compositions (see Section 3.2):

- Deep saline water
- Old meteoric and glacial waters, assumed to be a homogeneous mixed water
- Holocene glacial melt water
- Littorina sea water
- Altered meteoric water.

The definition of the initial condition for modelling from 10,000 years ago, and of how it has evolved since then, assumes how pre-Holocene groundwater is constituted including the distribution of glacial melt water that was already in the system at 10,000 years ago. Infiltration of glacial melt water as an ongoing process is not simulated in the model.

The two pre-Holocene reference waters, 'deep saline water' and 'old meteoric and glacial water', do not have specific origins and are end-members that have been judged to mix together in depth-dependent proportions to constitute water in the system at the start of Holocene evolution. The two Holocene reference waters, 'Littorina sea water' and 'altered meteoric water', have infiltrated the system in time-and depth-dependent proportions to produce the compositions observed in sampled groundwaters. Holocene infiltration and mixing of these two reference waters is simulated by the palaeohydrogeological transport model.

The modelled distributions of proportions of reference waters at the present day can be translated into values for hydrochemical and isotopic parameters. These modelled or 'reconstructed' groundwater compositions have been projected onto depth profiles at drillhole positions in SDM-Site, so that they can be compared directly with compositions of groundwaters sampled at Forsmark. Parameters studied in this way are TDS, Cl, Br/Cl, SO_4, HCO_3, Na, Ca and Mg plus the oxygen stable isotopic ratio $\delta^{18}O$ (Figures 8-46 to 8-49 in SKB 2008). Cl and $\delta^{18}O$ have also been modelled with the addition of diffusive exchange with pore waters in the rock matrix in two drillhole profiles, though there are relatively few measurements for comparison (Figure 8-50 in SKB 2008).

The spatial distribution of Cl concentrations and $\delta^{18}O$ values across the site has been modelled using the deterministic DFN representation of transmissive transport paths. The model was run from an initial state at 10,000 years ago for which a distribution of groundwater compositions was assumed in terms of proportions of reference waters. Subsequent time-dependent boundary conditions, represented as reference waters, were assigned according to the post-glacial history of Littorina marine inundation followed by meteoric water infiltration as the rock mass experienced subaerial uplift. The modelled output of groundwater compositions at the present time is illustrated as colour-contoured cross-sections (Figure 6). The contoured distribution of modelled Cl concentrations can be compared with the interpolated contours of measured Cl concentrations that are reported in SKB (2011; Figure 7). The deepest groundwater samples are from slightly less than 1000 m depth, so comparison is valid only above that depth. The cross-section of simulated present-day Cl concentrations versus depth (Figure 6) has a steeper salinity gradient than is observed in the distribution of measured Cl concentrations (Figure 7). This suggests that the large-scale hydrogeological properties assigned to the DFN in the model are less transmissive in the upper part (i.e. down to around 500 m depth) than in reality. It is unclear whether and how the model has been calibrated to address this apparent mismatch in properties that affect the rate of response of the model to future infiltration of dilute water or of seawater.

Potential sources of uncertainty in using proportions of reference waters and the derived chemical and isotopic parameter values to calibrate transient groundwater flow and solute transport modelling on the basis of 'goodness of match' to measured compositions include: (a) how hypothetical reference waters have been selected and the implicit assumptions and simplifications, and (b) assumptions that the end members in groundwaters with mixed sources can be represented by single water compositions that have remained invariant through time. Groundwater evolution, hydrogeologically and geochemically, in reality will have been more complex.

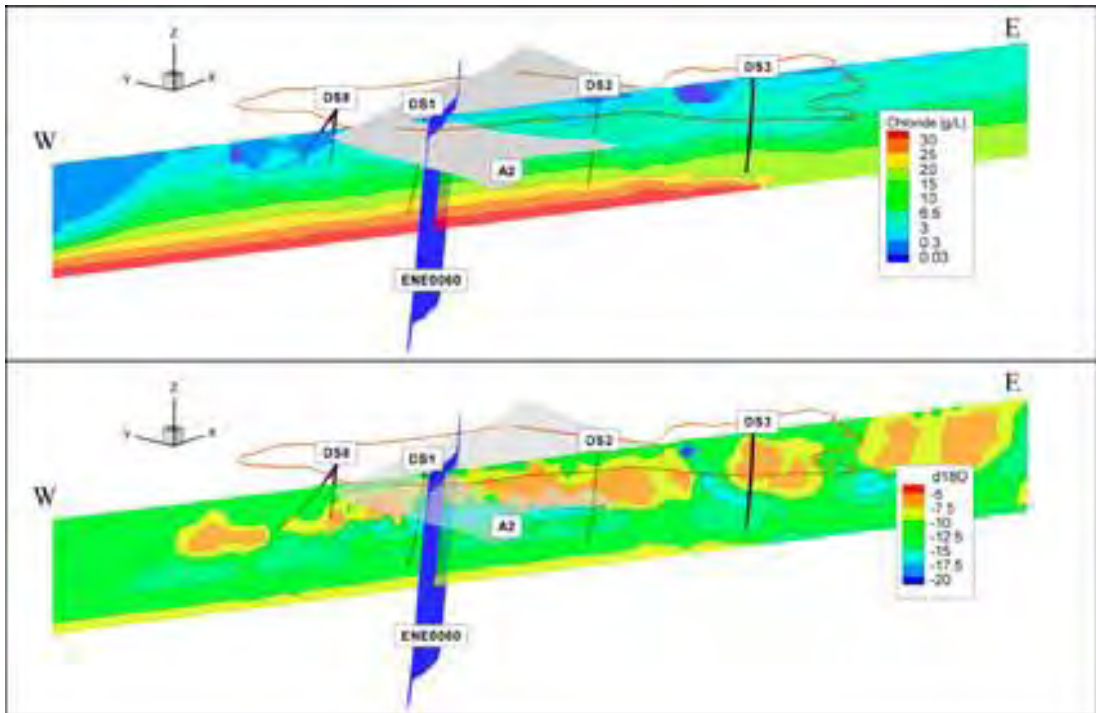**Figure 6.** Modelled Cl⁻ concentrations and δ¹⁸O values in W-E cross-section 1200 m deep and parallel to the shoreline at Forsmark (Fig 8-55 in SKB 2008).
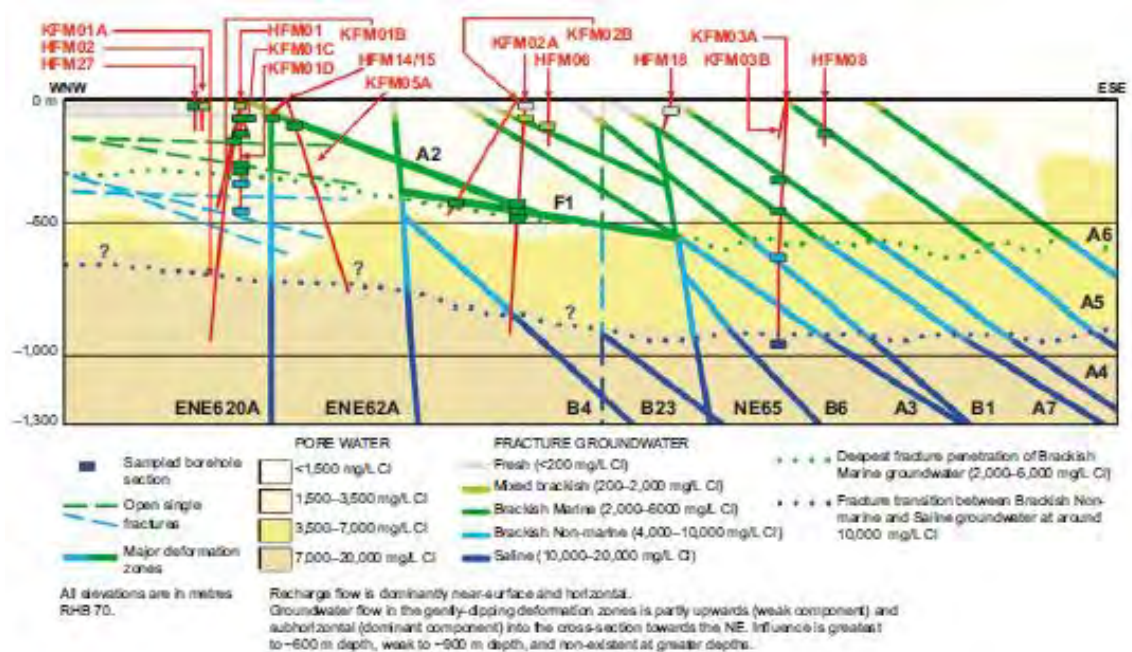

Figure 7. Distribution of Cl concentrations interpreted from analysed data for samples from boreholes along WNW-ESE cross-section to 1300 m depth through candidate area at Forsmark (Figure 4-22 in SKB 2011 and Figure 6-3 in Laaksoharju et al. 2008).

Sensitivity analysis of the transient flow-transport model calibration to alternative concepts and parameters was evaluated by SKB with three calibration targets: groundwater level responses during interference testing, present-day groundwater levels in superficial Quaternary deposits, and hydrochemical data (SKB 2008, Section 8.1.2). Calibration comprised the adjustment of parameters for deformation zones and fracture domains.

Further developments of this approach take into account the measured compositions of porewaters in the rock matrix, as well as the compositions of groundwaters sampled from the fracture network. Based on the concept that porewaters have been diffusively exchanging water and solutes with groundwaters in adjacent fractures, measured compositions of porewaters can be interpreted as a record of how groundwaters have evolved up to the present. Achieving a best match between modelled and measured porewater compositions provides a calibration of diffusion coefficients in the rock matrix. Conversely, failure to achieve a good match indicates that the concept and assumptions about past groundwater compositions and evolution might be erroneous.

Diffusion properties of intact rock matrix were adjusted according to the best match with pore water Cl and $\delta^{18}O$ data. Sensitivity analysis in this way shows that model calibration against interference testing and hydrochemical data is more sensitive and therefore effective than calibration against groundwater levels (Figure 8).

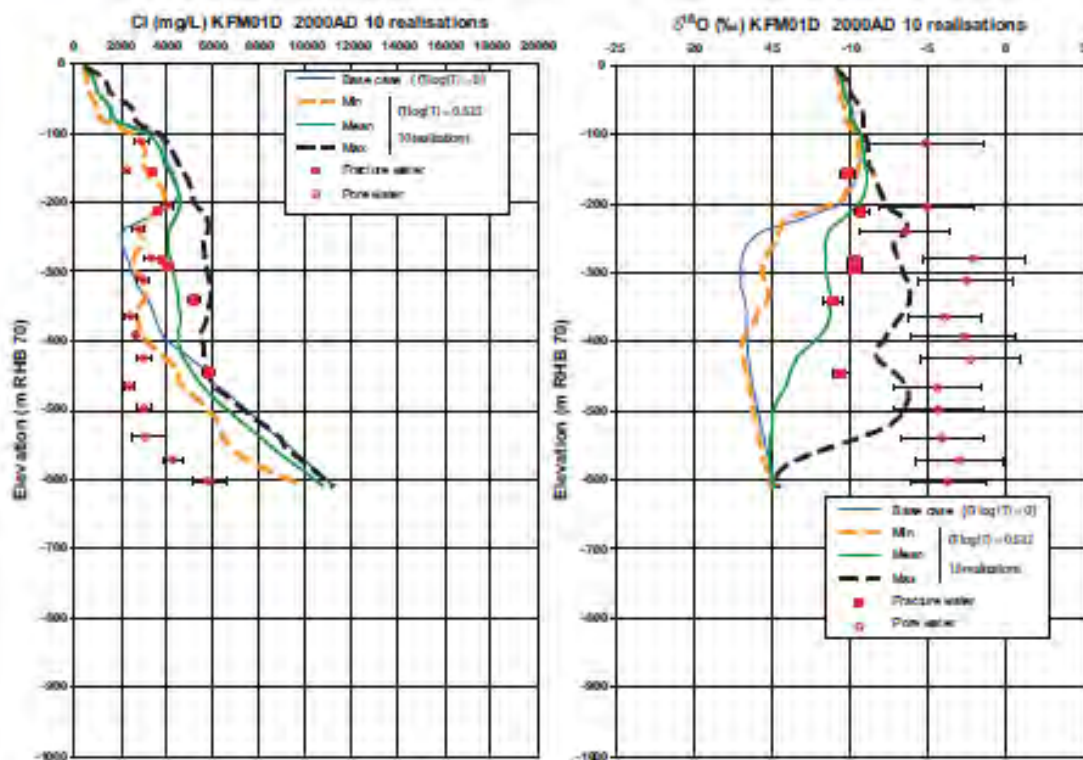**Figure 8.** Depth profiles of measured and simulated values of Cl⁻ and δ¹⁸O in fracture water and measured values for pore waters in borehole KFM01D at Forsmark. The different coloured lines illustrate sensitivities to variations of hydrogeological properties of deformation zones (Fig 8-68 in SKB 2008).

4 Hydrogeochemistry Model

The hydrogeochemistry model describes the features, processes and parameters that control present-day groundwater compositions and the geochemical 'initial state' of the repository volume. It also describes the processes that will control the evolution of water compositions and will influence the future performance of engineered barriers and transport of radionuclides.

Sources and types of water infiltrating the system in the past, and the extent to which that water has been able to displace pre-existing groundwaters, are major influences on present groundwater compositions. At Forsmark, the diverse sources and varying salinities of past water sources, represented by the reference waters (deep saline, Littorina, etc.), dominate over water-rock reactions as controls on groundwater compositions in terms of the major solutes. Other hydrochemical properties and trace solutes, i.e. pH, redox, sulphide and dissolved oxygen, are controlled by in situ hydrogeochemical and biogeochemical processes.

4.1 Hydrogeochemical processes

A conceptual model for hydrogeochemistry is developed in the SDM by showing that the processes can account for the observed compositions. Safety assessment involves forecasting of how groundwater compositions might evolve in the long term, specifically as they will impact on the engineered barriers. Confidence in this forecast depends on the conceptual model and on quantitative geochemical modelling of how groundwater compositions will evolve in response to external scenarios and to internal water-rock reactions in the geochemical, mineralogical and hydrogeological setting.

The hydrogeochemical processes that influence the long-term safety assessment are:

- Evolution and long-term buffering capacity of redox potential in groundwater at repository depth, taking account of redox-active solutes and biogeochemical processes;
- Reactions controlling the pH, dissolved inorganic carbon system and proton-buffering capacity of groundwater at repository depth;
- Control of dissolved sulphide concentration, sources and production at repository depth, specifically at deposition holes;
- Reactions that consume dissolved oxygen in infiltrating groundwaters between surface and repository depth;
- Reactions controlling groundwater compositions at repository depth that would affect the stability of bentonite buffer and backfill, i.e. pH, Ca, Na, K, dissolved silica, Fe, etc;
- Sources, hydrochemical stabilisation and mobility of colloidal materials e.g. organics, clays, iron oxides, microbial biomass;

- Reactions that dissolve or precipitate fracture-filling and matrix-sealing minerals that would affect radionuclide transport and retention properties.
-

Many of these processes are interdependent so they have data requirements in common and have similar approaches and tools for modelling. In the hydrogeochemical evolution model for SR-Site, the geochemical concept is simplified (Salas et al. 2010). For example: pH buffering is modelled in terms of reaction only with calcite; sulphate reduction to sulphide is dependent only on Eh and is not coupled to a specific electron donor reaction (DOC, acetate, H_2 and CH_4 data are evaluated qualitatively) ; oxygen consumption is modelled as a reaction with labile iron originating from pyrite, chlorite or biotite; ion exchange with rock matrix and secondary minerals and evolution of dissolved cations is simplified; alteration reactions producing secondary minerals in fractures are not modelled. It is recommended that further studies aimed at improving the modelling of these processes, for example groundwater monitoring and smaller-scale experiments with more intensive and localised sampling, could be carried out in future underground excavations.

It is suggested that a coherent biogeochemical model of redox processes could be further developed and calibrated with monitoring data and in situ experiments during a construction phase. The model would interpret and simulate redox buffering, sources of redox-active solutes and of electron donors that maintain redox conditions at repository depth stable (or otherwise) in the long term. It would need data for all redox-active solutes including concentrations, fluxes and sources of gases and organic C, plus characterisation of microorganisms and biogeochemical processes.

Stability and predictability of redox potential underpins confidence in the modelling of processes that are involved in corrosion of the copper canisters. Assessing redox in the system in these respects involves (a) comprehensive characterisation of the undisturbed hydrogeochemistry from surface to repository depth so that all the active and potentially-active redox processes are understood, (b) modelling of expected disturbance of the system during the excavation and open operation stages and the post-closure reinstatement of closed system equilibrium assuming continuation of present-day external influences on redox, and (c) modelling of long-term scenarios for responses of redox to external factors.
Eh in brackish groundwaters over most of the depth interval of interest (approx. 100 m to ~600 m) "seems to be controlled by the occurrence of amorphous iron oxyhydroxide" (SKB 2011, Section 4.8.2). This interpretation, that the amorphous iron oxyhydroxide is co-genetic with the present groundwater regime down to repository depth, implies that reduced iron, Fe^{2+}, released from iron-containing minerals has been oxidised. There is a question of whether the oxidation of dissolved Fe^{2+} is a continuing process or whether it has been episodic, for example occurring during infiltration conditions of palaeoclimatic episodes such as glacial melt water infiltration.

Evidence of Fe^{2+} oxidation raises a further question of what geochemical entity has been reduced. Dissolved sulphate reduction to sulphide, facilitated by sulphur-reducing bacteria (SRB), is theoretically excluded by the electrochemical potentials of the $Fe^{2+}/Fe(OH)_3$ and HS^-/SO_4^{2-} couples. It is more plausible in terms of relative redox potentials that Fe^{2+} has been oxidised by traces of dissolved oxygen. Dissolved oxygen (DO) in present-day infiltration or in infiltration, e.g. of melt water, that has moderately enhanced DO has been shown to be very probably consumed in the shallow subsurface (Sidborn et al. 2010). So, there is an apparent inconsistency between this model of oxygen consumption and the evidence from iron oxyhydroxide mineralisation at Forsmark that trace DO has penetrated to repository depth over some period in the past.

Iron oxyhydroxide mineralisation at Laxemar was reported to be rather different from that at Forsmark. Iron oxyhydroxide, identified as goethite, was found on fracture surfaces at 15-20 m depth at that site, below which pyrite mineralisation persists indicating that chemical conditions below 20 m have remained reducing (Drake et al. 2009). Occasional goethite occurrences as deep as ~80 m tend to correlate with high transmissivity fractures or fracture zones. In this case the mineralogical evidence is consistent with the hydrogeochemical model of DO consumption.

It is recommended that further studies in boreholes and underground at Forsmark will be needed to explain or rectify the apparent inconsistency between the iron oxyhydroxide distribution and the modelled consumption of DO. Greater confidence is needed in the hydrogeochemical model for redox, dissolved Fe, iron mineralisation, and attenuation of DO.

SKB have done mass budget calculations of the potential extent of corrosion by traces of O_2 if there were hydrogeological conditions in the future in which DO were to penetrate to repository depth (SKB 2011, Section 10.3.13; SKB 2010a, Section 3.5.4; SKB 2010b, Section 5.2.3). They suggest that the probable maximum extent of corrosion would not be of concern. However, the uncertainties in the scenarios and parameters for O_2 ingress, most notably in the case of glaciation, are such that improved confidence in the geochemical processes is desirable. Glacial melt water infiltration is usually considered to be the most likely scenario for this, but the general possibility of DO penetration in groundwater will become slightly more significant as meteoric water penetrates deeper, displaces the present brackish-marine groundwater, and reduces the effect of downwards-increasing density on the hydraulic gradient.

Another open question concerns the source and future evolution of the electron donor (or donors) that is capable of biogeochemical reduction of sulphate to sulphide. Considering the thermodynamics of redox potentials, those could only be labile dissolved organic carbon (DOC) or dissolved methane or hydrogen (Tullborg et al. 2010, Sections 5.3 & 5.4). For long-term buffering of redox to maintain stable persistence of the present-day reducing Eh, a flux of these one or more

of these entities is needed to maintain Eh. They have distinct sources: DOC is almost certainly derived by transport from the biosphere, H_2 is probably derived by transport from greater depth, and CH_4 could be biogenic or thermogenic and therefore originating from shallow depth or great depth.

4.2 Development of the model

The modelling of hydrogeochemical evolution of groundwater compositions over time is based on hydrodynamic transport and mixing of individual end-member components. End members are the reference waters and groundwater components that have been identified by the statistical method described in Section 3 for processing data for groundwater compositions.

Transport and mixing of the end member waters is simulated using the hydrogeological flow and solute transport model for which the calibration is described in Section 5.1. Calibration has been carried out by matching modelled reference water proportions, solute concentrations (Cl^-) or water stable isotopic ratio ($\delta^{18}O$) to measured parameters. The transport part of the evolution model is therefore conditioned by these conservative parameters of groundwater composition.

Mixing of equilibrated end members have been forward-modelled from a palaeo-hydrogeological starting point, typically at the end of the last period of ice cover (8000 BC i.e. 10,000 years ago), to the present. The groundwater flow and reactive transport modelling tool simulates past evolution of groundwater compositions along groundwater flow paths. The same method has been used to model the evolution of groundwater compositions forwards from the present time with a chosen scenario for future boundary conditions (see Section 4.3).

In addition to modelling hydrodynamic mixing of end members to give the spatial distributions of reference water proportions, concentrations of specific solutes are constrained by geochemical equilibria for reactions with mineral phases. For SR-Site, SKB have assumed equilibrium with calcite, quartz, hydroxyapatite, Fe(III) oxyhydroxide and/or amorphous Fe(II) sulphide (Salas et al. 2010). Cation exchange with clays and other mineral surfaces is not considered; neither are dissolution reactions of Na- and K-feldspar minerals and Mg,Fe-silicates, although Table 6-3 in the Data Report (SKB 2010c) suggests that other aluminosilicate minerals have been equilibrated. The hydrogeochemical model therefore is based on a simplified concept and, except for redox, is dominated by physical mixing of solutes.

'Box-and-whisker' plots showing the statistical distributions of calculated values for solute concentrations at 2000 AD, i.e. the present day, in the candidate repository volume at Forsmark are reported for TDS, Cl, Ca, $\sum$cations, and SO_4, plus the redox-active parameters HS^-, Fe and Eh, in SR-Site Main Report (SKB 2011), and additionally for K and pH in Salas et al. (2010). These have been compiled in Figures 9 and 10. Several of these parameters are directly or indirectly significant as safety function indicators.

Effects of hydrogeological variants on the results of hydrodynamic mixing modelling have been examined but are relatively insignificant for the limited range of variants considered (see Fig 6-25 in Salas et al, 2010).
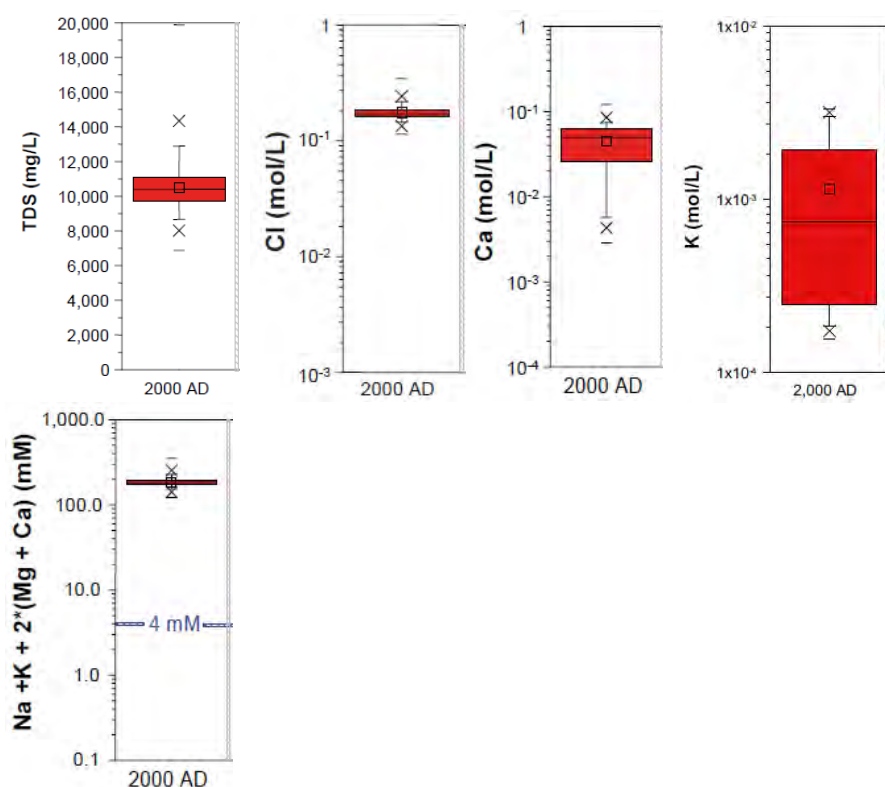
Figure 9. 'Box-and-whisker' plots (mean, 25th & 75th percentiles – box, 5th & 95th percentiles – whiskers, 1st & 99th percentiles – crosses, max & min - dashes) showing statistical distributions of modelled values for present-day values of TDS, Cl⁻, Ca^{2+}, K⁺ and ∑cations in the repository volume. These are data resulting from the hydrodynamic mixing model; the only geochemical constraint is that of calcite equilibrium on Ca^{2+}. From Figs 10-39, 10-40 & 10-46 in SKB (2011) and from Figs 6-2, 6-3, 6-6 & 6-8 in Salas et al. (2010).

The relatively wide ranges of calculated concentration values for redox-active parameters and for SO_4^{2-} in Figure 10 reflects the choice of buffer mineral, Fe(III) oxyhydroxide or Fe(II) sulphide, for Fe^{2+}/Fe^{3+} and HS^-/SO_4^{2-} redox equilibria. The spread of SO_4^{2-} concentrations in parallel with HS⁻ indicates that HS^-/SO_4^{2-} equilibrium is being assumed in the geochemical model. Fe^{2+} concentrations are constrained within narrower ranges if hematite or FeS equilibrium alone is assumed, the former in a lower Fe concentration range and the latter in a higher range (see Figs 6-20, 6-21 & 6-22 in Salas et al. 2010). These potential variations in calculated Fe^{2+} are propagated into variability in calculated HS⁻ concentrations. Uncertainties in identifying how Fe concentrations are controlled geochemically also produces uncertainties in HS⁻ concentrations which themselves are calculated on the basis of assumed equilibrium with a FeS mineral and HS^-/SO_4^{2-} redox equilibrium.
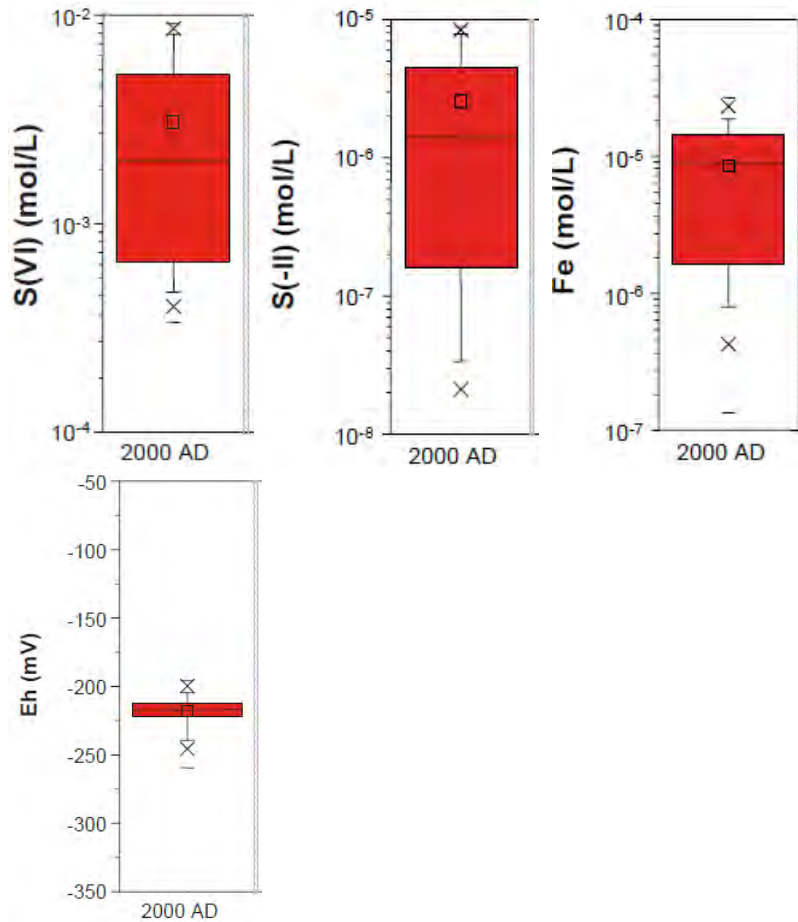
Figure 10. 'Box-and-whisker' plots showing statistical distributions of modelled values for present-day values of SO_4^{2-}, HS^-, Fe^{2+} and Eh in the repository volume. HS^-, Fe^{2+} and Eh are constrained geochemical by equilibrium with Fe(III) oxyhydroxide and/or amorphous Fe(II) sulphide. From Figs 10-44, 10-46 & 10-47 in SKB (2011).

Calculation results were displayed either as contours on slices through the modelled volume from surface to below repository depth (Figures 11 and 12) or as graphical depth profiles showing the range of variation of calculated data in each depth interval of ca. 10 m (Figures 13 and 14). The latter have been used as the only illustration of how modelled data for 2000 AD compare with observed values, presumably because it is more compatible with the low spatial density of observed data in comparison with the uniformly higher density of modelled values. Modelled and observed data for pH and Ca only are shown in the SR-Site Main Report (Figure 13). Similar graphical comparisons for Mg and phosphate (which is not of primary interest in relation to buffer stability or alteration) plus vertical slices of contoured Eh values are shown in Salas et al. (2010; Figure 14).
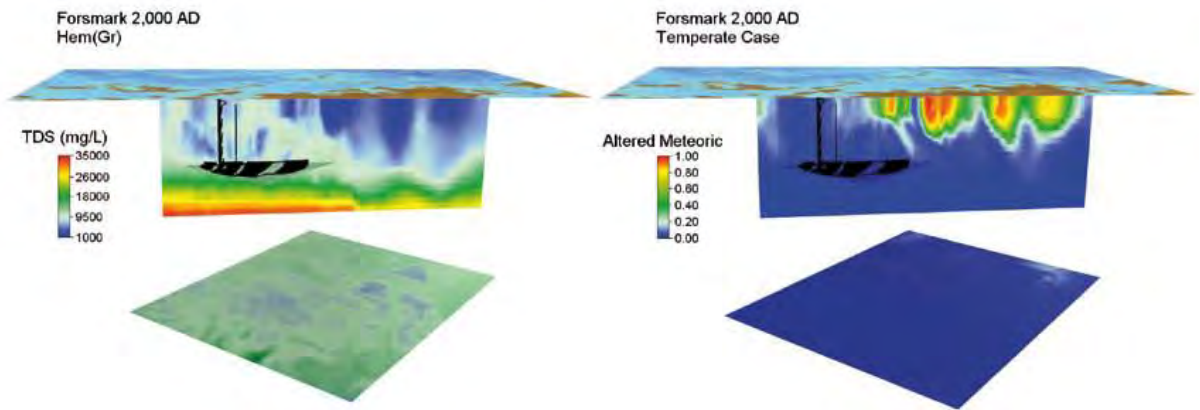
Figure 11. Modelled distributions of TDS (left) and fraction of 'altered meteoric' at 2000 AD in vertical slice through repository volume at Forsmark (extracted from Fig 10-37 in SKB 2011 and Fig 6-1 in Salas et al, 2010).
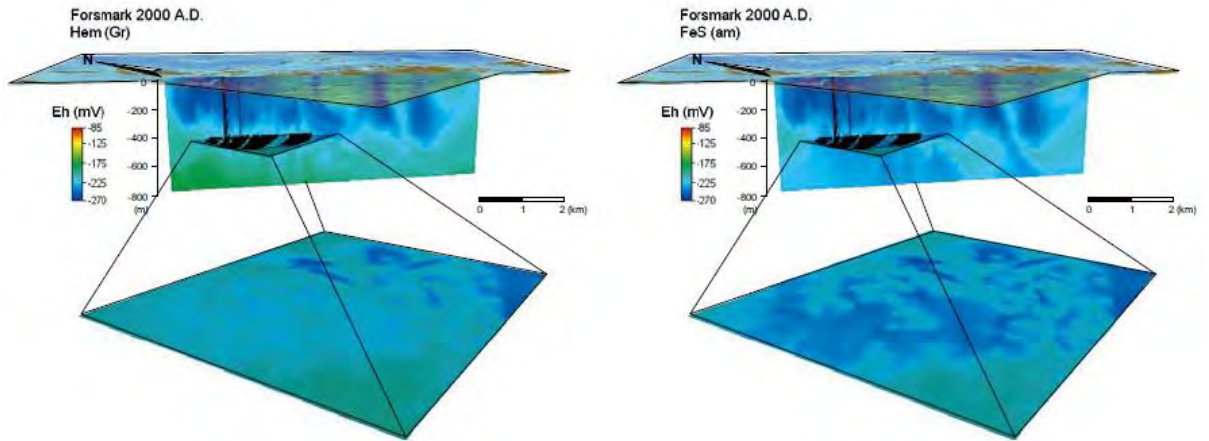
Figure 12. Modelled distributions of Eh for alternative geochemical model assumptions of hematite equilibrium (left) and FeS equilibrium (right) in vertical slice through repository volume at Forsmark (Fig 6-19 in Salas et al. 2010).
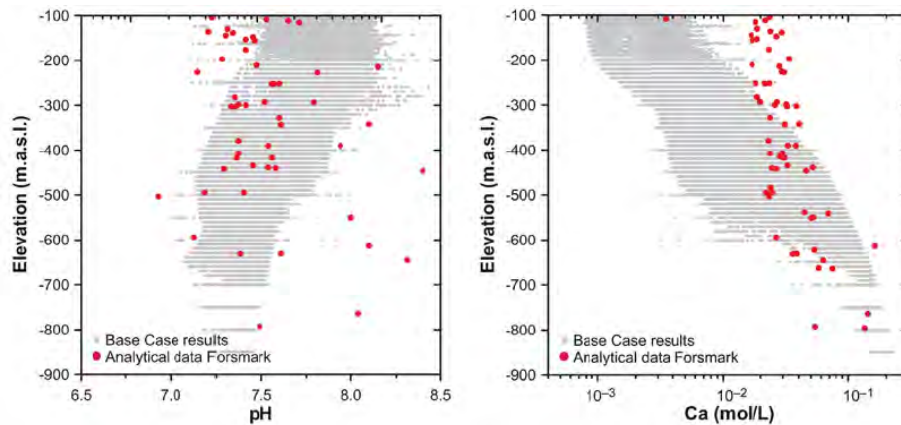
Figure 13. Ranges of modelled pH and Ca^{2+} for present-day groundwaters at depths from 100-700 m at Forsmark (grey bars) compared with values measured in boreholes (Fig 10-38 in SKB 2011).
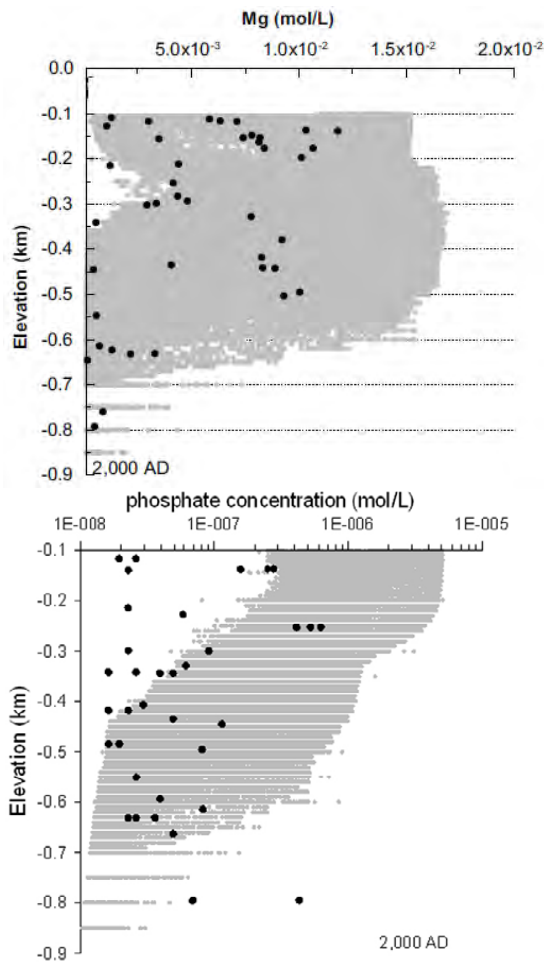
Figure 14. Ranges of modelled Mg and phosphate for present-day groundwaters at depths from 100-700 m at Forsmark (grey bars) compared with values measured in boreholes (Figs 6-5 & 6-9 in Salas et al. 2010).

35

Iterative calibration of the solute transport and hydrogeochemical model by comparison of modelled solute concentrations with observed data would improve confidence that the conceptual and numerical model for the evolution of the groundwater compositions by hydrodynamic mixing and reaction is a reasonable representation of the response to external drivers, i.e. climate-driven factors, over a timescale of at least 10,000 years or so of persistent temperate climate. It seems from the reports that this has been done only to a limited extent and the resulting effects on model parameters are unclear.

In the examples described above, the depth-dependent modelled solute concentrations do not match well the measured data for pH, Ca and phosphate. This suggests that the hydrogeochemical model requires further development and calibration to produce a reasonably good simulation of the time-dependent transport, dispersive mixing and geochemical processes controlling the evolution of groundwater solutes. It is recommended that further work to achieve this should be carried out, focussing effort on achieving more reliable simulations for solutes and other hydrochemical parameters, e.g. redox-active solutes and M^{2+}/M^+ proportions of major cations in dilute groundwaters, that have most significance for safety assessment.

4.3 Modelling of hydrogeochemical long-term evolution

Groundwater compositions have been projected into the future by modelling transport and mixing of end-member groundwaters using the same method and the same palaeohydrogeological starting point as used for modelling present groundwater compositions (Section 4.2) plus appropriate physical and hydrochemical boundary conditions for future climate scenarios. In most or all such modelling, the simulation from 10,000 years ago to the present has simply been extended to 7000 or 10,000 years into the future.

This approach is used in SKB TR-10-58 (Salas et al. 2010) to obtain statistical distributions of major cation and anion concentrations, ionic strength, pH, and redox potential (Eh). Box-and-whisker plots for projections of TDS and sum of cations to 7000 years in the future are shown in Figure 15. The spatial distributions of modelled TDS values on vertical cross sections to 800 m depth to 7000 years in the future are illustrated in Figure 16. Sources of uncertainties in the outputs from this modelling are the assumed initial compositions, the geochemical reaction concepts, and the hydrogeochemical heterogeneity.
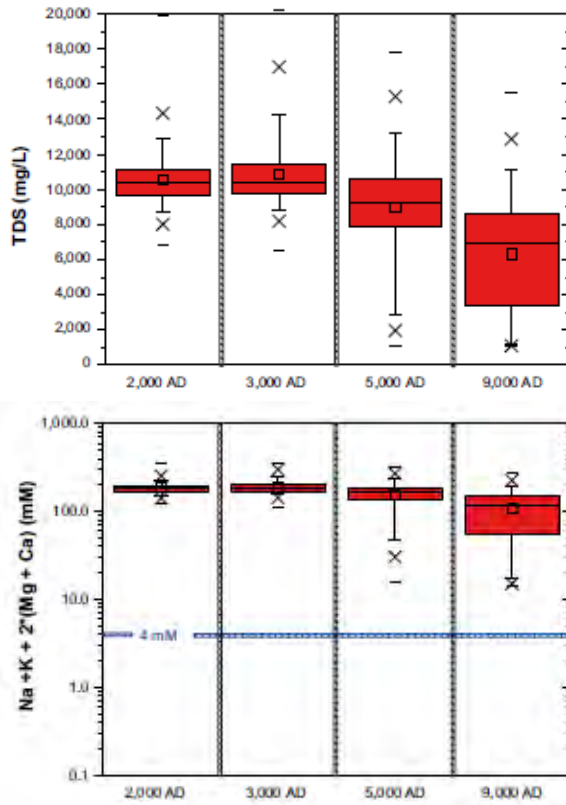
Figure 15. 'Box-and-whisker' plots (mean, 25th & 75th percentiles – box, 5th & 95th percentiles – whiskers, 1st & 99th percentiles – crosses, max & min - dashes) showing statistical distributions of modelled values for TDS and ∑cations in the repository volume at present day and at 1000, 3000 and 7000 years into the future. These are data resulting from the hydrodynamic mixing model; the only geochemical constraint is that of calcite equilibrium on Ca^{2+}. From Figs 6-2 & 6-3 in Salas et al, 2010.

In summary, understanding of end members, mixing and hydrogeochemical processes affecting specific geochemical parameters is the basis for forecasting of the possible ranges of variation and the most likely scenarios for groundwater compositions in the future. This modelling method has been used in SR-Site only as far as 10,000 years into the future.

It is suggested that forecasting of how groundwater compositions will evolve in a longer timescale with a persistent temperate climate is necessary to study how the system might evolve through an extended period of groundwater dilution. Other approaches and reasoning have been used in SR-Site for the much longer timescales and potentially greater variability of boundary conditions, reflecting changing climate states, that have to be considered in the safety assessment.
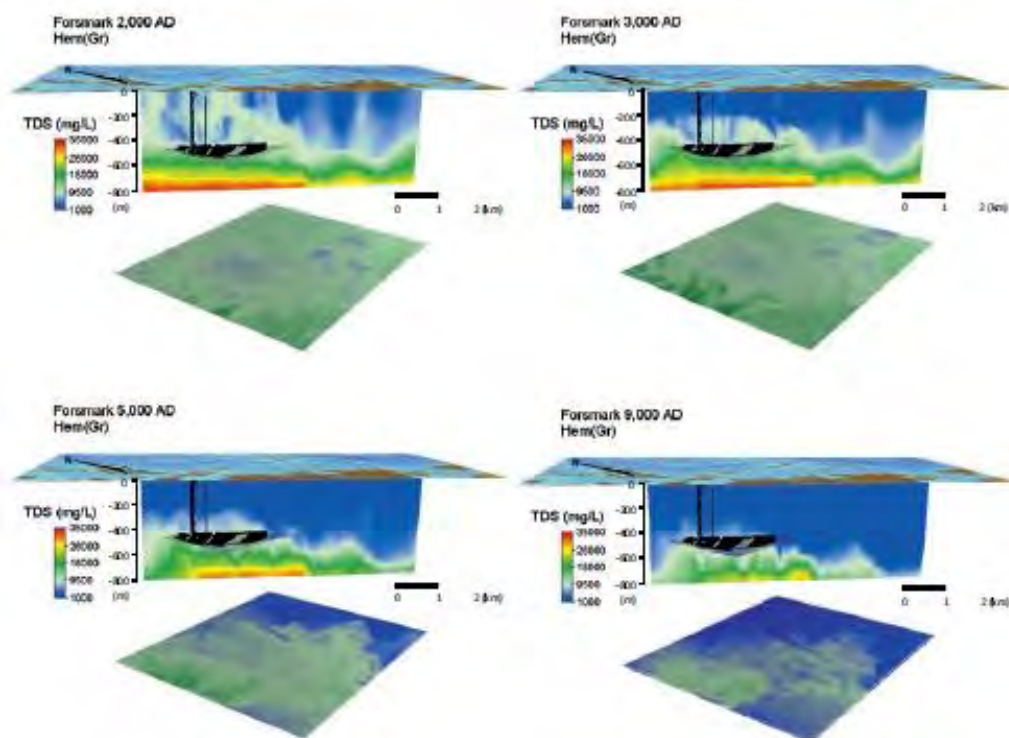
Figure 16. Modelled distributions of TDS in vertical slice through repository volume at Forsmark, at present day and at 1000, 3000 and 7000 years in the future. From Fig 6-1 in Salas et al, 2010.

4.4 Evaluation of data for redox-active solutes and colloids

Data for solutes and dissolved gases at trace concentrations that have specific significance in safety assessment have been processed and interpreted in SDM-Site to derive best estimates and ranges of uncertainty for their concentrations. Their significance for safety assessment relates for example to canister corrosion and to radionuclide transport. There is particular interest in how their concentrations will evolve in groundwater volumes around deposition holes and along groundwater flow paths that would be discharge routes for released radionuclides.

Trace solutes and gases are typically difficult to sample and analyse consistently so data tend to be sparse. They mostly cannot be forecast by geochemical modelling because their abundances and processes involve uncertain origins, microbially-catalysed kinetics and transformations, and complex reaction paths. They include, according to the Data Report for SR-Site (SKB 2010c), dissolved H_2 and methane (CH_4), dissolved organic carbon (DOC) and acetate (CH_3COO^-), ammonium (NH_4^+) and nitrite (NO_2^-).

The sulphur redox couple comprising reduced S as bisulphide (HS^-) and oxidised S as sulphate (SO_4^{2-}) are also in this category and are of direct interest for safety

assessment because of sulphide-promoted corrosion of copper. Measured data and modelled forecasts for sulphide concentrations at repository depth are considered in the context of canister corrosion in Section 5.3.

Best estimates of concentrations for these trace solutes and dissolved gases have been derived from measured data. These estimates take account of analytical detectability and sampling uncertainties, using expert judgement and background geochemical knowledge about likely present concentrations. There are likely to be various sources of uncertainty and variability for the estimated 'typical' and maximum abundances of redox-active chemical entities in a groundwater system which, on the basis of variations in analysed microbial populations, is biogeochemically heterogeneous.

Hydrogeochemical concepts for how concentrations might vary in the future have been considered for some of these entities and for others it has been assumed that present-day concentrations are adequate indicators of future variability in the scenarios considered for safety assessment. Values of DOC, acetate, methane, hydrogen, nitrite, ammonium and colloids concentrations for use in SR-Site as recommended by Salas et al. (2010) are in Table 6.
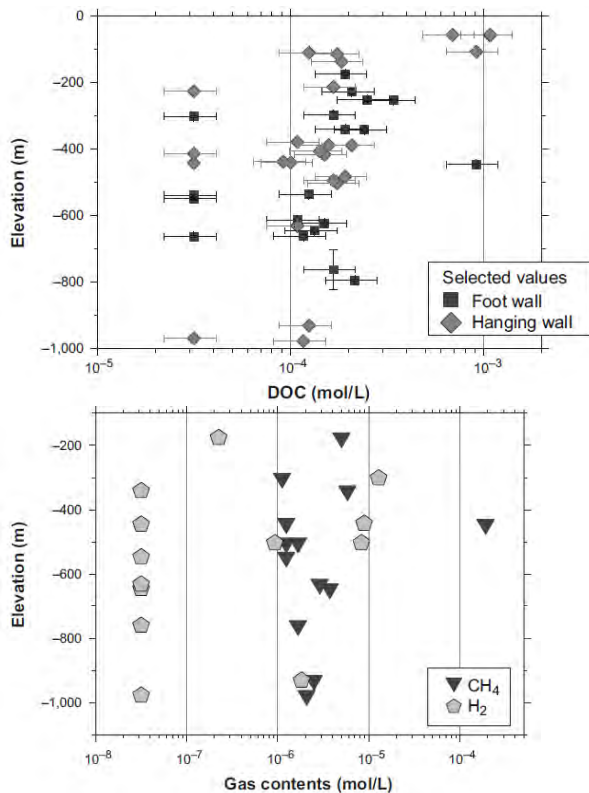

Figure 18. Measured concentrations in Forsmark groundwaters of redox-active electron donors that are considered as influencing the Fe-S redox system (Figures 10-42 & 10-43 in SKB 2011).

Table 6. Recommended values for DOC, acetate, CH_4, H_2, NO_2^-, NH_4^+ and colloids for the stages of evolution through the assessment timescale for use in SR-Site. Values in grey cells are based on mass balance using DOC and other data; other data are based on measured values and on consideration of factors that could control future values (Table 8-1 in Salas et al. 2010).

Evolutive Periods	DOC	Acetate	CH_4	H_2	NO_2^-	NH_4^+	Colloids (μg/L)
Excavation/Operation	$1.2 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$2.7 \cdot 10^{-6\,(1)}$	$< 2 \cdot 10^{-6}$	$< 3 \cdot 10^{-2}$	500
		μM range		$1.5 \cdot 10^{-7}$			
Temperate	$1.25 \cdot 10^{-3}$	μM range	$2 \cdot 10^{-4}$	$1.92 \cdot 10^{-6}$	$1.07 \cdot 10^{-7}$	$4.0 \cdot 10^{-6}$	< 180
Glacial	$4.2 \cdot 10^{-6}$		$2 \cdot 10^{-4}$	$1.92 \cdot 10^{-6}$	$\leq 1.07 \cdot 10^{-7}$	$< 4.0 \cdot 10^{-6}$	20,000
Submerged (marine)	$2.9 \cdot 10^{-3}$		$2 \cdot 10^{-4}$	$1.92 \cdot 10^{-6}$	$1.07 \cdot 10^{-7}$	$1.9 \cdot 10^{-4}$	< 180

(1) Value estimated from iron corrosion.

Measured data relating to redox conditions throughout the rock from surface to 1000 m depth have been scrutinised and interpreted in SR-Site to assess the evidence for the biogeochemical reactions that control groundwater redox in the Forsmark system. In addition to Fe, HS^- and pH, data for potential electron donors are also examined: dissolved organic carbon (DOC), dissolved hydrogen (H_2) and dissolved methane (CH_4) (Figure 18).

Analytical data for DOC and their significance for the safety assessment are discussed in more detail by Salas et al (Salas et al. 2010, Section 8.2). Whilst DOC concentrations in groundwaters below about 200 m depth at both the Forsmark and Simpevarp/Laxemar/Äspö are predominantly around 0.1 mM, there are occasional anomalous values up to an order of magnitude higher (Figure 19). These generally low values of DOC are discussed in Salas et al. (2010) in terms of relevance to microbial activity, i.e. redox control, and to the possibilities for natural colloids. However, SR-Site cautions that the natural values may be affected by artefacts of anthropogenic organic materials in the vicinity of a repository. The observed values are argued to be representative of future concentrations through a temperate climate period. Concentrations through a glacial period are thought to be lower due to sparse carbon sources.
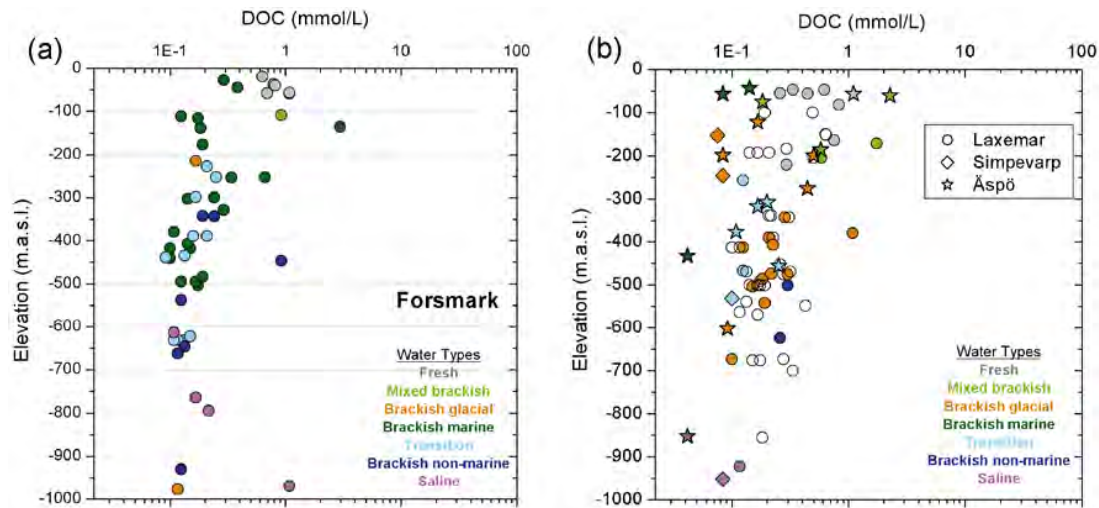
Figure 19. Depth distribution of DOC data in Forsmark and Simpevarp/Laxemar/Äspö (Figure 8-1 in Salas et al. 2010).

Acetate is the fraction of DOC that is more readily available for microbial metabolism. It is therefore of interest in conjunction with observations on microbial populations and their activity. In the absence of data for acetate in groundwaters at Forsmark, Salas et al refer to data from Äspö and Laxemar (Salas et al. 2010, Section 8.3). Results from the Microbe experiment in Äspö HRL are referred to in which the correlations of acetate concentrations, i.e. microbial production versus microbial consumption, and SRB leading to sulphide production were investigated.

There are a small number of measurements of dissolved methane (CH_4) and even fewer of dissolved hydrogen (H_2) in groundwaters at Forsmark and Simpevarp/Laxemar (Figure 20).

The CH_4 and H_2 measurements are used to support assumptions of maximum values for these dissolved gases in current groundwaters and to assess evidence for depth-dependent variations, for correlations with microbial populations, and evidence about their origin being biotic or abiotic (Salas et al. 2010, Sections 8.4 & 8.5). The highest value for CH_4 is 4×10^{-2} mM, comparing with the maximum amounts if acetate or hydrogen sources are assumed of 2×10^{-1} and 3×10^{-4} mM respectively. In discussing potential variability of CH_4 and H_2 in the evolution of the repository system through future climate stages, measurements of current amounts are inferred to be constraints on amounts through the temperate period.
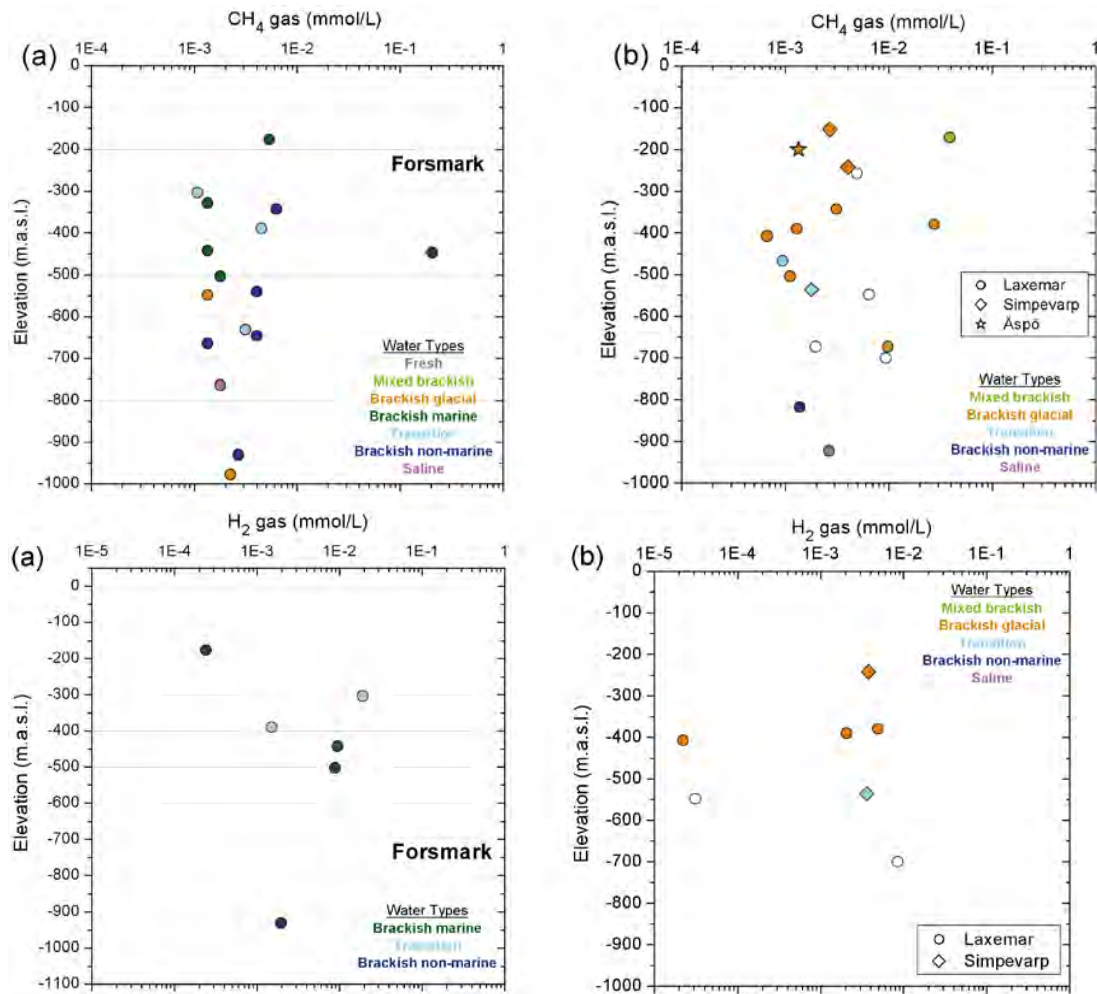
Figure 20. Dissolved methane and hydrogen in groundwaters at Forsmark and Simpevarp/Laxemar (Figs 8-3 & 8-4 in Salas et al. 2010; note that the concentration units or converted values for CH₄ in Fig 8-3 have some errors).

For a future glacial period, upwards fluxes of abiogenic gases could change. The steady state concentrations would depend, amongst other factors, on their biogeochemical consumption by O_2, Fe^{3+}, SO_4 and other electron acceptors. On the basis of qualitative arguments, the current concentrations of CH_4 and H_2 are assumed to be typical of abundances throughout the entire assessment timescale (Salas et al. 2010). However, there are gaps in knowledge about the sources, constraints and other factors affecting CH_4 and H_2 abundances in crystalline basement rock. Further generic and site-specific studies could improve confidence that future environmental changes will not cause significant changes. For example, a study could focus on understanding why CH_4 and H_2 concentrations in groundwaters at Forsmark are several orders of magnitude lower, especially for CH_4, than at Olkiluoto and whether that indicates a possibility of higher CH_4 at Forsmark in the future.

Colloids, both colloids derived from the engineered barrier of a repository and naturally-occurring mineral-derived and organic colloids, are significant because of the potential enhanced migration of radionuclides by 'colloid-facilitated radio-nuclide transport'. Data for concentrations of naturally-occurring colloids are considered by Salas et al (2010) as the basis for constraining likely concentrations in the future evolution of the groundwater system. They also have significance as analogues for the migration of bentonite colloids that could be dispersed from the buffer and act as potential vectors for radionuclide transport if chemical erosion of the buffer were to occur. Measurements in Forsmark and Laxemar groundwaters are shown in Figure 17.
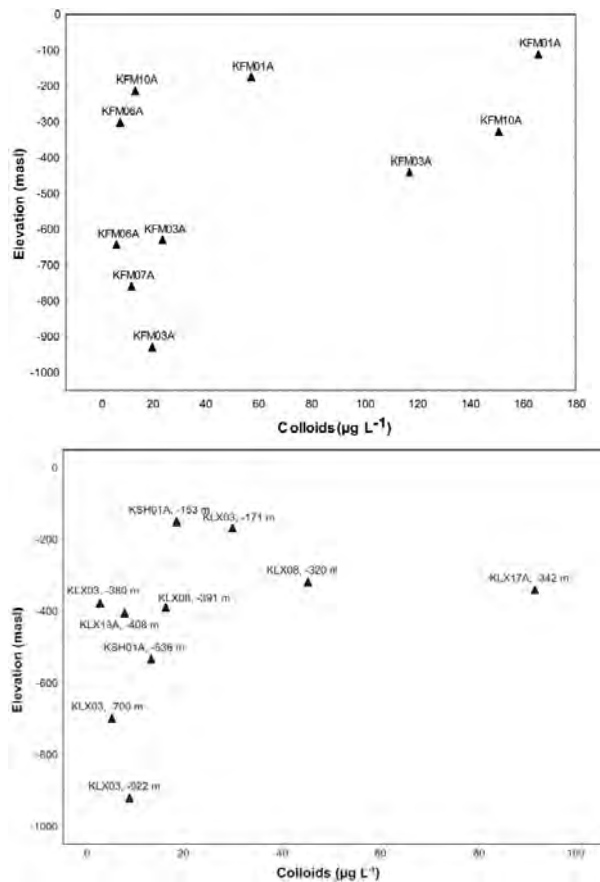
Figure 17. Measurements of naturally-occurring colloids at Forsmark (left) and Laxemar (right) (Fig 8-6 in Salas et al, 2010).

In discussion of the possible colloid concentrations during a future glacial period, Salas et al. state that glacial water would likely be more dilute than present groundwaters and therefore could support higher colloid contents. By comparison with current concentrations which are in sub-milligram per litre ranges, they suggest that a 'reasonable upper limit' is in the milligram per litre range (Salas et al. 2010, Section 8.7.2). The reasoning behind this assertion is presumably based on the observed present variability of natural colloid concentrations but needs further explanation and then needs to be coupled with an estimate of what concentrations

of colloids, both buffer-derived and natural, might rise to in groundwater dilution and glacial melt water infiltration scenarios.

It is suggested in Section 4.1 that a biogeochemical model should be developed to underpin the understanding of likely evolution of redox and redox-active solutes in the future. Microorganism numbers and activity, along with the trace chemical concentrations that influence microbial activity, are key parameters that would be needed to develop a biogeochemical model. SKB has made intensive efforts to characterise and quantify the naturally-occurring populations of microbes in the groundwater system especially at repository depth. There has also been an attempt to correlate the size of microbial populations, their metabolic activities and energetics, and their effects on redox-active entities. The potential causes and implications of variability in microbial populations in the future needs to be considered in SR-Site.

As summarised above, variable amounts of data have been acquired for trace solutes, dissolved gases, natural colloids and microorganisms in the hydrogeochemistry SDM for Forsmark (and also for Laxemar). Sampling and analysing reliably for these entities have been challenging tasks requiring significant developments of methods and supporting research. The data for these entities reported in the SDM and in supporting reports are mostly rather sparse and the ranges in concentration or abundance values make it difficult to be sure of the significance of variabilities for safety functions and other issues that are directly or indirectly relevant to safety assessment. For most of these trace entities, SR-Site has not considered the implications, if any, for safety assessment of measured data and of forecast future variations in scenarios for environmental change.

It is recommended that SKB could assess further the significance of existing data in the context of safety functions and safety assessment. That would allow the necessity of additional sampling, analyses and future projections to be prioritised. Opportunities for improving data and understanding of processes for these entities may arise in future underground investigations, in addition to possibilities in new and existing boreholes.

Processed or interpreted data and model outputs resulting from the processing and interpretation methods for the major hydrochemical parameters described in the earlier sections of this chapter, Sections 4.1 to 4.3, are used in three principal parts of safety analysis and assessment:

    i.   corrosion of copper canisters and modelling of the associated hydrochemical processes that will govern corrosion rates in future scenarios;

    ii.   alteration and chemical erosion of bentonite buffer in response to changing groundwater compositions in future scenarios; and

    iii.   palaeohydrogeological confirmation of concepts and parameters for groundwater movement and radionuclide transport.

These are considered in the following sections.

5 Use of Data for Assessment of Canister Corrosion

5.1 Corrosion parameters and processes

Two principal corrosion mechanisms affecting copper have been considered in SR-Site. They are mutually exclusive because one occurs in oxic conditions and the other occurs in anoxic conditions (SKB 2010b). The respective reactions are the formation of cuprous oxide, Cu_2O, and cuprous sulphide, Cu_2S.

Calculation of the extent of corrosion in each of the cases requires the concentrations of dissolved oxygen (DO) and sulphide (HS$^-$) respectively in water in contact with canisters plus the rate of supply of oxygen and sulphide to that interface. Migration is modelled as being constrained by the rate of diffusion across the bentonite buffer. Therefore, the relevant concentrations for DO and HS$^-$ are those in groundwater at the outer surface of the bentonite buffer, i.e. at the periphery of each deposition hole, over the time period that is relevant to long-term safety. The sulphide corrosion reaction is pH-dependent because of the speciation of HS$^-$/S^{2-}. The electrochemical corrosion of copper by HS$^-$ is also promoted by other aspects of water chemistry, primarily high chloride salinity. Therefore, SKB places additional safety function indicator criteria to minimise corrosion: pH > 4 and [Cl$^-$] < 2M (SKB 2011, Section 8.3.4).

5.2 Dissolved oxygen

The issue of whether DO could ever penetrate to repository depth and thus cause canister corrosion was handled in SR-Site with a conceptual and analytical model for oxygen consumption (SKB 2011, Section 10.4.7; Sidborn et al. 2010). SKB's position is stated in SR-Site (SKB 2011, Section 10.2.5) as follows: 'Microbial oxygen consumption takes place in the overburden and in the first metres of rock, as well as lacustrine, fluvial and marine sediments. Therefore, infiltrating waters are free of DO. This position is supported by scientific literature on O_2 consumption in soils and by experiment at the Äspö HRL where the observation of ubiquitous dissolved Fe^{2+} is inferred to prove the absence of significant DO.

As discussed in Section 4.1, however, the line of argument that DO would not reach repository depth appears to be somewhat inconsistent with the mineralogical observation of iron oxyhydroxide distribution on fracture surfaces.

SR-Site also considers a 'worst-case scenario' whereby DO would penetrate to repository depth in glacial meltwater infiltrating under the enhanced hydraulic gradient at the front of an ice sheet that is stationary over the repository location and that DO contacts one or more canisters directly because the buffer has been

eroded. An upper limit for DO concentration under such conditions was estimated to be 1.5 mM (48 mgO$_2$/L; SKB 2011). Mass budget calculations of the potential extent of corrosion by traces of O$_2$ in that pessimistic scenario suggested that the probable maximum extent of corrosion would not be of concern (SKB 2011, Section 10.3.13; SKB 2010a, Section 3.5.4; SKB 2010b, Section 5.2.3). It is suggested that the uncertainties in the scenarios and parameters for DO ingress, most notably in the case of glaciation, are such that improved confidence in the geochemical processes is desirable.

Measurements of DO in present-day groundwaters around the repository location have not been interpreted for Forsmark groundwaters in SDM-Site, although a few measurements of DO were reported as unapproved raw data in 'P' reports. The numbers of DO data reported from deep (>100 m) drillholes at the Laxemar and Forsmark site investigations are 8 and 2 respectively (Table 5). Values in this small data set are zero or within the error limits around zero so they support the concept and analytical modelling of DO consumption. It is recommended that additional monitoring should be carried out in relevant boreholes and in seepages to tunnels during excavation, to test whether the enhanced infiltration due to hydraulic drawdown is accompanied by DO drawdown.

5.3 Sulphide and related parameters

Occurrence of sulphide in groundwaters at repository depth is the dominant cause of canister corrosion and is therefore a major issue for the long-term safety assessment. Measured data for present-day bisulphide (HS$^-$) concentrations are used for corrosion calculations in SR-Site, based on the premise that the controls on dissolved sulphide concentrations: the available total sulphur budget (mostly as pyrite in bentonite and as sulphate in groundwaters) and the biogeochemistry of sulphate-sulphide conversion, will be the same in the long-term future as they are at present. Sulphide derived from pyrite, and also from biogeochemical reduction of sulphate, in buffer and backfill is discussed and calculated in SKB (2010c). Use of groundwater data for scoping potential maximum concentrations and budgets of sulphide and sulphate reaching the periphery of deposition holes is described below.

HS$^-$ in groundwaters is inferred to be controlled by a steady state between microbial sulphate reduction and sulphide removal by precipitation or oxidation (SKB 2010c). Measured HS$^-$ data for groundwaters at Forsmark have been reviewed and evaluated intensively by Tullborg et al. (2010). A number of the reported HS$^-$ values are at or below the assessed variable detection limit which is around 0.01 mg/L; these analyses were given a value of 1.2 x 10^{-7} M (0.004 mg/L). The outcome of Tullborg et al's review was a selected group of samples and sulphide concentrations that are believed to be representative of sulphide distribution in groundwaters around repository depth. The maximum HS$^-$ is assigned a value of 1.2 x 10^{-4} M (3.8 mg/L) whilst typical concentrations are below 1.3 x 10^{-5} M (0.42 mg/L). The probability distribution of observed HS$^-$ concentrations derived by

Tullborg et al. was recommended for use in SR-Site as an appropriate distribution of HS$^-$ values, especially with respect to the maximum probable value, in groundwaters at repository depth in the long-term future.

HS$^-$ concentrations in future groundwaters at repository depth can also be constrained by modelling its possible evolution in the context of overall hydrogeochemical equilibria. A groundwater flow and transport model was used to simulate mixing of end-member waters, assuming in the first instance non-reactive mixing of all solutes in the proportions and concentrations of the component reference waters (the 'base case'). Variant cases couple the PHREEQC geochemical equilibrium code loosely with the flow-transport model to further constrain the modelled hydrochemical parameters according to mineral phase equilibria. Two variant models have control of HS$^-$, Fe^{2+} and Eh by hematite equilibrium or amorphous FeS equilibrium. The results have been reported in Salas et al. (2010). The modelling is projected forwards for 7000 years, and results are therefore only illustrative with regard to the much longer timescale and possible hydrological boundary conditions of groundwater evolution for long-term safety assessment. The results of the flow-transport mixing modelling with variant geochemical constraints on the calculated concentrations of HS$^-$ and Fe^{2+} concentrations and on calculated Eh are shown in Figures 21, 22 and 23. The forecast values for HS$^-$ were not used directly in the corrosion calculations in SR-Site, but the conclusion by Salas et al. (2010) is that 'sulphide concentrations averaged over the temperate period will be at the levels found at present or lower, i.e. lower than 10^{-5} mol/L', though they qualify this conclusion by pointing out that sulphide concentrations as high as 10$^{-3.9}$ mol/L have been observed (Figure 24).
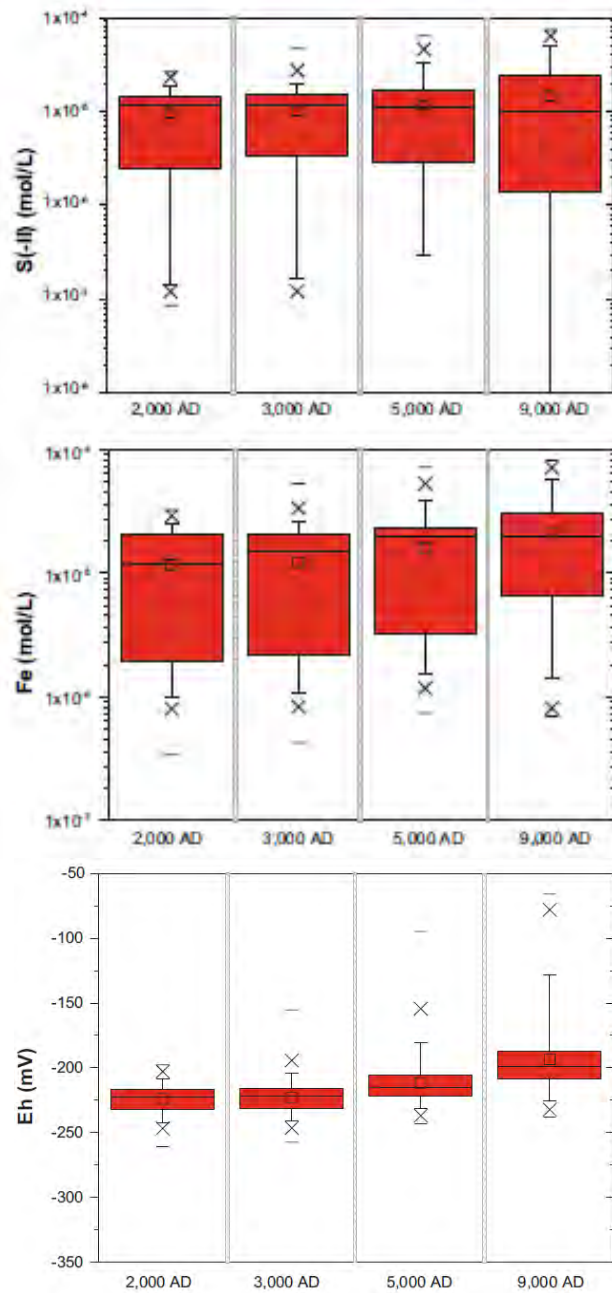
Figure 21. Box-and-whisker plots showing statistical distributions (mean, 25th & 75th percentiles – box, 5th & 95th percentiles – whiskers, 1st & 99th percentiles – crosses, max & min - dashes) of calculated values of sulphide and iron concentrations and Eh in repository volume groundwaters from present day to 7000 years into the future at Forsmark, based on flow-transport modelling of mixing between end-member waters. There is no geochemical constraint on sulphide, so the modelled values are just results of mixing between varying proportions of end members. The geochemical constraint on Fe is Fe(III) oxyhydroxide equilibrium. The ranges of Eh represent either Fe(III) oxyhydroxide or amorphous FeS equilibrium. From Figures 6-16 and 6-17 in Salas et al. (2010).
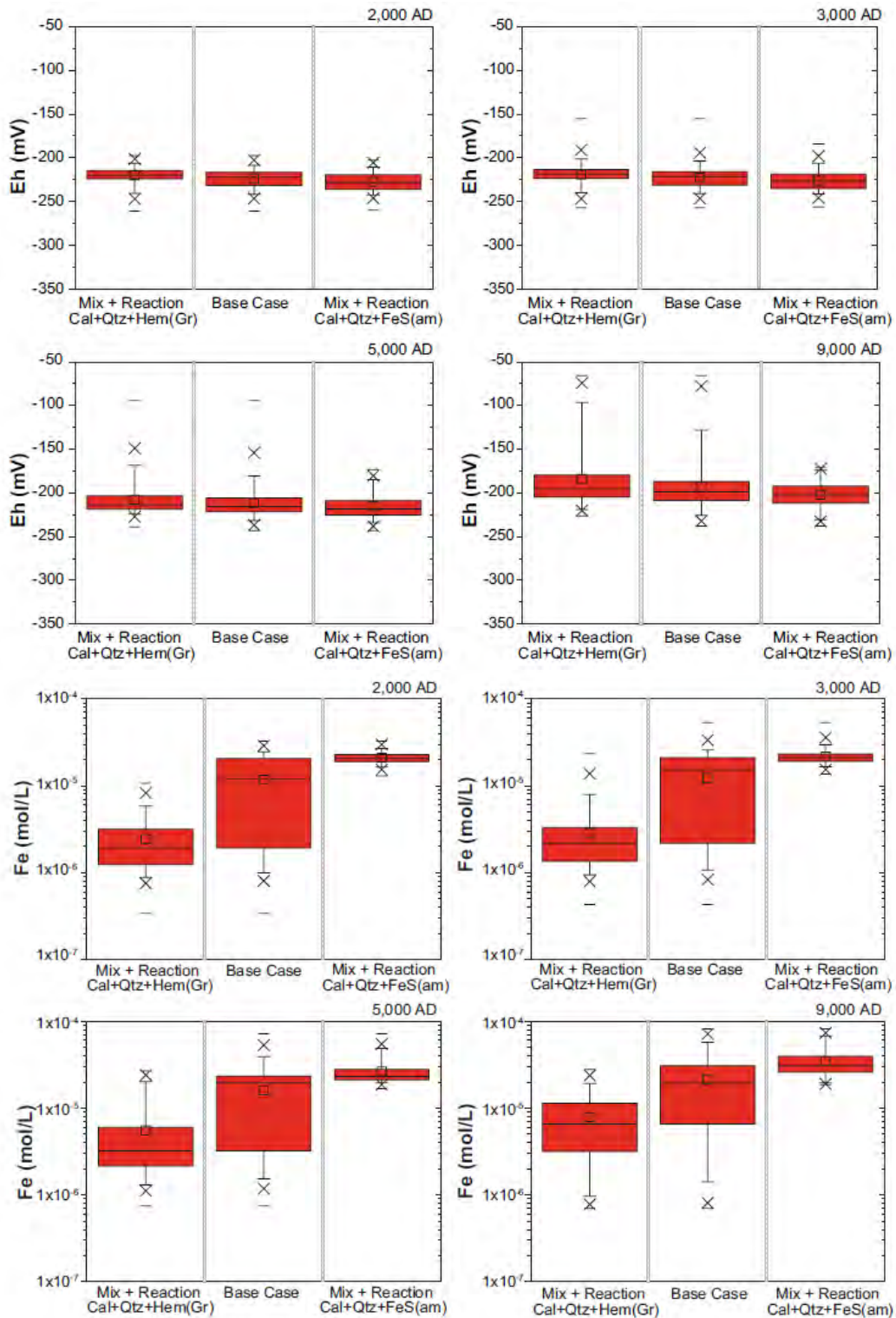
Figure 22. Box-and-whisker plots showing statistical distributions of calculated values of Eh and iron concentrations in repository volume groundwaters from present day to 7000 years into the future, based on flow-transport modelling of mixing between end-member waters and geochemical constraint by both Fe(III)

oxyhydroxide and amorphous FeS equilibria ('Base Case'). The variants are geochemically constrained by (i) hematite equilibrium and (ii) amorphous FeS equilibrium. From Figures 6-20 and 6-21 in Salas et al. (2010).
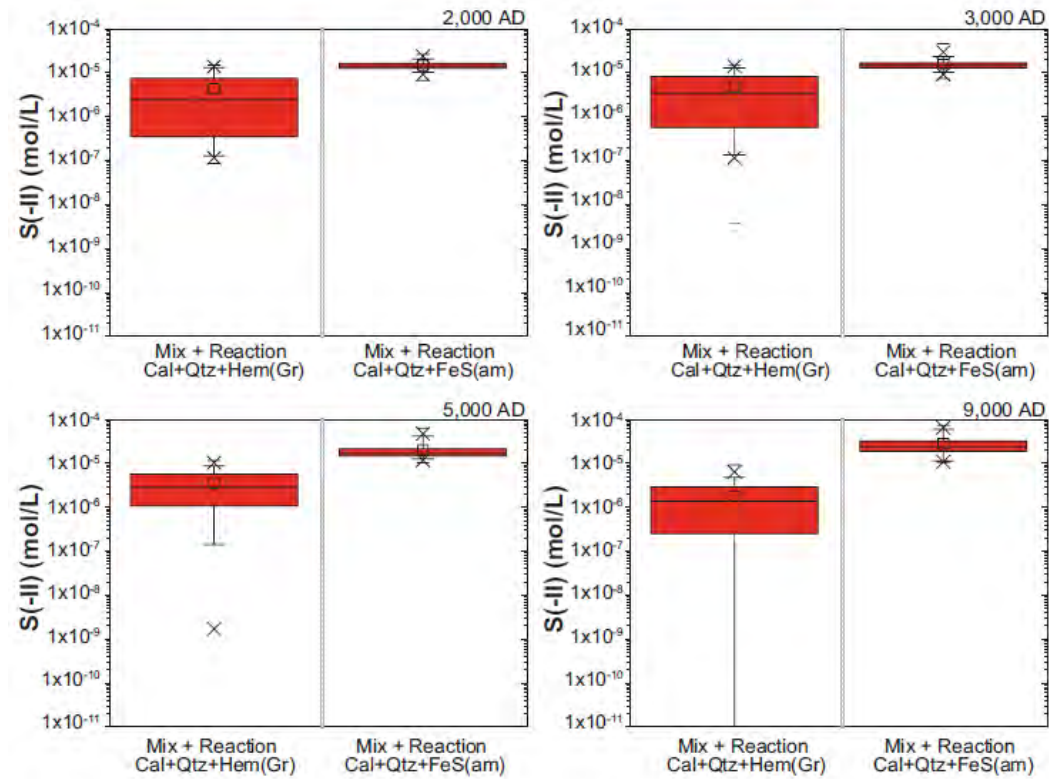
Figure 23. Box-and-whisker plots showing statistical distributions of calculated values of sulphide concentration in repository volume groundwaters from present day to 7000 years into the future, based on flow-transport modelling of mixing between end-member waters and geochemical constraints on S by (i) hematite equilibrium and (ii) amorphous FeS equilibrium. From Figures 6-22 in Salas et al. (2010).

Analytical data for microbial numbers and populations, specifically of sulphate-reducing bacteria (SRB), are not interpreted in SDM-Site beyond the conclusion that 'measured EH values corelate with the number of SRB, suggesting that the SO_4^{2-}/S^{2-} system is catalysed by SRB and probably plays an important role in the redox state of the system' (SKB 2008, Section 9.5.4). There is also some discussion in Section 8.4 of Salas et al. (2010) of whether their variability might promote or constrain HS^- or of whether the measurements might or might not be typical of how the biogeochemical system will evolve in the future.

Results from Tullborg et al's (2010) detailed evaluation and review of all HS^- measurements were used in SR-Site. 'Typical' maximum HS^- concentration is suggested to be 1.3×10^{-5} M, noting that this is exceeded in a few outlier samples (Figure 24). Measured concentrations of electron donors, DOC, CH_4 and H_2, have also been reviewed by Tullborg et al. Present-day HS^- data and the electron donor and SRB data have been qualitatively interpreted by Tullborg et al. to constrain

the maximum production of HS⁻ from SO₄²⁻ and to assess potential increases and decreases in HS⁻ during future periods with different climates (Table 6-1, Tullborg et al. 2010). The conclusion in SR-Site is that 'during the initial temperate period following repository closure the sulphide concentrations in the groundwaters will remain at the levels found at present in Forsmark' (SKB 2011, Section 10.3.7). Therefore SR-Site infers that the evaluated HS⁻ measurements are adequate for use in safety analysis at least in the intermediate timescale. SKB's statement that 'it cannot be concluded that the temporal variations will be sufficiently large that the time averaged concentration would correspond to the average of sulphide concentrations sampled at Forsmark today' (SKB 2011, Section 10.3.7) seems to have an error and presumably should be '.... sufficiently small....'. Considerations in Tullborg et al. and SR-Site concerning future variability of HS⁻ is exhaustive in the context of present knowledge. As SKB seems to admit, there are remaining uncertainties that could be reduced by better quantitative knowledge of sulphate sources, electron donor sources and variabilities, and of the processes of HS⁻ production and removal.
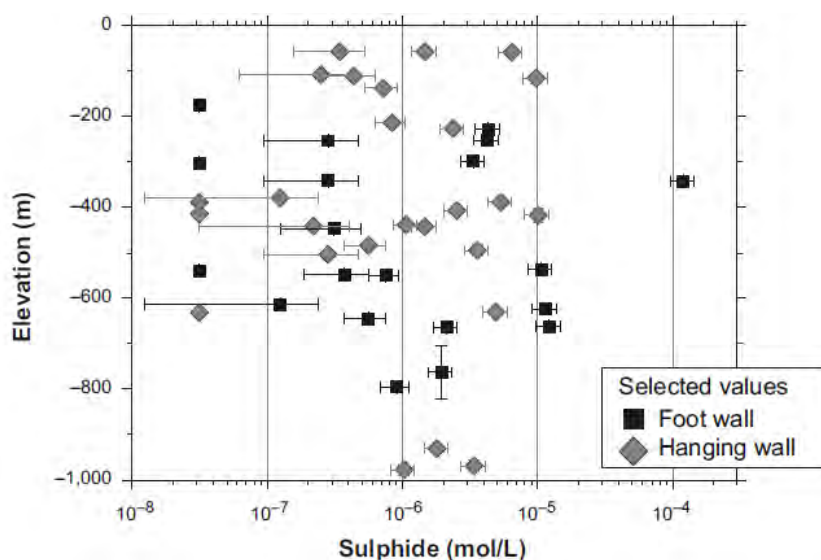
Figure 24. Selected HS⁻ measurements in present-day groundwaters that are considered in SR-Site as typical of future concentrations at least through the initial temperate period (Fig 10-41 in SKB 2011).

In the Fuel and Canister Process Report for SR-Site (SKB 2010a, Section 3.5.4), SKB refer to groundwater sulphide concentrations being 'mostly much lower than 5×10^{-5} M, based on Tullborg et al's (2010) review of measurements. This single value is used in the Process Report as the parameter for judging that, after saturation with oxygen-free groundwater, access of groundwater-derived sulphide to canisters will be transport-controlled and thus the resulting corrosion rate will be acceptably low.

Nitrite (NO_2^-), ammonium (NH_4^+) and acetate (CH_3COO^-) would contribute to stress corrosion cracking of the copper canister in the early post-closure oxidising conditions (SKB 2010a, Section 3.5.5). Safety analysis considers their future

abundance in groundwaters at repository depth. As with the biogeochemical and redox-active species considered above, future concentrations are assumed to be constrained by similar factors that influence current contents. Concentrations of nitrite and ammonium in a future glacial period are assumed to be lower than current concentrations because nitrate under an ice sheet is likely to be lower than current NO_3^-. Measured data are reported in this context in Salas et al. (2010) (Figure 25).

On the basis of review of experimental evidence and assessment of the process, SKB conclude that there is no evidence that stress corrosion cracking could occur in the Forsmark groundwater environment, but also that 'the possibility cannot be entirely ruled out' (SKB 2010a, Section 3.5.5).
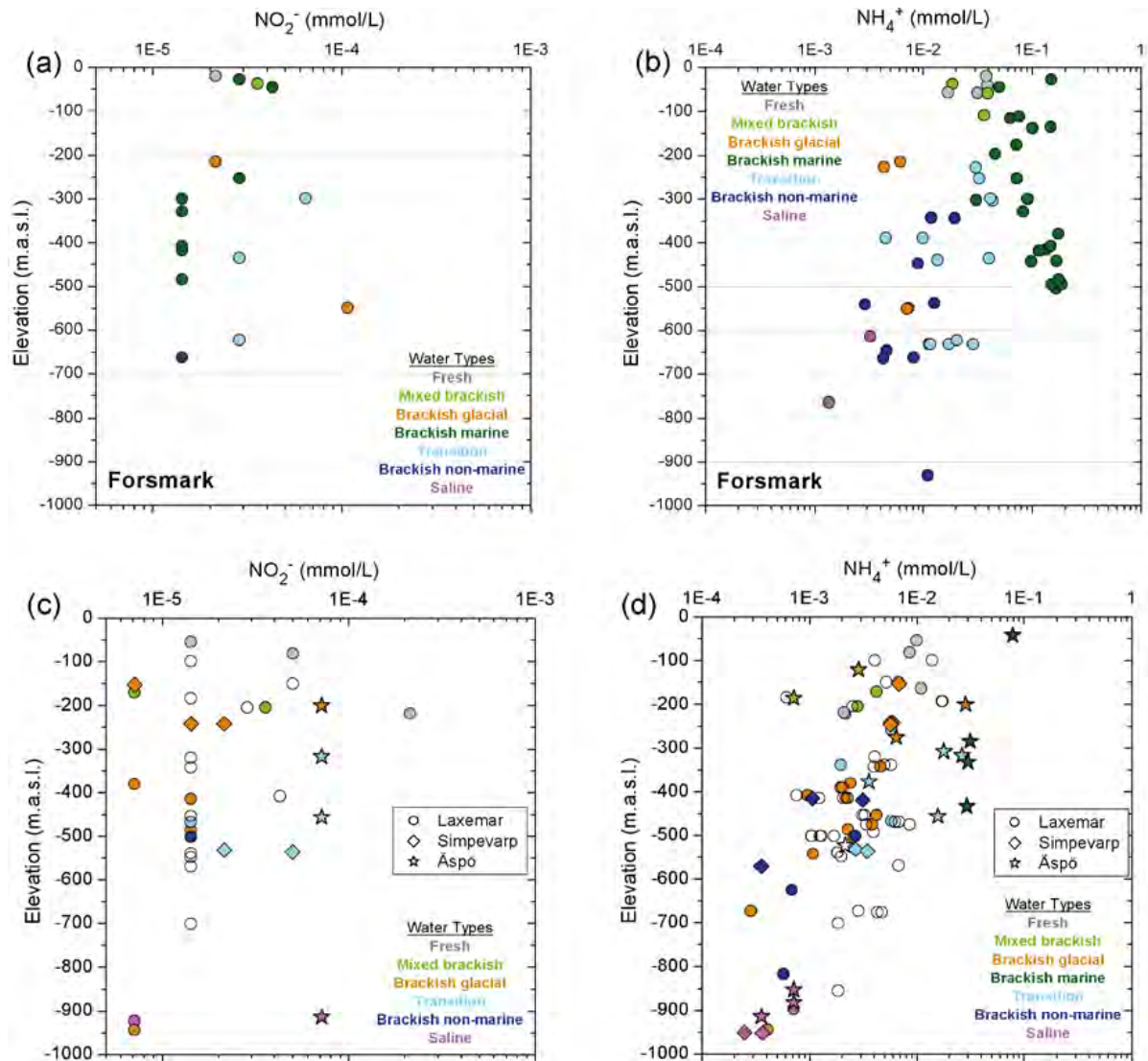
Figure 25. Measurements of nitrite (NO_2^-) and ammonium (NH_4^+) in groundwaters at Forsmark and Simpevarp/Laxemar/Äspö (Fig 8-5 in Salas et al. 2010).

6 Use of Data for Assessment of Buffer Alteration and Erosion

6.1 Source and composition of water that enters buffer

Buffer resaturation occurs when groundwater enters filled and sealed deposition holes. This poses questions of the source(s) of that resaturating water, the rate and prolonged timescale for resaturation, and the likely composition of water influx. Inflows, other than those that might come from the deposition tunnel through unintended pathways through seal and buffer, occur where transmissive fractures intersect deposition holes. Flow is driven by the hydraulic gradient towards the filled hole and by the capillary suction of unsaturated compacted bentonite. SKB have formulated a rejection condition that groundwater inflow to any deposition hole should cause no more than 100 kg of bentonite to be dispersed due to piping/erosion. For erosion of buffer by dilute groundwater, SKB judges that this design premise is met if inflow to a deposition hole is <0.1 L/min. (SKB 2011, Section 10.2.3).

The probabilistic discrete fracture network (DFN) model suggests that ~20% of deposition hole positions are intersected by transmissive fractures that would extend to the full perimeters of the deposition holes (Fig. 10-30, SKB 2011). This is interpreted to imply that around 80% of deposition holes will be expected to have undetectable or less significant flows of $<10^{-5}$ m^3/y per m^2 annular area. ($<10^{-11}$ m^3/min per m^2 = 10^{-8} L/min per m^2). Concerning the inflow criterion for buffer erosion, the model suggests that <1% of deposition hole positions would have inflows exceeding 0.1 L/min (Fig. 10-8, SKB 2011).

In the absence of a transmissive fracture intersecting a deposition hole, the potential sources of water entering the buffer are: (a) through the top of the hole either through the EDZ or a fracture intersecting the deposition tunnel (SKB's Q2 and Q3 pathways), or (b) the porewater in the very low transmissivity matrix and microfractures of intact rock. For porewater to pass from low permeability rock matrix and microfractures to compacted bentonite buffer will require the water potential ('capillary suction') in the buffer to be at a greater negative pressure than in the rock matrix.

Chemical compositions of matrix porewaters are measured by extraction experiments on drillcore samples with reasonable reliability only for Cl^- (and Br^-) concentrations, though SO_4^{2-} has also been analysed. In general, measurements suggest that porewaters have lower Cl^- concentrations than nearby fracture waters – sometimes more dilute by 50% or more but there is no general pattern. There is a dependence on the density of fracturing, as seen in the porewater compositions in the distinct fracture patterns of footwall and hanging wall structural blocks. SO_4^{2-} concentrations are prone to increase due to sulphide oxidation in the extraction procedure. pH, redox and related solutes such as HCO_3^-, Fe^{2+}, HS^-, DOC of porewaters are also not known reliably but could be estimated by modelling on the basis of the geochemical buffering by rock matrix minerals. No experimental measurements of these parameters have yet been reported for Forsmark rock. Major cation concentrations have been analysed in extractions but are affected by mineral dissolution. Based on model calculations of mineral dissolution, it has been concluded that the dissolution inputs of element concentrations are negligible for major cations and very minor for Mg^{2+}. SKB has not routinely reported the analytical data for the major cations in matrix porewater extractions and subsequently calculated in situ concentrations as they have done for Cl^-.

Porewaters also have $\delta^{18}O$ compositions that are distinctively heavier than corresponding fractures waters, adding to evidence that porewaters are relict from much older palaeohydrogeological conditions than the sources of fracture waters. It is deduced, supported by experimental findings, that the porewaters are exchanging diffusively with more mobile groundwater.

Resaturation of buffer in deposition holes with water derived from pores and microfractures in rock matrix would have the following characteristics:

- very low flux of water into buffer, depending on relative capillary suction potentials between compacted bentonite and rock matrix;
- less mineralised water compositions than current fracture waters; pore waters at repository depth and below are presently brackish-saline;
- pH, alkalinity, redox of pore waters parameters assumed similar to ambient conditions in adjacent fracture waters but probably with stronger buffering by reactions with the matrix minerals with which porewater is in contact;
- compositions of porewaters evolving more slowly than the compositions of fracture waters, so the long-term trend of dilution will be more sluggish.

Resaturation of buffer from rock matrix porewaters and continued diffusive equilibration of buffer porewater with rock matrix porewater will tend to maintain a more stable mineralisation of water in the buffer. There are uncertainties in redox and pH buffering but it is unlikely that there would be any process particularly deleterious to engineered barriers, for example sulphide production would be restricted by the supply of SO_4^{2-} from rock porewater and by the restriction on microbial activity in rock and buffer micro-porosity. The absence of fracturing intersecting a deposition hole would also decrease possibility of oxygenated water entering buffer and contacting copper canisters.

It is suggested that SKB could reduce the uncertainties around this issue by additional research and measurements:

- model calculations of the transfer of water between intact rock matrix and compacted bentonite buffer at a deposition hole periphery;
- experiments and geochemical model simulations to understand better the constraints on and possible ranges of rock matrix porewater chemistry, including redox conditions, cation compositions, anion exclusion;
- studying possibilities for solute fractionations during capillary transfer of solution between rock matrix and buffer;
- pilot experiments to study directly the water transfer across the interface of saturated rock and unsaturated compacted bentonite.

6.2 Geochemistry and buffer performance

A number of physicochemical processes could cause buffer alteration and/or erosion. These processes are to some extent interdependent because the same hydrochemical parameters are implicated in more than one process. The processes are considered separately by SKB. In summary, they and the relevant hydrochemical data and criteria are:

- Structural geochemical alteration of bentonite to illite ('illitization'). The relevant hydrochemical data are K^+ and dissolved SiO_2, as shown in Figure 3-23 in SKB (2010d) which is a mineral phase diagram in $\log(a_{K+}/a_{H+})$ versus $\log(a_{SiO2})$ space. K^+ and SiO_2 would also be buffered by dissolution of source minerals, e.g. feldspar, within bentonite and in surrounding rock. SKB do not have a safety function indicator criterion for K^+ concentrations. A limiting value for illitization has not been quantified for low temperature conditions in which alteration reaction kinetics is the limiting factor.
- Transformation of bentonite due to reaction of montmorillonite with other chemical components of groundwater, e.g. Fe^{2+}, Li^+ or due to dissolution of trace minerals in bentonite.
- Dissolution and degradation of bentonite by alkaline reaction. SKB have a safety function indicator criterion related to this process of pH <11.
- Precipitation of minerals from water, causing cementation in bentonite pores; potential mineral precipitates that might originate from groundwater solutes are gypsum, calcite, silica and iron oxides.
- Dispersion of colloids derived from bentonite; formation of a colloidal sol occurs when bentonite swells which is dependent on free volume for expansion and on interlayer forces in bentonite which vary in relation to concentrations in pore water of mono- and di-valent cations, i.e. Na^+, K^+, Ca^{2+} and Mg^{2+}. Divalent cations are more effective than monovalent cations at

lowering the critical coagulation concentration (CCC; Section 6.3) above which a colloidal sol will no longer be stable. SKB use a quantitative criterion based on sum of charge equivalents for all cations for the safety function indicator $\sum q[M^{q+}] > 4$ mM, rather than separate concentrations for different cations. That takes account of the ion exchange equilibrium effect described below (SKB 2011, Section 8.3.4).

- General electrostatic influences on swelling pressure and hydraulic conductivity of bentonite. Ca^{2+}/Na^+ ion exchange in bentonite affects how sensitive bentonite swelling is to the electrostatic environment in pore solution, therefore Na^+, Ca^{2+} and total ionic strength (or TDS, total dissolved solids) of groundwater are relevant. SKB use ionic strength criteria corresponding to 1.7M NaCl for the buffer bentonite and 0.6M NaCl for backfill.

These processes and safety functions for performance of the buffer and backfill are the basis of the hydrochemical data requirements that are set out in the Data Report for SR-Site (SKB 2010c) and were originally identified with preliminary target values by Andersson et al. (1998, 2000).

Geochemical alteration of bentonite buffer caused by dissolution of montmorillonite and precipitation of other minerals is covered by the processes described in the first four bullet points above. These processes depend on porewater compositions that are controlled by surrounding groundwater compositions. Forecasting of how groundwater compositions might evolve into the future for various scenarios have been achieved in SR-Site by using the forward modelling of reactive solute transport and groundwater mixing using the methods that are outlined in Section 4.3. For the initial thermal period and for the subsequent reference evolution, SR-Site concludes that for the modelled groundwater compositions, alteration will not proceed to a level where it will affect the physical properties, e.g. the swelling pressure and self-healing capacity, of the buffer (SKB 2011, Section 10.3.10). The fifth bullet point above concerns the potential dispersion of buffer bentonite as a colloid if dilute groundwater penetrates to repository depth at some time in the future (SKB 2011, Section 10.3.11). This is the process of 'chemical erosion' by which dilute groundwater would enter deposition holes via fractures with transmissivities above a threshold value and might disperse bentonite as a colloid. Loss of a substantial amount of buffer by erosion could eventually lead to advective movement of groundwater to the canister surface. Advective groundwater movement would enhance the transport of sulphide to the canister and thereby increase the rate of copper corrosion.

The sixth bullet point concerns the effect of ionic strength on the performance of the bentonite and places an upper limit on the safety function criterion in terms of ionic strength or total salinity. In this context, SKB uses criteria of 100 g/L and 35 g/L of NaCl salinity used on buffer and backfill performance respectively (SKB 2011, Section 8.3.4). There is uncertainty in these criteria depending on material properties and specific solutes contributing to salinity. Present salinity at

repository depth at Forsmark is well below these maxima and the model for long-term evolution forecasts only dilution. Upconing as a cause of increasing salinity might be a short-term issue in the operational period and shortly thereafter but there is no indication that groundwater within reasonable distance below repository depth has a level of salinity that would cause concern.

6.3 Groundwater dilution and the possibility of buffer erosion

The degree of dilution of the water composition that would cause colloidal dispersion of bentonite is governed by the Critical Coagulation Concentration (CCC) which can be calculated by DLVO theory. CCC is defined as the concentration of counter-ions (i.e. the cations in solution that counteract the repelling forces of negative charges on the colloid surfaces) below which a colloidal dispersion is stable. CCC is lower for divalent cations than for monovalent cations because of their higher charge.

There is a substantial amount of research evidence in support of the 4 mM threshold for colloidal dispersion of bentonite. The original research by SKB was reported by Birgersson et al (2009). The issue was further studied in more detail by the Euratom BELBaR project which more or less confirmed the threshold around 4 mM for NaCl solution (Missana et al. 2013). It also studied the sensitivity of threshold to the major interlayer cation in bentonite, i.e. Na- or Ca-bentonite, and found that Ca-bentonite is more resistant to dispersion so tends to have a slightly lower threshold of solution composition below which colloidal dispersion would occur. Posiva reported experiments that also found a dependence of the CCC on material properties and composition of bentonite (Schatz et al., 2013; Posiva 2013a).

There is a correlation between the safety function indicator $\sum q[M^{q+}]$ and TDS. SR-Site suggests that the criterion for $\sum q[M^{q+}]$ which has been evaluated as > 4mM could also be evaluated in modelling of future evolution of groundwaters through the proxy of TDS, the corresponding value being > 0.27 g/L (SKB 2011, Section 10.3.7).

Groundwater at repository depth at Forsmark has about 5-6 g/L Cl^- which is equivalent to 8-10 g/L NaCl. The cation composition comprises roughly similar charge equivalents of Na^+ and Ca^{2+} as the dominant cations, around 80 mM of Na^+ and 35 mM of Ca^{2+}. The trend of increasing total salinity with depth is associated with increasing proportion of Ca^{2+} whilst Na^+ concentrations are more variable and increase only slightly with depth.

In the scenario of a prolonged temperate climate followed by glacial climate in the long-distant future, progressive dilution of groundwaters will occur. Interpretation of present-day groundwater compositions indicates that the Na/Ca ratio will decline as dilution progresses.

Dilution of groundwater at repository depth due to glacial melt water penetration has been modelled at site scale by SKB (Vidstrand et al. 2010) and at repository scale (Joyce et al. 2010). SKB use these models in SR-Site and assume that glacial melt water penetration occurs transiently as an ice sheet advances. For example, penetration of melt water for 100 years in this scenario would result in inflow to 2% of deposition holes at 10% of the original salinity, i.e. <0.3 g/L TDS. This was reviewed more extensively in Bath (2014).

A key question is whether groundwater conditions could evolve to a state of dilution in which groundwater salinity would be significantly lower than 0.3 g/L TDS, i.e. <4 mM charge equivalents of Na^+ and Ca^{2+}.

SKB's probabilistic base case modelling in SR-Site suggests that advective conditions because of buffer erosion might develop at an average of 23 deposition holes within 1 million years (SKB 2011, Section 10.3.11). Adding sulphide concentrations and transport rates to the base case probabilistic model indicates that the average number of deposition holes that would fail in a million years varies from 0.12 to 0.65, depending on the assumption made concerning aperture-length correlation in the DFN model (SKB 2011, Section 10.4.9). SR-Site also points out that corrosion is slower than buffer erosion, implying that the latter process would not have immediate consequences for radionuclide release.

Evolution of groundwater compositions was modelled at the regional scale by 'loose coupling' of advection, transport and mixing of end-member waters with geochemical reaction (Salas et al. 2010; SKB 2011, Section 10.3.7). The modelled end-members were the altered meteoric, massive, glacial, brine, and older meteoric reference waters (SKB 2011, Section 10.3.6). Matrix diffusion affects the modelled proportions of reference waters in terms of diffusive exchange of solutes with rock matrix porewaters that were assigned different proportions of end-members, though it is unclear what these proportions were used in the reported model runs (Joyce et al 2010, Section 3.2.3; Salas et al. 2010).

The model starts from an initial depth-dependent mixture of reference waters that is assumed to be representative of the groundwater system 10,000 years ago (Joyce et al. 2010; Salas et al. 2010). Temperate climate conditions were modelled from that starting point at the end of the last glaciation until 10,000 years into the future. Cover of the site by the Littorina Sea and intrusion of brackish seawater is included in the variable boundary conditions for the model from about 8000 years ago until about 1000 years ago (Joyce et al. 2010).

The coupled model of transport and geochemical reaction was extended from the end of temperate conditions for a further 18,850 years during which boundary conditions representing a cycle of periglacial conditions, glacial advance and retreat. A different groundwater flow and transport model with an appropriate set of hydrogeological and hydrochemical boundary conditions were used for the simulation of the reference glacial cycle (Vidstrand et al. 2010).

Early water-rock reaction by infiltrating rainwater is taken into account by the 'altered meteoric' reference water. Ion exchange, calcite dissolution, microbial sulphate reduction, quartz and hydroxyapatite, iron oxides or amorphous iron sulphide have been equilibrated with the mixture of end-members (Salas et al. 2010). Uncertainties in groundwater flow modelling are not propagated into geochemical modelling (SKB 2011, Section 10.3.7).

Groundwater chemistry modelling makes various approximations, e.g. regarding the assemblage of mineral reactions minerals (calcite, SiO_2 and ion exchange only), and also that equilibrium with minerals in the 'active' shallow system is achieved (Salas et al. 2010). For example, the modelled Ca^{2+} does not match measured Ca^{2+} which is higher in shallow samples and lower in deeper samples (Fig 6-5, Salas et al. 2010). Another approximation is that only Littorina seawater is represented in geochemical modelling whereas less saline modern Baltic water should be simulated as a distinct component. The modelled pH, using these assumptions, is higher than measured at shallow depths and lower than measured at greater depths, providing further evidence that the geochemical modelling of buffering and evolution of groundwater composition is discrepant (Fig 6-10, Salas et al. 2010).

The conclusion from the modelling of Ca^{2+} (plus Mg^{2+}) and Na^+ evolution is that the safety function indicator for buffer erosion will be dominantly influenced by the mixing process. Mg^{2+} is not modelled and is uncertain due to source/sink uncertainties, mainly due to chlorite. The conclusion that mixing dominates ceases to be valid at very high dilutions, i.e. when pre-existing saline/brackish water components of 'deep' origin and marine (Littorina/Baltic) origin will have been flushed out of the system, for example in the scenarios of a prolonged temperate climate or of a massive intrusion of glacial melt water. In that case, Ca^{2+} and Na^+ concentrations and their relative proportions will be controlled by mineral reactions and ion exchange. SKB's hydrogeochemical modelling of the reference glacial cycle indicates a high probability that $\sum q[M^{q+}]$ will exceed 4mM by 1 to 2 orders of magnitude throughout expected conditions for periglacial and glacial climate stages. Propagation of parameter uncertainties through the model indicates low probabilities, due to outliers of parameters, that $\sum q[M^{q+}]$ of groundwater within the repository volume could be lower than 4 mM (Salas et al. 2010, Section 7.3.2, Fig 7-7).

Modelling carried out for SSM (Bath 2011) indicates that the range of scenarios for water-rock reaction outcomes at high dilution is rather broad, depending amongst other things on the mineral assemblage that is dissolving, equilibrating and precipitating and also on the exchangeable cation budgets. In most modelled cases, it was found that the dissolved cations would exceed the safety function indicator criterion of 4 mM charge equivalents and also that the Ca/Na ratio would be beneficial. There are, however, a small number of alternative scenarios for evolution of dilute groundwater compositions in which the mineralisation of solutions might remain below 4 mM and/or the Ca/Na ratio would be deleteriously low. The main prerequisite for very dilute groundwater at repository depth would,

of course, be very dilute rainwater or melt water input, specifically with a very low content of conservative anion Cl$^-$. Hydrogeochemical evolution pathways that could preserve a low level of mineralisation with low Ca/Na ratio involve reactions with plagioclase, feldspar, montmorillonite and illite (Bath 2011).

Fig 10-39 in SKB (2011) shows that SKB's model forecasts that salinity will decrease from 10,000 mg/L TDS to ~6000 mg/L (range 8000 to 3000 mg/L) in 7000 years' time. Additional transport-reaction modelling for an extended temperate period of around 58,000 years in a 'global warming' scenario was reported by Joyce et al. (2015). It forecasts that TDS and Cl$^-$ concentrations will not decrease much further over the extended period of meteoric water infiltration, typically falling to around 2500 mg/L Cl$^-$ (~4000 mg/L TDS, 95th to 5th percentile range 10,000 to 600 mg/L). Data from Forsmark, Laxemar and Simpevarp show good correlations of $\sum q[M^{q+}]$ with TDS, so the 4mM limit is equivalent to >270 mg/L TDS. SKB's modelling indicates that there is a very low probability of future dilution of groundwaters causing that criterion to be breached.

The composition of the (altered) meteoric reference water is based on groundwaters at 50-150 m depth at Forsmark. Ca^{2+} concentrations in the upper 200 m vary between 0.2 and 30 mM, but this variability of Ca^{2+}, specifically the occurrence of very low values (which tends to confirm the findings of the modelling in Bath 2011), is not represented in the meteoric reference water composition used in modelling. This supports the conclusion that there is a non-negligible probability that dilute water could penetrate to repository depth in the most direct transmissive pathways. Moreover such 'fast pathways' are not represented in simulations with the ECPM regional-scale flow model that is used in the model for evolution of groundwater composition.

SKB addressed these issues of timescale and fast flow using a simplified model to transport meteoric water with zero salinity from source along pathways identified in the ECPM regional scale model. The only process in this model that modifies salinity is out-diffusion of matrix salinity. This model has been run forwards for 10,000y (base case for temperate climate) and for 60,000 y (prolongation of present temperate conditions). It predicts that the number of deposition hole positions in which salinity will decrease to 10% of original salinity i.e. to 1 g/L TDS, is 1% of total at 10,000 y and 2% at 60,000 y (SKB 2011, Section 10.3.6).

This modelling represents heterogeneity of flow-paths, but it assumes homogeneity of matrix diffusion and flow rates. If matrix diffusion does not operate as effectively as is assumed, for example because fast water flow through fractures limits the effectiveness of out-diffusion of saline water from the matrix pores, then the effect of progressive flushing by dilute water will not be mitigated as much as the model suggests. There may be deposition hole positions where more dilute water could penetrate. A global warming temperate climate period might extend beyond 60,000y. It is probable that more dilute water, i.e. <1 g/L TDS and as low as <270 mg/L TDS (<4 mM cation equivalents) would penetrate and not be attenuated by matrix diffusion. This is the potential state of dilution in which reactions with minerals will be the process that would probably, but not certainly,

maintain mineralisation above the safety function indicator criterion. Reaction with minerals is therefore the most reliable process mitigating extreme dilution (Section 2.1.6 in Bath 2014). There is a question over whether reaction of dilute infiltration with minerals would always achieve the minimum level of mineralisation required to meet the required criterion.

Modelling for SSM of geochemical evolution of dilute waters (glacial melt waters, Forsmark soil water and shallow groundwater) by reaction with biotite, chlorite, pyrite, plagioclase, feldspar and quartz had two alternative model assumptions: kinetic dissolution to equilibrium and local 'instant' equilibrium with different mineral assemblages (Bath 2011). Results of kinetic dissolution modelling indicate that in early stages of hydrogeochemical evolution, Na, Ca, K and Mg increase due to albite, anorthite, feldspar and biotite dissolution. K is buffered by precipitation of illite. pH goes to very high values unless P_{CO2} is held constant. In unbuffered high-pH solutions, (Ca + Mg)/Na goes to 1 whereas in buffered lower-pH solutions, (Ca + Mg)/Na is mostly 0.01 to 0.1, i.e. low, and $\sum$cations is 10^{-3} to 10^{-2} M. i.e. 1 to 10 mM.

Results of local equilibrium modelling (Bath 2011) indicate that initial dissolution of calcite to saturation coupled with cation exchange raises pH and all cation concentrations to e.g. $\sum M = 4\text{-}5$ mg/L (10^{-5} to 10^{-4} M) and (Ca+Mg)/(Na) is ~3. Second and third stages of the model involve equilibration or dissolution-only equilibration with various secondary minerals, e.g. clays, zeolites, and dissolution-only equilibration with albite and feldspar or equilibration with illite and chlorite. In these second and third stages, concentrations of cations generally increase, pH increases and (Ca + Mg)/Na also increases. Na^+, Mg^{2+} and K^+ tend to decrease if these are taken up into precipitating montmorillonite and/or illite/chlorite. In the absence of a precipitating mineral sink once calcite is at equilibrium, Ca^{2+} tends to increase so (Ca + Mg)/Na tends to rise.

In the kinetic dissolution modelling, cation concentrations remain around 10^{-3} to 10^{-2} molar (1 to 10 mM) total for the modelled timescale of 1000 y. If groundwater flows rapidly through rock, e.g. under a high hydraulic gradient, reaction may not advance to this level of mineralisation. A similar conclusion was derived from reactive transport modelling of dissolved oxygen reaction with fracture minerals (Bath and Hermansson 2007). A comparable conclusion, that high flow velocities could enable glacial melt water to penetrate to repository depth in just a few years whilst pessimistically retaining a small fraction of its original dissolved oxygen content, was reached from SKB's research (Guimera et al. 2006).

Deep groundwaters in continental or coastal locations in fractured shield rock generally have mineralisation well in excess of 4 mM total cations and have Ca^{2+} as a sufficient proportion of total cations to meet this requirement. There are relatively few reliable groundwater samplings at the depth range of interest, 450-500 m in Fennoscandian and Canadian Shields and none of those have mineralisation that is as low as <270 mg/L TDS. Total flushing has evidently not occurred to the

depth of interest in these locations in the timescales for which they have been exposed to meteoric infiltration - extremely long periods for the non-coastal continental locations. The probability of extreme dilution occurring in the future at Forsmark is very low but cannot be completely discounted on the basis of the hydrodynamics and hydrogeochemical considerations discussed above. There is also a possibility that a prolonged period of dilute infiltration could deplete significantly the reactive fracture-coating minerals that are accessible for rapid reactions with rapid infiltration.

7 Comparable Properties of Olkiluoto Site, Finland

7.1 Posiva's safety assessment of Olkiluoto and geochemical data requirements

Posiva's 'TURVA 2012' safety assessment for the spent fuel repository at Olkiluoto comprises a portfolio of reports. At the top of the hierarchy of reports are 'Synthesis 2012' (Posiva 2012a) and 'Performance Assessment 2012' (Posiva 2013a). Relevant supporting reports with geochemical data are: 'Models and Data for the Repository System 2012 (Posiva 2013b), 'Radionuclide Migration Parameters for the Geosphere' (Posiva 2014a), 'Radionuclide Solubility Limits and Migration Parameters for the Canister and the Buffer' (Posiva 2014b) and 'Olkiluoto Site Description 2011' (Posiva 2013c).

Key parameters relating to chemical conditions that are required for PA, and the models and input site data from which the parameters have been derived, are in Table 7.

7.2 Geochemical data utilisation in safety assessment of Olkiluoto

Posiva's hydrogeological modelling of groundwater evolution over time is done by a solute transport simulation with an initial condition representing the groundwater system and salinity distribution at 8000 y BP (Posiva 2013b, Section 6.1). This is an initial condition of post-glacial groundwater, similar to that used by SKB for its groundwater evolution modelling though SKB start their model at 8000 BC, i.e. 2000 years earlier than Posiva's model. At the starting point of 8000 y BP, Posiva have three reference waters in their palaeohydrogeological model: brine, sub-glacial and glacial, which are assumed to account for all groundwater mixtures from surface to 1000 m depth. With advancing time, a fourth reference water, meteoric, is added to represent temperate climate infiltration. The groundwater flow and solute transport computer code that is used for the modelling, ConnectFlow, is common to SKB and Posiva, so it should be expected that the conceptual approach, assumptions and input data requirements are similar if not identical for the two safety assessments.

The hydrogeological model for Olkiluoto is calibrated against a large number of pressure head measurements. These head measurements are compared with the hydrostatic head versus depth profile which is calculated from the salinity profile indicated by EC logging and TDS values calculated from the compositions of groundwater samples (Fig 6-20, Posiva 2013b).

Table 7. Parameters describing chemical conditions that are required for PA, models producing those data, and required input hydrogeochemical data and other parameters (extracted from Tables 4-9 and 4-10 in Posiva 2013b).

Chemical parameters for PA	Model using site data	Input site data
Groundwater composition at repository depth, reference and bounding groundwater compositions at different times	Reactive-transport model for geochemical evolution of geosphere and buffering capacity of host rock; required for canister corrosion, buffer & backfill performance	Compositions of initial groundwater, i.e. present-day, and infiltrating waters at different times in the future
Backfill porewater composition and composition of water fluxes out of backfill for different groundwater compositions	Geochemical evolution of deposition tunnel backfill; required for swelling clay losses from backfill and for potential sulphate fluxes and sulphide production rates in near field	Groundwater composition at different times, mineral and geochemical data for bentonite plus foreign materials
Buffer porewater composition and composition of water fluxes out of buffer for different groundwater compositions including dilute groundwater	Geochemical and physical evolution of buffer; required for bentonite erosion losses and for potential sulphate fluxes and sulphide production rates adjacent to canister	Groundwater composition at different times, geochemical evolution in far field of dilute infiltration, mineral and geochemical data for bentonite
Near-field pH and Cl^- concentrations at different times	Corrosion of copper canisters in highly saline groundwaters	Groundwater compositions at present-day and at various times in the future
Mass transport rate for HS^- at canister surface	Corrosion of copper canisters by microbiologically-enhanced sulphide HS^-	HS^- concentrations in groundwaters at deposition holes at present-day and in the future; co-existing microbial populations
Oxidation state, speciation and solubility limits of radionuclides, diffusive fluxes and retardation	Near-field solubilities, transport and release rates of radionuclides from buffer and backfill	Composition of groundwater at bentonite/host rock interface, buffer & backfill porewater compositions based on bentonite-water reactions, sorption and diffusion parameters
Oxidation state, speciation and complexation of radionuclides, retardation by sorption and matrix diffusion	Transport of radionuclides in the geosphere	Redox and compositions of groundwaters along flow paths and in rock matrix, sorption and diffusion parameters, colloid concentrations (NB. Colloid transport is out of scope of PA and is treated only in Complementary Considerations report, Posiva 2012-11)
Maximum depth of transient permafrost and depth of perennial permafrost	Climate-driven model for geothermal conditions in rock mass and groundwater	Depth-dependent variation of groundwater salinity (TDS), radiogenic heat production by U/Th in rock, plus physical and hydromechanical parameters

The model for geochemical evolution of the geosphere at Olkiluoto is based on a concept that groundwater compositions evolve from present-day conditions by reaction with mineral phases that control pH, redox, major cation concentrations and ratios, and redox-sensitive trace solutes specifically HS^- and Fe^{2+}. Initial groundwater compositions are a set of reference waters that represent the depth-dependent changes of compositions observed in deep drillholes. With increasing depth, these salinities and water types are: brackish bicarbonate, brackish sulphate, brackish-saline, saline, and highly saline (Posiva 2013b, Section 6.2). As in SKB's hydrogeochemical modelling of the Forsmark site, these reference waters are derived from measured groundwater compositions although they are selected single representative groundwater samples (see Table 6-4, Posiva 2013b) rather than the statistically-processed ('M3') hypothetical compositions that are used for SR-Site. The mineral phases with which the initial reference water compositions, and subsequent mixed groundwaters, are reacted are: calcite, pyrite and/or amorphous FeS, iron oxide, albite, K-feldspar, illite and chlorite. Cation exchange is also modelled. The reactive transport modelling code used by Posiva is FASTREACT which couples 3D random-walk particle tracking realisations with the PHREEQC water-rock reaction code. This methodology is similar to, but slightly different from, the ConnectFlow code that SKB uses.

For assessing the performance of the EBS and for defining solubility limits and retention parameters for radionuclides in near- and far-fields, reference and bounding groundwater compositions were derived by Posiva in an earlier but similar exercise (Posiva 2013b, Section 6.2.2). The reference groundwaters represent the likely range of groundwaters at repository depth in the short-term evolution, whereas the bounding groundwater compositions represent possible future groundwater compositions in the long-term evolution of Olkiluoto. These water compositions are selected from observed groundwaters, except for glacial melt water which is based on water at the Grimsel test site. The measured compositions are adjusted to equilibrium with calcite and quartz. Measured data for pH, Eh, major cations and anions, plus HS^-, Fe^{2+}, Sr, Mn, F and Si are used in this way.For modelling corrosion of the copper canisters, Posiva have used a single value for sulphide concentration, 3 mg/L, which is believed to be the maximum value expected at repository depth in the long term (Posiva 2013b, Section 6.2.2; Wersin et al. 2013).

In their safety assessment for Olkiluoto, Posiva refer to natural colloids data from Olkiluoto and Onkalo and also from research projects in crystalline rock URLs at Äspö and Grimsel (Appendix K, Posiva 2013b; Posiva 2012b, Section 9.3). At Olkiluoto and in the Onkalo tunnels, inorganic colloids have been observed at concentrations in the range 0.001 to 200 ppb. Organic colloids, which comprise mostly fulvic and humic acids, have been measured at Olkiluoto at ppb level, whereas in Onkalo monitoring samples these have been at the ppm level. These data are not used in Posiva's safety assessment. Potential effects of colloids on radionuclide sorption and transport are scoped using experimental data for bentonite colloids (e.g. from FEBEX experiments).

It is evident that the general approach to conceptual models, processes, safety functions, assessment models and input data are very similar between SKB's SR-Site and Posiva's TURVA 2012 (Posiva 2012a). The main assessment targets in both cases are corrosion of the canisters, performance of bentonite buffer and backfill, and transport and retention of radionuclides in the geosphere. Considering the timescale of safety assessment, a major task in the safety assessment has been to use reactive transport modelling to forecast the likely evolution of groundwater compositions through the assessment timescale. This includes modelling a prolonged temperate period and then potentially through a glacial period in which the Forsmark and Olkiluoto sites would be affected by periglacial conditions with permafrost followed by advance and retreat of ice sheets.

In both Posiva's and SKB's safety assessments, geochemical evolution has been modelled from initial conditions that are defined in terms of reference waters. Although, as discussed above, these have been derived in rather diverse ways in the two safety assessments. Nevertheless, the two approaches both rely heavily on measured present-day groundwater compositions to define the reference waters and to constrain the mixing proportions between the reference waters.
The hypothetical groundwater compositions that are outputs from the geochemical evolution modelling are discretised both spatially and temporally, so they provide calculated values for TDS, pH, Eh and major cations and anions at points in the site rock volume for different times through the temperate and glacial stages of evolution. These modelled compositions are used as part of the evidence that the relevant hydrochemical safety functions will be achieved. Other lines of argument for some safety functions involve estimations such as mass budget calculations, e.g. for sulphide production based on observed abundance of sulphate combined with mass transport calculations.

It is notable that the safety assessment argument regarding canister corrosion is based on observed sulphide concentrations (supported by equilibrium calculations of HS^- concentration in equilibrium with FeS) combined with the mass transport constraint on sulphate, and that the observed concentrations of sulphide and sulphate are argued to be adequate estimates for the assessment timescale. Apart from this direct use of measured data, the safety assessments from both Posiva and SKB primarily use modelled data for future evolution of TDS/salinity and major cation concentrations for the other principal assessment targets, i.e. performance of the EBS and radionuclide transport.

In general, the hydrogeochemical behaviours of natural nuclides that are analogues of inventory radionuclides, e.g. U, Cl, I, Cs, Sr, Ni have not been interpreted specifically to support the conceptual model for transport, retardation and rock matrix diffusion. Posiva have compared the natural fluxes of U and ^{226}Ra from the proposed repository volume with the modelled flux of inventory-derived U and ^{226}Ra through the near field and geosphere as a 'complementary indicator' of radiological safety (Posiva 2012b, Section 11.2.1 & Table 11-5). SKB have not included such 'Complementary Considerations' in their safety assessment.

7.3 Summary comparison of hydrochemical characteristics of Forsmark and Olkiluoto sites

The comparisons in this section are concerned with the hydrochemistry of 'deep' groundwaters at each site that occur at >100 m depth. They have been extracted and edited from the report 'Comparison of site descriptive models for Olkiluoto, Finland and Forsmark, Sweden' (Geier et al. 2012) that was produced for the Finnish Radiation and Nuclear Safety Authority. Table 8 is a summary of the comparisons, organised according to the following hydrogeochemical topics.

Water sampling and hydrochemical measurements in deep boreholes at Olkiluoto

Most or all of the drillholes at Olkiluoto have been sampled, soon after drilling, at one or more depth intervals using pumped extraction with a double-packer down-hole tool. The downhole PAVE tool consists of a membrane pump operated from the surface and one or more sample vessels with an internal gas-driven piston that compensates for pressure changes and preserves water samples at in-*situ* pressure. Subsequently many of the boreholes have been re-sampled after the installation of multi-packer systems, however many of the boreholes were left open for extended periods (i.e. several years) prior to multi-packer installations so these water samples may not be representative due to cross-flow within drillholes.

Efforts aimed specifically at sampling fracture groundwaters in rock domains with lower transmissivity at Olkiluoto have not revealed any substantial contrast with groundwaters in more transmissive domains, though slightly higher Cl^- concentrations and lower HCO_3^- presumably reflect the tendency for less mixing of dilute meteoric water in the former. Groundwater samples collected from the hydrogeological zones HZ19A and HZ20A in the immediate vicinity of the Onkalo have compositions that are slightly dilute compared with earlier groundwater samples taken at comparable depths in surface-based boreholes (Penttinen et al, 2011, pp 98 & 110). This can be interpreted as evidence that there has been some drawdown of shallow dilute water towards the Onkalo excavation, though there is also evidence of a more general pattern of slightly greater infiltration of fresh waters in the hydrogeological zones.

Water samples have also been collected from 2005 onwards from 'groundwater stations' (PVA 1 to 6) and from 2004 onwards in pilot holes (PH 2 to 6, 8 to 11) in the Onkalo access tunnel (Posiva, 2009; Penttinen et al, 2011, p 123). These samples have had little significance for baseline hydrochemistry but have been used to search for perturbations due to excavation such as stray materials from blasting, injection and grouting, and also for studies focused on colloids, microbes and organics. The total number of water samples from drillholes that have been reasonably representative of baseline conditions is 41 (plus another 52 water samples of secondary quality). Another 102 water samples are considered to have some degree of perturbation. Samples have been taken down to about 850 m

depth, though most are at ≤ 500 m. The length of sampled intervals has been mostly in the range 2 to 10 m.

Posiva's PAVE equipment measures pH, Eh and dissolved oxygen (DO) in water pumped from a borehole to a flow-through cell at the surface. pH and Eh data have been obtained for most of the intervals from which water samples have been collected, but a large proportion (perhaps >50%) of these measurements appear to be unrepresentative especially for Eh, and thus also for DO. It is not clear from Posiva's reporting how many measurements are considered to be reliable. A report of PAVE sampling and monitoring of groundwaters from six open boreholes (sampling depths 50 to 867 m) provides data for pH, Eh and DO (Hirvonen and Hatenpää, 2006). A similar data set has been obtained during a long-term pumping test in an open borehole (Paaso et al, 2006). pH values are in the range 7.4 to 8.1, Eh values are in the range -270 to -30 mV, and DO values are consistently below detection limits of the electrochemical probes, i.e. either <0.01 or <0.001 mg/L O_2. In several cases (including the two least negative values) the Eh did not stabilize during monitoring, so the overall reliability is not certain though the data tend to indicate reducing conditions as expected.

The same issues apply to samples taken for analyses of redox-active solutes, i.e. Fe^{2+}, HS^- and probably also CH_4 and H_2. Data for ^{14}C and $\delta^{13}C$ might also have similar uncertainties. Water samples have been collected specially for microbial analyses down to about 450 m depth; about 25 such samples from drillholes have been analysed.

Salinity (total dissolved solids and ionic strength)

Olkiluoto and Forsmark both have brackish (≤10 g/L TDS) groundwaters down to at least proposed repository depths; these levels of salinity then transition to saline (>10 g/L TDS) waters over differing depth ranges. Salinities reach different maxima at maximum drilled depth, i.e. about 1000 m, at the two sites. Olkiluoto generally has brackish groundwater between 30 and 450 m depth, below which observed salinity rises to a maximum of about 84 g/L TDS (about 52000 mg/L Cl^-) at about 1000 m depth (Posiva, 2009, p314). Forsmark is brackish from about 60 m to 900 m depth in the southern part of the target area and to about 600-700 m in the northern part. The maximum observed salinity below those depths at Forsmark is about 24 g/L TDS (about 15000 mg/L Cl^-) at about 1000 m depth (Smellie et al, 2008).

Whilst SO_4^{2-} contents are similar for brackish-SO_4 water at Olkiluoto (up to 580 mg/L) and brackish-marine waters at Forsmark (up to 550 mg/L), they are dissimilar for brackish-Cl water at Olkiluoto (up to 100 mg/L) and brackish non-marine water at Forsmark (up to 200 mg/L).

The distribution of salinity is more spatially heterogeneous at Forsmark than at Olkiluoto; this may relate to the hydrogeological differences: the dominance of large scale vertical conductivity at Forsmark and the dominance of lateral conductivity at Olkiluoto. The distinction between the southern and northern parts of the

Forsmark siting area reflects the significance of distinct groundwater regimes (footwall and hanging wall domains that are separated by the major sub-horizontal gently dipping deformation zone A2. Although Olkiluoto also has sub-horizontal fracture zones that are known to be major hydrogeological features, i.e. to have relatively high transmissivities, they do not seem to cause the salinity heterogeneity seen at Forsmark.

These observations and comparisons lead to some conceptual interpretations on Olkiluoto and Forsmark:

- Brackish waters with higher SO_4^{2-} contents at both sites are of predominantly Littorina Sea origin.
- During post-glacial Holocene submergence, Littorina water penetrated deeper at Forsmark than at Olkiluoto. This may reflect longer duration of submergence at Forsmark than at Olkiluoto, and/or greater vertical transmissivity at Forsmark than at Olkiluoto, and/or a constraint on deep infiltration due to pre-existing deep groundwater at Olkiluoto being more saline than at Forsmark.
- Sub-horizontal gently-dipping deformation zones and the distribution and frequency of vertical hydrogeological zones are significant at both sites for groundwater movements and mixing, and thus for salinity distributions. The varying salinity distribution at Forsmark indicates that groundwater movement is more restricted down to proposed repository depths in the footwall domain where there are no (or fewer) deformation zones.
- Brackish groundwaters with lower SO_4^{2-} content at both sites are not derived from Littorina but predominantly from dilution of deeper saline waters that are of non-marine origins (based on Mg^{2+} interpretation).
- Differences of SO_4^{2-} concentrations in the deeper non-marine brackish waters at Olkiluoto and Forsmark may reflect contrasting sources of SO_4^{2-} in deep saline waters or differing efficiencies of SO_4^{2-} reduction. Posiva infer that the latter is the case and is linked with methane abundance in Olkiluoto groundwaters (see below).

Redox Conditions (dissolved oxygen, Eh, reduced S, C and N species)

Dissolved oxygen (DO) data obtained by electrochemical probe have not been consistently reported for groundwaters at Olkiluoto and Forsmark. DO measurements have variable reliability due primarily to the likelihood of contamination by air ingress into the sampling tubing and/or the flow-through cell at the surface. However, 'below detection limit' values of DO, coupled with negative Eh values, have been measured in some groundwaters at Olkiluoto in open borehole conditions. For both sites, DO is inferred to be absent on the basis of Eh values and of iron and sulphur speciation that indicate reducing conditions.

Redox conditions at proposed repository depth ranges are expected to be similar at both sites. Reported Eh values for groundwaters at Olkiluoto are scattered with a wide range of +100 to -400 mV and show no systematic variation with depth. The scatter of values is attributed by Posiva to problems with measurements and this is almost certainly the case. Eh values reported for groundwaters at Forsmark have higher reliability: 13 measurements in brackish and saline groundwaters fall in the range -143 to -281 mV (Laaksoharju et al, 2008a). Taking account of pH variations these Eh values for Forsmark are fairly consistent with electrochemical equilibrium for the SO_4^{2-}/HS^- and SO_4^{2-}/FeS_{am} couples and also with Fe^{2+} equilibrium with an iron oxide phase with intermediate crystallinity (cf Banwart, 1999).

The conceptual model proposed for redox at Olkiluoto based on distributions of redox-active solutes has two regimes, above and below a 'metastable interface' at 200-300 m (Posiva, 2009). Above that, SO_4^{2-}/HS^- is suggested as the control whereas below 300 m CH_4/CO_2 is suggested as the control. It is implied that microbially-mediated anaerobic oxidation of CH_4 and concurrent reduction of SO_4^{2-} take place in the interface at about 300 m where SO_4^{2-} concentrations decrease sharply with increasing depth and CH_4 concentrations decrease with decreasing depth.

The inferred change of redox-controlling biogeochemistry at Olkiluoto is related to the changing occurrence of CH_4 which is very low to 300 m depth below which it increases in brackish-Cl and saline groundwaters to ~1000 mL_{STP} per litre water (Figure 26). Below 300 m depth, HS^- is always <1 mg/L. H_2 concentrations at Olkiluoto increase with increasing depth, from μL/L to mL/L levels. Both CH_4 and H_2 are attributed by Posiva to a dominantly abiogenic source.
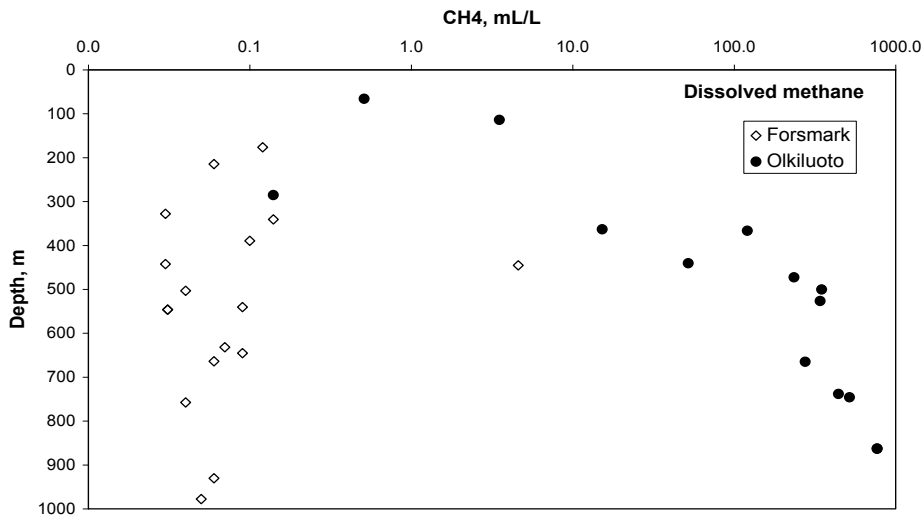

Figure 26. Methane concentrations (plotted on a logarithmic scale) versus depth at Olkiluoto and Forsmark.

CH$_4$ concentrations at Forsmark are mostly below 0.10 mL/L (Figure 26) whilst corresponding H$_2$ concentrations are scattered from below detection (around 3 µL/L) up to 370 µL/L.

Data for populations and distributions of microorganisms are similar for the two sites and do not really shed any clarity on variations of biogeochemical processes with depth. Total numbers of cells (TNC) at more than 100 m depth at Olkiluoto are mostly in the range 10^4-10^5 cells/mL (Posiva, 2009) whereas TNC at Forsmark is similar, between 10^4-10^6 cells/mL (Hallbeck and Pedersen, 2008b). Most probable numbers (MPN) for various groups of microbes, e.g. sulphate reducing bacteria (SRB), iron and manganese reducing bacteria (IRB and MRB), acetogens, and methanogens, generally do not show clear patterns at Forsmark though they seem to reach maxima at 250-330 m depth at Olkiluoto. These microbial groups are mostly present at all depths at Forsmark though methanogens are very sparse, more so than at Olkiluoto, being detected in only 2 samples. Acetogens are the dominant group at both Olkiluoto and Forsmark, and it is noted that SRB are a low proportion of total microbes. There seems to be a correlation between the MPN for SRB and the value of Eh at Forsmark, adding to evidence for Eh being controlled by the microbially-mediated SO$_4$/HS redox couple.

pH, Carbonate Alkalinity and Buffering Capacity

Values of pH in groundwaters at Olkiluoto vary between about 7 and 8.2 (Posiva, 2009). In shallow fresh-brackish HCO$_3$-type waters they are between 7 and 7.5, and then show a tendency to increase to 7.5 and 8.2 in brackish-SO$_4$ and brackish-Cl waters. In deep saline groundwaters, there is a trend of a slight decrease of pH from around 8 to 7.5 as TDS increases and water composition changes from Na-Ca-Cl to Ca-Na-Cl.

pH in groundwaters at Forsmark varies over similar ranges: 7.3-8.2 in brackish marine waters and 7.0-8.5 in brackish non-marine and saline waters, though there is no clear pattern of variation with depth or salinity in this case (Laaksoharju et al, 2008).

Total alkalinity, predominantly due to dissolved inorganic carbon i.e. HCO$_3^-$, is inversely correlated with salinity at both sites. It is <2 milliequivalents per litre (meq/L) in brackish SO$_4$ waters at Olkiluoto and <1 meq/L in brackish Cl and saline waters. It is mostly <3 meq/L in brackish marine waters at Forsmark and <1 meq/L in brackish and saline non-marine waters.

In both cases, the main buffering process for pH is interpreted as equilibration with calcite which is almost ubiquitous in fracture-filling mineral assemblages. Studies of fracture minerals at Forsmark indicate that calcite occurs in both the hydrothermal generations and the more recent low temperature generation of fracture minerals. It is one of the most common minerals in open and partly-open transmissive fractures. Similarly, at Olkiluoto, calcite is identified to be the most abundant mineral in coatings or surfaces of open fractures.

Calculations with measured values for pH and alkalinity indicate that pCO_2 decreases with depth from 10^{-2} to $10^{-4.5}$ atm. at Olkiluoto. Calculated pCO_2 values at Forsmark also tend to decrease with depth, but there is a small difference between the ranges calculated for the less transmissive 'footwall' fracture domain in the northern part of the area (10^{-3} to 10^{-5} atm) and for the 'hanging wall' domains in the rest of the area (10^{-2} to 10^{-4} atm). This is attributed to the difference in groundwater mixing in the two domains.

Reaction with aluminosilicate minerals is considered to be a minor process for pH buffering relative to reaction with calcite in the interpretation of both sites. However, models including aluminosilicate reactions and cation exchange as well as calcite equilibrium to account fully for the systematic variations and evolution of pH, alkalinity and relative cation concentrations, e.g. Ca:Na, have not been presented for either site.

Divalent (Ca^{2+}, Mg^{2+}) and Monovalent (Na^+, K^+) Cations

The water types at Olkiluoto change with depth from Ca-Na-Mg in fresh groundwaters to Na-(Ca) and Na-dominated in brackish groundwaters. Saline groundwaters change from Na-Ca to Ca-Na types as salinity increases to the maxima seen at Olkiluoto. A similar pattern is seen at Forsmark in the brackish non-marine waters, but the change to Ca-Na types occurs at lower salinities. At both Olkiluoto and Forsmark, Na^+ and Ca^{2+} increase regularly with increasing depth and increasing Cl^-, with the rates of increase changing so that Ca^{2+} predominance takes over from Na^+ predominance in saline groundwaters.

Maximum Na^+ at 1000 m depth is about 10000 mg/L at Olkiluoto and is about 2200 mg/L at Forsmark (with slightly higher Na^+ in more saline groundwaters in the northern part of the target area). Maximum Ca^{2+} at 1000 m depth is about 18000 mg/L at Olkiluoto and is about 4000 mg/L at Forsmark, with higher Ca^{2+} in the northern part of the target area.

K^+ concentrations at Olkiluoto are more variable in relation to depth and Cl^- but show a slight increase to a maximum of around 29 mg/L in the deepest samples. K^+ concentrations are variable in brackish marine groundwaters at Forsmark, varying between 5 and 60 mg/L. In contrast to the case at Olkiluoto, maximum K^+ values decrease with increasing depth at Forsmark and are around 10 mg/L at 1000 m.

The patterns of Mg^{2+} variation with depth and in relation to salinity at both Olkiluoto and Forsmark are strongly influenced by the distribution of brackish marine Littorina water. Maxima of Mg^{2+} between 250-300 mg/L are seen in the brackish-SO_4 and brackish marine groundwaters at Olkiluoto and Forsmark respectively. In deeper saline waters at Olkiluoto and Forsmark, Mg^{2+} is generally <60 mg/L except in the most saline waters sampled at Olkiluoto in which Mg^{2+} is 100-135 mg/L.

Ca:Na ratios are generally higher in groundwaters at proposed repository depth at Forsmark than at Olkiluoto. The hydrogeochemical reasons for these differences, apart from the clear link between Littorina water and Mg^{2+}, are not clear; for example, the reasons for different reaction stoichiometries in Ca-Na evolution and for differences in K^+ concentrations are not evident.

Compositions of Rock Matrix Pore Waters in Relation to Fracture Waters

The strong contrast in hydraulic properties between rock mass and transmissive fractures, and the resulting differences and lack of equilibration in hydrochemical compositions, is a recent and striking finding. The implications of this for hydrogeological and hydrochemical interpretation are not yet fully understood. Profiles of pore water Cl^- concentration and stable isotope ratios have been measured for two drillholes at Olkiluoto and for four drillholes at Forsmark. Estimated Cl^- concentrations in pore waters were calculated from results of leaching tests coupled with data for porosity and an estimation of the proportion that is anion-accessible. Pore water Cl^- concentrations at Olkiluoto are systematically more dilute than fracture waters at corresponding depths below about 100 m. The divergence, which appears to be much greater than the potential error on pore water data, increases substantially below about 300 m so that pore waters have brackish salinity whilst fracture waters are saline. For example, Cl^- is about 500 mg/L in pore waters and is about 19,000 mg/L in fracture waters at 600 m depth in borehole KR47. This is a very significant difference that has implications for hydrogeological and hydrochemical modelling of future groundwater conditions. Palaeohydrogeological concepts and modelling that might explain these observations and thus assess the implications for long term evolution have not yet been comprehensively presented by Posiva.

Estimated pore water Cl^- concentrations in boreholes at Forsmark show different patterns for locations in the 'footwall' and 'hanging wall' rock domains with respect to sub-horizontal deformation zone A2. Porewater Cl^- concentrations are generally lower than Cl^- in fracture waters but the contrast is greater and the porewater Cl^- values are lower (<1500 mg/L down to 550 m depth) in the boreholes that are located in the hanging wall domain (KFM02B and 06A upper part) versus boreholes in the footwall domain (KFM01D, 06A lower part and 08C). Water stable isotopic compositions ($^{18}O/^{16}O$) are heavier for pore waters than for fracture waters in the footwall rock domain samples at Forsmark. Isotopic compositions of pore waters in hanging wall rock at Forsmark are similar to those for fracture waters. Isotopic compositions of pore waters and fracture waters at Olkiluoto have so far been found to have a similar relationship.

SKB have inferred that pore waters in the hanging wall rock domain at Forsmark have equilibrated relatively recently with pre-Littorina fracture waters because of a higher frequency of vertical fracturing whereas pore waters in the less fractured footwall domain are much older, i.e. are pre-glacial.

The implications of these findings regarding pore water compositions are that the solute transport and water exchange behaviour of rock at Olkiluoto and in the footwall at Forsmark are quite similar. They also indicate that both systems had long periods of deep circulation, prior to glaciation, of water that was less saline than is presently seen in the fracture system, suggesting that groundwaters in the long-term future could also revert to low salinities. An additional consequence of these relatively dilute pore waters is that they should be taken into account in models of future evolution of hydraulic and hydrochemical conditions.

Isotopic and Dissolved Helium Compositions and Groundwater Ages

Brackish SO_4 rich groundwaters at Olkiluoto have carbon-14 (^{14}C) contents ≤ 50 pmC which is consistent with the dominant Littorina origin attributed to them (Posiva, 2009). Brackish-Cl and saline groundwaters have ^{14}C contents from 5 to 22 pmC.

The content of dissolved helium (^4He) increases generally with depth to >10 mL/L in saline groundwater. This supports the ^{14}C pattern qualitatively but is not interpretable, even semi-quantitatively, in terms of age for the saline water component in the deep mixed groundwaters. 8 analyses of ^{36}Cl data are reported for various groundwater types at Olkiluoto; the $^{36}Cl/Cl$ ratios are all low, $\leq 25 \times 10^{-15}$, and the interpretation with respect to water ages is unclear.

A component of glacial melt water (or other 'cold climate' water) is indicated by the $^{18}O/^{16}O$ ratio which increases with depth from -15 to -9‰ in brackish waters to -13 to -10‰ in saline water at Olkiluoto. The depth to which glacial water penetrated and mixed with deep pre-glacial saline water at Olkiluoto has been the subject of changing interpretation. This issue is tied in to Posiva's concept of 'subglacial initial water' which represents the inferred composition of groundwater in the system prior to the last glaciation. Preliminary modelling assumed that this composition was 3500 mg/L Cl^- and -12‰ $\delta^{18}O$ which in turn indicated 10-20% of glacial water in the brackish-Cl and saline groundwaters. However, this mixing calculation has been revised using slightly more dilute 'subglacial initial water' with 3000 mg/L Cl^- which thus leads to a lower degree of deep penetration of glacial water being modelled. Posiva's conclusion on this and on the related issue of Littorina water mixing is that there are only 'minor' proportions of Littorina and glacial water in the brackish-Cl and saline groundwaters below 300 m depth. The uncertainty on this is relatively large and is evidently dependent on assumptions about the compositions of various end-members. The reasoning and evidence for an assumed subglacial water composition needs to be clear if it is the basis for conclusions about these other aspects of palaeohydrogeology.

Brackish groundwaters between 150 and 500 m depth at Forsmark have ^{14}C contents mostly in the range 5-30 pmC (Laaksoharju et al, 2008). This suggests a range of groundwater ages from post-glacial to older for brackish non-marine waters; post-glacial ages are consistent with the Littorina origin for the bulk of brackish-marine waters. ^{14}C data for brackish-marine groundwaters are supplemented by measurements on dissolved organic carbon (DOC) for three samples

which contain 45-53 pmC, corresponding to contents in TIC of 13-17 pmC. The ^{14}C(DOC) data support the post-glacial age, 5000-6000 y, and Littorina origin for the brackish-marine waters.

Helium (^{4}He) contents of brackish groundwaters at Forsmark are around 1 mL/L whilst those of saline groundwaters are >10 mL/L. These values are comparable with helium contents of saline groundwaters at Olkiluoto.

There is a more complex picture at Forsmark than at Olkiluoto for the distribution of water of glacial or other cold-climate origins. ^{18}O/^{16}O ratios range between -14 and -8‰ δ^{18}O (with one measurement of -16‰ in a brackish-marine water). There is a slight overall tendency towards lighter δ^{18}O values with increasing depth which suggests that glacial water is a component of most or all of the groundwaters and that it penetrated to >500 m depth at Forsmark.

Abundance and composition of colloids and DOC

Water samples have been collected for colloid analyses in the 'groundwater stations' PVA 1 and 5 (at depths of about 20 and 240 m) in the Onkalo tunnel at Olkiluoto (Järvinen et al, 2011). Particle-counting and analyses of filtered colloids indicated concentrations of 0.5 and 0.15 μg/L respectively. Mineral and chemical compositions of these colloids have not been reported. Dissolved organic carbon (DOC) contents of groundwaters at Olkiluoto are reported to be 0-25 mg/L down to 100 m depth, <10 mg/L between 100-300 m (except 1 sample with 40 mg/L), and up to about 20 mg/L (1 sample with 37 mg/L) from 300-800 m (Posiva, 2009). However, it is noted that Posiva casts doubt on the validity of these data, suspecting contamination of samples.

Colloids contents in groundwaters at Forsmark are reported to be in the range 0-160 μg/L, having approx. values 160, 60 and 20 μg/L in 3 samples from depths of 112, 176 and 215 m, and <20 μg/L in saline waters at >600 m depth (Laaksoharju et al, 2008a). Colloidal particle counts are mostly 2-6×10^5 per mL, with higher outlier values in two boreholes. Information about mineral and chemical compositions is contradictory. Analysis of filtered/fractionated particles indicates Fe and S compounds, whilst LIBD/EDX analysis indicates Al, Si and Fe compounds. Therefore, some colloids concentrations at Forsmark are much higher than in the two samplings done at Olkiluoto. However, it is possible that this is attributable to the greater difficulty in obtaining representative samples for in-situ colloids from surface-based boreholes than from seepages into short boreholes underground in Onkalo.

DOC concentrations in Forsmark groundwaters are reported to be between 5 and 15 mg/L in shallow groundwaters (0-100 m depth; 1 outlier sample with 35 mg/L) and <5 mg/L from 100-1000 m (2 outlier samples with 10 and 15 mg/L). These ranges of DOC at Forsmark are fairly similar to those at Olkiluoto. The evidence suggests that, at both sites, DOC is not contributing to formation of colloids.

7.4 Groundwater end-members, palaeohydrogeology and mixing

Water types at Olkiluoto change from Ca-Na-HCO$_3$-SO$_4$ and Ca-Na-HCO$_3$ in shallow dilute groundwaters, to Na-(Ca)-Cl-(SO$_4$) in brackish-SO$_4$ waters, to Na-Ca-Cl and Ca-Na-Cl in the deep brackish-Cl and saline groundwaters (Posiva, 2009). Water types at Forsmark change from Na-(Ca)-HCO$_3$-(SO$_4$) in shallow fresh groundwaters, to Na-Ca-Mg-Cl-SO$_4$ in brackish marine waters to Ca-Na-Cl in brackish non-marine and saline waters. The overall pattern of water types is therefore similar to that at Olkiluoto.

Mixing of different end-member component waters with distinct origins at Olkiluoto has been interpreted by Posiva using a mass-balance and mixing-reaction inverse modelling method which attempts to consider non-conservative solute changes due to water-rock reaction as well as mixing of conservative solutes. Posiva have used five reference waters: meteoric, Littorina, glacial, subglacial and saline (Pitkänen et al, 2003). The 'meteoric' reference water dominates down to about 150 m depth, below which substantial proportions of 'subglacial' and 'Littorina' are mixed down to about 300 m. 'Subglacial' dominates from about 200 m to 600 m depth, below which 'saline' dominates. It is commented in the previous section that the significance and reality of the 'subglacial' end member is arguable and using it in mixing modelling may obscure the presence of glacial-origin and deep-saline waters.

Br/Cl ratios in groundwaters at Olkiluoto tend to increase with depth, from 0.002-0.005 in brackish-SO$_4$ waters, to 0.004-0.007 in brackish-Cl waters and 0.006-0.0085 in saline waters (Posiva, 2009). This pattern is consistent with the marine origin of salinity in brackish-SO$_4$ waters evolving towards a non-marine origin for salinity in deep bedrock groundwaters in which Br/Cl ratio has increased due to water-rock reaction. Br/Cl ratios in pore waters at Olkiluoto tend to mirror this pattern in fracture waters.

Mixing of end-member water components at Forsmark has been interpreted by SKB on the basis of a conceptual model for post-glacial groundwater evolution and statistical analysis of water chemical and isotopic compositions and, unlike the method used for Olkiluoto data, has not quantitatively taken account of geochemical reactions in the model. The principal components analysis (PCA) tool 'M3' has been used by SKB; this method is influenced most strongly by compositions of conservative solutes and water isotopes whilst solutes affected by water-rock reactions have a secondary effect on the PCA analysis and cannot be resolved in terms of explicit reactions and mass transfers.

Preliminary modelling with M3 was done with three different sets of end-member waters; the preferred set of end members used for the final analyses comprises: altered meteoric, Littorina, glacial, and deep saline (Laaksoharju et al, 2008b). The basic premise of the mixing modelling and analysis of end-member proportions

for Forsmark is therefore rather different from that for Olkiluoto. The resulting end-member proportions for Forsmark groundwaters are: (i) altered meteoric decreasing with depth from 95% maximum in shallow groundwaters to <10% at >500 m; (ii) Littorina decreasing with depth from 55% maximum to <10%; (iii) glacial (+old meteoric) increasing with depth from 10% to 70%; (iv) deep saline between 10-30% in saline groundwaters.

As at Olkiluoto, Br/Cl increases with depth at Forsmark from 0.003-0.005 in brackish-marine waters to 0.008-0.014 in brackish-saline non-marine waters. The brackish-marine Br/Cl ratios are similar to those at Olkiluoto, as expected, but the non-marine brackish and saline waters have rather higher Br/Cl ratios suggesting that a greater degree of water-rock reaction has enhanced Br in the deeper groundwaters at Forsmark.

Table 8. Comparison of hydrogeochemical characteristics of sites (Table 5.2 in Geier et al. 2012).

Property	Olkiluoto	Forsmark	Implications
Distribution and sources of salinity	Maximum salinity down to ca1000m: 84000 mg/L TDS, ca 52000 mg/L Cl; more homogeneous distribution and trend versus depth.	Maximum salinity down to ca1000m (central/northwest sectors): 17000/24000 mg/L TDS, 10000/15000 mg/L Cl; more heterogeneous distribution according to fracture domains and sectors.	Up-coning from below a repository at Olkiluoto would pose a greater hazard to the EBS (i.e. buffer swelling pressure, corrosion rate) than at Forsmark due to the proximity of significantly higher salinity and the uncertainty for salinity at >1000m
	Brackish-SO_4 water at 100-300m ($\leq$5000 mg/L Cl^-, 30-250 mg/L Mg^{2+}, $\leq$580 mg/L SO_4^{2-})	Brackish-marine water at 60-600m (<6000 mg/L Cl^-, 10-250 mg/L Mg^{2+}, $\leq$550 mg/L SO_4^{2-})	Deeper Littorina penetration at Forsmark suggests higher vertical connectivity
	Brackish-Cl water at 300-450m ($\leq$7000 mg/L Cl^-, $\leq$80 mg/L Mg^{2+}, <100 mg/L SO_4^{2-})	Brackish non-marine water at >350m (>5000 mg/L Cl^-, 10-80 mg/L Mg^{2+}, $\leq$200 mg/L SO_4^{2-})	Generally similar hydrochemistry at proposed repository depths for both sites; also transition to less conductive system
	Saline water at >450m (6000-45000 mg/L Cl^-, 0-130 mg/L Mg^{2+}, <10 mg/L SO_4^{2-})	Saline water at >500m (6000-15000 mg/L Cl^-, 0-20 mg/L Mg^{2+}, 20-150 mg/L SO_4^{2-})	The salinity gradient is steeper below proposed repository depth at Olkiluoto
	Interpreted mixing model end-members are: meteoric, Littorina, glacial, 'subglacial', saline	Interpreted mixing model end-members are: altered meteoric, Littorina, glacial, deep saline	Different end-members so mixing models are not comparable. Large uncertainties in water proportions propagate into palaeo-hydrogeological models
	Br/Cl increases with depth: 0.002-0.005 in brackish-SO_4, 0.004-0.007 in brackish-Cl, 0.006-0.0085 in saline water	Br/Cl increase with depth: 0.003-0.005 in brackish-marine, 0.008-0.014 in brackish non-marine	Similarities confirm Littorina water source for brackish waters at both sites; higher Br/Cl characterizes deep saline waters
Post-glacial palaeo-hydrogeology	Maximum Littorina salinity 5600 mg/L Cl^-	Maximum Littorina salinity 8400 mg/L	Unclear whether this difference is real or an interpretation artefact
	Sub-aerial emergence at 3000-2500 y ago	Sub-aerial emergence at 2500 y ago	Similar periods of meteoric water infiltration
	'Minor proportions' only of Littorina and glacial waters at >300m	Littorina penetrated to $\leq$600m; glacial water to >500m	Suggests that Forsmark has higher vertical conductivity from surface, but these interpretations have large uncertainties

Property	Olkiluoto	Forsmark	Implications
Redox and bioge-ochemistry	Eh +100 to -400 mV	Eh -143 to -281 mV	Inferred absence of dissolved oxygen at both sites; redox control and buffering for Olkiluoto are poorly characterized
	HS^- <1 mg/L at <250m & >350m, 0-12 mg/L at 250-350m	HS^- mostly <0.1 mg/L at 50-1000m except for 5 samples 0.2-1.6 mg/L	Corrodant HS^- concentrations are generally low at proposed repository depths at both sites, but there are spot anomalies at both sites that are not explained
	Fe^{2+} mostly 0-1 mg/L at >100m	Fe^{2+} mostly <3 mg/L at <300m, <2.5 mg/L at >300m	Additional evidence for uniformly reducing conditions
	CH_4 <10 mL/L at <300m, then increases with depth to ~1000 mL/L at 1000m	CH_4 mostly <0.10 mL/L	Large difference; source of much higher CH_4 at Olkiluoto is not known, nor is possible magnitude of future changes
	H_2 increases with depth from µL/L to mL/L magnitudes	H_2 below detection (3 µL/L) to 370 µL/L	Slightly higher H_2 at Olkiluoto but may be sampling artefact
	DOC ≤20 mg/L at >300m (contaminated?)	DOC mostly <5 mg/L at >100m	Similar low levels of dissolved organics at both sites, i.e. low significance for radionuclide speciation
	Microbial TNC 10^4-10^5 cells/mL at >100m; MPNs for all groups peaks at 250-350m; acetogens are dominant group	Microbial TNC 10^4-10^6 cells/mL; MPNs show no pattern; acetogens are dominant group, methanogens are very sparse; MPN for SRB are possibly correlated with Eh	Similar microbial data for both sites, but uncertain how representative data are. Biogeochemical model and implications for redox remain unclear
pH and dissolved inorganic carbon	pH 7 to 7.5 in brackish-HCO_3 water, ≤7.5 in brackish-SO_4, ≤8.2 in brackish-Cl, decreasing 8 to 7.5 in saline water as TDS increases	pH 7.3 to 8.2 in brackish marine water, 7.0 to 8.5 in brackish non-marine and saline water	Similar for both sites. pH variation is well within safety function requirement. Buffering in both cases is primarily due to calcite
	HCO_3^- inversely correlated with salinity; <2 meq/L in brackish-SO_4 water, <1 meq/L in brackish-Cl and saline water	HCO_3^- inversely correlated with salinity; <3 meq/L in brackish marine water, <1 meq/L in brackish non-marine and saline water	Similar values, consistent with the pH buffering model
	P_{CO2} decreases with depth from 10^2 to $10^{-4.5}$ atm	P_{CO2} decreases from 10^{-3} to 10^{-5} atm in footwall, from 10^{-2} to 10^{-4} in hanging wall	As above

Property	Olkiluoto	Forsmark	Implications
Cations hydro-chemistry	Increasing vs depth to max at 1000m: Na^+ ~10000 mg/L, Ca^{2+} ~18000 mg/L, Sr^{2+} ~190 mg/L	Increasing vs depth to max at 1000m: Na^+ ~2200 mg/L, Ca^{2+} ~4000 mg/L (>4000 mg/L in northern sector), Sr^{2+} ~70 mg/L	Na versus Ca, Mg and K differences indicate that hydrogeochemical evolution models for the two sites are slightly different; neither SDM has a full model for aluminosilicate reactions and cation exchange
	Mg^{2+} reaches maximum 250-300 mg/L in brackish-SO_4 water, generally <60 mg/L in saline water except 100-130 mg/L in deepestmost saline water	Mg^{2+} reaches max 250-300 mg/L in brackish-marine water, 10-80 mg/L in brackish non-marine decreasing to <20 mg/L in saline water	
	K^+ varying vs depth with max ~29 mg/L at 1000m	K^+ 5-68 mg/L at <100m, varying vs depth decreasing to ~10 mg/L at 1000m	
Pore waters	Cl^- 500 mg/L at 600m (KR47) vs 19000 mg/L in fracture water	Cl^- hanging wall domain: 3000 mg/L at 450m, 1000 mg/L at 550m vs 5500 mg/L in fracture water; footwall domain: <4000 mg/L to 600m vs 7000 mg/L in fracture water, <11500 mg/L to 850m (except peak of 15000 mg/L at 650m)	Dilute pore waters have hydraulic and hydrochemical effects on future groundwater evolution. Pore water chloride and water isotopic compositions have been included in palaeohydrogeological model for Forsmark but not yet for Olkiluoto
	$\delta^{18}O$ lighter than $\delta^{18}O$ of fracture waters at ≤100m; heavier than $\delta^{18}O$ of fracture waters at >300m	$\delta^{18}O$ heavier than $\delta^{18}O$ of fracture waters in footwall domain; $\delta^{18}O$ are similar in hanging wall domain	
Water ages	^{14}C ≤50 pmC in brackish-SO_4 water, 5-22 pmC in brackish-Cl and saline waters	^{14}C 5-30 pmC in brackish waters between 150-500m; ^{14}C(DOC) 45-53 pmC in brackish-marine waters	Consistent with Littorina source for brackish water at both sites. Deeper water ages cannot be resolved quantitatively due to mixing
	$\delta^{18}O$ -15 to -9‰ in brackish waters, -13 to -10‰ in saline waters	$\delta^{18}O$ -14 to -8‰ in brackish waters (except one sample at -16‰ in brackish marine), decreasing slightly vs depth to >500m	Additional evidence for complicated water mixing and palaeohydrogeology at both sites
	^4He increases generally to >10 mL/L in saline water	^4He increases from 1 to >10 mL/L from brackish to saline waters	Similar for both sites, but cannot be quantitatively interpreted
Colloids	0.15 and 0.5 µg/L by two methods	0-160 µg/L (lower values at >600m); $2-6 \times 10^5$ particles/mL	Data for the two sites are probably not comparable because of different sampling sources

8 Suggested Objectives of Future Geochemical Data Acquisition

8.1 Current position regarding geochemical data utilisation

Original objectives for using geochemical data and the associated data requirements at the outset of site characterisations at Simpevarp/Laxemar and Forsmark were straightforward and clearly documented. The ways that data have been used, requiring data processing, interpretative modelling and/or innovative methods of integration with a groundwater flow and transport model, have been less straightforward. The extent and reliability of available data raises issues of whether sources of uncertainties have been identified, and the complexities of the data processing methods and of the integration methods, e.g. using statistical proportions of hypothetical reference waters as the metrics for calibrating and confirming the flow-transport model, raises further questions about the degree of understanding of transient processes that will influence future evolution of the groundwater system.

Geochemical characterisation of the candidate siting areas has involved sampling, interpretation and modelling techniques that are state-of-the-art for investigating fractured crystalline rock. Data from the surface-based investigations that have been selected, approved and used by SKB in SDM-Forsmark and SR-Site are considered to be representative of in situ geochemical conditions with a reasonable degree of confidence.

8.2 General objectives of geochemistry in underground investigations

Underground investigations are an opportunity to build confidence in quality of samples and data and in knowledge of spatial variability of key hydrochemical parameters specifically in the target rock volume for a repository at Forsmark. It is recommended that SKB assess further the significance of existing data in the context of safety functions and safety assessment. That would help to set priorities for additional sampling, analyses, data processing and modelling.

Further research is suggested to develop and confirm the methods for using hydrochemical data in two of the key modelling components of SR-Site. These components of SR-Site are the use of hydrochemical and isotopic data to support and calibrate the groundwater flow and solute transport model, and the interpretation

of hydrogeochemical processes that will control the evolution of key chemical parameters of groundwater around the repository over the safety assessment timescale. Underground investigations would contribute substantially to research in these areas.

8.3 Additional geochemical data acquisition for confirmation of safety function indicators and understanding of processes

Specific tasks of geochemical data acquisition are suggested from this review. They would be carried out in underground investigations, by monitoring in deep boreholes, and as in situ or laboratory experiments. Interpretation and modelling of the enhanced data should be aimed at improving confidence in the values of safety function indicator criteria and in understanding of the geochemical processes that will control how the repository system will evolve.

Features and processes controlling the composition of water entering the EBS

It is suggested that the uncertainties in the chemistry of water resaturating bentonite buffer could be addressed further by additional research and measurements:

- Carry out model calculations of the transfer of water between intact rock matrix and compacted bentonite buffer at a deposition hole periphery;
- Develop a programme of experiments and geochemical model simulations to understand better the constraints on and possible ranges of rock matrix porewater chemistry, including redox conditions, cation compositions, anion exclusion;
- Study solute fractionations during capillary transfer of solution between rock matrix and buffer;
- Carry out, underground and/or in the laboratory, pilot experiments to study directly the water transfer across the interface of saturated rock and unsaturated compacted bentonite.

Statistical analysis of groundwater compositions and identity of reference waters

Statistical analysis of groundwater compositions and the identification of reference waters has been a substantial basis for calibration of the groundwater flow and solute transport model in SR-Site. Further studies would aim to improve the methodology, validate the method and understand better how uncertainties are propagated into transport model calibration.

- Update identities of reference waters and selection of end-member water compositions, i.e. deep saline, saline, glacial and old/recent meteoric waters, plus possibility of others, by new hydrochemical interpretations of high-quality groundwater samples from pilot holes and other drillholes and short boreholes drilled from tunnels at repository depth.
- Focus attention on justification for saline end members, i.e. components of saline and very saline groundwaters at and below repository depth, Littorina seawater, also on composition of glacial (cold climate) end-member water.
- Re-analyse SR-Site water data using alternative end-member and reference water compositions; assess implication of assumption that reference water compositions are invariant over time.

Calibration of groundwater flow and solute transport model

The hydrogeochemical model requires further development and calibration to produce a reasonably good simulation of the time-dependent transport, dispersive mixing and geochemical processes controlling the evolution of groundwater solutes.

- Make additional flow-mixing model calculations of groundwater compositions at repository depth and compare with measured data; re-calibrate the groundwater flow-transport model with new interpolations of spatial variations of water compositions and end-member mixing at repository depth in relation to deformation zones and structural units.
- Design and implement strategy for intensive monitoring of groundwater inflow compositions, flow rates and pressures during drawdown due to excavation; use approach and methodology developed in Task 5 of Äspö Groundwater Modelling Taskforce for integrating hydrogeological and hydrochemical data (Svensson et al. 2002; Bath & Jackson 2002; Rhén & Smellie 2003).
- Carry out time-series sampling for ^{3}H, ^{85}Kr, ^{14}C, ^{4}He, ^{36}Cl(?), plus CFCs, SF_6 for detection of young meteoric groundwater breakthrough and groundwater age interpretation using lumped parameter modelling.

Additional data for rock matrix porewater compositions in relation to fracture waters

There are various open questions concerning extraction and data processing methods for compositions of porewater in the intact rock matrix. Interpretations of data and spatial variations in relation to fracture water compositions have presented a number of interpretative uncertainties that have implications for palaeohydrogeology and future solute transport processes.

- Underground investigations offer the opportunity to take drillcores from pilot drillholes and short purpose-drilled boreholes from tunnels with varying orientations and known spatial relationships with respect to transmissive fractures.
- Additional studies are required to characterise the rock matrix porosity to understand the proportion that is connected and thus open to diffusive solute exchange with advective solutes, and also the proportion that is accounted for by microfracturing.
- Further studies could be carried out to study artefacts and other biases in porewater extractions that affect uncertainties in whether data are representative of in situ porewater compositions.
- Patterns of porewater compositions in relation to adjacent fracture water compositions can be studied to provide new knowledge of matrix diffusion and palaeohydro-geological significance.
- Make in situ measurements and carry out hydrogeochemical modelling to infer the in situ redox, pH, HS^-, Fe^{2+}, etc compositions for rock matrix pore waters and the overall buffering capacity of rock matrix.

Development of hydrogeochemistry model

A biogeochemical model of redox processes could be further developed and calibrated with monitoring data and in situ experiments during a construction phase. The model would interpret and simulate redox buffering, sources of redox-active solutes and of electron donors that maintain redox conditions at repository depth stable (or otherwise) in the long term. It would need data for redox-active solutes including concentrations, fluxes and sources of gases and organic C. Additionally, microorganism numbers and activity, along with the trace chemical concentrations that influence microbial activity, would be used in a biogeochemical model.

- Intensive mineralogical and petrographic characterisation of rock at repository depth to identify all potential components of water-rock reactions and to quantify rock buffering of redox, pH, HS^-, Fe^{2+}, also to characterise cation exchange capacity and exchangeable cations.
- Further develop the hydrogeochemical model with intensive data for groundwater compositions and time series changes due to perturbations of drawdown and changing hydraulic conditions, plus comprehensive suite of minerals and reactions; confirm buffering models for redox, pH and proportions of cations M^{2+}/M^+.
- Model forecasting over longer timescales of how the system might evolve through an extended period of groundwater dilution as well as through different climate scenarios. So far, qualitative lines of argument have been mostly used for timescales beyond 10,000 years.

- Monitor pH, Eh, Fe^{2+}, HS^- in underground niches and boreholes, plus microbiological sampling and analyses, plus DOC, CH_4, H_2 and other electron donor energy sources for microorganisms; characterisation of DOC and study of sources of electron donors.

- Establish inventory and release of Fe^{2+} and sulphide from rocks at repository depth.

- Studies to explain or rectify the apparent inconsistency between the iron oxyhydroxide distribution and the modelled consumption of DO. This may indicate the need for modifications in the interpretative model for redox, dissolved Fe, iron mineralisation, and attenuation of DO.

- Additional monitoring should be carried out in relevant boreholes and in seepages to tunnels during excavation, to test whether the enhanced infiltration due to hydraulic drawdown is accompanied by DO drawdown.

- Monitor trace elements of relevant analogue interest, i.e. U, Ra, I, Cs, etc and interpret the mineral sources and transport/immobilisation processes by modelling of water-rock reactions and rock matrix diffusion.

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2018:15

The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 300 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.