


Review Article

Methodology for Hydrogeochemical Sampling to Characterise Groundwaters in Crystalline Bedrock: Developments Made within the Swedish Radwaste Programme

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The search by SKB (Swedish Nuclear Fuel and Waste Management Co.) for a site to locate the deep geological repository for spent nuclear fuel in Sweden has involved geoscientific investigations at several locations since the 1970s. The objectives were to characterise geologically a bedrock volume as well as its hydrogeology and hydrochemistry. To acquire high-quality hydrogeochemical data, a complete system for groundwater sampling and analysis, as well as for interpretation strategies, has been developed through a continuous process of modification and refinement. Since the largest part of the Swedish bedrock is composed of granitoids, the site investigations had to adapt to the special difficulties of fractured crystalline rocks. This paper discusses the problems with groundwater sampling that are specific to fractured crystalline rocks and describes the solutions adopted and methods developed by SKB since the early 2000s during the site investigations. The methodology described in this paper for the characterisation of deep groundwaters in crystalline rocks is not only applicable in the context of radioactive waste disposal but also useful when sampling groundwaters for any purpose in such rocks. Sampling of groundwaters in fractured rocks at depth, often down to approximately 1,000 m, involves special challenges since the natural conditions of the groundwater are easily disturbed, especially by the initial drilling, but also by every subsequent activity performed in the borehole, including the actual groundwater sampling. The sampling strategy presented in this paper shows that planning of the sampling preferably starts already when the drilling procedure is decided. Each following step is described in detail and includes tracing the drilling fluid, selecting the best borehole sections to sample, procedures for the actual sampling, and selection of analytical protocol; all this with the goal of taking representative samples. Although the evaluation of the sampling uncertainties is not a straightforward procedure, an adequate categorisation routine has been established to classify groundwater samples regarding sample quality, representativeness, and suitability for further interpretations and modelling.

1. Introduction

The need for reliable groundwater sampling procedures has been recognised for years. The United States Geological Sur-

vey was one of the first institutions to publish rigorous sampling and analytical protocols and procedures [1–3]. Since then, and together with the United States Environmental Protection Agency, more detailed manuals of sampling

procedures, devices, techniques, etc. in different host rocks have been reported in various publications by these two organisations [4–15]. Along similar lines, other countries such as Australia and South Africa have recently published guidelines for groundwater sampling [16–20]. Nevertheless, the hydrogeochemical characterisation of groundwaters remains a challenging task [21–23].

In crystalline rocks, where groundwater flow is dependent on the fracture systems, the heterogeneous hydrogeological conditions imposed by the fractures and fracture zones result in a very inhomogeneous distribution of groundwater compositions. Therefore, in these environments, in addition to the usual groundwater sampling problems, it is necessary to monitor simultaneously the hydraulic pressure during sampling, in order to establish unambiguously that the groundwater sample represents the fractures intersecting the sealed-off borehole section [9]. In this way, the samples from boreholes drilled into intact rock will represent undisturbed conditions while sampling in boreholes close to a tunnel should give information on the disturbed system (often influenced by drawdown and/or artificial mixing).

In Sweden and Finland, deep geological disposal of spent nuclear fuel is being planned in fractured rock at approximately 400 to 500 m depth [24–28]. The planning for this type of repositories requires the characterisation of groundwaters in sparsely fractured rocks to depths down to ~1,000 m [29]. The aim of this paper is to provide insights in the difficulties of groundwater characterisation for such systems, and the solutions adopted within the site characterisation program conducted by the Swedish Nuclear Fuel and Waste Management Co. (SKB). The present paper therefore fills in the gap between technically detailed reports from SKB (available at <http://www.skb.com/publications>) and the peer-reviewed publications in the open literature, which concentrate on interpretation and modelling aspects, for example, [30–43]. This paper also is aimed at providing an overall picture of those aspects of geoscientific site investigations that have implications on the quality and the performance of the hydrogeochemical studies in fractured crystalline bedrocks, e.g., drilling technique and execution and investigation sequence.

One must emphasise that the techniques described here-with are the result of large efforts during a relatively long period of time (since the middle of the 1970s) by several organisations dedicated to the disposal of radioactive wastes around the globe. It is not the purpose of this paper to provide a detailed historical account of the developments in the field of groundwater characterisation in fractured rocks; however, the interested reader may find a short account in the Supplementary Material 1.

2. Investigations in Boreholes: Effects on the Representativity of Groundwater Samples

2.1. The Sequence of Borehole Drilling and Investigations. Investigations in deep groundwater systems imply borehole drilling followed by logging and sampling activities which, in fractured crystalline rocks, normally result in the mixing of groundwaters from different depths. As a consequence,

this can cause a variety of physical processes and chemical reactions that impact the representativity of the water samples.

To avoid disturbances in the system and to obtain as much useful information as possible, drilling and borehole investigations have to be carefully planned to follow a systematic sequence of proven strategies. A close cooperation among different disciplines is also needed during the planning and execution of the field work (and subsequent interpretations). A general investigation sequence is shown in Figure 1.

2.2. The Drilling. Drilling is one of the most important activities within the scope of site investigations for a deep repository, and its performance is of particular importance in order to achieve high-quality groundwater samples and representative measurements from the boreholes. The boreholes can be either percussion drilled or core drilled.

Percussion drilling is the faster and cheaper technique used to supplement and increase the number of sampling locations as well as to provide boreholes with diameters between 200 and 250 mm. The technique is restricted to relatively short boreholes in the range of 50 to 300 m. No flushing water is used for the drilling, and no drill cores are obtained since the rock is crushed.

Core drilling is used for deeper boreholes down to around 1,000 m depth or when information from a drill core is required for specific studies like mapping and sampling of fractures, of rock types, and of fracture infills. In the case of the site investigations performed by SKB, flushing water without recirculation is used to cool the drill bit and no-drill mud or lubricants are used to avoid unnecessary contamination. After the late 1980s, most core boreholes drilled by SKB from the ground surface are of the so-called telescopic type: the first 100 m correspond to a wider percussion-drilled borehole, followed by a core-drilled hole with a smaller diameter (76–77 mm). This technique was developed specifically for hydrochemical investigations. It allows efficient gas-lift pumping from the upper percussion-drilled part of the borehole during and after core drilling. This pumping decreases the amount of flushing water and of drilling debris which, otherwise, would be forced into conductive bedrock fractures by the high pressure prevailing during drilling. This type of borehole also allows the installation of standpipes to facilitate groundwater head measurements and sampling during the following long-term hydrochemical monitoring phase (Section 3.3).

In the case of boreholes drilled from tunnels, the conventional core or percussion drilling techniques are used. The telescopic design is not necessary since there is no need for standpipes or pumping during groundwater sampling. The water from the borehole is discharged during drilling and sampling due to the difference between the pressure in the bedrock and the atmospheric pressure in the tunnel.

Different equipment and investigation methods are in general required for the different borehole types, and they will be indicated in the corresponding sections of this paper. The most extensive hydrochemical investigations are performed in telescopic core boreholes, and their drilling protocol includes the following:

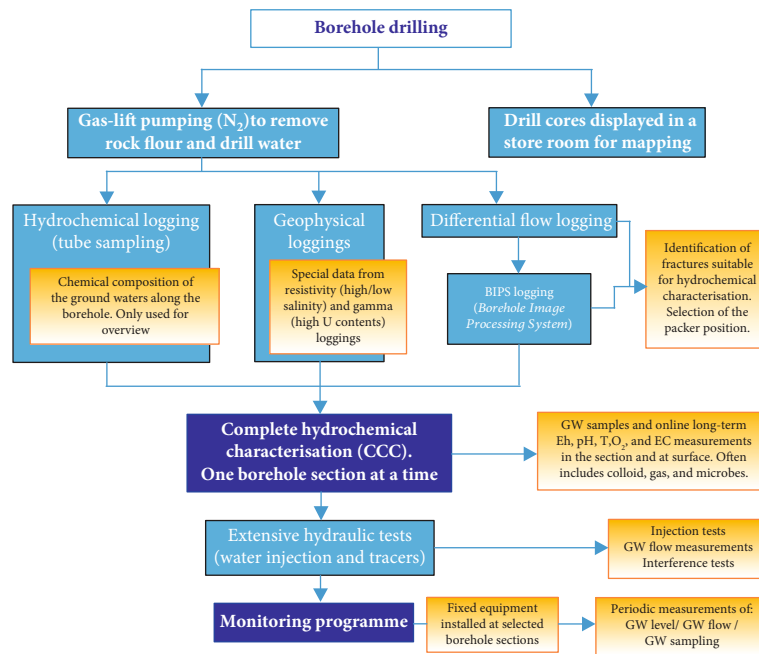


FIGURE 1: Schematic overview of a general investigation sequence in a telescopic core-drilled borehole designed for chemical characterisation. The most important hydrochemical sampling methods (Complete Chemical Characterisation, i.e., CCC, and monitoring) are shown in boxes with a darker blue colour and text in bold. GW: groundwaters; Eh: redox potential; T: temperature; EC: electrical conductivity. A more detailed description can be found in Supplementary Material 2.

- (i) The flushing water is spiked with a tracer (e.g., sodium fluorescein), and it is discharged as return water (i.e., a mixture of flushing water, formation groundwater, and drill cuttings) by gas-lift pumping during drilling. Due to contamination risks, the selection of the flushing water source and the possible impact of the flushing water on the groundwater composition are important issues that are discussed in more detail in Supplementary Material 2.
- (ii) The downhole drilling equipment and the flushing water system require a strict routine of cleanliness (more details can be found in Supplementary Material 2).
- (iii) The percussion drilled part of a telescopic borehole is cased, and the gap between the borehole wall rock and the casing is grouted with cement to prevent groundwater inflow from the upper part to the lower core-drilled borehole part during drilling.
- (iv) Grooves are milled into the borehole wall at certain intervals for length calibration to ensure reliable depth readings.
- (v) The use of a triple tube system is indispensable for preserving the fracture infillings (in the extracted drill cores) whose study, among other things, will facilitate the correlation of transmissive fractures with the flow log and the BIPS (Borehole Image Processing System, cf. Section 2.3.2).

2.3. Sampling Conditions: When, Where, and How

2.3.1. *When to Sample.* The time delay between drilling and chemical sampling is an important factor affecting the representativity of groundwater samples. Sampling close in time to the completion of the borehole may result in groundwater samples still impacted from the drilling, i.e., flushing water and groundwaters from different depths, introduced by the pressure impact during drilling. However, the problem could be even more serious if a borehole is kept open for some time without packers installed between the different hydraulically conductive fractures. In an inflow area, large volumes of shallow water are likely to intrude from fractures in the upper part of the borehole down to greater depths and mix with deeper groundwaters, and microbial activity and sulfide production could be promoted [44, 45], which drastically decreases the representativity of the groundwater samples.

For similar reasons, groundwater sampling should be avoided when activities such as drilling or hydraulic tests are ongoing in the vicinity of the borehole.

2.3.2. *Where to Sample: Selection of the Borehole Sections.* The main criteria for the selection of the borehole sections are (1) presence of one or more fractures with a suitable hydraulic transmissivity, (2) appropriate borehole wall conditions (less fractured rock) that allow isolation of the section by inflatable packers, and (3) favourable distribution of the water yielding fractures in the isolated borehole section to facilitate the removal of water in the section prior to sampling (Figure 2).

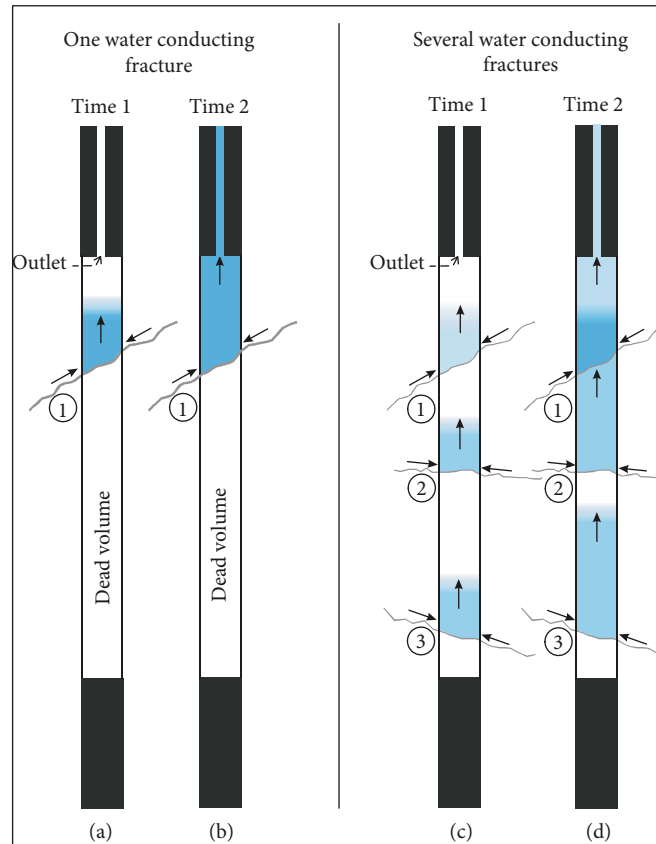


FIGURE 2: Schematic drawing of two different situations of the water yielding fractures in an isolated borehole section (modified from [49]). The blue colour intensity illustrates the amount of formation groundwater in the borehole section during pumping. The presence of a single water-bearing fracture in the upper part of the borehole section, close to the outlet of the section (fracture ^① in (a) and (b), on the left part of the figure), is a favourable situation since the rest of the water volume beneath the fracture will stay trapped, regardless of the removed amount of water from the borehole section (i.e., the lower part of the isolated section is a dead volume). Figure (a) illustrates the moment shortly after pumping starts (time 1) when the water from the only fracture has not reached the outlet yet. Figure (b) shows that after a while (time 2) all the water leaving the section is formation groundwater. If there are several fractures in the section ((c) and (d) in the right part of the figure), the section water between the fractures will contribute to the sample until the formation groundwater from the deepest fracture reaches the outlet: shortly after pump starts (c), no formation water has reached the outlet yet; after a certain time (time 2 in (d)), formation groundwater from fracture ^① has reached the outlet and formation groundwater from fracture ^② has passed fracture ^①; however, formation groundwater from fracture ^③ has not yet reached fracture ^② and the section water between fractures ^② and ^③ will still contribute to the sample. In this last case, the water volume that should be extracted prior to collecting a representative sample of the isolated borehole section may become unrealistically long.

The selection of water yielding fractures and the isolation of the borehole sections are based on the information provided by the flow logging [46, 47] and the BIPS [48]. In core-drilled boreholes, the differential flow logging method is especially useful. This method gives better information on the location of the water yielding fractures than other methods, and it also helps to estimate the groundwater volumes to be extracted prior to sampling. The BIPS logging is helpful to locate suitable packer positions and to identify each water-yielding fracture.

Borehole sections including fractures with moderate hydraulic transmissivities (around $10^{-7} - 10^{-8} \text{ m}^2 \text{ s}^{-1}$) or isolated borehole sections close to the bottom of the borehole are preferred from a practical point of view. In both cases, the amount of flushing water and/or water from other parts of the borehole, intruded into the fractures

during drilling, will be less either because of the low transmissivity or because the drill bit has stayed a shorter time in the lower part of the borehole. This lower amount of drilling fluid in the fractures will shorten the time needed for purging prior to sampling. Hydraulic transmissivities lower than $10^{-8} \text{ m}^2 \text{ s}^{-1}$ require special equipment and sampling methods, cf. Section 3.2.

Once the water yielding fracture(s) have been selected, the next important step is to optimise the position of the packers: (1) in order to decrease the required volume of water (Figure 2) to be exchanged prior to sampling and (2) to obtain a fully isolated borehole section without short circuits between the section and the borehole water above and/or below the section. The latter can be checked by observing the pressure responses in other parts of the borehole during pumping.

2.3.3. *How to Create Adequate Sampling Conditions.* Essential for the sampling procedure is (1) the evaluation of the contribution of flushing water from the drilling, (2) the adequate exchange of water from the borehole sections prior to sampling, and (3) the check of pressure responses in other parts of the borehole (or other boreholes in the vicinity) to exclude short-circuiting effects. Well-documented sampling conditions considering these aspects are important to facilitate the data evaluation during later stages of the site investigation.

The discharge of water prior to sampling is necessary to remove (1) the drilling debris and the remains of flushing water from the drilling and (2) the water initially present in the borehole section (section water). With respect to the flushing water, the calculation of its contribution requires a good homogeneous mixing of the tracer dye in the drilling fluid and frequent analyses of the tracer. The limit for the flushing water content for the best quality data in the SKB site investigations has been set to 2%; however, up to 10% may be considered acceptable if the groundwater data for such samples are used with care. The main problem associated with this task is the often long time needed to reach low enough flushing water content in the samples. With respect to the section water, its removal is needed to exchange the initial mixture of waters present in the borehole section. This water mixture may originate from different fractures at varying depths along the borehole, and in the case of monitored sections, the water may be affected by the stagnant conditions of the isolated section (e.g., microbial activity and corrosion, Section 3.3). The general recommendation to remove approximately five volumes of the sampled section [50] may be valid in the case of porous media but not for crystalline bedrock where the required purged volume is often larger. Individual discharge volumes for each section are calculated using plug flow estimations. These calculations consider the number of water yielding fractures, their hydraulic transmissivity, and their location in the isolated borehole section (Figure 2), and at least two plug flow volumes are discharged to compensate for the unknown contribution from laminar flow.

Finally, three ways to secure adequate sampling conditions are (1) checking the absence of pressure responses in other parts of the sampled borehole or adjacent boreholes, (2) estimation of the sampling-day hydraulic transmissivity (based on flow rate and pressure measurement during sampling) which can be compared with the hydraulic transmissivity values obtained from differential flow logging, and (3) collection of sample series of minimum three samples (if possible) to check their hydrochemical behaviour with time.

3. The Hydrogeochemical Sampling Methods

3.1. *Available Methods.* The hydrogeochemical investigations conducted by SKB involve groundwater sampling and measurements and analyses of different parameters (chemical and isotopic composition, electrical conductivity, Eh and pH, colloids, dissolved gas, and microbes). Some special topics such as matrix pore water, fracture mineralogy, microbes and gases, and new methods for detailed studies on isotopic

zoning in minerals, that require other types of sampling and treatment, have been described thoroughly elsewhere [30–41]. Archive samples are collected for back-up in case of failures or possible later need of additional analyses/constituents. Different groundwater sampling methods have been used for different purposes as summarised below.

- (i) Hydrochemical logging (tube sampling) with the purpose of obtaining the composition of the groundwater present along the borehole. A tube consisting of connected 50 m long tube sections is used for the sampling, and each 50 m section constitutes one sample. This type of sampling provides only an approximate characterisation of the depth dependency of the geochemical characteristics of the groundwaters.
- (ii) Comprehensive groundwater characterisation (also known as *Complete Chemical Characterisation*, CCC) is the premium type of sampling carried out on carefully selected transmissive structures in core boreholes based on flow and core logging (Section 2.3.2). A special sampling unit can be combined with parts of the equipment for CCC for the sampling of low transmissive fractures ($T < 10^{-8} \text{ m}^2 \text{ s}^{-1}$; Section 3.2).
- (iii) Long-term hydrochemical monitoring in core and percussion boreholes to study the evolution of the groundwater composition over time (several years; Section 3.3).

The data obtained with the tube sampling method are mainly used for initial discussion and to allow the comparison with the hydrochemical data obtained later. Even not being suitable for modelling purposes, these data may be useful for the understanding of the borehole hydraulic conditions and its evolution with time. The last two methods, including the special equipment used for sampling of low transmissive fractures, are described in more detail below.

3.2. *The CCC Sampling Method.* Among all the sampling methods used by SKB, the Complete Chemical Characterisation (CCC), developed during the 1980s [51, 52] and further improved during the first decade of the 21st century [53], involves the most extensive sampling schemes and the most advanced equipment (Figure 3). The method is almost exclusively used in core boreholes where more information on structural geology and on hydrogeology is available compared to the percussion boreholes. The equipment can be used in boreholes from the ground surface (preferably telescopic boreholes) or from vertical and subvertical boreholes in tunnels. It comprises an integrated system for (1) sealing off a borehole section by inflatable packers and pumping of groundwater from the section, (2) sampling of pumped groundwater as well as sampling *in situ* (downhole in the section) to obtain groundwater samples at maintained pressure, and (3) online long-term measurements (weeks to months) of the chemical and

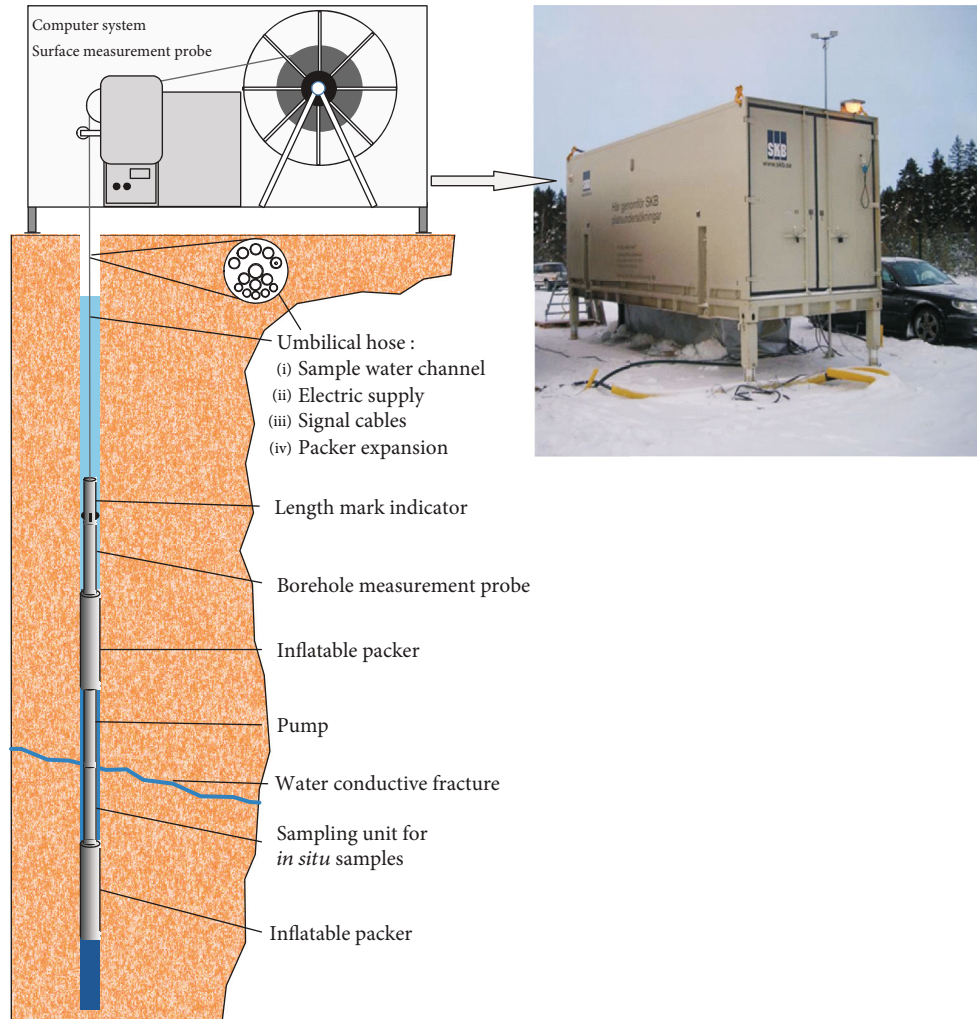


FIGURE 3: Outline of the integrated system comprising a carriage/container with downhole equipment (umbilical hose, inflatable packers, pump, downhole measurement probe, and downhole sampling unit) and facilities for lowering and raising this equipment. This system is placed over the borehole (see photo), and the container's indoor temperature is adjusted to maintain the temperature of the groundwater in the section to be investigated.

physicochemical parameters Eh (redox potential), pH, dissolved O_2 , EC (electrical conductivity), and T (groundwater temperature), both at the surface and at depth downhole (measurement probe in Figure 3).

The CCC sampling campaigns usually start as soon as the preceding logging activities (Figure 1) are finished which may take one or two months after the completion of drilling. The lengths of the packed-off borehole sections are often around seven meters, but they can also be shorter (from 0.5 m) or longer (up to approximately 15 m). The CCC investigations are performed in one borehole section at a time. Initially, the downhole equipment is internally rinsed and filled with deaerated and deionised water before use. The outside of the equipment and the hose is cleaned/wiped using 70% ethanol (being careful not to introduce it to the borehole since it may promote microbial activity) while being lowered into the borehole. Despite this cleaning, sterile equipment cannot be expected, and foreign microbes may anyhow be introduced into the borehole.

Finally, all surfaces in contact with the water sample are composed of either polyamide or high-quality stainless steel, and lubricants (Teflon spray or Vaseline) are used sparsely on O-rings in valves and other connections.

The water is pumped to the ground surface through the downhole equipment and then through the polyamide tube housed in the umbilical hose (Figure 3). The first sample in the series is collected when the groundwater from the section reaches the surface. This sample is important to understand the conditions in the borehole section (considering, for example, sulfide or organic carbon concentrations) before exchanging the section water to obtain representative groundwater samples from the bedrock formation (Sections 2.3.2 and 2.3.3). Experience shows that pumping flow rates of around 100 to 250 mL/minute are preferred to avoid unnecessary particle release and to optimise the function of the *in situ* flow-through cell in the borehole section. If the water yield is low, care has to be taken to avoid that the drawdown creates any leakage between the isolated section

being sampled and the rest of the borehole (the already mentioned pressure measurements in the borehole section and above it will help to control this; Section 2.3.2).

Online regular logging of pH, Eh, dissolved oxygen, electrical conductivity, and groundwater temperature starts as soon as the packers are inflated, and the pumping has started. Once the water is at the surface, sample portions are collected regularly for analysis during pumping (usually for a period of three weeks or until stable Eh readings are obtained).

The sample series of groundwater collected by the CCC method are of the best possible quality and include the most complete set of analyses as well as supporting information. Moreover, the series allow verification of stable conditions and identification and exclusion of single outliers. At the end of the pumping period, *in situ* samples (maximum four samples), maintaining the pressure from the borehole section, are enclosed in their containers and then lifted to the ground surface together with the rest of the equipment. These samples are used for gas analyses, as well as microbial and colloid determinations.

A variation of the CCC method was developed in order to sample low transmissive fractures ($T < 10^{-8} \text{ m}^2 \text{ s}^{-1}$). These fractures are important since they are likely to contain groundwaters representative of those associated with the bedrock volumes where the spent nuclear fuel repository will be located in the future.

The special sampling unit for low transmissive fractures, to be used with the umbilical hose of the CCC equipment, consists of (a) inflatable packers delimiting a borehole section of a fixed length of one metre (instead of adjustable length of up to 15 m); (b) a dummy, whose surface is coated with Teflon, that is mounted in between the packers to reduce the water volume in the section to 0.3 L (absent in the standard sampling unit); and (c) a single sample container (1.2 L) connected to the sampling section but placed above the upper packer, outside the section. The water is sucked into the evacuated sample container. The filling of water is recorded by a pressure sensor. Once the sampling is finished, the equipment is raised to the ground surface and the water is portioned into bottles and sent for analysis.

3.3. Monitoring. The main aim of the hydrogeochemical monitoring is to create a long time series of data to study the evolution of the composition of the groundwaters with time. Apart from obtaining base-line data covering the normal variations, monitoring is essential to study the impacts of the construction and operation of a facility at a later stage.

After completion of the general investigation activities in a borehole (Figure 1), packer equipment is installed to allow continuous pressure measurements (up to ten sections) as well as regular flow measurements and groundwater sampling (up to two sections). Besides packers, boreholes drilled from the ground surface also require standpipes in the upper part of the borehole that are connected to each section at depth (Figure 4). Only telescopic and percussion boreholes allow these standpipe installations due to the required diameter. In addition to the possibility of long-term evaluation of the pressure and the major groundwater chemistry (and environmental iso-

topes, $\delta^2\text{H}$, ^3H , and $\delta^{18}\text{O}$), the packer system prevents undesired short-circuiting effects that would occur if boreholes were kept open.

Tunnel boreholes are also monitored. The design of the equipment in these boreholes is basically similar although there are no standpipes since no pumping is needed to discharge the groundwater due to the hydrostatic pressure.

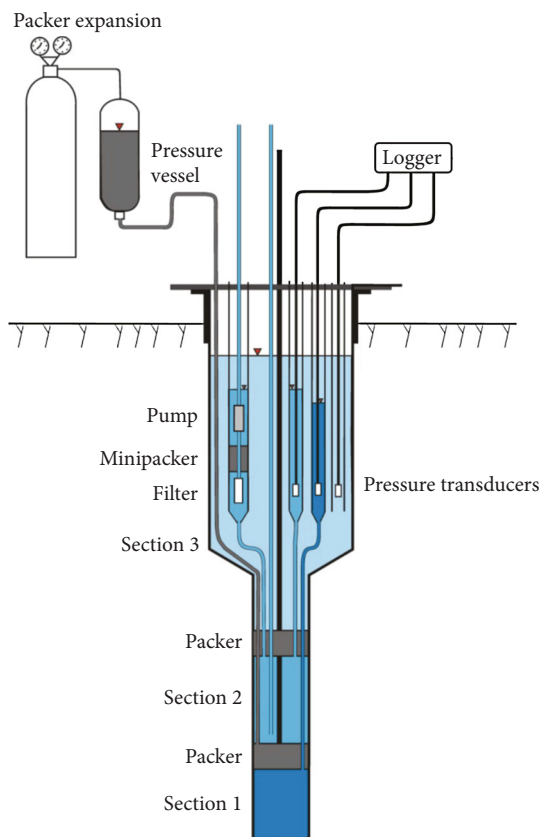
Hydrochemical monitoring includes the collection of sample series (minimum of three samples) during continuous pumping/discharge at each sampling occasion. As indicated above (Section 2.3.3), individual plug flow volumes are calculated for the monitored sections to estimate the volume of water needed to be discharged. This is particularly important in this case since the long contact time between the water isolated in the section and the installed borehole equipment may promote contamination, microbial activity, sulfide production, and corrosion. All this may have consequences on pH, organic carbon content, and trace- and redox-sensitive elements. Other sources of contamination are the biological remains (biofilm, pollen, insects, etc.) that are introduced into the standpipes between sampling occasions. With time, these contaminants will reach the isolated sections. Finally, the lowering and raising of equipment in the standpipes create pressure differences and water movements that may propagate down to the connected borehole section and promote contamination. Taking all these conditions into consideration, the recommendation is to omit (or consider with caution) the analysis of the monitoring data for the more sensitive geochemical parameters/constituents.

Besides the impact on sensitive constituents, monitored boreholes from the surface are also unsuitable for Eh measurements as the equipment cannot be lowered into the borehole due to the fixed packer system. Additionally, the system with standpipes does not allow completely oxygen-free operation (Figure 4).

4. Analyses and Measurements

4.1. Groundwater Chemical Components and Isotopes. Analytical programmes are designed to provide information/data for different purposes: (1) to describe the distribution, age, and geochemical evolution of groundwaters of different origins in the bedrock, (2) to complement the hydrogeological information in order to characterise the flow paths of the water and validate the hydrogeological models and *vice versa*, and (3) to evaluate some of the safety indicators in the repository performance assessment (pH, Eh, colloids, organic compounds, microbes, nitrogen compounds, sulfide, sulfate, inorganic carbon, phosphate, and total salinity).

The analytical protocol for groundwater analyses has included the same basic components and parameters since the beginning of the 1980s: major constituents, nutrient salts, and other anions of lower concentrations, DOC and TOC (dissolved and total organic carbon concentrations, respectively), trace metals, and stable and radioactive isotopes [54]. The list of isotopes in the early days contained $\delta^2\text{H}$, $\delta^{18}\text{O}$, ^3H , ^{14}C (percent modern carbon, pMC), and $\delta^{13}\text{C}$ on inorganic carbon, and a few have been added more recently, especially during the site investigations in Forsmark and



(a)



(b)

FIGURE 4: (a) Installed equipment for pressure, groundwater sampling, and groundwater flow monitoring in a telescopic borehole. A maximum of 10 pressure sections can be installed in a telescopic borehole, of which generally two are equipped for water sampling and circulation of tracers during flow measurements. These circulation sections are connected to three tubes. Two of them connect the section to the two standpipes for pressure measurements and groundwater sampling (the wider pipe), respectively, in the uppermost part of the borehole. The third tube leads all the way to the ground surface for the circulation experiments. (b) Lowering of a pump connected to a minipacker (for isolating the standpipe from the atmosphere) and a $50\ \mu\text{m}$ filter (polyamide) into a large diameter standpipe. To collect samples, pumping is conducted in the closed standpipe (cf. (a)); when the pressure decreases, groundwater from the connected borehole section is sucked into the standpipe and pumped to the ground surface. Modified from [48].

Laxemar ($^{10}\text{B}/^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{37}\text{Cl}$, $\delta^{34}\text{S}$, ^{36}Cl , and ^{14}C (pMC) and $\delta^{13}\text{C}$ on organic carbon). This list of analyses reflects the full protocol, but it is only used for some of the collected samples depending on the nature of the boreholes, types of samples, and/or the aims of the investigation.

Different sample classes are established to define the parameters to be included in the analytical protocol as well as the adequate sampling procedures and sample treatments. The lowest classes include basic measurements and analyses (pH, electrical conductivity, chloride, and alkalinity). An intermediate class includes the main chemical components and some of the isotopes. Sampling according to the highest classes demands trained personnel and specialised equipment since these classes comprise, in addition, components that need online filtering and/or special conservation/treatment of the water sample (trace elements, redox-sensitive components, and additional isotopes).

Analyses that need to be conducted soon after sampling (Fe^{2+} , Fe-tot , NH_4 , HCO_3^- , and lab-pH) are conducted onsite. In addition, Cl^- , EC, HS^- , and ion chromatographic (IC) determinations of SO_4^{2-} , Br^- , and F^- are generally per-

formed by SKB but not necessarily at the investigation site. Besides IC, the analyses performed by SKB laboratories are conducted by spectrophotometric, titrimetric, and potentiometric methods (additional methods, such as ICP, are conducted in external laboratories; see Supplementary Material 1; Table SM3-1). Most analyses and sample treatments (filtration, conservation, storage, etc.) follow standards from the Swedish Standards Institute (SIS) and from the Comité Européen de Normalisation (EN) or from the US Environmental Protection Agency (USEPA), but in some exceptional cases, suitable standards are missing (e.g., Fe^{2+}). Calculation of measurement uncertainties is made according to the EUR-ACHEM/CITAC guide [55].

4.2. Measurements of Eh and pH In Situ and at Ground Surface. Reliable and plausible Eh measurements at the very negative range observed for deep groundwaters [30] require optimal conditions from several aspects. For example, the smallest diffusion of oxygen into the measurement system will have a significant impact on the results. Furthermore, the most useful pH measurements for hydrogeochemical

modelling are those performed with maintained *in situ* (downhole) pressure and temperature. The CCC method (see Section 3.2) offers the best possibilities to meet these demands in telescopic core-drilled boreholes. However, a simplified equipment can also be used in tunnel boreholes. In this case, a flow-through cell is used, preferably located as close as possible to the opening of the borehole (to avoid oxygen diffusion through tubing, valves, and connections) and kept either at a pressure similar to the borehole section pressure or at atmospheric pressure, depending on the equipment.

The CCC method includes simultaneous measurements of Eh and pH at depth as well as in a flow-through cell at the ground surface. Three different redox electrodes (platinum, gold, and glassy carbon) measure Eh, and one or two glass electrodes are used for pH at each location (borehole and surface flow-through cells, respectively). Agreeing measurements by the different types of redox electrodes indicate stable conditions and reliable values. The logging continues until the parameters stabilise [30], and for Eh, this may take up to four weeks depending on the time needed to remove the very small amounts of oxygen initially present in the equipment.

The reference electrode for the Eh and pH measurements is of the Ag/AgCl, double junction type. The downhole reference electrodes and the glass (pH) electrodes are specially designed by SKB to stand high pressures by allowing compression of the electrolyte volume. The electrodes used at the surface are all commercially available. The electrical ground in the probes is galvanically isolated from earth.

With respect to the pH measurements, apart from those performed in the field together with the Eh, pH is also measured in the laboratory at 25°C (batch). The possibility of comparing different measurements to evaluate reliability has been proven to be important.

5. Data Quality Evaluation

5.1. Data Quality Control Sequence. The chemical data (analytical results and measured values) from different sources are checked in several steps before they are used in interpretations and modelling work.

- (1) First screening at the investigation site is important since it is conducted close in time to the sampling and analyses and by personnel familiar with the sampling and analytical performance. This screening involves charge balance calculations, simple consistency checks (Section 5.2), and judgments based on experience and previous results. In the case of questionable data, there is still the possibility of repeating analyses at this stage.
- (2) A further check is performed when the data are entered into SKB's geoscientific database, mainly to confirm correct entries by signing the quality check for each sample record. Further control is added by plotting large amounts of data in x - y scatter plots to check for trends and outliers.
- (3) Finally, when the dataset is delivered for hydrochemical interpretation and modelling, the quality of

the data is assessed with respect to sample representativity. At this stage, more information is available (a larger dataset, complete isotope data, hydrogeological and geological interpretations, etc.) allowing representativity assessments based on an integrated hydrochemical, geological, and hydrogeological approach (Section 5.3).

5.2. Consistency Checks. Some basic consistency checks are performed prior to inserting the data in the database. The usual checks are described below:

- (i) Comparison of the measured electrical conductivity (EC) with the concentration of the dominating dissolved ion (chloride in most of the Fennoscandian groundwaters) in order to discover outliers. Since the dominating ion contributes the most to the electrical conductivity, the comparison should result in a close to a straight line in the relevant salinity range for the considered deep groundwaters [56–58].
- (ii) Charge imbalance calculations provide verification of reliable major components. The acceptable range is set to $\pm 5\%$; however, in the case of dilute waters ($\text{Cl} < 50 \text{ mg/L}$), a range of $\pm 10\%$ is tolerable. Charge imbalances outside these limits often require repeated analyses or repeated sampling.
- (iii) Comparison between the values obtained by different analytical methods. In the analytical routine followed by SKB, this applies to iron, sulfate, and uranium (the element and the U-238 activity) which are all routinely determined by two methods that are based on different principles.
- (iv) Bromide concentrations are plotted versus corresponding chloride contents to give a rough check of the plausibility of the bromide concentrations. Some correlation is usually found for the entire dataset also in the case of groundwaters with different origins (marine and nonmarine).

5.3. Categorisation of Samples according to Quality. The quality and representativity of groundwater data may be influenced by different factors, for example, contamination from drilling, different sampling methods, the hydraulic conditions in the borehole at the sampling occasion, and the analytical performance. After some initial strategies developed for groundwater data evaluation during the 1980s and 1990s (see the Supplementary Material 1), a more refined approach for quality categorisation was developed during the site characterisation of the Forsmark and Laxemar sites [54, 59, 60]. This was further developed during the more recent site characterisation for the extension of the SFR (the repository for low- and intermediate-level short-lived radioactive wastes) and the Äspö Underground Laboratory data evaluation [57, 61].

The objective of the categorisation is to assess the data quality by grading the set of data corresponding to a sampling occasion from 1 to 5 according to several quality

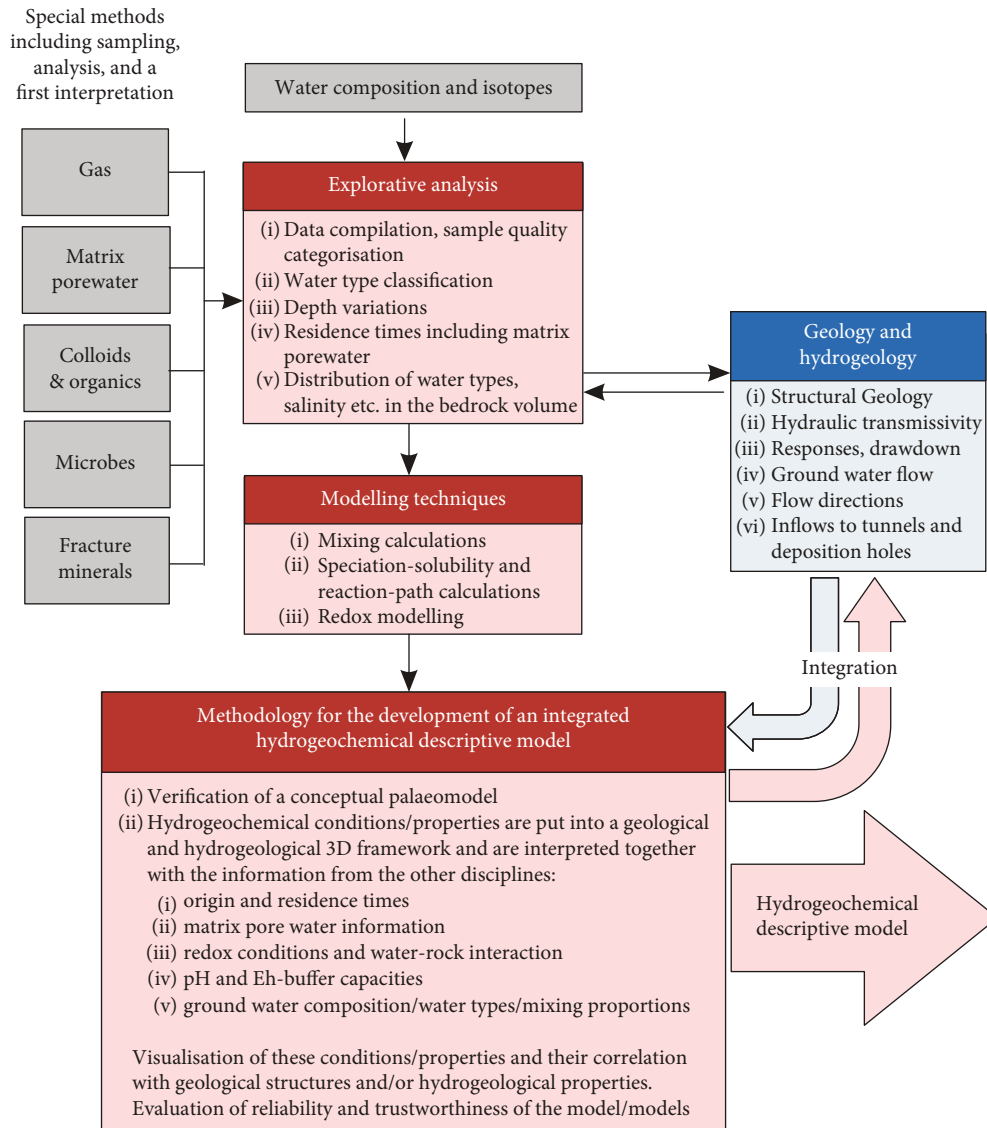


FIGURE 5: Schematic overview of the interpretation and modelling procedure to produce an integrated hydrogeochemical site model/description. Grey frames are used for hydrogeochemical input data. Blue colour indicates geological and hydrogeological methods and data flows, and red boxes indicate descriptive hydrogeochemical interpretation methods, generally performed with specific software.

criteria. Of these (1) is the highest quality, while quality (5) is not considered acceptable for modelling purposes (see Supplementary Material 3; Table SM3-2). The criteria include, for example, the flushing water content, the borehole section length, the hydraulic responses in other borehole sections or in other boreholes during sampling, and the possible concentration trends in sample time series.

The major reasons for performing this categorisation are to facilitate future interpretation and modelling work by providing well-structured data tables representing quality categorised data and also to guide users on how to select data for their purposes. Additionally, this evaluation is very useful to identify samples unsuitable for general modelling purposes (affected by experimental conditions, grouting, etc.). The first step for the categorisation needs to be a general overview of the dataset to establish the best categorisation criteria.

Once the data have been evaluated and categorised, they are ready to be used in the hydrogeochemical interpretation and modelling. The main objective is to use an integrated framework like the one shown in Figure 5 to produce a total conceptual hydrogeochemical model of the site (see some examples in [57, 62–65]).

6. Conclusions

The methodology developed by SKB for the characterisation of deep groundwaters in crystalline rocks has been based on forty years of experience and of collaboration with other international agencies and research institutions. This paper describes advances and improvements applicable to groundwater sampling, for any purpose, in crystalline rocks. The text also identifies the questions to be considered during data

interpretation for the hydrogeochemical characterisation of a crystalline bedrock system.

The sampling protocol emphasises the collection of hydrogeochemical data that accurately represent *in situ* conditions, minimising disturbances as much as possible and following quality assurance guidelines. However, it is important to keep in mind that no single method or procedure is universally applicable to all groundwater systems or to all types of groundwater sampling programmes. Therefore, the selection of appropriate sampling processes and equipment is vital to the success of any groundwater investigation. The same is applicable to the categorisation and quality assurance protocols, which are also site specific. The success of any site characterisation programme relies on a robust and comprehensive sampling protocol, coupled with proven analytical schemes, careful documentation, and the performance of quality assurance procedures.

Some general points/measures of importance in order to obtain representative groundwater samples of the best possible quality are as follows:

- (i) Planning of the hydrochemical investigations at an early stage, i.e., hydrochemical demands need to be considered already when preparing for the drilling of the boreholes.
- (ii) A thoughtful selection of borehole sections based on flow logging and BIPS data as well as specific hydrogeological evaluations to facilitate adequate sampling.
- (iii) Online measurements of Eh and pH, preferably *in situ* in the borehole section.
- (iv) Collection of sample time series to ensure hydrochemical stability.
- (v) Adequate data evaluation and quality check. Quality categorisation of data to provide guidance on their use for different purposes.

Finally, one of the most relevant issues to consider is the importance and usefulness of close cooperation and integration of hydrogeochemistry with other geoscientific disciplines, such as structural geology, hydrogeology, and geomicrobiology. This collaboration should start already during the planning and execution of the field work (and subsequent interpretations) in order to optimise the quality and the amount of information. The combination of different types of knowledge from all the geoscientific disciplines, ranging from field and laboratory studies to interpretation and modelling work, is the only way to obtain a final coherent and integrated understanding of the system.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

There is one file with supplementary information associated with this article. Inside that file, 3 supplementary sections are included: Supplementary Material 1 gives a summary of the background on the development of this type of methodology worldwide in the context of radioactive waste disposal. Supplementary Material 2 describes in detail some additional issues related to the drilling and after drilling procedures, especially about the flushing water. Finally, Supplementary Material 3 includes two tables with detailed information on some methodological aspects related to Sections 4.1 and 5.3. Table SM3-1 lists the analytical protocol followed for the groundwaters, including the detection limits and the measurement uncertainties, and Table SM3-2 displays an example of cornerstone criteria that were found to be relevant independently of the type of dataset. (*Supplementary Materials*)

References

- [1] W. W. Wood, "Guidelines for collection and field analysis of groundwater samples for selected unstable constituents," *U.S. Geological Survey Techniques for Water Resources Investigations, Book 1, Chapter D-2*, 1976.
- [2] US Geological Survey, *National Handbook of Recommended Methods for Water-Data Acquisition*. USGS Office of Water Data Coordination, Reston, Virginia, 1977.
- [3] J. D. Hem, *Study and interpretation of the chemical characteristics of natural water*, Geological Survey Water-Supply Paper 2254, U.S., 1985.
- [4] M. J. Barcelona, J. P. Gibb, J. A. Hellfrich, and E. E. Garske, *Practical guide for ground-water sampling*, Environmental Protection Agency, EPA/600/2-85/104, U.S., 1985.
- [5] R. W. Gillham, M. J. L. Robin, J. F. Barker, and J. A. Cherry, *Groundwater monitoring and sample bias*. Department of Earth Sciences University of Waterloo, Prepared for Environmental Affairs Department, American Petroleum Institute, API Pub. 4367, June, Waterloo, Ontario, 1983.
- [6] M. T. Koterba, F. D. Wilde, and W. W. Lapham, *Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—collection and documentation of water-quality samples and related data*, Geological Survey Open-File Report 95-399, U.S., 1995.
- [7] K. F. Pohlmann, C. Rosal, and B. Beldsoe, *Sample handling and analysis*. EPA Groundwater Sampling EPA/600/R-94/205, 94-98, 1993.

- [8] R. W. Puls and M. J. Barcelona, *Low-flow (minimal draw-down) ground-water sampling procedures*, Environmental Protection Agency, Ground Water Issue Report, EPA/540/S-95/504, U.S., 1996.
- [9] A. M. Shapiro, "Cautions and suggestions for geochemical sampling in fractured rock," *Groundwater Monitoring & Remediation*, vol. 22, no. 3, pp. 151–164, 2002.
- [10] US Environmental Protection Agency, *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide: Volume I: Solids and Ground Water Appendices A and B; EPA/625/R-93/003a*, 1993.
- [11] US Environmental Protection Agency, "Compendium of ERT groundwater sampling procedures," in *Report EPA/540/P-91/007, January 1991*, US Environmental Protection Agency, Washington DC, 1999.
- [12] US Geological Survey, *Characterizing ground-water chemistry and hydraulic properties of fracture-rock aquifers using the multifunction bedrock-aquifer transportable testing tool (BAT3). USGS Fact Sheet FS-075-01, August 2001*, 2001.
- [13] US Geological Survey, *National Field Manual for the Collection of Water-Quality Data*, Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, U.S., 2005, January 2005, <http://pubs.water.usgs.gov/twri9A/>.
- [14] D. Yeskis and B. Zavala, *Ground-water sampling guidelines for Superfund and RCRA project managers*, Environmental Protection Agency, EPA 542-S-02-001, U.S., 2002.
- [15] D. Johnston, *Regulatory Monitoring and Testing Groundwater Sampling*, Draft EPA Guidelines, Environment Protection Authority, 2006.
- [16] J. M. C. Weaver, "Groundwater sampling: a comprehensive guide for sampling methods," in *Report TT 54/92*, Water Research Commission, Pretoria, 1992.
- [17] J. M. C. Weaver, L. Cave, and A. S. Talma, *Groundwater sampling. A comprehensive guide for sampling methods*, WRC Report No. TT 303/07, South Africa, 2007.
- [18] Murray-Darling Basin Commission, *Murray-Darling basin groundwater quality sampling guidelines, Technical Report No. 3, MDBC Groundwater Working Group, Commonwealth of Australia*, 1997.
- [19] Standards Australia, *AS/NZS 5667.1:1998 water quality—sampling—guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples, standards Australia, New South Wales*, 1998.
- [20] V. E. P. Authority, *Groundwater Sampling Guidelines, Publication Number 669, (EPA Victoria), Melbourne*, 2000.
- [21] J. D. Pennino, "There's no such thing as a representative ground water sample," *Groundwater Monitoring & Remediation*, vol. 8, no. 3, pp. 4–9, 1988.
- [22] M. J. Barcelona, "Uncertainties in ground water chemistry and sampling procedures," in *Chemical Modeling of Aqueous Systems II*, D. C. Melchior and R. L. Bassett, Eds., pp. 311–320, American Chemical Society, Washington, D.C., 1990.
- [23] M. J. Barcelona, M. D. Varljen, R. W. Puls, and D. Kaminski, "Ground water purging and sampling methods: History vs. hysteria," *Groundwater Monitoring & Remediation*, vol. 25, no. 1, pp. 52–62, 2005.
- [24] P. Wikberg, K. Ahlbom, and O. Olsson, "Site investigations of potential repository sites in Sweden," in *Scientific Basis for Nuclear Waste Management XXVII*, V. M. Oversby and L. O. Werme, Eds., pp. 9–14, Materials Research Society (MRS), Warrendale, PA, 2004.
- [25] A. Ström, J. Andersson, K. Skagius, and A. Winberg, "Site descriptive modelling during characterization for a geological repository for nuclear waste in Sweden," *Applied Geochemistry*, vol. 23, no. 7, pp. 1747–1760, 2008.
- [26] N. Marcos, P. Hellä, M. Snellman et al., *The role of the geosphere in POSIVA's safety case. Stability and Buffering Capacity of the Geosphere for Long-term Isolation of Radioactive Waste: Application to Crystalline Rock. Workshop Proceedings Manchester, United Kingdom, 13-15 November 2007*, OECD Nuclear Energy Agency (NEA), Paris, France, 2009.
- [27] B. Pastina, J. Lehtikoinen, and I. Puigdomenech, "Safety case approach for a KBS-3 type repository in crystalline rock," *Proc. NEA-IGSC Workshop on cementitious materials in safety cases for geological repositories for radioactive waste: role, evolution and interactions*, OECD, Nuclear Energy Agency; NEA/RWM/R(2012)3, pp. 165–170, 2012.
- [28] J. Andersson, K. Skagius, A. Winberg, T. Lindborg, and A. Ström, "Site-descriptive modelling for a final repository for spent nuclear fuel in Sweden," *Environmental Earth Sciences*, vol. 69, no. 3, pp. 1045–1060, 2013.
- [29] J. A. T. Smellie, M. Laaksoharju, and P. Wikberg, "Äspö, SE Sweden: a natural groundwater flow model derived from hydrogeochemical observations," *Journal of Hydrology*, vol. 172, no. 1-4, pp. 147–169, 1995.
- [30] L. F. Auqué, M. J. Gimeno, J. Gómez, and A.-C. Nilsson, "Potentiometrically measured Eh in groundwaters from the Scandinavian shield," *Applied Geochemistry*, vol. 23, no. 7, pp. 1820–1833, 2008.
- [31] H. N. Waber and J. A. T. Smellie, "Characterisation of pore-water in crystalline rocks," *Applied Geochemistry*, vol. 23, pp. 1836–1861, 2008.
- [32] H. N. Waber, T. Gimmi, and J. A. T. Smellie, "Reconstruction of palaeoinfiltration during the Holocene using porewater data (Laxemar, Sweden)," *Geochimica et Cosmochimica Acta*, vol. 94, pp. 109–127, 2012.
- [33] L. Hallbeck and K. Pedersen, "Characterization of microbial processes in deep aquifers of the Fennoscandian shield," *Applied Geochemistry*, vol. 23, no. 7, pp. 1796–1819, 2008.
- [34] L. Hallbeck and K. Pedersen, "Culture-dependent comparison of microbial diversity in deep granitic groundwater from two sites considered for a Swedish final repository of spent nuclear fuel," *FEMS Microbiology Ecology*, vol. 81, no. 1, pp. 66–77, 2012.
- [35] H. Drake and E.-L. Tullborg, "Paleohydrogeological events recorded by stable isotopes, fluid inclusions and trace elements in fracture minerals in crystalline rock, Simpevarp area, SE Sweden," *Applied Geochemistry*, vol. 24, no. 4, pp. 715–732, 2009.
- [36] H. Drake, E.-L. Tullborg, J. Hogmalm, and M. Åström, "Trace metal distribution and isotope variations in low-temperature calcite and groundwater in granitoid fractures down to 1 km depth," *Geochimica et Cosmochimica Acta*, vol. 84, pp. 217–238, 2012.
- [37] H. Drake, M. Åström, E.-L. Tullborg, M. J. Whitehouse, and A. E. Fallick, "Variability of sulphur isotope ratios in pyrite and dissolved sulphate in granitoid fractures down to 1 km depth - evidence for widespread activity of sulphur reducing bacteria," *Geochimica et Cosmochimica Acta*, vol. 102, pp. 143–161, 2013.
- [38] B. Sandström and E.-L. Tullborg, "Episodic fluid migration in the Fennoscandian shield recorded by stable isotopes, rare earth elements and fluid inclusions in fracture minerals at

- Forsmark, Sweden,” *Chemical Geology*, vol. 266, no. 3-4, pp. 126–142, 2009.
- [39] B. Sandström, E.-L. Tullborg, J. Smellie, A. B. MacKenzie, and J. Suksi, *Fracture mineralogy of the Forsmark site. SDM-Site Forsmark. SKB Report R-08-102*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2008.
- [40] E.-L. Tullborg, H. Drake, and B. Sandstrom, “Palaeohydrogeology: a methodology based on fracture mineral studies,” *Applied Geochemistry*, vol. 23, no. 7, pp. 1881–1897, 2008.
- [41] A.-C. Nilsson, K. Pedersen, B. Hallbeck, J. Johansson, and E.-L. Tullborg, *Development and testing of gas samplers in tunnel environments*, SKB R-16-16, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2017.
- [42] M. J. Gimeno, L. F. Auqué, P. Acero, and J. Gómez, “Hydrogeochemical characterisation and modelling of groundwaters in a potential geological repository for spent nuclear fuel in crystalline rocks (Laxemar, Sweden),” *Applied Geochemistry*, vol. 45, pp. 50–71, 2014.
- [43] J. B. Gómez, M. J. Gimeno, L. F. Auqué, and P. Acero, “Characterisation and modelling of mixing processes in groundwaters of a potential geological repository for nuclear wastes in crystalline rocks of Sweden,” *Science of The Total Environment*, vol. 468-469, pp. 791–803, 2014.
- [44] H. Drake, L. Hallbeck, K. Pedersen et al., *Investigation of sulphide production in core-drilled boreholes in Äspö Hard Rock Laboratory. Boreholes KA3110A, KA3385A and KA3105A*, SKB TR-13-12, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2014.
- [45] P. Wersin, P. Alt-Epping, P. Pitkänen et al., “Sulphide fluxes and concentrations in the spent nuclear fuel repository at Olkiluoto,” in *Posiva report 2014-01*, Posiva Oy, Eurajoki, Finland, 2014.
- [46] J. Komulainen, “Posiva flow log (PFL), tool for detection of groundwater flows in bedrock,” in *13th International Mine Water Association Congress – Mine Water & Circular Economy*, C. Wolkersdorfer, L. Sartz, M. Sillanpää, and A. Häkkinen, Eds., pp. 556–563, Lappeenranta University of Technology (LUT) Scientific and Expertise Publications, Lappeenranta, Finland, 2017.
- [47] J. J. Komulainen, T. Vaitinen, P. Picken, and E. Heikkinen, “Hydrogeological bedrock characterisation based on Posiva flow log measurement data,” in *11th ICARD/IMWA/MWD Conference 2018*, C. Wolkersdorfer, L. Sartz, A. Weber, J. Burgess, and G. Tremblay, Eds., pp. 654–659, International Mine Water Association, Denver, Colorado, 2018.
- [48] M. Stigsson, “Orientation uncertainty of structures measured in cored boreholes: methodology and case study of Swedish crystalline rock,” *Rock Mechanics and Rock Engineering*, vol. 49, no. 11, pp. 4273–4284, 2016.
- [49] A.-C. Nilsson, C. Berg, J. Harrström et al., “Hydrochemical monitoring of groundwaters and surface waters. Results from water sampling in the Forsmark area, January-December 2009,” *Forsmark site investigation. SKB P-10-40*, p. 224, 2010.
- [50] L. A. Richards, D. Magnone, B. E. van Dongen, C. J. Ballentine, and D. A. Polya, “Use of lithium tracers to quantify drilling fluid contamination for groundwater monitoring in Southeast Asia,” *Applied Geochemistry*, vol. 63, pp. 190–202, 2015.
- [51] F. Karlsson and P. Wikberg, “Some highlights on the isotope geochemistry studies within the Swedish research program on radioactive waste disposal,” *Applied Geochemistry*, vol. 2, no. 1, pp. 25–31, 1987.
- [52] P. Wikberg, “The natural chemical background conditions in crystalline rocks,” in *Scientific Basis for Nuclear Waste Management XI*, M. J. Apted and R. E. Westerman, Eds., pp. 373–382, Materials Research Society (MRS), Pittsburgh, Pennsylvania, 1988.
- [53] A. Bergelin, A. Lindquist, K. Nilsson, P. Wacker, and A.-C. Nilsson, “Hydrochemical characterisation in borehole KFM08D,” *Results from two investigated borehole sections at 669.7-676.8 m and 828.4-835.5 m. Forsmark site investigation. SKB P-07-190*, p. 107, 2007.
- [54] A.-C. Nilsson, “Laxemar site investigation: quality of hydrochemical analyses (DF version 2.3),” in *Background complementary hydrogeochemical studies. SKB Report R-08-111*, B. Kalinowski, Ed., Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2009.
- [55] A.-C. Nilsson, “Forsmark site investigation: analytical uncertainties,” in *Background complementary hydrogeochemical studies. SKB Report R-08-87*, B. Kalinowski, Ed., Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2008.
- [56] R. B. McCleskey, D. K. Nordstrom, J. N. Ryan, and J. W. Ball, “A new method of calculating electrical conductivity with applications to natural waters,” *Geochimica et Cosmochimica Acta*, vol. 77, pp. 369–382, 2012.
- [57] A.-C. Nilsson, M. Gimeno, E.-L. Tullborg, F. Mathurin, and J. Smellie, “Hydrogeochemical data report,” in *Site descriptive modelling Äspö SDM. SKB R-13-26*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2013.
- [58] F. Visconti, J. M. De Paz, and J. L. Rubio, “An empirical equation to calculate soil solution electrical conductivity at 25 °C from major ion concentrations,” *European Journal of Soil Science*, vol. 61, no. 6, pp. 980–993, 2010.
- [59] J. Smellie, E.-L. Tullborg, A.-C. Nilsson et al., “Explorative analysis of major components and isotopes,” in *SDM-Site Forsmark. SKB Report R-08-84*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2008.
- [60] J. Smellie and E.-L. Tullborg, “Quality assurance and categorisation of groundwater samples from the Laxemar-Simpevarp area,” in *Background complementary hydrogeochemical studies. SKB Report R-08-111*, B. Kalinowski, Ed., Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2009.
- [61] A.-C. Nilsson, E.-L. Tullborg, J. Smellie et al., “SFR site investigation,” in *Bedrock Hydrogeochemistry. SKB R-11-06*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2011.
- [62] M. Laaksoharju, J. Smellie, E.-L. Tullborg et al., “Bedrock hydrogeochemistry, Forsmark,” in *Site descriptive modelling. SDM-Site Forsmark. SKB Report R-08-47*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2008.
- [63] M. Laaksoharju, J. Smellie, E.-L. Tullborg et al., “Hydrogeochemical evaluation and modelling performed within the Swedish site investigation programme,” *Applied Geochemistry*, vol. 23, no. 7, pp. 1761–1795, 2008.
- [64] M. Laaksoharju, J. Smellie, E.-L. Tullborg et al., “Bedrock hydrogeochemistry Laxemar,” in *Site descriptive model, SDM-Site Laxemar. SKB Report R-08-93*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2009.
- [65] J. Öhman, N. Bockgård, and S. Follin, “Bedrock hydrogeology,” in *Site Investigation SFR. SKB Report R-11-03*, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2012.