

**Methodology for hydrogeochemical sampling to characterise
groundwaters in crystalline bedrock: developments made within
the Swedish radwaste programme. Supplementary Material**

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Supplementary Material 1: **Background**

The need for reliable groundwater sampling procedures and chemical analyses has been internationally recognised for years. The USGS (United States Geological Survey) was one of the first institutions in the 1970s to publish rigorous sampling and analytical protocols and procedures related to studies of environmental groundwater contamination ([1], although the first edition was published in 1959; [2, 3]). Since then, and together with USEPA (United States Environmental Protection Agency), more detailed descriptions, proposals and manuals of sampling procedures, devices, techniques, etc. in different host rocks, have been reported in various publications by these two organisations [4-14]. Along similar lines, other countries such as Australia and South Africa have recently published guidelines for groundwater sampling [15, 16] which are based on previous experience developed since 1997, involving drilling, sampling, analytical methodologies and quality assessment [17-20].

There are many other domains in which the deep drilling and the related investigations have also evolved and improved over the years (geothermalism, ODP, etc) but in this summary we will focus on the context of radioactive waste disposal. In this context, most of the existing technologies for sampling in boreholes to around 1,000 m depth have been developed and documented in several international site characterisation projects. Furthermore, natural analogue studies have also provided valuable input in this respect (e.g. [21-22]). Overall, it is important to stress that collaboration between these international organisations has been close, particularly where similar rock types have been demarcated for radioactive waste disposal; some notable examples are briefly listed below.

Site investigations carried out by AECL (Atomic Energy of Canada Ltd.) and now by NWMO, (the Nuclear Waste Management Organization) on the Canadian Shield commenced in 1978 and resulted in important developments of borehole and sampling techniques for hydrogeochemical investigations in fractured crystalline rocks [5, 23-33].

In Switzerland, a major effort has been made since the 1980's by NAGRA (National Cooperative for the Disposal of Radioactive Waste) on drilling and development of characterisation methodologies related to deep boreholes initially in crystalline rocks [34-44] and more recently in clay formations [40].

The Finnish site investigation programme carried out initially by TVO (Teollisuuden Voima Oyj) and later by Posiva Oy, started in 1984 and was mainly focused on groundwater flow and geochemistry due to their importance in terms of long-term repository safety in crystalline rock. These studies resulted in, for example, the development of field instrumentation and tests and protocols for groundwater sampling and measuring groundwater flow [45-58]. Also included were analytical programmes which covered, for example evaluation of the representativeness of the groundwater samples, use of sampling equipment, and handling and preparation of groundwater samples, as well as field measurements and analyses.

In Spain, the main scientific and technological advance on the hydrogeochemical investigations for deep geological disposal started with ENRESA (Empresa Nacional de Residuos Radioactivos, SA) in 1984. Then, in the 1990s a specific and comprehensive protocol for the groundwater sampling and characterisation was developed in the framework of the International Natural Analogue Project at El Berrocal [59-63].

In Belgium and France, where radioactive wastes disposal in clay repositories are being considered by ONDRAF/NIRAS (Organisme National des Déchets RAdiactifs et des matières Fissiles enrichies) and ANDRA (Agence Nationale pour la gestion des Déchets RAdioactifs), technological and methodological developments have been carried out in relation to the hydrogeochemical characterisation of underground research laboratories in clay [64-67].

In the United Kingdom the first publications concerning deep borehole sampling, sample handling and storage and chemical analyses were associated with the Sellafield site investigations [68-73]. More recently the NDA-RWMD (Nuclear Decommissioning Authority - Radioactive Waste Management Directorate) have published several reports related to groundwater sampling and analytical strategies and techniques as part of a future site characterisation programme for a geological

radioactive waste disposal facility [74-79]. The work from Bath and Metcalfe [75] provides a thorough review of the available technologies for groundwater sampling and analyses developed in site characterisation projects on three relevant host rock types. The authors give a general overview of the sampling methods and techniques, the operational information about the equipment and information about the countries that have developed the equipment (Tables 5-1, 5-2, 5-5 and 6-1 in [75]). They also discuss the quality of groundwaters in terms of their representativity. The United Kingdom programme has still not been restricted to any specific rock type.

The Japanese hydrogeochemical investigations related to the deep geological disposal of radioactive wastes started in the 1990s and were carried out by the JNC (Japan Nuclear Cycle Development Institute). Some specific methodologies have been developed [80-81] and others have been applied based on experience from other countries. All these developments were initially studied in the Kamaishi and Tono Mines [82-86] and, more recently in the Mizunami and Horonobe Underground Research Laboratories [87-95]. This experience has been incorporated in the procedures that constitute the scientific and technical basis for HLW (High Level Wastes) disposal in Japan [96-100].

Sweden (through the Swedish Nuclear Fuel and Waste Management Company, SKB) together with Finland, has had the advantage of a continuous programme of scientific and technical development of a site characterisation for almost 40 years. Since 1977 SKB has performed activities with the overall objective of acquiring knowledge and data to develop methodologies and instrumentation required for the safe disposal of radioactive wastes in fractured crystalline rocks. An important part of this work has been the hydrogeochemical characterisation of the deep groundwaters in granitic rocks, in order to describe their chemistry, origin and distribution in the bedrock and the hydrogeochemical processes involved in their evolution. Close collaboration with other agencies, such as those listed above, has been a great benefit in this respect.

The Swedish site characterisation programme initially investigated a number of crystalline rock sites with the aim to increase knowledge of bedrock conditions in different types of rocks and at different locations in Sweden (SKB Study Site Programme; 1976-2001). Together with these investigations, a

final repository for low- and intermediate-level radioactive waste (SFR), located adjacent to Forsmark at the Baltic coast about 150 km north of Stockholm, commenced operations in 1988.

At the time of these early Study Site investigations (1976-1986) very little was known about the groundwater chemistry at 500 m depth in non-mineralised crystalline bedrock and therefore a progressive development of a specific investigation methodology was initiated. The initial reports on sampling and analysis protocols for groundwaters were published by SKB at the beginning of the 1980s associated with the establishment of the KBS-3 disposal concept [101-103], and the characterisation of several sites [104-112]. High quality groundwater data was already recognised at that time as a necessary pre-requisite in site characterisation and, therefore, evaluation of the quality of groundwater samples was an important part of the studies [113-116]. Due to the complexity of the fracture systems, these studies showed the lack of representative groundwater samples for hydrochemical considerations [113] and, therefore, an important effort was made to rectify this. It involved improving instrumental development, experimenting using different materials, testing drilling and sampling techniques and analysing their effects on the final chemical composition of the sampled groundwaters. These successful experiments and associated knowledge subsequently became an integrated part of the SKB approach.

One of the major improvements was the design and use of the first mobile chemistry equipment in 1984. It included a mobile laboratory for immediate chemical analyses and down-hole equipment for, among other uses, to carry out *in situ* Eh and pH measurements. This new methodology regarding redox measurements was of special relevance since the general belief at the time was that it was not possible to measure meaningful Eh values in natural waters.

However, despite the important advances made thanks to this mobile equipment, some problems still remained, for example it was not realised how difficult it was to obtain representative groundwater samples; another problem was the lack of good analytical methods for isotope determinations (especially for ^{14}C and ^3H) which prevented the reliable use of these isotopes for residence time interpretations.

Prior to the construction of the Äspö Hard Rock Laboratory (1986-1990), the *pre-investigation* studies represented important progress from the earlier KBS-3 groundwater studies in refining and establishing future borehole investigation methodology [117-118]. A major step forward was the introduction of a new drilling technique, telescope-type drilling, which improved the possibilities to remove flushing water and drilling debris, thereby increasing the quality of the groundwater samples. The investigations in boreholes from the Äspö tunnel during the following *construction phase* (1990-1995; [119-120]) were performed in parallel with the construction work which required careful planning. The *operation phase* in the late 1990s involved the introduction of differential flow logging measurements [49, 121] and BIPS logging measurements (Borehole Image Processing System; [122]) techniques which significantly improved the possibility of selecting water bearing fractures for sampling and determining the water yield situation in demarcated borehole sections. Furthermore, the tripple tube drilling system minimised the loss of fracture filling material therefore improving the quality of the fracture mineral samples, which are very important for the hydrogeochemical interpretations from several aspects. During this time much effort was also spent on the thorough assessment of all procedures involved in the localisation, sampling and analysis of groundwaters to find sources of uncertainties or inconsistencies in the final groundwater chemical data. Laaksoharju et al. [123], Smellie et al. [124] and Laaksoharju [125] describe in detail different quality evaluation approaches (expert judgement, statistical treatment and scoring system) used to identify representative chemical compositions for classification and modelling purposes.

Based on this experience gained over a period of about 20 years, SKB published a series of documents outlining the basis for the geoscientific programme for investigation and evaluation of sites for a deep repository ([126] and references therein). The general investigation programme was established in SKB [127] and the guidelines and strategy for the hydrogeochemical interpretation and modelling work were described in detail in Smellie et al. [128]). However, the details about the groundwater sampling issues were not addressed in any of these previous publications.

During the site characterisation investigations at Forsmark, Laxemar and SFR (2002 to 2010; 4-6) to select the location for the final repository of spent nuclear fuel (the two first) and for the extension of

the existing repository (SFR) for low and intermediate level waste, a large number of boreholes were drilled and newly developed or modified hydrochemical investigation methods were applied for studying the groundwater chemistry [129-132]. Although these investigations were planned based on the previous experience, modifications, updates and improvements on the methodologies and strategies had to be done and they are presented and discussed in this paper. SKB will use the same kind of methodological scheme during repository construction and operation with modifications and future technical developments. Additional publications concerning specific SKB methodologies related to the hydrogeochemical studies have been published and will not be described in detail here, e.g. the methodology developed for potentiometrical Eh measurements and their evaluation [133], the methodology used for the matrix porewater studies [134, 135], the studies on microbes and gases [136, 137], on fracture minerals [138-143], and on statistical and hydrogeochemical modelling techniques [144, 145].

ACKNOWLEDGMENTS

The authors gratefully acknowledge Dr. Russell Alexander (Bedrock Geosciences, Switzerland) for providing some of the references related to methodological developments in other countries that are included in this Supplementary Material.

REFERENCES

- 1 Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water-Supply Paper 2254, 264 p.
- 2 U.S. Geological Survey, 1977. National Handbook of Recommended Methods for Water-Data Acquisition. USGS Office of Water Data Coordination, Reston, Virginia.
- 3 Wood, W.W., 1976. Guidelines for Collection and Field Analysis of Groundwater Samples for Selected Unstable Constituents. *In*: U.S. Geological Survey Techniques for Water Resources Investigations, Book 1, Chapter D-2.
- 4 Barcelona, M.J., Gibb, J.P., Hellfrich, J.A., Garske, E.E., 1985. Practical Guide for Ground-Water Sampling; U.S. Environmental Protection Agency, EPA/600/2-85/104, 169 pp.

- 5 Gillham, R.W., Robin, M.J.L., Barker, J.F., Cherry, J.A., 1983. Groundwater monitoring and sample bias. Department of Earth Sciences University of Waterloo, Waterloo, Ontario. Prepared for Environmental Affairs Department, American Petroleum Institute, API Pub. 4367, June, 206 pp..
- 6 Koterba, M.T., Wilde, F.D., Lapham, W.W., 1995. Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.
- 7 Pohlmann, K.F., Rosal, C., Beldsoe, B., 1993. Sample handling and analysis. EPA Groundwater Sampling EPA/600/R-94/205, 94-98.
- 8 Puls, R.W., M.J. Barcelona, 1996. Low-flow (minimal drawdown) ground-water sampling procedures. U.S. Environmental Protection Agency, Gound Water Issue Report, EPA/540/S-95/504.
- 9 Shapiro, A.M., 2002. Cautions and suggestions for geochemical sampling in fractured rock. *Ground Water Monit. Remediat.* 22, 151-164.
- 10 U.S. Environmental Protection Agency, 1993. *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide: Volume I: Solids and Ground Water Appendices A and B*; EPA/625/R-93/003a.
- 11 U.S. Environmental Protection Agency, 1999. *Compendium of ERT groundwater sampling procedures*. Report EPA/540/P-91/007, January 1991, US Environmental Protection Agency, Washington DC.
- 12 U.S. Geological Survey, 2001. *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.
- 13 U.S. Geological Survey, variously dated, *National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations*, book 9, chaps. A1-A9, accessed Jan. 3, 2005, at <http://pubs.water.usgs.gov/twri9A/>.

- 14 Yeskis, D., Zavala, B., 2002. *Ground-water sampling guidelines for Superfund and RCRA project managers*, U.S. Environmental Protection Agency, EPA 542-S-02-001.
- 15 Johnston, D., 2006. *Regulatory monitoring and testing Groundwater sampling*. Draft EPA Guidelines. Environment Protection Authority.
- 16 Weaver, J.M.C., Cave, L., Talma, A.S., 2007. *Groundwater sampling. A comprehensive guide for sampling methods*. WRC Report No. TT 303/07, South Africa.
- 17 Murray-Darling Basin Commission, 1997. *Murray-Darling Basin groundwater quality sampling guidelines*, Technical Report No. 3, MDBC Groundwater Working Group, Commonwealth of Australia.
- 18 Standards Australia, 1998. *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.
- 19 Victorian Environment Protection Authority, 2000. *Groundwater sampling guidelines*, Publication Number 669, (EPA Victoria), Melbourne.
- 20 Weaver, J.M.C., 1992. *Groundwater sampling: a comprehensive guide for sampling methods*. Report TT 54/92, Water Research Commission, Pretoria.
- 21 Cramer, J.J., Smellie, J.A.T. (Ed.), 1994. *Final Report of the AECL/SKB Cigar Lake Analog Study*. (Tech. Rep SKB TR 94-04), AECL, Pinawa, Manitoba, Canada.
- 22 Nordstrom, D.K., McNutt, R.H., Puigdomènech, I., Smellie, J.A.T., Wolf, M., 1992. *Groundwater chemistry and geochemical modelling of water-rock interactions at the Osamu Utsumi mine and the Morro do Ferro analogue study sites, Poços de Caldas, Minas Gerais, Brazil*. *J. Geochem. Explor.* 45, 249-287.
- 23 Bottomley, D.J., Graham, B.W., Ross, J.D., 1980. *Investigations into the geochemistry of groundwater in precambrian crystalline rocks*, AECL Tech. Rec. TR-122, Atomic Energy of Canada Ltd., Pinawa, Manitoba, Canada.

- 24 Bottomley, D. J., Ross, J. D., Graham, B. W., 1984. A borehole methodology for hydrogeochemical investigations in fractured rock. *Water Resour. Res.* 20, p 1277-1300.
- 25 Gascoyne, M., 1994. Isotopic and geochemical evidence for old groundwaters in a granite on the Canadian Shield. *Mineral. Mag.* 58A, 319-320.
- 26 Gascoyne, M., 1997. Evolution of redox conditions and groundwater composition in recharge/discharge environments on the Canadian Shield. *Hydrogeol. J.* 5, 4-18.
- 27 Gascoyne, M., 2004. Hydrogeochemistry, groundwater ages and sources of salts in a granitic batholith on the Canadian Shield, southeastern Manitoba. *Appl. Geochem.* 19, 519-560.
- 28 Gascoyne, M.G., Elliot, L.C.M., 1986. A simple well-water dilution model. Atomic Energy of Canada Limited Technical Record, TR-391.
- 29 Gascoyne, M., Davison, C.C., Ross, J.D., Pearson, R., 1987. Saline groundwaters and brines in plutons in the Canadian Shield. In *Saline Water and Gases in Crystalline Rocks*, P. Fritz and S.K. Frappe (Editors), Geological Association of Canada Special Paper, 33, pp. 53-68.
- 30 Ross, J.D., Gascoyne, M., 1993a. Methods for sampling and analysis of groundwater in the Canadian nuclear fuel waste management program. Atomic Energy of Canada Limited Technical Record, TR-588, COG-93-36.
- 31 Ross, J.D., Gascoyne, M., 1993b. Comparison of surface and downhole electrochemical measurements in research area groundwater on the Canadian Shield. Atomic Energy of Canada Limited Technical Record, TR-591, COG-93-59.
- 32 Ross, J. D., Gascoyne, M., 1995. Methods for sampling and analysis of groundwaters in the Canadian Nuclear Fuel Waste Management Program. Atomic Energy of Canada Limited Technical Record TR-588, COG-93-36.
- 33 Whitaker, S. H., Brown, A., Davison, C. C., Gascoyne, M., Lodha, G. S., Stevenson, D.R., Thorne, G. A., Tomsons, D., 1994. AECL strategy for surface-based investigations of potential disposal sites and the development of a geosphere model for a site. SKB, Technical Report TR 94-18, Svensk Kärnbränslehantering AB, Stockholm, Sweden.

- 34 Baeyens, B., Bradbury, M.H., 1991. Characterisation of downhole water samples taken during pumping tests from borehole SB4, Wellenberg: Can the groundwater chemistry be deduced from such measurements? Nationale Genossenschaft f_r die Lagerung radioaktiver Abf_lle (NAGRA) Internal Report 91-38, Wettingen, Switzerland.
- 35 Blaser, P., Scholtis, A., 1991. Sondierbohrung Siblingen: Dokumentation der Wasserprobenentnahmen und Interpretation der hydrochemischen und isotopenhydrologischen Analysen. Nagra Technischer Bericht NTB 91-22, 54 p., Nagra, Wettingen, Schweiz.
- 36 Kickmaier, W., Alexander, W.R., Vomvoris, S., McKinley, I.G., 2001. Grimsel 2000 - status of international projects at the Grimsel Test Site (GTS). Sci. Basis Nucl. Waste Manag. XXIV, 893-900.
- 37 Meyer, J., Mazurek, M., Alexander, W.R., 1989. Ch 2 in The laboratory support for the Grimsel test site migration experiment, (ed. M.H.Bradbury). Nagra Technical Report Series NTB 88-23, Nagra, Wettingen.
- 38 Pearson, F.J. Jr., 1985. Sondierbohrung Bottstein-Results of Hydrochemical Investigations: Analysis and Interpretation. Nagra Technical Report NTB 85-05, 131 p. Nagra, Wettingen, Switzerland.
- 39 Pearson, F.J. Jr., Scholtis, A., 1993. Chemistry of Reference Waters of the Crystalline Basement of Northern Switzerland for Safety Assessment Studies. Nagra Technical Report 93-07.
- 40 Pearson, F.J., Arcos, D., Bath, A., Boisson, J.-Y., Fernández, A.M., Gåbler, H.-E., Gaucher, E., Gautschi, A., Griffault, L., Hernán, P., Waber, H.N., 2003. Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory-Synthesis Report. Reports of the Swiss Federal Office for Water and Geology, Geology Series, No. 5, 321 pp. Bern, Switzerland.
- 41 Pearson, F.J., Balderer, W., Loosli, H.H., Lehmann, B.E., Matter, A., Peters, Tj., Schmassmann, H., Gautschi, A., 1991. Applied Isotope Hydrogeology – A Case Study in Northern Switzerland. Nagra Technical Report 88-01.

- 42 Pearson, F.J. Jr., Lolcama, J.L., Scholtis, A., 1989. Chemistry of Waters in the Bottstein, Weiach, Riniken, Schafisheim, Kaisten and Leuggem Boreholes: A Hydrochemically Consistent Data Set. Nagra Technical Report NTB 86-19, 102 p. Nagra, Wettingen, Switzerland.
- 43 Scheweingruber, M., 1984. Deep-crystalline reference water for project "Gewahr". Eidgenossisches Institut für Reaktorforschung, Würenlingen, Switzerland, Technical Report TM-45-84-21, 8 p.
- 44 Witiwer, C., 1986. Sondierbohrungen, Bottstein, Weiach, Riniken, Schafisheim, Kaisten, Leuggem: Probenahmen und Chemische Analysen von Grundwassern aus den Sondierbohrungen. Nagra Technischer Bericht NTB 85-49, 142 p. Nagra, Wettingen, Schweiz.
- 45 Alexander, W.R., Neall, F.B., 2007. Assessment of potential perturbations to Posiva's SF repository at Olkiluoto caused by construction and operation of the ONKALO facility. Posiva Working Report 2007-35, Posiva Oy, Olkiluoto, Finland.
- 46 Hinkkanen, H., Öhberg, A., Ikonen, A., Heikkinen, E., Helenius, J., 1996. Investigation methods and equipment used in the detailed site investigations 1993-1996, summary report. Posiva Oy, Eurajoki. Work Report PATU-96-84.
- 47 Laaksoharju, M., Ahonen, L., Blomqvist, R., 1995. Handheld Double Packer Equipment for Water Sampling and Hydraulic Measurements in Deep Borehole, Groundwater Monitoring & Remediation, Vol. XV, No. 2.
- 48 Öhberg, A., 1991. Site investigation equipment developed by Teollisuuden Voima Oy. Tech. Rep. (YJT 91-06), Helsinki, Finland.
- 49 Öhberg, A., Rouhiainen, P., 2000. Posiva groundwater flow measuring techniques. Posiva Working Report 2000-12.
- 50 Öhberg, A., 2006. Investigation Equipment and Methods Used by Posiva. Posiva Working Report 2006-81.
- 51 Paaso, N. (ed.), Mäntynen, M., Vepsäläinen, A., Laakso, T., 2003. Field Manual for the water sampling of Posiva – Updated version 2003, rev. 3 (in Finnish with an English abstract). Olkiluoto, Finland. Posiva Oy. 209 p. Working report 2003-02.

- 52 Pitkänen, P., Snellman, M., Vuorinen, U., 1996. On the origin and chemical evolution of groundwater at the Olkiluoto site. Posiva report 96-14, Posiva Oy, Eurajoki, Finland.
- 53 Posiva, 2003. Baseline conditions at Olkiluoto. Report Posiva 2003-02, Posiva Oy, Helsinki, Finland.
- 54 Posiva, 2005. Olkiluoto Site Description 2004. Report Posiva 2005-03, Posiva Oy, Helsinki, Finland.
- 55 Rouhiainen, P., Lampén, P., Helenius, J., Snellman, M., 1992. Groundwater sampling system - Technical specifications and manual, Rev. III. TVO/Site Investigations, Work report 92-71.
- 56 Ruotsalainen, P., Snellman, M., 1998. Characterisation of deep groundwaters at Olkiluoto and Hästholmen (Finland). New results with PAVE, a sampling equipment maintaining the in situ pressure. 3rd Äspö International Seminar 1998-04-20.
- 57 Ruotsalainen, P., Snellman, M., Helenius, J., Keinonen M., Vaahtera, V., Kuusela, H., Oksa, M., 1994. The Field Guide for the Hydrogeochemical Studies of TVO (in Finnish with an English abstract). Helsinki, Finland: Teollisuuden Voima Oy. 96 p. Working report PATU-94-28.
- 58 TVO, 1992. Final disposal of spent nuclear fuel in the Finnish bedrock, preliminary site investigations. Nuclear Waste Commission of Finnish Power Companies, Helsinki. Report YJT-92-32E.
- 59 Gómez, P., 2002. Impacto de la Mina Ratones (Albalá, Cáceres) sobre las aguas superficiales y subterráneas: modelización hidrogeoquímica. Publicación Técnica N° 06/2000 ENRESA.
- 60 Gómez, P., Martínez, B., Turrero, M.J., 1994. Unidades Móviles para Caracterización Hidrogeoquímica. Publicación Técnica N° 08/94 ENRESA.
- 61 Gómez, P., Turrero, M.J., Martínez, B., Melón, A.M., Mingarro, M., Rodríguez, V., Gordienko, F., Hernández, A., Crespo, M.T., Ivanovich, M., Reyes, E., Caballero, E., Plata, A., Fernández, J.M., 1995. Methodologies used for water sampling and characterization at El Berrocal. Publicación Técnica de ENRESA. El Berrocal Project, Vol II, Hydrogeochemistry, pp. 7-206.

- 62 Gómez, P., Turrero, M.J., Bruno, J. Caballero, E., Crespo, M.T., Gimeno, M.J., Gordienko, F., Hernández, A., Ivanovich, M., Martínez, B., Melón, A., Mingarro, M., Peña, J., Plata, A., Rodríguez, V., Hernán, P., 1997. The Hydrogeochemistry of the El Berrocal site, Spain. EUR Nuclear Science and Technology, El Berrocal Project. EUR 17478 EN.
- 63 Gómez, P., Turrero, M.J., Garralón, A., Melón, A., 1998. Procedimiento de muestreo y caracterización de las aguas de Mina Ratones. CIEMAT/DIAE/54211/7/98, 10-CIE-IF-1-98.
- 64 ANDRA, 2005. Dossier 2005. ANDRA Research on the Geological Disposal of High-Level Long-lived Radioactive Waste - Results and Perspectives; Ref 265VA, Châtenay Malabry, France.
- 65 Beaucaire, C., Pitsch, H., Toulhoat, P., Motellier, S., Louvat, D., 2000. Regional fluid characterisation and modelling of water-rock equilibria in the Boom Clay Formation and in the Rupelian aquifer at Mol, Belgium. *Appl. Geochem.* 15, 667-686.
- 66 Buschaert, S., Giannesini, S., Lavastre, V., Benedetti, L.C., Gaucher, E., Lacroix, M., Lavielle, B., Michelot, J-L., France-Lanord, C., Bourlés, D., Lancelot, J., Benabderrahmane, H., Dewonck, S., Vinsot, A., 2007. The contribution of water geochemistry to the understanding of the regional hydrogeological system. In Lebon P. Ed. A multi-disciplinary approach to the eastern Jurassic border of the Paris Basin Meuse/Haute-Marne. *Mem. Soc. Geol. Fr.* 178, 91-114.
- 67 Gaudiani, P., Delay, J., Mari, J.-L., 2004. DIAPO: Combined pumping and wireline logging for detailed hydrological and hydrogeochemical characterization of wells at the Meuse/Haute-Marne underground research laboratory. *Geophysical Research Abstracts*, 6, 04612. European Geosciences Union.
- 68 Bath, A.H., McCartney, R.A., Richards, H.G., Metcalfe, R., Crawford, M.B., 1996. Groundwater chemistry in the Sellafield area: A preliminary interpretation. *Q. J.Eng. Geol.* 29, S39-S57.
- 69 Nirex, 1994. Report on the regional hydrogeology and geochemistry in the Sellafield area: Phase 2. Nirex report no. 499. Hydrotechnica Report.
- 70 Nirex, 1998a. Sellafield geological investigations: Acquisition of deep borehole groundwater compositions. UK Nirex Limited Science Report SA/97/072.

- 71 Nirex, 1998b. Sellafield geological and hydrogeological investigations: The hydrochemistry of Sellafield: 1997 update. Nirex report no. SA/97/089.
- 72 Richards, H.G., Bath, A.H., 1998. The Hydrogeochemistry of Sellafield: 1997 update. Nirex Report SA/97/089.
- 73 Sutton, J.S., 1996. Hydrogeological testing in the Sellafield area. *Q. J. Eng. Geol.* 29, S29-S38.
- 74 Alexander, W.R., Berry, J.A., Kelly, M.J., Swanton, S., 2011. Review of colloids in the geosphere and their treatment in performance assessment. Report to NDA-RWMD. Serco/TAS/002924/01, Serco, Didcot, UK.
- 75 Bath, A., Metcalfe, R., 2009. NDA-RWMD Geosphere Characterisation Project: Data Acquisition Report: Groundwater. Sampling and Analysis Techniques. Quintessa Report No. QRS-1421A-R2. Report for NDA.
- 76 Fretwell, B., Ingram, R., McCord, J., Rukin, N., Bath, A., Alexander, R., Tellam, J., 2012. Interpretation and Modelling - Hydrochemistry to support dev of integrated site descriptive model. AMEC Report for NDA (Nuclear Decommissioning Authority).
- 77 Golder Associates (UK) Limited, 2010. Report on state-of-the-art in groundwater sampling for colloids, microbes and organics. Report Number 10514270104.500/A.0. Report for the Nuclear Decommissioning Authority Radioactive Waste Management Directorate.
- 78 NDA, 2011a. Proposed strategy for the geoscientific aspects of site characterisation. NDA Report NDA/RWMD/017.
- 79 NDA, 2011b. Site characterisation for a geological disposal facility. Status Report March 2010. NDA Report NDA/RWMD/057.
- 80 Li, H., Horie, Y, Ishii, T., Shimada, J., 1997. Development of an apparatus to measure groundwater qualities in situ and to sample groundwater using boreholes. *Environ. Geol.* 32, 17-22.
- 81 Yoshida, T. and 16 authors, 2005. Development of micro-chemical probe for geological environment diagnosis (2005 fiscal year) Hitachi Corp for JGC, Japan (in Japanese).

- 82 Arthur, R., Iwatsuki, T., Hama, K., Amano, K., Metcalfe, R., Ota, K., 2002. The redox environment of deep groundwaters associated with the Tono uranium deposit, Japan. *Procs. Mat Res Soc Symp, Sci Basis for Nuclear Waste Management XXV*.
- 83 Hama, K., Seo, T., Yusa, Y., 1994. A sampling procedure of formation water and its application to geochemical investigation of groundwater in the Tono area, Japan. *Procs. NEA SEDE Clay Club Workshop, Nottingham, UK, 1994*.
- 84 Iwatsuki, T., Yoshida, H., 1999. Groundwater chemistry and fracture mineralogy in the basement granitic rock in the Tono uranium mine area, Gifu Prefecture, Japan– Groundwater composition, Eh evolution analysis by fracture filling minerals. *Geochem. J.* 33, 19-32.
- 85 Iwatsuki, T., Metcalfe, R., Amano, K., Hama, K., Noda, N., Arthur, R., Sasamoto, H. et al., 2001. Data book on groundwater chemistry in the Tono area. JNC TN 7450 2001-003. JAEA, Tono Geoscience Center, Toki, Japan.
- 86 Sato, T., Sugihara, K., Matsui, H., 1996. Geoscientific studies at the Tono and the Kamaishi mine in Japan. *Proc. 8th ISRM Int. Symp., Volume 1*, 47-52. Balkema, Rotterdam, ISBN 90 5410 5747.
- 87 Hama, K., Kunimaru, T., Metcalfe, R., Martin, A.J., 2007. The hydrogeochemistry of argillaceous rock formations at the Horonobe URL site, Japan. *Phys. Chem. Earth* 32, 170-180.
- 88 Iwatsuki, T., Furue, R., Mie, H., Ioka, S., Mizuno, T., 2005. Hydrochemical baseline condition of groundwater at the Mizunami underground research laboratory (MIU). *Appl. Geochem.* 20, 2283-2302.
- 89 Kunimaru, T., Ota, K., Alexander, W.R., Yamamoto, H., 2010a. Hydrochemistry of the groundwaters from JAEA's Horonobe URL: Data Freeze I - preliminary data quality evaluation of boreholes HDB9, -10 and -11. JAEA Report 2010-035, 2010. JAEA, Tokai, Japan
- 90 Kunimaru, T., Ota, K., Amano, K., Alexander, W.R., 2010b. Development of a QualityManagement System (QMS) for Borehole Investigations: Part 2—Evaluation of Applicability of QMS Methodology for the Hydrochemical Dataset. ASME 2010 13th International Conference on Environmental Remediation and Radioactive Waste Management,

- Tsukuba, Japan, October 3–7, 2010. Volume 2, Paper No. ICEM2010-40065, pp. 159-168; 10 pages, doi:10.1115/ICEM2010-40065.
- 91 Kunimaru, T., Ota, K., Alexander, W.R., Yamamoto, H., 2011. Hydrochemistry of the groundwaters from JAEA's Horonobe URL: Data Freeze II - preliminary evaluation of boreholes HDB1 to HDB8 and field manual for on-site practices. JAEA Report 2011-010, JAEA, Tokai, Japan.
- 92 Ota, K., Amano, K., Niizato, T., Alexander, W.R., Yamanaka, Y., 2010. Development of comprehensive techniques for coastal site characterization (1) Strategic Overview. Proc. ICEM 2010 Conference, ASME, Washington, USA.
- 93 Ota, K., Kunimaru, T., Amano, K., Alexander, W.R., 2011. Development of Quality Management System for Site Characterisation Programmes – experience in Japan. Proc. ICEM 2011 Conference, Reims, France, September, 2011, ASME, Washington, USA.
- 94 Sai, M., Shingu, S., Hagiwara, H., Mizuno, T., 2011. Hydrochemical investigation at the Mizunami Underground Research Laboratory; Compilation of groundwater chemistry in the Mizunami group and Toki granite, fiscal year 2008 (in Japanese) JAEA-Data/Code 2011-003; June 2011, 41p.
- 95 Sasamoto, H., Arthur, R.C., Hama, K., 2011. Interpretation of undisturbed hydrogeochemical conditions in Neogene sediments of the Horonobe area, Hokkaido, Japan. *Appl. Geochem.* 26, 1464-1477.
- 96 Japan Nuclear Cycle Development Institute (JNC), 2000a. H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Project Overview Report, JNC TN1410 2000-001 (2000).
- 97 JNC, 2000b. H12: Project to establish the scientific and technical basis for HLW disposal in Japan: Supporting report 1, geological environment in Japan, Appendix : Techniques for investigating the geological environment.

- 98 Nanjo, I., Amano, Y., Iwatsuki, T., Kunimaru, T., Murakami, H., Hosoya, S., Morikawa, K., 2011. Development of a groundwater monitoring system at Horonobe Underground Research Center (in Japanese), JAEA-Research 2011-048.
- 99 Amano, K., Niizato, T., Yokota, H., Ota, K., Lanyon, B., Alexander, W.R., 2011a. Development of comprehensive techniques for coastal site characterisation: integrated palaeohydrogeological approach for development of site evolution models. Proc. ICEM 2011 Conference, Reims, France, September, 2011, ASME, Washington, USA (*in press*).
- 100 Amano, K., Kunimaru, T., Ota, K., Alexander, W.R., 2011b. Hydrochemistry of the groundwater from JAEA's Horonobe URL 1. Field manual for on-site and off-site practices. Japan Atomic Energy Agency Technical Report, JAEA-Research 2011-0XX (*in press*).
- 101 Almén, K.-E., Andersson, O., Hansson, K., Hohansson, B.-E., Nilsson, G., Wikberg, P., Åhagen, H., 1983. Final disposal of spent nuclear fuel - equipment for site characterisation. SKBF/KBS Technical Report TR 83-44, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 102 Almén, K.E., Andersson, O., Fridh, B., Hohansson, B.-E., Sehlstedt, M., Hansson, K., Olsson, O., Nilsson, G., Wikberg, P., 1986. Site investigations. Equipment for geological, geophysical, hydrogeological and hydrochemical characterization. SKB Tech. Rep. 86-16, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 103 KBS-3, 1983. Final storage of spent nuclear fuel, Parts I-IV (1983). SKB Tech. Reps, Stockholm.
- 104 Laurent, S., 1982. Analysis of groundwater from deep boreholes in Kråkemåla, Sternö and Finnsjön. SKBF/KBS Technical Report TR-82-23, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 105 Laurent, S., 1986. Analysis of groundwater from Deep Boreholes in Klipperås. SKB TR 86-17, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 106 Wikberg, P., Grenthe, S., Axelson, K., 1983. Redox conditions in groundwaters from Svartboberget, Gideå, Fjällveden and Kamlunge. KBS Technical Report, 83-40, Stockholm.

- 107 Smellie, J.A.T., 1983a. Progress report of uranium series disequilibrium studies on surface - and groundwaters from the Kamlunge area, and the groundwaters from the Gideå, Fjällveden and Svartboberget areas. Swedish Geological Company (SGAB) Internal Report, Luleå.
- 108 Smellie, J.A.T., 1983b. Groundwater pump flow-rate and its effects on some physico-chemical parameters - A controlled experiment carried out at Kamlunge. Swedish Geological Company (SGAB). Internal Report IRAP 84055, Luleå.
- 109 Smellie, J.A.T., 1983c. Groundwater pump flow-rate and its effects on some physico-chemical parameters - A controlled experiment carried out at Taavinunnen, Norrbotten. SKBF/KBS Status Report AR 83-45. Stockholm, Sweden.
- 110 Smellie, J.A.T., 1985. Uranium series disequilibrium studies of drillcore Km 3 from the Kamlunge test site, northern Sweden. *Mineral. Mag.* 49, 271-279.
- 111 Nordstrom, D.K., Andrews, J.N., Carlsson, L., Fontes, J.C., Fritz, P., Moser, H., Olsson, T., 1985. Hydrogeological and hydrochemical investigations in boreholes. Final report of the Phase I geochemical investigations of the Stripa groundwaters. Stripa Project Technical Report 85-06, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 112 Nordstrom, D.K., Ball, J.W., Donahoe, R.J., Whitemore, D., 1989. Groundwater chemistry and water-rock interactions at Stripa. *Geochim. Cosmochim. Acta* 53, 1727-1740.
- 113 Smellie, J., Larsson, N.-Å., Wikberg, P., Carlsson, L., 1985. Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Experience from the SKB test sites in Sweden. SKB Tech Rep. 85-11. Stockholm, Sweden.
- 114 Smellie, J.A.T., Gustavsson, E., Wikberg, P., 1987. Ground water sampling during and subsequent to air-flush rotary drilling: hydrochemical investigations at depth in fractured crystalline rock. SKB Status Rep. AR 87-31, Stockholm, Sweden.
- 115 Karlsson, F., Wikberg, P., 1987. Some highlights on the isotope geochemistry studies within the Swedish research program on radioactive waste disposal. *Appl. Geochem.* 2, 25-31.
- 116 Smellie, J.A.T., Wikberg, P., 1991. Hydrochemical investigations at Finnsjön, Sweden. *J. Hydrol.* 126, 129-158.

- 117 Almén, K.-E., Zellman, O., 1991. Äspö Hard Rock Laboratory. Field investigation methodology and instruments used in the pre-investigation phase, 1986-1990. SKB TR 91-21, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 118 Smellie J.A.T., Laaksoharju, M., 1992. Äspö Hard Rock Laboratory. Final evaluation of the hydrogeochemical pre-investigations in relation to existing geologic and hydraulic conditions. SKB TR-92-31, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 119 Almén, K.-E., Olsson, P., Rhen, I., Stanfors, R., Wikberg, P., 1994. Äspö Hard Rock Laboratory. Feasibility and usefulness of site investigation methods. Experiences from the pre-investigation phase. SKB TR 94-24, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 120 Almén, K.-E., Stenberg, L., 2005. Äspö Hard Rock Laboratory. Characterisation methods and instruments. Experiences from the pre-investigation phase. SKB TR 05-11, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 121 Follin, S., Ludvigson, J.-E., Levén, J., 2011. A comparison between standard well test evaluation methods used in SKB's site investigations and the generalised radial flow concept. SKB P 06-54, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 122 Munier, R., Stigsson, M., 2007. Implementation of uncertainties in borehole geometries and geological orientation data in Sicada. SKB R-07-19, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 123 Laaksoharju, M., Smellie, J., Ruotsalainen, P., Snellman, M., 1993. An approach to quality classification of deep groundwaters in Sweden and Finland. SKB TR-93-27, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 124 Smellie, J.A.T., Laaksoharju, M., Snellman, M., Ruotsalainen, P.H., 1999. Evaluation of the quality of groundwater sampling: Experience derived from radioactive waste programmes in Sweden and Finland during 1980-1992. Posiva Tech. Rep. (TR-99-29). Posiva OY, Helsinki, Finland.

- 125 Laaksoharju, M., 1999. Groundwater characterisation and modelling: problems, facts and possibilities. PhD Thesis, Department of Civil and Environmental Engineering, Royal Institute of Technology, Sweden. ISSN 1400-1284.
- 126 SKB, 2000. Geoscientific programme for investigation and evaluation of sites for the deep repository. SKB TR-00-20, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 127 SKB, 2001. Site Investigations: Investigation Methods and General Execution Programme. SKB Technical Report TR-01-29, 264 p. Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 128 Smellie, J., Laaksoharju, M., Tullborg, E.-L., 2002. Hydrogeochemical site descriptive model – a strategy for the model development during site investigations. SKB R-Rep. (R-02-49), Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 129 Laaksoharju, M., Smellie, J., Tullborg, E.-L., Gimeno, M., Hallbeck, L., Molinero, J., Waber, N., 2008a. Bedrock hydrogeochemistry, Forsmark. Site descriptive modelling. SDM-Site Forsmark. SKB Report R-08-47, 158 p. Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 130 Laaksoharju, M., Smellie, J., Tullborg, E.-L., Gimeno, M., Molinero J., Gurban, I., Hallbeck, L., 2008b. Hydrogeochemical evaluation and modelling performed within the Swedish site investigation programme. *Appl. Geochem.* 23, 1761–1795.
- 131 Laaksoharju, M., Smellie, J., Tullborg, E.-L., Wallin, B., Drake, H., Gascoyne, M., Gimeno, M., Gurban, I., Hallbeck, L., Molinero, J., Nilsson, A.-C., Waber, N., 2009. Bedrock hydrogeochemistry Laxemar. Site descriptive model, SDM-Site Laxemar. SKB Report R-08-93, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 132 Nilsson, A.-C., Tullborg, E.-L., Smellie, J., Gimeno, M., Gómez, J., Auqué, L., Sandstrom, B., Pedersen, K., 2011. SFR site investigation. Bedrock Hydrogeochemistry. SKB R-11-06, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 133 Auqué, L.F., Gimeno, M.J., Gómez, J., Nilsson, A.-C., 2008. Potentiometrically measured Eh in groundwaters from the Scandinavian Shield. *Appl. Geochem.* 23, 1820-1833.
- 134 Waber, H.N., Smellie, J.A.T., 2008. Characterisation of porewater in crystalline rocks. *Appl. Geochem.* 23, 1836-1861.

- 135 Waber, H.N., Gimmi, T., Smellie, J.A.T., 2012, Reconstruction of palaeoinfiltration during the Holocene using porewater data (Laxemar, Sweden). *Geochim. Cosmochim. Acta* 94, 109–127.
- 136 Hallbeck, L., Pedersen, K., 2008. Characterization of microbial processes in deep aquifers of the Fennoscandian Shield. *Appl. Geochem.* 23, 1796-1819.
- 137 Hallbeck, L., Pedersen, K., 2012. Culture-dependent comparison of microbial diversity in deep granitic groundwater from two sites considered for a Swedish final repository of spent nuclear fuel. *FEMS Microbiol. Ecol.* 81, 66-77.
- 138 Drake H., Tullborg, E.-L., 2009. Paleohydrogeological events recorded by stable isotopes, fluid inclusions and trace elements in fracture minerals in crystalline rock, Simpevarp area, SE Sweden. *Appl. Geochem.* 24, 715-732.
- 139 Drake, H., Tullborg, E.-L., Hogmalm, J., Åström, M., 2012. Trace metal distribution and isotope variations in low-temperature calcite and groundwater in granitoid fractures down to 1 km depth. *Geochim. Cosmochim. Acta* 84, 217-238.
- 140 Drake H., Åström, M., Tullborg E.-L., Whitehouse M. J., Fallick A.E., 2013. 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. *Geochim. Cosmochim. Acta* 102, 143–161.
- 141 Sandström, B., Tullborg, E.-L., 2009. Episodic fluid migration in the Fennoscandian Shield recorded by stable isotopes, rare earth elements and fluid inclusions in fracture minerals at Forsmark, Sweden. *Chem. Geol.* 266, 135–151.
- 142 Sandström, B., Tullborg, E.-L., Smellie, J., MacKenzie, A.B., Suksi, J., 2008. Fracture mineralogy of the Forsmark site. SDM-Site Forsmark. SKB Report R-08-102, Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 143 Tullborg, E.-L., Drake, H., Sandstrom, B., 2008. Palaeohydrogeology: A methodology based on fracture mineral studies. *Appl. Geochem.* 23, 1881-1897.

- 144 Gimeno, M.J., Auqué, L.F., Acero, P., Gómez, J., 2014. Hydrogeochemical characterisation and modelling of groundwaters in a potential geological repository for spent nuclear fuel in crystalline rocks (Laxemar, Sweden). *Appl. Geochem.*, 45, 50-71.
- 145 Gómez, J.B., Gimeno, M.J., Auqué, L.F., Acero, P., 2014. Characterisation and modelling of mixing processes in groundwaters of a potential Geological Repository for Nuclear Wastes in crystalline rocks of Sweden. *Sci. Total Environ.* 468–469, 791–803.

Supplementary Material 2: **Drilling and after drilling procedures**

This file contains some detailed description on different steps of the drilling and after drilling procedures (see Figure 1 in the main paper), including the issues about the flushing water and the cleaning, that complement the summary included in the main paper.

SM2.1 THE FLUSHING WATER

One of the most important aspects when evaluating groundwater samples and groundwater data from core boreholes drilled from the ground surface is the degree of contamination with flushing water and its impact on the groundwater chemistry and sample representativity. Typically, about 1,000 m³ flushing water (spiked with sodium fluorescein as tracer) is used for a 1,000 m long SKB type telescopic core borehole drilled from the ground surface. About twice this volume (2,000 m³) is discharged (depending on water yield) from a borehole during gas-lift pumping from the uppermost 100 m of the borehole at a flow rate between 20 and 50 L/min. The gas-lift pumping removes the return water, i.e. a mixture of flushing water, groundwater and drill cuttings, from the borehole.

The risk of flushing water contamination is much lower in samples collected from boreholes drilled in underground tunnels since the flow direction is out from the borehole due to the hydrostatic overpressure. However, special conditions may arise where contamination is difficult to avoid, for example if two boreholes are hydraulically connected or if there is a hydraulic gradient along the borehole.

In any case, due to contamination risks, the choice of a flushing water source is very important. Two possible strategies are used: 1) flushing water with a chemical composition similar to the groundwater expected to be found in the borehole to minimise the influence on the samples, i.e. flushing water taken from an adjacent percussion borehole, implicitly assuming that the composition will be quite

close, or 2) tap water with much lower concentrations of most components and therefore not likely to affect the interpretation of the groundwater origin (e.g. marine or non-marine signatures). The first alternative has been the most common choice but its main disadvantage is that the groundwater composition is unknown beforehand, and it varies with depth. Consequently, the composition of the flushing water and the groundwater in the borehole being drilled may differ considerably. The second alternative, on the other hand, results in dilution of the groundwater sample. This dilution is usually manageable when interpreting the data. However, parameters such as TOC/DOC may be significantly higher in the tap water and can therefore obstruct the evaluation of the organic component in the formation water. The tap water contribution is also a problem when analysing ^{14}C in organic material and in inorganic carbon.

Another important aspect when selecting the flushing water source is the probable effect of its oxygen content on the groundwater redox conditions. Therefore, nitrogen gas is bubbled into the flushing water (irrespective of its source) before use (cf. Figure SM2.1). An estimation of the impact of the flushing water on the groundwater composition is always carried out during the data interpretation process. A flushing water budget is calculated [146] for each drilled borehole.

With respect to the cleaning, for hydrochemical and microbial investigations the specialised SKB telescopic borehole requires a strict routine of cleanliness and sterility. The down-hole equipment and the flushing water system (see below) undergo rigorous cleaning procedures: 1) the pipe string and drilling crown are steam cleaned before use, 2) the drilling water supply tube line is cleaned and scanned using UV-light for sterilisation (Figure 2), and 3) the bioaccessibility of all the used chemical products are also thoroughly addressed including the choice of lubricants for connecting the pipe string. However, despite these precautions, it would be unrealistic to expect total sterile conditions.

SM2.2. AFTER DRILLING

After drilling (see Figure 1 in the main manuscript), the boreholes are usually cleared of rock debris and drilling water by gas-lift pumping (N_2). The detailed core mapping activity starts as soon as the drill core is removed and transported to the core mapping hall/facility. Hydrochemical logging (tube sampling) is performed relatively early in the investigation sequence with the purpose of obtaining the

composition of the groundwater present along the borehole. Also obtained early in the sequence are data from the different geophysical logging methods which are needed to proceed with the ongoing core mapping activity. The same applies to the differential flow logging which is used, together with the information from the BIPS logging (Borehole Image Processing System), to select the water yielding fracture(s) to be hydrochemically characterised and to isolate suitable borehole sections to be investigated. Extensive hydrochemical characterisation (Complete Chemical Characterisation or CCC) implies investigations in one packed-off borehole section at a time, and most often it also includes colloid, gas and microbial studies.

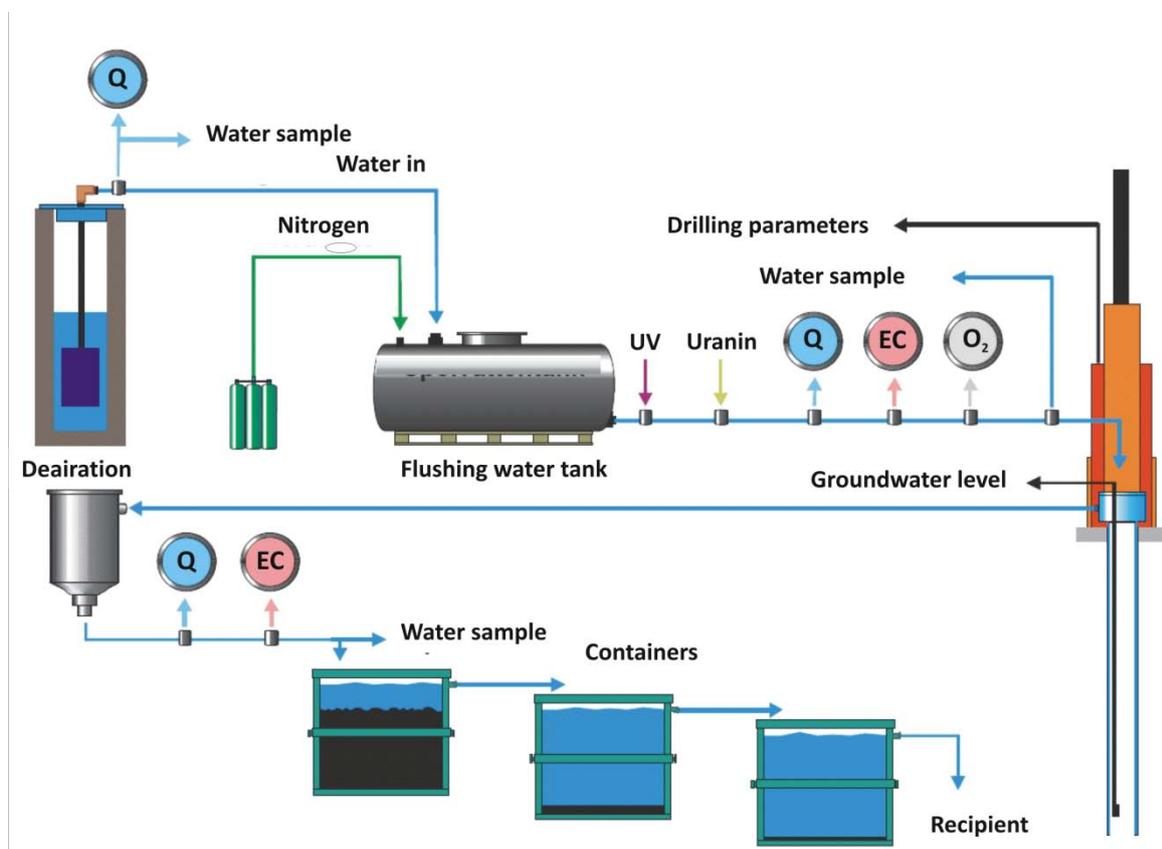


Figure SM2.1. Schematic outline of the flushing water line and the treatment of returned water. The different measurement stations and sampling points are also displayed (modified from drilling method description SKB MD 640.001) UV = Ultra Violet light used for sterilisation, Uranine = injection location for uranine (sodium fluoresceine; the flushing water is spiked with uranine as tracer), Q = water flow rate measurement, EC = Electrical Conductivity measurement, O₂ = dissolved oxygen measurement. Figure courtesy of Göran Nilsson.

Once the main hydrochemical characterisation campaign has finished, other more extensive hydraulic tests are performed that are likely to contaminate the groundwater; these include injection and interference tests and groundwater flow measurements. These are not performed until any pressure disturbances caused by water sampling have disappeared, i.e. if water sampling has been carried out for two weeks, then the hydraulic tests are postponed for at least another two weeks after the water sampling.

When the above basic investigation activities have finished, fixed packer equipment is installed to prevent groundwater flow along the borehole and ultimately to allow regular groundwater level monitoring, sampling and flow measurements in the packed-off borehole sections. Thereafter, hydrochemical monitoring is performed in selected borehole sections (i.e. regular yearly sampling; [147]).

REFERENCES

- 146 Nilsson, A-C., 2008. Forsmark site investigation: Analytical uncertainties. In: B. Kalinowski (Ed) Background complementary hydrogeochemical studies. SKB Report R-08-87. pp. 139-154. Svensk Kärnbränslehantering AB, Stockholm, Sweden.
- 147 SKB, 2007. RD&D Programme 2007. Programme for research, development and demonstration of methods for the management and disposal of nuclear waste. SKB Technical Report TR-07-12, 509 p. Svensk Kärnbränslehantering AB, Stockholm, Sweden.

Supplementary Material 3: **Supplementary Tables**

This file includes two tables that give detailed information on some of the methodological aspects treated in the paper, specifically in 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. Table SM3-2 displays an example of cornerstone criteria that were found to be relevant independently of the type of dataset.

Table SM3-1. List of components usually analysed in the hydrochemical investigations. Many elements may be determined by more than one ICP technique depending on concentration range. The most relevant technique and measurement uncertainty for the concentrations normally encountered in groundwater are indicated. In cases where two techniques were frequently used, both are displayed under the Method column. The analyses generally follow the standards from the Swedish Standards Institute (SIS) and Comité Européen de Normalisation (EN) or the US Environmental Protection Agency (USEPA). Reporting limits (RL) are generally 10×standard deviation. Measured values below RL or DL are stored as negative values in SICADA (i.e. –RL value and –DL value). The reporting limits are given if not otherwise stated. Measurement uncertainty reported by the laboratory is generally as ±percent of measured value in question at 95% confidence interval, calculated according to the EURACHEM/CITAC guide (2000).

Component	Method*	Reporting limits (RL), detection limits (DL) or range	Units	Measurement uncertainty
pH	Potentiometric	3-10	pH unit	±0.1
EC	Conductivity meter	1-150 150-10,000	mS/m	5% 3%
HCO ₃	Alkalinity titration	1	mg/L	4%
Cl ⁻	Mohr- titration	≥ 70	mg/L	5%
Cl ⁻	IC	0.5 – 70	mg/L	8%
SO ₄	IC	0.5	mg/L	12%
Br ⁻	IC	DL 0.2, RL 0.5	mg/L	15%
Br	ICP SFMS	0.001, 0.004, 0.010 ¹	mg/L	25% ²
F ⁻	IC	DL 0.2, RL 0.5	mg/L	13%
F ⁻	ISE	DL 0.1, RL 0.2	mg/L	12%
I ⁻	ICP SFMS	0.001, 0.004, 0.010 ¹	mg/L	25% ²
Na	ICP AES	0.1	mg/L	13%
K	ICP AES	0.4	mg/L	12%
Ca	ICP AES	0.1	mg/L	12%
Mg	ICP AES	0.09	mg/L	12%
S(tot)	ICP AES	0.16	mg/L	12%
Si(tot)	ICP AES	0.03	mg/L	14%
Sr	ICP AES	0.002	mg/L	12%
Li	ICP AES	0.004	mg/L	12.2%
Fe	ICP AES	0.02	mg/L	13.3% ³
Fe	ICP SFMS	0.0004, 0.002, 0.004 ¹	mg/L	20% ²
Mn	ICP AES	0.003	mg/L	12.1% ²
Mn	ICP SFMS	0.00003, 0.00004, 0.0001 ¹	mg/L	53% ³
Fe(II), Fe(tot)	Spectrophotometry	DL 0.006, RL 0.02	mg/L	0.005 (0.02-0.05 mg/L) 9% (0.05-1 mg/L) 7% (1-3 mg/L)
HS-	Spectrophotometry, SKB	SKB DL 0.006, RL 0.02	mg/L	30%
HS-	Spectrophotometry, external laboratory	0.01	mg/L	0.02 (0.01-0.2 mg/L) 12% (>0.2 mg/L)
NO ₂ as N	Spectrophotometry	0.1	µg/L	2%
NO ₃ as N	Spectrophotometry	0.2	µg/L	5%
NO ₂ +NO ₃ as N	Spectrophotometry	0.2	µg/L	0.2 (0.2-20 µg/L) 2% (> 20 µg/L)
NH ₄ as N	Spectrophotometry, SKB	11	µg/L	30% (11-20 µg/L) 25% (20-50 µg/L) 12% (50-1200 µg/L)
	Spectrophotometry external laboratory	0.8	µg/L	0.8 (0.8-20 µg/L) 5% (> 20 µg/L)
PO ₄ as P	Spectrophotometry	0.7	µg/L	0.7 (0.7-20 µg/L) 3% (> 20 µg/L)
SiO ₄	Spectrophotometry	1	µg/L	2.5% (>100 µg/L)
O ₂	Iodometric titration	0.2 – 20	mg/L	5%

Table SM3-1. Continuation.

Component	Method	Reporting limits (RL), detection limits (DL) or range	Units	Measurement uncertainty
O ₂	Iodometric titration	0.2 – 20	mg/L	5%
Al	ICP SFMS	0.2, 0.3, 0.7 ¹	µg/L	17.6% ³
Zn	ICP SFMS	0.2, 0.8, 2 ¹	µg/L	15.5, 17.7, 25.5% ³
Ba, Cr, Mo,	ICP SFMS	0.01, 0.04, 0.1 ¹	µg/L	Ba 15% ¹ , Cr 22% ² Mo 39% ³
Pb	ICP SFMS	0.01, 0.1, 0.3 ¹	µg/L	15% ³
Cd	ICP SFMS	0.002, 0.02, 0.5 ¹	µg/L	15.5% ³
Hg	ICP AFS	0.002	µg/L	10.7% ³
Co	ICP SFMS	0.005, 0.02, 0.05 ¹	µg/L	25.9% ³
V	ICP SFMS	0.005, 0.03, 0.05 ¹	µg/L	18.1% ³
Cu	ICP SFMS	0.1, 0.2, 0.5 ¹	µg/L	14.4% ³
Ni	ICP SFMS	0.05, 0.2, 0.5 ¹	µg/L	15.8% ³
P	ICP SFMS	1, 5, 40 ¹	µg/L	16.3% ³
As	ICP SFMS	0.01 (520 mS/m)	µg/L	59.2% ³
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	ICP SFMS	0.005, 0.02, 0.05 ¹	µg/L	20%, 20%, 25% ³
Sc, In, Th	ICP SFMS	0.05, 0.2, 0.5 ¹	µg/L	25% ³
Rb, Zr, Sb, Cs	ICP SFMS	0.025, 0.1, 0.25 ¹	µg/L	15%, 20%, 20% ² 25% ³
Tl	ICP SFMS	0.025, 0.1, 0.25 ¹	µg/L	14.3% ^{2 and 3}
Y, Hf	ICP SFMS	0.005, 0.02, 0.05 ¹	µg/L	15%, 20%, 20% ² 25% ³
U	ICP SFMS	0.001, 0.005, 0.01 ¹	µg/L	13.5%, 14.3%, 15.9% ² 19.1%, 17.9%, 20.9% ³
DOC	UV oxidation, IR detection Carbon analysator	0.5	mg/L	8%
TOC	UV oxidation, IR detection Carbon analysator	0.5	mg/L	10%
δ ² H	MS	2	‰ SMOW ⁴	0.9 (one standard deviation)
δ ¹⁸ O	MS	0.1	‰ SMOW ⁴	0.1 (one standard dev.)
³ H	LSC	0.8	TU ⁵	0.8
δ ³⁷ Cl	AMS	0.2	‰ SMOC ⁶	0.2 ¹²
δ ¹³ C	AMS	-	‰ PDB ⁷	0.3 ¹²
¹⁴ C pmc	AMS	-	PMC ⁸	0.4 ¹²
δ ³⁴ S	MS	0.2	‰ CDT ⁹	0.4 (one standard dev.)
⁸⁷ Sr/ ⁸⁶ Sr	TIMS	-	No unit (ratio) ¹⁰	0.00002
¹⁰ B/ ¹¹ B	ICP SFMS	-	No unit (ratio) ¹⁰	-
²³⁴ U, ²³⁵ U, ²³⁸ U, ²³² Th, ²³⁰ Th	Alfa spectr.	0.0001	Bq/L ¹¹	≤5% (Counting statistics uncertainty)
²²² Rn, ²²⁶ Ra	LSC	0.015	Bq/L	≤5% (Counting statistics uncertainty)

* Analytical methods abbreviations:

AMS: Accelerator Mass Spectrometry
 IC: Ion Chromatography
 ICP-AES: Inductively Coupled Plasma Atomic Emission Spectrometry
 ICP-AFS: Inductively Coupled Plasma Atomic Fluorescence Spectrometry
 ICP-SFMS: Inductively Coupled Plasma Sector Field Mass Spectrometry
 ISE: Ion Selective Electrode
 LSC: Liquid Scintillation Counting
 MS: Mass Spectrometry
 TIMS: Thermal Ionisation Mass Spectrometry

Table SM3-1. Continuation.

1. Reporting limits at electrical conductivity 520 mS/m, 1440 mS/m and 3810 mS/m respectively.
2. Measurement uncertainty at concentrations 100×RL
3. Measurement uncertainty at concentrations 10×RL
4. Per mille deviation from SMOW (Standard Mean Oceanic Water). Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as: $\delta^y\text{‰} = 1000 \times (K_{\text{sample}} - K_{\text{standard}}) / K_{\text{standard}}$, where K= the isotope ratio and $y = {}^2\text{H}$, ${}^{18}\text{O}$, ${}^{37}\text{Cl}$, ${}^{13}\text{C}$ or ${}^{34}\text{S}$ etc.
5. TU=Tritium Units, where one TU corresponds to a tritium/hydrogen ratio of 10⁻¹⁸ (1 Bq/L Tritium = 8.45 TU).
6. Per mille deviation from SMOC (Standard Mean Oceanic Chloride).
7. Per mille deviation from PDB (the standard PeeDee Belemnite).
8. The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: $\text{pmC} = 100 \times e^{((1950-y) \cdot 1.031) / 8274}$ where y = the year of the C-14 measurement and t = C-14 age.
9. Per mille deviation from CDT (the standard Canyon Diablo Troilite).
10. Isotope ratio without unit.
11. The following expressions are applicable to convert activity to concentration; for uranium-238 and thorium-232: 1 ppm U = 12.4 Bq/kg ²³⁸U, 1 ppm Th = 3.93 Bq/kg ²³²Th.
12. SKB estimation from duplicate analyses by the contracted laboratory.

Table SM3-2. An example of a criteria table with category grading. Each criterion has its grade and the final category grading for the sample is determined by the worst grade/highest number. The table presented here is derived from similar tables developed during past SKB site investigations (Table 3-2 in [148]; Table 4-1 in [149]; Table 3-2 in [150]; and Table A1-1 in [151]). These categorisation criteria should be adapted to the conditions of the specific conditions for each site investigation.

Criteria	Category grade				
	1	2	3	4	5
Drill water					
(<2 %)	X				
(<5 %)		X			
(<10 %)			X		
(>10 %)					X
Sampling method					
Sampling during drilling					X
Sampling in an isolated section in a surface (CCC) or in a tunnel borehole	X				
Monitoring in fixed borehole sections in surface boreholes				X	
Monitoring in fixed borehole sections in tunnel boreholes	X				
Available data (major constituents and basic components with lower concentrations)					
Complete major constituents (Na, K, Ca, Mg, Cl, HCO ₃ ⁻ , SO ₄ ²⁻) and ions with lower concentration (Si, Br, Sr, Li, F, S(II) Fe, Mn).	X				
Ions with lower concentrations are incomplete: one or more of them are missing.		X			
Uncertain pH-value			X		
One of the following components are missing: K, Mg, HCO ₃ , or SO ₄ .				X	
The major constituents are incomplete: more than one of them are missing.					X
Charge imbalance					
>±5% (±10% at <50 mg/L Cl)					X
Available isotope data					
Complete: δ ¹⁸ O, δ ² H, ³ H, ¹⁴ C, δ ¹³ C (except in samples with HCO ₃ < 10 mg/L)	X				
δ ¹⁸ O, δ ² H, ³ H		X			
δ ¹⁸ O, δ ² H			X		
Incomplete: lack of δ ¹⁸ O and/or δ ² H				X	
Section length					
(<10 m)	X				
(<20 m)		X			
(<100 m)			X		
(>100 m)				X	
Sample series*					
Adequate number of samples (to follow the development during months- years)	X				
Inadequate number of samples			X		
Time series**:					
Adequate number of samples (at least three samples during days-weeks).	X				
One or two samples				X	
Significant impact from injection of grout (enhanced pH value)					
					X

REFERENCES

Note: the following reports may be downloaded from <http://www.skb.com/publications/>

- [148] Laaksoharju M, Smellie J, Tullborg E-L, Gimeno M, Hallbeck L, Molinero J, Waber N (2008) Bedrock hydrogeochemistry Forsmark. Site descriptive modelling. SDM-Site Forsmark. Report SKB-R-08-47. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co.
- [149] Smellie J, Tullborg E-L, Nilsson A-C, Sandström B, Waber N, Gimeno M, Gascoyne M (2008) Explorative analysis of major components and isotopes. SDM-Site Forsmark SKB R-08-84
- [150] Laaksoharju M, Smellie J, Tullborg E-L, Wallin B, Drake H, Gascoyne M, Gimeno M, Gurban I, Hallbeck L, Molinero J, Nilsson A-C, Waber N (2009) Bedrock hydrogeochemistry Laxemar. Site descriptive modelling. SDM-Site Laxemar. Report SKB-R-08-93. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co.
- [151] Nilsson A-C, Tullborg E-L, Smellie J, Gimeno M J, Gómez J B, Auqué L F, Sandström B, Pedersen K (2011) SFR site investigation. Bedrock hydrogeochemistry. Report SKB-R-11-06. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Co. (SKB).