P-03-94

Forsmark site investigation

Complete hydrochemical characterisation in KFM01A

Results from two investigated sections, 110.1–120.8 and 176.8–183.9 metres

Pia Wacker, Anette Bergelin
ÅF Energi och Miljö AB/Geosigma AB

Ann-Chatrin Nilsson
Geosigma AB

December 2003

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19

ISSN 1651-4416
SKB P-03-94

Forsmark site investigation

Complete hydrochemical characterisation in KFM01A

Results from two investigated sections, 110.1–120.8 and 176.8–183.9 metres

Pia Wacker, Anette Bergelin
ÅF Energi och Miljö AB/Geosigma AB

Ann-Chatrin Nilsson
Geosigma AB

December 2003

Keywords: Groundwater, Measurements on line, "In situ" sampling, Measurements "in situ", Redox potential, Dissolved gas, Humic and fulvic acids, Colloids, Microbes, Chemical analyses, Isotope determinations, AP PF 400-02-38, Field notes No. Forsmark 69.

Summary

Complete chemical characterisation has been conducted in the two sections 110.1–120.8 m and 176.8–183.9 m of borehole KFM01A. Complete chemical characterisation is the most extensive chemical investigation method performed in core drilled boreholes. The method entails pumping, measurements on-line and regular water sampling for chemical analyses in isolated borehole sections during approximately three weeks per section.

The results obtained from the investigation includes on line measurements of redox potential, pH, dissolved oxygen, electric conductivity and water temperature in the borehole section as well as chemical analyses of major constituents, trace components and isotopes. Furthermore, gas content and composition, inorganic colloids as well as humic and fulvic acids were investigated in the groundwater.

The water composition was stable during the entire pumping and sampling period in both borehole sections. The chloride concentrations amounted to approx. 4500 mg/L and 5200 mg/L in the sections at 110.1 and 176.8 m respectively. The redox potential measurements stabilised at practically the same level (–180 to –190 mV) in the two sections. The reducing conditions in the groundwater were proved also by the presence of ferrous iron Fe(+II) at relatively high concentrations in both borehole sections. The content of inorganic colloids was very low or nonexistent and the organic constituents were present as fulvic acids and possibly other low molecular weight organic acids (citric acid, oxalic acid etc).

Sammanfattning

Fullständig kemikarakterisering har utförts i två sektioner av borrhålet KFM01A, nämligen vid 110,1–120,8 m och 176,8–183,9 m. Fullständig kemikarakterisering är den mest omfattande undersökningsmetoden som utförs i kärnborrhål. Metoden innebär pumpning, mätningar on-line och regelbunden vattenprovtagning för kemiska analyser i avmanschetterade borrhålssektioner under cirka tre veckor per sektion.

De resultat som erhållits från undersökningen omfattar on-line mätningar av redoxpotential, pH, syre, elektrisk konduktivitet och temperatur samt kemiska analyser av huvudkomponenter, spårämnen och isotoper. Dessutom undersöktes gasinnehåll och gassammansättning, oorganiska kolloider samt humus och fulvosyror i grundvattnet.

Vattensammansättningen var stabil under pump- och provtagningsperioderna i båda borrhålssektionerna. Kloridhalterna uppgick till ca 4500 och 5200 mg/L i sektionerna vid 110,1 m respektive 176,8 m. Redoxpotential-mätningarna stabiliserade sig vid praktiskt taget samma nivå (–180 till –190 mV) i de två sektionerna. De reducerande förhållandena i grundvattnet bevisas också av närvaron av tvåvärt järn i relativt höga koncentrationer i båda borrhålssektionerna. Halten av oorganiska kolloider var mycket låg eller obefintlig och de organiska komponenterna förekom som fulvosyror eller möjligen andra organiska syror med låg molekylvikt (citronsyra, oxalsyra etc).

Contents

1 Introduction

This document reports performance of and results from the activity: “Complete Chemical Characterisation” of cored borehole KFM01A performed within the site investigation programme at Forsmark /1/. The work was conducted according to activity plan AP PF 400-02-38 (SKB internal controlling document). The report presents hydrochemical data from two borehole sections:

- 110.1–120.8 m
- 176.8–183.9 m

The fieldwork was carried out during the period March 2003–May 2003. Sampling for microbe studies, based on activity plan AP PF 400-02-35 (SKB internal controlling document), was also performed within the present activity. The microbe investigations and results are reported in /2/.

Borehole KFM01A is the first deep (1001.5 m) telescopic borehole drilled at Forsmark /3/. Its location and that of the drilling site DS1 is shown in Figure 1-1. Between 0–100 m the borehole section is percussion drilled and cased with a stainless steel casing with the internal diameter of 200 mm, whereas the 100–1001.5 m interval is core drilled with a diameter of 76 mm.

The borehole is of the so-called SKB chemical-type; see method descriptions MD 620.003 (Method Description for drilling cored boreholes) and MD 610.003 (Method Description for percussion drilling). A SKB chemical-type borehole requires cleaning procedures to be carried out on all downhole equipment to be used in the borehole, both during and after drilling, according to Level 2 in the cleaning instructions outlined in MD 600.004 (Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning). All method descriptions and instructions are SKB internal controlling documents.

Basic borehole information is given in Table 2-1 and the design of the borehole is presented in Appendix 1. A map showing the location of borehole KFM01A, the percussion boreholes and the shallow monitoring wells at drilling site DS1 are presented in Figure 1-2.

Figure 1-1. *The investigation area at Forsmark (approximately the area inside the marked square) including the candidate area selected for more detailed investigations. Drilling sites DS1–3 (BP1–3) are marked with circles.*

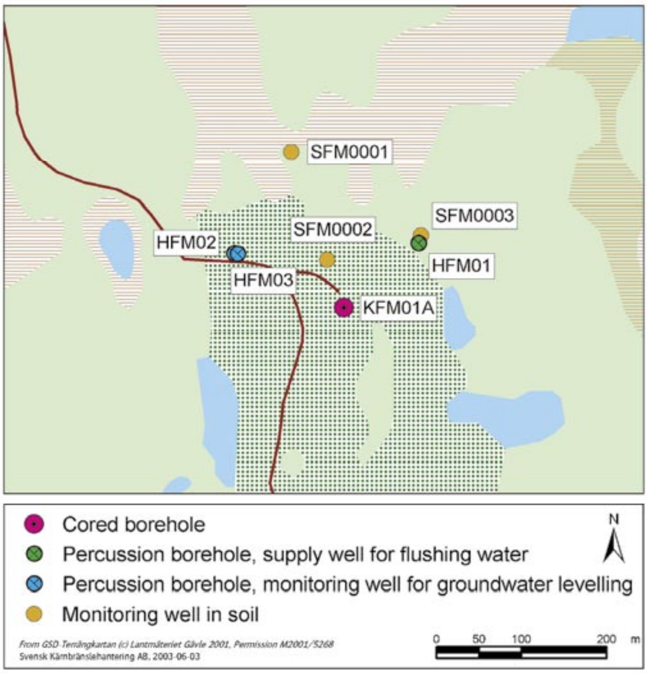


Figure 1-2. *Location of the cored borehole KFM01A, the percussion boreholes and the monitoring wells at drilling site DS1. A second, near-vertical borehole, KFM01B, was drilled at drilling site DS1 after the completion of the hydrochemical characterisation (not included in this map).*

2 Objectives and scope

"Complete Chemical Characterisation" is the most extensive chemical investigation method performed in core drilled boreholes and is carried out in order to obtain as much information as possible about the groundwater chemical conditions in individual water bearing fractures or local fracture zones. Considerable effort is put into obtaining representative samples from a limited rock volume. Careful pumping and continuous control of the pressure in the sampled borehole section, as well as above the section, is maintained in order to minimise the risk of mixing with water from other fracture systems.

According to the original planning of the site investigation in Forsmark, the first core drilled borehole was predestined for chemical investigations. However, borehole KFM01A was found to have unexpectedly few flow yielding fractures in the core drilled part. There was a fear that also the following core drilled boreholes might show similar properties/characteristics. If this was to be the case, there would be a shortage of chemical groundwater data at depth for the subsequent modelling work. Therefore, in order to collect as much data as possible from the borehole, it was important to investigate the two available water bearing fractures at 110.1–120.8 m and 176.8–183.9 m, although the distance between them was relatively short.

The analysis programme is carried out according to the SKB Class 4 and Class 5 levels, including all options. In addition, pH, redox potential (Eh) and water temperature are measured in a downhole flow-through cell as well as at the surface. Surface measurements include also electric conductivity and dissolved oxygen. Furthermore, in-situ samples are collected in the borehole section: a) to determine gas contents and composition, b) for microbe content and characterisation, and c) for determination of colloid content and composition. The in situ samples maintain the pressure of the borehole section when lifted to the surface. Fractionation of humic and fulvic acids as well as inorganic species is performed to obtain information about the size distribution. In addition, enrichment of the organic acids is carried out in order to determine $\partial^{13}C$ and pmC (percent modern carbon).

3 Background

3.1 Flushing water history

The percussion drilled borehole HFM01, see Figure 1-2, served as the supply well for the flushing water used for the drilling of borehole KFM01A /4/. The chemical composition of the flushing water was checked before and during use and the analytical data from the supply well HFM01 are reported in /5/. The core drilling of the 1000 m long borehole consumed 999 m^3 of flushing water and the volume of returned water pumped from the borehole during drilling was 1030 m^3. The nominal concentration of the dye Uranine, added as a tracer to mark the flushing water, was 0.2 mg/L. The Uranine concentration in the flushing water was checked regularly during the drilling and a total of 64 samples were analysed and the average Uranine concentration in the samples was 0.194 ± 0.014 mg/L. The total amount of Uranine added to the borehole via the flushing water was 186 g and the amount that was recovered in the return water was roughly estimated to be 142 g. In Figure 3-1, the cumulative amount of Uranine introduced in the borehole and recovered in the return water is plotted versus borehole length.

The Uranine budget in the diagram below suggests that about 220 m^3 flushing water was lost in the borehole. However, in this particular borehole, this cannot be the case since the yield of water from the borehole itself is extremely small and the volume of return water pumped out is somewhat larger than the volume introduced. A conclusion that can be drawn from the Uranine budget is that a more frequent sampling is needed in order to obtain correct information.

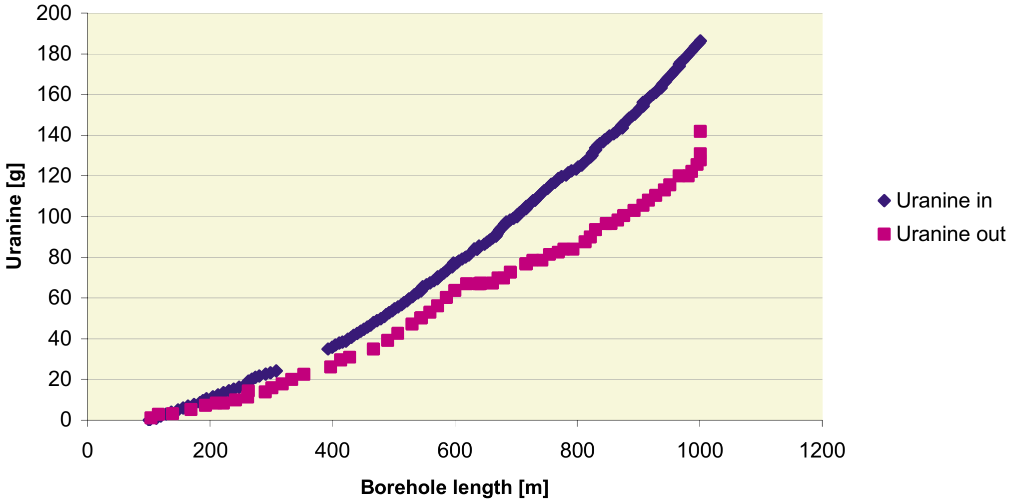


***Figure 3-1.** Cumulated amount of Uranine added to the borehole via the flushing water (in) and in the return water (out) from the borehole plotted versus borehole length.*

As borehole KFM01A is of SKB chemistry type, the following special precautions were taken in order to minimise contamination via the flushing water:

- The supply well was also of SKB chemistry type (entailing special cleaning procedures).
- An active carbon filter system was installed in order to reduce the content of organic components in the pumped groundwater from HFM01. The concentration of total organic carbon (TOC) in the flushing water should be low, preferably below 5 mg/L. The concentration in untreated samples collected in HFM01 was in the range 10–12 mg/L.
- An UV-system for disinfecting the flushing water was mounted in-line before the flushing water tank where the addition of Uranine takes place, see description in /3/. This design was necessary as the dye decomposes by light, although it would be more favourable from a disinfecting point of view to place the UV-system as close to the drilling machine as possible.

Control of microbe content in the flushing water before and after the active carbon filter, after the UV-system and in flushing water tanks was performed during the drilling /6/. The results showed that the UV-system worked very well although growth of algae and bacteria in the water tank placed after the UV-system was considerable.

3.2 Previous events and activities in the borehole

KFM01A is a SKB chemical-type telescopic borehole and thus specially intended for complete hydrochemical characterisation. Only investigations that are necessary in order to select suitable borehole sections are carried out in the borehole prior to the chemistry campaign. The more equipment that is used in the borehole, the greater is the risk of groundwater contamination and effects on the in situ microbiological conditions. The activities/investigations performed in KFM01A prior to the chemistry campaign are listed in Table 3-1 below.

The hydrochemical logging activity included in the basic investigation programme for core drilled boreholes was not performed in this borehole. The downhole electric conductivity measurements that were conducted in connection with the differential flow logging activity, see Table 3-1, revealed that the water column below 300 m consisted of flushing water from the drilling, see also Appendix 2, Figure A2-1. Therefore, it was concluded that hydrochemical logging would not give any further useful information about the initial conditions along the borehole.

Table 3-1. Activities performed in borehole KFM01A prior to the chemistry campaign.

Activities performed	Date of completion	Length (m)	Comment
Percussion drilling	2002-05-22	0–100	A fractured interval was encountered at approx. 48–52 m, which turned out to be heavily water yielding. The flow rate was estimated at approx. 800 L/min at a drawdown of 50–60 m.
Pumping tests and water sampling	2002-05-25	0–100	Sample no SKB 4165 /5/.
Geophysical logging and BIPS logging	2002-05-28	0–51	/7/
Casing installed	2002-06-10	0–100	After the hydraulic tests a casing was installed and the gap between the casing and the borehole wall was cement grouted in order to prevent surface water and shallow groundwater to reach deeper parts of the borehole and further into the formation. The grouting was very successful, thus sealing borehole section 0–100 m completely from water inflow.
Core drilling No Wireline sample	2002-10-28	1001.5	HFM01 was the source of flushing water for drilling the cored part of KFM01A. HFM01 is a SKB chemistry type borehole /3, 5/. Due to the small water yield from KFM01A, it was not possible to collect samples using the WL-sond.
Flushing water treatment	-	-	An active carbon filtering system was used in order to decrease the content of organic components in the flushing water /3/.
Microbe control	2002-10-14	-	Check of microbe content in flushing water /6/.
Differential flow logging	2002-11-28	1000	/8/
BIPS-logging	2002-12-11	1000	/9/
Complete chemical characterisation including sampling for microbe investigation	2003-04-07	-	Presented in this report
Microbe investigation	-	-	/2/

3.3 Choice of borehole sections

During drilling of the core drilled part, it was soon established that KFM01A yields only small amounts of water below the cased and grouted percussion drilled section 0–100 m. The total inflow of water into the borehole, estimated from pumping tests during the drilling, was 1–2 L/min. This inflow appeared between 100 and 200 m during drilling and did not change as the borehole length increased. Results from the subsequent differential flow logging showed that the small inflow was restricted to mainly two water bearing fracture zones. This fact was favourable from a water sampling point of view. The zones were situated at approx. 118 m and approx. 178 m along the borehole, see Appendix 2, Figures A2-2, A2-3 and A2-4.

The zone at 118 m was regarded as suitable for complete chemical characterisation. The flow during the difference flow logging /7/ was about 10 L/h at a drawdown of approx. 10 m. The calculated hydraulic transmissivity (T) for the borehole section 110.1–120.8 m amounts to 9×10^{-8} m^2/s which is sufficient for sampling ($T=10^{-8}$ to $T=10^{-6}$ m^2/s is optimal). As can be seen from the flow logging diagram in Figure A2-2, there are several fractures in the vicinity and therefore it was decided to increase the section length to 10 m to ensure fracture free rock beneath the inflatable packers.

The zone at 178 m was somewhat more doubtful as the corresponding flow was 2 L/h giving a hydraulic transmissivity of $T=5\times10^{-8}$ m^2/s for the section 176.8–183.9 m. However, it was decided to conduct pumping also in this section. There is solid bedrock above and below the fracture zone and a feasible section length of 7 m could be used.

4 Equipment

4.1 The mobile field laboratory

The mobile field laboratories used by SKB for water sampling and downhole measurements consist of a laboratory unit, a hose unit with downhole equipment and a Chemmac measurement system; these are presented schematically in Figure 4-1. It is also possible to include a separate unit for computer work (MYC-wagon). The different parts of equipment are described in the SKB internal controlling documents SKB MD 434.004, 434.005, 434.006, 434.007 and SKB MD 433.018 (Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation).

The Chemmac measurement facilities include a communication system, measurement application and flow-through cells with electrodes and sensors at the surface (surface Chemmac) and downhole (borehole Chemmac).

The downhole equipment consists of inflatable packers, pump, borehole Chemmac and the in situ sampling unit (PVP) allowing measurement (borehole Chemmac) and sampling in situ in the borehole section (PVP sampling unit). The four sample portions collected with the PVP sampling unit maintain the pressure from the borehole section when lifted to the surface. The portions are used for colloid filtration, gas analyses and microbe investigations.

The mobile units used in borehole KFM01A consisted of the hose unit S3, the laboratory unit L3 and the extra MYC 3 unit for computer work. The special parts of equipment used for colloid filtration, enrichment of humic and fulvic acids and fractionation of humic and fulvic acids are described below.

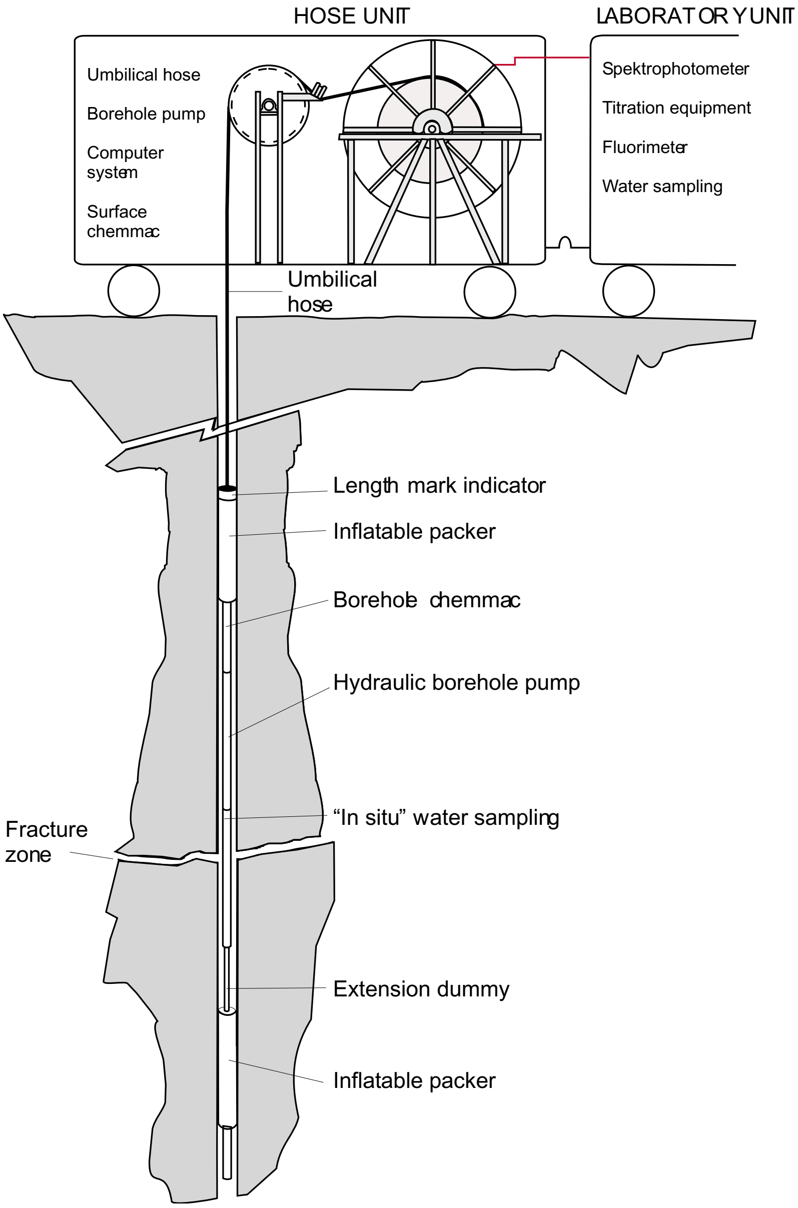


Figure 4-1. *The mobile chemistry laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.*

4.2 Colloid filtering equipment

The colloid filtering system is a prototype and still at the development stage. The equipment is adapted to the sample containers (PVB) belonging to the PVP sampling unit consisting of holders for two PVB-containers, a tube and valve system for water and gas, a filter holder package for five filters, and a collecting container. The pore sizes of the five connected filters are 0.40, 0.40, 0.20, 0.05 and 0.05 µm. The equipment is described in SKB MD 431.045 (Mätsystembeskrivning för kolloidfiltreringssystem, handhavandedel (SKB internal controlling document to be published)). Figure 4-2 shows the equipment setup.

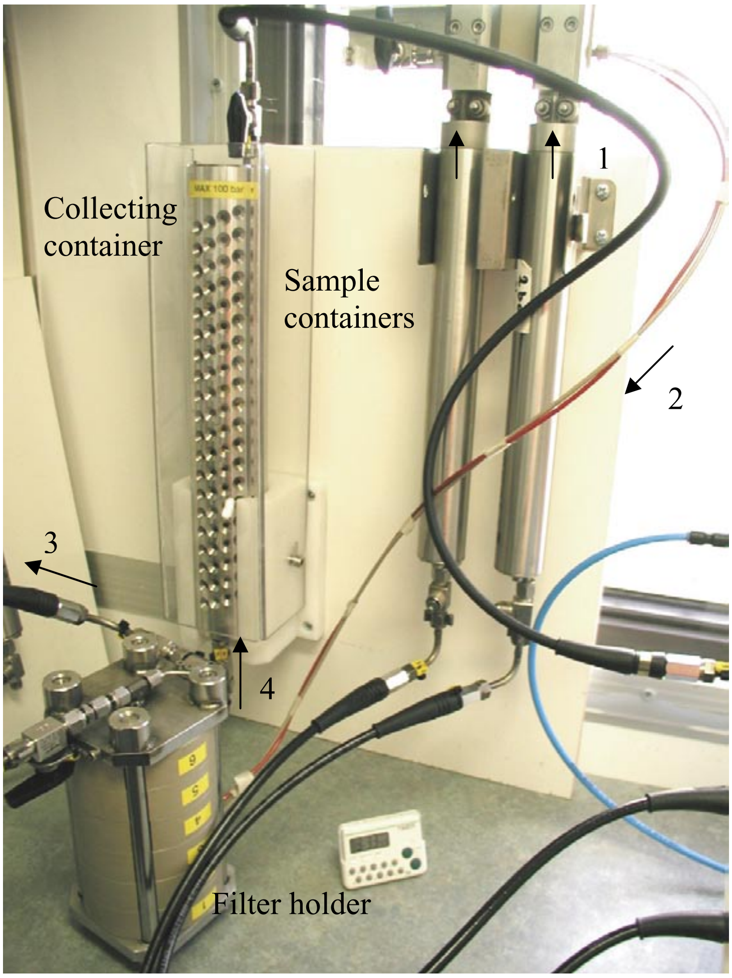


Figure 4-2. *The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1–4, give the flow direction of the sample water through the system.*

The major equipment features are:

- Filtering is performed in a closed system at argon atmosphere thus avoiding the risk of iron precipitation due to contact between the groundwater sample and air.
- Filtering is performed at a pressure similar to that of the groundwater in the borehole section since the sample container maintains the pressure. The system is adjusted to create a pressure difference between the inlet of the filter package and the outlet side and the pressure difference drives the sample water through the filters.
- The design of the sample containers and the mounting with the outlet at the top prevents migration of the larger particles, which may clog the filters. Furthermore, clogging is prevented also by the first two filters with pore size 0.40 µm which are mounted parallel to each other.

Disadvantages/drawbacks, which may cause modifications of the equipment later on, are:

- The sample volume is limited to maximum of 2×190 mL.
- The PVB sample containers are made of stainless steal and contamination may occur. If the filtering method proves to be successful, an improvement would be to use Teflon coating on the inside of the cylindrical containers.

4.3 Equipment for enrichment of humic and fulvic acids

The enrichment of humic and fulvic acids is conducted in order to collect enough material to determine ∂^{13}C and pmC on organic constituents in the groundwater. The equipment for enrichment includes a porous column and a textile filter with defined pore size and filled with an anion exchanger (DEAE-cellulose). The textile filter is placed inside the column in order to prevent the ion exchange resin from diffusing through the column. The equipment and performance is described in SKB MD 431.044 (Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror, SKB internal controlling document). Figure 4-3 shows the equipment setup.

Figure 4-3. *The ion exchange column mounted to the outlet of pumped groundwater from the borehole section.*

4.4 Equipment for fractionation of humic and fulvic acids

The equipment consists of membrane filters with defined cut off (pore size), a peristaltic pump, flexible tubing and vessels. Generally, one water sample from each section is filtered through two filters with different cut off pore sizes (1000 D and 5000 D). The equipment and performance is described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror, SKB internal controlling document). Figure 4-4 presents the equipment setup.

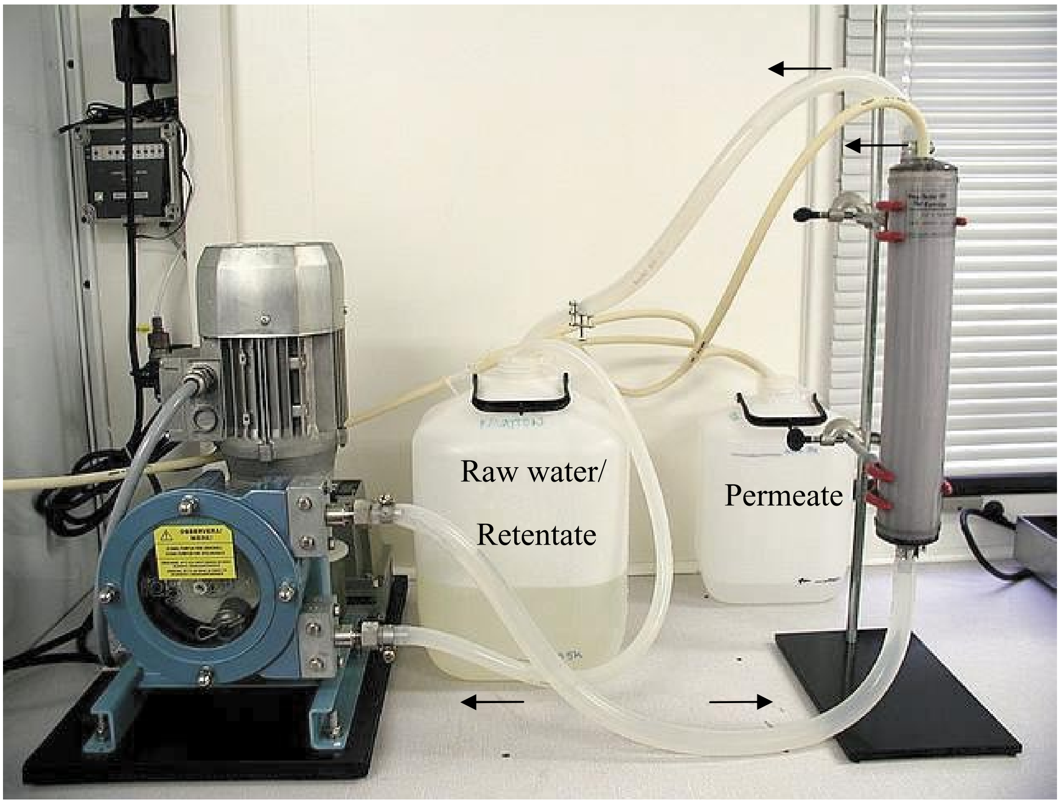


Figure 4-4. *Equipment for fractionation of humic and fulvic acids.*

5 Performance

Complete chemical characterisation in KFM01A was performed according to activity plan AP PF 400-02-38 (SKB internal controlling document) following the method described in SKB MD 430.017 (Metodbeskrivning för fullständig kemikarakterisering med mobilt fältlaboratorium, SKB Internal Control Document).

5.1 Overview of field work procedure

A short chronological summary of the different steps that constitute complete chemical characterisation of groundwater in a borehole section is given below.

The preparations that are conducted before the downhole equipment is lowered in the borehole include:

- Cleaning of the inside of the umbilical hose (the sample water channel) with minimum 2 ppm sodium hypochlorite solution followed by rinsing with de-ionised, deoxygenated water. Finally, the sample water channel is filled with de-ionised and deoxygenised water prior to the lowering.
- Cleaning and preparation of the four sample containers (PVB) belonging to the in situ water sampling unit (PVP). The containers are cleaned using 70% denaturised ethanol. One of the containers will be used for microbe sampling and sterile conditions are desirable. The containers are purged with nitrogen gas and a small nitrogen gas pressure is maintained in the containers. The magnitude of the pressure depends on the depth of the intended section.
- Calibration of the pH and redox electrodes in the borehole Chemmac.

The different downhole units are assembled together during the lowering of the equipment in the borehole and the following steps are taken:

- The outside of the umbilical hose is cleaned with 70% denaturised ethanol (SKB MD 600.004).
- Calibration of the umbilical hose length is conducted at least once for each borehole. For this a length mark detector unit (caliper) is mounted together with the ordinary downhole equipment. The length mark detector indicates the milled length calibration marks situated at almost every 50 m along the borehole /3/. At each indication a reading is made of the corresponding length mark on the umbilical hose. The correct distance to each length mark is obtained from the SICADA database.

When the pump is started and the packers are inflated at the desired positions in the borehole, a minimum pumping and measurement period of three weeks begins. Typical measures taken and activities carried out during this period are:

- Calibration of the pH and redox electrodes as well as the electric conductivity and oxygen sensors in the surface Chemmac is conducted when the pumped water from the borehole section has reached the surface.

- Careful attention is paid in order to make sure that the packed off section is joint tight. A noticeable drawdown in the section during pumping is one indication that the section is isolated. Leakage would cause pumping of water from the borehole column above and/or below the packers and not only from the fracture zone of interest. However, the drawdown in the borehole section must not be too large since the greater the drawdown, the larger the bedrock volume affected by the pumping and the risk of mixing with water from other fracture systems increases. The pumping flow rate is adjusted to between 50 and 300 mL/min depending of the flow yield from the fracture or fracture zone and maintained more or less constant during the pumping and measurement period.
- Water samples are collected regularly twice a week during the pumping period. Changes in water composition are monitored by conductivity measurements and by a few immediate analyses at the site.
- Enrichment of humic and fulvic acids is conducted for as long a time as possible in each section. The time needed depends on the carbon concentration in the water and the flow rate through the ion-exchanger. Generally, a period of at least two weeks is needed to collect the amount of carbon required to determine ∂^{13}C and pmC.
- Fractionation of humic and fulvic acids as well as inorganic species to determine the size distribution, is performed at the end of the pumping period.
- A decision when to terminate the sampling work in the section is made during the third week of the pumping and measurement period. The investigation might be prolonged if the concentration of flushing water exceeds 1% or if the redox potential measurements have not reached stable values. A final SKB Class 5 sample including all options is collected the day before termination.

Completion of the investigation in the section and lifting of the downhole equipment entails:

- Collection of in situ samples is performed prior to lifting the equipment. The valves to the PVB sampling containers in the borehole section are opened from the surface in order to rinse the system and fill the containers. After a few hours, the valves are closed and the water sample portions for analyses of colloids, dissolved gases and microbes are contained.
- Following stopping of the borehole pump and deflation of the packers, the equipment is lifted and the different downhole units are de-assembled.
- Calibration of the electrodes in the borehole and surface Chemmac units. The final calibration for a section can be used as the initial calibration for the next section.

5.2 Performance in section 110.1–120.8 m

The configuration of the downhole units in the borehole was, from the top down; umbilical hose, upper packer, borehole Chemmac, borehole pump, in situ water sampler (PVP), extension dummy and lower packer. Due to this configuration with the two measurement units in the borehole section, the pressure within the section was measured using three sensors, whereas the pressure above the borehole section was not measured at all.

The pumping was performed at a flow rate of about 80–100 mL/min with a drawdown (estimated from the pressure difference before and after inflating the packers) in the borehole section of about 0.7 m. Diagrams showing the flow rate and the pressure in the borehole section during the pumping/measurement period are given in Appendix 3, Figures A3-1 and A3-2.

The events during the pumping and measurement period are listed in Table 5-1.

Table 5-1. Events during the pumping/measurement period in section 110.1–120.8 m.

Date	Events	SKB sample no. *Improvement/deviation*
030113	Calibration of borehole Chemmac.	
030114	Lowering of downhole equipment (110.00–120.67).	
	A wheel on the length mark indicator (caliper) is broken.	
	Lifting.	
030115	Lowering of downhole equipment (110.00–120.67).	
	Calibration of surface Chemmac.	
030116	Lifting.	
	Leakage scanning.	
	Lowering of downhole equipment (110.00–120.67).	
	Leakage observed in packer-system.	
030117	Lifting.	
	Leakage in packer.	1
	Lowering of downhole equipment (110.00–120.67).	
	Water sampling: SKB class 2.	4461
030121	Uneven pump flow. Change of pump circuit breaker.	2
030122	Water sampling: SKB class 3.	4466
	No contact with the measurement system. Installation of new “modbus” application.	3
030127	No communication with the downhole equipment. Faulty coupling is repaired.	4
030129	Momentary stop of borehole pump for change of valve.	
030131	Lifting.	
030203	Lowering of downhole equipment (110.10–120.77 m).	
030207	Water sampling: SKB class 4.	4480
030210	Water sampling: SKB class 5.	4481
030213	Water sampling: SKB class 4.	4484
030217	Water sampling: SKB class 5.	4520
	Humic and fulvic acids; enrichment start.	
030220	Water sampling: SKB class 4.	4524
030224	Water sampling: SKB class 5.	4538
	Humic and fulvic acids; fractionation.	
030225	PVP-sampler; opening of valve at 7:15 and closure at 08:15.	4538
	Humic and fulvic acids; enrichment stop.	
	Lifting.	
	Calibration of surface and borehole Chemmac.	
030226	Humic and fulvic acids; enrichment eluation.	4538
	Colloid filtration.	

5.3 Performance in section 176.8–183.9 m

The configuration of the downhole units in the borehole was, from the top down; umbilical hose, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP), extension dummy and lower packer. The pressures above and within the sampled section were measured using the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping was performed at a flow rate of about 50 mL/min with a drawdown of about 1.3 m. Diagrams showing the flow rate and the pressures within and above the borehole section during the pumping/measurement period are given in Appendix 3, Figures A3-3 and A3-4.

The pumping and measurement period in the section was extended to four weeks due to remaining flushing water in the samples (about 5%) and a sudden decrease in the redox potential measured by one of the six electrodes (the gold electrode) at the end of the third week. The events during the investigation are listed in Table 5-2.

Table 5-2. Events during the pumping/measurement period in section 176.8–183.9 m.

Date	Events	SKB sample no. *Improvement/deviation*
030226	Re-calibration of pH in surface chemmac due to change of pH electrode.	
	Lowering of downhole equipment (176.80–183.90).	
030227	Water sampling: SKB class 2.	4542
030227	*Lack of immersion heater in the water collecting tank. Enrichment of humic- and fulvic acids delayed.*	*4*
030303	Water sampling: SKB class 4.	4610
030305	Humic and fulvic acids; enrichment start.	
030307	Water sampling: SKB class 5.	4620
030311	Water sampling: SKB class 4.	4637
030314	Water sampling: SKB class 5.	4663
030317	Water sampling: SKB class 4.	4664
030320	Water sampling: SKB class 5.	4665
	Momentary stop of borehole pump; change of valve.	
030324	Water sampling: SKB class 4.	4666
030325	Humic and fulvic acids; fractionation.	
030328	Water sampling: SKB class 5.	4700
030331	Water sampling: SKB class 5.	4724
	PVP-sampler; opening of valve at 16:24.	
030401	PVP-sampler; closure of valve at 07:25.	4724
	Humic and fulvic acids; enrichment stop.	
	Lifting.	
	Calibration.	
	Lowering of downhole equipment (176.80–183.90).	
030402	Humic and fulvic acids; enrichment, eluation.	4724
	Colloid filtration.	
030407	Lifting.	
	PVP-sampler; opening of valve at 06:40 and closure at 08:13.	
	Colloid filtration.	

5.4 Water sampling, sample treatment and analyses

The pumped water from the borehole section is led into the laboratory unit where sampling and sample filtration is carried out. Filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. A ‘water sample’ is defined as water collected during one day and consists of several sample portions, labelled with the same sample number.

An overview of sample treatment and analysis routines is given in Appendix 6. The routines are applicable independently of sampling method or sampling objective.

5.5 Collection of in situ water samples

The in situ water sampling was conducted successfully in both of the investigated borehole sections. The sampling was repeated in the deeper section in order to increase the number of samples and test the reproducibility of the colloid filtration method. The samples were collected in the borehole section and lifted to the surface, maintaining the same pressure in the sample as in the sampling section. In the first borehole section, the sample water was allowed to flow through and rinse the PVP-system and its four sample containers (PVB) for a few hours before the valves were closed. In the second section, the rinsing time was 15 hours. The purpose of each sample portion is given in Table 5-3.

It turned out that all the PVB-containers used during the period 2003-02-26 and 2003-04-02 behaved differently and in some cases it was difficult to force the water out. An initial check of the PVB-containers before use was therefore introduced prior to the use 2003-04-07. This procedure includes de-assembling the container, thorough cleaning, re-assembling and measurement of piston friction.

The two PVB-containers for determination of microbes and dissolved gases, respectively, were immediately transported to the relevant laboratories. The PVB-containers were packed together with ice packs in insulated bags and sent by express delivery service. The microbe sample arrived at the laboratory in Gothenburg before three o’clock the same day and the gas sample arrived at the laboratory in Finland the next morning.

Table 5-3. Collection and purpose of in situ water sample portions.

Sample portion No.	**Section 110.1–120.8 m 2003-02-26**	**Section 176.8–183.9 m 2003-04-02**	**Section 176.8–183.9 m 2003-04-07** Initial control of PVB-containers at workshop. The friction of the piston was measured.
1	Dissolved gas No water. One of the valves was not closed.	Dissolved gas	Colloid filtration
2	Microbes	Microbes	Colloid filtration
3	Colloid filtration	Colloid filtration	Colloid filtration
4	Colloid filtration	Colloid filtration	Colloid filtration

5.6 Colloid filtration

The method for sampling of colloids in groundwater entails filtering the groundwater through a series of connected filters in a closed system under an argon atmosphere. The pressure in the system is maintained at the same level as the pressure in the sampled borehole section. The intention is that colloids should be collected on the different filters (descending pore sizes) according to their size. Since the method had not been used earlier under realistic conditions, borehole KFM01A was used to test and verify the method according to the activity plan AP PU 400-03-002 (SKB internal controlling document). Generally, two of the four sample containers (PVB) involved in collecting in situ groundwater in each borehole section are used for colloid filtration. In the second borehole section the lowering of the downhole equipment was repeated to obtain four extra sample portions in order to test the reproducibility of the method. As the water volume of two PVB-containers are used in each filtration, the six containers collected in the second section allowed three filtration runs. Data from the different filtration runs are given below in Table 5-4. Each filtration results in five filter samples (two 0.40 µm, one 0.20 µm and two 0.05 µm filter pore sizes) and two water samples (water in and water out). All samples were sent for ICP analyses (major components and common trace metals); analyses of unused filters and analyses of filters when deionised water has flowed through the system, were used as sample blanks.

The filtering time is an important parameter which is difficult to optimise. For example, it is an advantage if the time is short due to the risk of oxygen intrusion. On the other hand, it is a disadvantage to force the water through the filters as the size distribution may be affected and the risk of broken filters will increase.

Table 5-4. Colloid filtration; performance.

Section/date	Entering pressure (bar)	Max. diff. pressure over filter package (bar)	Temp. (°C)	Filtering time (min)	Filtered volume (ml)	Comments
110.1–120.8 m/ 20030226	~10	4	~8	138	58.7	
176.8–183.9 m/ 20030402	~18,5	7 (the differential pressure was increased from 4 bars during the filtration in order to force the water through the filters)	~9	70	303.5	A small leakage from the filter holder package was noticed during the filtration.
20030407	~18,5	3.9	~9	38	163.5	Leakage test prior to filtration. No leakage was noticed.
20030407	~18.5	5.1	~8	44	319.0	Leakage test prior to filtration. No leakage was noticed. Both the 0.05 µm filters were broken.

5.7 Enrichment of humic and fulvic acids

The enrichment of humic and fulvic acids was conducted in order to collect enough material to determine $\partial^{13}C$ and pmC in organic constituents in the groundwater. The enrichment method entails collection of organic acids on an ion exchanger, eluation of the resin and evaporation of the resulting solution. The method is described in SKB MD 431.044 (Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror). The dry residue is used for the isotope determination; a minimum amount of 10 mg organic carbon is needed. In addition to organic material the residue also contains sodium hydroxide from the eluation. The sample is acidified at the relevant laboratory prior to analysis in order to exclude the carbon dioxide.

The water was allowed to flow through the ion exchanger for 10 days in section 110.1–120.8 m and 24 days in section 176.8–183.9 m. The total water volume is estimated at about 1.5 m^3 in each section. Theoretically, if all carbon is adsorbed by the ion exchange resin it would amount to about 4.5 and 6 g respectively.

5.8 Fractionation of humic and fulvic acids

Humic and fulvic acids were fractionated with respect to molecular weight using an ultra filtration technique. The method is described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror).

Sampled water from the two sections at 110.1–120.8 m and 176.8–183.9 m were filtered through membrane filters with a cut off of 1000 D (Dalton) and 5000 D (D=g/mol). The initial water volumes prior to filtration were approximately 5 litres. The final retentate and permeate volumes following filtration were approximately 1 and 4 litres respectively, which gave an enrichment factor of five in the retentate.

Water samples were collected from the retentate and the permeate as well as from the original groundwater in the borehole section. Each sample was analysed for dissolved organic carbon (DOC), major components and common trace metals. The analyses of metal ions are conducted in order to detect any precipitation of metals that could possibly lead to co-precipitation of the humic and fulvic acids. Furthermore, the analyses of metal ions should indicate if metals such as Al, Si, Mn and Fe exist as colloidal species.

6 Nonconformities

The complete chemical characterisation of the two sections in KFM01A has been conducted according to the SKB internal controlling documents AP PF 400-02-38 and SKB MD 434.004, 434.005, 434.006, 434.007 without any serious deviations. Some equipment malfunctions have occurred during the pumping/measurement periods but none of those will cause decrease in the quality of the data. The equipment malfunctions are listed in Tables 5-1 and 5-2. The flushing water content exceeded the upper limit (1%) for the allowed flushing water content in the section 176.8–183.9 m although this condition has not been reported in a nonconformity report.

7 Data handling

7.1 Chemmac measurement data

7.1.1 Data file types and calculation software

The on-line measurement in one borehole section produces the following types of raw data files:

- Calibration files (altogether 16 files) from calibration measurements (*.CRB) and corresponding comment files (also 16 files) (*.CI). The files are used for calculation of calibration constants (pH and Eh) and the calibration factor (electric conductivity).
- Raw data file containing the logged data measurements from the borehole section and the surface (*K.MRB) as well as a corresponding comment file (*.MI). The logged voltage values need to be recalculated to pH and Eh (also in mV) using the calibration constants obtained from calibration.
- Measurement file including equipment and environment parameters (*O.MRB) such as power consumption in the downhole Chemmac unit and temperature inside the hose unit.

The original raw data files as listed above are stored in the SICADA file archive. Furthermore, the files are recalculated and evaluated to obtain pH and redox potential values and to correct the electric conductivity values using the specially designed calculation software (Hilda). The resulting files containing calculated and evaluated values as well as comments on the performance are:

- A file **constants.mio* containing all the calculated calibration constants (one constant for each electrode in each buffer solution). The file is stored in the SICADA file archive and is useful in order to follow the development of single electrodes.
- A file **measurements.mio* containing the calculated and evaluated measurement values (pH, redox potential, electric conductivity and water temperature). The data from the file are exported to the data tables "redox" and "ph_cond" in SICADA. As the file contains some measured parameters that are not included in the tables mentioned above (e.g. pressure registrations) the complete file is also stored in the SICADA file archive.
- A file **comments.mio* containing comments on the fieldwork and the calculation/evaluation. The comments in the file are imported as activity comments in SICADA.

7.1.2 Calculations and evaluation of pH and redox potential

The redox potential is measured by six electrodes (three at the surface and three in the downhole borehole section) and pH is measured by four electrodes (two at the surface and two downhole in the borehole section). Furthermore, the registrations by the redox and the pH electrodes are logged each hour during a measurement period of approximately three weeks and a calibration is performed before and after the measurement period. The treatment of the raw data includes the following steps:

- Calculation and choice of calibration constants.
- Calculation of one pH and one redox potential sequence for each electrode (i.e. six redox electrodes and four pH electrodes).

- Evaluation to obtain representative pH and redox potential values as well as estimated measurement uncertainties for the investigated borehole section.

One calibration constant is selected for each electrode using one of the following alternatives:

- Case 1: Calculation of the average calibration constant value and the standard deviation. The initial and the final calibration measurements give rise to four constants for each redox electrode (in pH 4 and pH 7 buffer solutions) and six constants for each pH electrode (in pH 4, 7 and 10 buffer solutions).
- Case 2: The calibration constant obtained from the initial calibration measurement at pH 7 is selected since it is closest to the pH of the borehole water. This alternative is chosen if the calibration constants obtained in the different buffers show a large variation in value (generally a difference more than 20 mV between the highest and the lowest value). The standard deviation is calculated in the same way as in Case 1.
- Case 3: If the final calibration constants turn out to be very different (more than 20 mV) from the initial constants, a linear drift correction is needed. The reason is most often a drift in the reference electrode. The average values and standard deviations are calculated for the initial and the final calibration constants separately and a linear correction is made between the selected initial and the selected final constant. The higher of the two standard deviation values is used in the estimation of the total measurement uncertainty.

The values in the measurement raw data file are recalculated to pH and Eh measurement sequences for each pH and redox electrode using the calibration constant selected as stated above.

The next step is to choose a logging occasion in a stable part of the measurement period and select a result for each electrode. The average values are calculated for each electrode group in order to obtain one representative value of redox potential, pH (borehole Chemmac) and pH (surface Chemmac) respectively. Obviously erroneous electrodes are omitted. The corresponding total measurement uncertainties are estimated by including the standard deviations of the calibration constants and the standard deviations of the Eh and the pH values obtained by the three sets of electrodes. It is useful to evaluate pH at the surface and pH in the borehole section separately, since pH in the pumped water might differ from the pH measured in the borehole section. This is due to the decreasing pressure and its effects on the carbonate system.

Factors considered when evaluating the measurement uncertainties in pH and redox potential (Eh) values are:

- Difference in calibration constants for each electrode and calibration/buffer solution.
- Drift in calibration constants between the initial and the final calibration.
- Stability in voltage value during the last part of the on-line measurement. A successful measurement shows no tendency of a slope.
- Agreement between the different pH and redox electrodes on the surface and in the downhole borehole Chemmac.
- Number of electrodes showing reasonable agreement. Obviously erroneous electrodes are excluded from the calculation.

7.2 Water analysis data

The following routines for quality control and data management are generally applied for hydrogeochemical analysis data, independently of sampling method or sampling object.

Several components are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure on each fifth or tenth collected sample. All analytical results are stored in the SICADA database. The applied hierarchy path "Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database" contains two types of tables, raw data tables and primary data tables (final data tables).

Data on *basic water analyses* are inserted into raw data tables for further evaluation. The evaluation results in a final reduced data set for each sample. These data sets are compiled in a primary data table named "water composition". The evaluation is based on:

- Comparison of the results from different laboratories and/or methods. The analyses are repeated if a large disparity is noted (generally more than 10%).
- Calculation of charge balance errors. Relative errors within ± 5% are considered acceptable (in surface waters ± 10%).

$$\text{Rel. error (\%)} = 100 \times \frac{(\sum \text{cations(equivalents)} - \sum \text{anions(equivalents)})}{(\sum \text{cations(equivalents)} + \sum \text{anions(equivalents)})}$$

- General expert judgement of plausibility based on earlier results and experience.

All results from *special analyses of trace metals and isotopes* are inserted directly into primary data tables. In those cases where the analyses are repeated or performed by more than one laboratory, a "best choice" notation will indicate those results which are considered most reliable.

An overview of the data management is given in Figure 7-1.

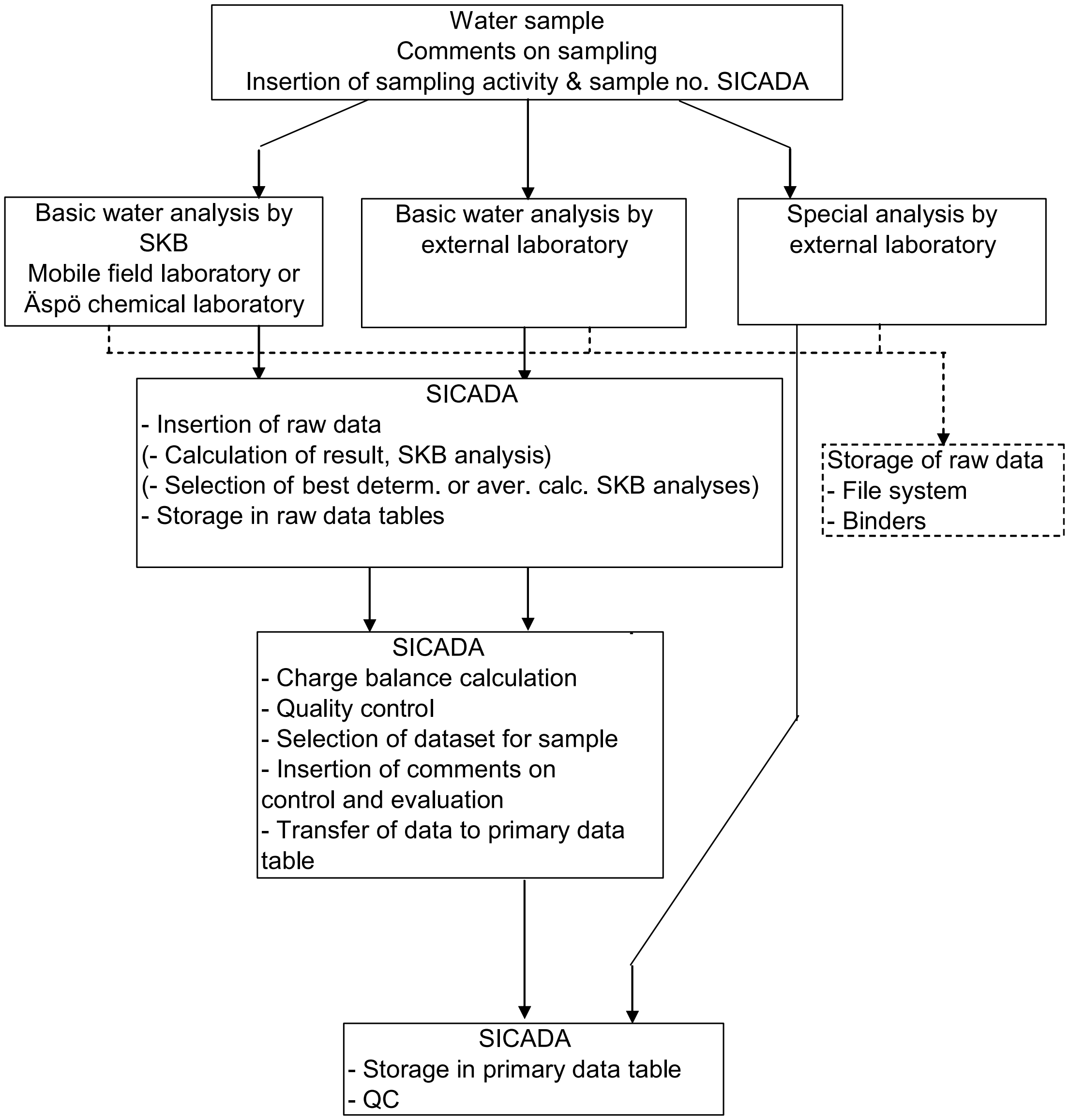


***Figure 7-1.** Overview of data management for hydrogeochemical data.*

7.3 Data from special sampling methods

Special sampling methods include collection of in situ samples, colloid filtration, enrichment of humic and fulvic acids and fractionation of humic and fulvic acids. All analytical data are subjected to quality control and stored in the SICADA database. Separate sampling activities, methods and sample numbers are defined for the data on dissolved gases, microbes, colloids, fractions of humic and fulvic acids and $\partial^{13}C$ and pmC determined on organic constituents.

8 Results

8.1 Chemmac measurements

The Chemmac measurements were conducted successfully in both of the investigated borehole sections. The whole measurement sequences of pH, Eh, electric conductivity, dissolved oxygen and water temperature values are plotted versus time in Appendices 4 and 5. The pH and redox potential data measured by the downhole Chemmac electrodes in section 110.1–120.8 were calculated using linear drift correction.

The measurement data sequences were evaluated in order to obtain one representative value of Eh, pH (surface), pH (downhole section), electric conductivity and dissolved oxygen for each borehole section as described in Section 6.1. Data were selected from the last part of the measurement sequences. The glassy carbon electrode at the surface (EHCY) was omitted from the average calculation in both cases due to an erroneous amplifier, causing noisy and somewhat diverging measurement values. The measurement of dissolved oxygen in the section 110.1–120.8 m showed a noisy behaviour due to disturbance from the climate system and was therefore omitted. In the section 176.8–183.9 m the oxygen concentration decreased to below detection limit after a few days of measurement. The evaluated results from the measurements in the two sections are given in Table 8-1.

Table 8-1. Evaluated results from the Chemmac measurements in KFM01A.

Borehole section (m)	Electric conductivity* (mS/m)	pH (surface Chemmac)***	pH (borehole Chemmac)***	Eh (borehole and surface Chemmac)*** (mV)	Dissolved oxygen** (mg/L)
110.1–120.8	1519 ± 20	7.62 ± 0.06	7.68 ± 0.22	–195 ± 32	xx
176.8–183.9	1548 ± 20	7.41 ± 0.25	7.41 ± 0.18	–188 ± 16	0.00 ± 0.01

* The electric conductivity is measured between 0–10 000 mS/m with a resolution of 1% of the measurement interval.

** Measuring interval 0–15 mg/L, resolution 0.01 mg/L.

*** Evaluated result and measurement uncertainty calculated as described in section 6.1.

8.2 Water analyses

8.2.1 Basic water analyses

The basic water analyses includes the major components Na, K, Ca, Mg, S, SO_4^{2-}, Cl^-, Si and HCO_3^- as well as the minor constituents Fe, Li, Mn, DOC, Br, F, HS^- and NH_4^+. Furthermore, batch measurements of pH and electric conductivity are included. Another important parameter is the flushing water content in each sample. The basic water analysis data and relative charge balance errors are compiled in Appendix 7, Table A7-1. Existing batch measurement values of pH and electric conductivity are compared to the corresponding on-line Chemmac measurement values in the diagrams in Appendices 4 and 5.

The charge balance errors give an indication of the quality and uncertainty of the analyses of major components. The errors do not exceed ± 5% in any case. Furthermore, the last sample in each section was analysed also by an independent laboratory as a quality control. A comparison between results from different laboratories and methods shows that the agreement is acceptable in most cases. Generally, the difference in concentrations between each analysed component is less than 10%.

The flushing water contents in the sample series collected in the first and second borehole sections are presented in Figure 8-1. The flushing water content should not exceed 1% in a sample considered representative for the groundwater of the sampled fracture zone. This condition was met for most of the samples collected in the first section (110.1–120.8 m). However, in the second section (176.8–183.9 m) the flushing water content was 5% in the final water sample. The prolonged pumping and measurement period did not improve the situation.

The concentration levels of sodium, calcium and chloride are presented in Figure 8-2 and Figure 8-3. The concentrations of all major components remained practically constant during the pumping and sampling periods.

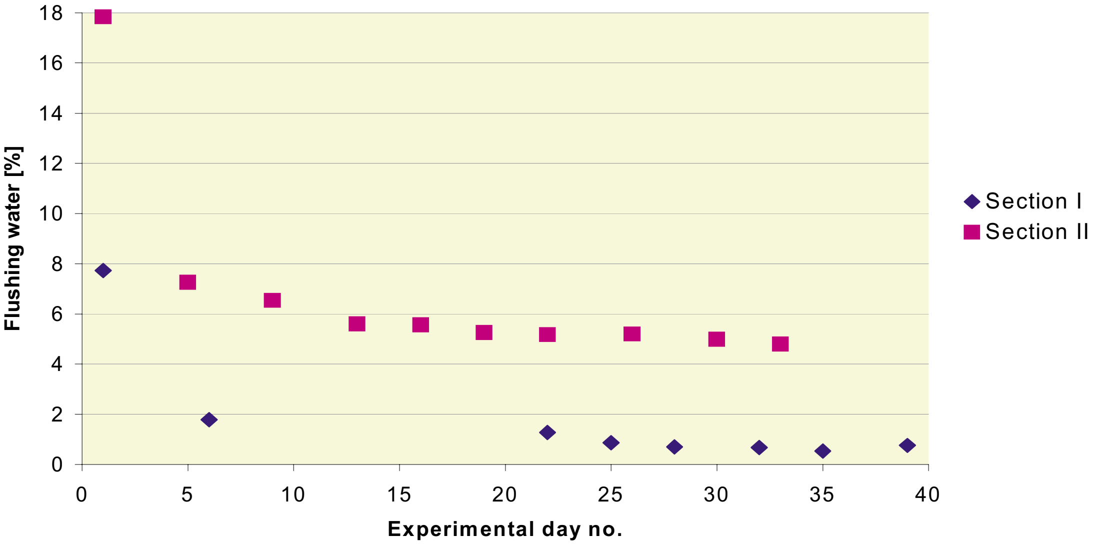


Figure 8-1. *Flushing water content plotted versus experimental day number.*

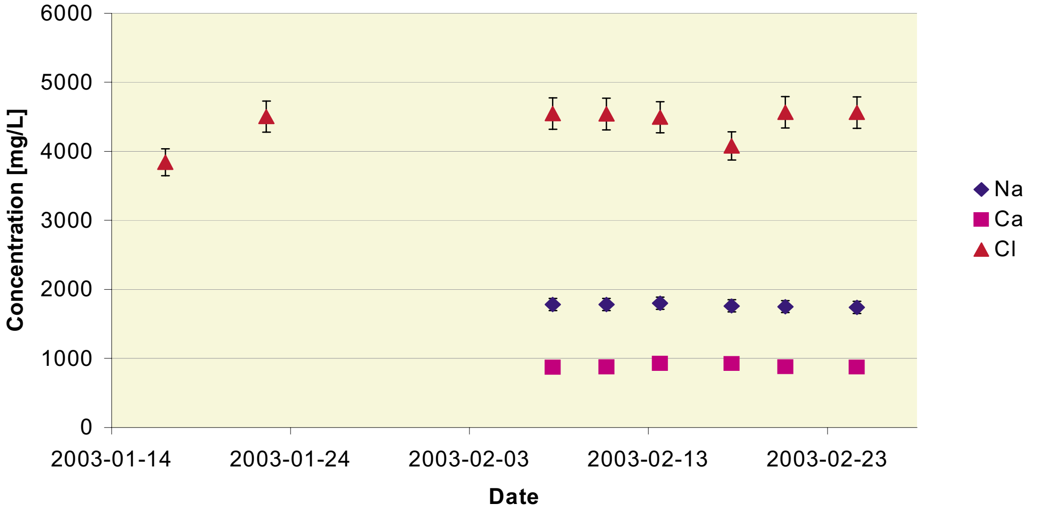


Figure 8-2. *Sodium, calcium and chloride concentration trends from sample series at 110.1–120.8 m.*

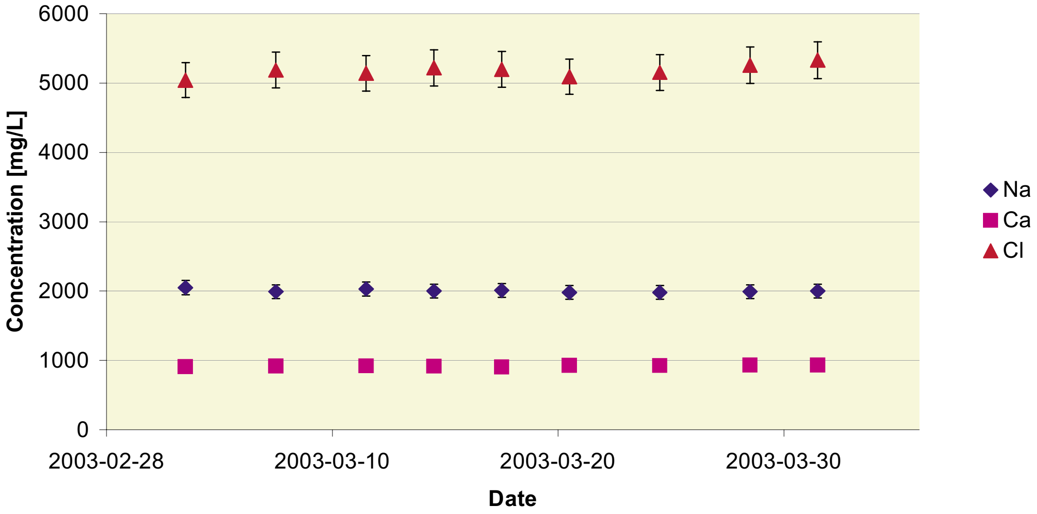


Figure 8-3. *Sodium, calcium and chloride concentration trends from sample series at 176.8–183.9 m.*

The iron concentrations determined by ICP-AES (total Fe) and by spectrophotometry (Fe(+II) and Fe-tot) are compared in Figure 8-4 and Figure 8-5. The concentrations show a decreasing trend in both sections. Furthermore, the ICP-results are lower compared to the results obtained by spectrophotometry, except for the late samples collected in the second section. Any colloidal iron present in a sample would give the opposite effect, as the spectrophotometric method excludes (or only partly includes) colloids, while the ICP technique makes no distinction between different iron-containing species.

The DOC results from the two borehole sections are plotted versus experimental day in Figure 8-6. DOC analyses in saline waters are by experience considered less reliable. The irregularly placed data points of section II (176.8–183.9 m) seem to support this view/opinion. However, data from the first section show a clearly decreasing trend and the last value is confirmed by the duplicate analysis.

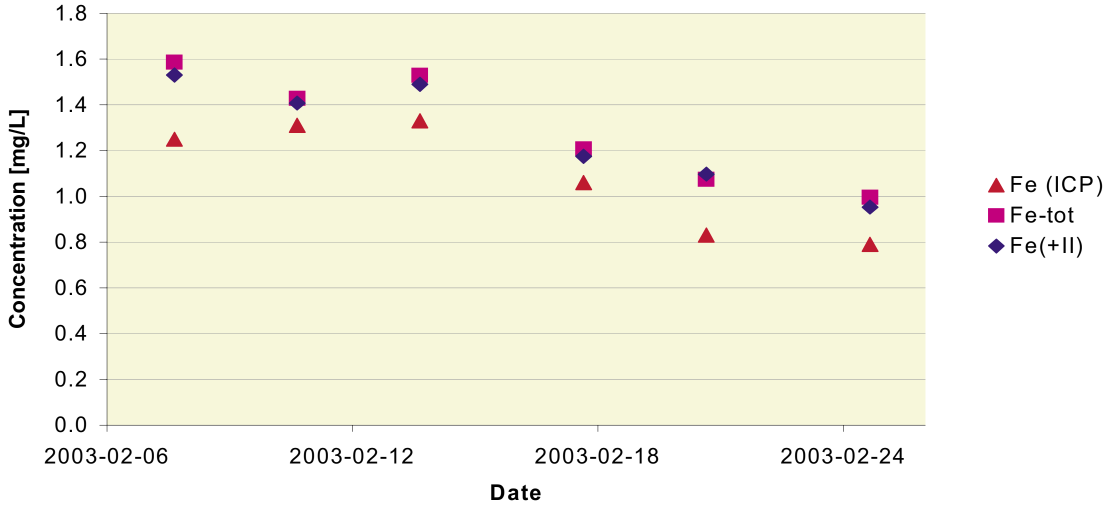


Figure 8-4. *Comparison of iron concentrations obtained by ICP-AES and spectrophotometry from borehole section 110.1–120.8 m.*

Figure 8-5. *Comparison of iron concentrations obtained by ICP-AES and spectrophotometry from borehole section 176.8–183.9 m.*

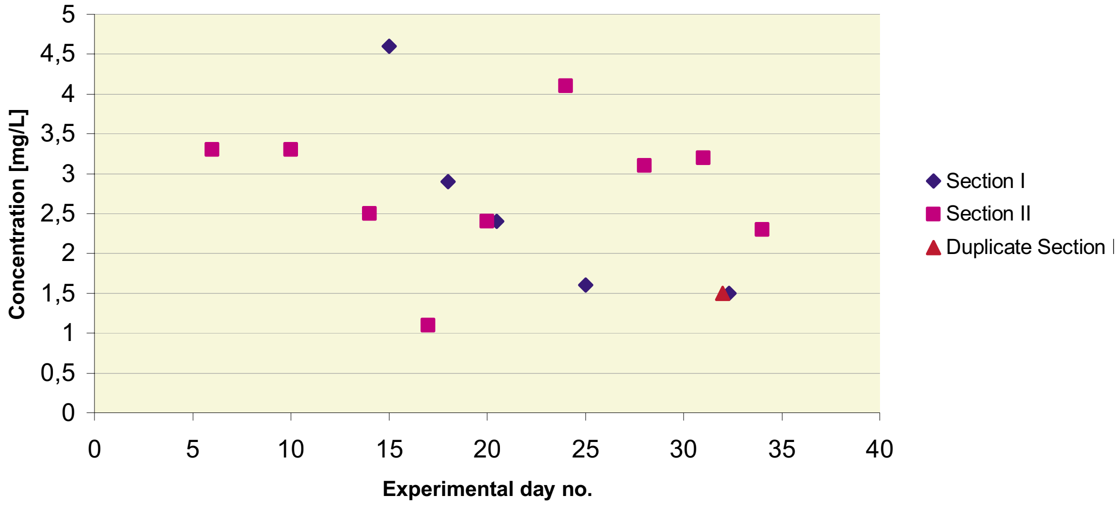


Figure 8-6*. DOC concentrations versus experimental day number from sections 110.1–120.7 m (I) and 176.8–183.9 m (II).*

Sulphate analysed by ion chromatography (IC) is compared to sulphate determined as total sulphur by ICP-AES in Figures 8-7 and 8-8. As shown there is a satisfactory agreement. However, the results from the ICP measurements are considered more reliable by experience since the variation between the samples in a time series is often smaller.

The chloride concentrations are plotted versus the corresponding electric conductivity values in Figure 8-9. The plot gives a rough control that the values are reasonable. The data from the two borehole sections agree well with the line obtained by earlier data from the Äspö Hard Rock Laboratory.

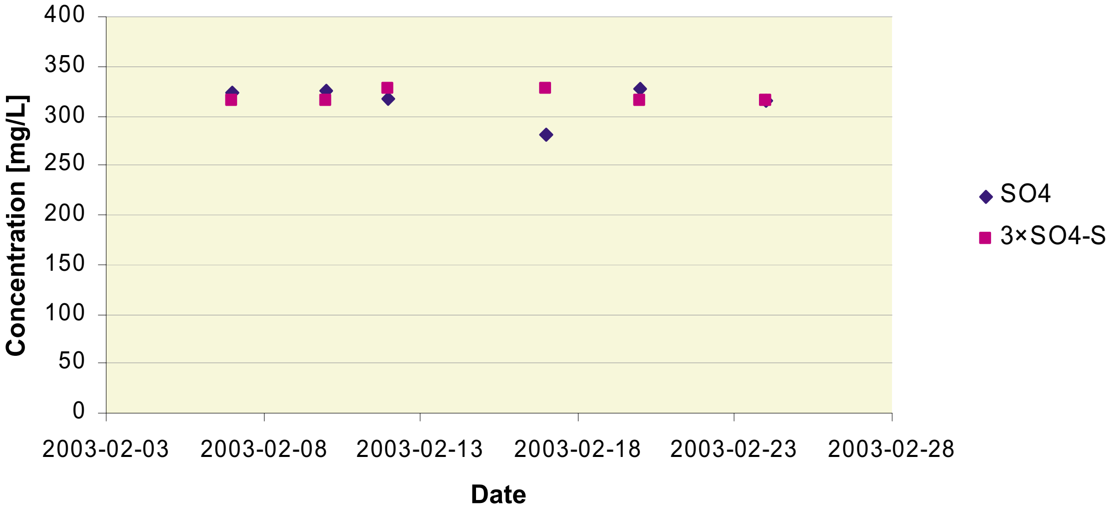


***Figure 8-7**. Sulphate (SO_4 by IC) compared to sulphate recalculated from total sulphur ($3×SO_4$-S by ICP) versus date. Samples collected in section 110.1–120.8 m.*

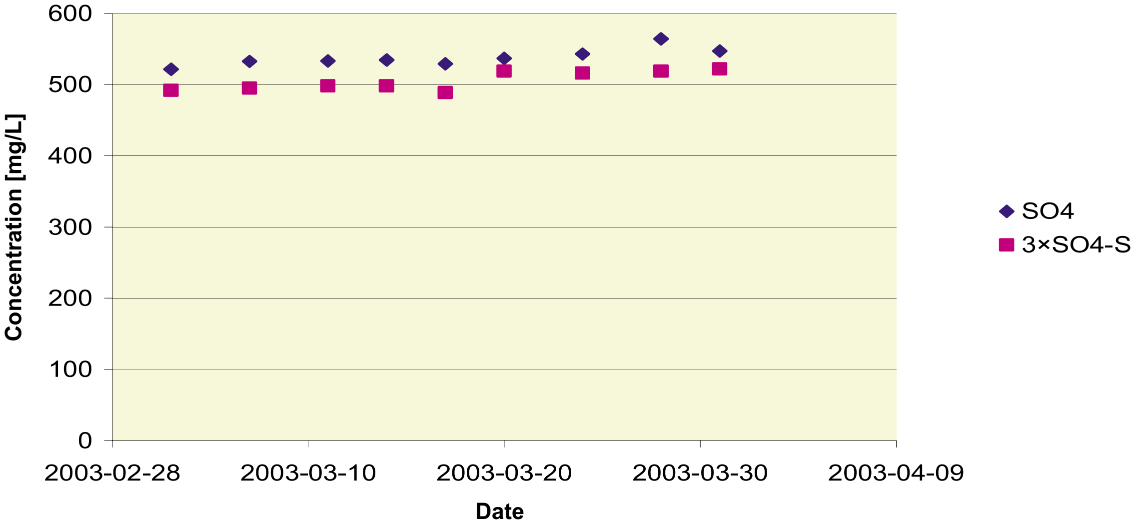


***Figure 8-8**. Sulphate (SO_4 by IC) compared to sulphate recalculated from total sulphur ($3×SO_4$-S by ICP) versus date. Samples collected in section 176.8–183.9 m.*

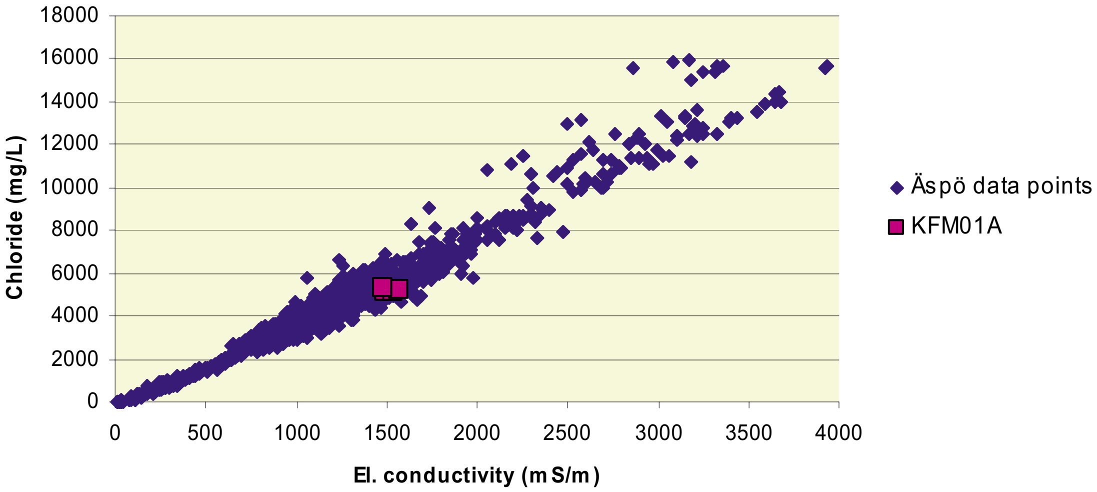


Figure 8-9*. Chloride concentration versus electric conductivity. Data from earlier investigations at the Äspö Hard Rock Laboratory are used to show the linear trend. Data from KFM01A do not deviate from a regression line.*

8.2.2 Trace elements (rare earth metals and others)

The analyses of trace and rare earth metals include U, Th, Sc, Rb, Y, Zr, In, Sb, Cs, Ba, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and V. Commonly occurring metals, such as Cu, Zn, Pb and Mo are not included in the analysis programme due to contamination considerations. The trace element data are compiled in Appendix 7, Table A7-3. The results from the analyses of common trace metals show no large variations.

8.2.3 Stable and radioactive isotopes

The isotope determinations include the stable isotopes δD, $\delta^{18}O$, $^{10}B/^{11}B$, $\delta^{34}S$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ as well as the radioactive isotopes Tr (TU), ^{14}C (pmC), ^{238}U, ^{235}U, ^{234}U, ^{232}Th, ^{230}Th, ^{226}Ra and ^{222}Rn. The isotope data are compiled in Appendix 7, Table A7-2 and Table A7-4.

The tritium and $\delta^{18}O$ results are presented in Figures 8-10 and 8-11. The tritium content was below the detection limit (0.8 Tritium Units) in most of the samples. The two deviating tritium values in the second borehole section are possibly due to the higher content of remaining flushing water in this section. The $\delta^{18}O$ ratios remained stable during the sampling period in both sections.

The carbon isotopes ($\delta^{13}C$ and pmC) were determined both in inorganic carbon (hydrogen carbonate) and in organic constituents. The results are compared in Table 8-2 below. Enrichment of organic carbon was necessary in order to get enough organic material, see Section 5.7.

As shown, the pmC values obtained from the organic acids are approximately three to four times higher than the inorganic values. This discrepancy is common and is explained by the different origin of the carbon and by substitution reactions that occur between dissolved carbonates in the water and carbonate minerals, which alter the isotope signature of the inorganic carbon in the water.

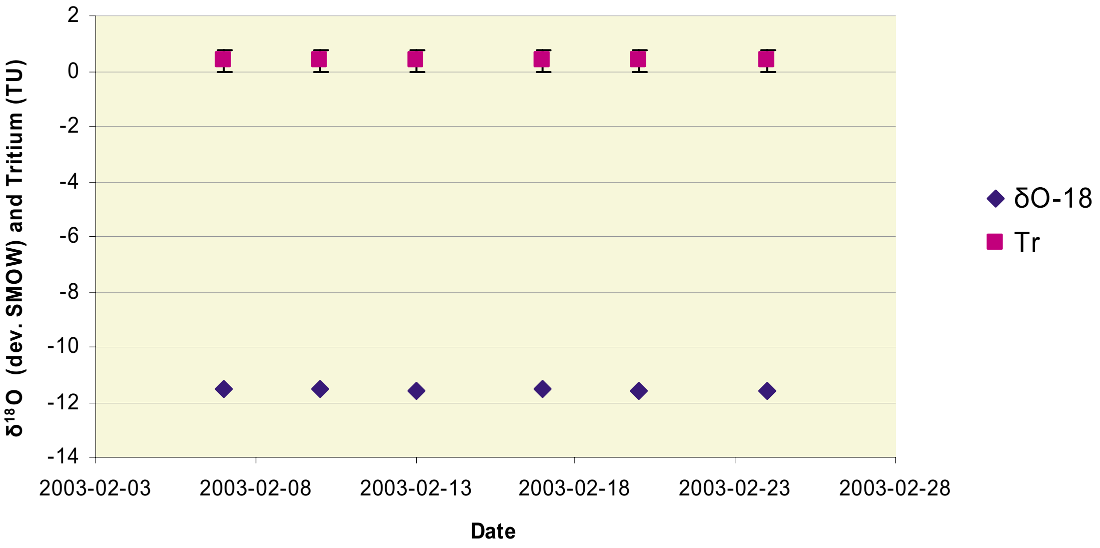


Figure 8-10. *Tritium and δ^{18}O data from samples collected in section 110.1–120.8 m.*

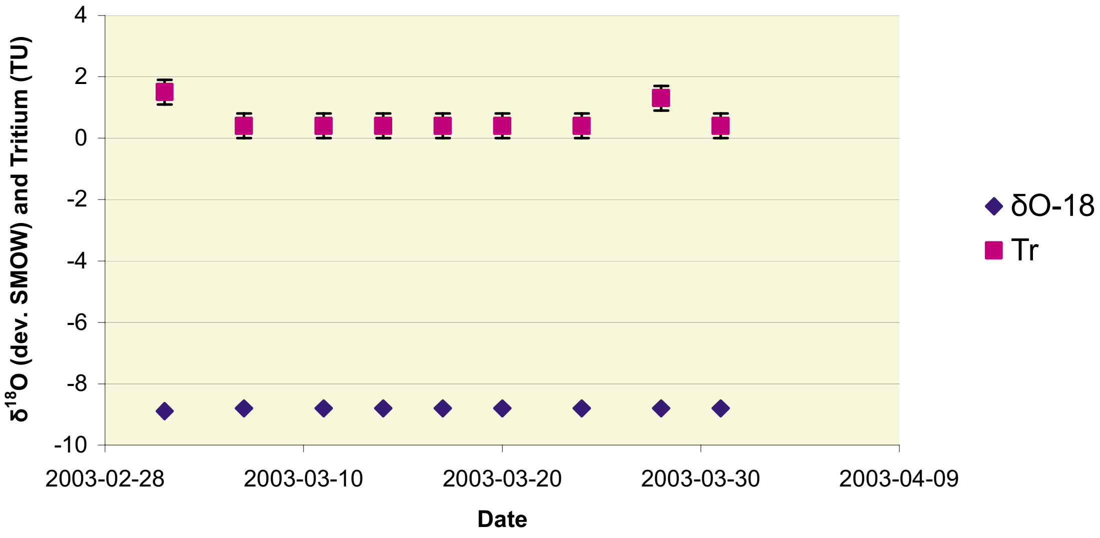


Figure 8-11. *Tritium and δ^{18}O data from samples collected in section 176.8 to 183.9 m.*

Table 8-2. Inorganic and organic δ^{13}C and pmC.

Borehole section (m)	Inorg. δ^{13}C (dev PDB)	Org. δ^{13}C (dev PDB)	Inorg. pmC	Org. pmC
110.1–120.8	–9.02	–28.3	13.38	53.2
176.8–183.9	–6.50	–27.4	16.68	46.4

A comparison between recalculated uranium and thorium isotope determinations and ICP-analyses are given in Table 8-3. The isotopes uranium-238 and thorium-232 are recalculated to element concentrations. Generally the same order of magnitude indicates a satisfactory agreement. All thorium results are below the detection limits.

Table 8-3. Comparison of isotope determinations (^{238}U and ^{232}Th) and ICP-analyses of the elements uranium and thorium.

Borehole section (m)	Sample No.	Date	U (µg/L)	U* (µg/L)	Th (µg/L)	Th** (µg/L)
110.1–120.8	4481	2003-02-10	-	< 4	-	< 12.3
110.1–120.8	4520	2003-02-17	-	5	-	< 12.3
110.1–120.8	4538	2003-02-24	1.51	< 4	< 0.2	< 12.3
176.8–183.9	4620	2003-03-07	20.3	19.4	< 0.5	< 12.3
176.8–183.9	4663	2003-03-14	17	8.9	< 0.5	< 12.3
176.8–183.9	4665	2003-03-20	17.7	8.9	< 0.2	< 12.3
176.8–183.9	4700	2003-03-28	15	-	< 0.2	-
176.8–183.9	4724	2003-03-31	14.6	13.8	< 0.2	< 12.3

* recalculated from ^{238}U (mBq/L)

** recalculated from ^{232}Th (mBq/L)

"-" not performed

8.3 Dissolved gases

The analyses of dissolved gases include argon (Ar), helium (He), nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), hydrogen (H_2), carbon monoxide (CO), ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2) and propane (C_3H_8). The gas data are compiled in Appendix 7, Table A7-5. Data from gas analyses are available from borehole section 176.8–183.9 m but not from section 110.1–120.8 m due to sampling problems.

The total gas content in the groundwater of borehole section 176.8–183.9 m was 57.8 mL/L and Figure 8-12 illustrates the percentage distribution of the different gases. The oxygen content of 0.095 mL/L indicates that there was an air leakage into the purging system at the consulted laboratory. The results can be corrected by removing the air effect (nitrogen, oxygen and argon) assuming that the oxygen content is zero.

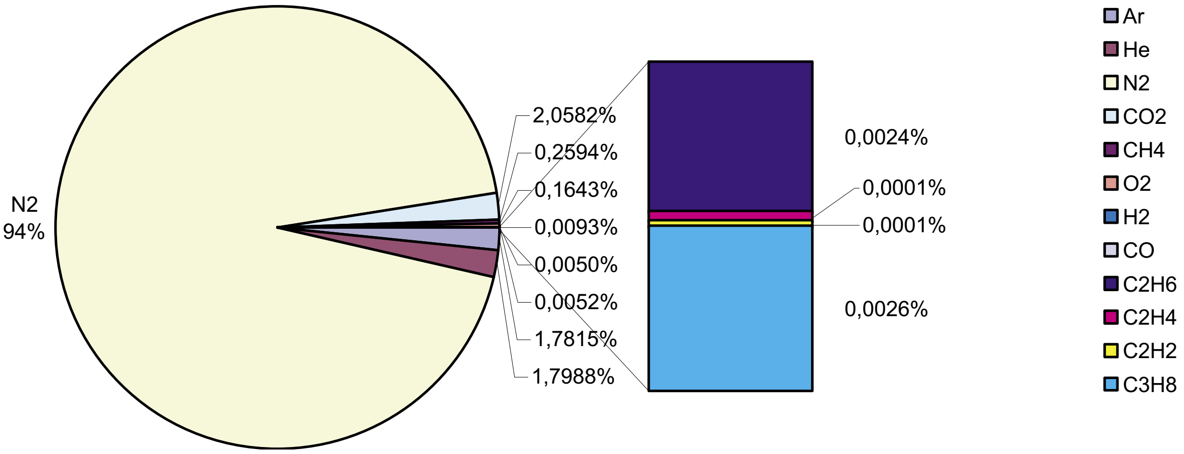


__Figure 8-12__. Percentage composition of gases (Ar, He, N_2, CO_2, CH_4, O_2, H_2, CO, C_2H_6, C_2H_4, C_2H_2 and C_3H_8).

8.4 Inorganic colloids

The presence of inorganic colloids was investigated by two different methods. One method was colloid filtration through a series of connected filters of different pore sizes. This method is new and the performance in KFM01A should be regarded as merely a method test. A second method was fractionation/ultra filtration using cylindrical membrane filters with a cut off of 1000 D and 5000 D respectively. The results of the two methods are difficult to compare quantitatively but a qualitative agreement is identified.

8.4.1 Inorganic colloids – colloid filtration

The main results from the first testing of the colloid filtration method conducted in sections 110.1–120.8 m and 176.8–183.9 m are presented in Figures 8-13 to 8-16 and Figures 8-17 to 8-20 respectively. A more thorough evaluation of the achievements, the contamination sources and the results are given in a final method evaluation report /8/.

The results are presented as amount (μg) of aluminium, iron, silicon and manganese going into the filter package, in each filter and in the collecting container. The amount is calculated with the assumption that the water volume coming out in the collecting container is equal to the volume going into the system. This is not quite true as up to ten millilitres will be left in cavities in the filter holder package, in the tubing and in valves. A small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its content of the different elements is included in the analysis.

Comments and conclusions regarding the results presented in Figures 8-13 to 8-20 follow below:

- The input amounts differ considerably from time to time. This is mainly due to different input volumes but also to contaminant contributions.
- The generally larger amounts in the filter samples from the first section than from the second section are most probably due to improved performance in the second case and thereby less contamination.
- In some cases (aluminium, iron and also silicon in section II) the input amount is larger than the sum of the amounts recovered in the filters and in the output. The output concentrations are close to the concentrations in the corresponding final class 5 sample. The input sample is collected after the filtration, from the small residual volume in the PVB-container. A possible explanation to the apparently too high input concentrations is that the sample water, when poured from the PVB-container, gets in contact with dirty surfaces on the outlet. The dirt source is probably the borehole section. The same increased input concentration did not occur when the PVB-containers were filled with pumped water at the surface.
- There is a need for an improved control of contamination sources in order to better understand the results. Nevertheless, it can be concluded that the content of colloidal species in the groundwater in the two borehole sections is very low or non-existent.

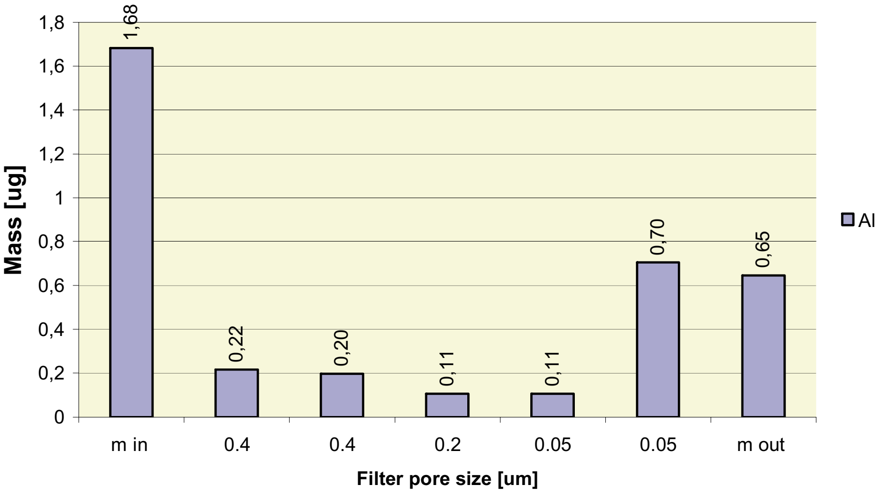


Figure 8-13. *Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out), section 110.1–120.8 m. Zero value = below detection limit.*

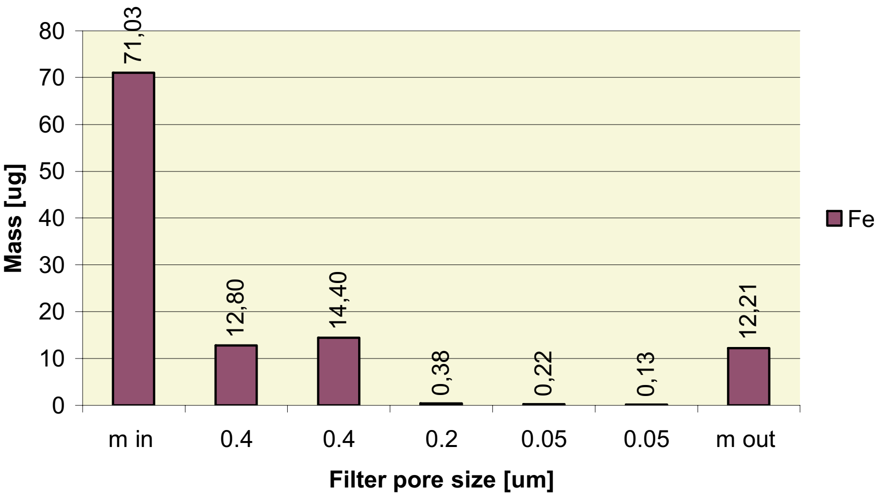


Figure 8-14. *Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out), section 110.1–120.8 m. Zero value = below detection limit.*

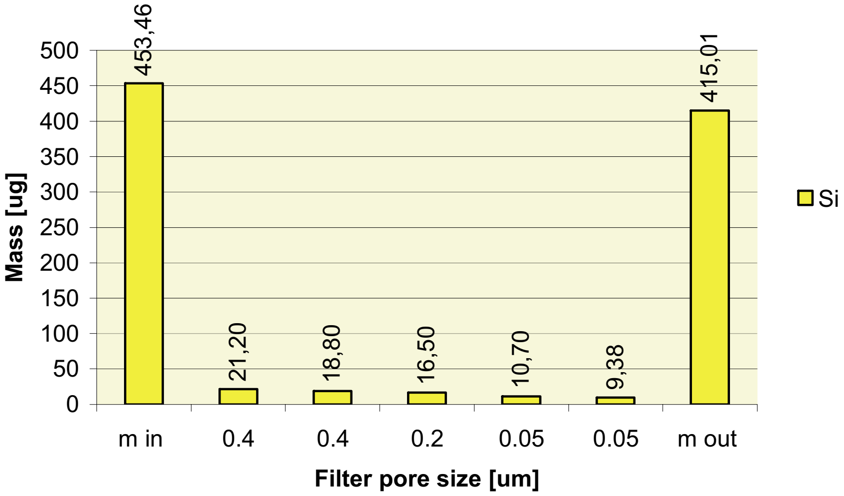


Figure 8-15. *Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out), section 110.1–120.8 m. Zero value = below detection limit.*

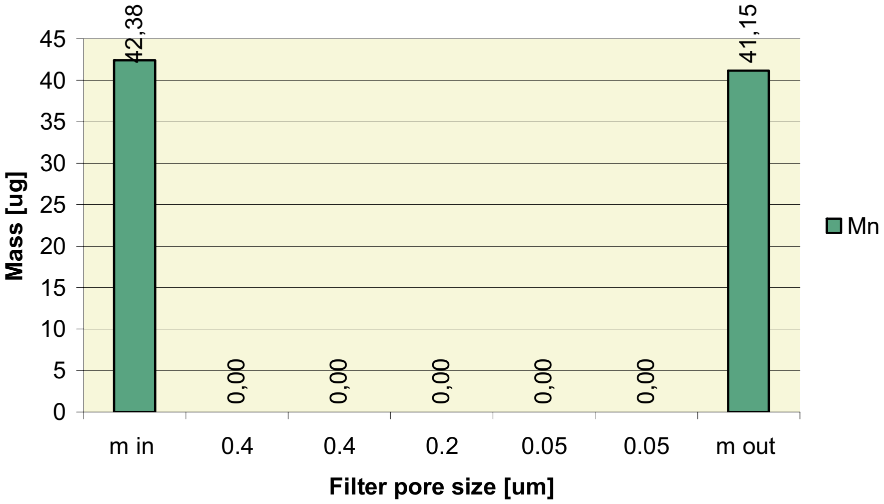


Figure 8-16. *Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out), section 110.1–120.8 m. Zero value = below detection limit.*

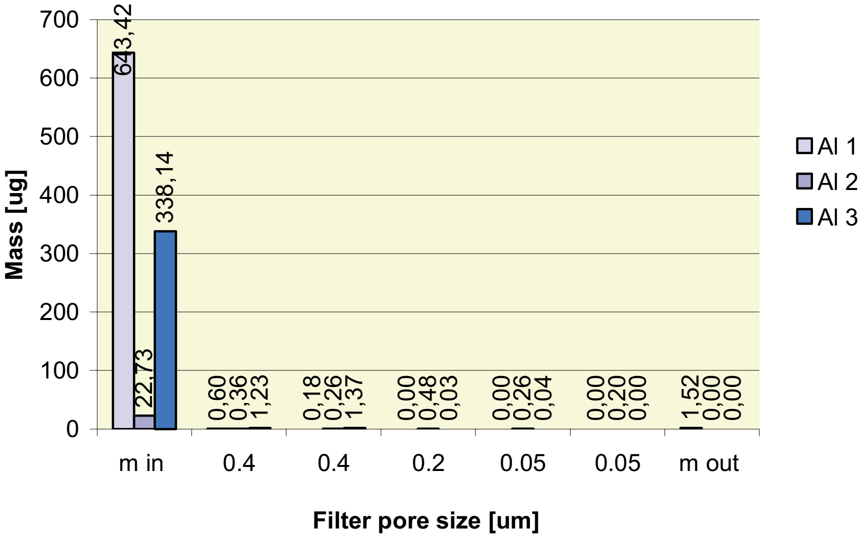


Figure 8-17. *Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out), section 176.8–183.9 m. Zero value = below detection limit.*

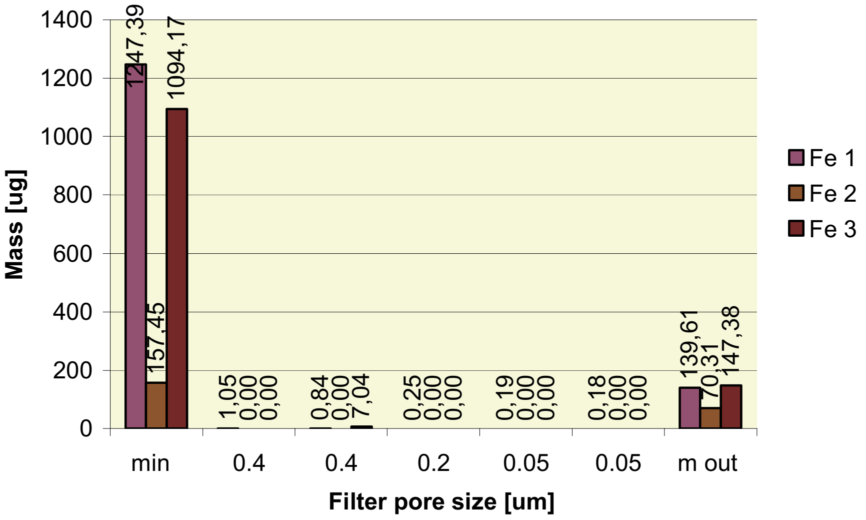


Figure 8-18. *Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out), section 176.8–183.9 m. Zero value = below detection limit.*

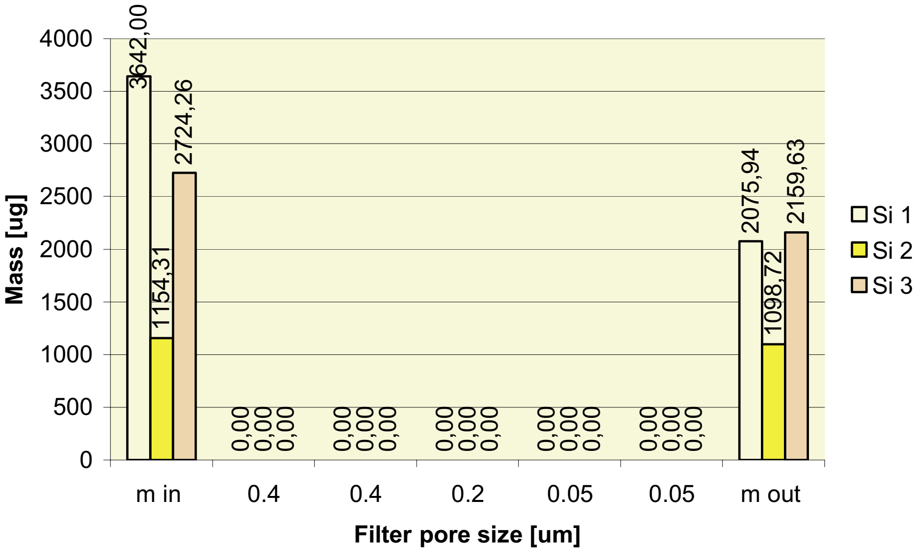


Figure 8-19. *Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out), section 176.8–183.9 m. Zero value = below detection limit.*

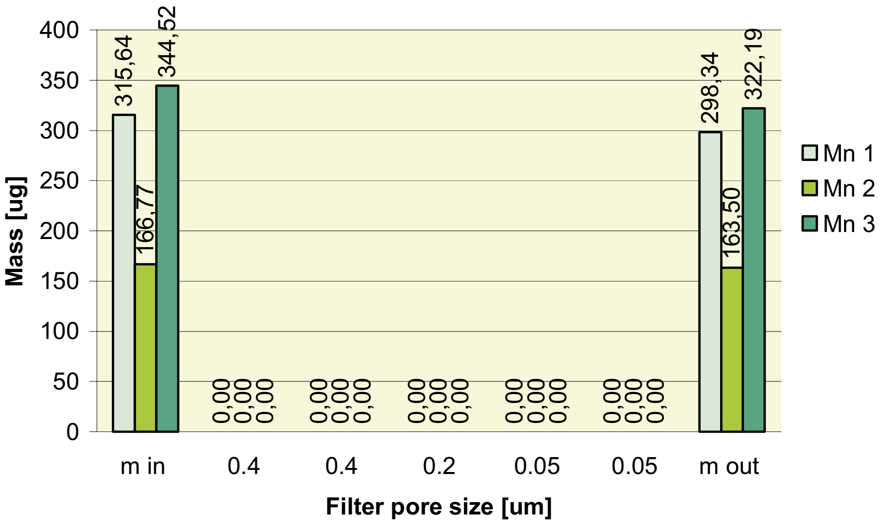


Figure 8-20. *Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out), section 176.8–183.9 m. Zero value = below detection limit.*

8.4.2 Inorganic colloids – fractionation

Besides the DOC analyses, the samples from fractionation experiments were also analysed by ICP-AES. The determined elements were; Ca, Fe, K, Mg, Na, S, Si, Al, Ba, Cd, Co, Cr, Cu, Hg, Li, Mn, Mo, Ni, P, Pb, Sr, V and Zn. Only iron, silicon, aluminium and manganese were considered important as colloid species.

The results presented in Tables 8-4 and 8-5 were calculated using mass balance equations (SKB MD 431.043). As shown, Fe, Si, Al and Mn exist as species (associated or non-associated with humic and fulvic acids) with a molecular weight less than 1000 g/mol. Such species are too small to be referred to as colloids. Iron was partly precipitated during the fractionation, since oxygen is present in the filtering system (pump, filter, hose etc). However unlikely, the presence of iron containing species of a larger fraction cannot be completely excluded.

In section 176.8–183.9 m additional aluminium was present, probably originating from the filter itself. Therefore, it was not possible to draw any conclusions regarding fractions of aluminium.

The filters were carefully washed before use and samples of de-ionised water (after passing through the washed filters) were analysed as sample blanks. The concentrations in the sample blanks were insignificant. The results from both sections show that Calcite was not precipitated to any significant extent during the filtrations.

Table 8-4. Inorganic fractions (1000 D and 5000 D filters) in section 110.1–120.8 m.

Fraction	Fe (mg/L)	Si (mg/L)	Al (µg/L)	Mn (mg/L)
< 1000 D	0.60 ± 0.07	7.1 ± 0.8	0.8 ± 0.1	0.67 ± 0.08
< 5000 D	0.02 ± 0.002	7.4 ± 0.9	1.0 ± 0.1	0.71 ± 0.08
> 1000 D but < 5000 D	-	-	-	-
> 5000 D	-	-	-	-
Adsorption 1000 D	0.30 ± 0.12	-	-	-
Adsorption 5000 D	0.75 ± 0.01	-	-	-

Table 8-5. Inorganic fractions (1000 D and 5000 D filters) in section 176.8–183.9 m.

Fraction	Fe (mg/L)	Si (mg/L)	Mn (mg/L)
< 1000 D	0.38 ± 0.04	6.7 ± 0.8	0.97 ± 0.12
< 5000 D	0.35 ± 0.04	7.2 ± 0.8	1.06 ± 0.12
> 1000 D but < 5000 D	-	-	-
> 5000 D	-	-	-
Adsorption 1000 D	0.14 ± 0.08	-	-
Adsorption 5000 D	0.16 ± 0.07	-	-

8.5 Humic and fulvic acids

The results from fractionation of organic acids in the sections at 110.1–120.8 m and 176.8–183.9 m are summarised in Table 8-6. The DOC-analyses were repeated for the samples from borehole section 176.8–183.9 m, since the results for the 1000 D and 5000 D filters did not agree the first time. As shown, the water in the sections contains organic acids with a molecular weight less than 1000 D, except for a very small fraction larger than 5000 D in section 176.8–183.9 m. This means that the organic constituents are present as low molecular weight fulvic acids and possibly other low molecular weight organic acids (eg. citric acid, oxalic acid etc).

Table 8-6. Summary of fractionation results.

Fraction	Section 110.1–120.8 m DOC concentration (mg/L)	Section 176.8–183.9 m DOC concentration (mg/L)
< 1000 D	3.8 ± 0.5	2.9 ± 0.3
> 1000 D but < 5000 D	-	-
> 5000 D	-	0.3 ± 0.1 (almost within the error)

- = Not found

9 Conclusions

The complete chemical characterisation of the groundwater in the two investigated sections in borehole KFM01A was performed successfully. Minor equipment malfunctions occurred on a few occasions, but none of those caused any serious problems or long delays. The main conclusions from the experimental results are:

- The redox potential measurements in the two borehole sections appear to be of very good quality. The electrodes stabilised at practically the same level (–180 mV) in both sections. The fact that the first measurement results were repeated in the second borehole section increases the credibility. It is reasonable to measure the same redox potential value in both sections since they are close to each other and have a similar water composition.
- The presence of remaining flushing water in the borehole sections seems to contradict the statement that no flushing water was lost during the drilling. However, a volume of a few cubic metres intruding into the fracture/fractures at the section 176.8–183.9 m is enough to create the recognised sampling problem.
- An upper limit for the allowed flushing water content in a representative water sample is set to 1%. This condition was met in section 110.1–120.8 m, but not in section 176.8–183.9 m. Possible effects of the higher flushing water content (5%) in the second section are:
  1. Some of the water samples show Tritium values above the detection limit.
  2. The determined inorganic pmC values are higher compared to the first section.
  3. The suggested presence of an organic fraction larger than 5000 Dalton.
- The water composition was stable during the whole pumping and sampling periods, indicating that there was no contribution of water from more distant fracture systems with a different water composition.
- The generally reducing conditions in the groundwater, as shown by the negative redox potentials, are supported by the presence of ferrous iron Fe(+II) at relatively high concentrations in both borehole sections. Furthermore, the on-line measurements of dissolved oxygen show zero values and do not contradict this statement.
- The content of colloidal components in the groundwater is very low and far below the recommended upper limit of 0.5 mg/L (safety assessment criterion).
- The organic constituents in the groundwater are present as fulvic acids and possibly other low molecular weight organic acids (citric acid, oxalic acid etc).

10 References

/1/ **SKB, 2001.** Generellt genomförande program för platsundersökningar. SKB R 01-10, Svensk Kärnbränslehantering AB.

/2/ **Pedersen Karsten, Kalmus Annika, 2003.** Forsmark site investigation. Total numbers and metabolic diversity of microorganisms in borehole KFM01A and KFM02A. Results from three investigated sections, 110.1– 120.8 m and 176.8–183.9 m in KFM01A and section 509.0–516.0 m in KFM02A. SKB P-03-91, Svensk Kärnbränslehantering AB.

/3/ **Claesson L-Å, Nilsson G, 2003.** Forsmark site investigation. Drilling of the telescopic borehole KFM01A at drilling site DS1. SKB P-03-32, Svensk Kärnbränslehantering AB.

/4/ **Claesson L-Å, Nilsson G, 2003.** Forsmark site investigation. Drilling of a flushing water well, HFM01 and two groundwater monitoring wells, HFM02 and HFM03, at drilling site DS1. SKB P-03-30, Svensk Kärnbränslehantering AB.

/5/ **Nilsson A-C, 2003.** Forsmark site investigation. Sampling and analyses of groundwater in percussion drilled boreholes and shallow monitoring wells at drilling site DS1. Results from the percussion boreholes HFM01, HFM02, HFM03, KFM01A (borehole section 0–100 m) and the monitoring wells SFM0001, SFM0002 and SFM0003. SKB P-03-47, Svensk Kärnbränslehantering AB.

/6/ **Pedersen Karsten, 2003.** Site investigations in the Forsmark area. Control of microorganism content in flushing water used for drilling in KFM01A. SKB P-03-03, Svensk Kärnbränslehantering AB.

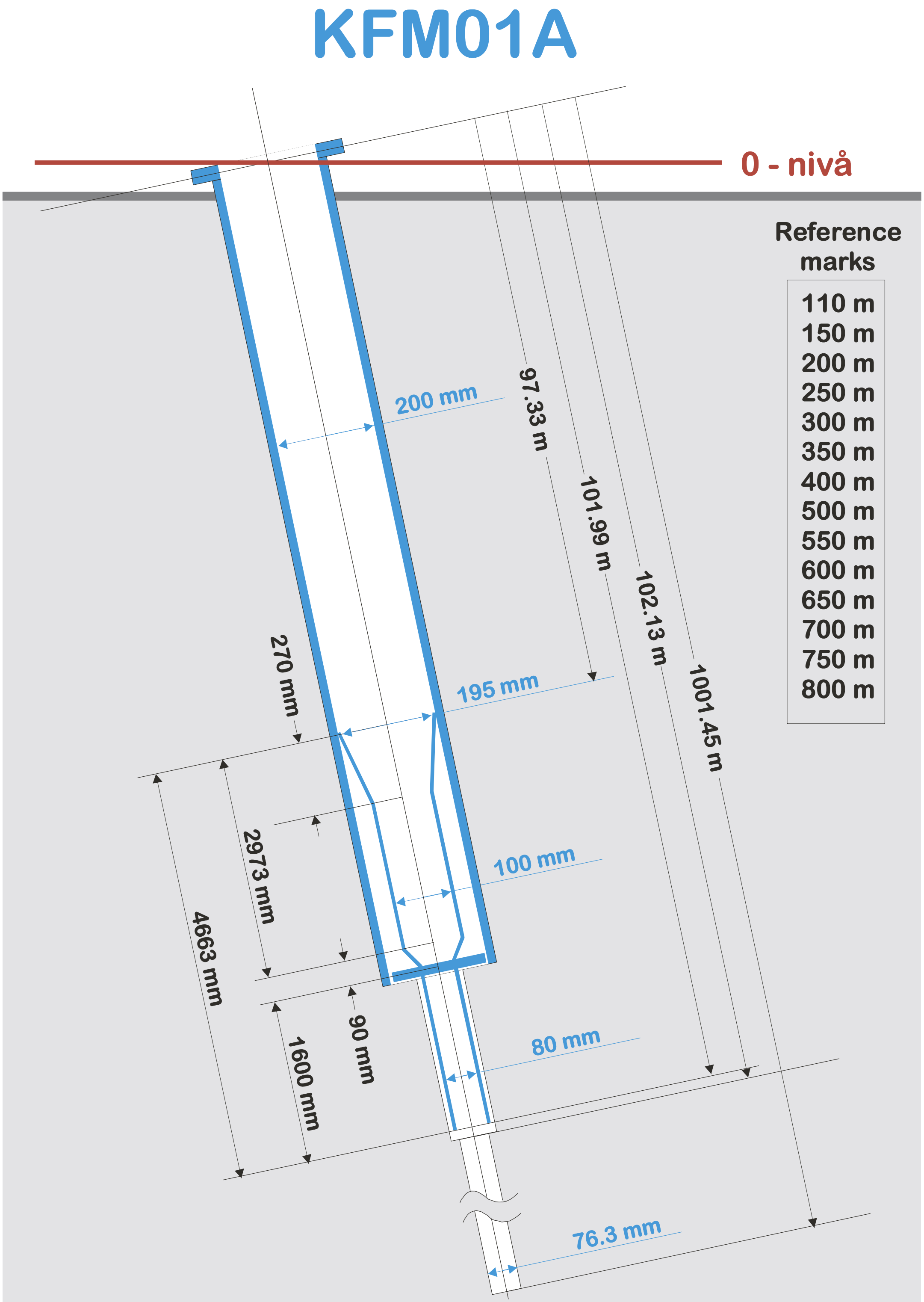
/7/ **Gustafsson P, Nilsson P, 2003.** Forsmark site investigation. Geophysical, radar and BIPS logging in boreholes HFM01, HFM02, HFM03 and the percussion drilled part of KFM01A. SKB P-03-39, Svensk Kärnbränslehantering AB.

/8/ **Rouhiainen P, Pöllänen J, 2003.** Forsmark site investigation. Difference flow logging of borehole KFM01A. SKB P-03-28, Svensk Kärnbränslehantering AB.

/9/ **Aaltonen Jaana, Gustafsson Christer, 2003.** Forsmark site investigation. RAMAC and BIPS logging in borehole KFM01A. SKB P-03-45, Svensk Kärnbränslehantering AB.

/10/ **Wacker Pia, Nilsson A-C, 2004.** Evaluation and verification of a colloid filtration method (in progress)

Design of cored borehole KFM01A

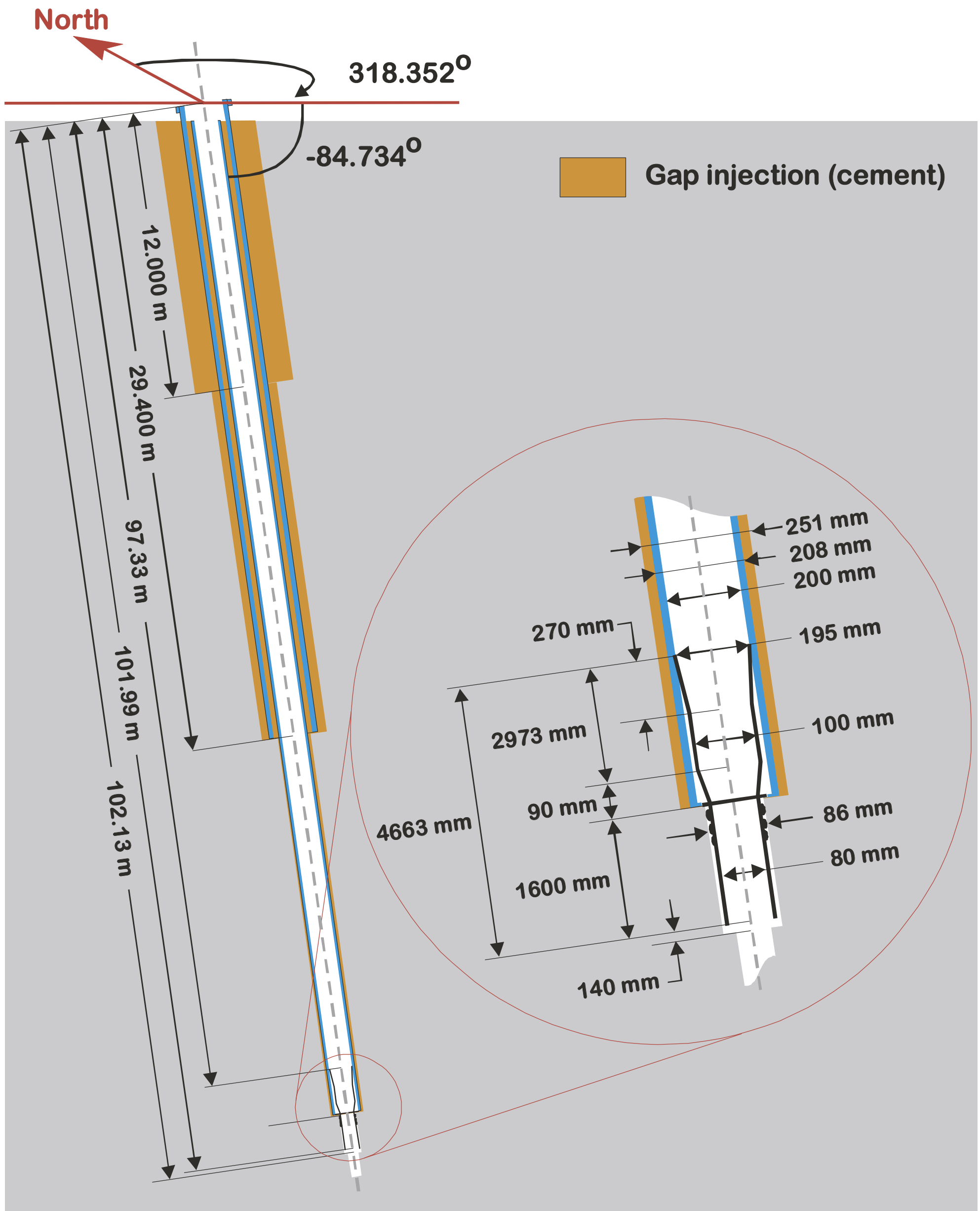


Drilling period
Drilling start date: 2002-05-27
Drilling stop date: 2002-10-28

Drilling reference point
Northing: 6699529.813 (m), RT90 2,5 gon □ 0:-15
Easting: 1631397.160 (m), RT90 2,5 gon □ 0:-15
Elevation: 3.125 (m), R□□ 70

Technical data

Borehole KFM01A



Drilling reference point

Northing:	6699529.813 (m), RT90 2,5 gon V 0:-15
Easting:	1631397.160 (m), RT90 2,5 gon V 0:-15
Elevation:	3.125 (m), RHB 70

Drilling period

Drilling start date:	2002-05-27
Drilling stop date:	2002-10-28

Borehole

Length:	1001.45 m

Appendix 2

Results of difference flow logging in KFM01A

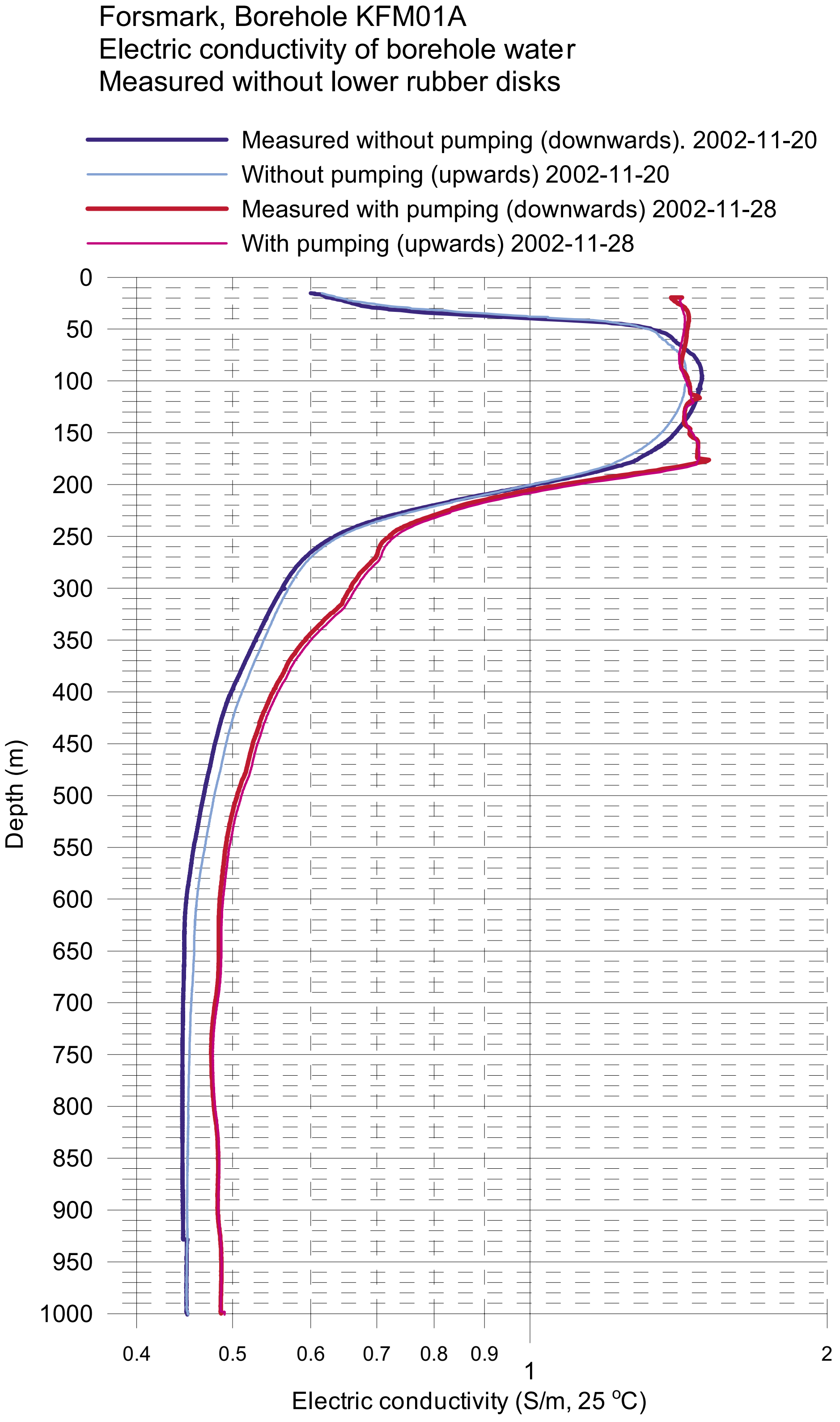


Figure A2-1. Borehole KFM01A: open hole electric conductivity measurements /7/.

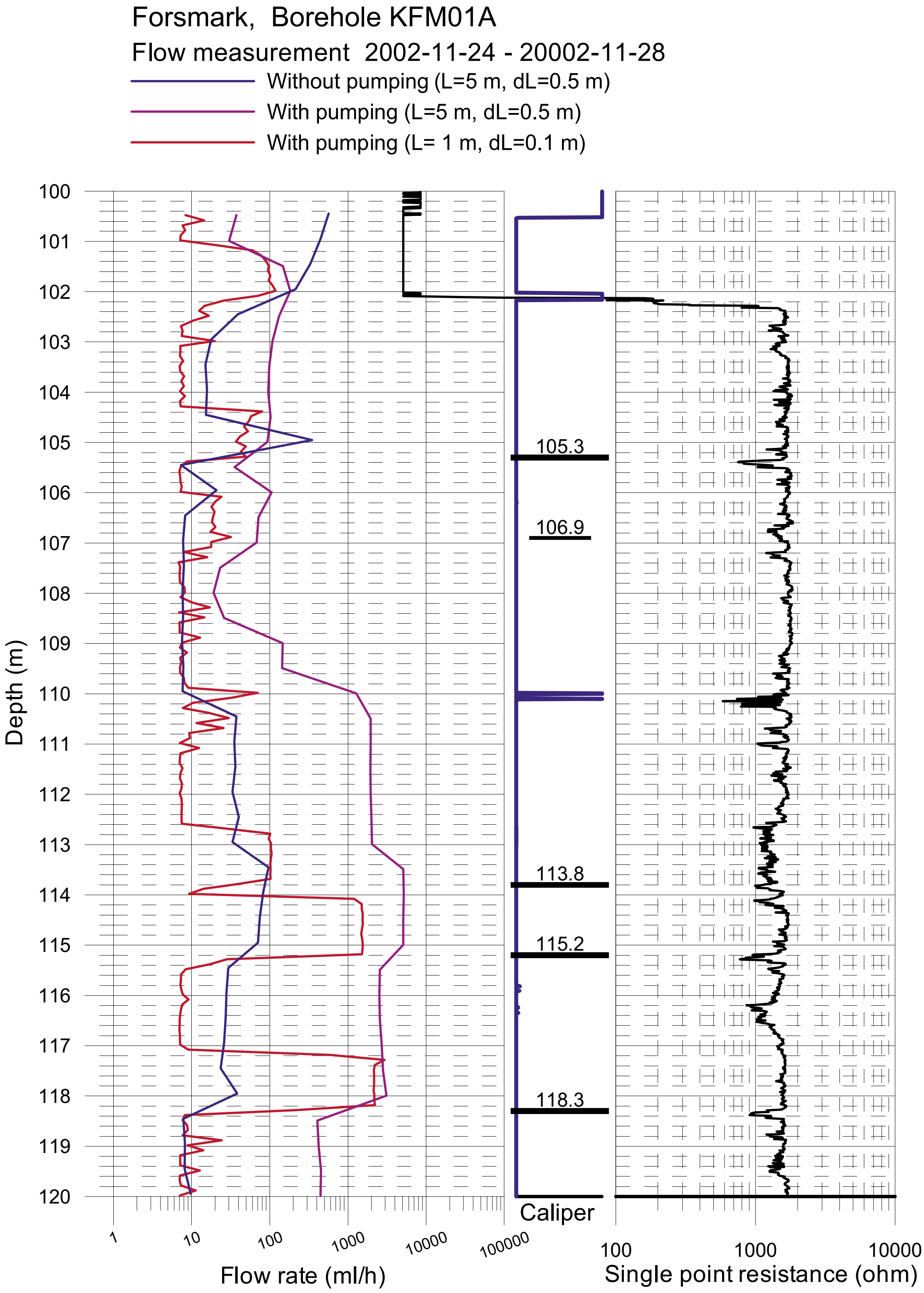


Figure A2-2. *Boreholoe KFM01A: Differential flow measurements from 100–120 m including the water bearing fracture zone at 118 m /7/.*

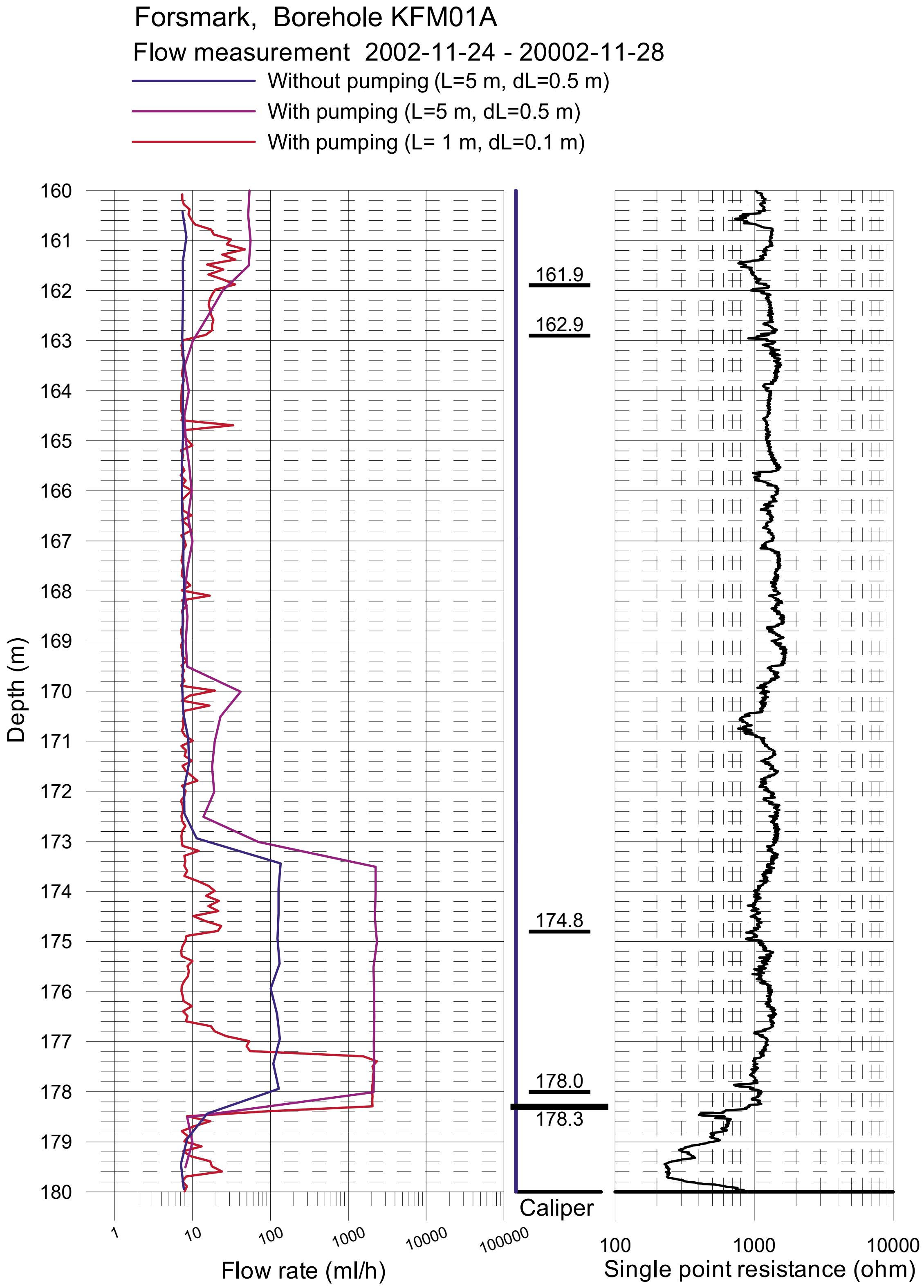


Figure A2-3. *Borehole KFM01A: Differential flow measurement from 160–180 m including the water bearing fracture zone at 178 m /7/.*

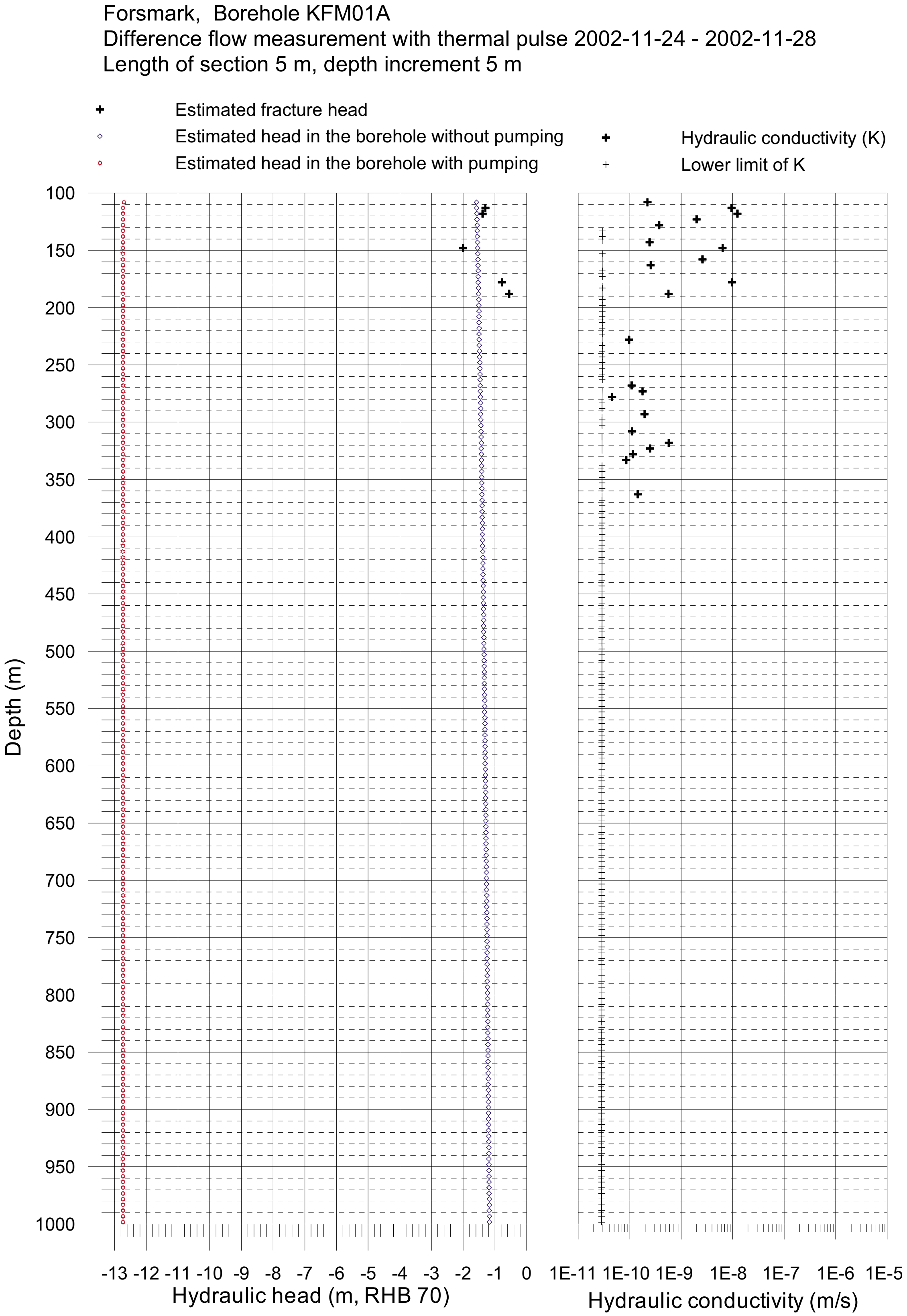


Figure A2-4. *Borehole KFM01A: Estimated fracture head and hydraulic conductivity /7/.*

Appendix 3

Flow and pressure measurements

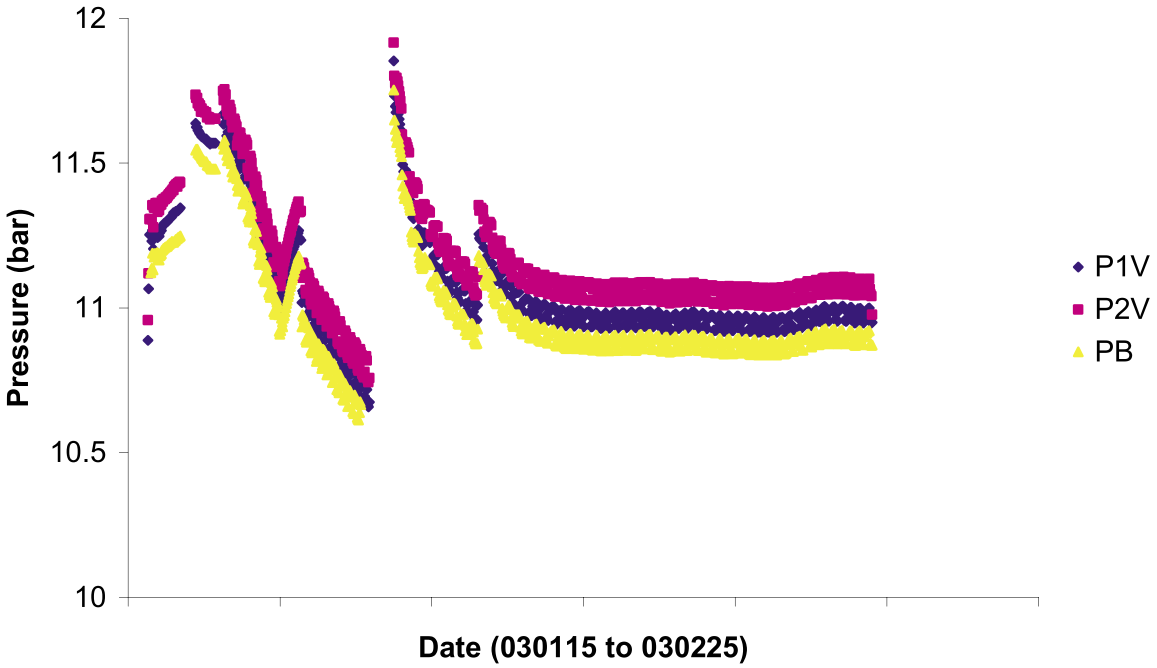


Figure A3-1. *Pressure measured in the borehole section 110.1–120.8 m. P1V and P2V are pressure sensors placed in the in situ sampling unit. PB is the sensor in the downhole Chemmac.*

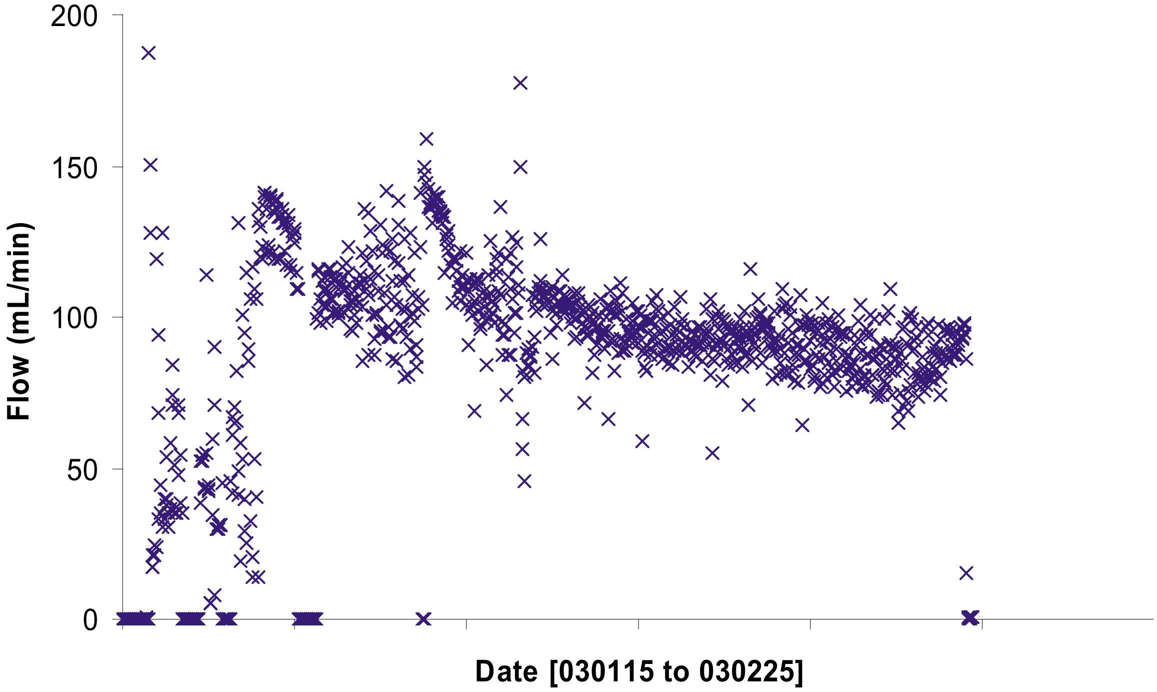


Figure A3-2. *Variation in flow rate during the pumping and measurement period from section 110.1–120.8 m.*

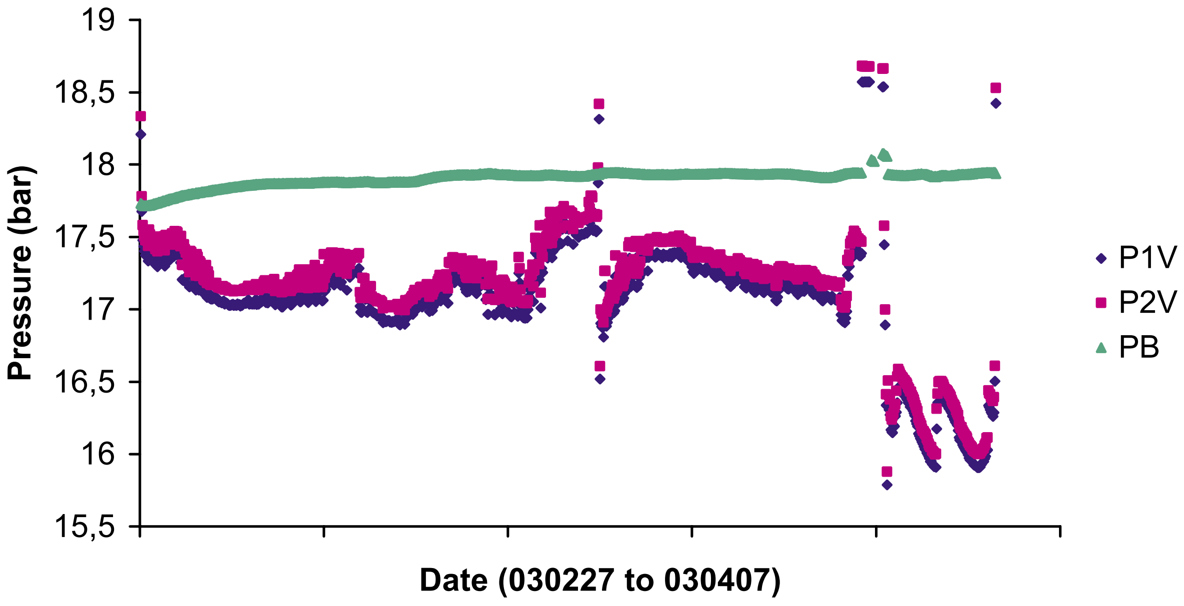


Figure A3-3. Pressure measured in the borehole section 176.8–183.9 m (P1V and (P2V) and above the section (PB). P1V and P2V are pressure sensors placed in the in situ sampling unit (PVP). PB is the sensor in the downhole Chemmac, which in this case was situated above the section. The difference in pressure corresponds to the drawdown in the section.

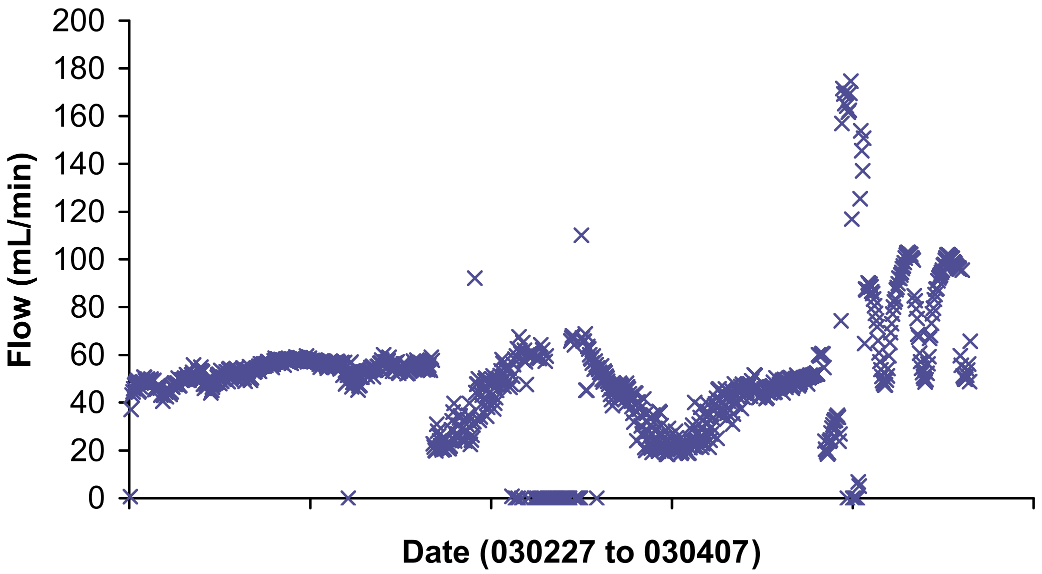


Figure A3-4. Variation in flow rate during the pumping and measurement period from section 176.8–183.9 m.

Appendix 4

Chemmac measurements, section 110.1–120.8 m

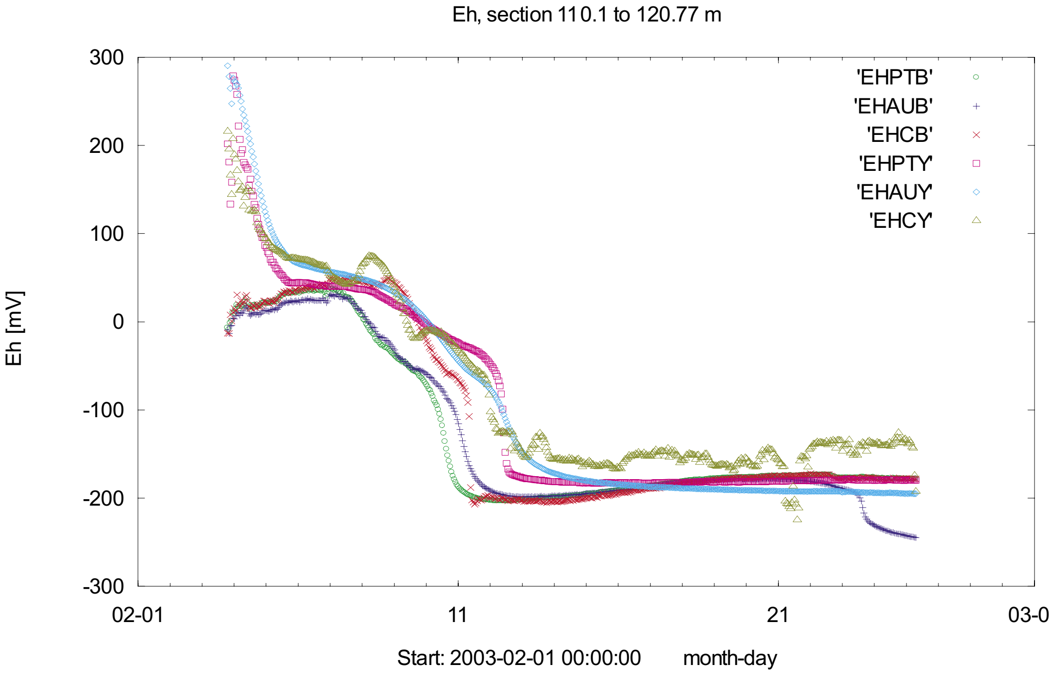


Figure A4-1. Redox potental measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCY). The glassy carbon electrode at the surface shows a noisy signal due to an erroneous amplifier.

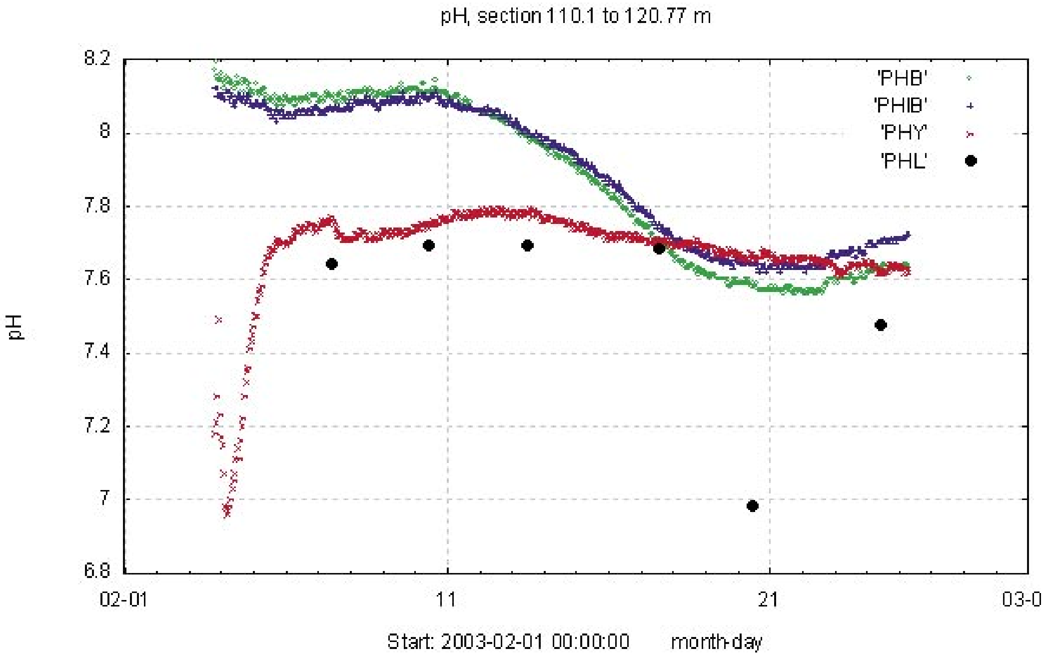


Figure A4-2. Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and one glass electrode at the surface (PHY). The laboratory pH in each collected sample (PHL) is given for comparison.

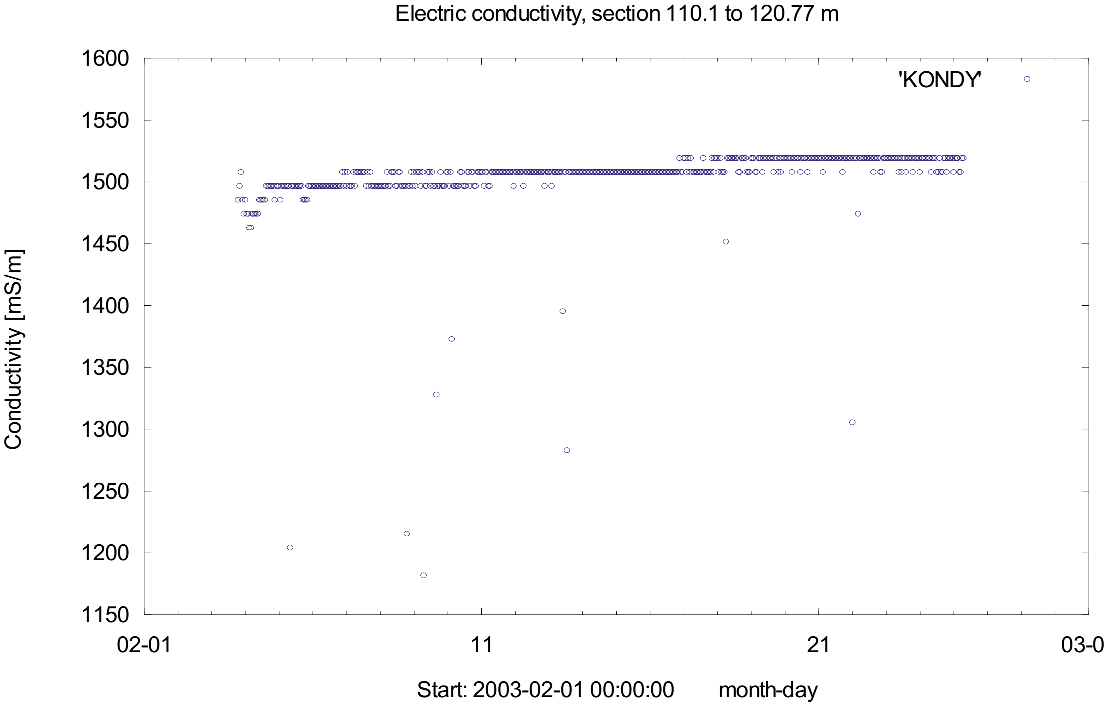


***Figure A4-3.** Electric conductivity measurement in the surface measurement cell (KONDY).*

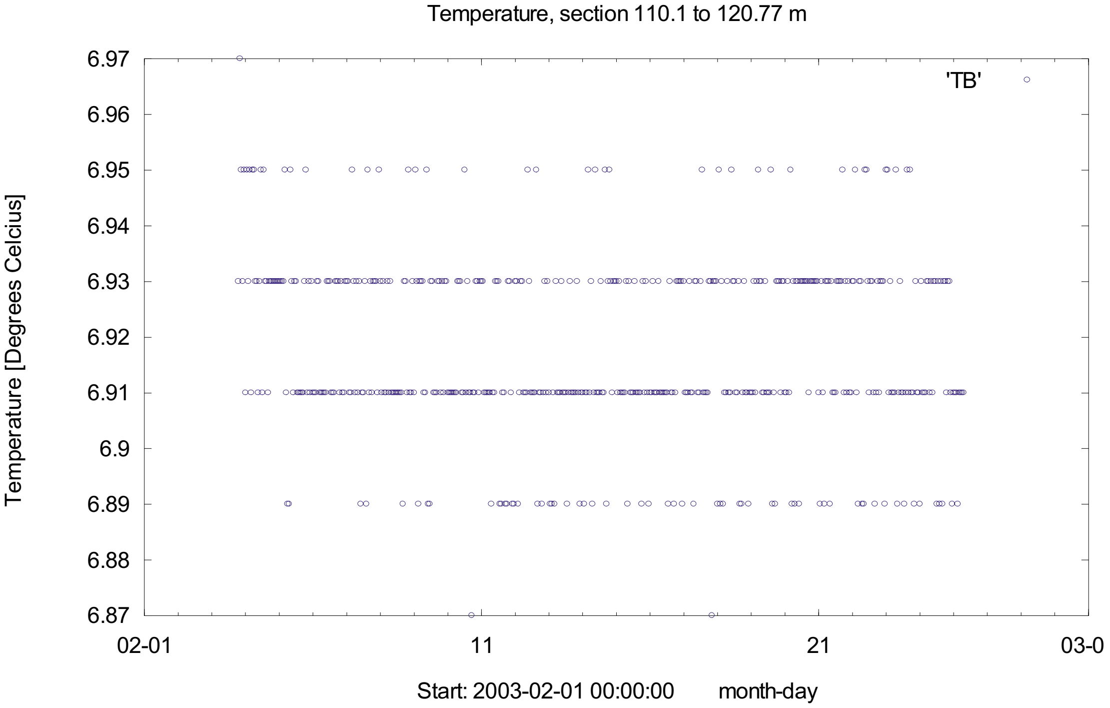


***Figure A4-4.** Temperature of the groundwater in the borehole section (TB).*

Chemmac measurements, section 176.8–183.9 m

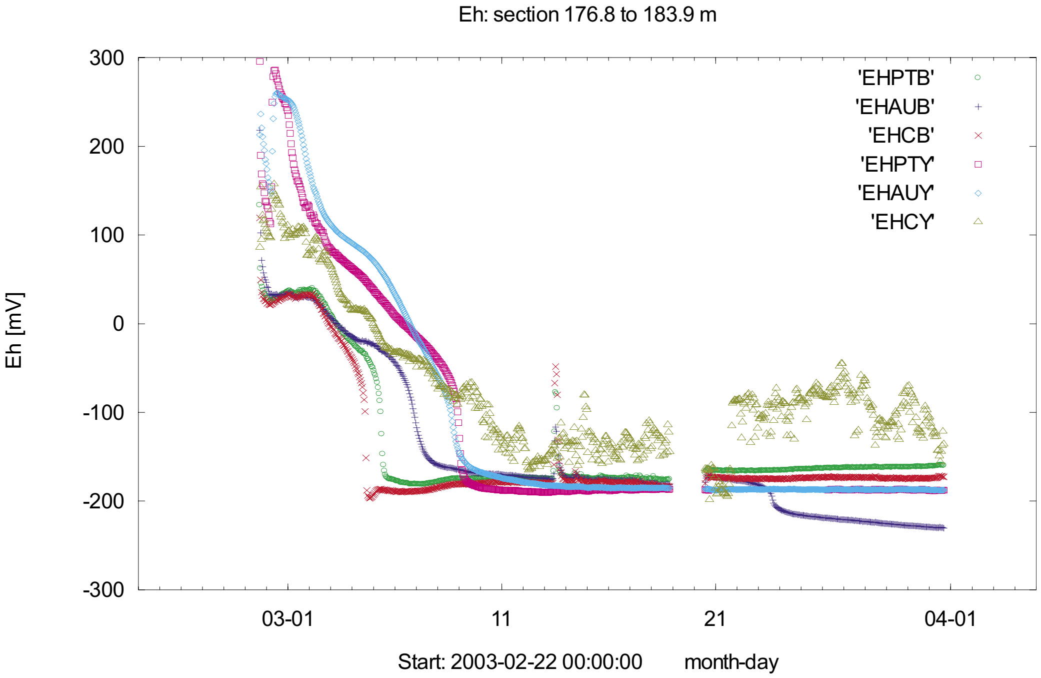


Figure A5-1. *Redox potental measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCY). The glassy carbon electrode at the surface shows a noisy signal due to an erroneous amplifier.*

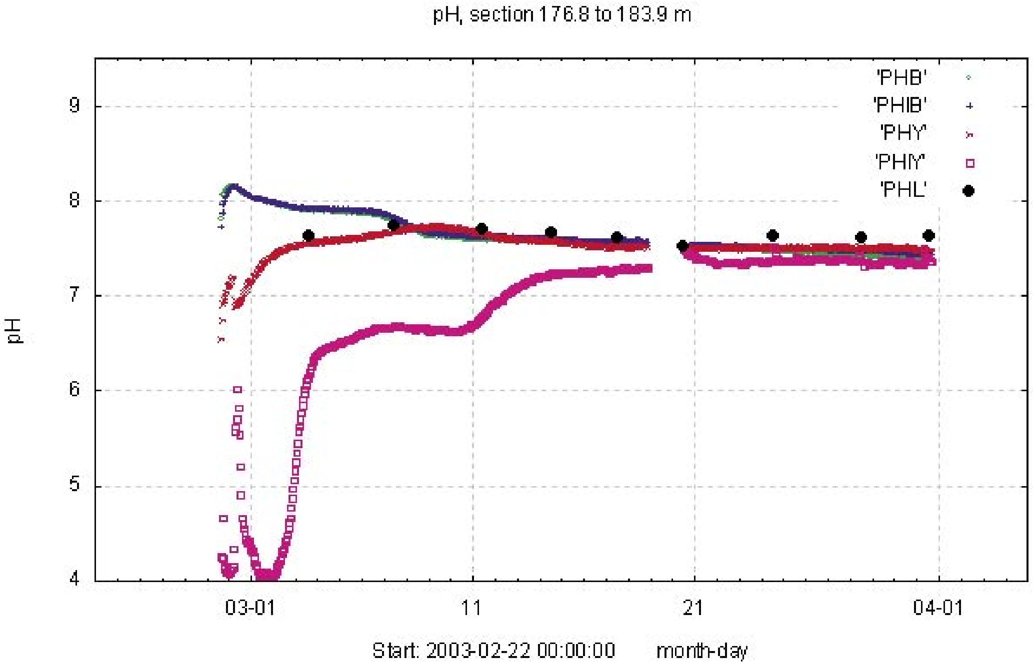


Figure A5-2. *Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison.*

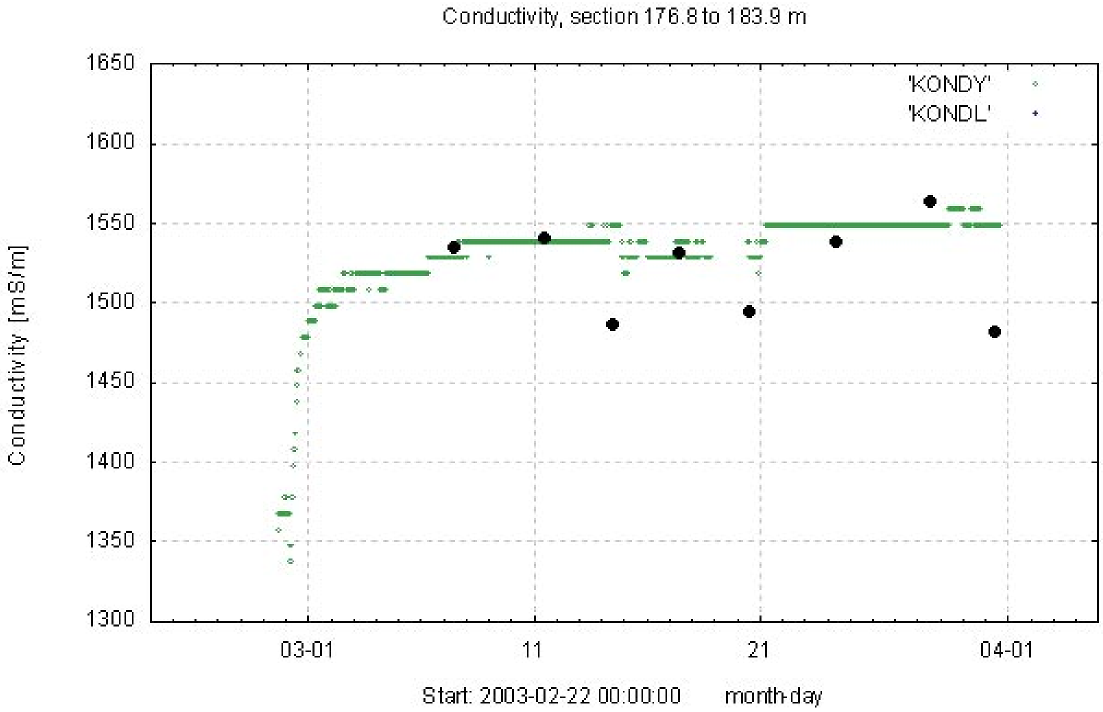


***Figure A5-3.** Electric conductivity measurement in the surface measurement cell (KONDY). The electric conductivity measured in each collected sample (KONDL) is given for comparison.*

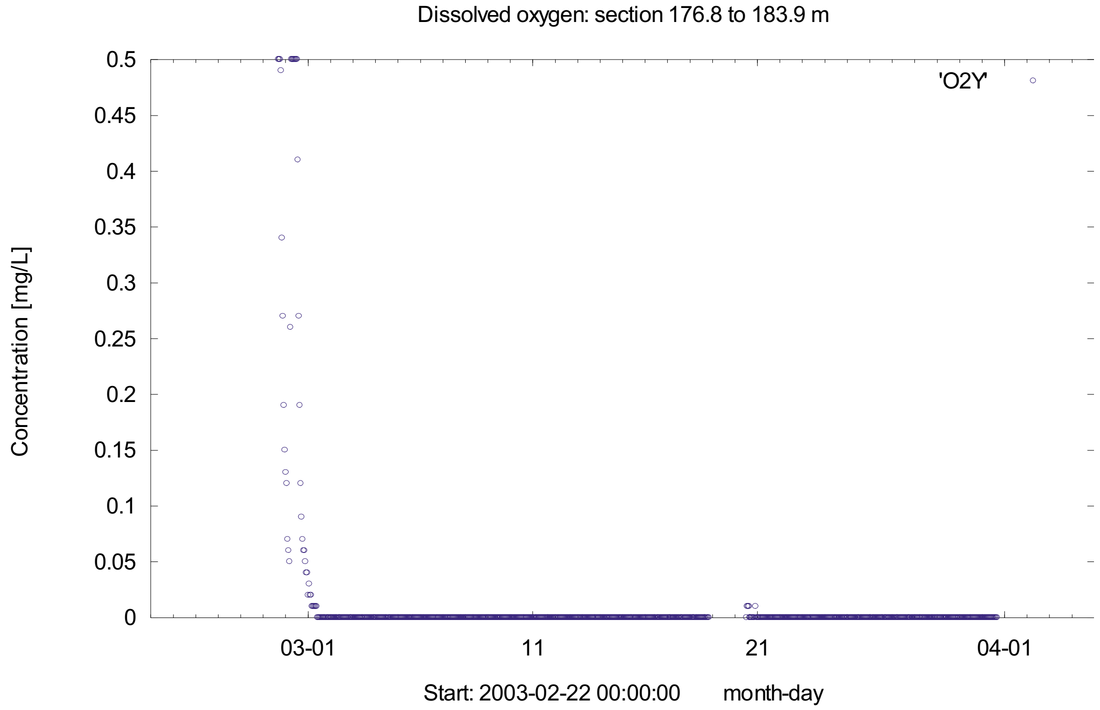


***Figure A5-4.** Dissolved oxygen measurement (O2Y) in the surface measurement cell.*

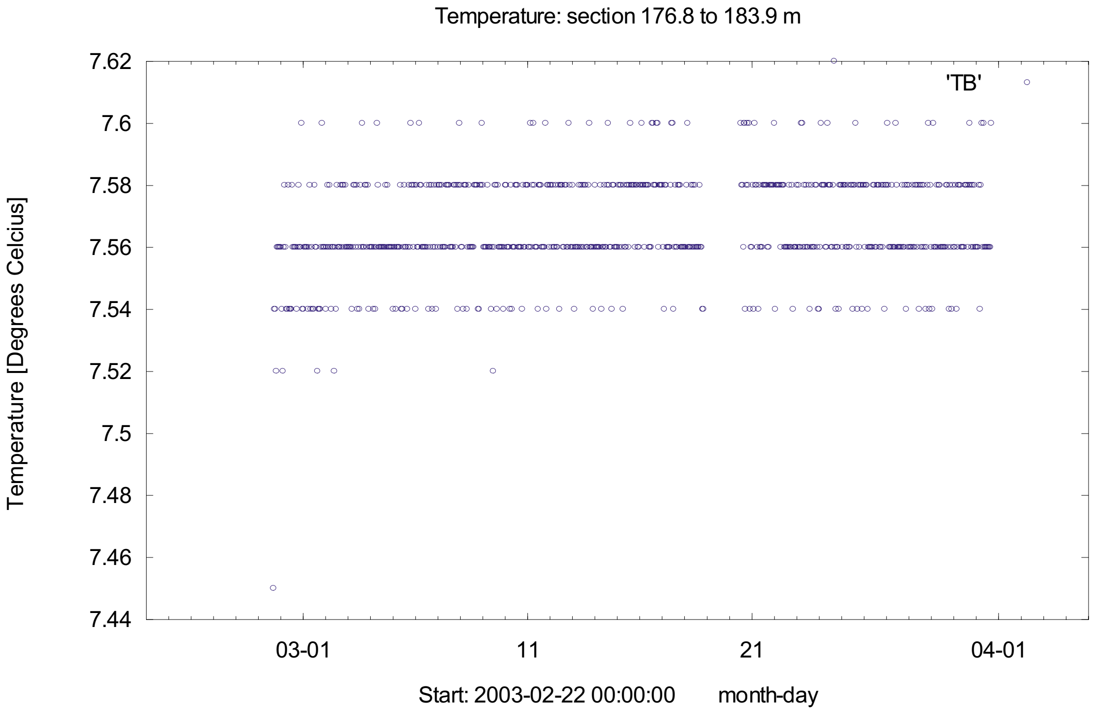


Figure A5-5. *Temperature of the groundwater in the borehole section (TB).*

Appendix 6

Sampling and analysis methods

Table A6-1. Sample handling routines and analysis methods.

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Anions 1.	HCO_3 pH(lab) cond (lab)	Plastic	250	Yes (not in the field)	No	Titration Pot. meas, Cond. meas	Mobile field lab. AnalyCen	The same day – maximum 24 hours
Anions 2	Cl, SO_4, Br^-, F^-, I^-	Plastic	100	Yes (not in the field)	No	Titration (Cl^-) IC (Cl^-, SO4, Br^-, F^-) ISE (F^-)	Äspö:s chemistry lab. AnalyCen	Not critical (month)
	Br, I	Plastic	100	Yes (not in the field)	No	ICP MS	Paavo Ristola OY Analytica AB,	Not critical (month)
Cations, Si and S according to SKB class 3	Na, K, Ca, Mg, S(tot), Si(tot), Li, Sr	Plastic (at low conc. acid washed bottles)	100	Yes (not in the field)	Yes (not in the field, 1 mL HNO_3)	ICP-AES ICP-MS	Analytica AB, AlnalyCen	Not critical (month)
Cations, Si and S according to SKB class 4 and 5	Na, K, Ca, Mg, S(tot), Si(tot), Fe, Mn, Li, Sr	Plastic (Acid washed)	100	Yes (immediately in the field)	Yes (1mL HNO_3)	ICP-AES ICP-MS	Analytica AB, AlnalyCen	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic (Acid washed)	500	Yes	Yes (5 mL HCl))	Spectrophotometry Ferrozine method	Mobile field lab.	As soon as possible the same day
Hydrogen sulphide	HS^-	Glass (Winkler)	About 120×2	No	Ev 1 mL 1 M NaOH+ 1 mL 1M ZnAc	Spectrophotometry	AlnalyCen I Äspö:s chemistry lab.	Immediately or if conserved, a few days
Nutrient salts	NO_2, NO_3+NO_2, NH_4, PO_4	Plastic	250	No	No	Spectrophotometry	Äspö:s chemistry lab. AlnalyCen I	Maximum 24 hours
Environmental metals	Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	Analytica AB, AnalyCen	Not critical (month)
Lantanoids, U, Th and so on.	Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	SGAB Analytica, AnalyCen	Not critical (month)
Dissolved organic Carbon, dissolved inorganic Carbon	DOC, DIC	Plastic	250 25	Yes	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Paavo Ristola OY Dept. of System ecology, SU	Short transportation time

Component group	**Component/ element**	**Sample container (material)**	**Volume (mL)**	**Filtering**	**Preparation/ Conservation***	**Analysis method**	**Laboratory*****	**Analysis within - or delivery time to lab.**
Total organic Carbon	TOC	Plastic	250 25	No	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Paavo Ristola OY Dept. of System ecology, SU	Short transportation time
Environmental isotopes	∂^2H, $\partial^{18}O$	Plastic	100	No	- -	MS	IFE	Not critical (month)
Tritium, Chlorine-37	^3H (enhanced.) $\partial^{37}Cl$	Plastic (dry bottle) Plastic	500 100	No No	- -	LSC ICP MS	Univ.of Waterloo	Not critical (month)
Carbon isotopes	$\partial^{13}C$, pmC (^{14}C)	Glass (brown)	100×2	No	-	(A)MS	Univ. of Waterloo	A few days
Sulphur isotopes	$\partial^{34}S$	Plastic	500 –1000	Yes	-	Combustion, ICP MS	IFE	No limit
Strontium-isotopes	$^{87}Sr/^{86}Sr$	Plastic	100	Yes	-	TIMS	IFE	Days or Week
Uranium and Thorium isotopes	^{234}U, ^{235}U, ^{238}U, ^{232} Th, ^{230}Th,	Plastic	50	No	-	Chemical separat. Alfa/gamma spectrometry	IFE	No limit
Boron isotopes	$^{10}B/^{11}B$	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP – MS	Analytica AB	No limit
Radon and Radium isotopes	^{222}Rn, ^{226}Ra	Plastic	500	No	No	EDA, RD-200	IFE	Immediate transport
Dissolved gas (content and composition)	Ar, N_2, CO_2, O_2, CH_4, H_2, CO, C_2H_2, C_2H_4, C_2H_6, C_3H_8	Cylinder of stainless steel	200	No	No	GC	Paavo Ristola OY	Immediate transport
Colloids	Filter series and fractionation (see below)	Polycarbonate filter	0.45, 0.2 and 0.05 µm	-	N_2 atmosphere	ICP-AES ICP-MS	Analytica AB	Immediate transport
Humic and fulvic acids	Fractionation	Fractions are collected in plastic bottles	250	-	N_2 atmosphere	UV oxidation, IR (DOC)	Paavo Ristola OY	Immediate transport
Archive samples with acid	-	Plast (washed in acid)	100×2 **	Yes	Yes (1 mL HNO_3)	-	-	Storage in freeze container
Archive samples without acid	-	Plastic	250×2 **	Yes	No	-	-	Storage in freeze container
Carbon isotopes in humic and fulvic acids	$\partial^{13}C$, pmC (^{14}C)	DEAE cellulose (anion exchanger)	-	-	-	(A)MS	The Ångström laboratory, Uppsala	A few days

* Suprapur acid is used for conservation of samples.

** Minimum number, the number of archive samples can vary depending on how many similar samples that are collected at the same occasion.

*** Full name and address is given in Table A2-3.

Abbreviations and definitions:

IC	Ion chromatograph
ISE	Ion selective electrode
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
MS	Mass Spectrometry
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
GC	Gas Chromatography

Table A6-2. Reporting limits and measurement uncertainties.

Component	**Method**	**Detection limit**	**Reporting limit or range**	**Unit**	**Measurement uncertainty**[2]	**"Total" uncertainty**[3]
HCO_3	Alkalinity titration	0.2	1	mg/L	4 %	<10 %
Cl^- Cl^-	Mohr titration IC	5 0.2	70 0.5	mg/L	5 % 6 %	<10 % 10 %
SO_4	IC	0.2	0.5	mg/L	6 %	15 %
Br^- Br^-	IC ICP	0.2 -	0.7 0.001 – 0.010[1]	mg/L	9 % 15 %	20 %
F^- F^-	IC Potentiometri	0.2 -	0.6 -	mg/L	10 % -	20 % -
I^-	ICP	-	0.001 – 0.010[1]	mg/L	15 %	20 %
Na	ICP	-	0.1	mg/L	4 %	10 %
K	ICP	-	0.4	mg/L	6 %	15 %
Ca	ICP	-	0.1	mg/L	4 %	10 %
Mg	ICP	-	0.09	mg/L	4 %	10 %
S(tot)	ICP	-	0.160	mg/L	10 %	15 %
Si(tot)	ICP	-	0.03	mg/L	4 %	15 %
Sr	ICP	-	0.002	mg/L	4 %	15 %
Li	ICP	-	0.2 - 2[1]	µg/L	10 %	20 %
DOC	See tab. 1	-	0.5	Mg/L	8 %	30 %
TOC	See tab. 1	-	0.5	Mg/L	10 %	30 %
$\delta^{2}H$	MS	-	2	‰ SMOW[4]	1.0 ‰	-
$\delta^{18}O$	MS	-	0.1	‰ SMOW[4]	0.2 ‰	-
^{3}H	LSC	-	0.8 or 0.1	TU[5]	0.8 or 0.1 TU	-
$\delta^{37}Cl$	ICP MS	-	0.2 ‰ (20 mg/L)	‰ SMOC[6]	-	-
$\delta^{13}C$	A (MS)	-	>20 mg Carbon	‰ PDB[7]	-	-
pmC (^{14}C)	A (MS)	-	>20 mg kol	PmC[8]	-	-
δ^{34} S	ICP MS	-	0.2 ‰	‰ CDT[9]	0.2 ‰	-
$^{87}Sr/^{86}Sr$	MS	-	-	No unit (ratio)[10]	0.000020	-
$^{10}B/^{11}B$	ICP MS	-	-	No unit (ratio)[10]	0,0020	-

[1] Reporting limits at salinity ≤ 0.4 % (520 mS/m) and ≤ 3.5 % (3810 mS/m) respectively.

[2] Measurement uncertainty reported by consulted laboratory.

[3] Estimated total uncertainty by experience (includes effects of sampling and sample handling).

[4] Per mill deviation[11] from SMOW (Standard Mean Oceanic Water).

[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 mill deviation[11] from SMOC (Standard Mean Oceanic Chloride).

[7] Per mill deviation[11] from PDB (the standard PeeDee Belemnite).

[8] The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: $pmC = 100 \times e^{((1950-y-1.03t)/8274)}$
where y = the year of the C-14 measurement and t = C-14 age

[9] Per mill deviation[11] from CDT (the standard Canyon Diablo Troilite).

[10] Isotope ratio without unit.

[11] Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:
$\delta^{y}I = 1000 \times (K_{sample}-K_{standard})/K_{standard}$, where K= the isotope ratio and $^{y}I = {}^{2}H$, ^{18}O, ^{37}Cl, ^{13}C or ^{34}S etc.

Table A6-3. Participant laboratories.

Äspö water chemical laboratory (SKB) Mobile field laboratory, Forsmark (SKB)
Inainööritoimisto Paavo Ristola Oy Teollisuus-ja Voimalaitoskemia Rajantorpantie 8, C-talo 01600 Vantaa FINLAND
Dept. of System ecology Stockholm University 10691 Stockholm
Analytica AB Aurorum 10 977 75 Luleå (Nytorpsvägen 16 Box 511 183 25 Täby)
Environmental Isotope Laboratory Dep. Of earth sciences University of Waterloo Waterloo, Ontario N2L 3G1 CANADA
Institutt for energiteknik (IFE) Insituttveien 18 P.O Box 40 2027 Kjeller NORGE
AlnalyCen Nordic AB Box 905 531 19 Lidköping
The Ångström laboratory Box 534 Se-751 21 Uppsala

Appendix 7

Water Composition

Table A7-1. Compilation December 2003

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Charge Bal %	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	HCO_3 mg/L	Cl mg/L	SO_4 mg/L	SO_4-S mg/L	Br mg/l	F^- mg/L	Si mg/L	Fe mg/L	Fe-tot mg/L	Fe(II) mg/L
KFM01A	110,1	120,77	4461	2003-01-17		-	-	-	-	72	3840	286	-	16,1	0,90	-	-	-	-
KFM01A	110,1	120,77	4466	2003-01-22	-0,9	1760	22,0	875	136	69	4500	309	96,2	18,6	1,17	7,1	1,61	-	-
KFM01A	110,1	120,77	4480	2003-02-07	-1,6	1780	22,3	871	140	61	4550	324	105	18,4	1,15	7,5	1,25	1,59	1,53
KFM01A	110,1	120,77	4481	2003-02-10	-1,5	1780	22,5	875	140	62	4540	326	105	17,2	1,21	7,8	1,31	1,43	1,41
KFM01A	110,1	120,77	4484	2003-02-12	0,3	1800	22,6	927	144	62	4500	317	109	17,7	1,12	8,1	1,33	1,53	1,49
KFM01A	110,1	120,77	4520	2003-02-17	4,2	1760	23,6	924	143	62	4080	280	109	15,9	1,02	8,0	1,06	1,21	1,18
KFM01A	110,1	120,77	4524	2003-02-20	-2,1	1750	25,1	879	143	61	4570	327	105	20,4	1,28	7,3	0,831	1,07	1,10
KFM01A	110,1	120,77	4538	2003-02-24	-2,3	1740	25,6	874	142	61	4560	316	105	18,4	1,36	7,2	0,790	0,996	0,953
KFM01A	176,8	183,9	4542	2003-02-27		-	-	-	-	105	-	-	-	-	-	-	-	-	-
KFM01A	176,8	183,9	4610	2003-03-03	-1,3	2050	32,9	909	199	103	5040	522	164	17,6	1,20	6,3	0,876	1,02	1,03
KFM01A	176,8	183,9	4620	2003-03-07	-3,5	1990	35,5	918	194	105	5190	533	165	18,0	0,95	6,6	1,59	1,88	1,85
KFM01A	176,8	183,9	4637	2003-03-11	-2,3	2030	34,7	920	200	106	5140	533	166	18,1	1,20	6,7	1,24	1,76	1,75
KFM01A	176,8	183,9	4663	2003-03-14	-3,6	2000	36,4	916	197	100	5220	534	166	18,8	1,05	6,7	0,914	1,14	1,11
KFM01A	176,8	183,9	4664	2003-03-17	-3,3	2010	35,4	904	198	100	5200	529	163	15,8	0,90	6,6	0,708	0,852	0,825
KFM01A	176,8	183,9	4665	2003-03-20	-2,6	1980	28,5	928	200	100	5090	537	173	19,5	1,19	6,8	0,768	0,788	0,807
KFM01A	176,8	183,9	4666	2003-03-24	-3,2	1980	28,6	925	200	98	5150	543	172	19,8	0,88	6,8	0,551	0,585	0,570
KFM01A	176,8	183,9	4700	2003-03-28	-3,8	1990	29,0	934	202	99	5260	564	173	20,3	1,02	6,9	0,512	0,526	0,525
KFM01A	176,8	183,9	4724	2003-03-31	-4,3	2000	29,2	934	204	99	5330	547	174	20,1	1,02	6,9	0,515	0,537	0,475

- = Not analysed
x = No result due to sampling problems
xx = No result due to analytical problems
- "value" = concentration below detection limit
ChargeBal % = Relative charge balance error %

SICADA: water_composition

Table A7-1. Compilation December 2003

Idcode	Secup m	Seclow m	Sample no.	Mn mg/L	Li mg/L	Sr mg/L	pH	DOC mg/L	HS^- mg/L	Drill_water %	ElCond mS/m	NH_4N (mg/L)
KFM01A	110,1	120,77	4461	-	-	-	7,50	-	-	7,7	-	-
KFM01A	110,1	120,77	4466	0,72	0,042	6,66	7,58	-	<0.03	1,8	-	-
KFM01A	110,1	120,77	4480	0,70	0,044	6,53	7,64	4,6	<0.03	1,3	-	0,924
KFM01A	110,1	120,77	4481	0,70	0,054	6,57	7,69	2,9	<0.03	0,9	-	1,07
KFM01A	110,1	120,77	4484	0,73	0,043	6,69	7,69	2,4	<0.03	0,7	-	1,07
KFM01A	110,1	120,77	4520	0,72	0,041	6,60	7,68	1,6	<0.03	0,7	-	1,01
KFM01A	110,1	120,77	4524	0,69	0,046	6,41	6,98	-	<0.03	0,5	-	1,06
KFM01A	110,1	120,77	4538	0,69	0,046	6,40	7,47	1,5	<0.03	0,8	-	1,07
KFM01A	176,8	183,9	4542	-	-	-	7,05	-	-	17,8	-	-
KFM01A	176,8	183,9	4610	0,97	0,056	7,10	7,63	3,3	<0.03	7,3	-	1,16
KFM01A	176,8	183,9	4620	0,97	0,056	6,81	7,74	3,3	<0.03	6,5	1530	1,34
KFM01A	176,8	183,9	4637	1,00	0,056	6,94	7,72	2,5	<0.03	5,6	1540	1,41
KFM01A	176,8	183,9	4663	0,99	0,056	6,83	7,68	1,1	<0.03	5,6	1490	1,17
KFM01A	176,8	183,9	4664	1,01	0,055	6,82	7,61	2,4	<0.03	5,3	1530	1,06
KFM01A	176,8	183,9	4665	0,99	0,057	6,89	7,49	4,1	<0.03	5,2	1490	1,26
KFM01A	176,8	183,9	4666	0,99	0,061	6,87	7,62	3,1	<0.03	5,2	1540	1,41
KFM01A	176,8	183,9	4700	1,01	0,059	6,92	7,62	3,2	<0.03	5,0	1560	1,09
KFM01A	176,8	183,9	4724	1,02	0,061	6,94	7,60	2,3	<0.03	4,8	1480	1,01

- = Not analysed
x = No result due to sampling problems
xx = No result due to analytical problems
- "value" = concentration below detection limit
ChargeBal % = Relative charge balance error %

SICADA: water_composition

Table A7-2. Compilation of H-, O-, B-, S-, Cl-, Sr and C-isotopes and isotope ratios.

Idcode	Secup m	Seclow m	Sample no	Sampling date	∂D dev SMOW	Tr TU	$\partial^{18}O$ dev SMOW	$^{10}B/^{11}B$ no unit	$\partial^{34}S$ dev CDT	$\partial^{13}C$ dev PDB	$\partial^{37}Cl$ dev SMOC	$^{87}Sr/^{86}Sr$ no unit	^{14}C pmC	AGE_BP years
KFM01A	110,1	120,77	4481	2003-02-10	-87,3	<0.8	-11,5	0,2388	23,9	-13,7	0,24	0,720399	50,7	5400
KFM01A	110,1	120,77	4520	2003-02-17	-89,2	<0.8	-11,5	0,2326	25,4	-	0,34	0,720375	-	-
KFM01A	110,1	120,77	4538	2003-02-24	-88,2	<0.8	-11,6	0,2399	25,5	-13,0	0,49	0,720373	12,20	16830
KFM01A	176,8	183,9	4620	2003-03-07	-70,2	<0.8	-8,8	0,2374	25,0	-7,7	0,24	0,720966	18,53	13490
KFM01A	176,8	183,9	4663	2003-03-14	-69,6	<0.8	-8,8	0,2374	25,1	-7,5	0,04	0,721080	17,98	13733
KFM01A	176,8	183,9	4665	2003-03-20	-73,0	<0.8	-8,8	0,2368	25,4	-7,5	-0,09	0,721157	17,89	13774
KFM01A	176,8	183,9	4724	2003-03-31	-69,3	<0.8	-8,8	0,2369	25,6	-6,5	-0,12	0,721196	16,68	14355

- = Not analysed
A = result will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
SICADA: h_o_isotopes, b_s_cl_sr_isotopes, c_s_isotopes

Table A7-3. Trace elements.

Idcode	Secup m	Seclow m	Sample no,	Sampling date	U ug/L	Th ug/L	Sc ug/L	Rb ug/L	Y ug/L	Zr ug/L	In ug/L	Sb ug/L	Cs ug/L	La ug/L	Hf ug/L	Tl ug/L	Ce ug/L
KFM01A	110,1	120,77	4538	2003-02-24	1,5	<0,2	<0,5	62,0	0,36	<0,30	-	xx	0,95	<0,05	<0,05	<0,3	<0,05
KFM01A	176,8	183,9	4620	2003-03-07	20,3	<0,5	<0,5	83,0	1,33	<0,25	<0,5	<0,2	1,68	<0,05	<0,05	<0,25	<0,05
KFM01A	176,8	183,9	4663	2003-03-14	17,0	<0,5	<0,5	84,6	1,31	<0,25	<0,5	<0,2	1,80	<0,05	<0,05	<0,25	<0,05
KFM01A	176,8	183,9	4665	2003-03-20	17,7	<0,2	<0,5	81,1	13,1	0,382	<0,5	0,447	2,15	0,0791	<0,05	<0,3	0,0847
KFM01A	176,8	183,9	4700	2003-03-28	15,0	<0,2	0,916	77,2	12,2	0,445	<0,5	0,215	1,74	0,0945	<0,05	<0,3	0,0699
KFM01A	176,8	183,9	4724	2003-03-31	14,9	0,61	<0,5	81,2	1,3	0,389	xx	0,165	1,61	<0,05	<0,05	<0,3	<0,05

Idcode	Secup m	Seclow m	Sample no,	Pr ug/L	Nd ug/L	Sm ug/L	Eu ug/L	Gd ug/L	Tb ug/L	Dy ug/L	Ho ug/L	Er ug/L	Tm ug/L	Yb ug/L	Lu ug/L
KFM01A	110,1	120,77	4538	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM01A	176,8	183,9	4620	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM01A	176,8	183,9	4663	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM01A	176,8	183,9	4665	<0,05	<0,05	<0,05	0,0877	<0,05	<0,05	<0,05	0,145	0,124	<0,05	0,0838	<0,05
KFM01A	176,8	183,9	4700	<0,05	<0,05	<0,05	0,0683	<0,05	<0,05	<0,05	<0,05	0,115	<0,05	0,0898	<0,05
KFM01A	176,8	183,9	4724	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05

- = Not analysed
x = No result due to sampling problems
xx = No result due to analytical problems
- "value" = concentration below detection limit
SICADA: trace_elements

Table A7-4. Compilation of U-, Th, Ra- and Rn-isotope data.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	U-238 mBq/L	U-235 mBq/L	U-234 mBq/L	Th-232 mBq/L	Th-230 mBq/L	Ra-226 Bq/L	Rn-222 Bq/L
KFM01A	110,1	120,77	4481	2003-02-10	<50	<50	<50	<50	<50	-	-
KFM01A	110,1	120,77	4520	2003-02-17	60	<50	60	<50	60	-	-
KFM01A	110,1	120,77	4538	2003-02-24	<50	<50	<50	<50	<50	1,80	181
KFM01A	176,8	183,9	4620	2003-03-07	240	<50	240	<50	160	-	-
KFM01A	176,8	183,9	4663	2003-03-14	110	<50	110	<50	<50	-	-
KFM01A	176,8	183,9	4665	2003-03-20	110	<50	110	<50	80	-	-
KFM01A	176,8	183,9	4724	2003-03-31	170	<50	170	<50	100	1,30	291

- = Not analysed
A = Results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
- "value" = concentration below detection limit
SICADA: u_th_isotope_t, ra_rn_isotope_t

Table A7-5. Dissolved gases.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Ar mL/L	He mL/L	N_2 mL/L	CO_2 mL/L	CH_4 mL/L	O_2 mL/L	H_2 µL/L	CO µL/L	C_2H_6 µL/L	C_2H_4 µL/L	C_2H_2 µL/L	C_3H_8 µL/L	DISS_GAS mL/L H_2O
KFM01A	176,8	183,9	4724	2003-04-01	1,03	1,04	54,3	1,19	0,12	0,095	5,4	<2.9	1,4	0,08	<0.05	1,5	57,8

- = Not analysed
A = Results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
- "value" = concentration below detection limit
SICADA: gas_dissolved