P-05-178

Forsmark site investigation

Chemical characterisation in borehole KFM06A

Results from the investigated sections at 266.0–271.0 m, 353.5–360.6 m and 768.0–775.1 m

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October 2005

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Abstract

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. This is carried out over a period of approximately three weeks per section at a flow rate of between 50 and 200 mL/min.

The method has been used in two sections from borehole KFM06A, at 353.5–360.6 m and 768.0–775.1 m, respectively. An attempt was also made to investigate a section at 740–747 m borehole length, but the investigation was interrupted due to high amounts of residual flushing water (46%) from core drilling. Furthermore, a simple water sample (SKB klass 3) was collected in borehole section 266.0–271.0 m in connection with subsequent injection tests in the borehole.

The results obtained from the complete chemical characterisation in sections 353.5–360.6 m and 768.0–775.1 m include on-line measurements of redox potential, pH, dissolved oxygen, electrical conductivity and water temperature in the borehole section as well as chemical analyses of major constituents, trace metals and isotopes. Furthermore, gas content and composition, inorganic colloids as well as humic and fulvic acids were investigated. In section 353.5–360.6 m the investigation was extended by one week and the downhole equipment was raised and lowered on two occasions to collect four extra in situ groundwater samples (totally eight samples). This was done in order to allow testing of Laser-Induced Breakdown Detection (LIBD) for quantifying the amount of colloids and also to perform repeated analyses of dissolved gases and microbes in order to check the reproducibility.

The water composition was reasonably stable during the pumping and sampling period in both investigated sections. The chloride concentrations amounted to approximately 4,800 mg/L (353.5–360.6 m) and 7,000 mg/L (768.0–775.1 m). The in situ redox potential measurements showed quite stable negative values at approximately –155 mV (353.5–360.6 m) and –200 mV (768.0–775.1 m). The reducing conditions in the groundwaters were also verified by the presence of ferrous iron, Fe(+II), at relatively high concentrations. The content of inorganic colloids was low or nonexistent, and the organic constituents were present mainly as fulvic acids or other low molecular weight acids (citric acid, oxalic acids, etc).

The chloride concentration in the single sample from section 266.0–271.0 m amounted to 5,200 mg/L and the flushing water content was 1.6%.

Sammanfattning

Fullständig kemikarakterisering är den mest omfattande kemiska undersökningsmetoden för kärnborrhål. Metoden innebär pumpning, mätning on-line och regelbunden vattenprovtagning för kemiska analyser i avgränsade borrhålssektioner under cirka tre veckor per sektion med ett pumpflöde på mellan 50 och 200 mL/min.

Metoden har utförts i de två sektionerna vid 353,5–360,6 m och 768,0–775,1 m i borrhålet KFM06A. Ett försök gjordes att även undersöka en sektion vid 740–747 m. Detta avbröts dock på grund av att halten kvarvarande spolvatten efter kärnborrningen var mycket hög (46 %). Förutom dessa undersökningar togs ett enstaka vattenprov (SKB klass 3) i borrhålssektionen vid 266,0–271,0 m i samband med de efterföljande injektionstesterna i borrhålet.

Resultaten som erhölls från den fullständiga kemikaraktäriseringen i de två sektionerna omfattar mätningar on-line av redoxpotential, pH, löst syre, elektrisk konduktivitet och vattentemperatur i borrhålssektionen samt kemiska analyser av huvudkomponenter, spårelement och isotoper. Vidare undersöktes gasinnehåll och sammansättning, oorganiska kolloider samt humus- och fulvosyror i grundvattnet. I sektionen 353,5–360,6 m förlängdes undersökningsperioden med en vecka och en extra sänkning/lyft av i-hålet utrustningen gjordes för att kunna ta ytterligare fyra in situ provportioner (totalt åtta provportioner). Detta för att ge möjlighet att testa Laser-Induced Breakdown Detection (LIBD) för kvantifiering av mängden kolloider och dessutom göra dubbelanalyser av lösta gaser och mikrober med avsikt att undersöka reproducerbarheten.

Vattensammansättningen var i det närmaste stabil under pump-/provtagningsperioderna i båda undersökta borrhålssektionerna. Kloridkoncentrationen uppgick till ca 4 800 mg/L (353,5–360,6 m) respektive 7 000 mg/L (768,0–775,1 m). Redoxmätningarna i sektionen visade samlade och ganska stabila negativa värden på cirka –155 mV (353,5–360,6 m) respektive –200 mV (768,0–775,1 m). De reducerande förhållandena i grundvattnet verifierades även av närvaron av tvåvärt järn i relativt höga koncentrationer. Mängden oorganiska kolloider var mycket låg eller icke existerande och de organiska komponenterna förelåg huvudsakligen som fulvosyror eller andra lågmolekylära syror (citronsyra, oxalsyra etc).

Kloridkoncentrationen i det enda provet från sektionen 266.0–271.0 m uppgick till 5 200 mg/L och spolvattenhalten var 1.6 %.

Contents

1 Introduction

This document reports performance and results of the activity: Complete chemical characterisation in KFM06A within the site investigation programme at Forsmark /1/. The report presents hydrogeochemical data from borehole sections at 266–271 m, 353.5–360.6 m and 768.0–775.1 m. The work was conducted according to the activity plans AP PF 400-04-10 (conducted by ÅF process AB) and AP PF 400-04-122 (conducted by SKB); the latter one concerns section 266–271 m. Most of the fieldwork was carried out during January and February 2005, although pumping in the borehole started already in December 2004. The controlling documents are listed in Table 1-1. Both activity plans and method descriptions are SKB's internal controlling documents. Sampling for microbe studies, based on the activity plan AP PF 400-05-53, was also performed within the present activity. The microbe investigations are reported in a separate primary data report /2/. The obtained data from the activity are reported in the database SICADA and traceable from the activity plan numbers.

Borehole KFM06A is the sixth approx 1,000 m deep telescopic borehole drilled at Forsmark /3/. The location of the borehole and the other current deep telescopic boreholes within the investigation area are shown in Figure 1-1, whereas Figure 1-2 is a detailed map of drill site DS6 with KFM06A and nearby situated percussion drilled boreholes in rock and soil. KFM06A is inclined at 60°, dipping northwest. The borehole section between 0–100.75 m is percussion drilled and has a stainless steel casing with an internal diameter of 200 mm. Section 100.75–102.04 m is core drilled with a diameter of 860 mm and also cased, whereas the 102.04–1,000.64 m interval is core drilled with a diameter of 77.3 mm and uncased. The design of the borehole is presented in Appendix 1.

The borehole is of the so-called SKB chemical-type; see the SKB method descriptions MD 620.003 (Method description for drilling cored boreholes) and MD 610.003 (Method description for percussion drilling). An 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.

Table 1-1. Controlling documents for performance of the activity.

Activity plans	Number	Version
Fullständig kemikaraktärisering med mobilt fältlaboratorium i KFM06A.	AP PF 400-04-110	1.0
Hydraulic injection tests in borehole KFM06A with PSS3.	AP PF 400-04-122	1.0
Method descriptions/instructions	**Number**	**Version**
Metodbeskrivning för fullständig kemikaraktärisering med mobilt fältlaboratorium.	SKB MD 430.017	1.0
Enkel vattenprovtagning i hammarborrhål och kärnborrhål.	SKB MD 423.002	2.0

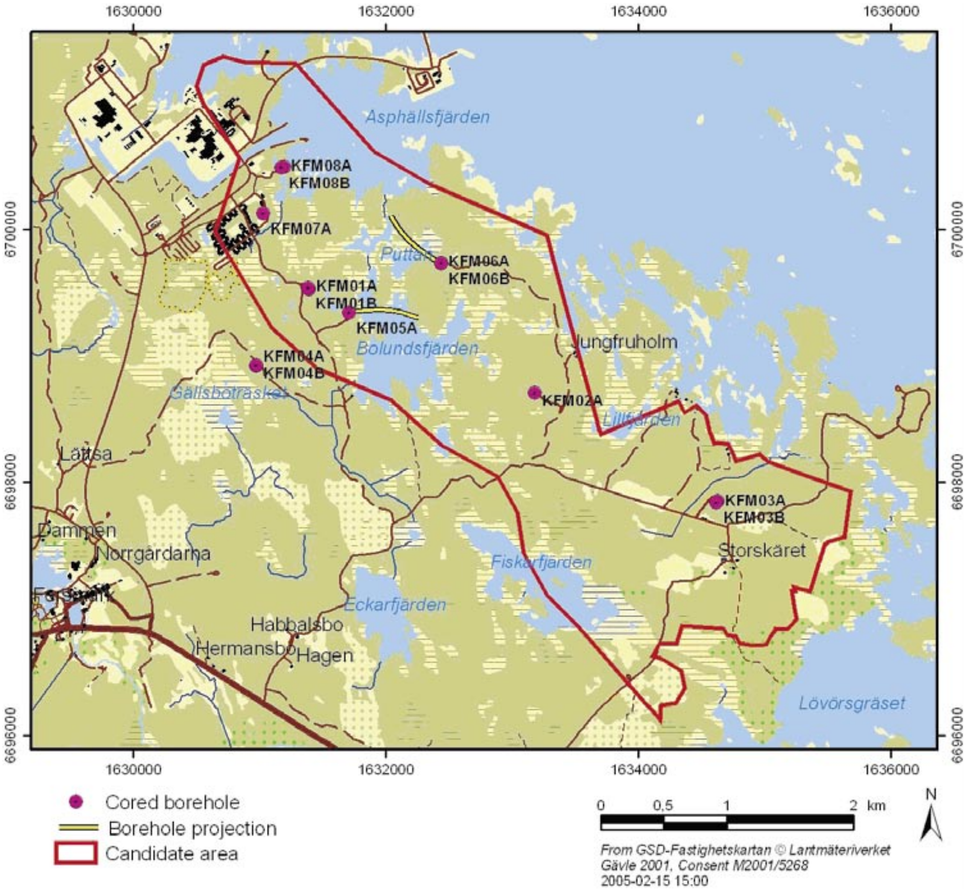


__Figure 1-1__. The investigation area at Forsmark (approximately the area inside the black square) including the candidate area selected for more detailed investigations. The deep and semi-deep (approx 100–450 m) cored boreholes, KFM01A to KFM08B, are marked with pink infilled circles.

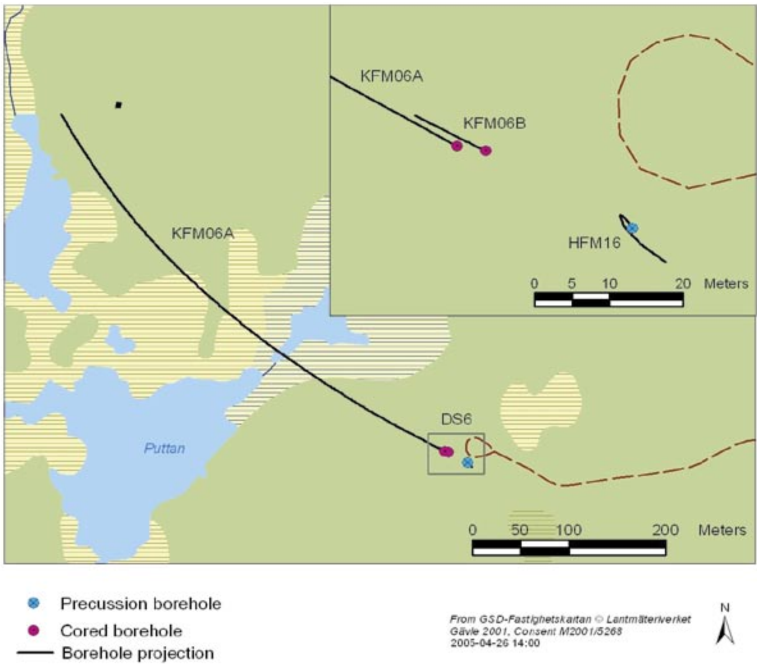


***Figure 1-2.** Location and projection on the horizontal plane of the cored boreholes KFM06A and KFM06B and the percussion borehole HFM16 at drill site DS6.*

2 Objectives and scope

"Complete chemical characterisation" is the most extensive chemical investigation method performed in core drilled boreholes. The method is carried out in order to achieve as much information as possible about the groundwater chemical conditions in individual water bearing fractures or 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.

A decision has been made to prioritise the northwestern part of the candidate area for continuing investigations /4/. In this part, there are no representative chemical data from borehole sections at depths greater than 200 m, prior to the present investigation. Furthermore, there are reasons to believe that there will be very few water yielding fractures at depth also in the coming boreholes. Therefore, every opportunity to conduct chemical investigations at depth in this part of the candidate area needs to be taken. In addition, it was important to gain hydrochemical data from at least three fracture zones at different depths in order to allow comparison with corresponding data from the matrix pore water study performed in this borehole /5/.

The analytical programme was carried out according to SKB chemistry class 4 and class 5 including all options /1/ (except the single sample from section 266–271 m which was analysed according to SKB class 3). Furthermore, pH, redox potential (Eh) and water temperature were measured in downhole flow-through cells in the pumped borehole section as well as at the surface. The flow-through cell at the surface also measured electrical conductivity and dissolved oxygen. Samples were collected in situ in the borehole section for determination of gas content and composition, microbe content and their characterisation as well as for determinations of colloid content and composition. A method to determine colloid content by a laser technique (LIBD) was tested in section 353.5–360.6 m. Fractionation of organic acids and inorganic species were performed in order to investigate size distribution (DOC and ICP analyses), and enrichment of organic acids was conducted in order to determine ∂^{13}C and pmC in organic constituents.

3 Background

3.1 Flushing water history

The percussion drilled borehole HFM05 served as a supply well for the flushing water used to drill borehole KFM06A /6/. The chemical composition of the flushing water was checked before and during use. The analytical data from the supply well HFM05 are reported in /7/. The core drilling of the 1,000 m long borehole consumed 1,087 m^3 of flushing water and the volume of returned water pumped from the borehole during drilling was 1,968 m^3. The nominal concentration of the dye Uranine, added as a tracer to mark the flushing water, was 0.2 mg/L. Automatic dosing equipment to introduce Uranine was installed in the flushing water line to supply flushing water to the drilling of KFM06A. The Uranine concentration in the flushing water was checked regularly during drilling and a total of 125 samples were analysed. A systematic error caused too high Uranine concentrations and the values were therefore corrected by a factor 0.7. The average Uranine concentration in the sample series without correction was 0.27 ± 0.04 mg/L and with correction 0.19 ± 0.03 mg/L. The corrected Uranine concentrations in flushing water as well as of the return water are presented in Figure 3-1. Further, the amount of Uranine added to the borehole via the flushing water and the estimated amount recovered in the return water are given in Table 3-1.

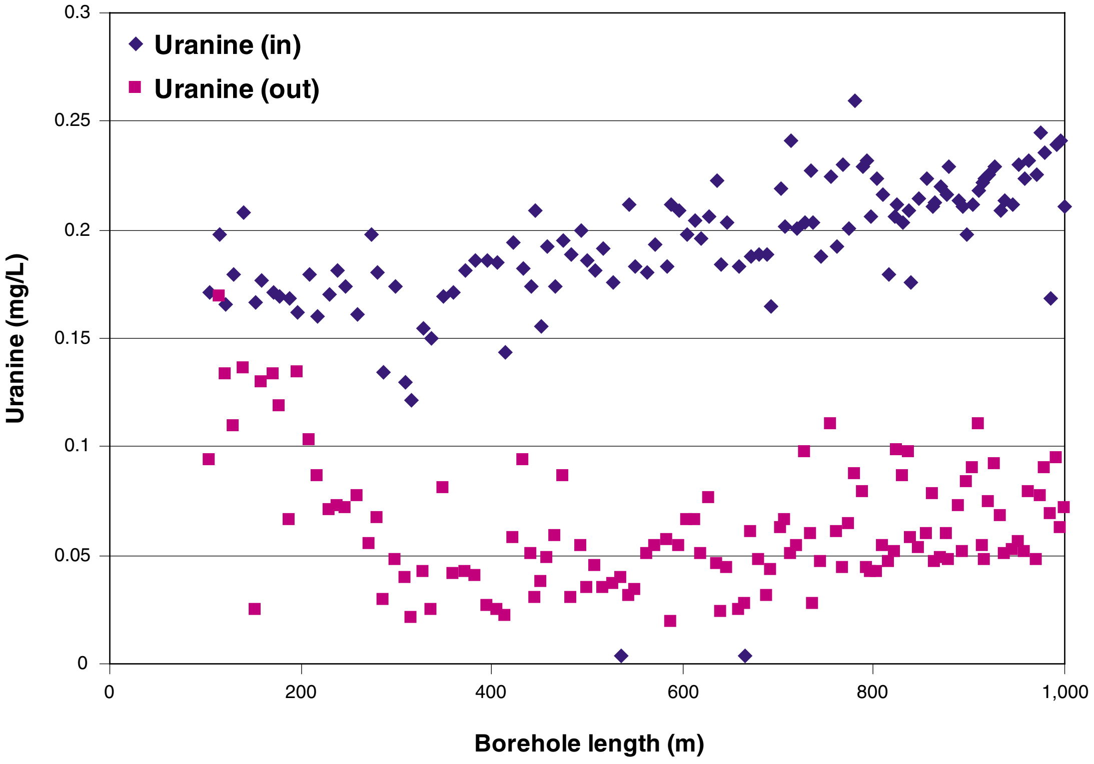


Figure 3-1. *Corrected Uranine concentrations in the flushing water and in the return water versus borehole length. The addition of Uranine was carried out using the automatic dosing equipment which is controlled by a flow meter.*

Table 3-1. Amount of Uranine added to KFM06A via the flushing water during core drilling and the amount recovered from the contemporary mammoth pumping.

Uranine	(g)
Added, according to the log book.	200.5
Added, calculated from the average corrected Uranine concentration and the total volume of flushing water.	210
Recovered, estimated from the average corrected Uranine concentration and the total volume of return water.	122

The Uranine budget in Table 3-1 suggests that approximately 400 m^3 of the flushing water was lost to the borehole and the adjacent host bedrock. However, the estimation should be regarded as rather uncertain due to the systematic error and the correction. It became clear later on that the remaining flushing water was going to be a major problem that required extra long pumping periods /8/.

As borehole KFM06A is of SKB chemical-type, the following special precautions were taken in order to minimise contamination via the flushing water:

- The supply well was also of SKB chemical-type.
- Borehole HFM05 was selected to supply flushing water because of the low concentration of total organic carbon (TOC). The concentration should preferably be below 5 mg/L and the concentration in the samples collected in HFM05 was in the range 4.8–6.1 mg/L.
- Dosing equipment for Uranine was installed, thereby removing the need for an in-line flushing water storage tank after the UV-system. Using a storage tank involves a potential risk of bacterial growth.

The microbe content in the flushing water was determined during the drilling of this borehole and the results are presented in /9/. The results showed, in a convincing way, that the cleaning procedure works well.

3.2 Previous events and activities in the borehole

KFM06A is an SKB chemical-type core borehole and thus specially intended for complete hydrochemical characterisation. Only those investigations that are necessary in order to select borehole sections are carried out in the borehole prior to the chemistry campaign. The more downhole equipment used in the borehole, the greater is the risk of contamination and effects on the in situ microbiological conditions. The activities/ investigations performed in KFM06A prior to the chemistry campaign are listed in Table 3-2 below.

Table 3-2. Activities performed in KFM06A prior to and immediately subsequent to the chemical characterisation.

Activities performed	Date of completion	Length or section (m)	Comment
Percussion drilling	2003-11-21	0–100.75	
Hydraulic tests (HTHB)	2003-12-09	0–100.3	
Water sampling class 3 Water sampling class 3	2003-12-08 2003-12-08	0–100.3 0–100.3	Sample no 8186 Sample no 8187
Core drilling	2004-09-21	100.64–1,000.64	HFM05 was the source of flushing water for drilling the cored part of KFM06A. HFM05 is an SKB chemical-type borehole /3, 6/.
Flushing water treatment	–	–	Automatic dosing of Uranine was used during drilling of KFM06A. In this way no in-line storage tank was needed after the UV-system /3/.
Check of microbe content in the flushing water	2004-09-21	–	/9/
Pore water sampling	2004-09-21	100.64–1,000.64	Sample nos 8550 to 8572 /5/.
Sampling of return water prior to disposal	 2004-08-23 2004-09-07 2004-09-21	–	Sampling in order to check effects in Bolundsfjärden /3/. Sample no 8621 Sample no 8624 Sample no 8636
Differential-flow logging	2004-10-21	0–1,000.64	/10/
Hydrochemical logging	2004-10-28	0–995	Sample nos 8695 to 8711 /8/.
BIPS-logging	2004-11-02	500–998.47	/11/
Geophysical logging	2005-01-12	100–1,000	/12/
Hydrochemical characterisation	2005-03-08	353.5–360.6 768.0–775.1	Presented in this report.
Microbe investigation	2005-03-08	353.5–360.6 768.0–775.1	/2/
Water sampling in connection to injection test	2005-04-21	266–271	Presented in this report
Single hole injection test	2005-04-21	–	/13/

3.3 Choice of borehole sections

The differential flow logging prior to the chemical investigation revealed several major water bearing zones in the shallow part of the borehole between 100 and 360 m. Furthermore, two deep, and therefore especially important zones to investigate, were identified below 700 m. The fracture zones with a water yield large enough to allow water sampling (hydraulic transmissivity ≥ 10E–8 m^2/s) are listed in Table 3-3.

Samples of the drill core were collected regularly during the drilling of KFM06A in order to investigate the chemical composition of the rock matrix interconnected pore water /5/. This would then be compared to the composition of formation groundwaters sampled from nearby hydraulically active fracture zones. To allow comparison between pore water and "fracture water" at corresponding depths, it was desirable therefore to sample fracture groundwater at several depths along the borehole. Selection of one of the two zones below 700 m was obvious, also because of the lack of chemical data deeper than 200 m in this part of the candidate area. Furthermore, the zone at 353 m was selected as the only possible one at intermediate depth. The more shallow depths were regarded as less important and it was considered that sampling in connection with a later injection test in one of the remaining and shallower fractures could fulfil the requirements. A section length of 7.5 m was suitable for both selected fracture zones. Section limits and corresponding hydraulic transmissivity values for the sections selected for hydrochemical characterisation are given in Table 3-4.

The diagrams from the differential flow logging in the two selected borehole sections are given in Appendix 2 and the corresponding pictures from BIPS (Borehole Image Processing System) logging are presented in Appendix 3.

Table 3-3. Water yielding fractures/fracture zones and approximate flow rates (drawdown 9 m) identified from differential flow logging /10/. Selected fractures/fracture zones are given in bold text.

Borehole length (m)	Flow (L/h)	Flow direction (into or out from borehole)	Comments
110–117	10	Into	Two major fractures/zones
125 –145	200	Into	Several fractures
157	50	Into	–
177–181	500	Into	Two major fractures/zones, 100+400 L/h
218–221	500	Into	Two major fractures/zones, 500+20 L/h
237–240	500	Into	Two major fractures/zones, 500+10 L/h
267–269	800	Into	This zone was selected for sampling in connection to injection tests.
355–357	30	Out from	–
737–742	10	Out from	A flow direction from the borehole into the bedrock increased the amount of flushing water contaminating the fracture system. Sampling was tried but interrupted due to excessively high flushing water contents.
770–771	3	Into	–

Table 3-4. Selected borehole sections for hydrochemical characterisation and their hydraulic transmissivity calculated from differential flow logging (T_D) and from injection tests (T_T). The results are preliminary.

Section (m)	T_D (m^2/s) /10/	T_T (m^2/s) /13/	Comments
353.5–360.6	9.1×10^{-7}	Section 345.5–365.5 m 3.1×10^{-6}	*Differential flow logging*: One dominating fracture at 356.6 m within the section.
		Section 353.0–358.0 m 3.4×10^{-6}	*Injection tests*: Section length 20 m and 5 m, respectively.
740.0–747.1	3.1×10^{-7}	Section 725.5–745.5 m 1.2×10^{-7}	*Differential flow logging:* One dominating fracture at 743.3 m within the section.
			Injection test: Section length 20 m.
768.0–775.1	2.7×10^{-8}	Section 765.5–785.5 m 1.8×10^{-8}	*Differential flow logging*: 0.36 L/h. Two similar fractures at 770.6 and 770.8 m.
			Injection test: Section length 20 m.

4 Equipment

4.1 The mobile field laboratory (MFL)

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; the equipment is presented schematically in Figure 4-1. It is also possible to include a separate unit for computer work (MYC). The different parts of the system 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).

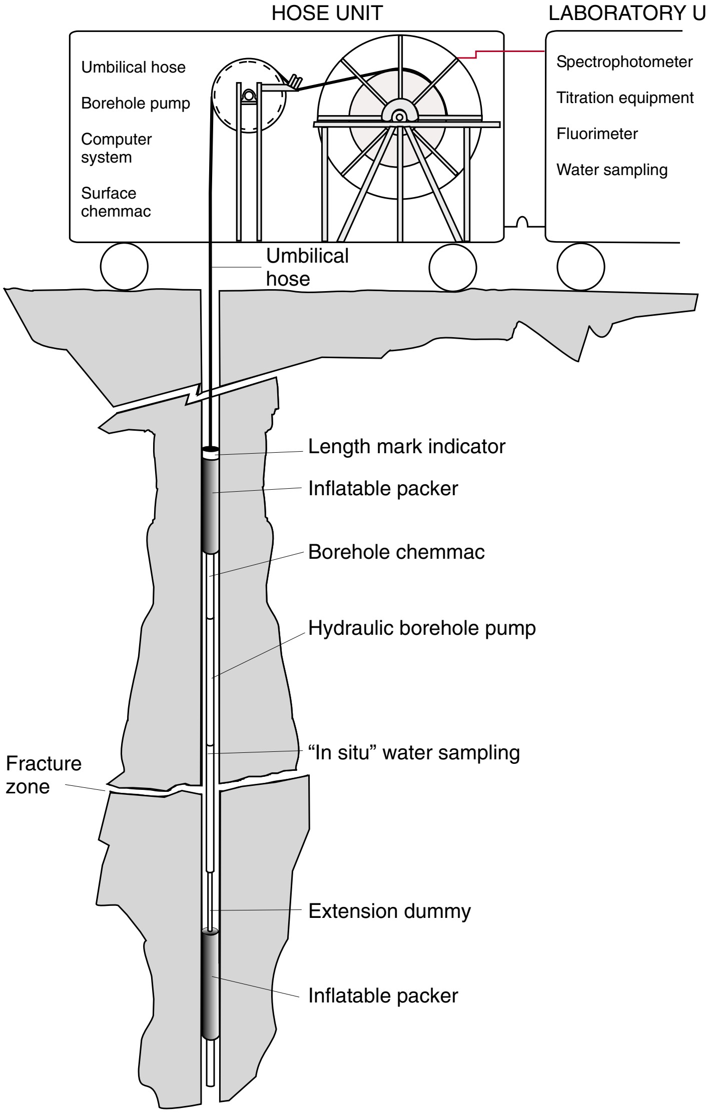


Figure 4-1. *The mobile laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.*

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

The downhole equipment comprises 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 sampled groundwaters collected with the PVP sampling unit maintain the pressure from the borehole section when raised to the surface. These samples are used for colloid filtration, gas analyses and microbe investigations.

The mobile units used for the investigation of borehole KFM06A consisted of the hose unit S3 and the MYC 3 unit for computer work. The laboratory unit L3 was employed for analytical work but was located close to the core mapping facility and not at drill site DS6.

4.2 Colloid filtering equipment

The colloid filtering equipment is adapted to the sample containers (PVB) from the PVP water sampling unit and consists of holders for two PVB-containers, a separated 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 0.4, 0.4, 0.2, 0.05 and 0.05 µm. The equipment is described in SKB MD 431.045 (Mätsystembeskrivning för kolloidfiltrerin gssystem, handhavandedel, SKB internal controlling document to be published). Figure 4-2 shows the equipment set up.

The major equipment features are:

- Filtering is performed in a closed system under an 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. The system is adjusted to create a pressure difference between the inlet of the filter package and the outlet side. 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 larger particles which may clog the filters. Furthermore, clogging is prevented by the first two filters with pore sizes 0.4 µm which are mounted parallel to each other.

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

- The sample volume is limited to a maximum of 2×190 mL.
- The PVB sample containers are made of stainless steel which may contaminate the samples. An improvement could be to use Teflon coating on the insides of the cylindrical containers.

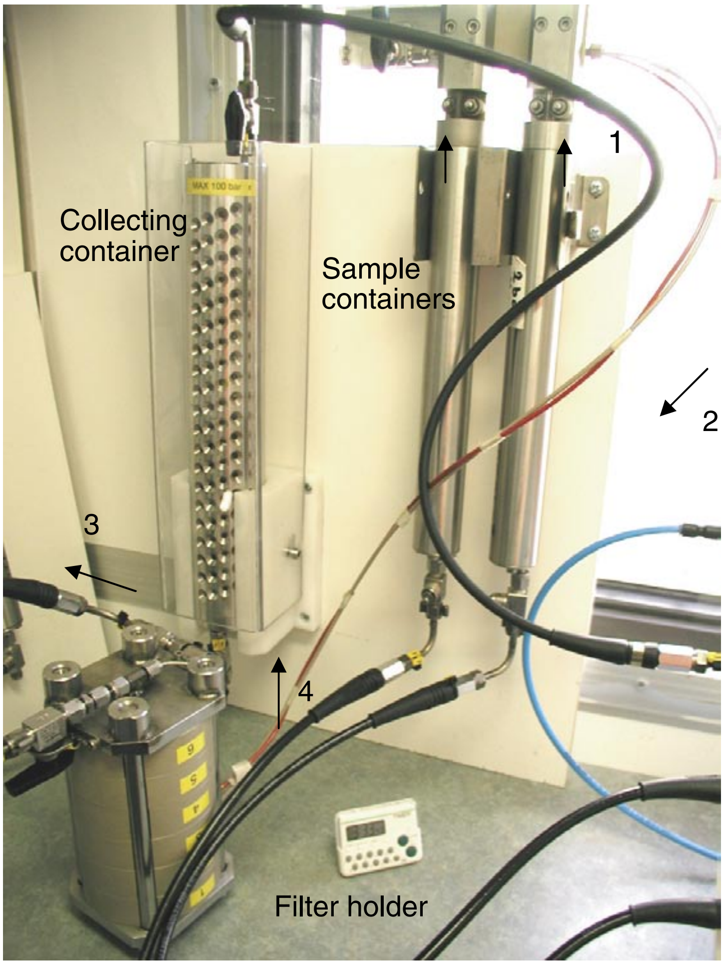


Figure 4-2. The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1 to 4, show the flow direction of the sample water through the system.

4.3 Equipment for enrichment of humic and fulvic acids

Enrichment of humic and fulvic acids is conducted in order to collect enough material to determine $\partial^{13}C$ and pmC (percent modern carbon) on organic constituents in the groundwater. The equipment for enrichment includes a porous column filled with an anion exchanger (DEAE-cellulose) and a textile filter with a well-defined pore size. 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. Since the ion exchange resin in the column creates a counter-pressure, which disturbs the water flow through the surface Chemmac, a pump was used for pumping a portion of the outlet water through the column (approximately 1.8 L/hour).

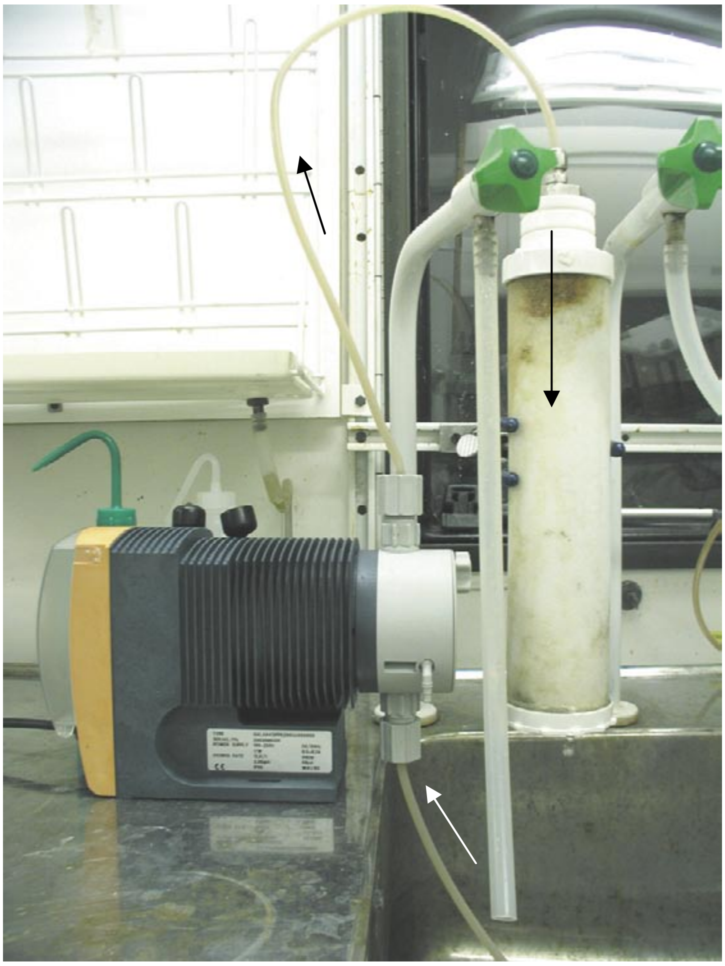


Figure 4-3. *The ion exchange column. The arrows show the water flow direction.*

4.4 Equipment for fractionation of humic and fulvic acids

The equipment consists of membrane filters with a defined cut-off (pore size), a membrane pump, flexible tubing and vessels. Generally, one water sample from each section is filtered through two filters with different pore sizes (1,000 D and 5,000 D, D = Dalton, 1 D = 1 g/mol). The equipment and performance are described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror, SKB internal controlling document). Figure 4-4 describes schematically the function of a membrane filter and Figure 4-5 shows the equipment setup.

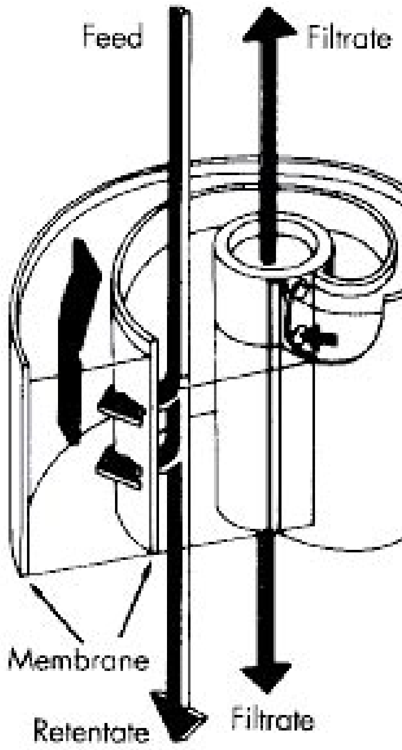


Figure 4-4. *Outline of membrane filter with water flow directions.*

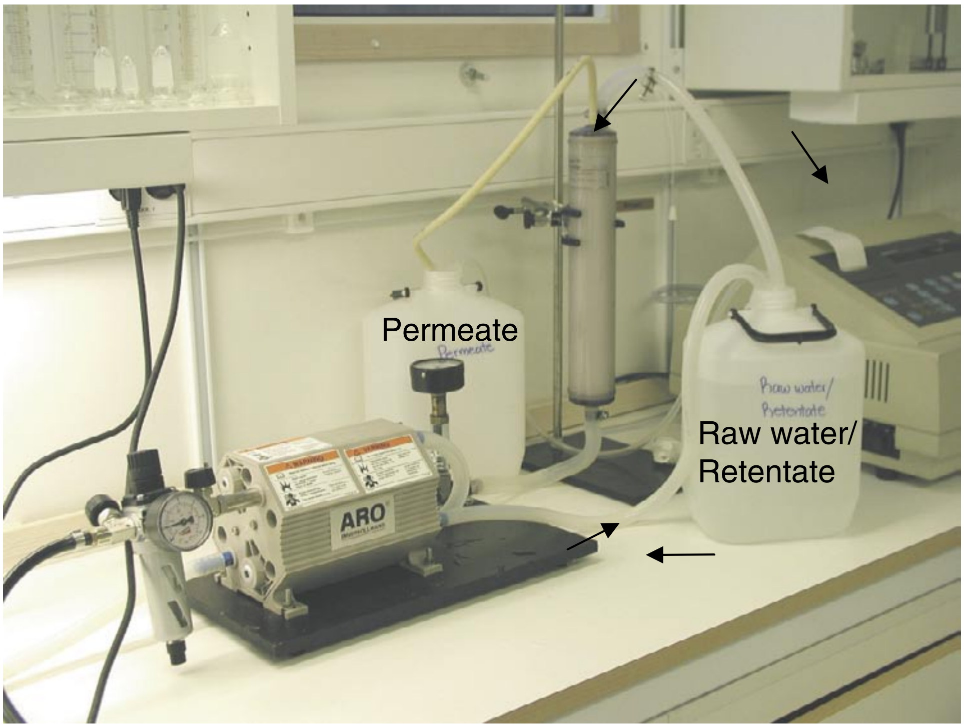


Figure 4-5. *Equipment for fractionation of humic and fulvic acids.*

5 Performance

5.1 General

Chemical characterisation of two sections in borehole KFM06A was planned according to activity plan AP PF 400-04-110 following the method described in SKB MD 430.017 (Metodbeskrivning för fullständig kemikarakterisering med mobilt fältlaboratorium, SKB internal controlling document). Initially, a section at 740 m was selected but due to very high flushing water content (46%) it was changed to the one at 768.0–775.1 m. The belief was that it aught to be easier to obtain samples with an acceptably low flushing water content due: a) to the lower hydraulic transmissivity (see Table 3-3), i.e. lower probability of flushing water entering the fracture during drilling, and b) to an undisturbed (i.e. non-pumped) groundwater flow direction under natural conditions where flow is from the bedrock to the borehole, i.e. a natural removal of some of the accumulated flushing water. An overview of the final investigation sequence is given in Table 5-1.

Table 5-1. Investigation sequence in KFM06A.

Start date/ Stop date	Investigation	Section (m)	Comment
2004-11-09/ 2004-11-19	Interrupted investigation due to high flushing water content.	(740.0–744.9) (740.2–747.3) 740.0–747.1	Pumped volume = 1.9 m^3. Flow rate 200 mL/min and drawdown 11 m.
2004-11-24/ 2005-02-01	Complete chemical characterisation.	768.0–775.1	Pumped volume = 8.5 m^3 from which approximately 1.6 m^3 was conveyed back to the upper part of the borehole during Christmas break (see Table 5-4).
2005-02-10/ 2005-03-14	Complete chemical characterisation.	353.5–360.6	Pumped volume = 8.8 m^3.
2005-04-21	Sampling/pumping using equipment for injection tests (PSS 3). Simple performance not described in text below.	266.0–271.0	Pumped volume = approx 64 m^3 prior to sampling. Check of flushing water content during the pumping period. One single sample SKB no 8860 (SKB klass 3). PSS – Pipe String System.

5.2 Overview of field work procedure

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

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

- Cleaning of the inside of the umbilical hose (the sample water channel) with de-oxygenated water. Finally, the sample water channel is filled with de-ionised and de-oxygenated water prior to 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% denatured ethanol. One of the containers is 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 section to be sampled.
- Calibration of the pH and redox electrodes in the borehole Chemmac.

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

- The outside of the umbilical hose is cleaned with 70% denatured ethanol (SKB MD 600.004).
- Calibration of the umbilical hose length is conducted at least once for each borehole. For this purpose, a length mark detector unit (caliper) is mounted together with the ordinary downhole equipment. The length mark detector indicates length calibration marks milled into the borehole wall 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 pumping and measurement period begins. Typical measures taken and activities carried out during this period are:

- Calibration of the pH and redox electrodes as well as the electrical 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 ensure that the packed-off section is well isolated from the rest of the borehole. A significant drawdown in the section during pumping is one indication that the section is thoroughly sealed off. 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 shallower and/or deeper fracture systems increases. The pumping flow rate is adjusted depending on the flow yield from the fracture or fracture zone (to between 50 and 200 mL/min) and maintained more or less constant during the pumping and measurement period.
- Water samples are collected regularly once or twice a week during the pumping period. Changes in water composition are monitored by conductivity measurements and by immediate analyses (pH, chloride, alkalinity, ferrous and total iron, and ammonium) at the site.

- Enrichment of humic and fulvic acids is conducted for as long 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 ∂13C 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 a suitably stable stage of the pumping and measurement period. The investigation might be prolonged if the concentration of flushing water exceeds 1% or if the redox potential and electrical conductivity 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 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 secured.
- Following stopping of the borehole pump and deflation of the packers, the equipment is lifted and the different downhole units are dismantled.
- Calibration of the electrodes in the borehole Chemmac and surface Chemmac. The final calibration for a borehole section can be used as the initial calibration for the next section.

5.3 Performance in section 353.5–360.6 m

The investigation carried out in section 353.5–360.6 m was performed using the following configuration of the downhole equipment starting from the top: umbilical hose, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP) and lower packer, see Appendix 4. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping flow rate was about 160–210 mL/min and the drawdown approx 2.5–3.5 m. Diagrams showing the pressures within and above the borehole section and the flow rate during the pumping/measurement period are given in Appendix 5.

The events during the investigation are listed in Table 5-2.

Table 5-2. Events during the pumping/measurement period in section 353.5–360.6 m.

Date	Events *Improvement/deviation*	SKB sample no
050210	Calibration of borehole Chemmac.	
	Lowering of downhole equipment (353.50–360.62 m).	
	Start of Chemmac measurements.	
050211	Calibration of surface Chemmac (conductivity).	
050214	Calibration of surface Chemmac (pH and redox).	
050215	Water sampling: SKB class 4	8802
050217	Water sampling: SKB class 5	8803
050222	Water sampling: SKB class 4	8804
050224	Water sampling: SKB class 5	8806
	Momentary stop of borehole pump during control of irregular flow rate.	
050228	Water sampling: SKB class 4	8807
	Adjustment of pump pressure to receive “normal” flow rate.	
050302	Humic and fulvic acids; enrichment start.	
050303	Water sampling: SKB class 5	8808
	Restart of measurement application due to alarm.	
	Humic and fulvic acids; fractionation 5 kD.	8809
050304	Humic and fulvic acids; fractionation 1 kD.	8809
050307	Water sampling: SKB class 5, all options.	8809
	PVP-sampler: opening of valve at 15:40.	
050308	PVP-sampler: closure of valve at 07:50.	
	Sampling of colloids (LIBD and chemical analyses*).	
	Sampling of colloids (filtration).	
	End of Chemmac measurements.	
	Lifting.	
	Colloid filtration.	8809
	Calibration borehole Chemmac.	
	Lowering of downhole equipment (353.50–360.62 m).	
050309	Calibration of surface Chemmac.	
	Start of Chemmac measurements.	
050311	Water sampling: SKB class 3.	8838
	PVP-sampler: opening of valve at 09:43.	
050314	PVP-sampler: closure of valve at 05:32.	
	Sampling for microbes and dissolved gases.	8809
	End of Chemmac measurements.	
	Lifting.	
	Humic and fulvic acids; enrichment stop.	
050322	Humic and fulvic acids; enrichment eluation.	8809

* See Appendix 10.

5.4 Performance in section 768.0–775.1 m

The investigation in section 768.0–775.1 m was performed using the following configuration of the downhole equipment, starting from the top: umbilical hose, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP) and lower packer, see Appendix 4. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping was performed at a flow rate of about 90 mL/min and a drawdown of approximately 50 m. Diagrams showing the pressures within and above the borehole section and the flow rate during the pumping/measurement period are given in Appendix 5. The events during the investigation are listed in Table 5-3.

Table 5-3. Events during the pumping/measurement period in section 768.0–775.1 m.

Date	Events *Improvement/deviation*	SKB sample no
041124	Calibration of borehole Chemmac.	
	Lowering of downhole equipment (768.00–775.12 m).	
	Start of Chemmac measurements.	
041125	Calibration of surface Chemmac.	
041125	Momentary stop of borehole pump while lowering a second pump in the upper part of the borehole for "clean up" pumping.	
	Water sampling: Uranine (flushing water content 24%).	
041129	Water sampling: Uranine (flushing water content 21%).	
041202	Water sampling: Uranine (flushing water content 14%).	
041207	Water sampling: Uranine (flushing water content 11%).	
041214	Water sampling: SKB class 4.	8746
041223	Water sampling: Uranine (flushing water content 8%).	
041229	Water sampling: SKB class 5.	8747
	In order to avoid flooded collecting tank, the outlet of the pumped borehole water was led back to the borehole (upper part of the borehole) during Christmas break.	
050105	Humic and fulvic acids; enrichment start.	
050111	Water sampling: SKB class 4.	8748
	Resuming collection of outlet water from the borehole to a tank instead of back to the borehole.	
050113	Water sampling: SKB class 5.	8749
050118	Water sampling: SKB class 4.	8781
050120	Water sampling: SKB class 5.	8782
050125	Water sampling: SKB class 4.	8783
050126	Humic and fulvic acids; fractionation 1 kD and 5 kD.	8785
050128	Water sampling: SKB class 5.	8784
050131	Water sampling: SKB class 5, all options.	8785
	Humic and fulvic acids; enrichment stop.	
	PVP-sampler: opening of valve at 14:11.	
050201	PVP-sampler: closure of valve at 06:58.	
	Sampling of microbes and dissolved gases.	8785
	Sampling of colloids.	
	End of Chemmac measurements.	
	Lifting.	
	Colloid filtration.	8785
	Humic and fulvic acids; enrichment eluation.	8785

5.5 Water sampling, sample treatment and analyses

The pumped water from the borehole section is conveyed from the hose unit into a container furnished with a sink and a tank for collecting the outlet water. Filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. A water sample is defined as groundwater collected during one day and consists of several sample portions, labelled with the same sample number.

An overview of sample treatment and analysis methods is given in Appendix 8. The routines are applicable independently of sampling method or type of sampling object.

5.6 Collection of in situ water samples

The in situ water sampling was conducted successfully in both borehole sections. In section 353.5–360.6 m the in situ sampling was repeated in order to obtain an additional set of sample portions. The increased number of sample portions allowed testing of a new method which combines quantification and average size determination of colloids as well as measurements and analyses of pH, Eh, electrical conductivity, dissolved oxygen and element composition, see Appendix 10.

The PVB-containers/vessels were all controlled before use; this procedure includes disassembling of the container, thorough cleaning, reassembling and measurement of piston friction.

The purpose of each sample portion is given in Table 5-4.

The colloid filtration was conducted on the sampling day. The LIBD (Laser-Induced Breakdown Detection) sample portions as well as the PVB-containers for dissolved gases and microbes were packed together with ice packs in insulated bags and sent by express delivery service immediately after sampling. The microbe sample arrived at the laboratory in Gothenburg before three o'clock the same day. The gas and LIBD sample portions arrived at the laboratories in Finland and Germany respectively, the next morning.

5.7 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 sizes. Two of the four sample portions collected in situ in each borehole section are used for colloid filtration. Data on performance of the filtration runs are given in Table 5-5.

A leak test of the system at 10 bars was also done prior to the sampling in order to eliminate the risk of leakage.

Each filtration results in five filter samples (two 0.4 µm, one 0.2 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 constituents and common trace metals).

5.8 Enrichment of humic and fulvic acids

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 method is described in SKB MD 431.044 (Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror). The enrichment method entails collection of organic acids on an ion exchanger, elution of the resin and evaporation of the resulting solution. The dry residue is used for isotope determination and 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 in order to prevent the formation of carbon dioxide.

Estimations of total duration time and water volume through the ion exchanger are given in Table 5-6.

Table 5-4. Collection and purpose of in situ water sample portions.

Sample portion no	Section 353.5–360.6 m 2005-03-08	Section 353.5–360.6 m 2005-03-14	Section 768.0–775.1 m 2005-02-01
1	Colloid filtration	Dissolved gas	Dissolved gas
2	Colloid filtration	Microbes	Microbes
3	LIBD and chemical analyses*	Microbes	Colloid filtration
4	LIBD and chemical analyses*	Dissolved gas	Colloid filtration

* See Appendix 10.

Table 5-5. Colloid filtration, data on performance.

Section/date	Entering pressure (bar)	Max differential pressure over filter package (bar)	Temp (°C)	Filtering time (min)	Filtered volume (ml)	Comments
353.5–360.6 m /20050308	~ 32	3.4	~ 11	53	308.5	Leakage test prior to filtration. No leakage was noticed. No broken filters.
768.0–775.1 m /20050201	~ 66	4.2 (during most of the filtration the diff pressure was 3 ± 0.2 bar)	~ 15	31	321.5	Leakage test prior to filtration. No leakage was noticed. No broken filters.

Table 5-6. Enrichment time and water volume through the ion exchanger

Borehole section (m)	Duration of enrichment (days)	Volume through ion exchanger (L)
353.5–360.6	9	419
768.0–775.1	23	1,018

5.9 Fractionation of humic and fulvic acids

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

Sampled water from each investigated section was first filtered through a 0.45 µm filter and then filtered through membrane filters with cut-off sizes of 1,000 D and 5,000 D, respectively. The initial water volume, prior to filtration, was approximately 5 litres. The final retentate and permeate volumes following the filtration runs 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 untreated groundwater. Each sample was analysed for dissolved organic carbon (DOC), major constituents and common trace metals. The analyses of metal ions should indicate if metals such as Al, Si, Mn and Fe exist as colloidal species. For section 353.5–360.6 m uranium analyses were included also.

6 Nonconformities

The hydrochemical characterisation of the two sections in KFM06A has been conducted according to the SKB internal controlling documents AP PF 400-03-38 and SKB MD 430.017. Some equipment malfunctions, listed in Tables 5-2 and 5-3, occurred during the pumping/ measurement periods.

The allowed upper limit for flushing water content, 1%, was exceeded in both sections 353.5–360.6 m (7%) and 768.0–775.1 m (2%).

The results from fractionation of iron species are rejected due to inconsistent analyses and considerable adsorption on the filters (section 353.5–360.6 m) as well as unlikely low concentration values below the detection limit (section 768.0–775.1 m).

7 Data handling and interpretation

7.1 Chemmac measurement data

The processing of Chemmac data is described in SKB MD 434.007-02 (Mätsystembeskrivning för Chemmac mätsystem, SKB internal controlling document, in progress).

7.1.1 Data file types and calculation software

The on-line measurements in a borehole section produce the following types of raw data files:

- Calibration files from calibration measurements (*.CRB) and corresponding comment files (*.CI). The files are used for calculation of calibration constants (pH and Eh) and the calibration factor (electrical conductivity). For surface Chemmac ten *.CRB and ten *.CI files are produced, and for borehole Chemmac six *.CRB and six *.CI files.
- Raw data file containing the logged 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 converted to pH and Eh values (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 listed above are stored in the SICADA file archive. Furthermore, the files are re-calculated and evaluated to obtain pH and redox potential values and to correct the electrical 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, electrical conductivity and water temperature). The data from the file are exported to the data tables "redox" and "ph_cond" in SICADA. As the file also 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 redox potential and pH

The redox potential is measured by three electrodes at the surface and three downhole in the borehole section. In addition, pH is measured by two electrodes at the surface and two downhole in the borehole section. 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. three or six redox electrodes and two or four pH electrodes).
- Determination of 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 results in 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 larger 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 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 converted 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 representative 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 using the standard deviations of the calibration constants and the standard deviations of the Eh and the pH values obtained by the different 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 changing gas pressure conditions with depth 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 final 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.

Some 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 the 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 according to the equation below. Relative errors within ± 5% are considered acceptable (in surface waters ± 10%).

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

- 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.

7.3 Data from special sampling methods

Special sampling methods include collection of in situ samples (colloid filtration and dissolved gases), enrichment and fractionation of humic and fulvic acids.

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

7.3.1 Colloid filtration

The concentration of the colloid portion caught on each filter 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. The measurement uncertainty of each colloid concentration is calculated according to the equation below.

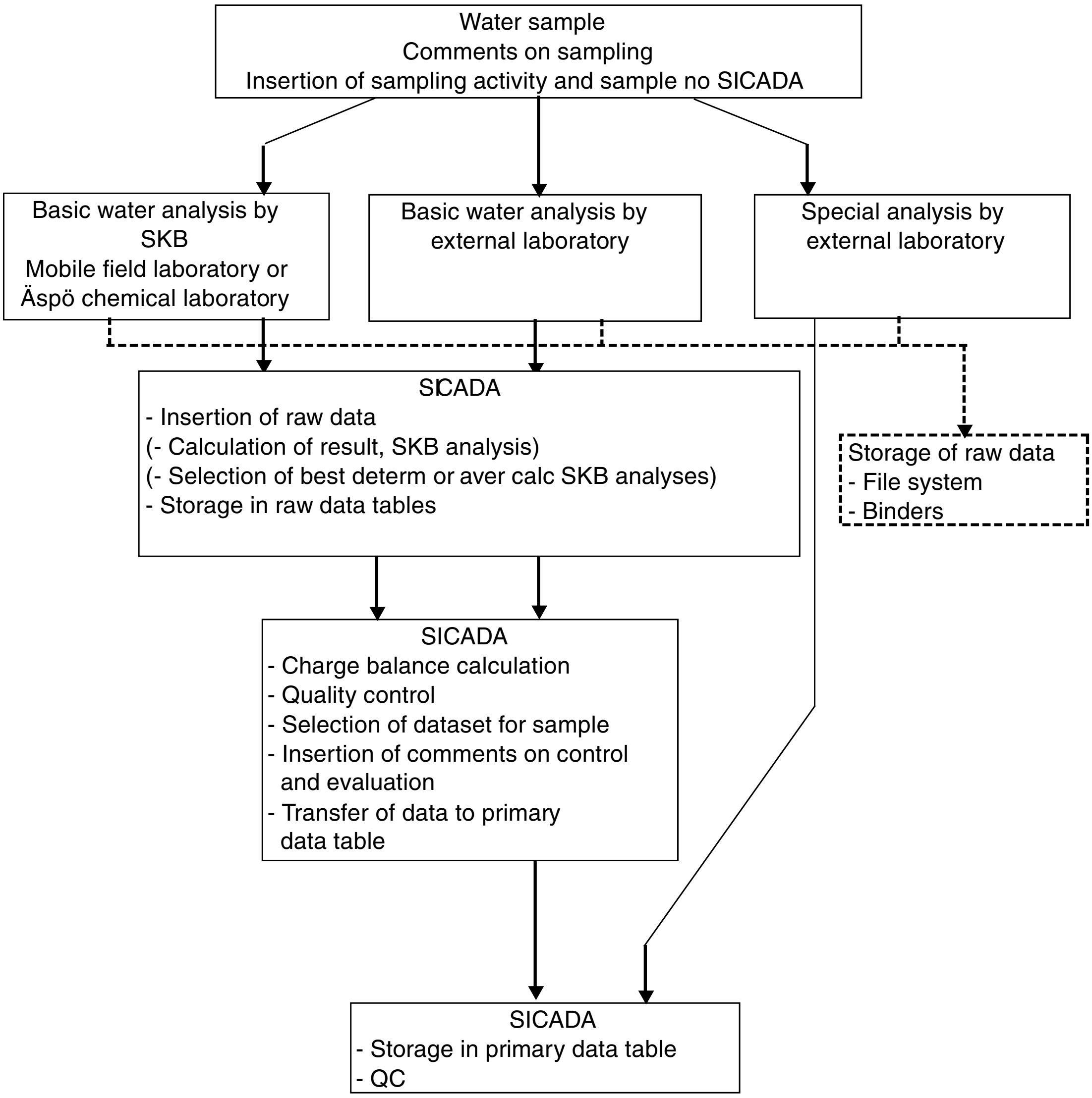


Figure 7-1. *Overview of data management for hydrogeochemical data.*

$$U = \sqrt{\left(\frac{1}{V^2}\times(\Delta m)^2 + \frac{m^2}{V^4}(\Delta V)^2\right)}$$

where

U = measurement uncertainty (µg/L)
V = ater volume through the system (L)
ΔV = estimated volume error, 0.010 L
m = amount on filter (µg)
Δm = measurement uncertainty of the filter analysis, 20% (µg)

The calculated results of the colloid filtration, filters, are stored in SICADA.

7.3.2 Dissolved gases

Results from gas analyses are stored in a primary data table in SICADA without post processing or interpretations.

7.3.3 Enrichment of humic and fulvic acids

The pmC and δ^{13}C values for enriched organic acids are stored in SICADA without post processing or interpretations.

7.3.4 Fractionation of humic and fulvic acids

The concentrations of organic and inorganic constituents in the retentate and permeate are recalculated to concentrations of each fraction of carbon and metal ions with molecular weight lower or higher than the cut-off size of the filter. This is done using mass balance equations as described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror). Comparison of the four concentration values from the two filters results in values for three fractions, i.e. < 1,000 D, 1,000–5,000 D and > 5,000 D.

8 Results

8.1 Chemmac measurements

The measurement sequences of pH, Eh, electrical conductivity, dissolved oxygen and temperature values are plotted versus time in Appendices 6 and 7.

The measured monitoring time series data sequences were evaluated in order to obtain one representative value of Eh, pH, electrical conductivity and dissolved oxygen for the borehole section as described in Section 7.1. The redox electrodes in the surface Chemmac measured high values between –30 and 50 mV in both investigated borehole sections and were therefore not included in the evaluation.

Data were selected from a part of the measured time series sequences where the electrodes show stable values, marked with an arrow in the diagrams. The evaluated results from the measurements in the two investigated sections are given in Table 8-1. Unusually high measurement uncertainties were estimated for pH (section 353.5–360.6 m) and for Eh (section 768.0–775.1 m). However, the surface Chemmac pH is probably better than indicated. The results obtained by the LIBD-laboratory (PVB-sample portions) are given for comparison, see Appendix 10.

Table 8-1. Evaluated results from Chemmac measurements in KFM06A.

Borehole section (m)	Electrical conductivity* (mS/m)	pH (surface Chemmac)**	pH (borehole Chemmac)**	Eh (borehole and surface Chemmac)** (mV)	Dissolved oxygen*** (mg/L)
353.5–360.6	1,343 ± 40	7.33 ± 0.63	6.91 ± 1.53	–155 ± 7	0.00 ± 0.01
353.5–360.6 (PVB)	1,347	7.33	–	94	< 0.094
768.0–775.1	1,947 ± 60	8.22 ± 0.17	8.31 ± 0.32	–200 ± 51	0.00 ± 0.01

* The electrical conductivity is measured between 0–10,000 mS/m with a measurement uncertainty of 3%.
** Evaluated result and measurement uncertainty calculated as described in Section 7.1.
*** Measurement interval 0–15 mg/L, resolution 0.01 mg/L.

8.2 Water analyses

8.2.1 Basic water analyses

The basic water analyses include the major constituents Na, K, Ca, Mg, S, Sr, SO_4^{2-}, Cl^-, Si and HCO_3^- as well as the minor constituents Fe, Li, Mn, DOC, Br, F, I, HS^- and , NH_4^+. Furthermore, batch measurements of pH and electrical 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 9, Table A9-1. Existing batch measurement values of pH and electrical conductivity are compared to the corresponding on-line Chemmac measurement values in Appendices 6 and 7.

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

The flushing water contents in the sample series collected from the borehole sections are presented in Figure 8-1. The content should not exceed 1% in order for a sample to be considered representative for the groundwater of the sampled fracture zone. This condition was not achieved for any of the samples collected in the two sections. The final samples showed 7.1% and 1.6% in section 353.5–360.6 m and 768.0–775.1 m, respectively. The contents in the samples were calculated using the nominal Uranine concentration (0.20 mg/L) in the flushing water.

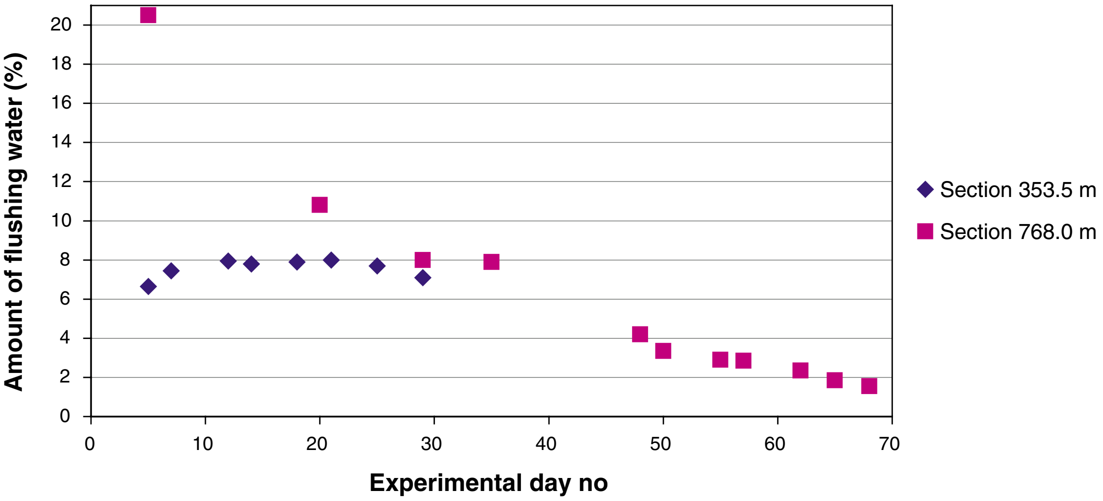


Figure 8-1. Flushing water content in the groundwater samples versus experimental day number.

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

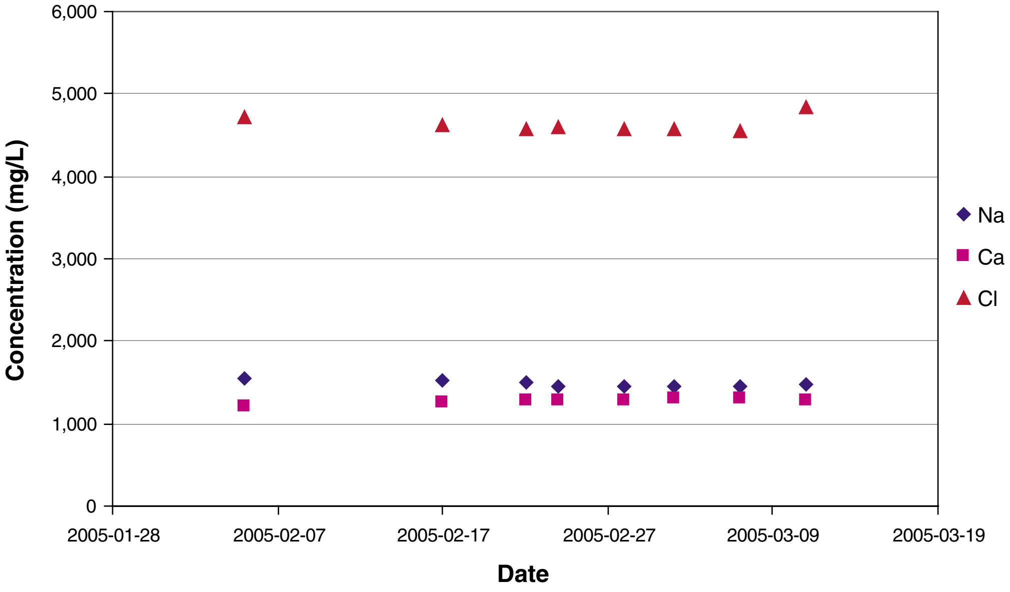


Figure 8-2. *Sodium, calcium and chloride concentrations from sample series at 353.5–360.6 m.*

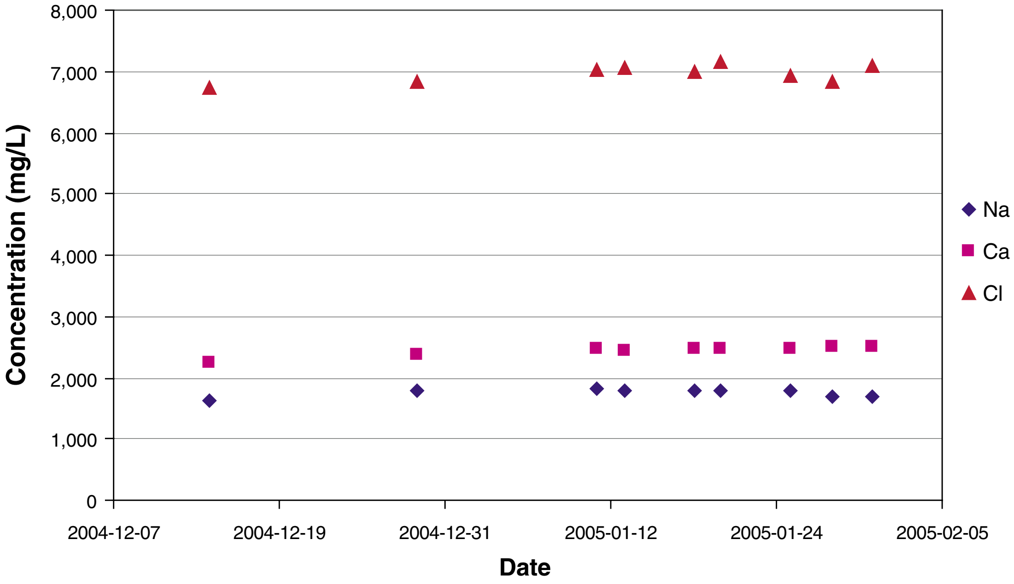


Figure 8-3. *Sodium, calcium and chloride concentrations from sample series at 768.0–775.1 m.*

The iron concentrations determined by ICP-AES (total Fe) and by spectrophotometry (Fe(+II) and Fe-tot) are compared in Figures 8-4 and 8-5. The total iron concentrations determined by ICP agree reasonably well with the results obtained by spectrophotometry. However in section 353.5–360.6 m, the ICP results are somewhat lower. 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.

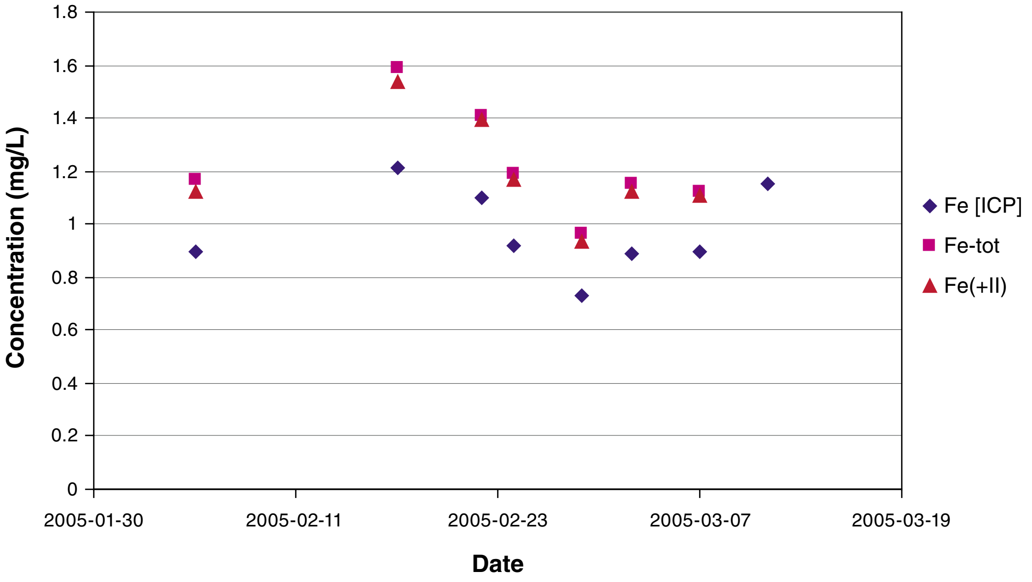


Figure 8-4. *Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole section 353.5–360.6 m.*

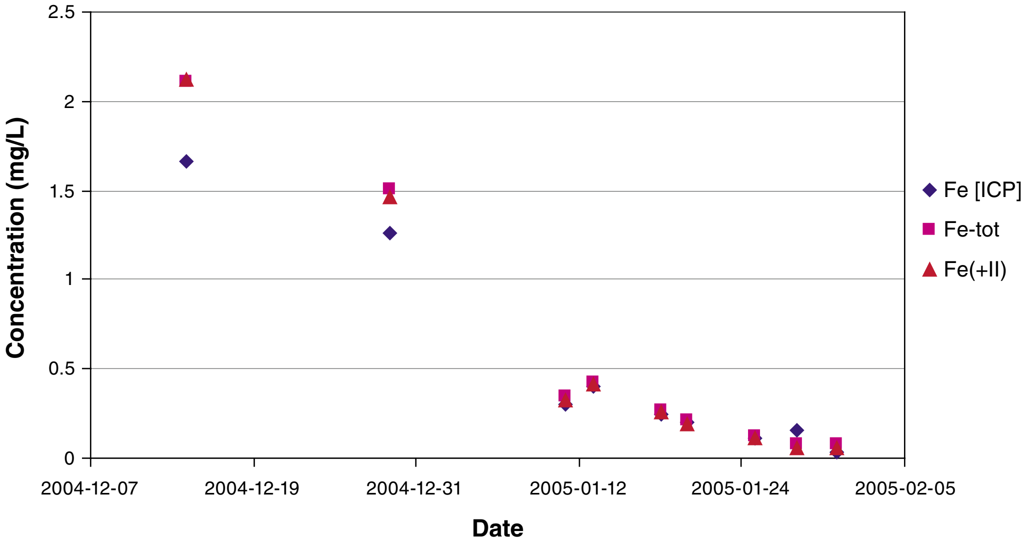


Figure 8-5. *Comparison of iron concentrations obtained by ICP-AES and spectrophotometry, borehole section 768.0–775.1 m.*

Sulphate analysed by ion chromatography (IC) is compared to sulphate determined as total sulphur by ICP-AES in Figures 8-6 to 8-7. As shown, there is a satisfactory agreement. The results from the ICP measurements are considered more reliable, by experience, since the variation between the samples in a time series often is smaller.

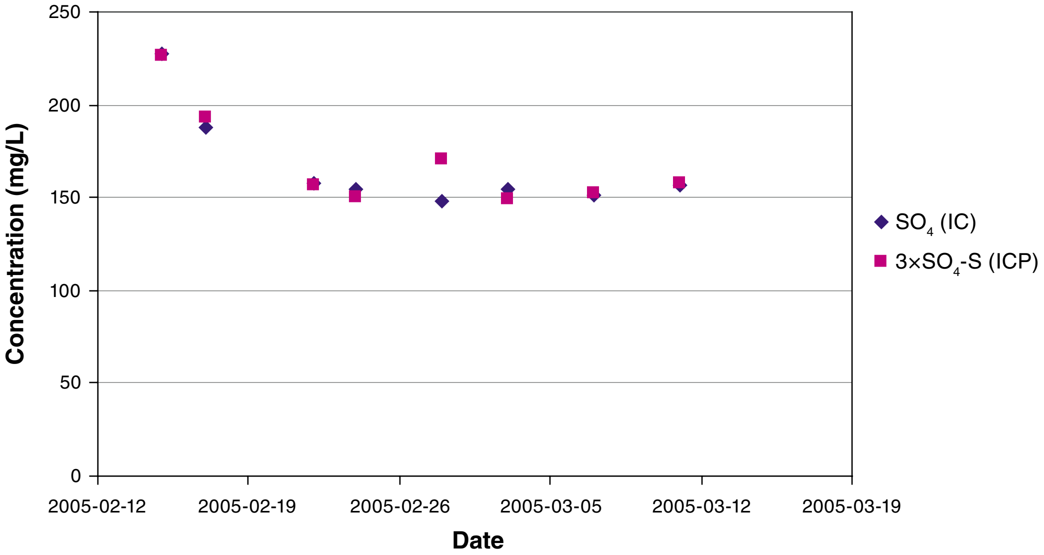


Figure 8-6. *Sulphate (SO_4 by IC) to total sulphate calculated from total sulphur ($3\times SO_4$-S by ICP) versus date, borehole section 353.5–360.6 m.*

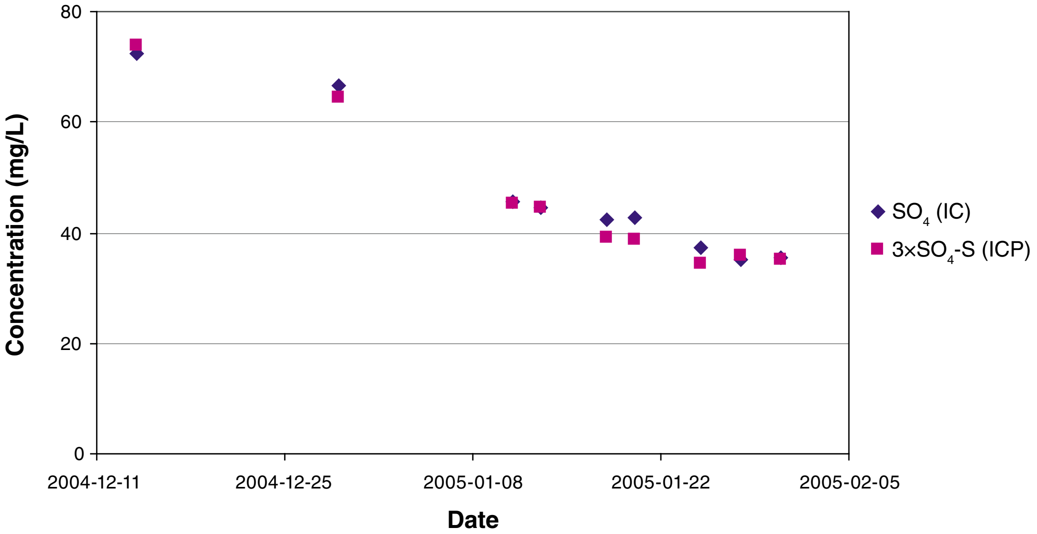


Figure 8-7. *Sulphate (SO_4 by IC) to total sulphate calculated from total sulphur ($3\times SO_4$-S by ICP) versus date, borehole section 768.0–775.1 m.*

The DOC results from the borehole sections are plotted versus experimental day number in Figure 8-8. DOC analyses in saline waters are, by experience, considered less reliable than in fresh waters. However, in this case the concentrations appear to be quite consistent.

The chloride concentrations are plotted versus the corresponding electrical conductivity values in Figure 8-9. The plot gives a rough check of the data. As shown, the data from the borehole sections agree well with a thought regression line obtained by earlier data from the Äspö Hard Rock Laboratory.

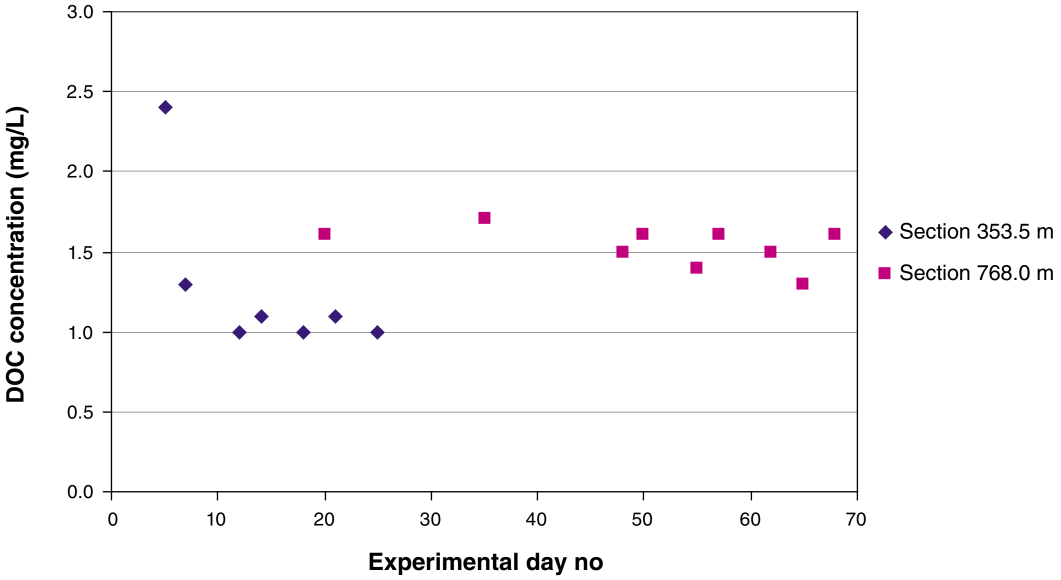


***Figure 8-8**. DOC concentrations in the sample series versus experimental day number.*

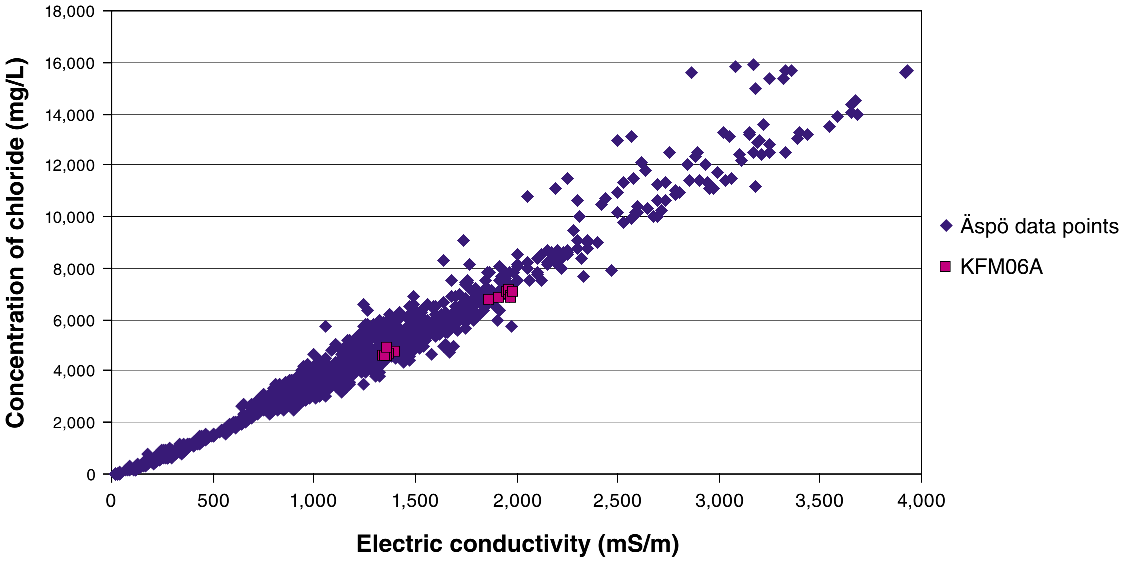


***Figure 8-9.** Chloride concentration versus electrical conductivity. Data from earlier investigations at the Äspö Hard Rock Laboratory are used to show the linear trend. Data from KFM06A do not deviate significantly from a thought regression line.*

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, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Commonly occurring metals, such as Cu, Zn, Pb and Mo are not included in the analysis programme due to contamination considerations. However, aluminium analyses are included in the colloid experiments and, due to special request, it is from now on also reported among the trace elements but only for the last sample in each series. The trace element data are compiled in Appendix 9, Table A9-3.

8.2.3 Stable and radioactive isotopes

The isotope determinations include the stable isotopes δD, δ^{18}O, ^{10}B/^{11}B, δ^{34}S, δ^{13}C, ^{37}Cl 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 9, Table A9-2 and Table A9-4. Some of the isotope data were not available at the printing date of this report.

The tritium and δ^{18}O results for sections 355.5–360.6 m and 768.0–775.1 m are presented in Figures 8-10 and 8-11. The tritium content was below the detection limit (0.8 Tritium Units) in all samples except the first one from section 768.0–775.1 m. Both sample series showed more or less constant δ^{18}O values.

The carbon isotopes (δ^{13}C and pmC) were determined both in inorganic carbon (hydrogen carbonate) and in organic constituents. The results are compared in Table 8-2. Enrichment of organic carbon was conducted in order to collect enough organic material.

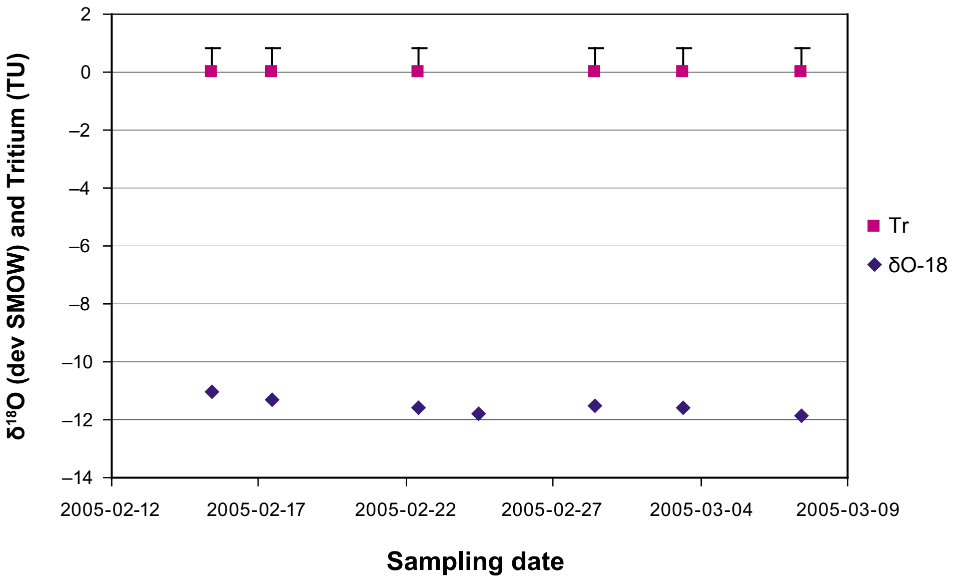


Figure 8-10. *Tritium and δ^{18}O data versus sampling date, section 355.5–360.6 m.*

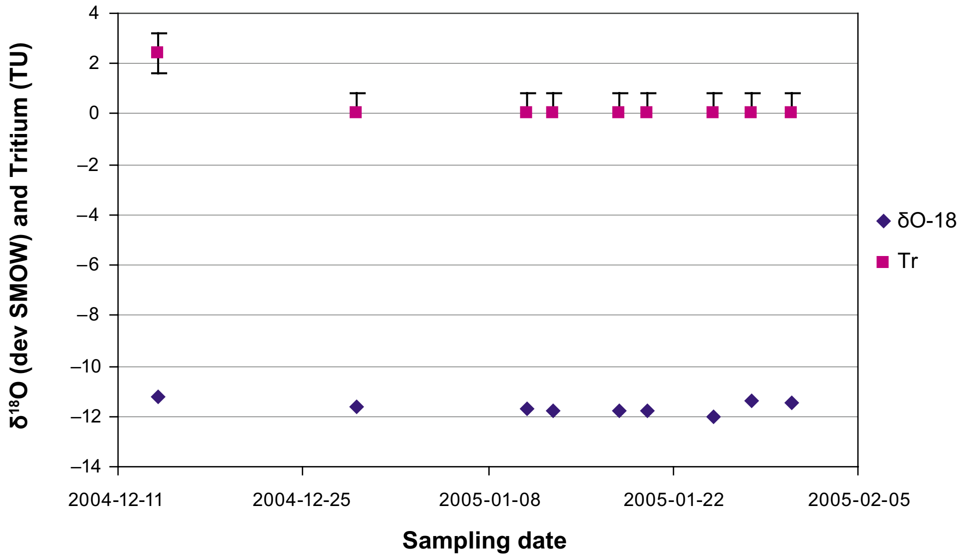


Figure 8-11. *Tritium and $\delta^{18}O$ data versus sampling date, section 768.0–775.1 m.*

Table 8-2. Inorganic and organic $\delta^{13}C$ and pmC.

Borehole section (m)	Inorg $\delta^{13}C$ (‰ PDB)	Org $\delta^{13}C$ (‰ PDB)	Inorg pmC	Org pmC
353.5–360.6	A	–26.6	A	70.1
768.0–775.1	–20.41	–21.3	36.92	68.2

A = Analytical results yet to be reported.

Previous chemical investigations in boreholes KFM02A and KFM03A revealed very high uranium concentrations in the groundwater at a depth ranging between 200–600 m (up to 90 µg/L). Furthermore, earlier uranium isotope results have been questioned since the consulted laboratory always reported identical values for ^{238}U and ^{234}U. Therefore, two more laboratories were consulted to check the different uranium determinations. A compilation of all the uranium data for both sections in KFM06A is presented in Table 8-3. The isotope uranium-238 is converted to element concentration using the expression given in Appendix 8. The relatively high uranium concentration of section 353.5–360.0 m is verified by the independent determination of uranium-238 and the four different analytical results for section 768.0–775.1 m also agree quite well.

The following conclusions may be drawn from the interlaboratory comparison:

- Normally, reliable isotope determinations do not give identical values of ^{238}U and ^{234}U in deep groundwater.
- One of the new laboratories will be used for future uranium and thorium isotope determinations.
- Earlier results (identical values for ^{238}U and ^{234}U) will not be rejected in SICADA but a comment will be made saying that the results should be used only as an indication of low or high activities.

Table 8-3. Comparison of different uranium determinations.

Borehole section (m)	Sample no	U µg/L	^{238}U mBq/L	^{235}U mBq/L	^{234}U mBq/L	$^{234}U/^{238}U$	$^{235}U/^{238}U$
353.5–360.0	8803	11.0 (1)					
353.5–360.0	8806	9.15 (1)					
353.5–360.0	8808	9.22 (1)					
353.5–360.0	8809	9.57 (1) 9.35* (3)	90 (2) 116 (3)	< 50 (2)	230 (2) 295 (3)		0.0071 (1)
768.0–775.1	8747	2.85 (1)					
768.0–775.1	8749	0.927 (1)					
768.0–775.1	8782	0.656 (1)					
768.0–775.1	8784	0.506 (1)					
768.0–775.1	8785	0.484 (1) 0.505 (4) 0.508 (4) 0.806* (3)	< 50 (2) 10 (3)	< 50 (2)	60 (2) 18 (3)	1.74 (3) 2.09 (4)	0.0073 (1)

(1), (2), (3) and (4) are different consulted laboratories.
* recalculated from ^{238}U (mBq/L).

8.3 Dissolved gas

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), ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2), propane (C_3H_8) and propene (C_3H_6). In order to check the reproducibility (i.e. using two separate sample containers), repeated analyses were conducted in section 353.5–360.6 m. The gas data are compiled in Appendix 9, Table A9-5.

Total gas content in the groundwater as well as the detected oxygen content is given in Table 8-4. Presence of oxygen indicates air leakage into the purging system at the consulted laboratory. The results may be corrected by removing the air effect (nitrogen, oxygen and argon) assuming that the oxygen content is zero.

The gas composition of the two different borehole sections – as well as the extra sample from section 353.5–360.6 m is compared in Figures 8-12 and 8-13.

Table 8-4. Total content of dissolved gas.

	Section 353.5–360.6 m (1)	Section 353.5–360.6 m (2)	Section 768.0–775.1 m
Total gas content (mL/L)	95	96	106
Oxygen content (mL/L)	0.48	0.35	0.17

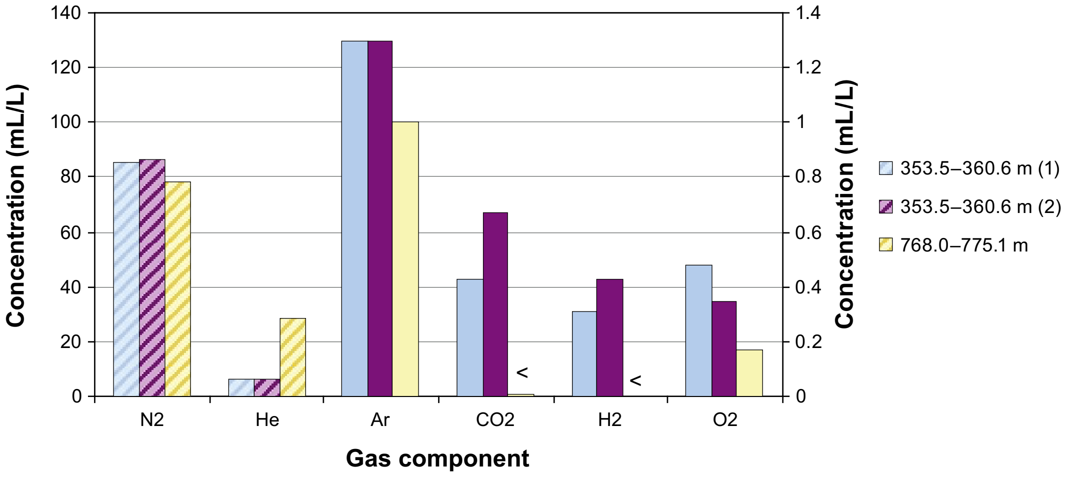


Figure 8-12. *Gas components (N_2, He, Ar, CO_2, H_2 and O_2) of high concentrations in samples collected in KFM06A using the in situ sampling equipment. Striped and unstriped bars refer to the scales on the left and right axis, respectively.*

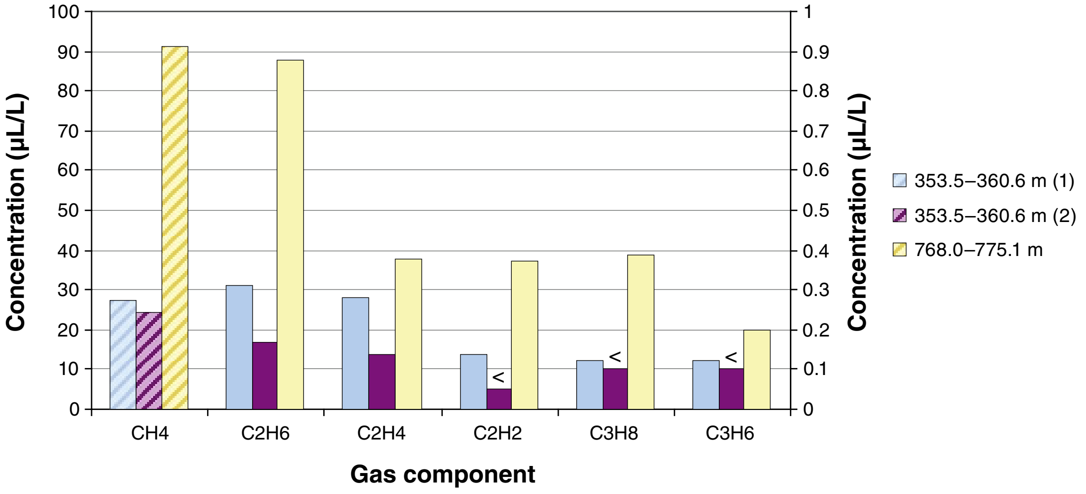


***Figure 8-13**. Gas components (CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8 and C_3H_6) of low concentrations in samples collected in KFM06A using the in situ sampling equipment. Striped and unstriped bars refer to the scales on the left and right axis, respectively.*

8.4 Inorganic colloids

The presence of inorganic colloids in the groundwaters was investigated by two standard methods, 1) filtration through a series of connected filters, and 2) fractionation /ultra filtration using special cylindrical filters with a cut-off of 1,000 D and 5,000 D. Furthermore, a third method (LIBD) for quantification of colloids was used in section 353.5–360.6 m, see Appendix 10.

8.4.1 Inorganic colloids – colloid filtration

The results from the colloid filtration method for sections 353.5–360.6 m and 768.0–775.1 m are presented in Figures 8-13 to 8-19 and Figures 8-20 to 8-25, respectively.

The bars in the diagrams represent amounts (µg) of aluminium, iron, silicon, manganese, calcium and sulphur (and uranium for section 353.5–360.6 m) entering the filter package, incorporated on each filter and present in the collecting container. The amounts are calculated assuming that the water volume coming out in the collecting container is equal to the volume going into the system. This is not quite the case, as up to ten millilitres will be left in cavities in the filter holder package, in the tubing and in valves. Further, a small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its salt content is included in the analysis. The presented input amounts, in the diagrams below, represent the sample taken on-line at the surface just before opening the PVB-containers for sampling.

The concentrations in blank samples (rinsing water), PVB-containers, collecting container and pumped groundwater are given in Table 8-5. The remaining water in the PVB containers after filtration was in both cases contaminated by aluminium and possibly by iron. The deviating iron concentrations may also be due to precipitation followed by settling down of particles.

Analysis of blank filters showed that the contributions of aluminium, iron, silica, manganese and uranium from filters were insignificant.

The following conclusions may be drawn from the colloid filtration results:

- Aluminium and iron results are somewhat difficult to evaluate since the output amount plus the amounts incorporated on filters do not balance the input amount. As can be seen in Table 8-5, the reasons are contamination and/or precipitation in the PVB-containers. Further, the imbalance of aluminium may also be due to analytical uncertainty, since the concentrations are very low.
- Calcium is present at high concentrations in the groundwater and water volumes left to dry in the filters will give significant contribution to the filter analyses. A remaining sample volume of 0.06 mL gives calcium contributions of 0.08 mg (353 m) or 0.15 mg (768 m) to the filters.
- Aluminium, iron and possibly calcium and manganese are detected in significant amounts on the filters. Addition of corresponding amounts of aluminium as K-Mg-illite, $Fe(OH)_2$ and $Mn(OH)_2$ (0.4 µm pore size excluded) gives colloid concentrations of 10.8 µg/L (section 353.5–360.6 m) and 3.5 µg/L (section 768.0–775.1 m). It is most probable that real background concentrations are lower because precipitated iron as well as contamination by iron and aluminium contributes.
- The colloid concentration determined in the groundwater of section 353.5–360.6 m is somewhat higher compared to the result obtained by using the LIBD-method, see Appendix 10.
- The amount of uranium in the filters from section 353.5–360.6 m exceeded the detection limit which may indicate that colloidal uranium is present in this groundwater.

8.4.2 Inorganic colloids – fractionation

Besides the DOC analyses, the samples from fractionation experiments were analysed by ICP. 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, calcium, sulphur and manganese were considered important as colloid species. For section 353.5–360.6 m, uranium was added to the analysed elements.

Table 8-5. Element concentrations in blank water, remaining water in PVB container, collected output water from filter system and in pumped water that has not passed the filter system.

Section m	Sample origin	Al µg/L	Ca mg/L	Fe mg/L	Mn µg/L	Si mg/L	S mg/L	U µg/L
353.5–360.6	Blank	9.73	< 1	0.028	17.8	< 0.3	< 2	–
	Rest volume PVB (input conc)	100 89.2	1,260 1,230	1.48 1.42	619 620	7.59 6.12	52.0 53.7	9.54 9.69
	Collecting container	7.42	1,280	0.997	677	5.30	48.6	8.95
	Pumped water (alt input conc)	4.29	1,280	0.860	690	5.27	47.7	9.0
768.0–775.1	Blank	1.55	< 0.1	0.0085	3.71	0.737	< 0.2	–
	Rest volume PVB (input conc)	325 220	2,530 2,470	0.968 0.684	127 105	6.38 6.33	11.8 11.5	–
	Collecting container	7.27	2,500	0.0907	94.8	4.13	12.1	–
	Pumped water (alt input conc)	5.02	2,540	0.175	88.3	4.15	12.3	–

Blank = rinsing water, leakage test.
Rest volume PVB = remaining water in the PVB container after filtering experiment.
Collecting container = water that has passed the filter system.
Pumped water = ordinary sample collected at the surface and not in situ in the borehole section.

The results presented in Tables 8-6 and 8-7 were calculated using mass balance equations (SKB MD 431.043). As shown, Si, Al , Ca, S and Mn exist as species (associated or non-associated with humic and fulvic acids) with a molecular weight less than 1,000 g/mol. Such species are too small to be referred to as colloids. In section 353.5–360.6 m there seems to be a small but probably significant uranium fraction with a molecular weight larger than 1,000 D but smaller than 5,000 D. No precipitation of iron, and to a certain extent also of calcite, is an indication of a successful fractionation experiment. During the fractionation in section 353.5–360.6 m, most of the iron was precipitated. Investigations in the previous boreholes at Forsmark were generally more successful and it can not be excluded that changed handling of protection gas is the major cause. Moreover, the iron analyses from the two filtrations were not consistent. Therefore, the iron fractions are rejected for section 353.5–360.6 m. The iron concentrations obtained from fractionation in section 768.0–775.1 m are not consistent (too low) with the concentrations in the ordinary samples (for example, sample no 8785), probably due to forgotten acid addition. Calcite was, in neither case, precipitated to any significant extent.

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 blank concentrations of iron, silicon, aluminium, calcium, sulphur and manganese were insignificant.

Table 8-6. Inorganic size fractions (1,000 D and 5,000 D filters) in section 353.5–360.6 m.

Fraction	Fe (mg/L)	Si (mg/L)	S (mg/L)	Ca (mg/L)	Al (µg/L)	Mn (µg/L)	U (µg/L)
< 1,000 D	*	4.9 ± 0.7	48.2 ± 6.7	1,210 ± 145	2.3 ± 0.5	655 ± 66	7.51 ± 0.75
< 5,000 D	*	5.0 ± 0.8	47.7 ± 6.7	1,200 ± 144	2.2 ± 0.4	660 ± 66	7.98 ± 0.80
> 1,000 D but < 5,000 D	*	–	–	–	–	–	0.41 ± 0.04
> 5,000 D	*	–	–	–	–	–	–
Adsorption 1,000 D	*	–	–	–	–	–	–
Adsorption 5,000 D	*	–	–	–	–	–	–

– = Not found.
*The iron results are rejected due to inconsistent analyses and considerable adsorption on the filters.

Table 8-7. Inorganic size fractions (1,000 D and 5,000 D filters) in section 768.0–775.1 m.

Fraction	Fe (mg/L)	Si (mg/L)	S (mg/L)	Ca (mg/L)	Al (µg/L)	Mn (µg/L)
< 1,000 D	*	3.9 ± 0.6	12.9 ± 1.8	2,430 ± 292	4.0 ± 0.8	98.0 ± 9.8
< 5,000 D	*	4.0 ± 0.6	13.2 ± 1.8	2,430 ± 292	3.0 ± 0.6	86.2 ± 8.6
> 1,000 D but < 5,000 D	–	–	–	–	–	–
> 5,000 D	–	–	–	–	–	–
Adsorption 1,000 D	–	–	–	–	–	–
Adsorption 5,000 D	–	–	–	–	–	–

– = Not found.
*The iron results are rejected due to inconsistent data.

8.5 Humic and fulvic acids

The results from fractionation of organic acids in sections 353.5–360.6 m and 768.0–775.1 m are summarised in Table 8-8. As shown, the water in the sections contains organic acids with a molecular weight less than 1,000 D. This means that the organic constituents are present as low molecular weight fulvic acids and possibly other low molecular weight organic acids such as citric acid and oxalic acid. The results from the 1,000 D filter and 5,000 D filters were consistent.

Table 8-8. Summary of fractionation results.

Section / Fraction	353.5–360.6 m DOC (mg/L)	768.0–775.1 m DOC (mg/L)
< 1,000 D	1.2 ± 0.2	1.6 ± 0.2
> 1,000 D but < 5,000 D	–	–
> 5,000 D	–	–

– = Not found.

Results of colloid filtering experiment, section 353.5–360.6 m

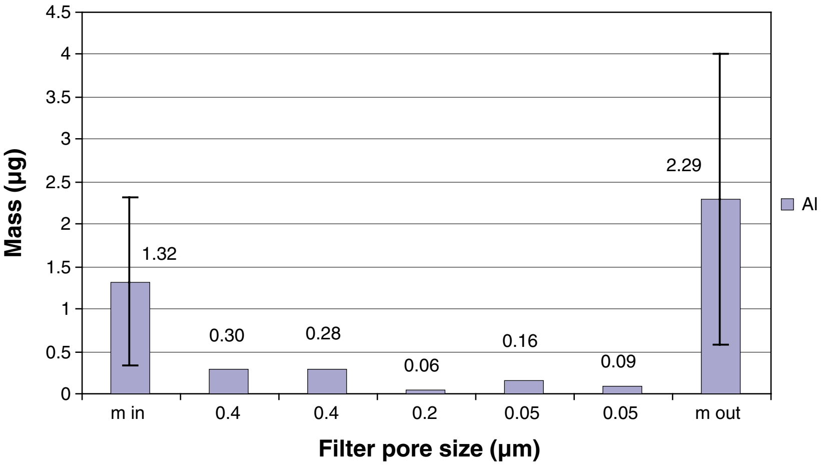


Figure 8-14. *Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out).*

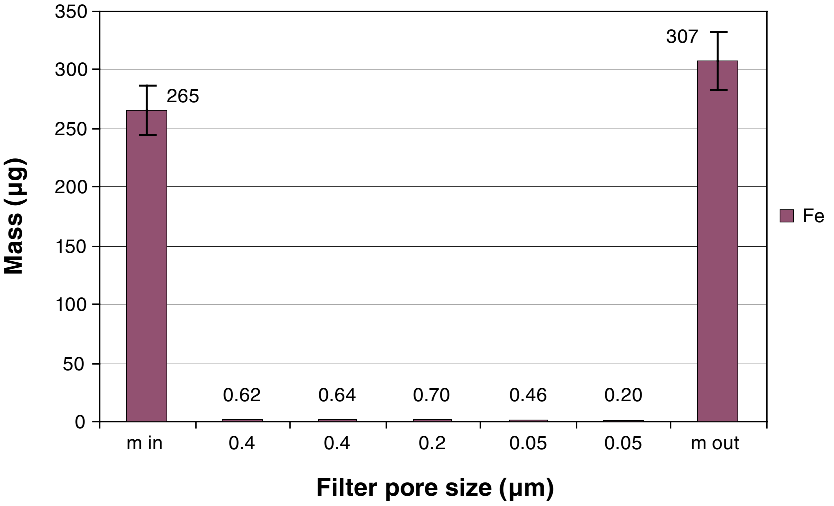


Figure 8-15. *Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out).*

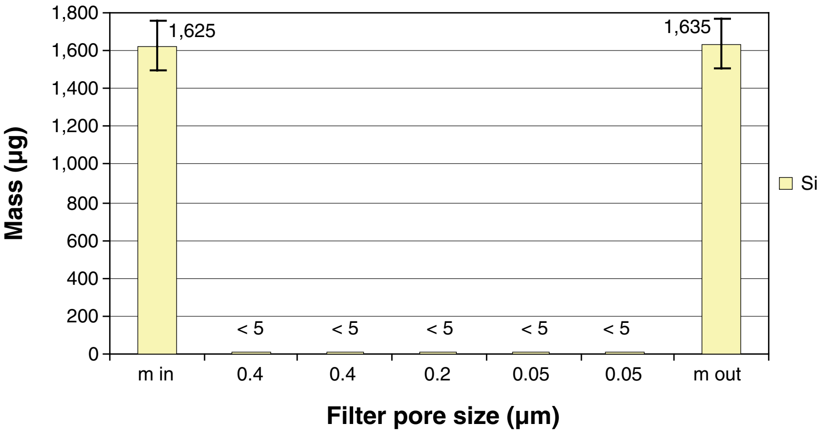


Figure 8-16. *Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out).*

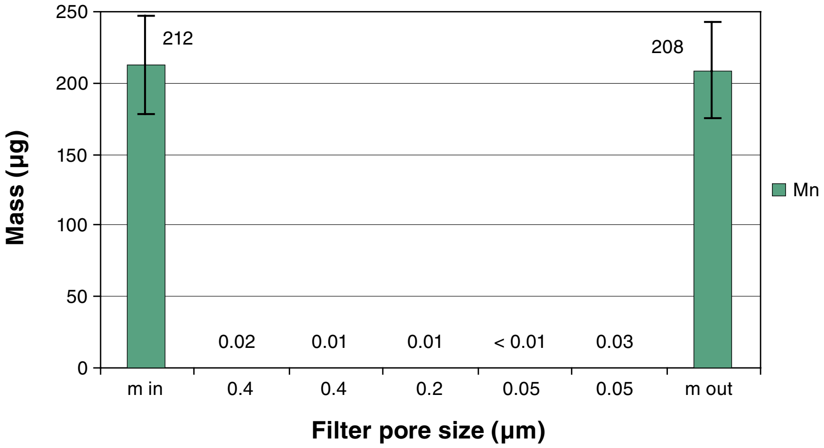


Figure 8-17. *Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out).*

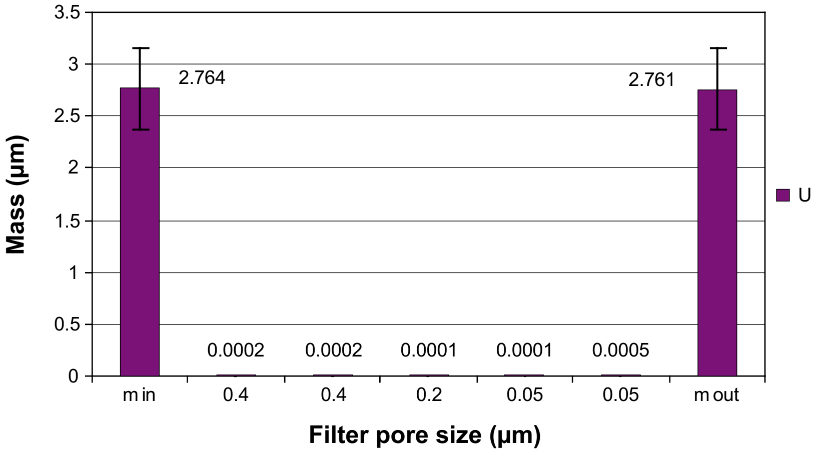


Figure 8-18. *Amount of uranium entering the filter system (m in), in the filters and in the collecting container (m out).*

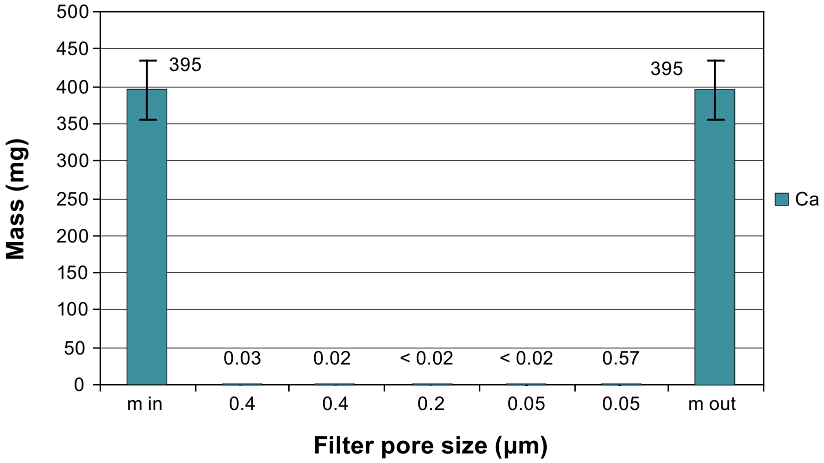


Figure 8-19. *Amount of calcium entering the filter system (m in), in the filters and in the collecting container (m out).*

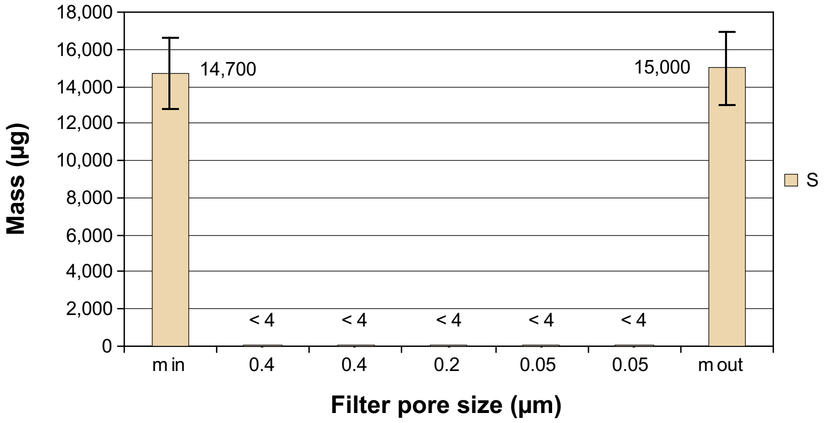


Figure 8-20. *Amount of sulphur entering the filter system (m in), in the filters and in the collecting container (m out).*

Results of colloid filtering experiment, section 768.0–775.1 m

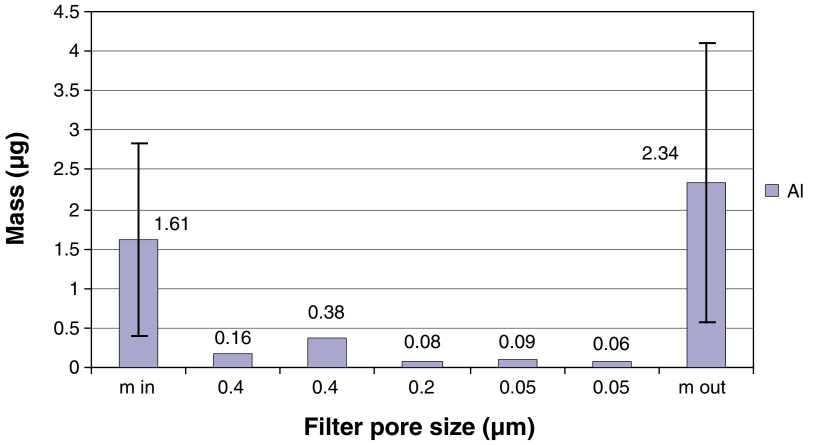


Figure 8-21. *Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out).*

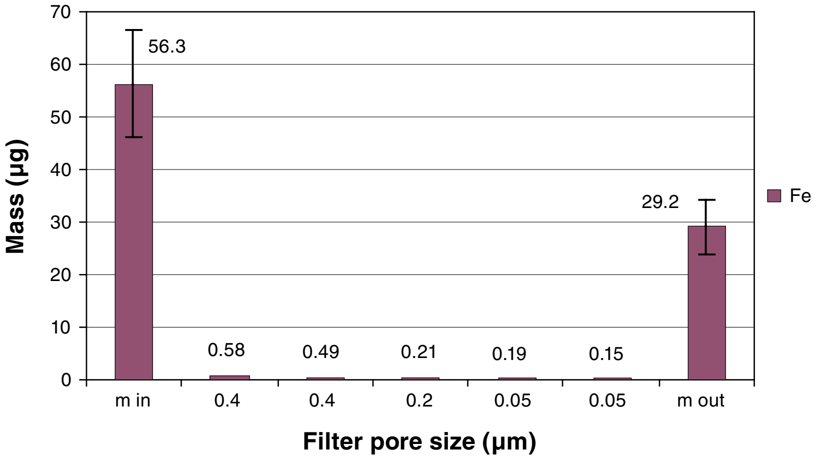


Figure 8-22. *Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out).*

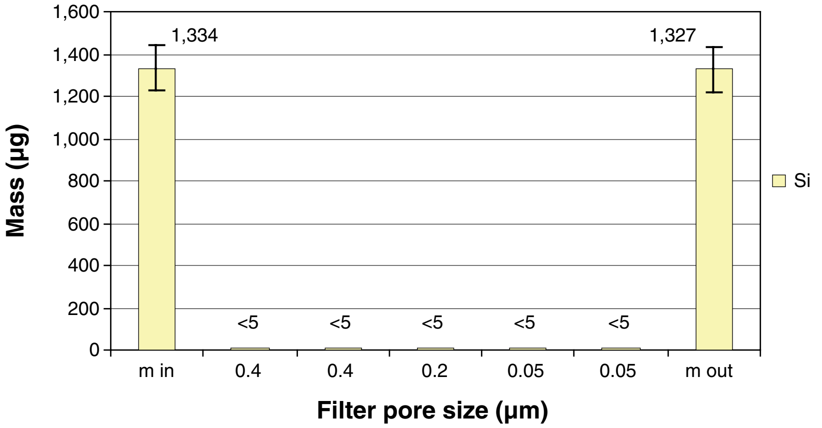


Figure 8-23. *Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out).*

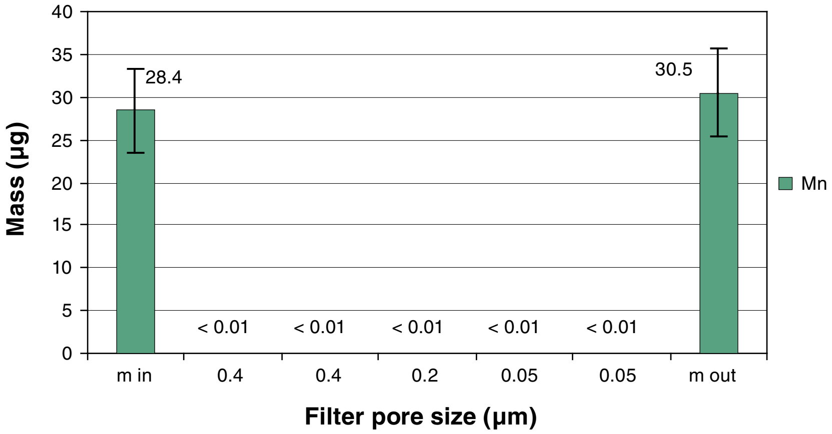


Figure 8-24. *Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out).*

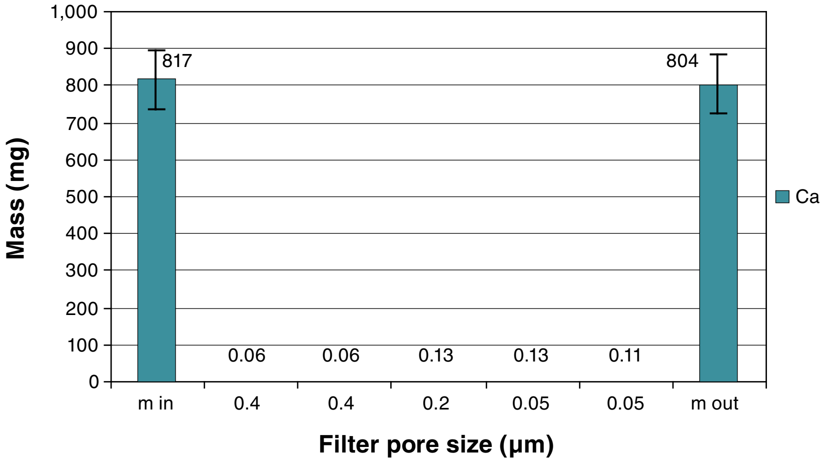


Figure 8-25. *Amount of calcium entering the filter system (m in), in the filters and in the collecting container (m out).*

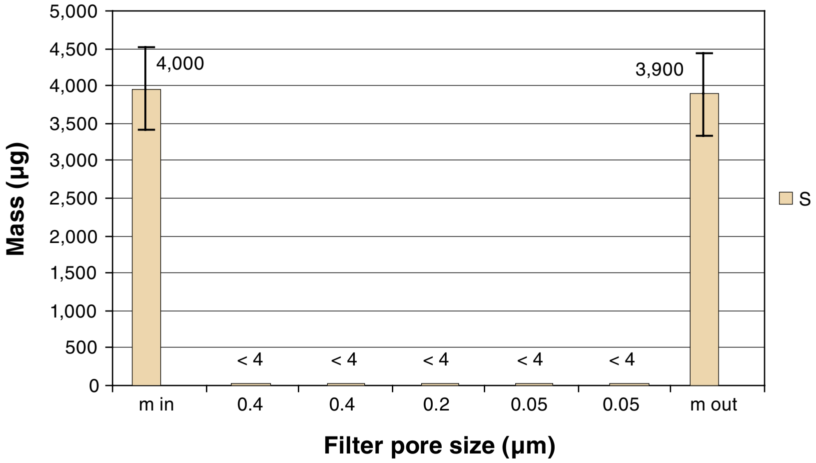


Figure 8-26. *Amount of sulphur entering the filter system (m in), in the filters and in the collecting container (m out).*

9 Summary and discussion

The chemical characterisation in borehole KFM06A was, on the whole, performed quite successfully without any major equipment malfunctions. However, high contents of remaining flushing water caused problems in this borehole in common with several previously investigated boreholes at Forsmark /14, 15, 16/. Figure 9-1 presents the chloride concentration versus depth dependence of investigated groundwaters in KFM06A together with corresponding data from other boreholes at Forsmark.

The main conclusions from the experimental results are:

- The redox potential measurement by the borehole Chemmac in the shallow section 353.5–360.6 m appears to be of very good quality (–155 mV) and the quality of the measurement in section 768.0–775.6 m is also acceptable (–200 mV). However, the surface Chemmac electrodes did not measure credible values in any of the sections. Possible reasons are air intrusion or gas bubbles on electrode surfaces.
- An upper limit for the allowed flushing water content in a representative water sample is set to 1%. This content was exceeded in both borehole sections. The flushing water contents were 7% and 2% for sections 353.5–360.6 m and 768.0–775.6 m respectively.
- The water composition was stable during the pumping/sampling periods which indicates that no mixing occurred with groundwaters from other fracture systems with different water compositions.
- In a few cases, the ferrous iron concentration is somewhat lower than the total iron concentration. It is unlikely that the difference represents the Fe(+III) concentration of the undisturbed groundwater. It is more probable that the time interval between sampling and reagent addition for the subsequent analyses was too long.

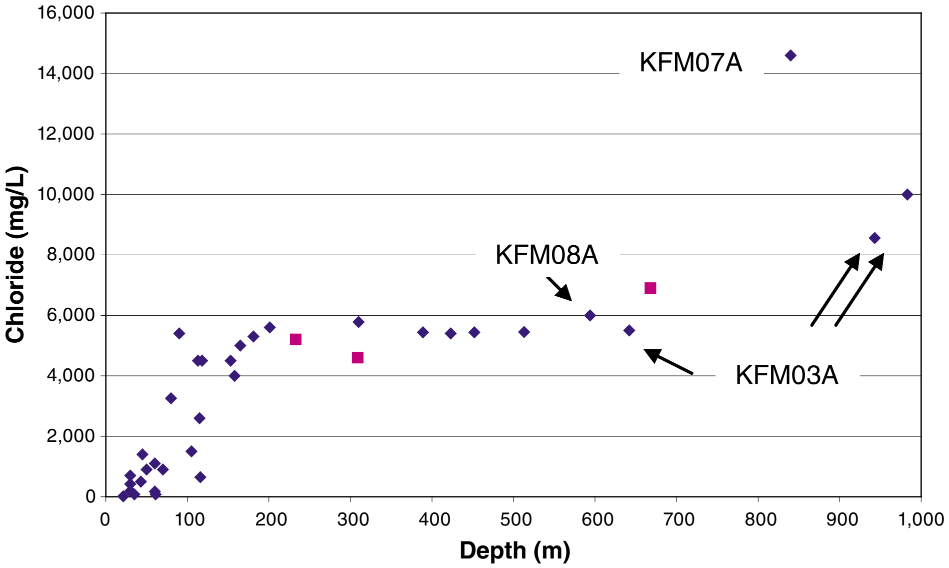


Figure 9-1. Chloride concentrations versus depth at the Forsmark site. Chloride data from KFM06A are plotted in pink colour. The diagram presents also those available data that will be included in subsequent reports.

- The previous boreholes KFM02A and KFM03A revealed very high uranium concentrations in the groundwater between 200 and 600 m depth (up to 90 µg/L). To some extent this was also the case in the shallow section 353.5–360.6 m of KFM06A. Here the uranium concentration amounted to approximately 9 µg/L. The independent determination of uranium-238 verified the element concentration obtained by ICP-MS technique.
- The results from the LIBD experiment and the enclosed PVB-container analyses, as well as the colloid filtering experiment, show the necessity to improve the tightness of the PVB-containers. Further, possible contamination sources need to be traced and excluded before the next borehole investigation.
- The content of inorganic colloids in the groundwater is low. The filtering experiments resulted in concentrations of approximately 11 µg/L (353.5–360.6 m) and 3.5 µg/L (768.0–775.1 m) while the LIBD-method (353.5–360.6 m) indicates concentrations in the range 1–7 µg/L. It is most probable that the real background concentrations are even lower, especially in the deep section (768.0–775.1 m), since precipitated iron as well as contamination by aluminium obviously contributes.
- Possibly, both the colloid filtering experiment and the colloid fractionation in section 353.5–360.6 m indicate a small fraction of colloidal uranium.
- The organic constituents present in the groundwaters in KFM06A (both sections) are of low molecular weight (< 1,000 D).

10 References

/1/ **SKB, 2001.** Site investigations. Investigation methods and general execution programme. SKB TR-01-29, Svensk Kärnbränslehantering AB.

/2/ **Pedersen K, 2005.** Forsmark site investigation. Numbers and metabolic diversity of microorganisms in boreholes KFM06A and KFM07A. Results from sections 353.5–356.6 and 768–775 m in KFM06A and section 848–1,001.6 m in KFM07A. SKB P-05-177, Svensk Kärnbränslehantering AB.

/3/ **Claesson L-Å, Nilsson G, 2005.** Forsmark site investigation. Drilling of the telescopic borehole KFM06A and the core drilled borehole KFM06B at drill site DS6. SKB P-05-50, Svensk Kärnbränslehantering AB.

/4/ **SKB, 2005.** Forsmark site investigation. Programme for further investigations of geosphere and biosphere. SKB R-05-14, Svensk Kärnbränslehantering AB.

/5/ **Waber H N, Smellie J A T, 2005.** Forsmark site investigation. Borehole KFM06A: Characterisation of pore water. Part I: Diffusion experiments. SKB P-05-196, Svensk Kärnbränslehantering AB.

/6/ **Claesson L-Å, Nilsson G, 2003.** Forsmark site investigation. Drilling of a flushing water well, HFM05 and a monitoring well, HFM04, at drill site DS2. SKB P-03-51, Svensk Kärnbränslehantering AB.

/7/ **Nilsson A-C, 2003.** Forsmark site investigation. Sampling and analyses of groundwater in percussion drilled boreholes and shallow monitoring wells at drillsite DS2. Results from the percussion boreholes HFM04, HFM05, KFM02A (borehole section 0–100 m) and the monitoring wells SFM0004 and SFM0005. SKB P-03-48, Svensk Kärnbränslehantering AB.

/8/ **Berg C, Nilsson A-C, 2005.** Forsmark site investigation. Hydrochemical logging in KFM06A. SKB P-05-33, Svensk Kärnbränslehantering AB.

/9/ **Pedersen K, 2003.** Forsmark site investigation. Control of microorganism content in flushing water used for drilling of KFM06A. SKB P-05-81, Svensk Kärnbränslehantering AB.

/10/ **Rouhiainen P, Sokolnicki M, 2005.** Forsmark site investigation. Difference flow logging in borehole KFM06A. SKB P-05-15, Svensk Kärnbränslehantering AB.

/11/ **Gustafsson J, Gustafsson C, 2005.** Forsmark site investigation. RAMAC and BIPS logging in boreholes KFM06A and HFM22. SKB P-05-01, Svensk Kärnbränslehantering AB.

/12/ **Nielsen U T, Ringgard J, Horn F, 2005.** Forsmark site investigation. Geophysical borehole logging in borehole KFM06A, HFM20, HFM21, HFM22 and SP logging in KFM01A and KFM04A. SKB P-05-17, Svensk Kärnbränslehantering AB.

/13/ **Hjerne C, Ludvigsson J-E, Lindquist A, 2005.** Forsmark site investigation. Single-hole injection tests in boreholes KFM06A and KFM06B. SKB P-05-165, Svensk Kärnbränslehantering AB.

/14/ **Wacker P, Bergelin B, Nilsson A-C, 2004.** Forsmark site investigation. Complete hydrochemical characterisation in KFM01A. Results from two investigated sections, 110.0–120.7 m and 176.8–183.9 m. SKB P-03-94. Svensk Kärnbränslehantering AB.

/15/ **Wacker P, Bergelin B, Nilsson A-C, 2004.** Forsmark site investigation. Hydrochemical characterisation in KFM02A. Results from three investigated sections, 106.5–126.5 m, 413.5–433.5 m and 509.0–516.1 m. SKB P-04-70, Svensk Kärnbränslehantering AB.

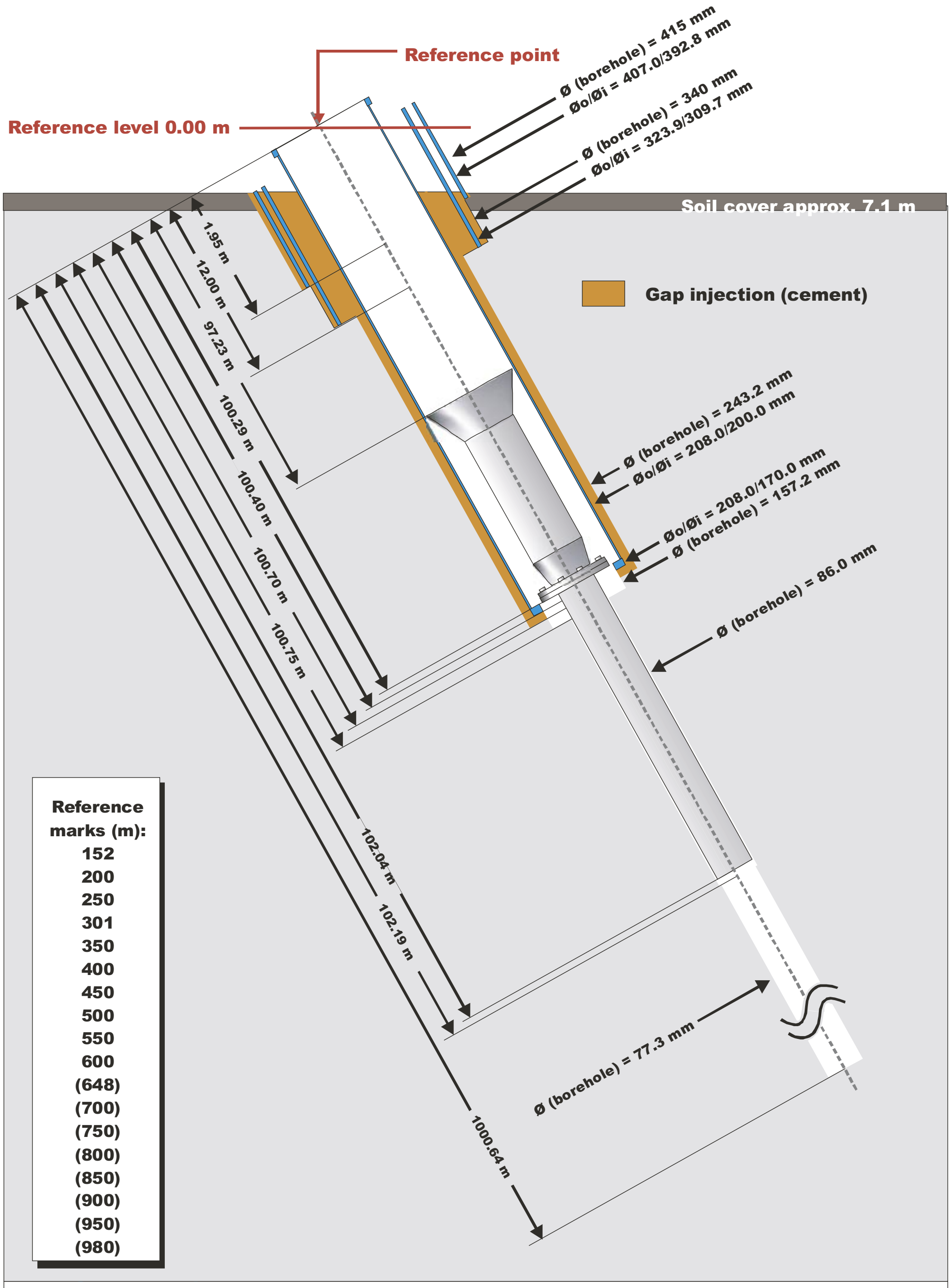
/16/ **Wacker P, Bergelin B, Berg C, Nilsson A-C, 2004.** Forsmark site investigation. Hydrochemical characterisation in KFM03A. Results from six investigated sections; 386.0–390.1 m, 448.0–453.0 m, 448.5–455.6 m, 639.0–646.1 m, 939.5–946.6 m, 980.0–1,001.2 m. SKB P-04-108, Svensk Kärnbränslehantering AB.

Appendix 1

Design of cored borehole KFM06A

Technical data

Borehole KFM06A



Northing: 6699732.88 (m), RT90 2,5 gon V 0:-15
Easting: 1632442.51 (m), RT90 2,5 gon V 0:-15
Elevation: 4.10 (m), RHB 70

Orientation
Bearing (degrees): 300.92°
Inclination (degrees): -60.25°

Borehole
Length: 1000.64 m

Percussion drilling period
Drilling start date:
Drilling stop date:

Core drilling period
Drilling start date: 2004-06-14
Drilling stop date: 2004-09-21

Appendix 2

Selected results from differential flow logging in KFM06A

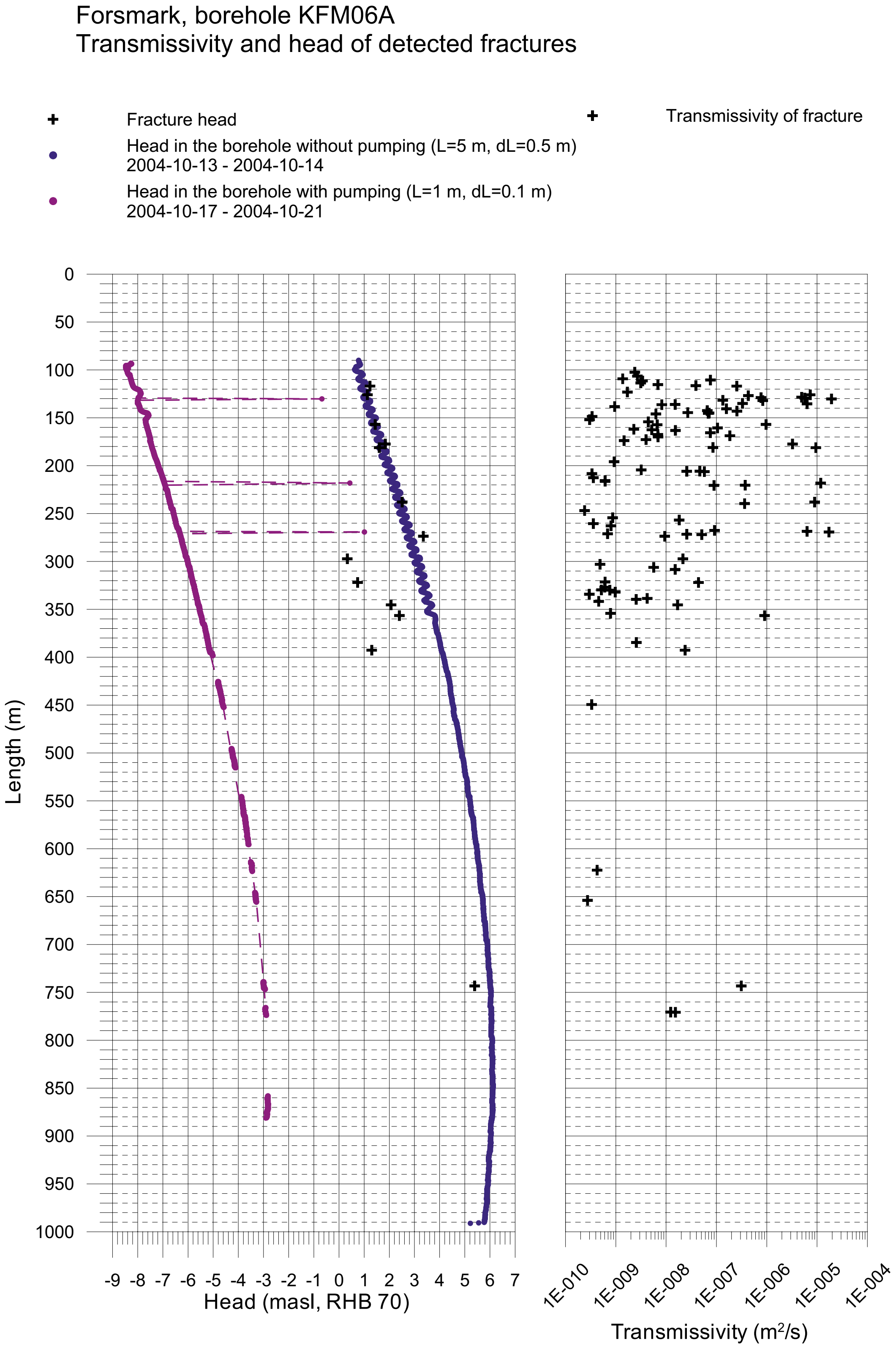


Figure A2-1. Borehole KFM06A: Head of detected fractures and hydraulic transmissivity /10/.

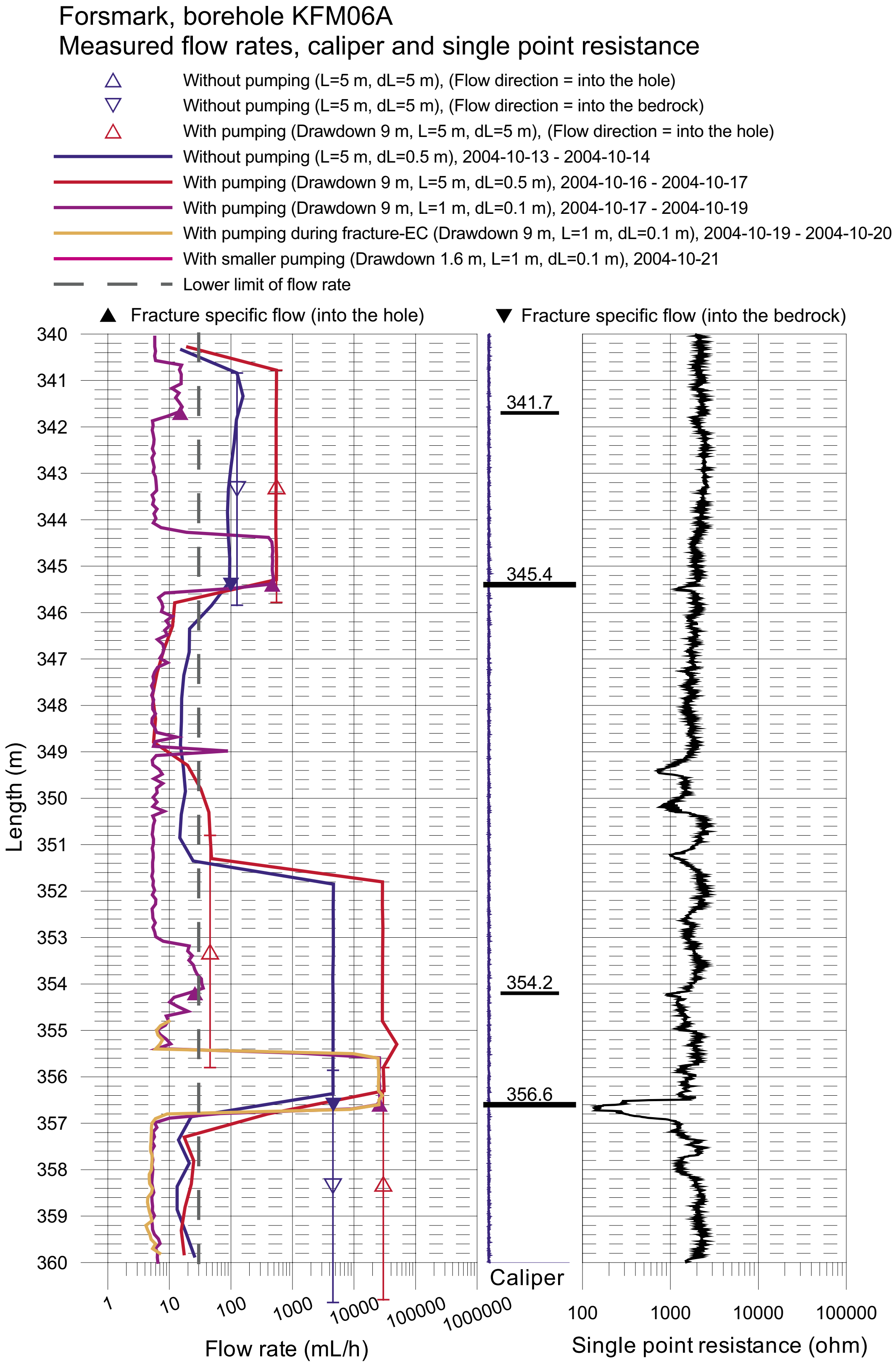


Figure A2-2. *Borehole KFM06A: Differential flow measurements from 340–360 m including the water bearing fracture zone at 356.6 m /10/.*

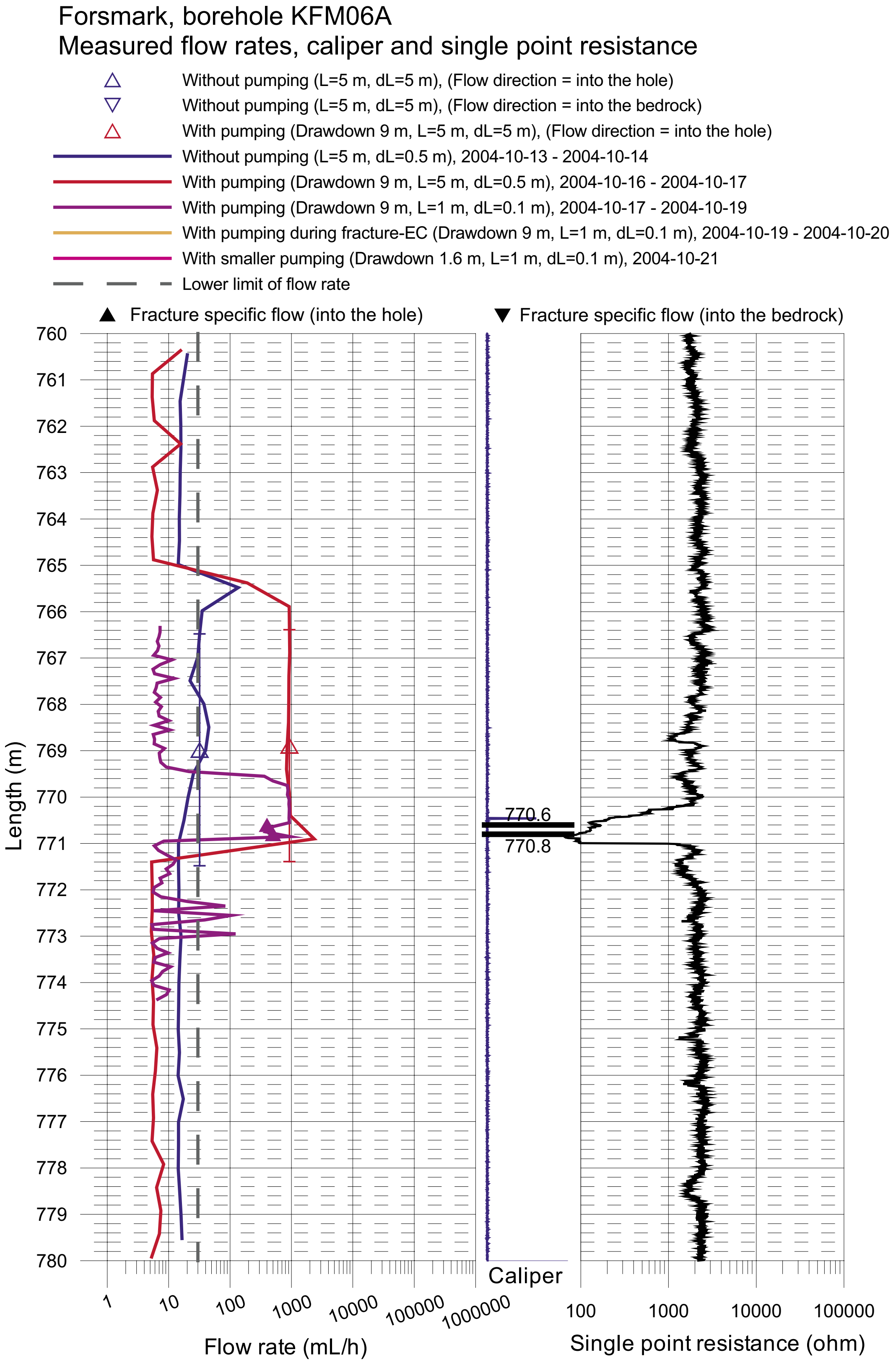


***Figure A2-3.** Borehole KFM06A: Differential flow measurements from 760–780 m including the water bearing fracture zone at 770.6 m /10/.*

Appendix 3

Selected images from BIPS logging in KFM06A

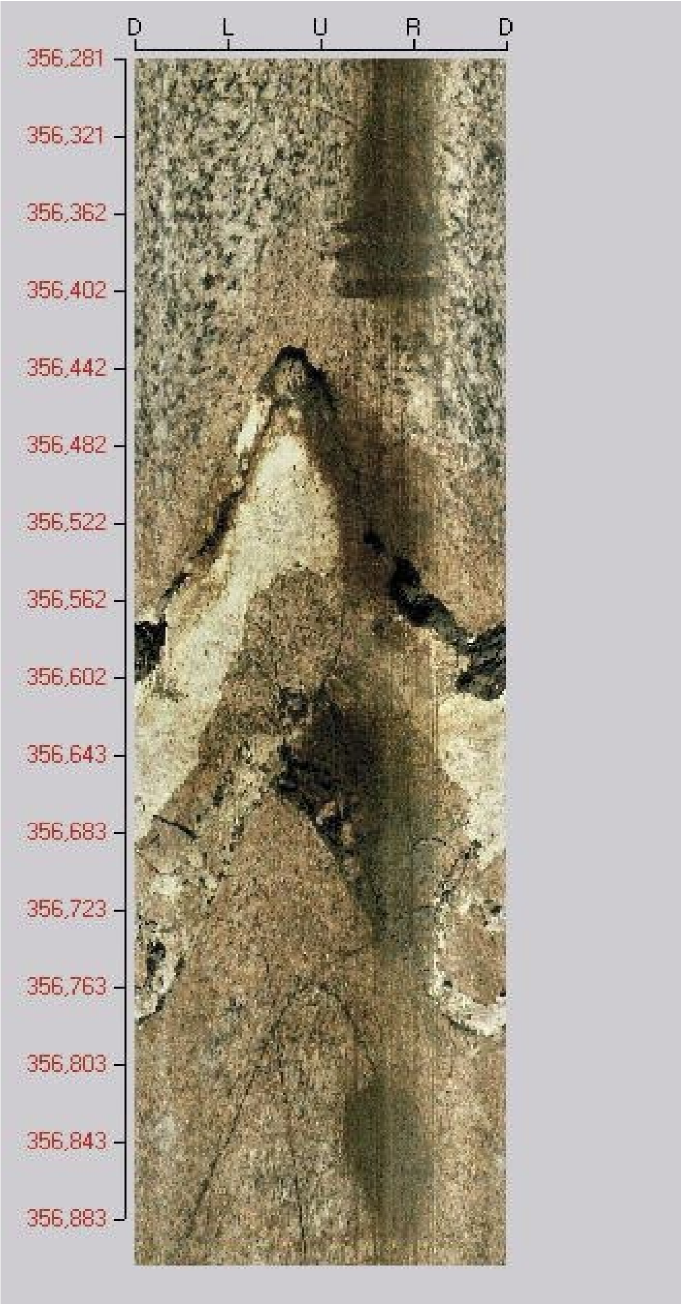


Figure A3-2. *Borehole KFM06A: BIPS logging from 356.3 to 356.9 m.*

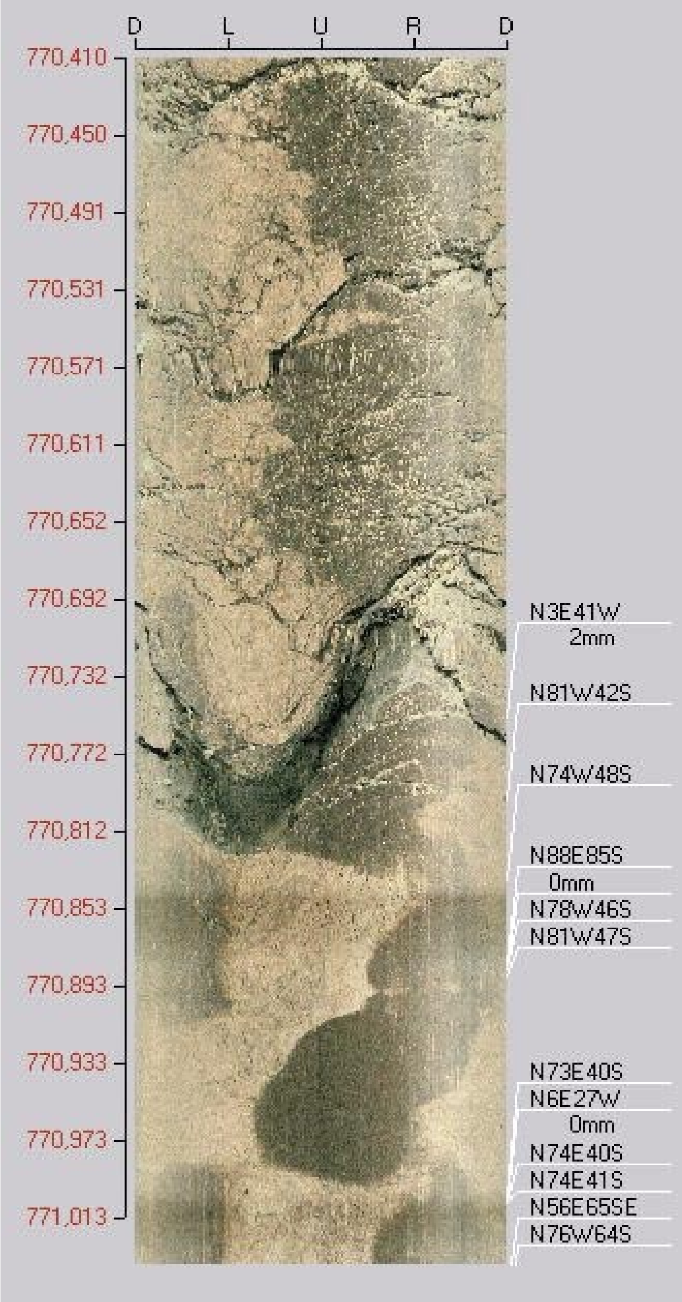
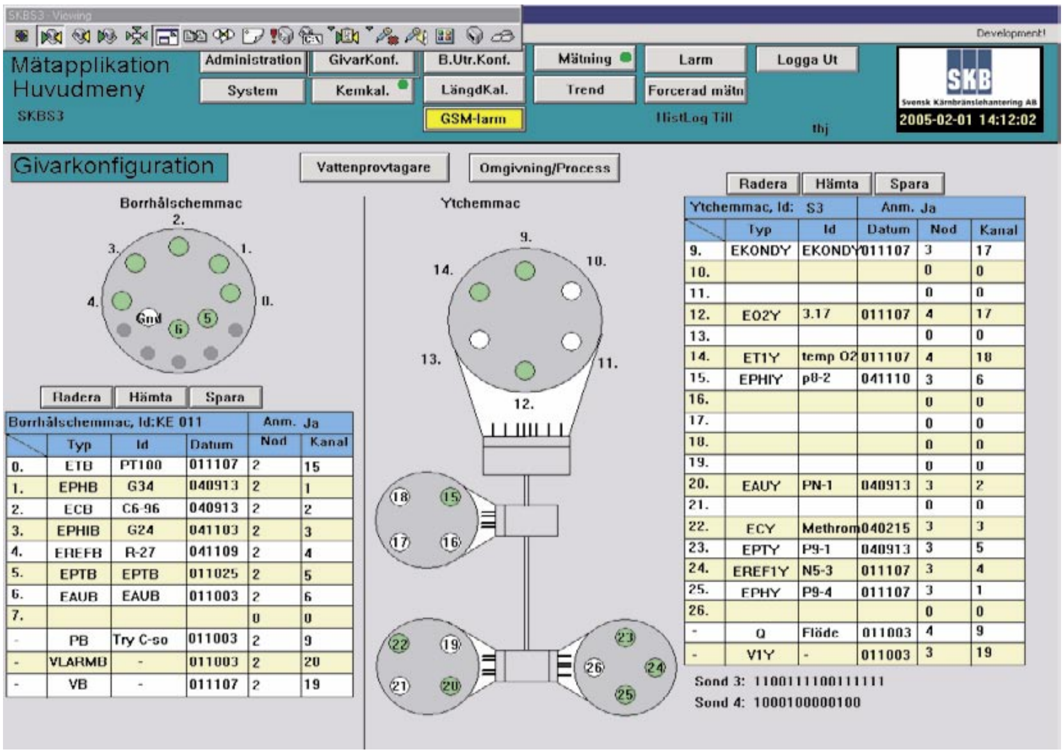


Figure A3-2. *Borehole KFM06A: BIPS logging from 770.4 to 771.0 m.*

Appendix 4

Measurement information, KFM06A

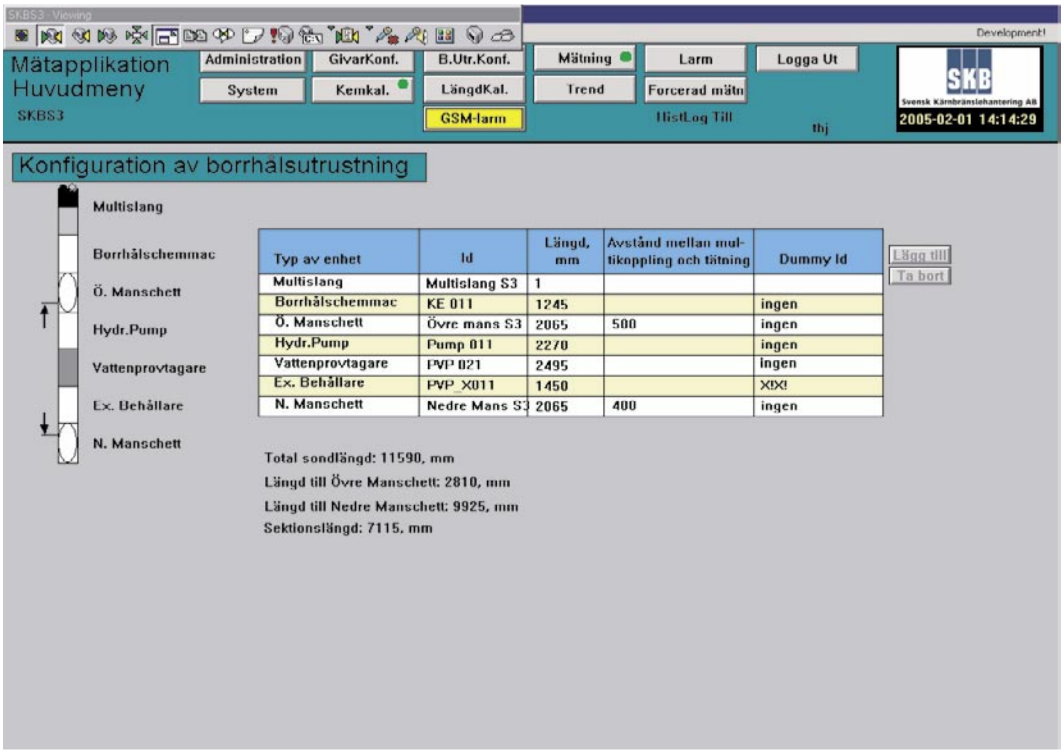


Borrhålschemmac, Id:KE 011				Anm. Ja	
	Typ	Id	Datum	Nod	Kanal
0.	ETB	PT100	011107	2	15
1.	EPHB	G34	040913	2	1
2.	ECB	C6-96	040913	2	2
3.	EPHIB	G24	041103	2	3
4.	EREFB	R-27	041109	2	4
5.	EPTB	EPTB	011025	2	5
6.	EAUB	EAUB	011003	2	6
7.				0	0
-	PB	Try C-so	011003	2	9
-	VLARMB	-	011003	2	20
-	VB	-	011107	2	19

Ytchemmac, Id: S3			Anm. Ja		
	Typ	Id	Datum	Nod	Kanal
9.	EKONDY	EKONDY	011107	3	17
10.				0	0
11.				0	0
12.	EO2Y	3.17	011107	4	17
13.				0	0
14.	ET1Y	temp O2	011107	4	18
15.	EPHIY	p8-2	041110	3	6
16.				0	0
17.				0	0
18.				0	0
19.				0	0
20.	EAUY	PN-1	040913	3	2
21.				0	0
22.	ECY	Methrom	040215	3	3
23.	EPTY	P9-1	040913	3	5
24.	EREF1Y	N5-3	011107	3	4
25.	EPHY	P9-4	011107	3	1
26.				0	0
-	Q	Flöde	011003	4	9
-	V1Y	-	011003	3	19

```
Sond 3:  1100111100111111
Sond 4:  1000100000100
```

Figure A4-1. Electrode configuration, section 768.0–775.1 m.



Typ av enhet	Id	Längd, mm	Avstånd mellan multikoppling och tätning	Dummy Id
Multislang	Multislang S3	1		
Borrhålschemmac	KE 011	1245		ingen
Ö. Manschett	Övre mans S3	2065	500	ingen
Hydr.Pump	Pump 011	2270		ingen
Vattenprovtagare	PVP 021	2495		ingen
Ex. Behållare	PVP_X011	1450		X!X!
N. Manschett	Nedre Mans S3	2065	400	ingen

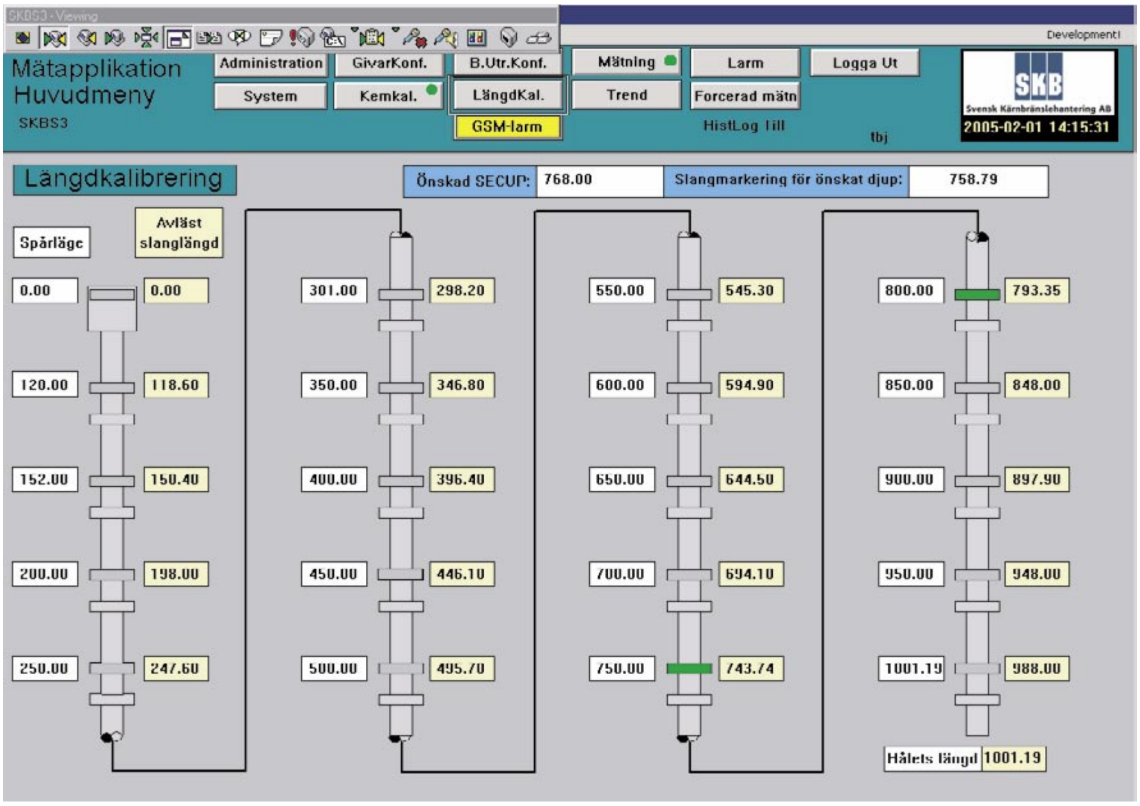
Total sondlängd: 11590, mm

Längd till Övre Manschett: 2810, mm

Längd till Nedre Manschett: 9925, mm

Sektionslängd: 7115, mm

Figure A4-2. Configuration of downhole equipment, section 768.0–775.1 m.



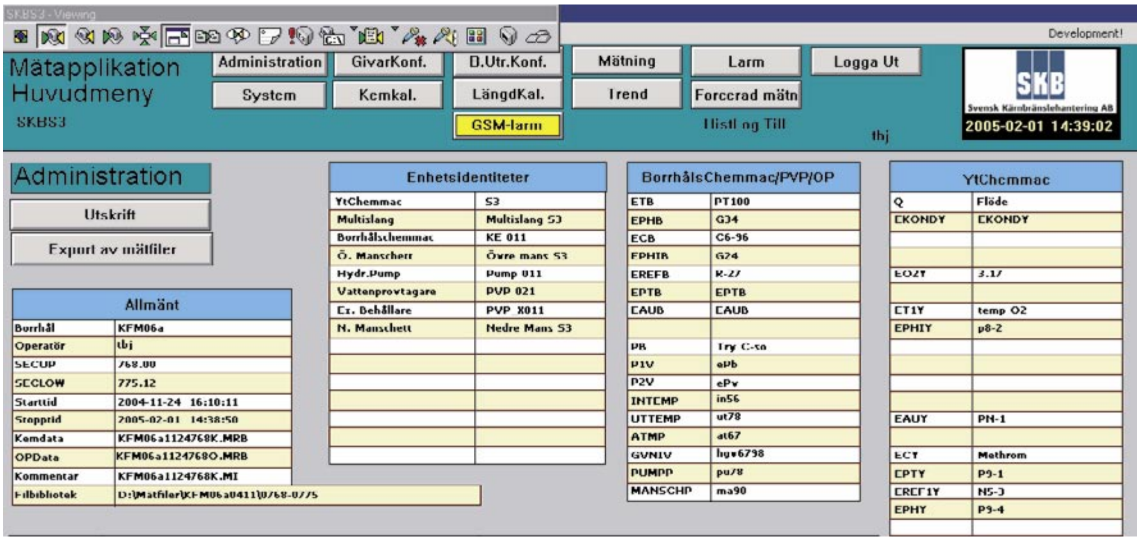
Önskad SECUP: 768.00

Slangmarkering för önskat djup: 758.79

Spårläge	Avläst slanglängd
0.00	0.00
120.00	118.60
152.00	150.40
200.00	198.00
250.00	247.60
301.00	298.20
350.00	346.80
400.00	396.40
450.00	446.10
500.00	495.70
550.00	545.30
600.00	594.90
650.00	644.50
700.00	694.10
750.00	743.74
800.00	793.35
850.00	848.00
900.00	897.90
950.00	948.00
1001.19	988.00

Hålets längd 1001.19

Figure A4-3. *Length calibration, section 768.0–775.1 m.*



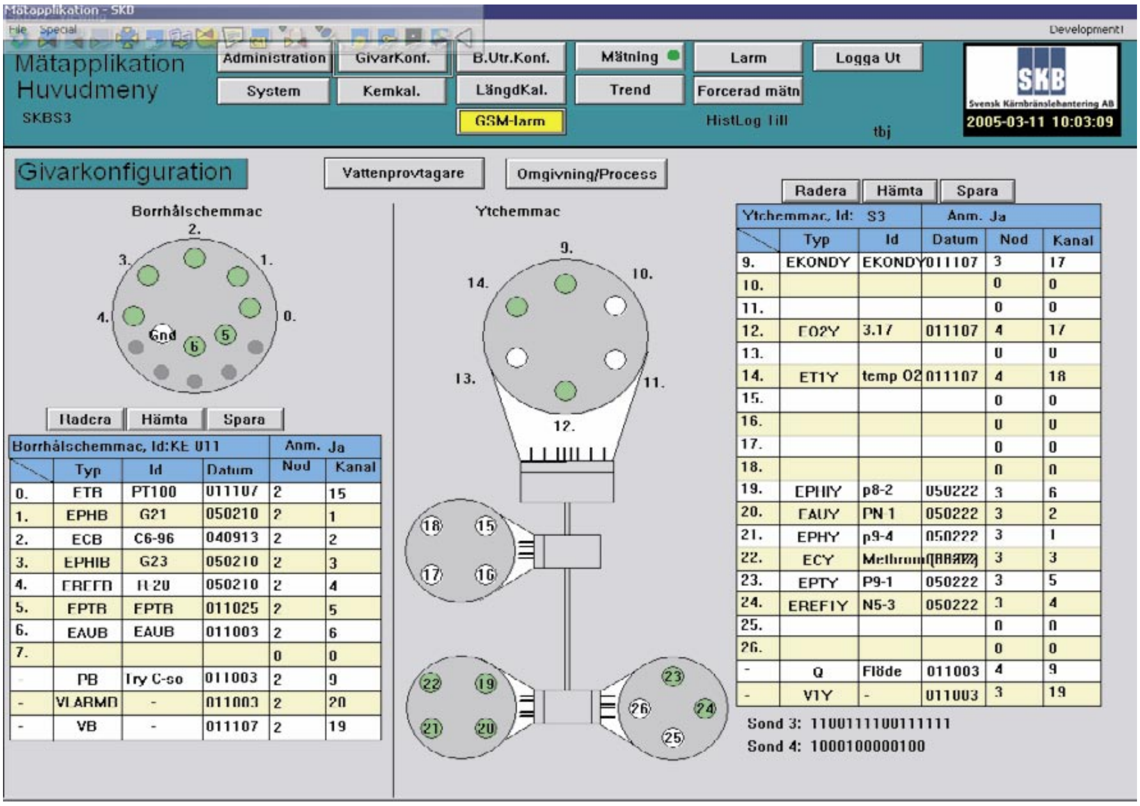
Allmänt	
Borrhål	KFM06a
Operatör	tbj
SECUP	768.00
SECLOW	775.12
Starttid	2004-11-24 16:10:11
Stopptid	2005-02-01 14:38:50
Kemdata	KFM06a1124768K.MRB
OPData	KFM06a1124768O.MRB
Kommentar	KFM06a1124768K.MI
Filbibliotek	D:\Matfiler\KFM06a0411\0768-0775

EnhetsIdentiteter	
YtChemmac	S3
Multislang	Multislang S3
Borrhålschemmac	KE 011
Ö. Manschett	Övre mans S3
Hydr.Pump	Pump 011
Vattenprovtagare	PVP 021
Ex. Behållare	PVP_X011
N. Manschett	Nedre Mans S3

BorrhålsChemmac/PVP/OP	
ETB	PT100
EPHB	G34
ECB	C6-96
EPHIB	G24
EREFB	R-27
EPTB	EPTB
EAUB	EAUB
PB	Try C-so
P1V	aPb
P2V	ePv
INTEMP	in56
UTTEMP	ut78
ATMP	at67
GVNIV	hgv6798
PUMPP	pu78
MANSCHP	ma90

YtChemmac	
Q	Flöde
EKONDY	EKONDY
EO2Y	3.17
ET1Y	temp O2
EPHIY	p8-2
EAUY	PN-1
ECT	Methrom
EPTY	P9-1
EREF1Y	N5-3
EPHY	P9-4

Figure A4-4. *Administration (050201), section 768.0–775.1 m.*



Borrhålschemmac, Id:KE 011				Anm. Ja	
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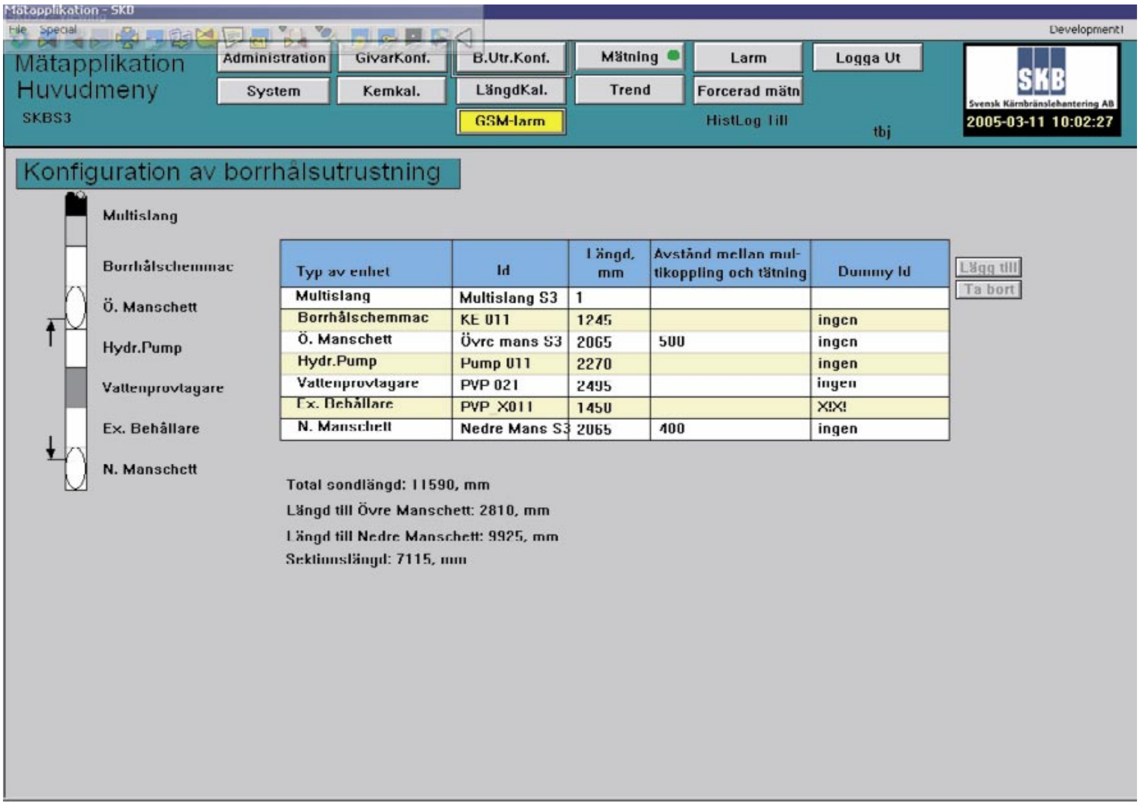
1.	EPHB	G21	050210	2	1
2.	ECB	C6-96	040913	2	2
3.	EPHIB	G23	050210	2	3
4.	EREFB	R 20	050210	2	4
5.	EPTR	EPTR	011025	2	5
6.	EAUB	EAUB	011003	2	6
7.				0	0
-	PB	Try C-so	011003	2	9
-	VLARMD	-	011003	2	20
-	VB	-	011107	2	19

Ytchemmac, Id: S3			Anm. Ja		
	Typ	Id	Datum	Nod	Kanal
9.	EKONDY	EKONDY	011107	3	17
10.				0	0
11.				0	0
12.	EO2Y	3.17	011107	4	17
13.				0	0
14.	ET1Y	temp 02	011107	4	18
15.				0	0
16.				0	0
17.				0	0
18.				0	0
19.	EPHY	p8-2	050222	3	6
20.	EAUY	PN 1	050222	3	2
21.	EPHY	p9-4	050222	3	1
22.	ECY	Methrom	[illegible]	3	3
23.	EPTY	P9-1	050222	3	5
24.	EREFIY	N5-3	050222	3	4
25.				0	0
26.				0	0
-	Q	Flöde	011003	4	9
-	V1Y	-	011003	3	19

Sond 3: 1100111100111111
Sond 4: 1000100000100

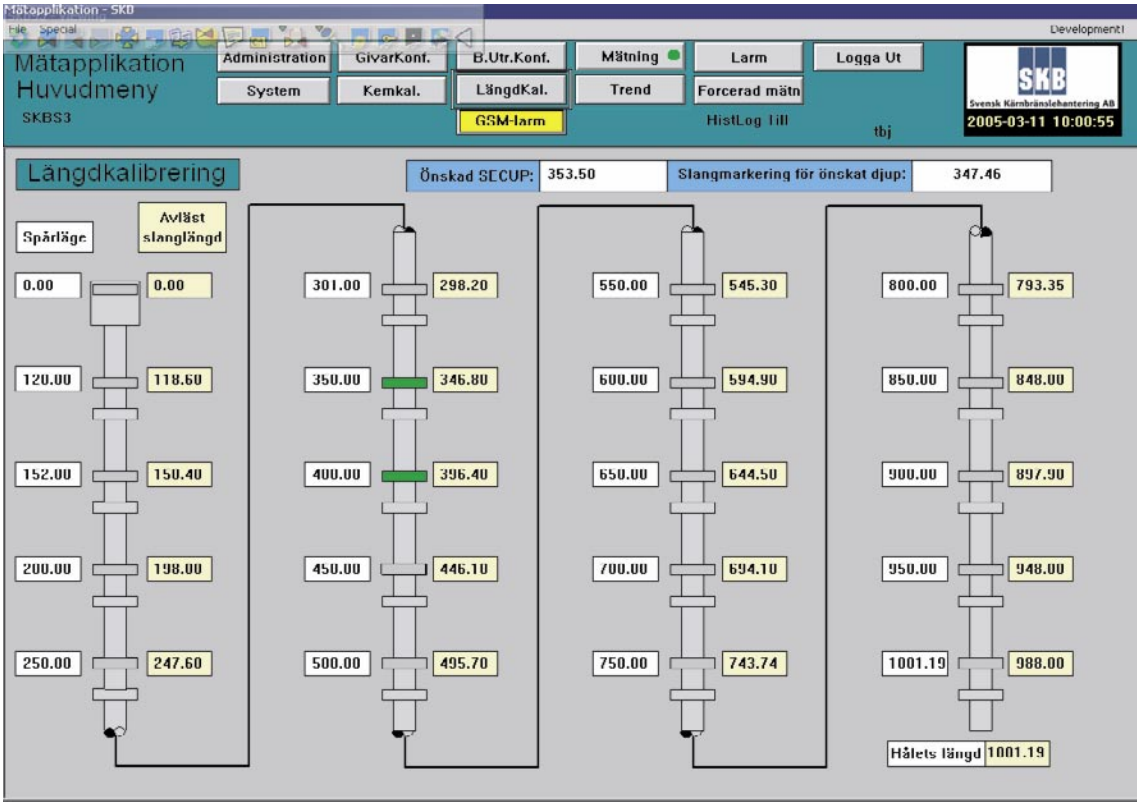
Figure A4-5. Electrode configuration, section 353.5–360.6 m.



Typ av enhet	Id	Längd, mm	Avstånd mellan multikoppling och tätning	Dummy Id
Multislang	Multislang S3	1		
Borrhålschemmac	KE 011	1245		ingen
Ö. Manschett	Övre mans S3	2065	500	ingen
Hydr.Pump	Pump 011	2270		ingen
Vattenprovtagare	PVP 021	2495		ingen
Ex. Behållare	PVP X011	1450		X!X!
N. Manschett	Nedre Mans S3	2065	400	ingen

Total sondlängd: 11590, mm
Längd till Övre Manschett: 2810, mm
Längd till Nedre Manschett: 9925, mm
Sektionslängd: 7115, mm

Figure A4-6. Configuration of downhole equipment, section 353.5–360.6 m.



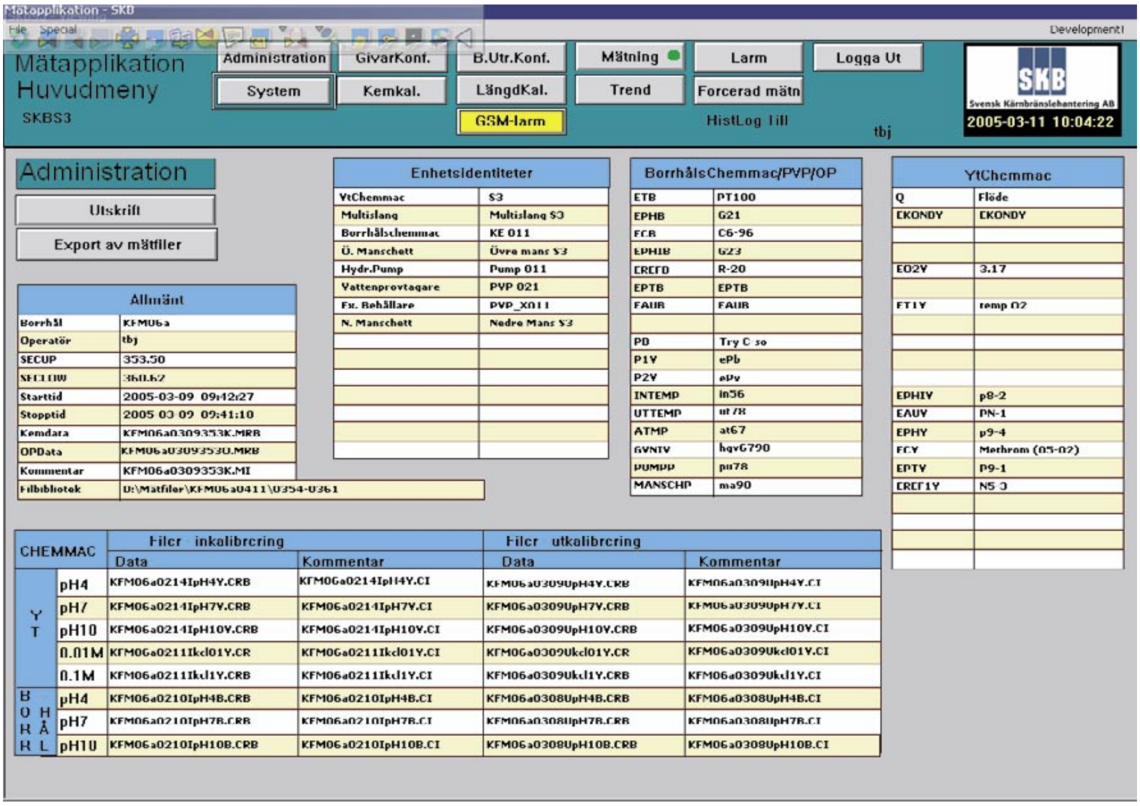
Önskad SECUP: 353.50

Slangmarkering för önskat djup: 347.46

Spårläge	Avläst slanglängd
0.00	0.00
120.00	118.60
152.00	150.40
200.00	198.00
250.00	247.60
301.00	298.20
350.00	346.80
400.00	396.40
450.00	446.10
500.00	495.70
550.00	545.30
600.00	594.90
650.00	644.50
700.00	694.10
750.00	743.74
800.00	793.35
850.00	848.00
900.00	897.90
950.00	948.00
1001.19	988.00

Hålets längd 1001.19

Figure A4-7. *Length calibration, section 353.5–360.6 m.*



Allmänt	
Borrhål	KFM06a
Operatör	tbj
SECUP	353.50
SECLOW	360.62
Starttid	2005-03-09 09:12:27
Stopptid	2005 03 09 09:41:10
Kemdata	KFM06a0309353K.MRB
OPData	KFM06a0309353O.MRB
Kommentar	KFM06a0309353K.MI
Filbibliotek	D:\Mätfiler\KFM06a0411\0354-0361

Enhetsidentiteter	
YtChemmac	S3
Multislang	Multislang S3
Borrhålschemmac	KE 011
Ö. Manschett	Övre mans S3
Hydr.Pump	Pump 011
Vattenprovtagare	PVP 021
Ex. Behållare	PVP_X011
N. Manschett	Nedre Mans S3

BorrhålsChemmac/PVP/OP	
ETB	PT100
EPHB	G21
ECB	C6-96
EPH1B	G23
ERCFD	R-20
EPTB	EPTB
FAUR	FAUR
PD	Try C so
P1Y	ePb
P2Y	ePv
INTEMP	in56
UTTEMP	ut78
ATMP	at67
GVNIV	hgv6790
PUMPP	pu78
MANSCHP	ma90

YtChemmac	
Q	Flöde
EKONDY	EKONDY
EO2Y	3.17
ET1Y	temp O2
EPHIY	p8-2
EAUY	PN-1
EPHY	p9-4
ECY	Methrom (05-02)
EPTY	P9-1
ERCF1Y	N5-3

CHEMMAC		Filer inkalibrering		Filer utkalibrering	
		Data	Kommentar	Data	Kommentar
YT	pH4	KFM06a0214IpH4Y.CRB	KFM06a0214IpH4Y.CI	KFM06a0309UpH4Y.CRB	KFM06a0309UpH4Y.CI
	pH7	KFM06a0214IpH7Y.CRB	KFM06a0214IpH7Y.CI	KFM06a0309UpH7Y.CRB	KFM06a0309UpH7Y.CI
	pH10	KFM06a0214IpH10Y.CRB	KFM06a0214IpH10Y.CI	KFM06a0309UpH10Y.CRB	KFM06a0309UpH10Y.CI
	0.01M	KFM06a0211Ikcl01Y.CR	KFM06a0211Ikcl01Y.CI	KFM06a0309Ukcl01Y.CR	KFM06a0309Ukcl01Y.CI
	0.1M	KFM06a0211Ikcl1Y.CRB	KFM06a0211Ikcl1Y.CI	KFM06a0309Ukcl1Y.CRB	KFM06a0309Ukcl1Y.CI
BORR HÅL	pH4	KFM06a0210IpH4B.CRB	KFM06a0210IpH4B.CI	KFM06a0308UpH4B.CRB	KFM06a0308UpH4B.CI
	pH7	KFM06a0210IpH7B.CRB	KFM06a0210IpH7B.CI	KFM06a0308UpH7B.CRB	KFM06a0308UpH7B.CI
	pH10	KFM06a0210IpH10B.CRB	KFM06a0210IpH10B.CI	KFM06a0308UpH10B.CRB	KFM06a0308UpH10B.CI

Figure A4-8. *Administration (050311), section 353.5–360.6 m.*

Appendix 5

Flow and pressure measurements in KFM06A

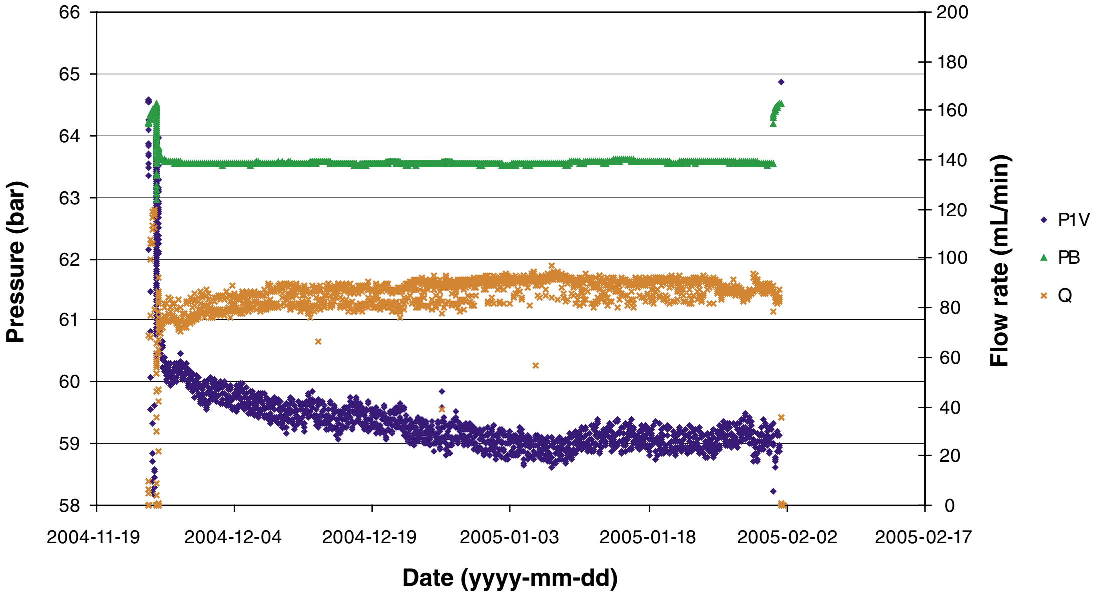


Figure A5-1. *Pressure (P1V and PB) and flow rate (Q) measurements from the borehole section 768.0–775.1 m. The sensors P1V and P2V measure the pressure in the section and are both placed in the in situ sampling unit. P1V- and P2V-measurements coincide and P2V is omitted in order to make the diagram clearer. PB is the sensor in the borehole Chemmac and measures the pressure above the section.*

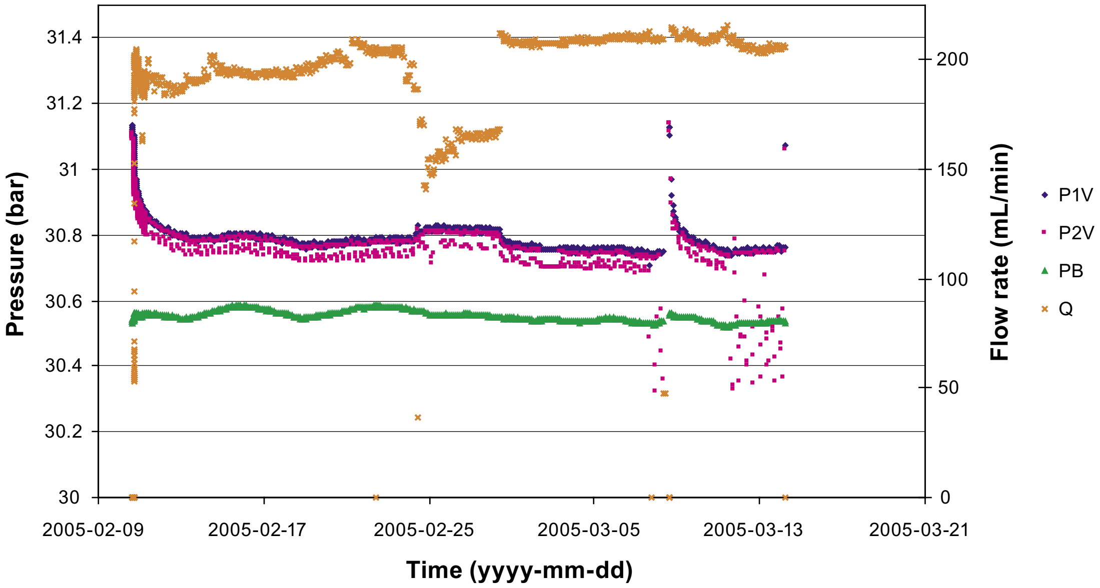


Figure A5-2. *Pressure (P1V, P2V and PB) and flow rate (Q) measurements from the borehole section 353.5–360.6 m. The sensors P1V and P2V measure the pressure in the section and are both placed in the in situ sampling unit. PB is the sensor in the borehole Chemmac and measures the pressure above the section.*

Chemmac measurements in KFM06A, section 353.5–360.6 m

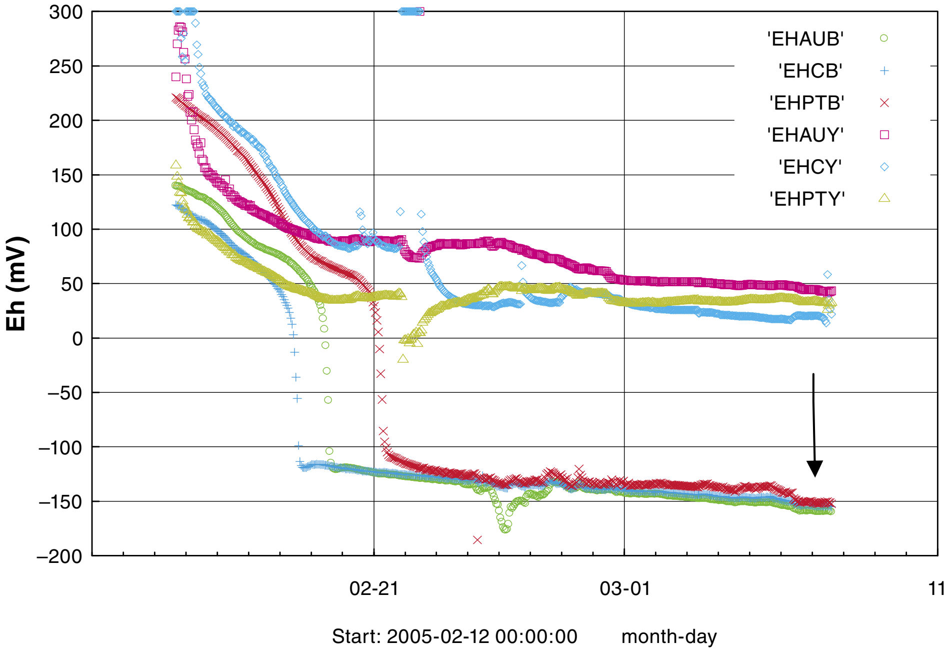


Figure A6-1. *Redox potential measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCY). The arrow shows the chosen representative Eh values for the borehole section.*

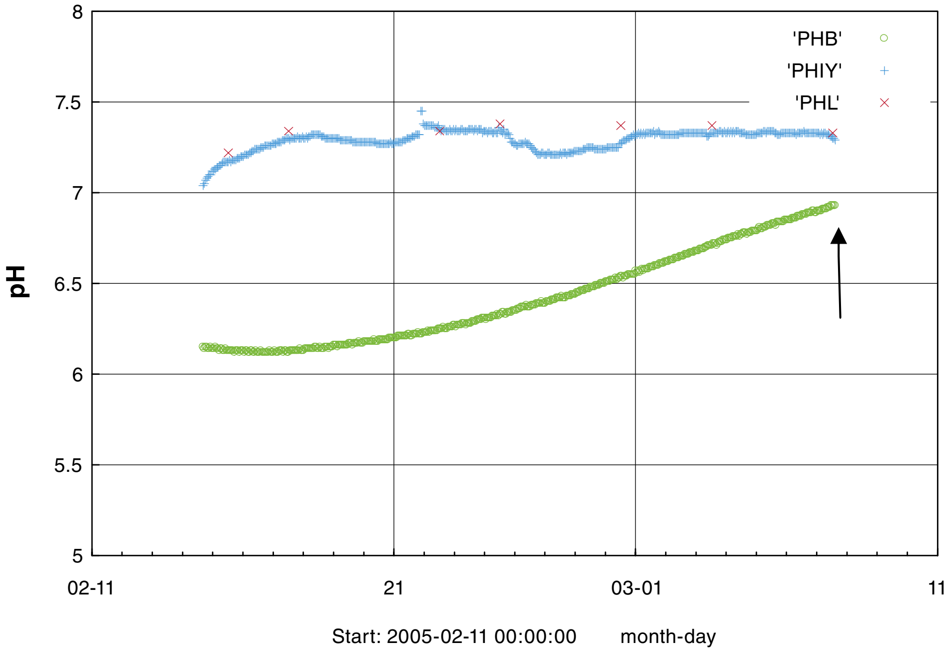


Figure A6-2. *Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.*

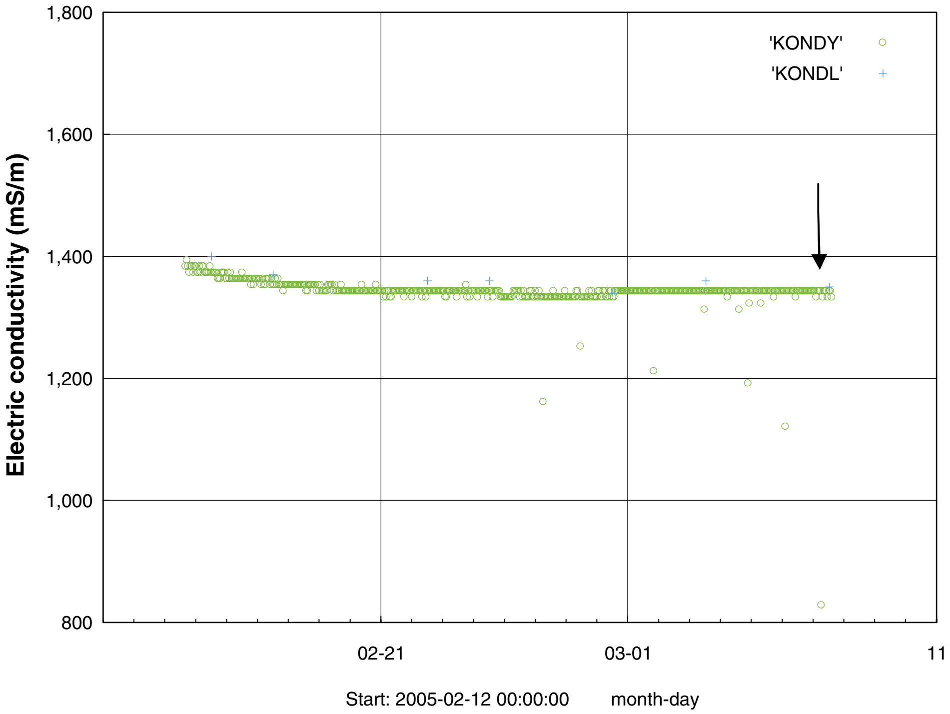


Figure A6-3. *Electric conductivity measurements in the surface measurement cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.*

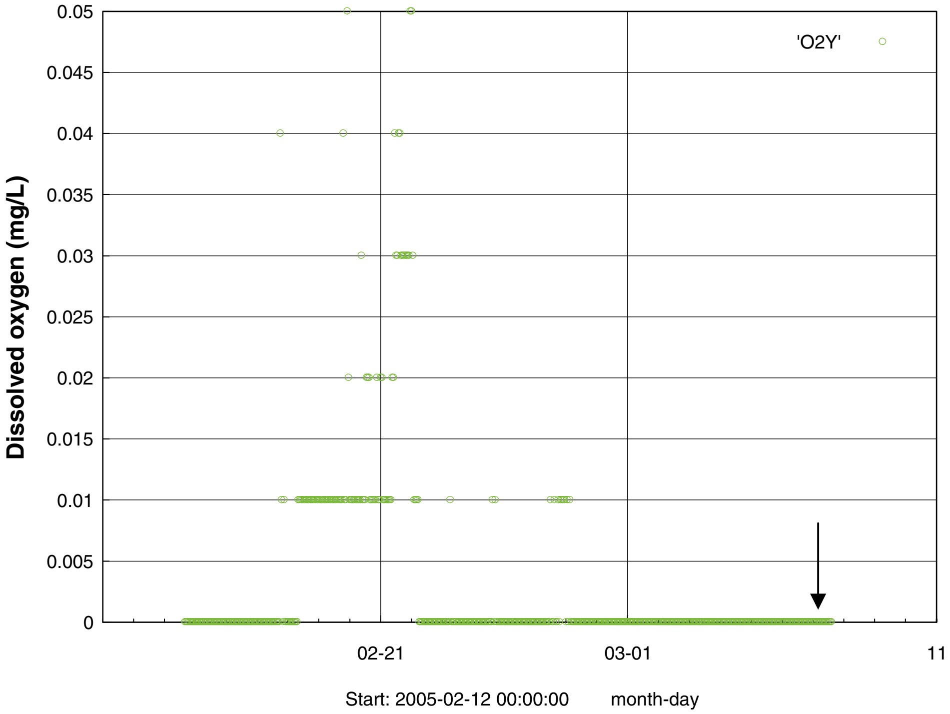


Figure A6-4. *Dissolved oxygen measurements (O2Y) in the surface measurement cell.*

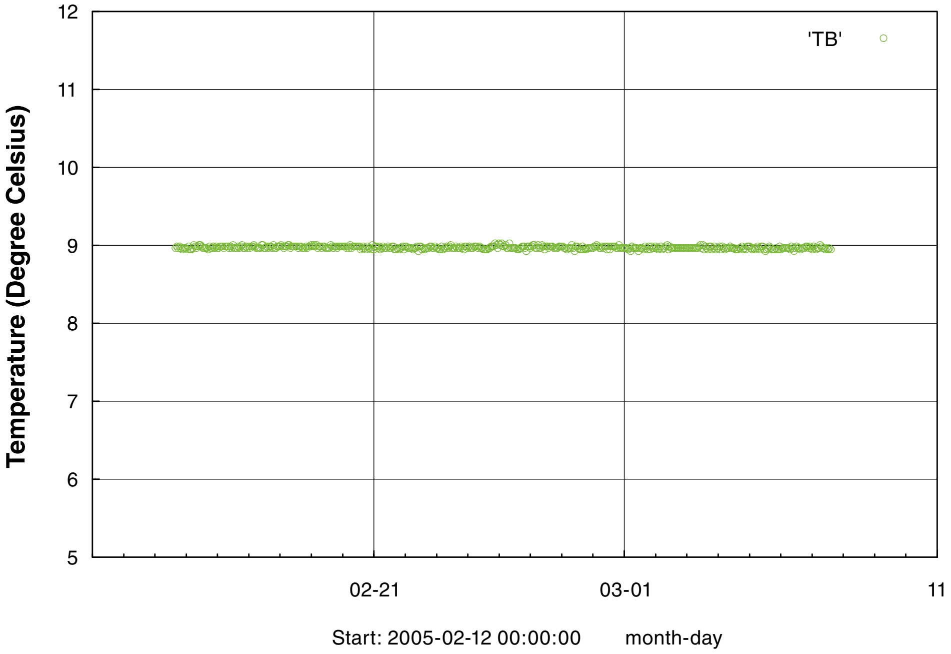


Figure A6-5. *Temperature of the groundwater in the borehole section (TB).*

Chemmac measurements in KFM06A, section 768.0–775.1 m

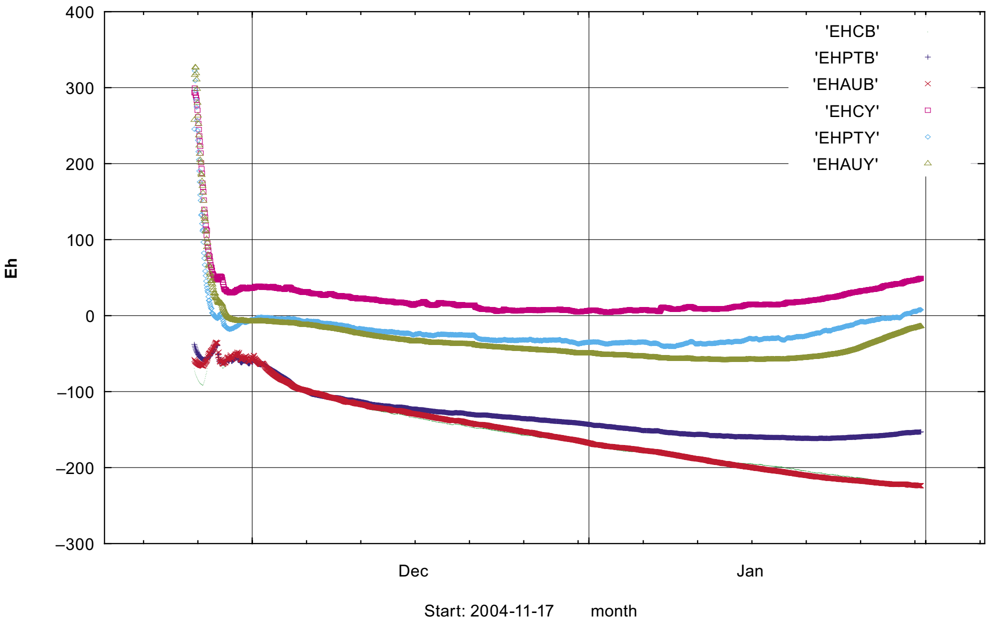


Figure A7-1. *Redox potential measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCY). The arrows show the chosen representative Eh values for the borehole section.*

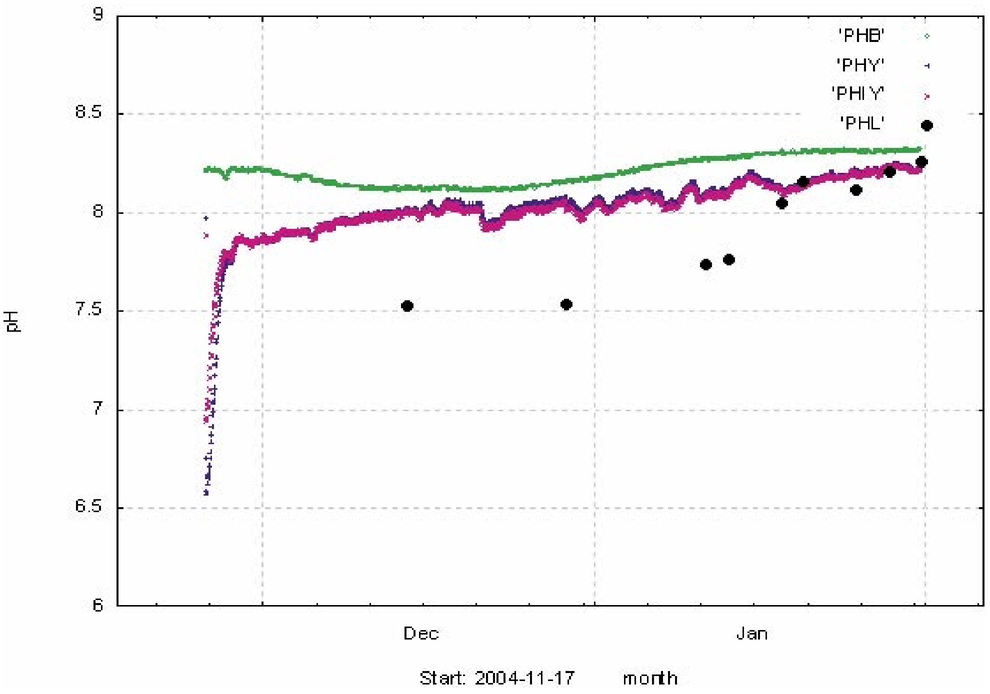


Figure A7-2. *Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrows show the chosen representative pH values for the borehole section.*

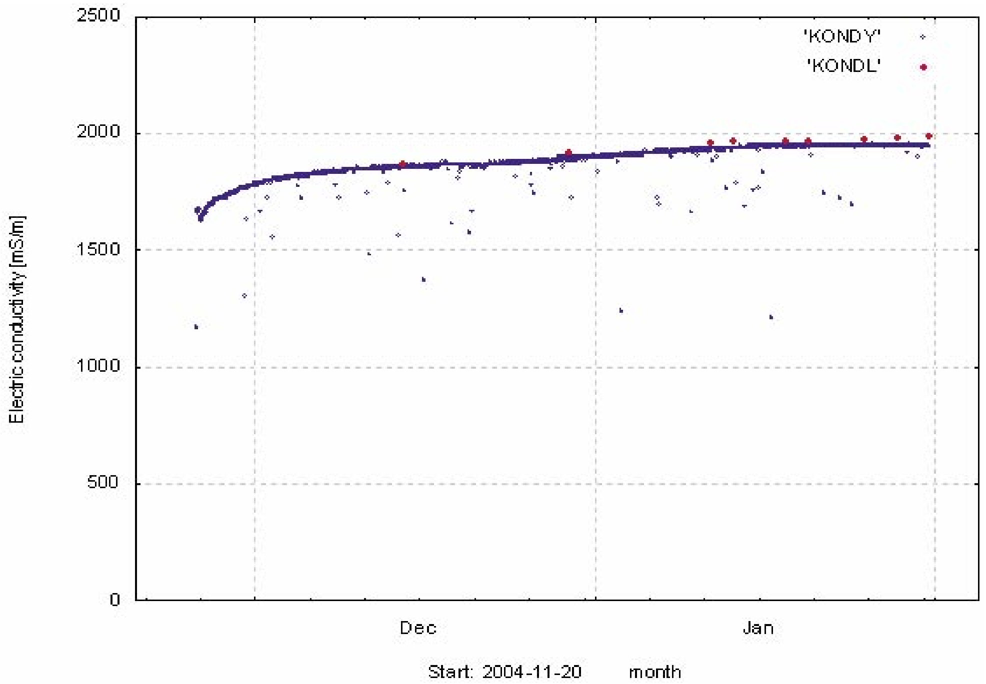


Figure A7-3. *Electric conductivity measurements in the surface measurement cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.*

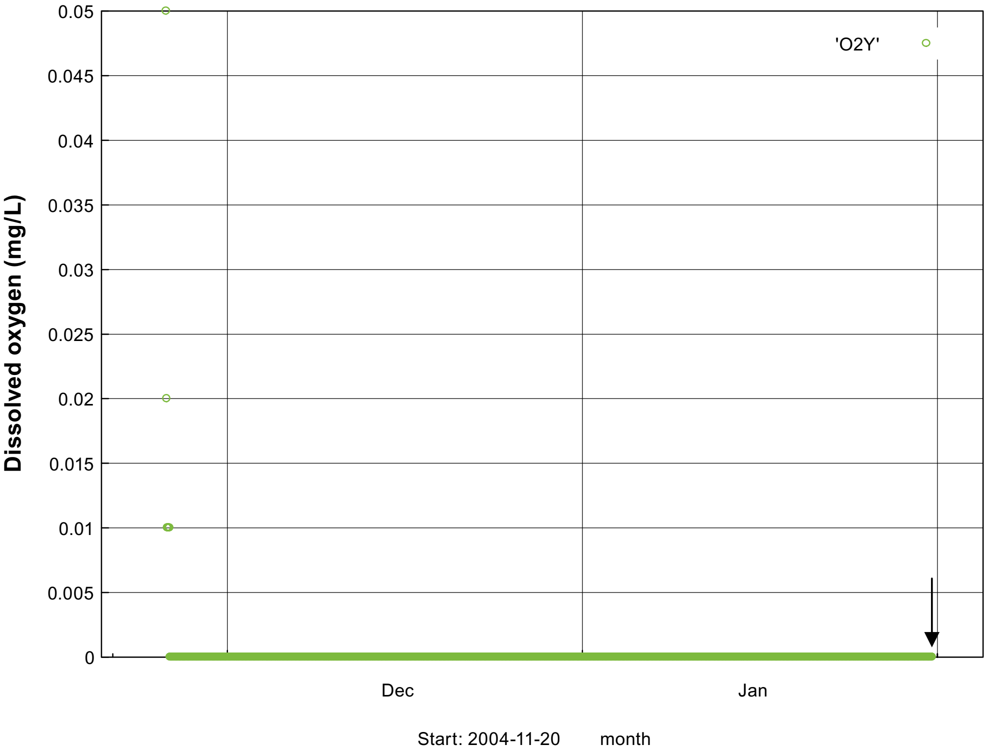


Figure A7-4. *Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section.*

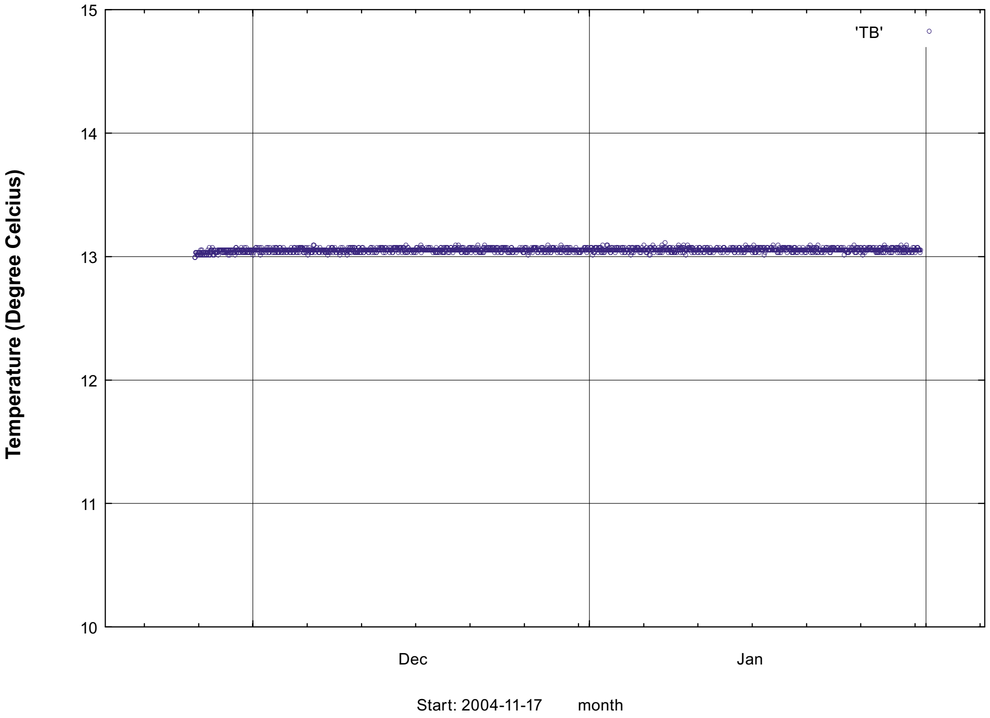


Figure A7-5. *Temperature of the groundwater in the borehole section (TB).*

Appendix 8

Sampling and analytical methods

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	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	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^-)	Not critical (month)
	Br, I	Plastic	100	Yes (not in the field)	No	ICP MS	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	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	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic (Acid washed)	500	Yes	Yes (5 mL HCl))	Spectrophotometry Ferrozine method	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	Immediately or if conserved, a few days
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	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	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	Short transportation time

Component group	**Component/element**	**Sample container (material)**	**Volume (mL)**	**Filtering**	**Preparation/ Conservation***	**Analysis method**	**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	Short transportation time
Environmental isotopes	^{2}H, ^{18}O	Plastic	100	No	– –	MS	Not critical (month)
Tritium, Chlorine-37	^{3}H (enhanced.) Chlorine-37	Plastic (dry bottle) Plastic	500 100	No No	– –	LSC ICP MS	Not critical (month)
Carbon isotopes	^{13}C, ^{14}C	Glass (brown)	100×2	No	–	(A)MS	A few days
Sulphur isotopes	^{34}S	Plastic	500–1,000	Yes	–	Combustion, ICP MS	No limit
Strontium-isotopes	$^{87}Sr/^{86}Sr$	Plastic	100	Yes	–	TIMS	Days or week
Uranium and Thorium isotopes	^{234}U, ^{235}U, ^{238}U, ^{232}Th, ^{230}Th,	Plastic	50	Nej	–	Chemical separat. Alfa/ gamma spectrometry	No limit
Boron isotopes	^{10}B	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP – MS	No limit
Radon and Radium isotopes	^{222}Rn, ^{226}Ra	Plastic	500	No	No	EDA, RD-200	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	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	Immediate transport
Humic and fulvic acids	Fractionation	Fractions are collected in plastic bottles	250	–	N_2 atmosphere	UV oxidation, IR (DOC)	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	^{13}C, ^{14}C (pmc)	DEAE cellulose (anion exchanger)	–	–	–	(A)MS	A few days
Nutrient salt + silicate	NO_2, NO_3, NO_2+NO_3, NH_4, PO_4, SiO_4	Sample tubes, plastic	25×2	Yes (in the field)	No, frozen immediately***	Spectrophotometry	Short transportation time

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Analysis within – or delivery time to lab
Total concentrations of Nitrogen and Phosphorous	N-tot, P-tot	Plastic	100	No	No, frozen immediately***	Spectrophotometry	Short transportation time
Particulate Carbon, Nitrogen and Phosphorous	POC, PON, POP	Plastic	1,000	Yes (within 4 h) prepared filters. Blank filters	Filtering, the filters are frozen immediately 2 filters/sample	Elementar-analysator (N, C) own method 990121 (P)	Short transportation time
Chlorophyll	Chlorophyll a, c and pheopigment	Plastic	1,000–2,000	Yes (within 4 h)	Filtering, the filters are frozen immediately	Spectrophotometry Fluorometry	Short transportation time
Oxygen	Dissolved O_2	Winkler, glass	2×ca 120	No	Mn (II) reagent Iodide reagent	Spectrophotometry SIS SS-EN 25813	Within 3 days
Archive samples for supplementary radio nuclides		Plastic	5,000	No	50 mL HNO_3	–	Storage in freeze container

* Suprapur acid is used for conservation of samples.

** Minimum number. The number of archive samples can vary depending on the number of similar samples collected at the same occasion.

*** The sample is transported in frozen condition to the laboratory. It is possible that the silicate concentration can change due to polymerisation for this reason.

**** Full name and address is given in Table A1-5.

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
TIMS	Thermal Ionization Mass Spectrometer
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
GC	Gas Chromatography

Table A8-2. Reporting limits and measurement uncertainties.

Component	Method	Reporting limits or range	Unit	Measurement uncertainty [2]	"Total" uncertainty [3]
HCO_3	Alkalinity titration	1	mg/L	4%	< 10%
Cl^- Cl^-	Mohr- titration IC	> 70 1–100	mg/L	5% 6%	< 10% 10%
SO_4	IC	1	mg/L	10%	15%
Br^- Br^-	IC ICP	0.2 0.001	mg/L	9% 15%	20%
F^- F^-	IC Potentiometric	0.1 –	mg/L	10% –	20%
I^-	ICP	0.001	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	21%	15%
Si(tot)	ICP	0.03	mg/L	4%	15%
Sr	ICP	0.002	mg/L	4%	15%
Li	ICP	0.2[1] 2	mg/L	10%	20%
Fe	ICP	0.4[1] 4	mg/L	6%	10%
Mn	ICP	0.03[1] 0.1	µg/L	8%	10%
Fe(II), Fe(tot)	Spectrophotometry	0.02 (DL = 0.005 mg/L)	mg/L	15% (> 30 µg/L)	20%
HS^-	Spectrophotometry	SKB 0.03 (DL = 0.02)	mg/L	10%	30%
NO_2 as N	Spectrophotometry	0.1	µg/L	2%	20%
NO_3 as N	Spectrophotometry	0.2	µg/L	5%	20%
NO_2+NO_3 as N	Spectrophotometry	0.2	µg/L	0.2 (0.2–20 µg/L) 2% (> 20 µg/L)	20%
NH_4 as N	Spectrophotometry	0.8 50 (SKB)	µg/L	0.8 (0.8–20 µg/L) 5% (> 20 µg/L) 20%	20%
PO_4 as P	Spectrophotometry	0.7	µg/L	0.7 (0.7–20 µg/L) 3% (> 20 µg/L)	20%
SiO_4	Spectrophotometry	1	µg/L	3% (> 200 µg/L)	–
O_2	Jodometrisc titration	0.2–20	mg/L	5%	–
Chlorophyll a, c pheopigment[4]	See Table A1-2	0.5	µg/L	5%	–
PON[4]	See Table A1-2	0.5	µg/L	5%	–
POP[4]	See Table A1-2	0.1	µg/L	5%	–
POC[4]	See Table A1-2	1	µg/L	4%	–
Tot-N[4]	See Table A1-2	10	µg/L	4%	–
Tot-P[4]	See Table A1-2	0.5	µg/L	6%	–
Al, Zn	ICP	0.2	µg/L	12%	20%[5]
Ba, Cr, Mo, Pb	ICP	0.01	µg/L	7–10%	20%[5]
Cd, Hg	ICP	0.002	µg/L	9 resp 5%	20%[5]
Co, V	ICP	0.005	µg/L	8 resp 5%	20%[5]
Cu	ICP	0.1	µg/L	8%	20%[5]
Ni	ICP	0.05	µg/L	8%	20%[5]
P	ICP	1	µg/L	6%	10%

As	1CP	0.01		µg/L	20%	Correct order of size(low conc)
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb	ICP	0.0051	0.05	µg/L	10%	Correct order of size (low conc)
Sc, In, Th	ICP	0.05^{1}	0.5	µg/L	10%	Correct order of size (low conc)
Rb, Zr, Sb, Cs, Tl	ICP	0.025^{1}	0.25	µg/L	10%	Correct order of size (low conc)
Y, Hf	ICP	0.005^{1}	0.05	µg/L	10%	Correct order of size (low conc)
U	ICP	0.001^{1}	–	µg/L	12%	Correct order of size (low conc)
DOC	See Table A1-1	0.5		mg/L	8%	30%
TOC	See Table A1-1	0.1		mg/L	10%	30%
$\delta^{2}H$	MS	2		‰ SMOW[5]	1‰	–
$\delta^{18}O$	MS	0.1		‰ SMOW[5]	0.2‰	–
^{3}H	LSC	0.8 eller 0.1		TU[6]	0.8 eller 0.1	–
^{37}Cl	ICP MS	0.2‰◦ (20 mg/L)		‰ SMOC[7]	–	–
$\delta^{13}C$	A (MS)	–		‰ PDB[8]	–	–
^{14}C pmc	A (MS)	–		PMC[9]	–	–
$\delta^{34}S$	ICP MS	0.2‰		‰ CDT[10]	0.3‰	–
$^{87}Sr/^{86}Sr$	TIMS	–		No unit (ratio)[11]	–	–
$^{10}B/^{11}B$	ICP MS	–		No unit (ratio)[11]	–	–
^{234}U, ^{235}U, ^{238}U, ^{232}Th, ^{230}Th	Alfa spectr.	0.0005		Bq/L[13]	5%	–
^{222}Rn, ^{226}Rn	LSC	0.03		Bq/L	5%	–

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1. Reporting limits at salinity ≤ 0.4% (520 mS/m) and ≤ 3.5% (3,810 mS/m) respectively.
2. Measurement uncertainty reported by consulted laboratory, generally 95% confidence interval.
3. Estimated total uncertainty by experience (includes effects of sampling and sample handling).
4. Determined only in surface waters and near surface groundwater.
5. Per mille deviation[13] from SMOW (Standard Mean Oceanic Water).
6. TU=Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10^{-18} (1 Bq/L Tritium = 8.45 TU).
7. Per mille deviation[13] from SMOC (Standard Mean Oceanic Chloride).
8. Per mille deviation[13] from PDB (the standard PeeDee Belemnite).
9. 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.
10. Per mille deviation[13] from CDT (the standard Canyon Diablo Troilite).
11. Isotope ratio without unit.
12. The following expressions are applicable to convert activity to concentration, for uranium-238 and thorium-232:
    1 ppm U = 12.4 Bq/kg^{238}U
    1 ppm Th = 3.93 Bq/kg^{232}Th
13. Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:
    $\delta^{y}I = 1{,}000\times(K_{sample}-K_{standard})/K_{standard}$, where K= the isotope ratio and ^{y}I = ^{2}H, ^{18}O, ^{37}Cl, ^{13}C or ^{34}S etc.

Appendix 9

Compilation of water analysis data

Table A9-1. Water composition. Compilation Sept 2005.

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^{2-} mg/L	SO_4-S mg/L	Br mg/l	F^- mg/L	Si mg/L	Fe mg/L	Fe-tot mg/L	FeII mg/L	Mn mg/L
KFM06A	266.00	271.00	8860	2005-04-21	–1.3	1,960	27.3	996	215	101	5,190	436	145.0	38.0	1.27	6.52	1.85	–	–	2.20
KFM06A	353.50	360.62	8802	2005-02-15	–0.5	1,560	19.3	1,200	113	67.5	4,710	228	75.5	–	1.22	5.87	0.896	1.17	1.12	0.905
KFM06A	353.50	360.62	8803	2005-02-17	0.8	1,530	16.4	1,260	91.4	58.2	4,620	188	64.4	28.0	1.24	5.72	1.21	1.59	1.54	0.748
KFM06A	353.50	360.62	8804	2005-02-22	0.8	1,490	13.7	1,290	77.1	49.8	4,580	158	52.3	–	1.26	5.47	1.10	1.41	1.39	0.616
KFM06A	353.50	360.62	8806	2005-02-24	–0.1	1,440	13.3	1,290	73.2	47.8	4,600	155	50.2	29.5	1.22	5.41	0.920	1.19	1.17	0.589
KFM06A	353.50	360.62	8807	2005-02-28	0.1	1,460	12.8	1,290	67	45.6	4,570	148	56.7	–	1.25	5.38	0.733	0.967	0.932	0.560
KFM06A	353.50	360.62	8808	2005-03-03	0.7	1,450	13.1	1,310	72.3	46.8	4,570	155	49.8	29.9	1.23	5.43	0.889	1.15	1.12	0.581
KFM06A	353.50	360.62	8809	2005-03-07	0.6	1,450	13	1,300	71.2	45.7	4,560	151	50.8	29.5	1.25	5.47	0.900	1.12	1.11	0.578
KFM06A	353.50	360.62	8838	2005-03-11	–2.6	1,470	13.4	1,280	74.1	47.7	4,850	157	52.5	–	1.26	5.50	1.15	–	–	0.621
KFM06A	768.00	775.12	8746	2004-12-14	–1.8	1,620	10.0	2,260	21.7	28.6	6,730	72.5	24.6	–	–	4.19	1.66	2.11	2.12	0.271
KFM06A	768.00	775.12	8747	2004-12-29	0.9	1,790	8.79	2,370	16.2	11.2	6,830	66.7	21.5	59.0	–	4.23	1.26	1.51	1.46	0.215
KFM06A	768.00	775.12	8748	2005-01-11	0.8	1,810	6.29	2,480	8.1	6.91	7,040	45.5	15.1	–	–	4.01	0.298	0.345	0.325	0.124
KFM06A	768.00	775.12	8749	2005-01-13	0.1	1,800	7.55	2,430	7.2	6.76	7,050	44.5	14.8	59.0	–	4.08	0.406	0.425	0.416	0.116
KFM06A	768.00	775.12	8781	2005-01-18	0.7	1,780	6.21	2,480	5.6	6.50	7,000	42.2	13.0	–	–	3.95	0.241	0.268	0.253	0.0952
KFM06A	768.00	775.12	8782	2005-01-20	–0.0	1,800	6.97	2,480	5.4	5.97	7,150	42.7	12.9	58.0	–	4.02	0.197	0.211	0.188	0.0927
KFM06A	768.00	775.12	8783	2005-01-25	1.0	1,790	6.20	2,460	4.4	5.78	6,940	37.4	11.5	–	–	3.95	0.110	0.127	0.111	0.0802
KFM06A	768.00	775.12	8784	2005-01-28	1.3	1,690	6.46	2,500	4.1	5.96	6,840	35.1	12.0	52.4	–	3.94	0.158	0.077	0.052	0.0859
KFM06A	768.00	775.12	8785	2005-01-31	–0.5	1,690	6.75	2,500	3.9	5.72	7,080	35.5	11.7	54.0	1.47	3.90	0.0376	0.077	0.051	0.0816

Cont Table A9-1. Water composition.

Idcode	Secup	Seclow	Sample	Sr	I$^-$	pH	DOC	HS$^-$	Drill_water	ElCond	NH$_4$N
	m	m	no	mg/L	mg/L		mg/L	mg/L	%	mS/m	mg/L
KFM06A	266.00	271.00	8860	11	0.250	7.17	–	–	1.6	1,520	–
KFM06A	353.50	360.62	8802	12.9	–	7.22	2.4	0.004	6.7	1,400	1.02
KFM06A	353.50	360.62	8803	13.8	0.101	7.34	1.3	< 0.002	7.5	1,370	0.730
KFM06A	353.50	360.62	8804	14.5	–	7.34	1	< 0.002	8.0	1,360	0.556
KFM06A	353.50	360.62	8806	14.7	0.104	7.38	1.1	< 0.002	7.8	1,360	0.653
KFM06A	353.50	360.62	8807	14.8	–	7.37	1	0.002	7.9	1,340	0.619
KFM06A	353.50	360.62	8808	14.0	0.103	7.37	1.1	0.003	8.0	1,360	0.622
KFM06A	353.50	360.62	8809	14.9	0.105	7.33	< 1	< 0.002	7.7	1,350	0.609
KFM06A	353.50	360.62	8838	14.9	–	7.41	–	–	7.1	1,360	–
KFM06A	768.00	775.12	8746	23.6	–	7.53	1.6	0.006	10.8	1,870	0.303
KFM06A	768.00	775.12	8747	25.8	0.224	7.54	1.7	0.009	7.9	1,920	0.201
KFM06A	768.00	775.12	8748	26.8	–	7.74	1.5	0.033	4.2	1,960	0.102
KFM06A	768.00	775.12	8749	27.1	0.239	7.76	1.6	0.019	3.4	1,970	0.0977
KFM06A	768.00	775.12	8781	26.7	–	8.04	1.4	0.013	2.9	1,970	0.0698
KFM06A	768.00	775.12	8782	27.2	0.240	8.15	1.6	0.022	2.9	1,970	0.0706
KFM06A	768.00	775.12	8783	27.0	–	8.11	1.5	0.010	2.4	1,980	0.0479
KFM06A	768.00	775.12	8784	26.7	0.237	8.21	1.3	0.015	1.9	1,980	0.0659
KFM06A	768.00	775.12	8785	26.7	0.232	8.26	1.6	0.022	1.6	1,990	0.0642

– = Not analysed
A = results will be reported later
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< ”value” = below detection limit

Table A9-2. Isotopes I (H-, O-, B-, S-, Cl- and C-isotopes). Compilation Sept 2005.

Idcode	Secup m	Seclow m	Sample no	Sampling date	δ^{2}H ‰ SMOW	^{3}H TU	δ^{18}O ‰ SMOW	^{10}B/^{11}B no unit	δ^{34}S ‰ CDT	δ^{13}C ‰ PDB	^{87}Sr/^{86}Sr no unit	^{14}C pmC	δ^{37}Cl ‰ SMOC
KFM06A	266.00	271.00	8860	2005-04-21	–70.7	–0.8	–9.4	0.2379	25.7	A	0.71793	A	0.27
KFM06A	353.50	360.62	8802	2005-02-15	–82.3	< 0.8	–11.0	0.2397	–	–	–	–	–
KFM06A	353.50	360.62	8803	2005-02-17	–86.3	< 0.8	–11.3	0.2406	27.6	–	0.71734	–	0.08
KFM06A	353.50	360.62	8804	2005-02-22	–83.5	< 0.8	–11.6	0.2396	–	–	–	–	–
KFM06A	353.50	360.62	8806	2005-02-24	–89.1	< 0.8	–11.8	0.2408	27.3	–	0.71727	–	0.13
KFM06A	353.50	360.62	8807	2005-02-28	–85.5	< 0.8	–11.5	0.2394	–	–	–	–	–
KFM06A	353.50	360.62	8808	2005-03-03	–85.6	< 0.8	–11.6	0.2408	27.0	–	0.71728	–	0.30
KFM06A	353.50	360.62	8809	2005-03-07	–86.0	< 0.8	–11.8	–	27.5	A	0.71727	A	0.07
KFM06A	353.50	360.62	8838	2005-03-11	–	–	–	–	–	–	–	–	–
KFM06A	768.00	775.12	8746	2004-12-14	–80.5	2.4	–11.2	0.2339	–	–	–	–	–
KFM06A	768.00	775.12	8747	2004-12-29	–78.4	< 0.8	–11.6	0.2389	27.9	–	0.71719	–	0.05
KFM06A	768.00	775.12	8748	2005-01-11	–79.0	< 0.8	–11.7	–	–	–	–	–	–
KFM06A	768.00	775.12	8749	2005-01-13	–81.3	< 0.8	–11.8	0.2400	35.1	–	0.71717	–	–0.01
KFM06A	768.00	775.12	8781	2005-01-18	–81.5	< 0.8	–11.8	–	–	–	–	–	–
KFM06A	768.00	775.12	8782	2005-01-20	–79.4	< 0.8	–11.8	0.2407	34.4	–	0.71718	–	0.05
KFM06A	768.00	775.12	8783	2005-01-25	–78.3	< 0.8	–12.0	–	–	–	–	–	–
KFM06A	768.00	775.12	8784	2005-01-28	–79.9	< 0.8	–11.4	0.2338	35.6	–	0.71718	–	0.31
KFM06A	768.00	775.12	8785	2005-01-31	–81.7	< 0.8	–11.5	0.2334	38.4	A	0.71719	A	0.23

– = Not analysed
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Table A9-3 Trace elements. Compilation Sept 2005.

Idcode	Secup m	Seclow m	Sample no	Sampling date	Al µg/L	U µg/L	Th µg/L	Sc µg/L	Rb µg/L	Y µg/L	Zr µg/L	In µg/L	Sb µg/L	Cs µg/L	La µg/L	Hf µg/L	Tl µg/L	Ce µg/L
KFM06A	353.50	360.62	8803	2005-02-17	–	11.0	< 0.4	< 0.8	43.7	0.181	< 0.2	–	0.761	1.0	< 0.04	< 0.04	< 0.2	< 0.04
KFM06A	353.50	360.62	8806	2005-02-24	–	9.15	< 0.4	< 0.8	31.5	0.188	< 0.2	–	1.03	0.725	< 0.04	< 0.04	< 0.2	< 0.04
KFM06A	353.50	360.62	8808	2005-03-03	–	9.22	< 0.4	< 0.8	31.4	0.15	< 0.2	–	1.07	0.758	< 0.04	< 0.04	< 0.2	< 0.04
KFM06A	353.50	360.62	8809	2005-03-07	4.29	9.57	< 0.4	< 0.8	34.5	0.172	< 0.2	–	1.16	0.781	< 0.04	< 0.04	< 0.2	< 0.04
KFM06A	768.00	775.12	8747	2004-12-29	–	2.85	< 0.2	< 0.5	22.6	0.219	< 0.3	< 0.5	0.393	0.48	< 0.05	0.432	< 0.3	< 0.05
KFM06A	768.00	775.12	8749	2005-01-13	–	0.927	< 0.2	< 0.5	18.1	0.178	< 0.3	< 0.5	0.219	0.43	< 0.05	0.279	< 0.3	< 0.05
KFM06A	768.00	775.12	8782	2005-01-20	–	0.656	< 0.2	< 0.5	17.4	0.19	< 0.3	< 0.5	0.198	0.389	< 0.05	0.224	< 0.3	< 0.05
KFM06A	768.00	775.12	8784	2005-01-28	–	0.506	< 0.4	< 0.8	16.5	0.223	< 0.2	< 0.4	0.205	0.48	0.042	< 0.04	< 0.2	< 0.04
KFM06A	768.00	775.12	8785	2005-01-31	5.02	0.484	< 0.4	< 0.8	15.5	0.218	< 0.2	< 0.4	<0.2	0.469	< 0.04	< 0.04	< 0.2	< 0.04

Cont Table A9-3 Trace elements.

Idcode	Secup m	Seclow m	Sample no	Nd µg/L	Sm µg/L	Eu µg/L	Gd µg/L	Tb µg/L	Dy µg/L	Ho µg/L	Er µg/L	Tm µg/L	Yb µg/L	Lu µg/L
KFM06A	353.50	360.62	8803	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
KFM06A	353.50	360.62	8806	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
KFM06A	353.50	360.62	8808	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
KFM06A	353.50	360.62	8809	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
KFM06A	768.00	775.12	8747	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KFM06A	768.00	775.12	8749	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KFM06A	768.00	775.12	8782	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.1	< 0.05
KFM06A	768.00	775.12	8784	< 0.04	< 0.04	0.13	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
KFM06A	768.00	775.12	8785	< 0.04	< 0.04	0.122	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04

– = Not analysed
A = Results will be reported later
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xx = No result due to analytical problems
< ”value” = below reporting limit

Table A9-4. Isotopes II (U-, Th, Ra- and Rn-isotopes). Compilation Sept 2005.

Idcode	Secup m	Seclow m	Sample no	Sampling date	^{238}U mBq/L	^{235}U mBq/L	^{234}U mBq/L	^{232}Th mBq/L	^{230}Th mBq/L	^{226}Ra Bq/L	^{222}Rn Bq/L
KFM06A	353.50	360.62	8809	2005-03-07	116	< 50	295	< 50	4.4	3.1	146
KFM06A	768.00	775.12	8785	2005-01-31	10	–	18	–	< 0.4	–	–

– = Not analysed
A = Results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< ”value” = below reporting limit

Table A9-5. Dissolved gases. Compilation Sept 2005.

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	C_2H_6 µL/L	C_2H_4 µL/L	C_2H_2 µL/L	C_3H_8 µL/L	C_3H_6 µL/L	DISS_GAS mL/L H_2O
KFM06A	353.50	360.62	8838	2005-03-14	1.3	6.3	84	0.43	0.027	0.48	310	0.31	0.28	0.14	0.12	0.12	95
KFM06A	353.50	360.62	8838	2005-03-14	1.3	6.2	85	0.67	0.024	0.35	430	0.17	0.14	< 0.05	< 0.1	< 0.1	96
KFM06A	768.00	775.12	8785	2005-02-01	1.0	28	77	< 0.004	0.09	0.17	< 3.2	0.88	0.38	0.37	0.39	0.2	106

– = Not analysed
A = Results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< ”value” = result below detection limit

Colloid Detection in Natural Ground Water from Forsmark by Laser-Induced Breakdown Detection

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Introduction

Colloid analysis has been performed in ground water samples collected during the site investigation program at Forsmark, Sweden. Two samples of the same ground water have been collected in a stainless steel cylinder avoiding water contact with the atmosphere. They were sent to INE for laboratory analysis. Colloid analysis was subsequently performed by the laser-induced breakdown detection (LIBD) in the laboratory using a closed flow-through detection cell again without atmosphere contact. Furthermore, a thorough chemical analysis of the water samples was performed.

It is supposed that the geological situation is similar to that found at various places in the Äspö tunnel. The aim of this study is to investigate the natural amount of background colloids in this specific borehole and to compare the data with those obtained in the Äspö underground laboratory.

Experimental

LIBD instrumentation

The principle of LIBD is based on the generation of a dielectric breakdown in the focus region of a pulsed laser beam. As the threshold energy (irradiance) to induce a breakdown is lower for solids than for liquids or gas, the breakdown can be generated selectively in particles dispersed in solution at a suitable pulse energy.

A schematic diagram of the mobile LIBD set-up used in the present work is shown Fig. 1. A pulsed laser beam with a frequency of 15 Hz at 532 nm wavelength from a small Nd:YAG-laser (Continuum Minilite I) is focused (15 mm focal length) into the center of a flow-through detection cell, after passing through a variable attenuator and a beam splitter. The plasma generated at a breakdown event is monitored by a microscope equipped with a CCD monochrome camera triggered by the incident laser pulse and recorded by a PC controlled image processing system. A breakdown shock wave propagated in the sample solution is detected simultaneously by an acoustic sensor (piezoelectric transducer) that is connected to the surface of the cell. Both, the energy and the acoustic signal are recorded by an analog-digital converter interface in a PC. Colloid concentrations are derived from the respective breakdown probability, represented by the number of breakdown events per number of laser shots, and the range of breakdown events within the laser beam axis determined by optical inspection of the laser focus area within the flow through cell. Colloid number concentrations (Pt/L) are given relative to a calibration with polystyrene reference colloids. Mass concentrations are calculated by assuming an average colloid density of 2.7 g/ml and spherical particle shape. A more detailed description of data evaluation is given in [1].

The mobile instrumentation of LIBD is combined with a Millipore ultra-pure water processing unit for on-line cleaning the flow-through detection cell of LIBD and to allow for the frequent control of the instrument background. The whole system, which is set up to a compact mobile unit can be transported by a van for field experiments.

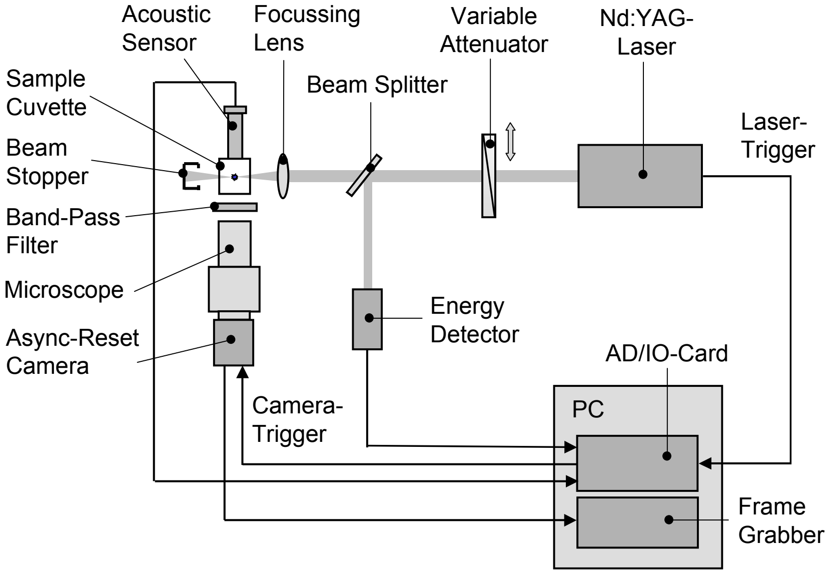


Fig. 1: Schematic diagram of the mobile laser-induced breakdown detection system

High-pressure flow-through detection cell

The LIBD has been operated in the CRR migration experiments (Grimsel Test-Site, Switzerland)[1] under low pressure conditions with commercially available quartz detection cells (fluorescence cells) for batch (laboratory experiments) or flow-through sampling. These cells have a sample volume of 3 ml at 10 mm absorption length. A new flow-through detection cell has been developed constraining water pressures of about 35 bar for in situ investigations in the Äspö Hard Rock Laboratory access tunnel (Sweden) [2], and in the Kraftwerke Oberhasli (KWO) access tunnel close to the Grimsel Test Site [3]. This detection cell has also been applied in connection with a borehole sampling system for the detection of ground water colloids sampled at a natural analogue site (Ruprechtov, Czech Republic).

Fig. 2 presents the high-pressure detection cell developed by INE. Without changing the optical path of the laser light, the detection cell fits into the same mount used for the silica cell. The new cell, fabricated from PEEK (polyether etherketone) is lined outside with a stainless steel housing (black parts in Fig. 2). Four optical windows, one at each side are applied for the passing laser light (absorption length 12 mm), the microscope and for inspection. They consist of sapphire with 2 mm thickness. The ground water flow enters the inner cell volume of 0.8 ml from the base via a PEEK tubing. The outlet is on the top of the cell. The high-pressure detection cell is successfully tested for a water pressure up to 60 bar.

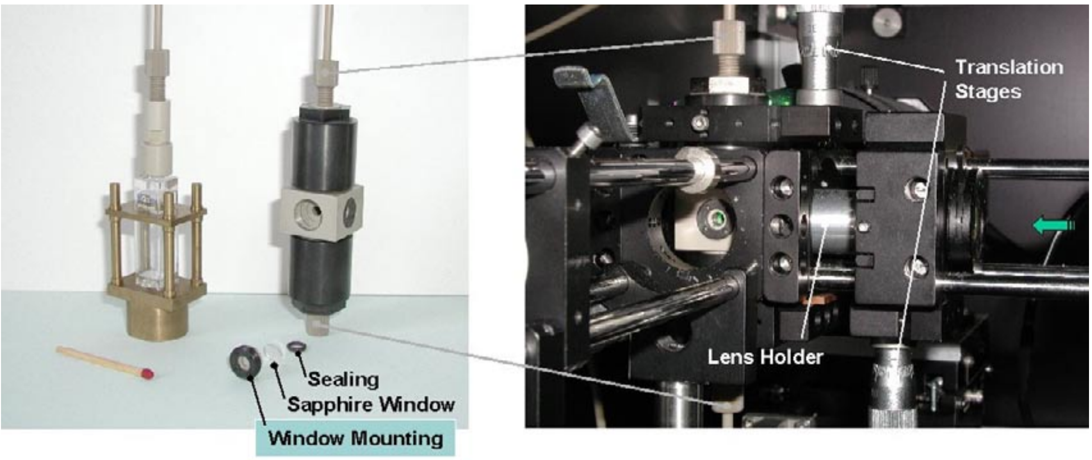


Fig. 2: LIBD high-pressure flow-through detection cell
(left: conventional flow-through silica detection cell)

Borehole sampling

Forsmark borehole KFM06A was sampled by SKB at March 7, 2005. Two samples were taken from a borehole section between 353.50 – 360.62 m. The vertical depth was approximately 307 m (inclination 60 degrees) with a measured pressure in the borehole section of 30.77 bar.

The stainless steel cylinders (Fig. 3) are ground water sampling cylinders from SKB with a sample volume of about 190 ml each. They are supplied with an internal piston and 3 valves. Further information concerning the sampling procedure is given elsewere.

At March 9 the cooled samples arrived at the INE where they have been stored in a fridge (Temp. about 10 deg. C) until colloid detection at April 6, 2005.

Fig. 3: SKB stainless steel sampling cylinder
(left: piston side, right: mounting adapter side)

Configuration of laboratory experiments

Each sampling cylinder is connected with the LIBD detection cell and the detection cells for pH-, Eh-, electrical conductivity-, oxygen content-detection and for taking samples for chemical ground water analysis. A scheme of the corresponding laboratory setup is plotted in Fig. 4 with an image of the experimental configuration in Fig. 5.

At first the tubings around the sampling cylinder are intensively cleaned by evacuation and flushing with Argon. Then a HPLC-pump is used to fill all tubings with ultra-pure water. Now one of the top valves of the sampling cylinder can be opened without contact of the sampled ground water with atmosphere oxygen. With Argon gas the ground water is pressed out from the sampling cylinder through the LIBD detection cell via a degasser to avoid occasionally occurring gas bubbles which interfere the colloid detection. Behind the LIBD system additional detection cells with pressure resistant electrodes (p < 15 bar) for pH, Eh, a sensor for electrical conductivity and a sensor for the pressure detection are arranged downstream. The Eh is detected with an electrode from Hamilton (Oxytrode). Before the sampling outlet a pressure regulator (PR), set to 8 bar, is installed. This overpressure in the whole system avoids further contact to oxygen. Data of this geo-monitoring system are stored on a personal computer with a data logger as a function of time. This allows to separate temporary fluctuating data, especially during the starting period when the detection cell and the geo-monitoring system are contaminated and does not contain the sampled ground water, respectively.

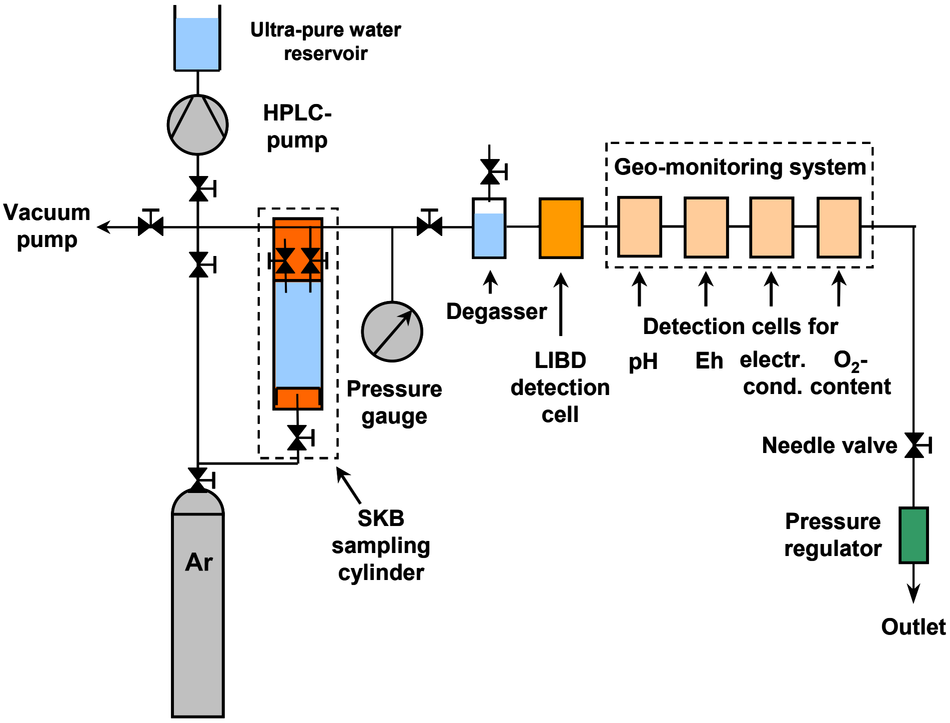


Fig. 4: Scheme of the laboratory setup for in-line LIBD colloid analysis and ground water monitoring

Ground water batch samples are collected at the outlet of the pressure regulator for chemical analysis with ICP-AES, ICP-MS and for the detection of inorganic carbon (IC) and dissolved organic carbon (DOC).

Additionally, track-etched Polycarbonate filter samples (pore size 50 nm) have been taken for colloid analysis with REM/EDX.

Fig. 5: Experimental configuration

Results

Data from geo-monitoring as well as the chemical composition of the two ground ground water samples, taken from the same ground water are displayed in table 1.

The chemical composition of the ground water is characterized mainly by the high salinity with about 4500 mg/l chloride. A pH of 7.3 and the chemical composition come close to the composition of ground water KXTT3/3, KXTT4/4 from boreholes used in the TRUE-1 project [4] at Äspö. The detected DOC is absolutely not conformable with any data obtained for Äspö ground water. It is more than a factor of 10 higher than the DOC of adequate Äspö ground water. For us it is not clear if this is an artefact (e.g. contamination of the sample) or if it results from microbial activities, which were found on a 50 nm filter taken by filtering the ground water at the outlet of the detection system (Fig.6).

Table 1: Monitored data of pH, Eh, el. conductivity, oxygen content and chemical analysis of the ground water samples from Forsmark borehole KFM06A

		SKB 9506-5 PVB	**SKB 9506-6 PVB**
		FOR1a	FOR2a
pH		n.d.	7.33
Eh	mV	n.d.	94
el. cond.	mS/m	n.d.	1347
O_2 content	mg/l	n.d.	0.094
Na^+	mg/l	1518	1455
K^+	mg/l	13.6	12.4
Ca^{2+}	mg/l	1246	1275
Mg^{2+}	mg/l	80	70.7
Cl^-	mg/l	4643	4419
SO_4^{2-}	mg/l	145	127
Br^-	mg/l	33.4	34.4
F^-	mg/l	8.9	9
Si^{4+}	mg/l	4.4	4.3
Fe-ICP	mg/l	0.18	0.21
Mn^{2+}	mg/l	1.01	0.71
Li^+	mg/l	0.1	0.106
Sr^{2+}	mg/l	12.5	12.6
DOC	mg/l	54.9	78.0
IC (HCO_3^-)	mg/l	8.7 (44.2)	5.6 (28.5)

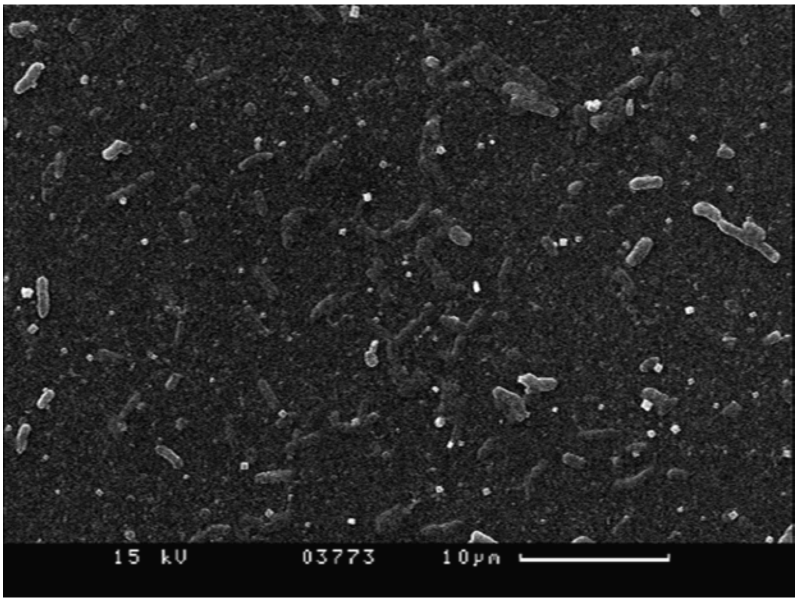


Fig. 6: SEM image with Forsmark ground water filter sample (50 nm Polycarbonate filter).

Data determined with the laser-induced breakdown detection system are listed in table 2. 190 ml sample was sufficient for two colloid measurements, one with 10000 and for a better statistic with 25000 laser pulses. The derived breakdown probability (Bd-events / Trigger-pulses) varied between 3.9 % and 5.4 %.

With these data together with the evaluation of image processing, average colloid diameters of 105 – 270 nm and mass concentrations of 1.1 - 6.8 µg/l in the samples are calculated for the same ground water. These concentrations are about 2 orders of magnitude higher than the LIBD detection limit. They are far below these colloid amounts in the range of mg/l, which are generated when an access of oxygen to the ground water may have occurred (fracture zone, Excavation Disturbed Zone).

It is remarkable that a higher colloid concentration always resulted from the 2nd measurement of each sampling cylinder. It may be explained by a settling down of a larger colloid fraction in the sampling cylinder and an additional washing out of this larger fraction with decreasing sample volume.

Table 2: LIBD data with average colloid diameter and colloid concentration of the analyzed Forsmark KFM06A ground water

		SKB 9506-5 PVB		**SKB 9506-6 PVB**	
		FOR1a	FOR1b	FOR2a	FOR2b
BD-events		426	976	485	1074
Trigger-pulses		10000	25000	11073	20000
BD-probability		0.0426	0.039	0.0438	0.0537
Colloid diam.	nm	117	217	105	270
Colloid mass conc.	µg/l	1.3	3.4	1.1	6.8

In the Äspö colloid project [5] a series of boreholes along the access tunnel have been sampled and their ground water was directly analyzed with the mobile LIBD system. A correlation was drawn (Fig. 7) between the colloid concentration and the Cl^- concentration of the ground water. At a Cl^- concentration of about 4000 mg/l a remarkable decrease of the colloid concentration over 4 orders of magnitude down to the LIBD detection limit of about 10 ng/l was observed.

The Forsmark sample data fit quite well into this correlation. But it is not clear, if at Forsmark during sampling additional small colloid quantities have been mobilized and washed out by erosion of borehole-/fracture filling material. SEM / EDX analysis from the filter samples of the ground water indicates iron containing colloids which might have been caused by contact with oxygen (Fig. 8) even though measured Eh-values were low. Real background colloid concentrations might then be even lower (Fig. 7).

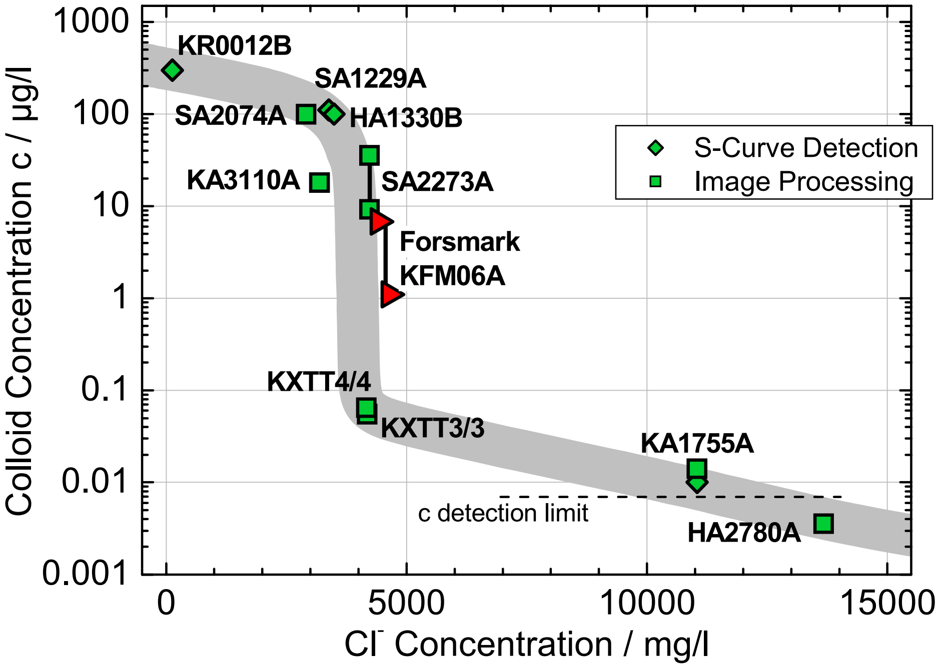
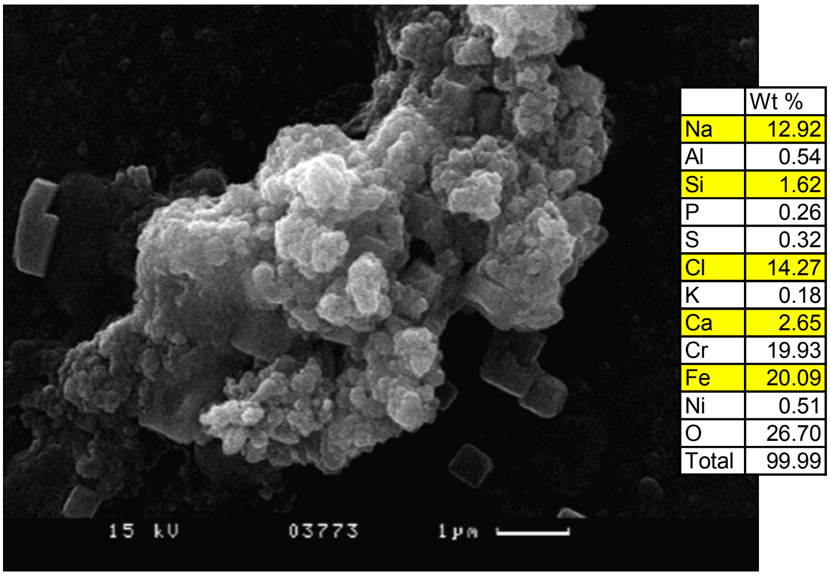


Fig. 7: Correlation between colloid concentration and chloride concentration in different ground water from Äspö [2, 5] (M,O) and in the Forsmark sample (χ).



	Wt %
Na	12.92
Al	0.54
Si	1.62
P	0.26
S	0.32
Cl	14.27
K	0.18
Ca	2.65
Cr	19.93
Fe	20.09
Ni	0.51
O	26.70
Total	99.99

Fig. 8: SEM / EDX colloid analysis from Forsmark ground water filter sample (50 nm Polycarbonate filter).

As a conclusion from such considerations, we can say that the colloid abundance in Forsmark ground water sample KFM06A is fairly consistent to that in Äspö ground water of the same salinity.

References

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