P-07-100

Forsmark site investigation

Hydrochemical characterisation in borehole KFM11A

Results from two investigated borehole sections at 447.5–454.6 m and 690.0–710.0 m

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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 during approximately three weeks per section at a flow rate of between 50 and 200 mL/min.

The method has been used in section 447.5–454.6 m borehole length (vertical depth 390 m) in borehole KFM11A. The results include on-line measurements of redox potential (Eh), pH, dissolved oxygen, electrical conductivity and water temperature, together with chemical analyses of major constituents, trace metals and isotopes as well as determinations of gas content and composition and microbe content and their physiological characteristics. Furthermore, the content of inorganic colloids in the groundwater was measured in situ by Laser Induced Breakdown Detection (LIBD) and colloids collected on filters were studied by the SEM technique.

In addition, a borehole section at 690.0–710.0 m (vertical depth 594 m) was investigated using the PSS equipment for pumping and sealing off the borehole section. Three water samples were collected from the section. The first two samples were analysed according to SKB class 3 and the last one followed the SKB class 5 protocol.

The water composition in section 447.5–454.6 m was stable during the second half of the pumping and sampling period. The chloride concentration amounted to 4,210 mg/L while the flushing water content was 5.9%. The Eh measurements worked satisfactory and the borehole electrodes stabilised at approximately –203 mV. The colloid content by LIBD gave approximately 100 µg/L while the estimated concentrations from the SEM images amounted to about 2 µg/L.

The three samples from section 690.0–710.0 m showed an increasing chloride concentration trend from 4,410 to 5,360 mg/L during five days of pumping, accompa-nied by a decrease in flushing water content from 5.2% to 3.3%. The increase in chloride can not be explained by depletion of flushing water and probably reflects an intrusion of old non-marine brackish groundwater, similar to that sampled in KFM01D.

Neither of the groundwaters from the two borehole sections revealed the dominating Littorina signature that was observed in some of the previously investigated boreholes in Forsmark. However, the lower section below the Singö zone displayed a moderate contribution of marine Littorina water in contrast to the upper section located close to or at the Singö zone. Here the contribution from Littorina is weak or missing.

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 en sektion av borrhålet KFM11A vid 447,5–454,6 m borrhålslängd (vertikalt djup 390 m). Resultaten omfattar mätningar on-line av redoxpotential, pH, löst syre, elektrisk konduktivitet och vattentemperatur i borrhålssektionen liksom kemiska analyser av huvudkomponenter, spårelement och isotoper liksom bestämningar av gasinnehåll och sammansättning samt antal mikroorganismer och deras fysiologi. Vidare undersöktes oorganiska kolloider i grundvattnet med hjälp av laserinducerad nedbrytning (LIBD), medan kolloider som insamlats genom filtrering studerades med SEM teknik.

Ytterligare en borrhålssektion undersöktes vid 690,0–710,0 m (vertikalt djup 594 m). Här användes PSS-utrustning för pumpningen och för att avgränsa borrhålssektionen. Tre vattenprov togs ut i sektionen. De första två proven analyserades enligt SKB klass 3 och det sista i ordningen följde SKB klass 5 protokollet.

Vattensammansättningen i sektionen 447,5–454,6 m var stabil under andra hälften av pump-/provtagningsperioden. Kloridkoncentrationen uppgick till 4 210 mg/l medan spolvattenhalten var 5,9 %. Redoxpotentialmätningarna fungerade tillfredsställande och borrhålselektrodererna stabiliserade sig på ca –203 mV. Kolloidkoncentrationen från Laser Induced Breakdown Detection (LIBD) mätte ca 100 µg/L medan den beräknade koncentrationen från SEM-analyser uppgick till ca 2 µg/L.

De tre proven från sektionen vid 690,0–710,0 m visade en ökande kloridtrend från 4 410 till 5 360 mg/L under fem dagars pumpning medan spolvattenhalten minskade från 5,2 % till 3,3 %. Ökningen i klorid kan inte enbart förklaras av bortpumpning av spolvatten utan reflekterar troligen inträngning av äldre icke-marint grundvatten, liknande det som observerades i KFM01D.

Inget av grundvattnen från de två borrhålssektionerna uppvisade den väldigt tydliga Littorina signatur som observerats i några av de tidigare undersökta borrhålen i Forsmark. Däremot avslöjade den djupare sektionen under Singözonen ändå ett bidrag av vatten från Littorinahavet i motsats till den övre sektionen vid/i Singö zonen där Littorina bidraget är obetydligt eller saknas.

Contents

1 Introduction

This document reports performance and results of the activity Complete Chemical Characterisation in borehole KFM11A within the site investigation programme at Forsmark /1/. The work was conducted according to the activity plan AP PF 400-07-004 (Kemikarakterisering i KFM11A). The activity plan includes Supplement 1 (Kemikarakterisering i KFM11A; kolloidfiltrering för SEM-analys) and Supplement 2 (Kemikarakterisering i KFM11A; uttag av vattenprov under pumpning med PSS-utrustning). The report presents hydrogeochemical data from field work carried out during January to March 2007 and includes also sampling using the PSS equipment, performed in July 2007.

The controlling documents for the activity are listed in Table 1-1. The activity plan, the method description and the measurement system descriptions constitute SKB's internal controlling documents. Original data from the reported activity are stored in the primary database Sicada. Data are traceable by the activity plan number (AP PF 400-07-004) and only data in the databases are accepted for further interpretation and modelling. The data presented in this report are regarded as copies of the original data. Data in the database may be revised if needed. However, such revision of the database will not necessarily result in a revision of this report, although major revisions are the normal procedure for a P-report. Minor revisions are normally presented as supplements, available at www.skb.se. Sampling for microbe studies, based on the activity plan AP PF 400-05-66, was also performed within the present activity. The microbe investigations will be reported in a separate primary data report /2/.

The location of the telescopic borehole KFM11A at DS11 /3/ (inclined at 61° and dipping NE) is shown in Figure 1-1 together with nearby situated percussion-drilled boreholes, and its position within the investigation area is shown in the small inset. The borehole section between 0–71.06 m is percussion drilled and has a stainless steel casing with an internal diameter of 200 mm, whereas the 71.06–851.21 m interval is core drilled with a diameter of 77.3 mm. 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 equipment 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).

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

Activity plan	Number	Version
Fullständig kemikaraktärisering med mobilt fältlaboratorium i KFM11A.	AP PF 400-07-004, Suppl. 1 and 2	1.0
Method descriptions and documentations	**Number**	**Version**
Metodbeskrivning för fullständig kemikaraktärisering med mobilt fältlaboratorium.	SKB MD 430.017	2.0
Enkel provtagning i hammarborrhål och kärnborrhål.	SKB MD 423.002	2.0
Instruktion för rengöring av borrutrustning och viss markbaserad utrustning.	SKB MD 600.004	1.0
Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation.	SKB MD 434.004 SKB MD 434.005 SKB MD 434.006 SKB MD 434.007 SKB MD 433.018	1.0 1.0 1.0 1.0 1.0
Provtagning och analys-kemilaboratorium.	SKB MD 452.001–019	–

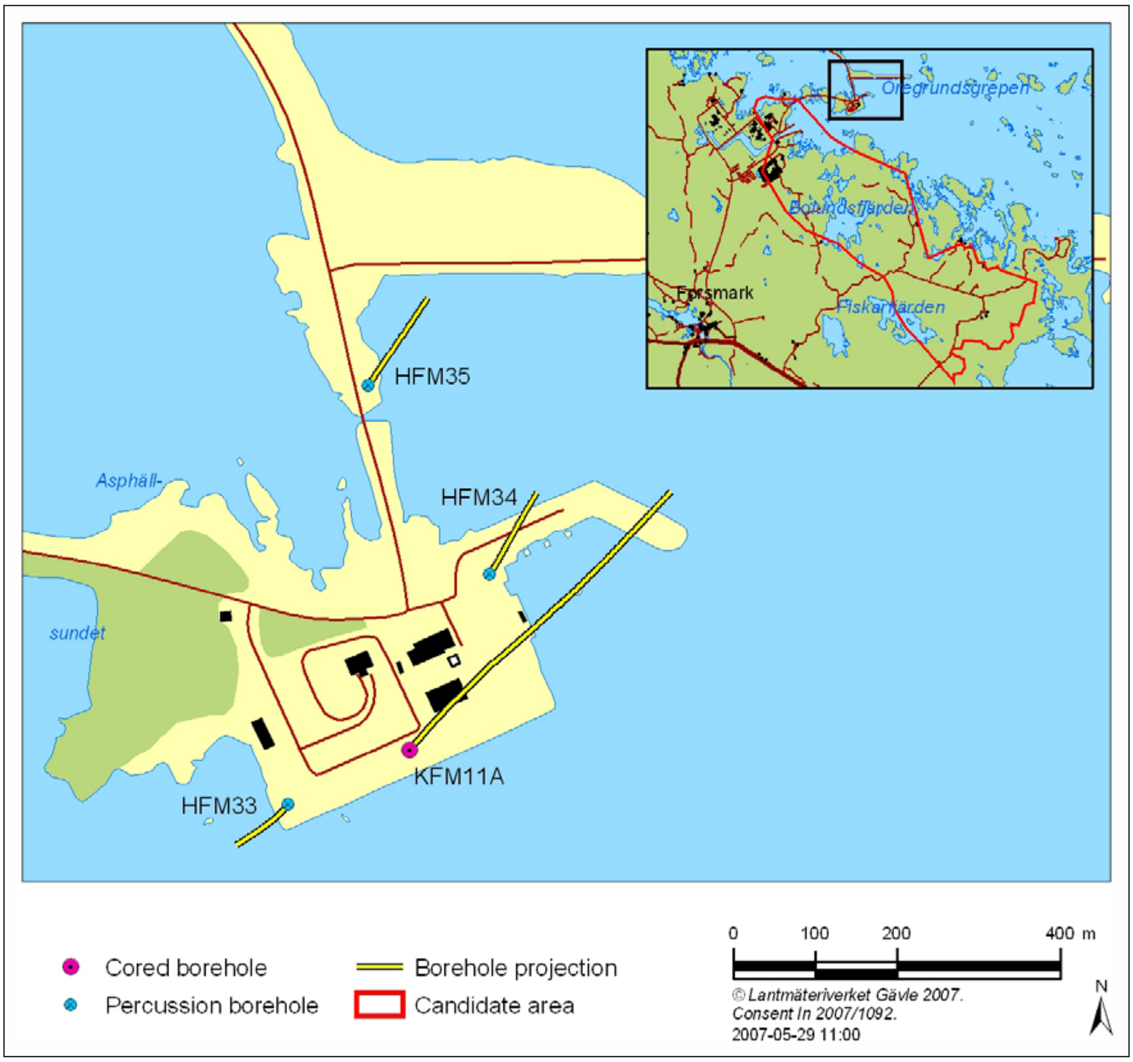

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Figure 1-1. *Locations and projections on the horizontal plane of the telescopic borehole KFM11A and nearby situated percussion boreholes, including the flushing water well HFM33, at drill site DS11. The inset in the upper right corner shows the location of DS11 within the investigation area at Forsmark.*

2 Objectives and scope

Complete chemical characterisation (CCC) is the most extensive chemical investigation method performed in core-drilled boreholes. The method is carried out in order to obtain as much information as possible about the chemical conditions in the groundwater from 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 groundwaters from other fracture systems.

It has been decided to prioritise the north-western part of the Forsmark candidate area for the continuing investigations /4/. Borehole KFM11A is situated north of this prioritised part, inclined below the Baltic Sea. However, the borehole intersects the Singö zone, a regional fracture zone between the mainland and Gräsö Island. The zone might constitute a discharge area and serve as a hydraulic boundary for the groundwater in the tectonic lens. Characterisation of the groundwaters at both sides of the zone may be of importance for both the hydrogeological and hydrogeochemical models. For this reason, hydrochemical investigations were performed in two sections, one above and the other below the zone.

The analytical programme in section 447.5–454.6 m borehole length was carried out according to SKB chemistry class 4 and class 5 including all options /1/. Furthermore, pH, redox potential (Eh) and water temperature were measured in flow-through cells downhole as well as at the ground 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 physiological characteristics as well as colloid content by two techniques, direct measurement by LIBD and colloid filtration followed by SEM (Scanning Electron Microscopy).

The investigation at 690.0–710.0 m borehole length was much less extensive and included only water sampling and analyses (totally three samples) according to SKB class 3 and SKB class 5 routines.

3 Background

3.1 Flushing water history

The percussion drilled borehole HFM33 /5/ served as a supply well for the flushing water used to drill borehole KFM11A and the chemical composition of the flushing water was checked three times before use and twice during the drilling of KFM11A /6/. The composition of the flushing water is typically Littorina in type and the salinity does not deviate very much from the groundwaters in sections 447.5–454.6 m and 690.0–710.0 m. The core drilling of the 851.21 m long borehole consumed 959 m^3 of flushing water and the volume of returned water pumped from the borehole by air-lift pumping during drilling was 2,712 m^3. After drilling, nitrogen flushing was carried out four times from the bottom of the borehole, resulting in discharge of an additional 10 m^3 of borehole water.

Automatic dosing equipment for injection of Uranine was installed in the water line that supplies flushing water to the drilling head. The Uranine concentration in the flushing water and returned water was checked regularly and a total of 121 samples of each sample type were analysed. The Uranine concentrations in the flushing water and in the returned water are presented in Figure 3-1. A water budget, presenting the amount of Uranine added to the borehole via the flushing water and the estimated amount recovered in the return water, is given in Table 3-1.

Table 3-1. Amount of Uranine added to KFM11A via the flushing water during core drilling and the amount recovered from the air-lift pumping.

Uranine	(g)
Added, according to the log book.	195
Added, calculated from the average Uranine concentration and the total volume of flushing water.	160
Recovered, estimated from the average Uranine concentration and the total volume of returned water.	244

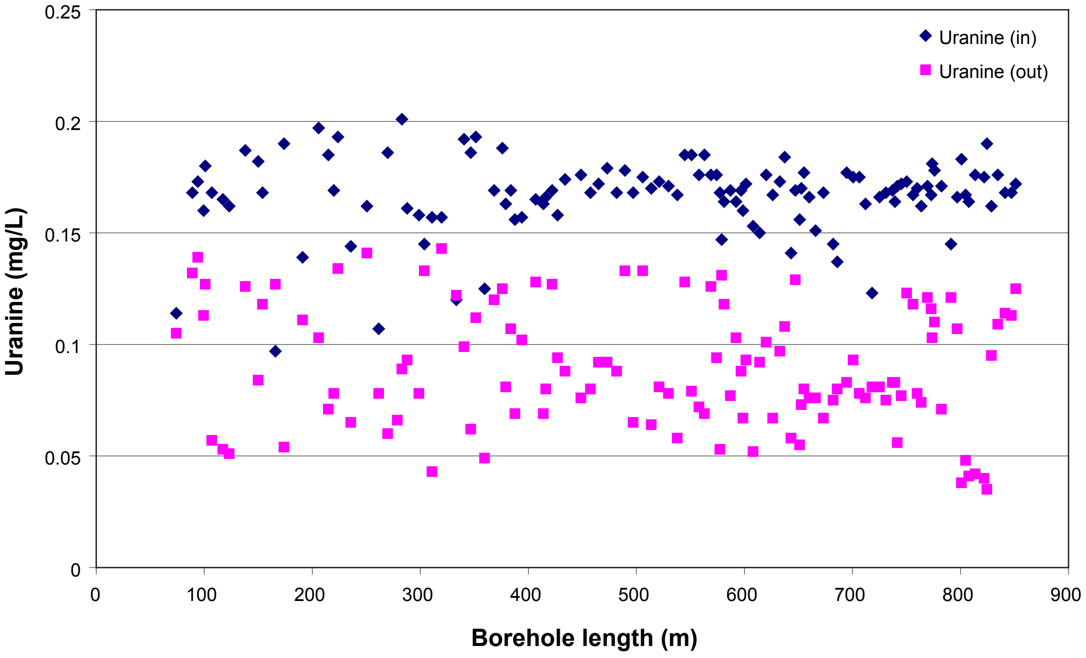


Figure 3-1. Uranine concentrations in the flushing water and in the recovered water versus borehole length.

The Uranine budget in Table 3-1 suggests that no flushing water was lost to borehole KFM11A and the adjacent host bedrock during drilling. This rarely happens and the subsequent chemical characterisation campaign, documented in this report, proved that flushing water remained in the borehole after drilling. It seems clear that the average values were not very representative in these two cases. Additional cleaning was carried out by nitrogen flushing after drilling. No Uranine analyses were performed on the water discharged during cleaning.

As borehole KFM11A 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.
- Dosing equipment for Uranine was installed, thereby removing the need for an in-line flushing water storage tank placed after the UV-system.
- In order to minimise oxygen contamination, pressurised nitrogen gas was flushed through the water storage tank placed before the UV-system in the flushing water line.

High contents of organic constituents or microbes in the flushing water may affect the microbiological conditions in the borehole. The TOC concentration in the flushing water varied between 1.3 and 2 mg/L and a concentration below 5 mg/L is considered acceptable. The microbe content in the flushing water was not determined during drilling of this borehole. Results from borehole KFM06A /7/ convincingly showed that the cleaning procedure works well and it was concluded that checking for microbes at all drilling occasions was no longer necessary.

3.2 Previous events and activities in the borehole

KFM11A is an SKB chemical-type core borehole and thus specially intended for complete hydrochemical characterisation. Only those borehole activities 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, for example, the in situ microbiological conditions. The activities/investigations performed in KFM11A prior to the chemistry campaign are listed in Table 3-2.

Table 3-2. Activities performed in KFM11A prior to and in connection with chemical characterisation and water sampling using PSS3.

Activities performed	Date of completion	Length or section (m)	Comment
Percussion drilling	2006-05-02	0–71.1	
Core drilling	2006-11-20	71.1–851.2	HFM33 was the source of flushing water for drilling the cored part of KFM11A. HFM33 is a SKB chemical-type borehole /3, 5/. Flushing water volume = 959 m^3. Return water volume = 2,712 m^3.
Flushing water treatment	–	–	Automatic dosing of Uranine was used during drilling of KFM11A. In this way there was no need for an in-line storage tank placed after the UV-system /3/.
Nitrogen flushing/lifting four times from the bottom of the borehole	2006-11-21	0–851.2	Exchanged volume 10 m^3
Geophysical logging	2006-11-23	71.0–848.8	/8/
BIPS-logging	2006-10-01 2006-11-24	70.0–250.0 72.0–847.0	/9/

Activities performed	Date of completion	Length or section (m)	Comment
Differential flow logging	2006-12-10	64.4–492.8	/10/
Core drilling, reaming and PLEX setting	2007-04-02	71.1–851.2	/3/
Complete chemical characterisation	2007-03-13	447.5–454.6	This report
Nitrogen lifting combined with pumping in the upper, wider part of the borehole	2007-04-04 to 2007-04-12	71.1–851.2	Exchanged volume 460 m^3
Injection tests	2007-06-12	470.0–840.0	/11/
Pumping test at 700 m borehole length	2007-07-10	690.0–710.0	/11/
Hydrochemical sampling using PSS3	2007-07-16	690.0–710.0	This report

3.3 Choice of borehole sections

Borehole KFM11A intersects the regional Singö deformation zone and the primary objective was to select two borehole sections for hydrochemical characterisation, one above and the other below the zone, respectively. Differential flow logging /10/ in the upper part of the borehole down to about 500 m revealed a number of shallow flow anomalies suitable for hydrochemical investigations and information from drilling of the borehole indicated the presence of a possible deep flow anomaly at about 700 m borehole length. Unfortunately, blocking by fall outs from the borehole wall at approximately 500 m borehole length prevented flow logging in the lower part of the borehole and this method was replaced by injection tests after restoration of the borehole. No injection tests were conducted in a 20 m interval close to 700 m borehole length in order not to obstruct the subsequent hydrochemical investigation. The hydraulic transmissivity in this interval was estimated from later pumping tests.

Figure 3-2 presents the hydraulic transmissivities along the borehole. Besides the water-yielding fracture at approximately 700 m borehole length and below the Singö zone, the water yielding fracture at 433 m borehole length was the first choice above the Singö zone. Due to high flushing water content, this section was replaced by one at around 450 m borehole length with several possible water yielding fractures and a lower total transmissivity. The water-yielding fracture at around 700 m borehole length and below the Singö zone was sampled using PSS equipment in connection with injection tests. This was because of time constraints and also to reduce the risk to get caught in the borehole. This risk is larger when using the umbilical hose compared to when using a pipe string.

The section investigated using the PSS equipment is indicated by the green arrow in Figure 3-2, and the two sections of interest for complete chemical characterisation are indicated by red arrows. Section limits, vertical depths and hydraulic transmissivity values are given in Table 3-3.

Table 3-3. Selected borehole sections for hydrochemical sampling and hydraulic transmissivity calculated from differential flow logging (T_D) and single hole hydraulic tests (T_R).

Section (m)	Elevation mid sect. (m.b.s.l.)	T_D (m^2/s) /10/	T_R (m^2/s) /11/	Comments
429.70–434.70	374	8.60E–7		T (5 m), hydrochemical characterisation planned but not performed (MFL)
449.71–454.71	391	4.40E–8		T (5 m), hydrochemical characterisation performed (MFL)
690–710	594		7.59E–7	(PSS)

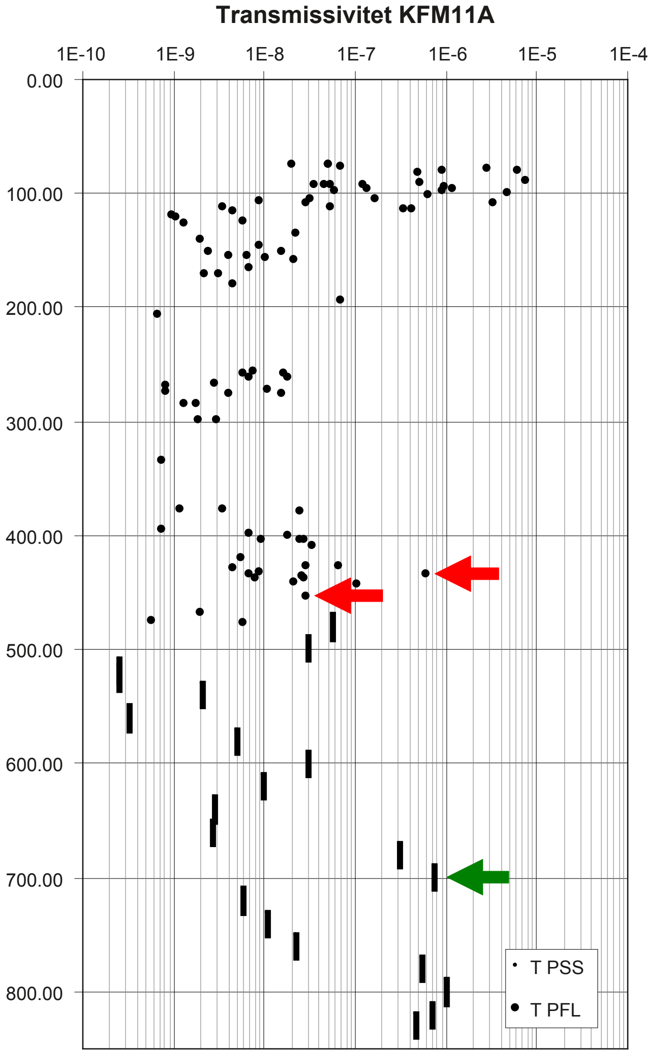


Figure 3-2. *Hydraulic transmissivity along borehole KFM11A. Selected fractures planned to be investigated are indicated with arrows or circles; red = hydrochemical characterisation, green = sampling using PSS equipment.*

The differential flow logs for relevant parts of the borehole are presented in Appendix 2 and the corresponding images from BIPS-logging (Borehole Image Processing System) are presented in Appendix 3.

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 separate computer unit (MYC), a hose unit with downhole equipment and a Chemmac measurement system. The equipment setup is presented in Figure 4-1. 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 mobila kemienheter – Allmän del, Slangvagn, Borrhålsutrustning, Mobil Yt-chemmac and Dataapplikation).

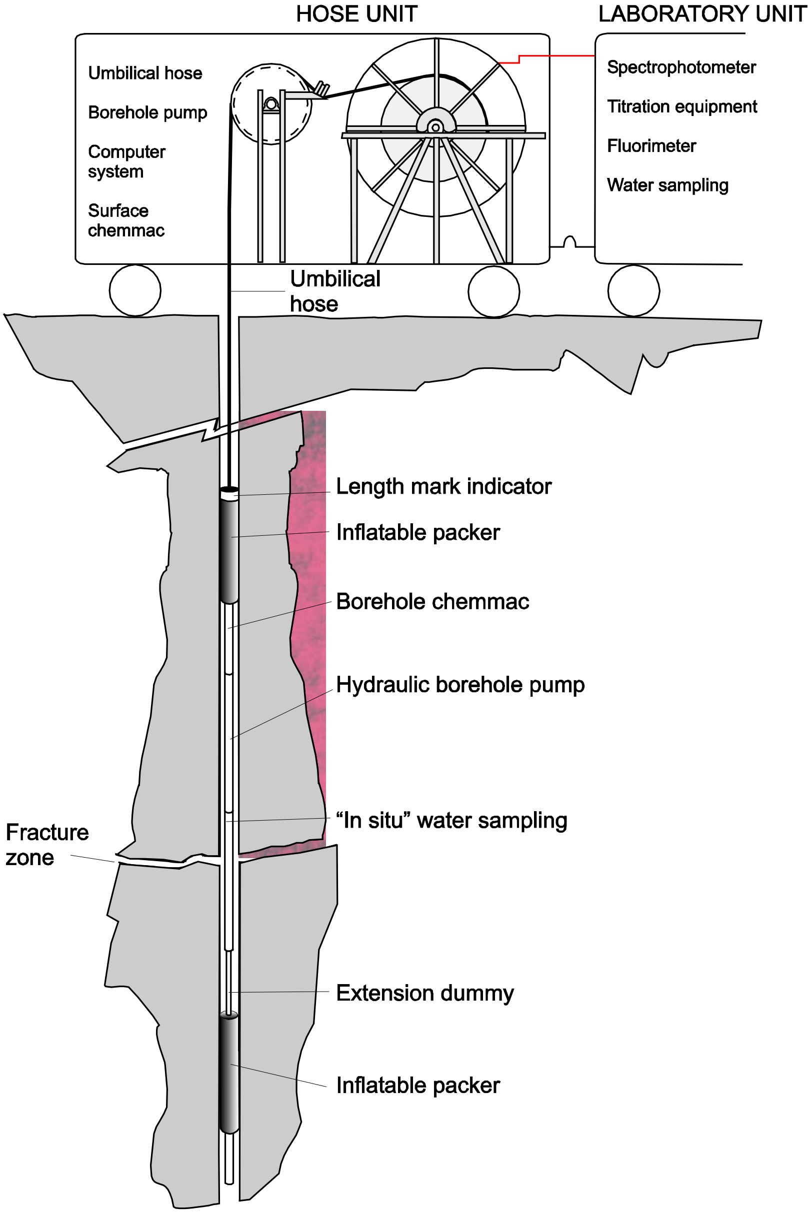


Figure 4-1. *The mobile laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.*

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 sample portions of groundwater collected with the PVP sampling unit maintain the pressure from the borehole section when raised to the surface. The portions are used for colloid and gas analysis and microbe investigations.

The mobile units used for the investigation of borehole KFM11A consisted of the hose unit S3 including surface Chemmac together with the computer unit MYC 3. The laboratory unit L3 was employed for analytical work but was located close to the core mapping facility and not at drill site DS11.

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 separate 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 in section 447.5–454.6 m were 2.0, 2.0, 0.4, 0.2 and 0.05 µm. The equipment is described in SKB MD 431.045 (Mätsystembeskrivning för kolloidfiltreringssystem, handhavandedel, SKB internal controlling document to be published) and in complement 1 to the activity plan AP PF 400-07-004. Figure 4-2 shows the equipment set-up. The major equipment performance 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 and temperature 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 that may clog the filters. Furthermore, clogging is prevented by the first two filters with pore sizes 2.0 µm which are mounted parallel to each other.

Disadvantages/drawbacks, which may cause subsequent modifications to the equipment 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.

When performing the filtration prior to the colloid study by SEM, the equipment is supplemented with a portable argon-filled glove-box for handling the filters containing the oxygen-sensitive colloids.

4.3 Pipe String System (PSS)

The SKB downhole pipe string system (PSS) is normally used for hydraulic injection and pumping tests but in this case it was used for pumping and chemical sampling. The system is designed for flow rates between 5 to 40 L/min when used for pumping. The equipment is described in SKB MD 345.100–124 (Pipe String System, SKB internal document).

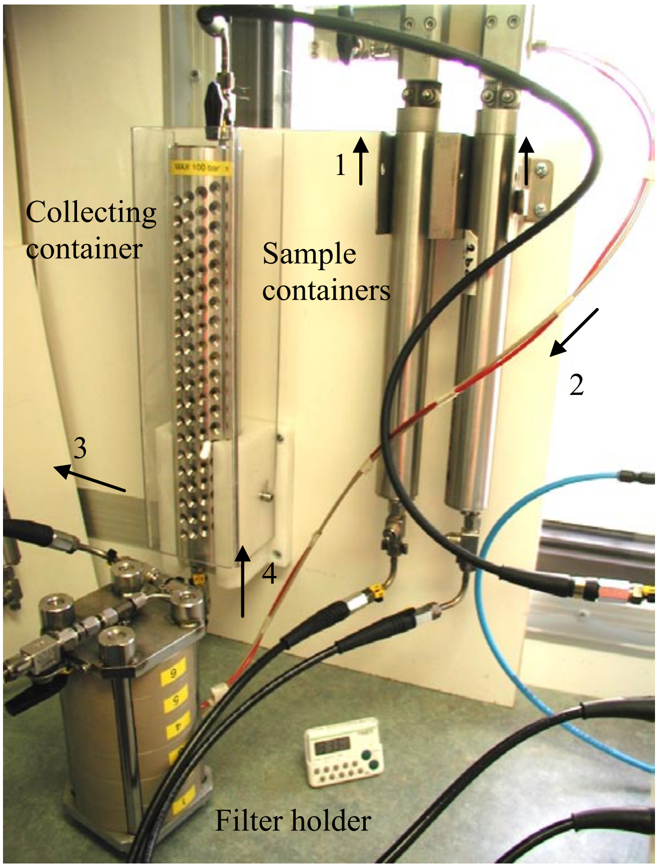


***Figure 4-2.** The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1 to 4, show the flow direction of the sample water through the system.*

4.3.1 PSS equipment facility container

The PSS is primarily designed for pumping and injection tests in packed-off borehole sections. All of the equipment needed to perform the tests is located in a steel container, which is placed on pallets in order to ensure a suitable working level in relation to the borehole casing. The container is divided into a computer-room and a workshop compartment, see Figure 4-3.

The hoisting rig is of a hydraulic chain-feed type. The jaws, holding the pipe string, are opened hydraulically and closed mechanically by springs. The rig is equipped with a load transmitter and the load limit may be adjusted. The maximum load is 22 kN.

The packers and the test valve are operated hydraulically by water filled pressure vessels. Expansion and release of packers, as well as opening and closing of the test valve, is done using magnetic valves controlled by the software in the data acquisition system.

4.3.2 Downhole equipment

A schematic drawing of the downhole equipment is shown in Figure 4-4. The pipe string consists of aluminium pipes of 3 m length, connected by stainless steel taps sealed with double o-rings. Pressure is measured above (P_a), within (P) and below (P_b) the test section, which is isolated by two packers. The groundwater temperature in the test section is also measured. The hydraulic connection between the pipe string and the test section can be closed or opened by a test valve operated by the measurement system.

At the lower end of the borehole equipment, a level indicator (caliper type) gives a signal as the reference depth marks along the borehole are passed.

The length of the test section may be varied (5, 20 or 100 metres).

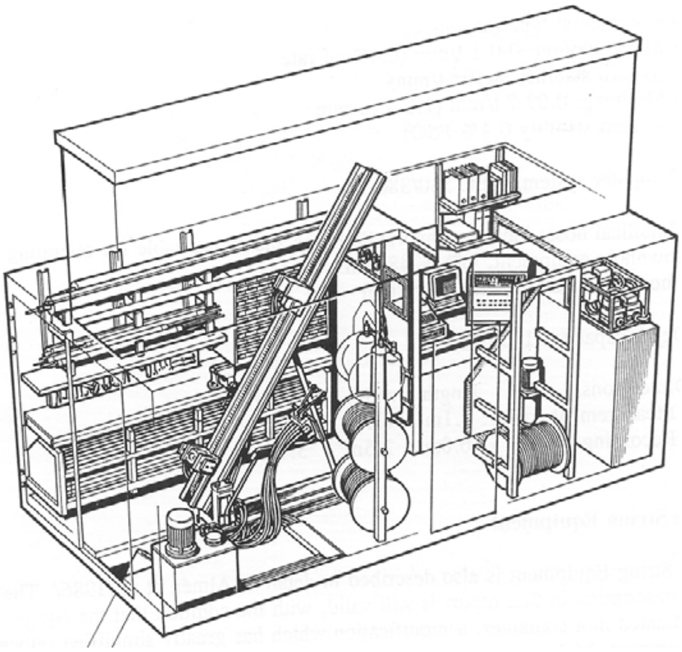


Figure 4-3. *Outline of the PSS3 container with equipment.*

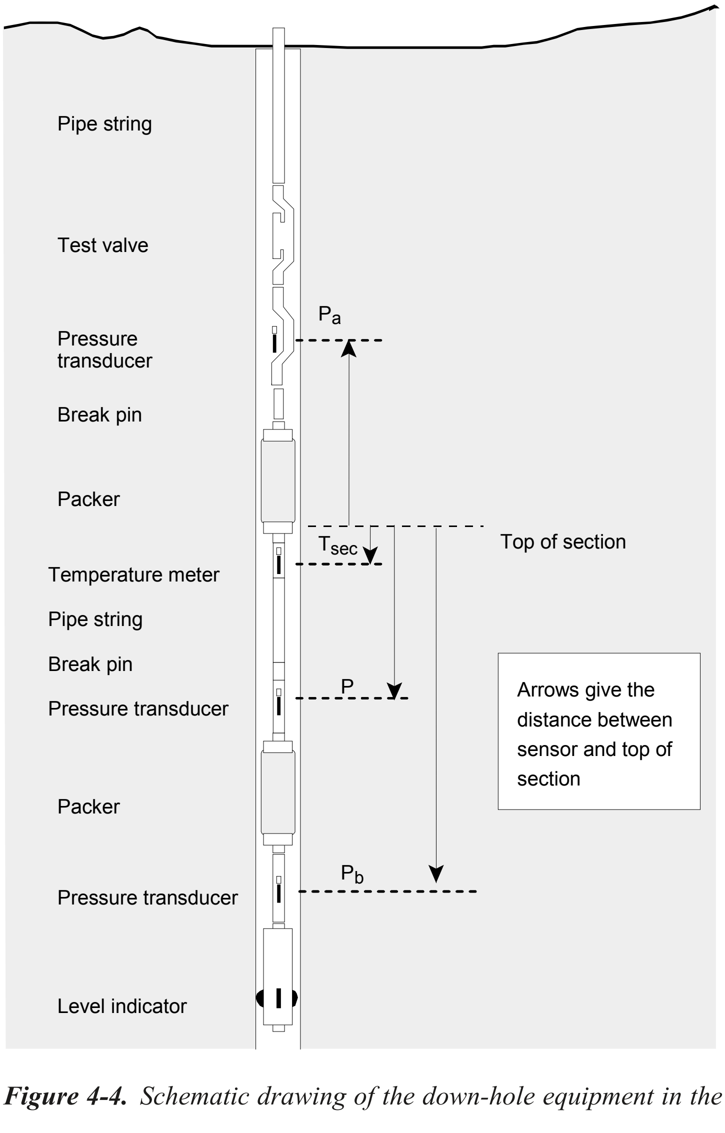


Figure 4-4. *Schematic drawing of the down-hole equipment in the PSS3 system.*

5 Performance

5.1 General

Chemical characterisation in borehole KFM11A was conducted according to activity plan AP PF 400-07-004 including two supplements. The methods are described in SKB MD 430.017 (Metodbeskrivning för fullständig kemikarakterisering med mobilt fältlaboratorium) and SKB MD 423.002 (enkel provtagning i hammarborrhål och kärnborrhål). Table 5-1 gives an overview of the investigation sequence in KFM11A.

5.2 Chemical characterisation

5.2.1 Overview of field work procedure

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

Preparations prior to lowering the downhole equipment in the borehole include:

- Cleaning of the inside of the umbilical hose (the sample water channel) with de-ionised and 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/vessels are cleaned on the outside using 70% denatured ethanol and on the inside using chlorine dioxide. 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 and in this case an overpressure of 5 bars was used.
- Calibration of the pH and redox electrodes in the downhole Chemmac equipment.

Table 5-1. Investigation sequence in KFM11A.

Start date/ Stop date	Investigation	Section (m)	Comment
2007-01-09/ 2007-01-17	Complete chemical characterisation	429.0–437.4	High flushing water content. The section was abandoned.
2007-01-17/ 2007-03-13	Complete chemical characterisation	447.5–454.6	Pumped volume = 5.3 m^3. Flow rate approx. 110 mL/min.
2007-04-04/ 2007-04-12	Nitrogen lifting combined with pumping	71.1–851.2	Exchanged volume 460 m^3.
2007-07-09/ 2007-07-16	Pumping/sampling with Pipe String System (PSS)	690.0–710.0	Pumped volume = 6.8 m^3. Flow rate 810–980 mL/min.

The different downhole units are assembled during lowering of the equipment down 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 on the regular downhole equipment. The length mark detector indicates length calibration marks milled into the borehole wall at intervals of almost every 50 m /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 properly 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, because the greater the drawdown, the larger the bedrock volume affected by the pumping, and the risk of mixing with groundwater 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, Uranine, chloride, alkalinity, ferrous and total iron, and ammonium) at the site.
- Enrichment of humic and fulvic acids is conducted for as long as possible in each section. The time needed depends on the organic 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 $\partial^{13}C$ and pmC. This activity is only performed when the flushing water content is sufficiently low.
- 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. This activity is only performed when the flushing water content is sufficiently low.
- A decision when to terminate the sampling work in the section is made during a suitable 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 measurements have not reached stable values. A final SKB class 5 sample including 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 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.

- When the borehole pump is stopped and the packers deflated, the equipment is lifted and the different downhole units are dismantled.
- Calibration of the electrodes in the downhole Chemmac and surface Chemmac equipment.

5.2.2 Performance in section 447.5–454.6 m

The chemical characterisation in section 447.5–454.6 m was performed using the following configuration of the downhole equipment in the borehole 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/measurement period was interrupted several times due to the difficulties with high flushing water content. A new method was used on the 12th of February in a last attempt to decrease the flushing water content to an acceptable level. The technique, using nitrogen lifting from the bottom of the borehole in combination with pumping from the top of the borehole, was rather successful and the flushing water content decreased from 11% to close to 7%.

The pumping flow rate was about 110 mL/min and the drawdown approximately 6 m at the end of the measurement period. However, a regular pressure variation of around 4 bars was observed within the section. This variation was not observed from manual registrations in a log book and it is most probably due to an unsuitable combination of pump-piston return time and logging interval. A diagram showing the pressures above and within the borehole section (the manually registered data) and the flow rate during the pumping/measurement period, is presented in Appendix 5. The events during the investigation are listed in Table 5-2.

Table 5-2. Events during the complete chemical characterisation pumping/measurement period in section 447.5–454.6 m.

Date	Event	Sample no.
070109	Calibration of borehole Chemmac.	
070112	Calibration of surface Chemmac.	
070117	**Lowering of downhole equipment S3 (447.50–454.64 m).**	
	Start of Chemmac measurements.	
070118	Water sampling: SKB class 2	12589
070119	Water sampling: Uranine	
070122	Water sampling: Uranine	
070123	Water sampling: Uranine	
	Stop of Chemmac measurements.	
	Raising of equipment due to clean-up pumping. Pumped volume: approx. 560 m^3	
070129	**Lowering of downhole equipment S3 (447.50–454.64 m).**	
	Start of Chemmac measurements.	
070130	Water sampling: Uranine	
	Stop of Chemmac measurements.	
	Raising of equipment due to clean-up pumping. Pumped volume: approx. 545 m^3	
070205	**Lowering of downhole equipment S3 (447.50–454.64 m).**	
	Start of Chemmac measurements.	
	Change of ground level indicator due to failure.	
070206	Water sampling: Uranine	
	Stop of Chemmac measurements.	
	Raising of equipment due to clean-up pumping. Pumped volume: approx. 665 m^3	
070212–13	Further cleaning by nitrogen lifting (60 bars) from the bottom of the borehole in combination with pumping from the upper part of the borehole (in the casing).	
070214	Calibration of borehole Chemmac.	

Date	Event	Sample no.
	Lowering of downhole equipment S3 (447.50–454.64 m).	
	Start of Chemmac measurements.	
070215	Water sampling: Uranine	
	Calibration of surface Chemmac, S3.	
	Computer failure; fault localisation, defragmentation and restart of the computer.	
070216	Water sampling: SKB class 2	12702
070219	Water sampling: SKB class 4	12703
070222	Water sampling: SKB class 4	12705
070226	Change of membrane in oxygen meter.	
	Water sampling: SKB class 4	12706
070301	Water sampling: SKB class 5	12707
	Oxygen meter control.	
070305	Water sampling: SKB class 5	12724
070308	Water sampling: SKB class 4	12725
070312	PVP-sampler: raised pressure and opening of valve at 13:52.	
	Water sampling: SKB class 5, all options except for colloid filtration followed by chemical analysis.	12727
070313	PVP-sampler: closure of valve at 05:37.	
	Sampling for colloids (SEM and LIBD), microbes and dissolved gases.	12727
	Colloid filtration.	12727
	End of Chemmac measurements.	
	Raising of equipment.	
	Calibration of borehole Chemmac.	
	Calibration of surface Chemmac.	
	Water sampling at the end/bottom of the of the umbilical hose after the sampling period: SKB class 2.	12728

5.2.3 Collection of in situ water samples

The in situ water sampling in the borehole section was conducted successfully and the purpose of each sample portion is given in Table 5-3. Two of the sample portions were used for colloid determination using different methods; laser-induced breakdown detection, LIBD, see Appendix 7, and detection by SEM /12/. All of the PVB-containers were quality controlled before use; this procedure includes disassembling the container, thorough cleaning, reassembling and measurement of piston friction. The filled PVB-containers for gas, microbes and LIBD were packed together with ice packs in insulated bags and sent to the laboratories by express delivery service immediately after sampling.

5.2.4 Colloid filtration followed by SEM investigation

One of the water sample portions collected in situ in section 447.5–454.6 m was used for colloid filtration, see Table 5-3, and two of the resulting five filters were studied by SEM. The colloid samples on filters were obtained by filtering the groundwater through a series of connected filters in a closed system under an argon atmosphere. The pressure and temperature in the system were maintained at the same level as in the sampled borehole section. The intention was that colloids should be collected on the different filters (descending pore sizes) according to their sizes. The general filtration method which is normally combined with colloid determinations by ICP-MS was somewhat modified prior to the SEM studies. The modifications are documented in Supplement 1, activity plan AP PF 400-07-004. Data on performance of the filtration runs are given in Table 5-4.

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

Sample portion no.	Section 447.5–454.6 m 2007-03-13
1	Dissolved gas
2	Colloids (LIBD)
3	Microbes
4	Colloids (SEM)

Table 5-4. Colloid filtration, data on performance runs.

Section/date	Entering pressure [bar]	Max. differential pressure over filter package [bar]	Temp. [°C]	Filtering time [min]	Filtered volume [mL]	Comments
447.5–454.6/ 20070313	~ 40	3	~ 8–9	7	145	Leakage test prior to filtration. No leakage was noticed. No broken filters.

After filtration of the sample water, the filters were rinsed with 50 mL of oxygen-free deionised water kept at borehole pressure and temperature. The source of the rinsing water was from the Milli Q system at Äspö Chemistry laboratory and it was used also for washing the PVB container before use. Dismounting of the filter holder package and packing of the filters took place inside an argon filled glove box. The filters were placed in plastic Petri-dishes covered in the inside with an anti-static material and kept closed with tape. Marks on the dishes indicated the active sides of the filters. The dishes were placed in gas-tight heat sealed plastic bags filled with argon and kept cool before transport to the laboratory.

Two water samples (water in and water out) were sent for ICP analyses (major constituents and common trace metals) and the 0.2 µm and 0.05 µm filters were sent for SEM investigation.

To check the validity of the approach, a test was performed using two different commercial Latex Microspere Suspensions containing particles with pore sizes of 0.08 µm and 0.24 µm, respectively. The filters were weighed before and after filtering (at a pressure of 10 bars) a suspension containing 0.1 mg of each pore size. The weighed amounts on the 0.4 µm and 2.0 µm filters (on which neither of the commercial colloids should be present) were rather high (0.03–0.09 mg). The average weight value, calculated from the weights on these filters, was subtracted from the weighed amounts on the 0.2 µm and 0.05 µm filters. The final results of the weights on the 0.2 µm and 0.05 µm filters were 0.11 and 0.14 mg, respectively, close to the expected values.

A leakage test of the system at approximately 10 bars was also conducted prior to the sample filtrations in order to eliminate this potential risk.

5.3 Simple water sampling using PSS-equipment

5.3.1 Performance in section 690.0–710.0 m

The pumping flow rate used was about 900 mL/min and the drawdown approximately 17 m at the end of the measurement period. The less extensive hydrochemical sampling performed using the PSS-equipment differs from the CCC investigations also in the following aspects.

- The water is pumped through a pipe string made of aluminium at a higher flow rate compared to when the mobile chemistry unit is used and therefore aluminium contaminated samples are expected.
- A flow rate of 900 mL/min is too low for this type of pump and an additional water volume is needed. This was solved by recirculating the pumped water back to the pump; however this may affect the quality of the samples.

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

5.4 Water sampling, sample treatment and analyses

The pumped water from borehole section 447.5–454.6 m was led from the hose unit into a container furnished with a sink and a tank for collecting the outlet water. When PSS3 was used for sampling in section 690.0–710.0 m, the outlet water was led directly into the nearby sea. Filtration of sample portions was performed on-line by connecting the filter holders for 0.40 µm polycarbonate membrane filters directly to the water outlet or, in the PSS3 case, the sample water was pressed through disposable 0.40 µm filters by using a syringe. During the entire sampling, laboratory gloves were used to minimise the risk of contaminating the samples. 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 6. The routines are applicable independently of the sampling method or the type of sampling object.

Table 5-5. Events during pumping and sampling using PSS3 equipment in section 690.0–710.0 m.

Date	Event	Sample no.
070710	Start	
070711	Water sampling: SKB class 3	12843
070713	Water sampling: SKB class 3	12844
070716	Water sampling: SKB class 5	12845
070716	Stop	

6 Nonconformities

The hydrochemical characterisation in KFM11A has been conducted according to the SKB internal controlling documents AP PF 400-07-004, including Supplements 1 and 2, and SKB MD 430.017 with the following deviations and remarks:

- The allowed upper limit for flushing water content, 1%, was exceeded in both investigated sections.
- Neither fractionation of organic and inorganic species nor enrichment of humic and fulvic acids were performed due to the high flushing water content.
- The high flushing water content was also the reason for excluding the standard colloid filtration method. Therefore, four in situ samples were sufficient (gas, microbes, SEM and LIBD) and only one raising of the down-hole units was needed.

7 Data handling and interpretation

7.1 Chemmac measurement data

The processing of Chemmac data is described in SKB MD 434.007, version 2 (Mätsystembeskrivning för Chemmac mätsystem, SKB internal controlling document).

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 for following 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 field work and the calculation/evaluation. The comments in the file are imported as activity comments in Sicada.

7.1.2 Calculation and evaluation of redox potential and pH

The redox potential is measured by three electrodes at the surface and three 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 result 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 for this 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 changes in gas pressure conditions which affects 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 Chemmac.
- Number of electrodes showing reasonable agreement. Obviously erroneous electrodes are excluded from the calculation.

7.2 Water analysis data

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

Several components are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure on every fifth or tenth 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 which 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 the results that are considered most reliable.

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

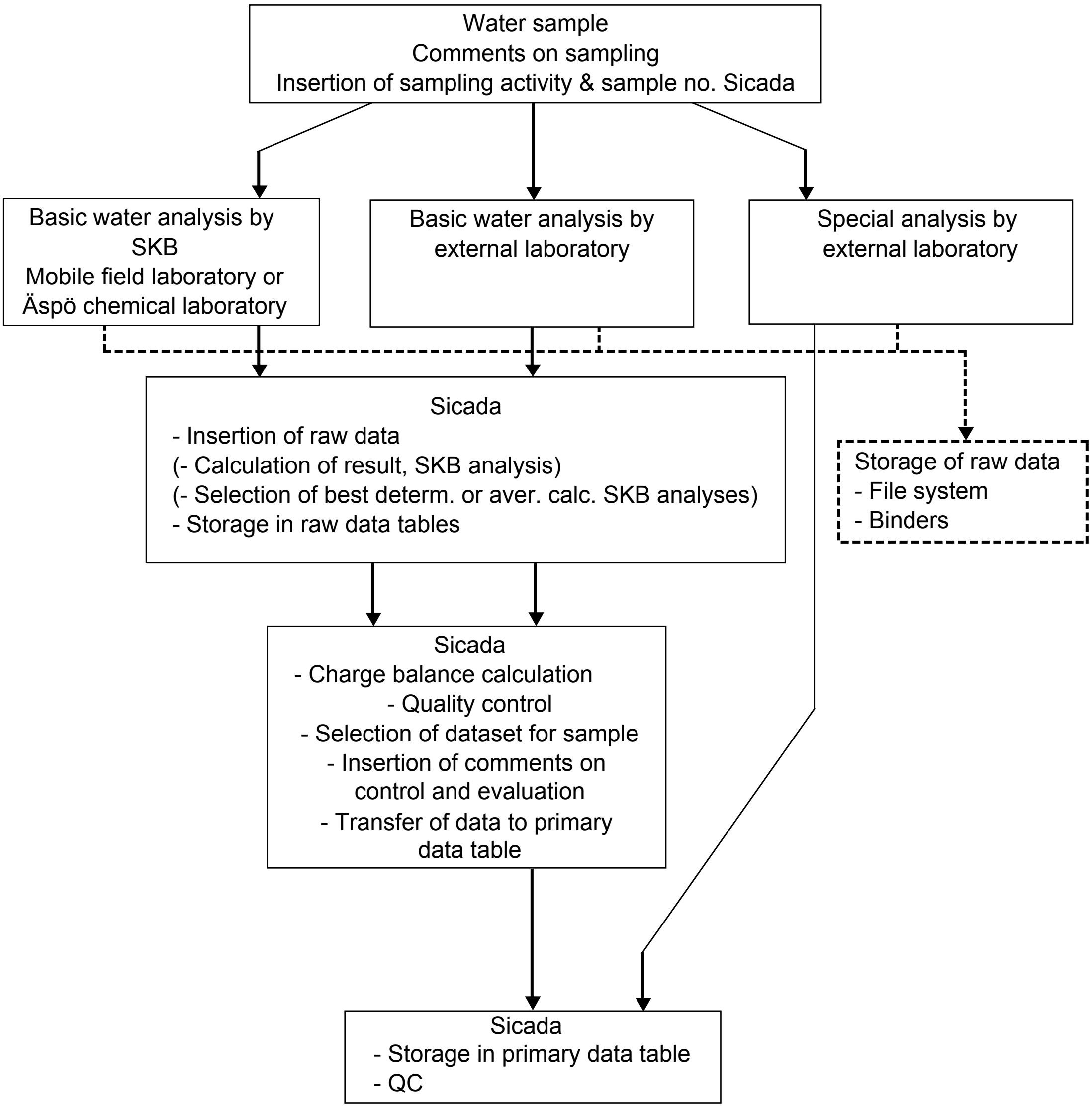


***Figure 7-1.** Overview of data management for hydrogeochemical data.*

7.3 Data obtained using special sampling methods

Separate activities, methods and sample numbers are defined in Sicada for data on dissolved gases and colloids. All data are subjected to quality control and the results are stored in primary data tables in Sicada without post processing or interpretation.

8 Results

8.1 Chemmac measurements

The data sequences of pH, Eh, electrical conductivity, oxygen and temperature values from the Chemmac measurements in borehole section 447.5–454.6 m are plotted versus time in Appendix 8. The measured time series were evaluated in order to obtain one representative value of Eh, pH, electrical conductivity and dissolved oxygen for the borehole sections as described in Section 7.1. Data were selected from the last part of the measured time series (where the electrodes show stable values), marked with an arrow in the diagrams in Appendix 8. The selected values from the measurements are given in Table 8-1 together with the corresponding results from the in situ sample used for LIBD experiments.

The borehole Chemmac electrodes stabilised at a lower level than the surface Chemmac electrodes. A possible reason is the contribution from very small amounts of air/oxygen somewhere in the sample water line at the surface; this is very difficult to avoid at times. Therefore, only the borehole electrodes were used for calculating a representative Eh value.

The pH-electrodes in the borehole and at the surface show excellent agreement. Even though minor discrepancies between pH measured at the ground surface, and pH measured in situ in the borehole section, are likely to occur due to the effect of pressure decrease on the carbonate system.

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 (lab-pH) and electrical conductivity (lab-EC) 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 lab-pH and lab-Eh values are compared to the corresponding on-line Chemmac measurement values in Appendix 8.

Table 8-1. Evaluated results from the Chemmac measurement in KFM11A.

Borehole section [m]	EC* [mS/m]	pH (surface Chemmac)**	pH (borehole Chemmac)**	Eh (Chemmac)** [mV]	Dissolved oxygen*** [mg/L]
447.5–454.6	1,200 ± 40	7.5 ± 0.1	7.5 ± 0.2	–203 ± 36 B	0.00 ± 0.01
447.5–454.6 LIBD****	1,131	7.88	–	380	0.004

* 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.

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

**** See Appendix 7.

B = Values from borehole Chemmac have been used in the calculation.

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 of the analysed samples. Furthermore, the last sample in section 447.5–454.6 m was also analysed by a second laboratory; in general, comparison between results from different laboratories and methods show an acceptable agreement.

The flushing water contents in the sample series collected from borehole sections 447.5–454.6 m and 690.0–710.0 m are presented in Figures 8-1 and 8-2, respectively. The content should not exceed 1% in order for a sample to be considered representative for the groundwater of the sampled fracture. This condition was not met in either of the sampled sections. The flushing water contents reached their lowest values at the end of each measurement period; 5.9% in section 447.5–454.6 m and 3.3% in section 690.0–710.0 m. The percentage of flushing water in the samples was calculated using the measured average Uranine concentration (0.170 mg/L).

The concentrations of chloride, calcium and sodium are presented in Figures 8-3 and 8-4. The concentrations of all major constituents remained practically constant during the second half of the pumping and sampling period in section 447.5–454.6 m. In section 690.0–710.0 m, the amounts of major constituents were still changing by the end of the pumping period.

The iron concentrations from section 447.5–454.6 m are compared in Figure 8-5. The determinations by ICP-AES (total Fe) and spectrophotometry (Fe(II) and Fe-tot) agree well. First there is an increasing trend from a very low concentration to a common level in deep groundwaters and then the concentration drops again in the end of the measurement period. None of the other analysed parameters show this behaviour. The iron concentration (total Fe) in the last sample from section 690.0–710.0 m was very high (3.0 mg/L). As the PSS technique was used for pumping, this iron concentration might be due to contamination from the equipment.

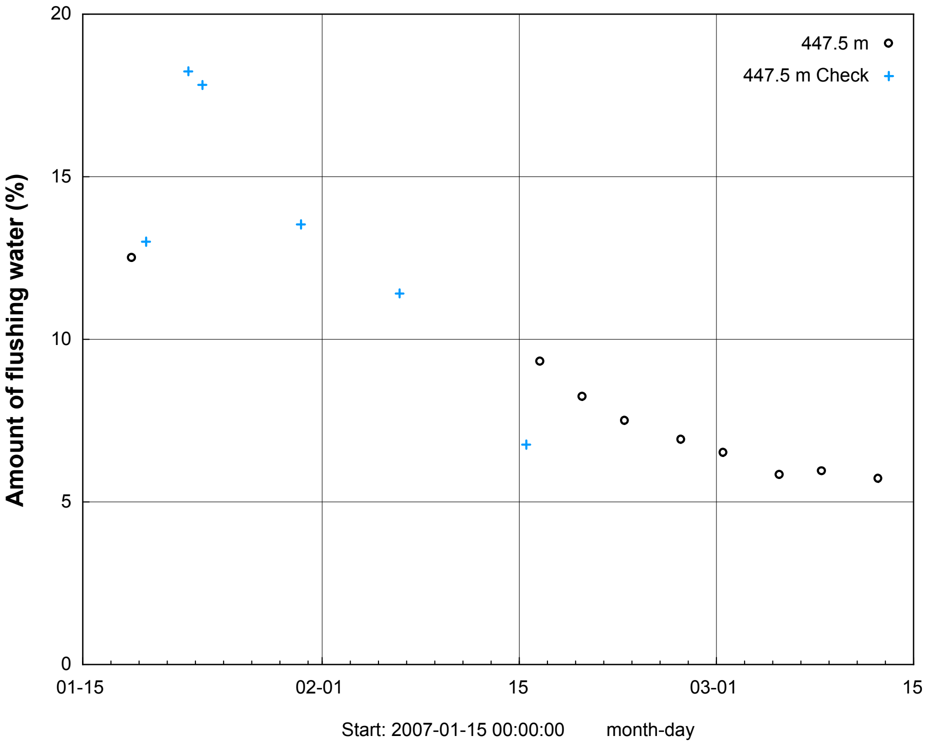


***Figure 8-1.** Flushing water content in the groundwater samples from section 447.5–454.6 m.*

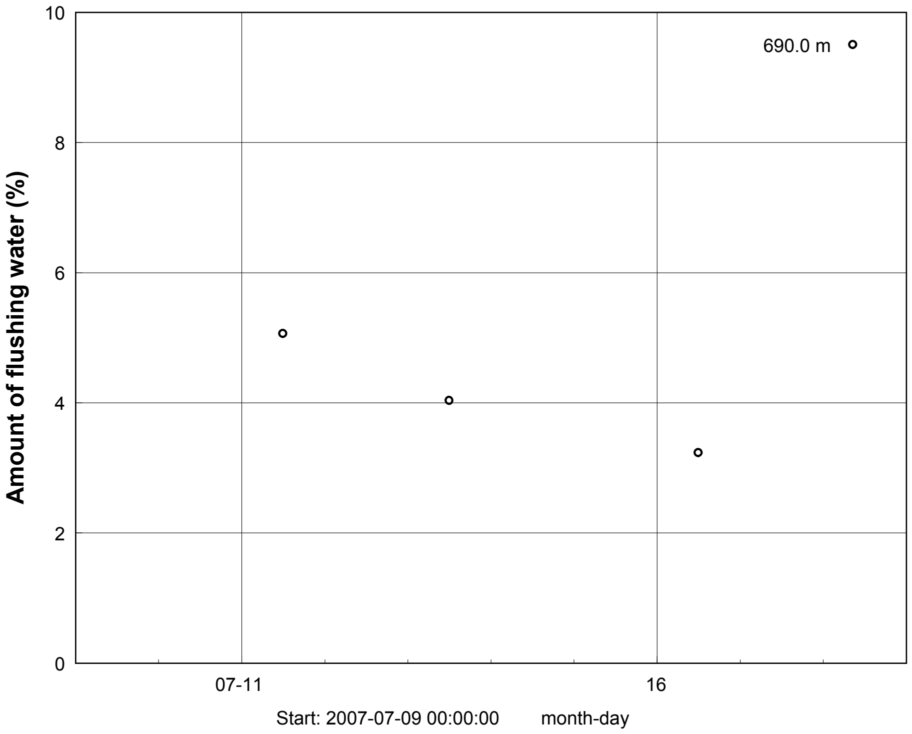


Figure 8-2. *Flushing water content in the groundwater samples from the sample series at 690.00–710.00 m collected during pumping with the PSS equipment..*

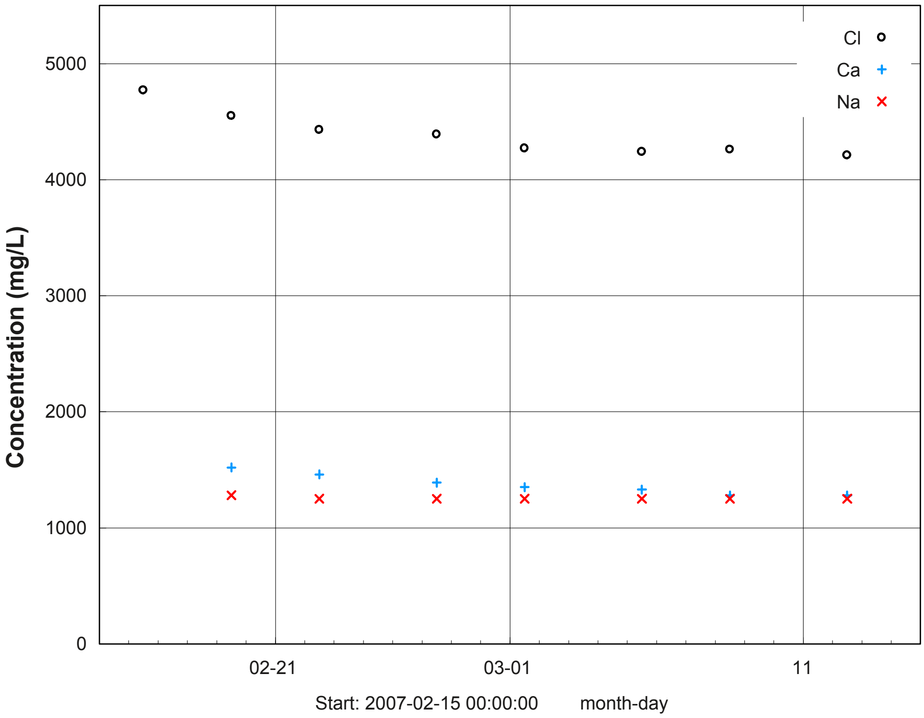


Figure 8-3. *Chloride, calcium and sodium concentration from the sample series at 447.5–454.6 m.*

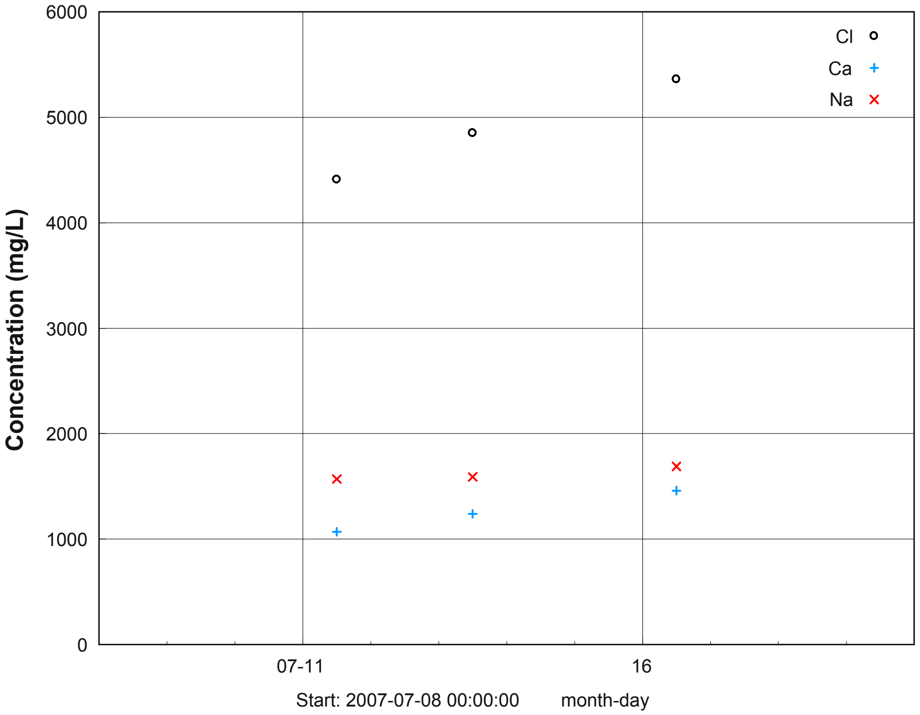


***Figure 8-4.** Chloride, calcium and sodium concentration from the sample series at 690.00–710.00 m collected during pumping with the PSS equipment.*

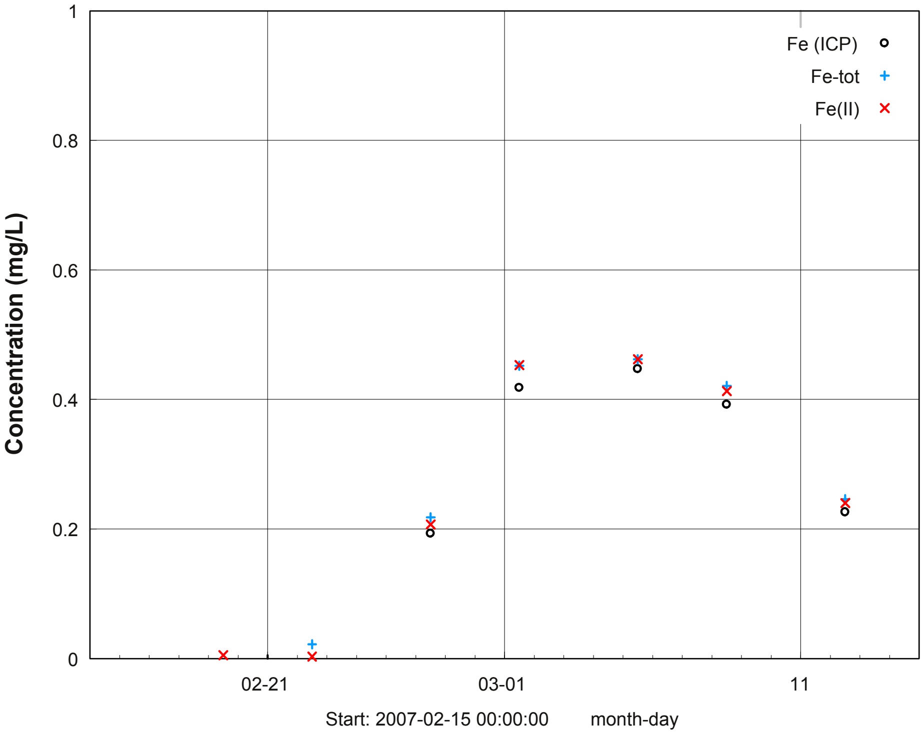


***Figure 8-5.** Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole section 447.5–454.6 m. The values plotted on the x-axis are below the detection limit; 0.02 mg/L.*

Sulphate analysed by ion chromatography (IC) is compared to sulphate determined as total sulphur by ICP-AES for sections 447.5–454.6 m and 690.0–710.0 m in Figures 8-6 and 8-7, respectively. The agreement between the two analysis methods (IC and ICP-AES) is rather good and the discrepancies correspond to the size of the analytical error. The results from the ICP measurements are considered to be more reliable, by experience, since the variations in time series usually are smaller.

The chloride concentrations are plotted versus the corresponding electrical conductivity values in Figure 8-8. The plot gives a rough check of the measured EC values and the chloride concentrations. As shown, the data from the KFM11A agree well with the line obtained by previous data from the site investigation at Forsmark.

The uncertainty in the bromide analyses is somewhat high compared with most other analyses and a plot of bromide versus chloride gives a check if the measured values are within reason, see Figure 9-3.

8.2.2 Trace elements (rare earth metals and others)

The analyses of trace and rare earth metals include Al, B, Ba, 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. The risk of contamination is large also for aluminium, and even more so when the PSS equipment has been used for sampling. The aluminium concentration is still reported due to its importance for the modelling work. The trace element data are compiled in Appendix 9, Table A9-2.

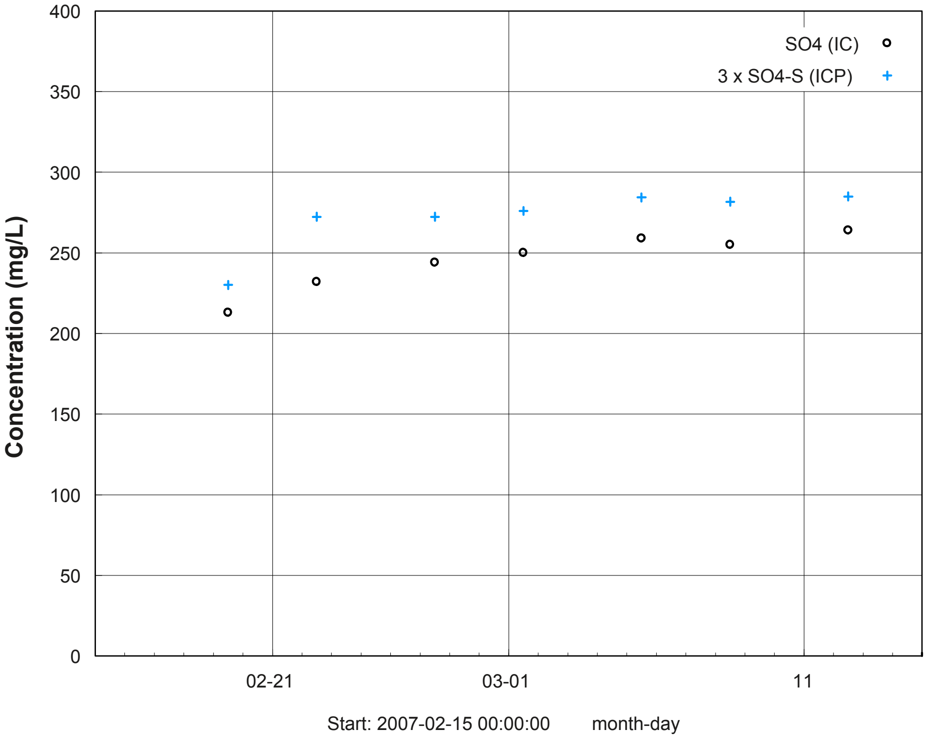


Figure 8-6. *Sulphate (SO_4 by IC) to total sulphate calculated from total sulphur ($3 \times SO_4$-S by ICP) versus date, borehole section 447.5–454.6 m.*

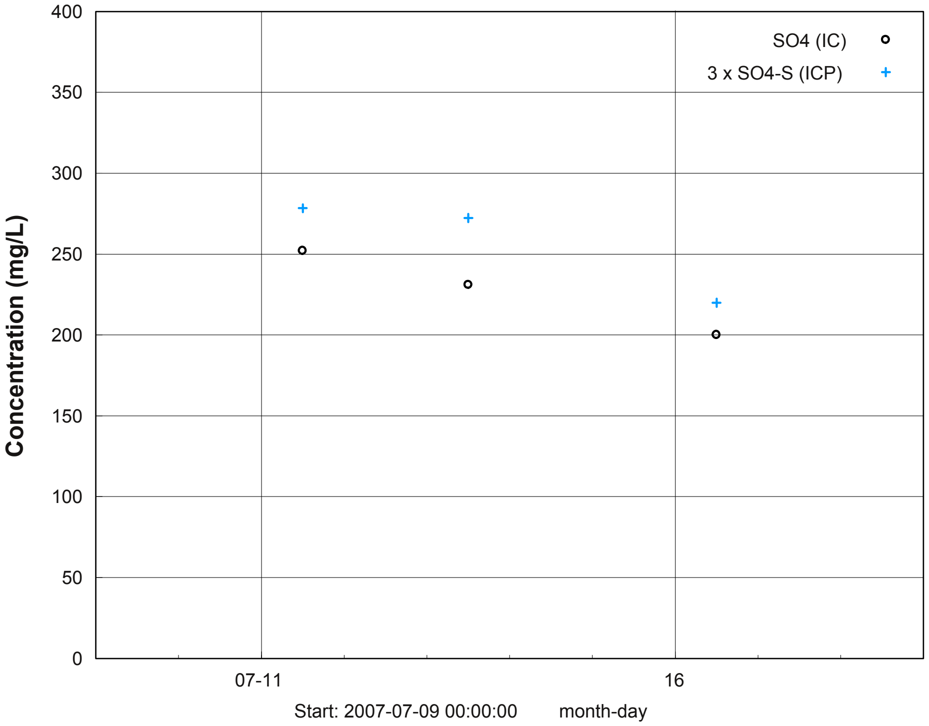


Figure 8-7. *Sulphate (SO_4 by IC) to total sulphate calculated from total sulphur (3×SO_4-S by ICP) versus date. Groundwater samples from the sample series at 690.00–710.00 m collected during pumping with the PSS equipment.*

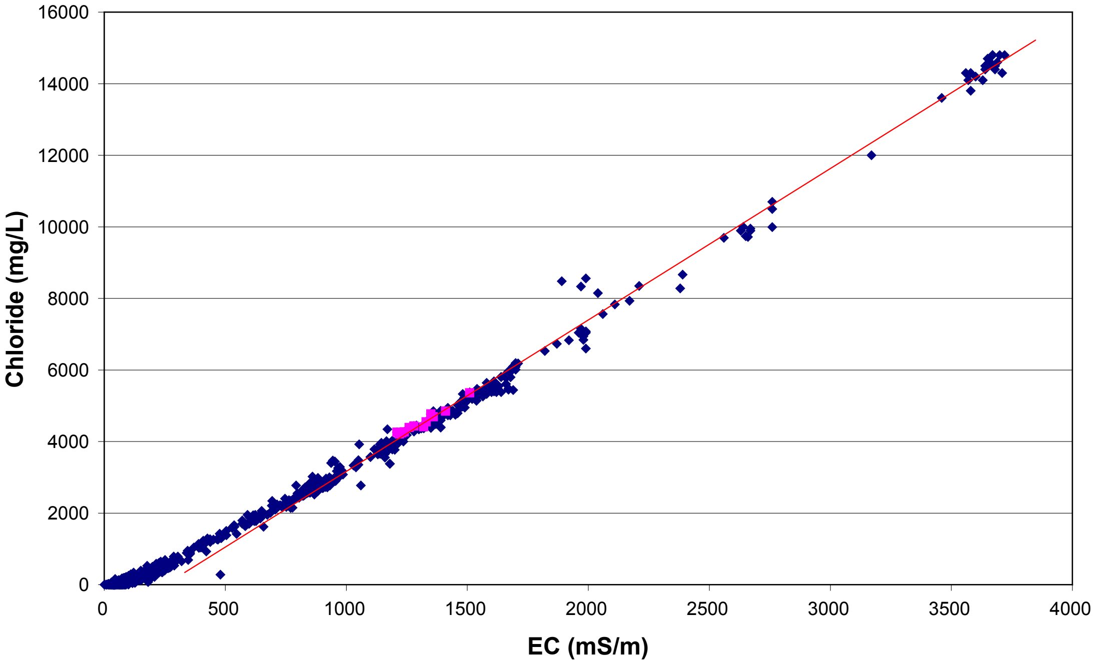


Figure 8-8. *Chloride concentration versus electrical conductivity. Data from previous investigations at Forsmark are used to show the linear trend. Data from KFM11A are shown in pink.*

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. Available isotope data at the time of reporting are compiled in Appendix 9, Table A9-3 and Table A9-4.

The ^{3}H and δ^{18}O results for section 447.5–454.6 m are presented in Figure 8-9. The δ^{18}O results in section 690.0–710.0 m, are in the range –10.0 to –10.7‰ SMOW but the tritium results are not available at the date of printing this report.

The carbon isotopes (δ^{13}C and pmC) are determined only in inorganic carbon (hydrogen carbonate), as no enrichment of humic and fulvic acids was performed.

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), carbon monoxide (CO), ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2), propane (C_3H_8) and propene (C_3H_6). The gas data are compiled in Appendix 9, Table A9-5. Total gas contents in the groundwater as well as the detected oxygen contamination are given in Table 8-2. The effects of air leakage may be corrected for, assuming that the oxygen contents are zero, by removing the air effect (nitrogen, oxygen and argon).

Table 8-2. Total contents of dissolved gas.

	Section 447.5–454.6
Total gas content [mL/L]	104
Oxygen content [mL/L]	0.028

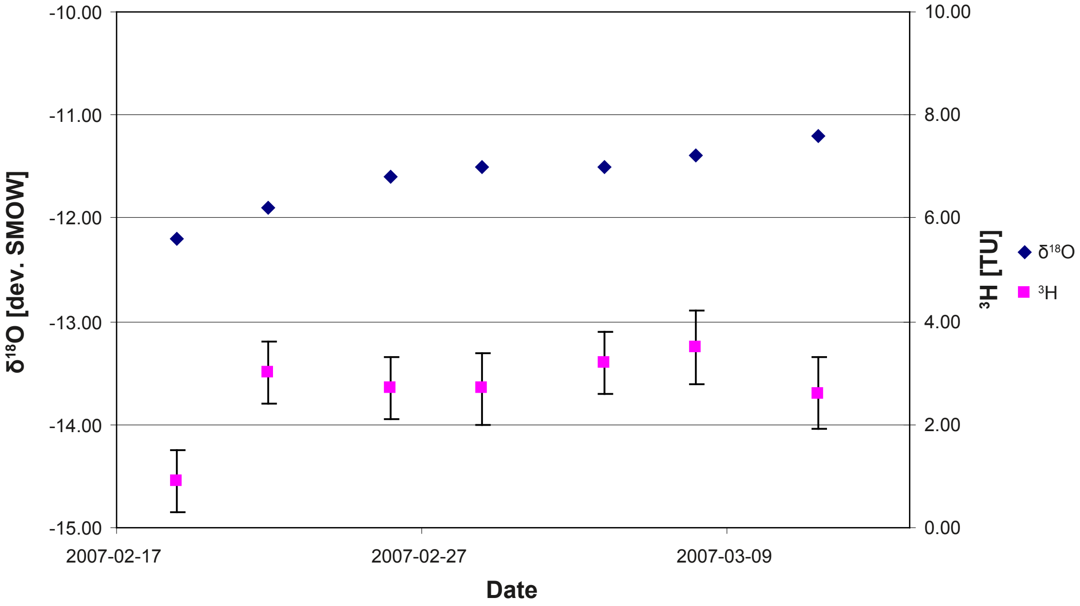


Figure 8-9. *δ^{18}O and ^{3}H data versus sampling date, section 447.5–454.6 m.*

---

* The B-isotope ratio is given as ^{10}B/^{11}B (the result reported from the consulting laboratory). The notation according to international standard for environmental isotopes is ^{11}B/^{10}B, i.e. 1/(^{10}B/^{11}B).

The contents of nitrogen are somewhat high, and it cannot be excluded that some leakage of nitrogen into the PVB-container has occurred, when purging the sample at the consulting laboratory. However, the gas data from this borehole fits well into the general trend when comparing gas data from several boreholes and borehole sections.

The gas composition of the groundwater is presented in Figures 8-10 and 8-11.

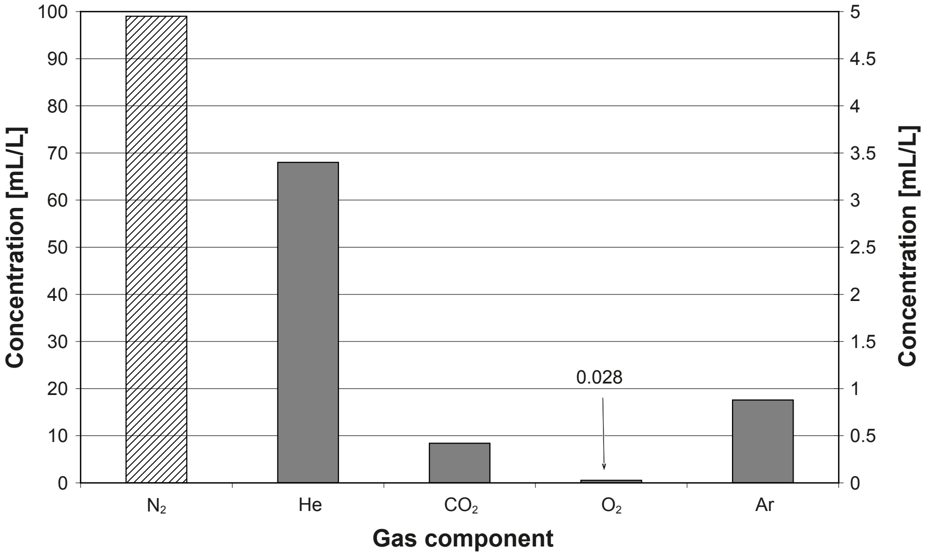


Figure 8-10. *Gas components of high concentrations (N_2, He, Ar, CO_2, and O_2) in the samples collected in section 447.5–454.6 m using the in situ sampling equipment. Bars with striped and solid colour fill patterns refer to left and right hand axis, respectively.*

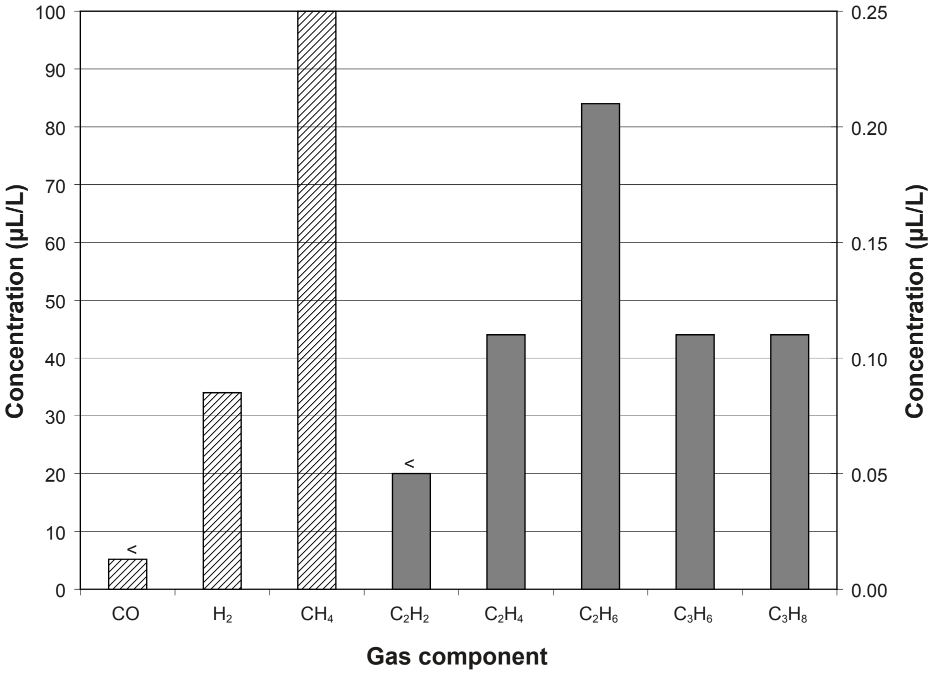


Figure 8-11. *Gas components of low concentrations (CO, H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8), in the samples collected in section 447.5–454.6 m using the in situ sampling equipment. Bars with striped and solid colour fill patterns refer to left and right hand axis, respectively.*

8.4 Colloids

The presence of colloids in section 447.5–454.6 m was investigated using two methods; 1) filtration through a series of connected filters in an argon atmosphere, followed by investigation using SEM /12/, and 2) Laser-Induced Breakdown Detection, LIBD, see Appendix 7.

The colloid contents evaluated from SEM and LIDB amounted to 2 µg/L and 100 µg/L, respectively. The discrepancy may be due to the presence of additional particles/colloids created from drilling and the wearing out of different equipment that are not included in the SEM data (i.e. removed by the prefilters during filtering), but are included in the data (probably constituting fraction 2) obtained from LIBD.

9 Summary and discussion

The results from the hydrochemical investigation in KFM11A provide information about the groundwater compositions above and below the Singö zone, a presumed hydraulic boundary in the northern part of the investigation area.

The diagrams in Figures 9-1 to 9-3 display chloride concentrations versus depth as well as magnesium and bromide concentrations versus chloride concentrations. KFM11A-data are presented together with corresponding data from other core boreholes at Forsmark. The chloride concentrations in both borehole sections follow more or less the general depth trend and the magnesium concentrations indicate a somewhat larger contribution of marine (Littorina) water in the deeper section. The marine signature in section 447.5–454.6 m (340 m vertical depth) is weak or missing while section 690.0–710.0 m (600 m vertical depth) shows a moderate influence from Littorina water. Two somewhat different trends (mixing lines) can be observed from the bromide diagram. The trend with low bromide to chloride ratio represents the marine mixing line while the high ratio represents the non-marine mixing line. The bromide data from the two sections in KFM11A plot between the two mixing lines and are difficult to interpret.

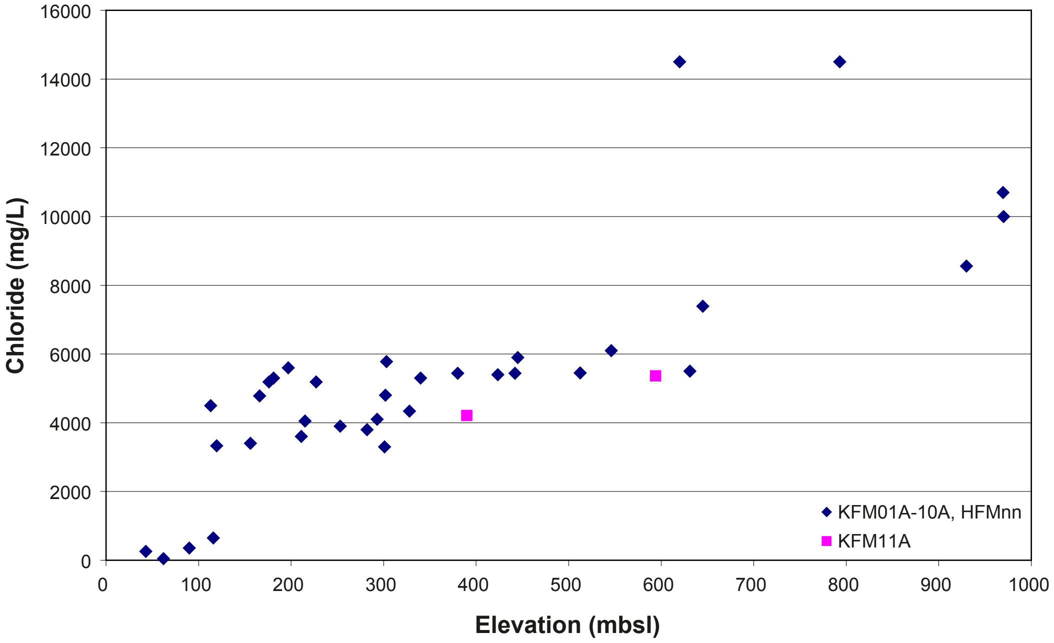


Figure 9-1. *Chloride concentrations versus depth (m) at the Forsmark site. The data points from KFM11A are shown in pink.*

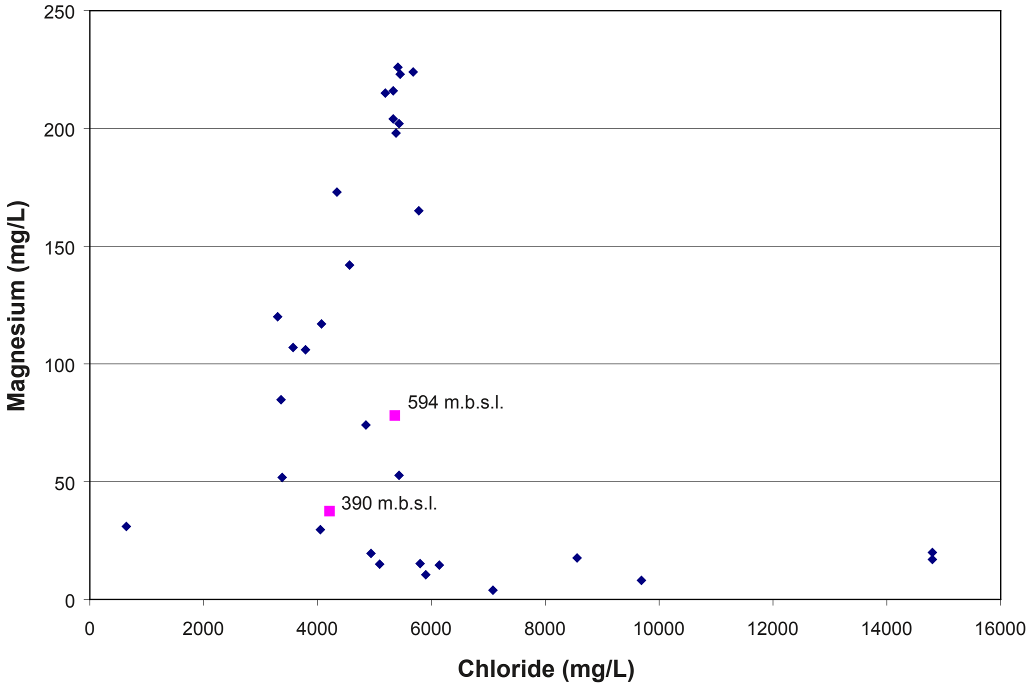


***Figure 9-2.** Magnesium concentrations versus chloride concentrations based on data from core drilled boreholes in Forsmark. The data points from KFM11A are shown in pink.*

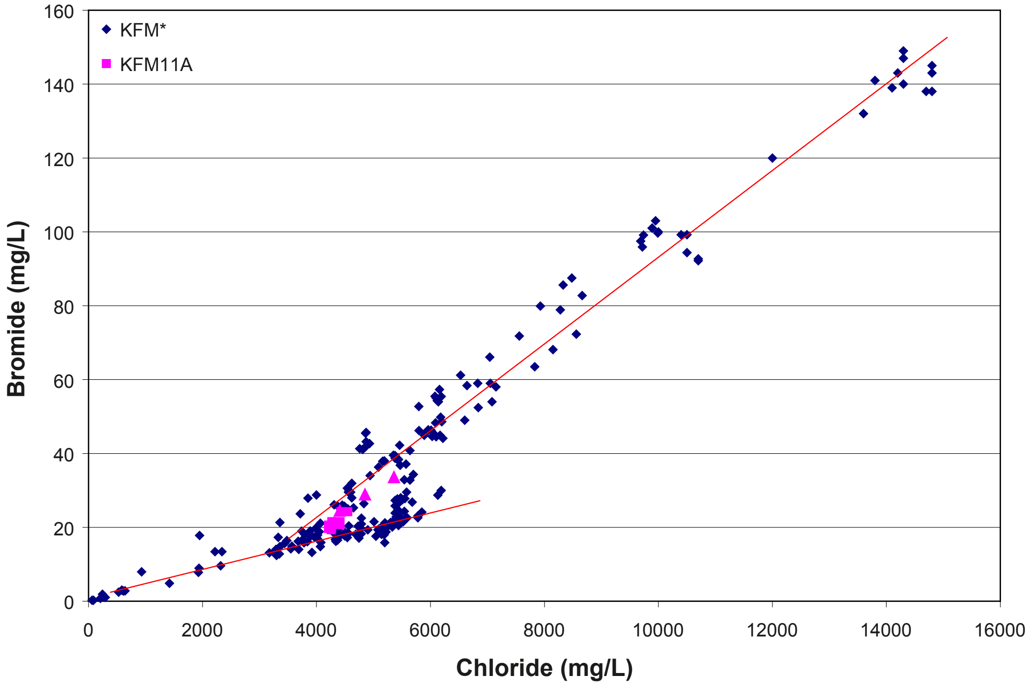


***Figure 9-3.** Bromide concentrations versus chloride concentrations based on data from core drilled boreholes in Forsmark. The data points from KFM11A are shown in pink.*

The main conclusions from the hydrochemical characterisation in KFM11A are:

- The groundwater in the two borehole sections in KFM11A differs somewhat with respect to a marine signature. The magnesium concentrations indicate a small or nonexistent contribution of Littorina sea water in the shallow section and a moderate contribution in the deeper section.
- The redox measurements in section 447.5–454.6 m performed quite well and the borehole electrodes measured stable and agreeing potentials around –203 mV.
- The flushing water contents were somewhat high in both sections; 5.9% at 447.5–454.6 m and 3.3% at 690.0–710.0 m.
- The quality of the water analyses is generally high, based on comparison between results from different laboratories and methods as well as acceptable charge balance errors. The relative charge balance errors are within ± 5%.
- In section 447.5–454.6 m, the major constituents showed stable concentrations during the second half of the pumping/sampling period. In section 690.0–710.0 m, the major constituents did not reach stable values and also the flushing water contents varied considerably. Therefore, it is difficult to assess the representativity of the deeper samples.
- The colloid contents in section 447.5–454.6 m was determined by LIBD as well as by filtration followed by SEM studies. The values diverge and amount to 100 µg/L and 2 µg/L, respectively. It has been observed that colloid contents may vary a lot in this chloride concentration range, see Appendix 7, therefore both values fit the expected colloid versus chloride trend reasonably well. However, with the SEM method it is possible to distinguish particles and artefacts from natural colloids and this may result in a lower and more reliable value.
- The uranium concentrations in the groundwaters from borehole KFM11A were rather low (1–3 µg/L) compared to the extremely high concentrations (80–120 µg/L) obtained in some of the other investigated boreholes and borehole sections in Forsmark.

10 References

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

/2/ **Pedersen K, 2007.** Forsmark site investigation. Total numbers and metabolic diversity of microorganisms in boreholes KFM10A, KFM11A and KFM08D. SKB P-07-198, Svensk Kärnbränslehantering AB.

/3/ **Claesson L-Å, Nilsson G, 2007.** Forsmark site investigation. Drilling of the telescopic borehole KFM11A at drill site DS11. SKB P-07-45, 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/ **Claesson L-Å, Nilsson G, 2007.** Forsmark site investigation. Drilling of flushing water well HFM33 and monitoring wells HFM34 and HFM35 at drill site DS11. SKB P-07-11, Svensk Kärnbränslehantering AB.

/6/ **Berg C, 2006.** Forsmark site investigation. Sampling and analyses of groundwater from percussion drilled boreholes. Results from the boreholes HFM14, HFM23, HFM24, HFM25, HFM26, HFM27, HFM28, HFM29, HFM30, HFM32, HFM33 HFM34 and HFM35. SKB P-06-231, Svensk Kärnbränslehantering AB.

/7/ **Pedersen K, 2005.** Control of microorganism content in flushing water used for drilling of KFM06A. SKB P-05-81, Svensk Kärnbränslehantering AB.

/8/ **Nielsen U T, Ringgaard J, 2007.** Forsmark site investigation. Geophysical borehole logging in the boreholes KFM11A and KFM90B. SKB P-07-92, Svensk Kärnbränslehantering AB.

/9/ **Gustafsson J, Gustafsson C, 2007.** Forsmark site investigation. RAMAC and BIPS logging in borehole KFM1A. SKB P-07-10, Svensk Kärnbränslehantering AB.

/10/ **Väisäsvaara J, Pekkanen J, 2007.** Forsmark site investigation. Difference flow logging in borehole KFM11A. SKB P-07-85, Svensk Kärnbränslehantering AB.

/11/ **Harrström J, Svensson T, Ludvigson J-E, 2007.** Forsmark site investigation. Single hole hydraulic tests in borehole KFM11A. SKB P-07-177, Svensk Kärnbränslehantering AB.

/12/ **Nilsson A-C, Degueldre C, 2007.** Forsmark site investigation. Granitic Groundwater Colloids sampling and characterisation. Colloids Analysis from KFM11A. SKB P-07-169, Svensk Kärnbränslehantering AB.

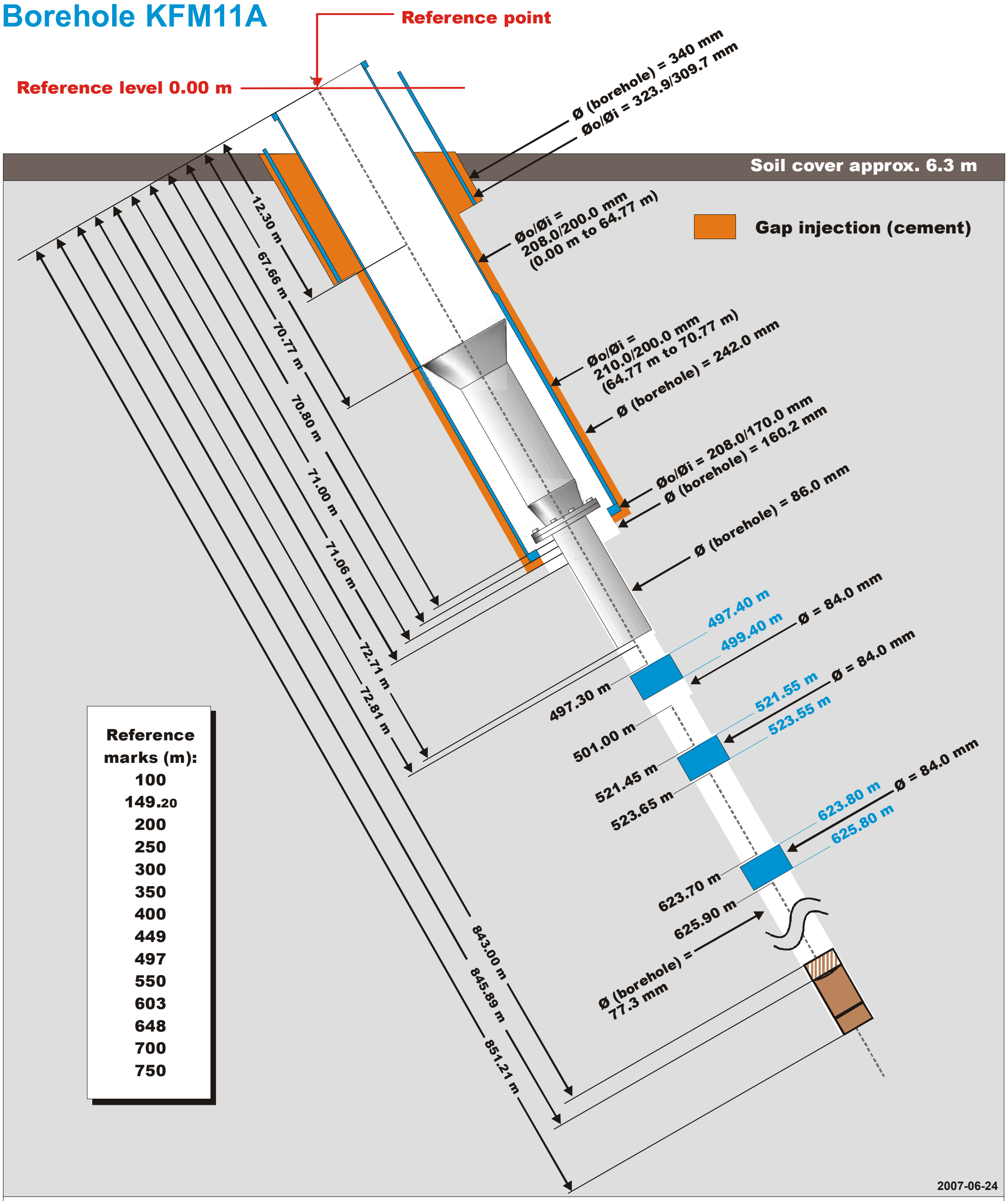
/13/ **Nilsson K, Bergelin A, Lindquist A, Nilsson A-C, 2006.** Forsmark site investigation. Complete chemical characterisation in borehole KFM01D. SKB P-06-227, Svensk Kärnbränslehantering AB.

/14/ **Bergelin A, Lindquist A, Nilsson K, Nilsson A-C, 2007.** Forsmark site investigation. Hydrochemical characterisation in borehole KFM10A. SKB P-07-42, Svensk Kärnbränslehantering AB.

Design of cored borehole KFM11A

Technical data

Borehole KFM11A



Drilling reference point

Northing:	6701103.82 (m), RT90 2,5 gon V 0:-15
Easting:	1632366.75 (m), RT90 2,5 gon V 0:-15
Elevation:	2.95 (m), RHB 70

Orientation

Bearing (degrees):	40.25°
Inclination (degrees):	-60.86°

Borehole

Length:	851.21 m

Percussion drilling period

Drilling start date: 2006-04-12
Drilling stop date: 2006-05-02

Core drilling period

Drilling start date: 2006-08-29
Drilling stop date: 2006-11-16

Additional work

Reaming and PLEX setting

Start date:	2007-03-14
Stop date:	2007-04-02

Appendix 2

Selected results from differential flow logging, KFM11A

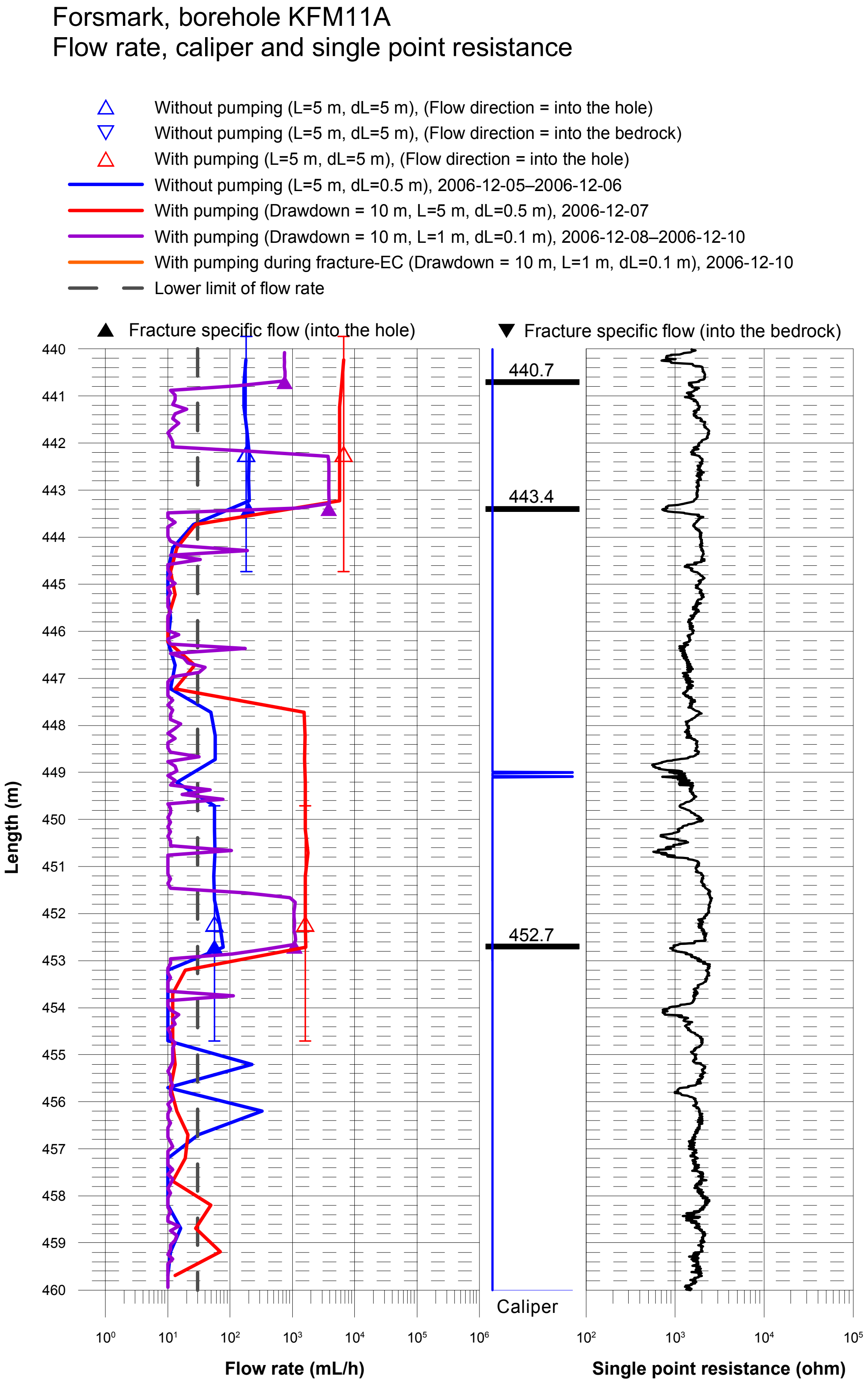


Figure A2-1. *Borehole KFM11A: differential flow measurements from 447.5–454.6 m including the water bearing fracture zone at approx.. 450 m /10/.*

Appendix 3

Selected BIPS logging images, KFM11A

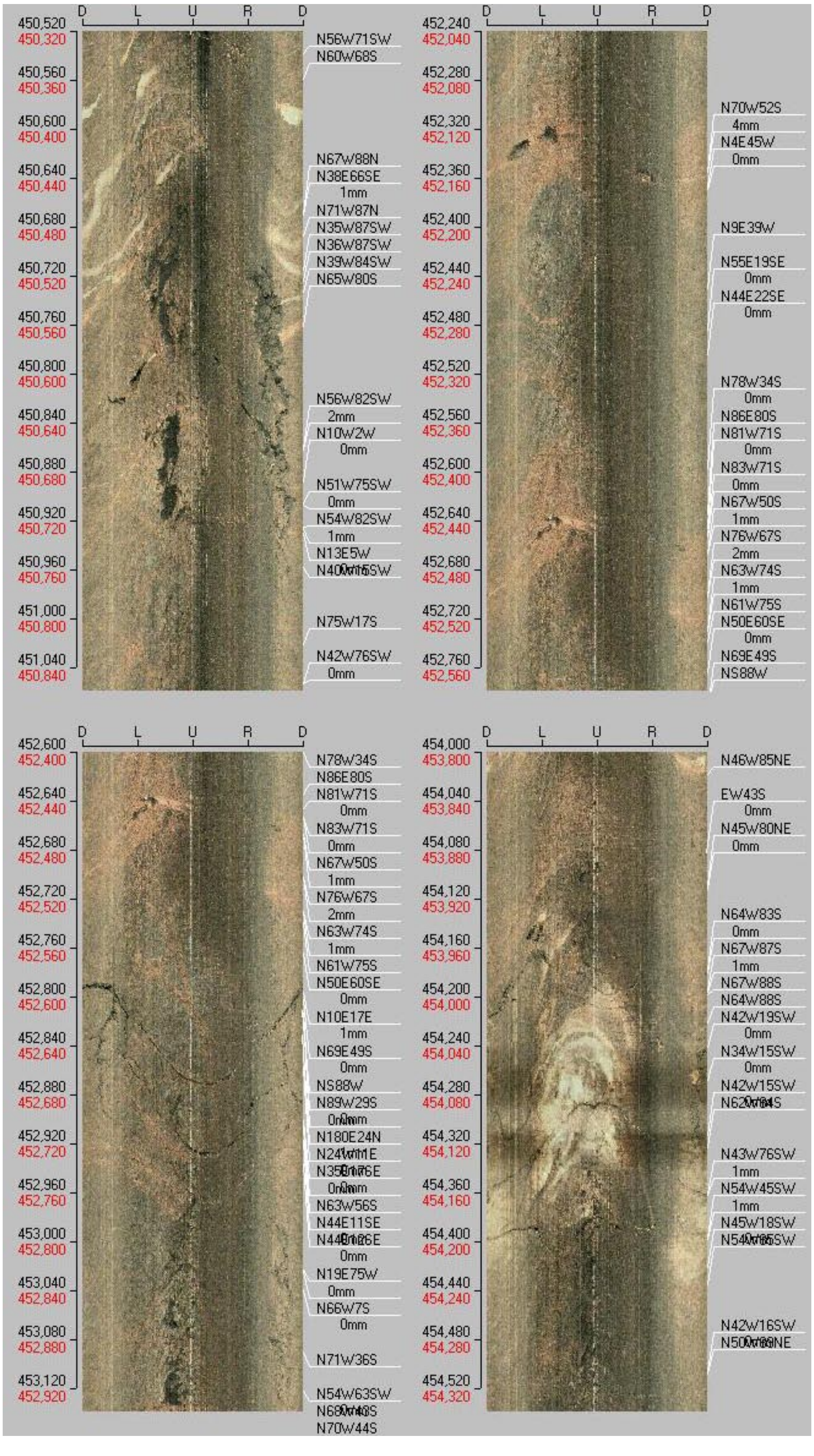


Figure A3-1. *Borehole KFM11A: selected BIPS logging images from 450.3 to 452.9 m borehole length, including several possible water bearing fractures. The non-adjusted length is marked with black and the adjusted true length is marked with red /9/.*

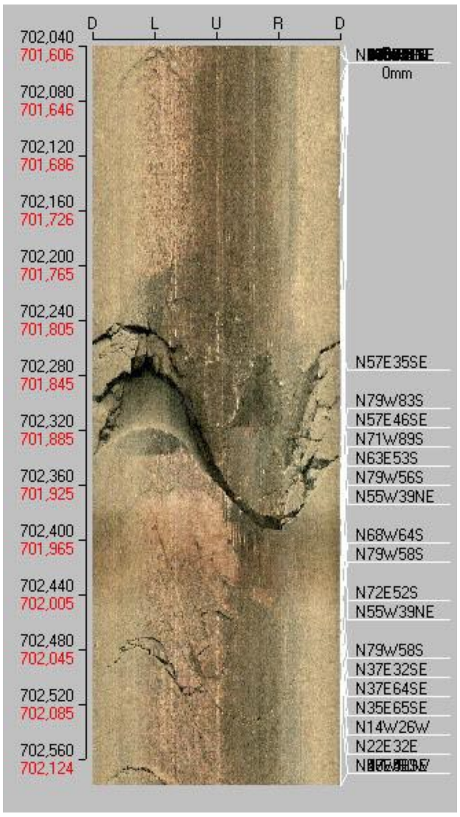
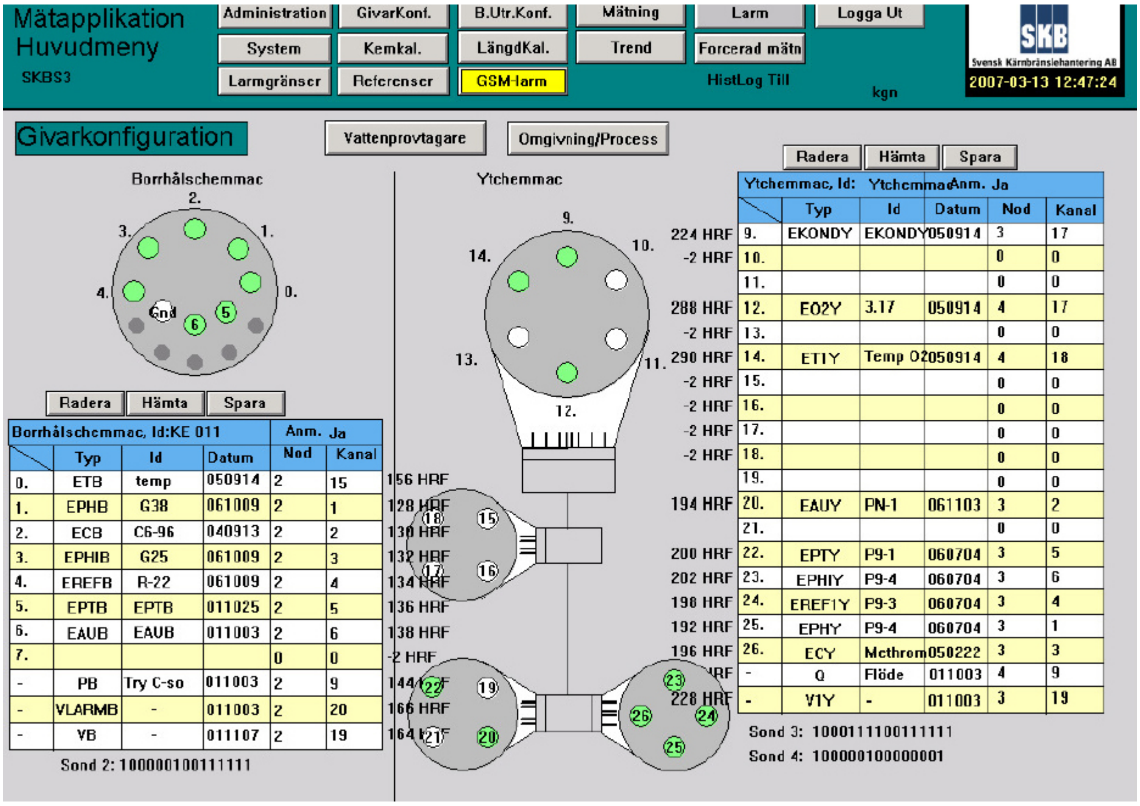


Figure A3-2. *Borehole KFM11A: selected BIPS logging image from 701.6 to 702.1 m borehole length, including the water bearing fracture at 701.9 m. The non-adjusted length is marked with black and the adjusted true length is marked with red /9/.*

Appendix 4

Measurements information, KFM11A



Borrhålschemmac, Id:KE 011 Anm. Ja

	Typ	Id	Datum	Nod	Kanal
0.	ETB	temp	050914	2	15
1.	EPHB	G38	061009	2	1
2.	ECB	C6-96	040913	2	2
3.	EPHIB	G25	061009	2	3
4.	EREFB	R-22	061009	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

Sond 2: 100000100111111

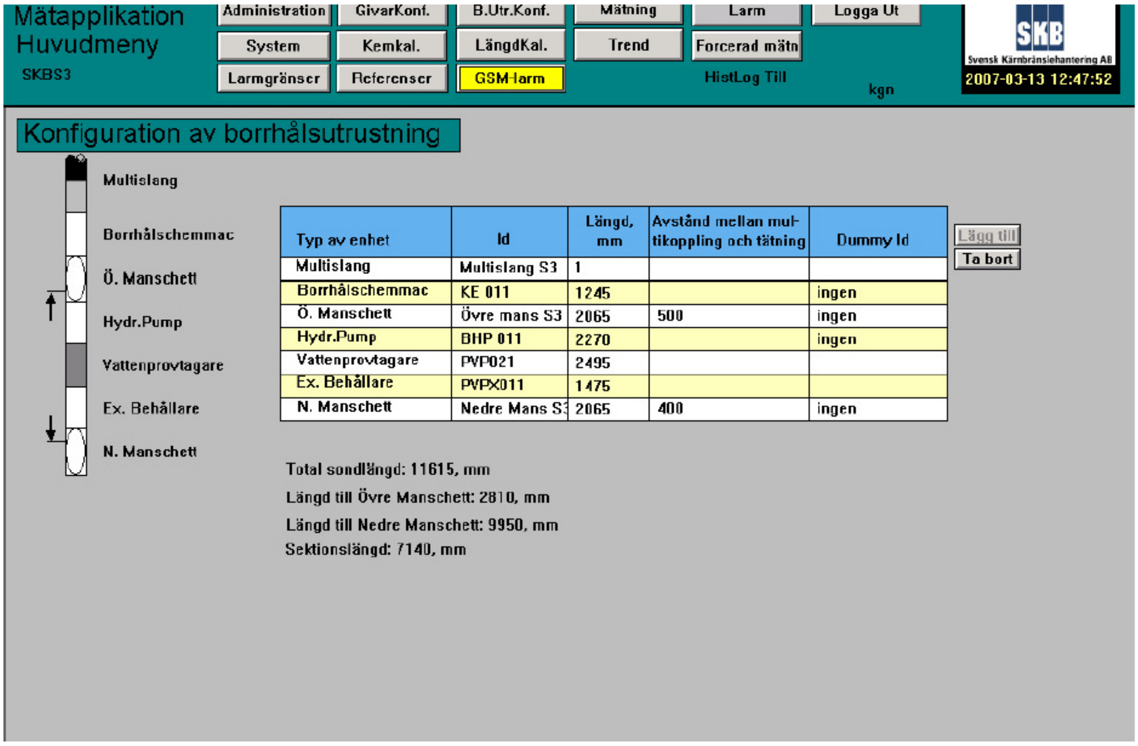
Ytchemmac, Id: Ytchemmac Anm. Ja

	Typ	Id	Datum	Nod	Kanal
9.	EKONDY	EKONDY	050914	3	17
10.				0	0
11.				0	0
12.	EO2Y	3.17	050914	4	17
13.				0	0
14.	ETIY	Temp O2	050914	4	18
15.				0	0
16.				0	0
17.				0	0
18.				0	0
19.				0	0
20.	EAUY	PN-1	061103	3	2
21.				0	0
22.	EPTY	P9-1	060704	3	5
23.	EPHIY	P9-4	060704	3	6
24.	EREF1Y	P9-3	060704	3	4
25.	EPHY	P9-4	060704	3	1
26.	ECY	Mcthrom	050222	3	3
-	Q	Flöde	011003	4	9
-	V1Y	-	011003	3	19

Sond 3: 100011100111111

Sond 4: 100000100000001

Figure A4-1. Electrode configuration, section 447.5–454.6 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	BHP 011	2270		ingen
Vattenprovtagare	PVP021	2495		
Ex. Behållare	PVPX011	1475		
N. Manschett	Nedre Mans S3	2065	400	ingen

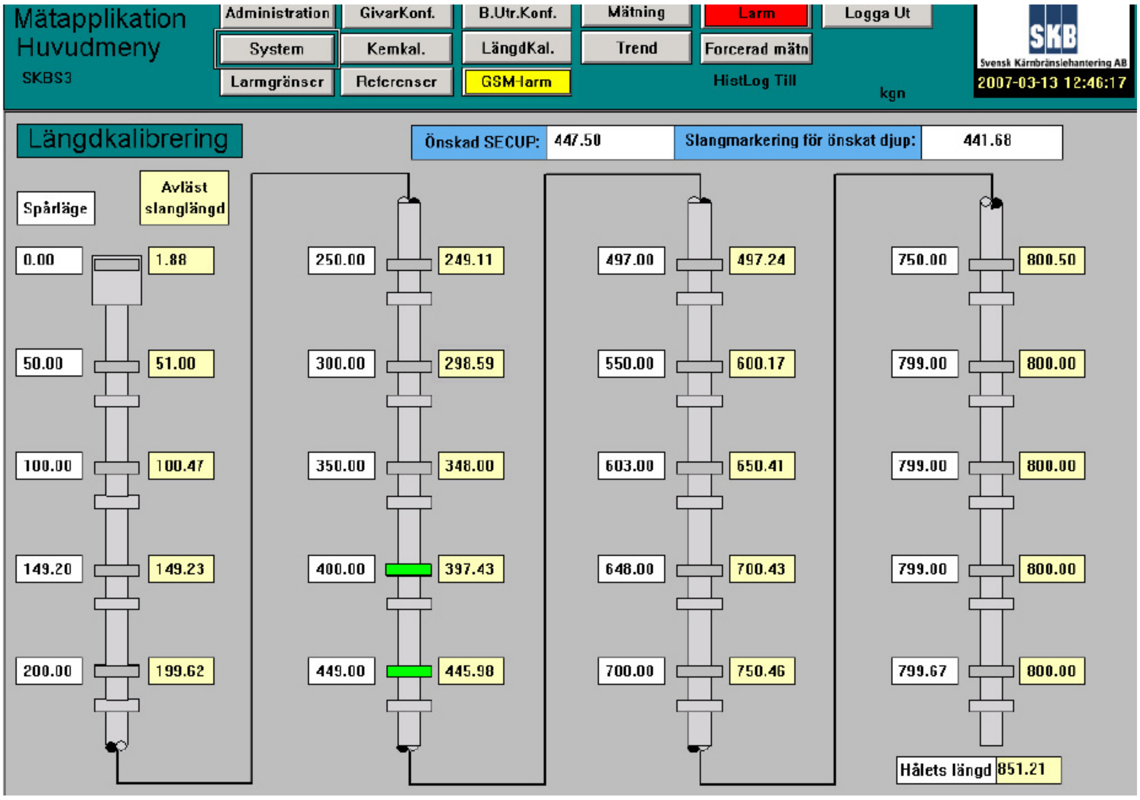
Total sondlängd: 11615, mm

Längd till Övre Manschett: 2810, mm

Längd till Nedre Manschett: 9950, mm

Sektionslängd: 7140, mm

Figure A4-2. Configuration of downhole equipment, section 447.5–454.6 m.



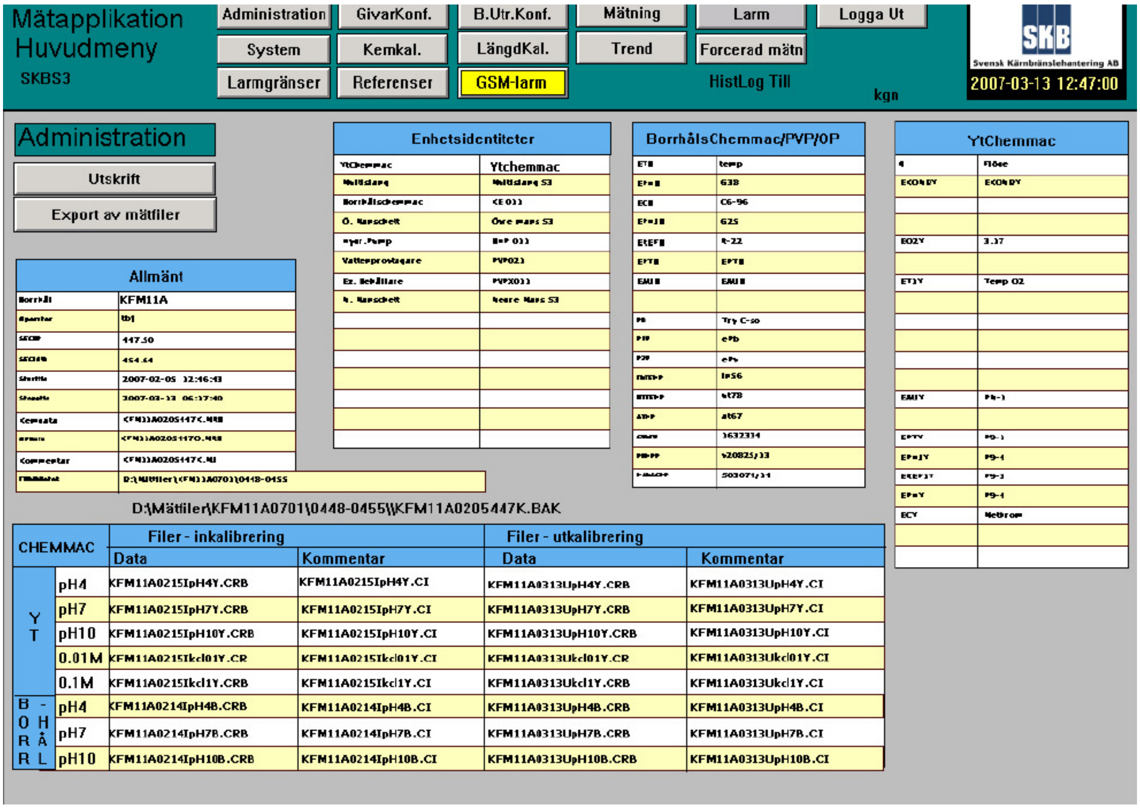
Önskad SECUP: 447.50

Slangmarkering för önskat djup: 441.68

Spårläge	Avläst slanglängd
0.00	1.88
50.00	51.00
100.00	100.47
149.20	149.23
200.00	199.62
250.00	249.11
300.00	298.59
350.00	348.00
400.00	397.43
449.00	445.98
497.00	497.24
550.00	600.17
603.00	650.41
648.00	700.43
700.00	750.46
750.00	800.50
799.00	800.00
799.00	800.00
799.00	800.00
799.67	800.00

Hålets längd 851.21

Figure A4-3. Length calibration, section 447.5–454.6 m.



Allmänt	
Borrhål	KFM11A
[illegible]	[illegible]
SECUP	447.50
SECLOW	454.64
Starttid	2007-02-05 12:46:43
Stopptid	2007-03-13 06:17:40
Kemdata	KFM11A0205447K.NRB
[illegible]	KFM11A0205447O.NRB
Kommentar	KFM11A0205447K.NI
[illegible]	D:\Mätfiler\KFM11A0701\0448-0455

D:\Mätfiler\KFM11A0701\0448-0455\\KFM11A0205447K.BAK

Enhetsidentiteter	
YtChemmac	Ytchemmac
Multislang	Multislang S3
Borrhålschemmac	KE011
Ö. Manschett	Övre mans S3
Hydr.Pump	[illegible]
Vattenprovtagare	PVP021
Ex. Behållare	PVPX011
N. Manschett	Nedre Mans S3

BorrhålsChemmac/PVP/OP	
[illegible]	temp
[illegible]	638
[illegible]	C6-96
[illegible]	625
[illegible]	R-22
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	Try C-so
[illegible]	ePb
[illegible]	[illegible]
[illegible]	Ir56
[illegible]	[illegible]
[illegible]	at67
[illegible]	1632314
[illegible]	[illegible]
[illegible]	[illegible]

YtChemmac	
[illegible]	Flöde
EKONDY	EKONDY
EO2Y	3.17
ET1Y	Temp O2
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
ECY	Metrom

CHEMMAC		Filer - inkalibrering		Filer - utkalibrering	
		Data	Kommentar	Data	Kommentar
YT	pH4	KFM11A0215IpH4Y.CRB	KFM11A0215IpH4Y.CI	KFM11A0313UpH4Y.CRB	KFM11A0313UpH4Y.CI
	pH7	KFM11A0215IpH7Y.CRB	KFM11A0215IpH7Y.CI	KFM11A0313UpH7Y.CRB	KFM11A0313UpH7Y.CI
	pH10	KFM11A0215IpH10Y.CRB	KFM11A0215IpH10Y.CI	KFM11A0313UpH10Y.CRB	KFM11A0313UpH10Y.CI
	0.01M	KFM11A0215Ikcl01Y.CR	KFM11A0215Ikcl01Y.CI	KFM11A0313Ukcl01Y.CR	KFM11A0313Ukcl01Y.CI
	0.1M	KFM11A0215Ikcl1Y.CRB	KFM11A0215Ikcl1Y.CI	KFM11A0313Ukcl1Y.CRB	KFM11A0313Ukcl1Y.CI
BORR - HÅL	pH4	KFM11A0214IpH4B.CRB	KFM11A0214IpH4B.CI	KFM11A0313UpH4B.CRB	KFM11A0313UpH4B.CI
	pH7	KFM11A0214IpH7B.CRB	KFM11A0214IpH7B.CI	KFM11A0313UpH7B.CRB	KFM11A0313UpH7B.CI
	pH10	KFM11A0214IpH10B.CRB	KFM11A0214IpH10B.CI	KFM11A0313UpH10B.CRB	KFM11A0313UpH10B.CI

Figure A4-4. Administration, section 447.5–454.6 m.

Flow and pressure measurements, KFM11A

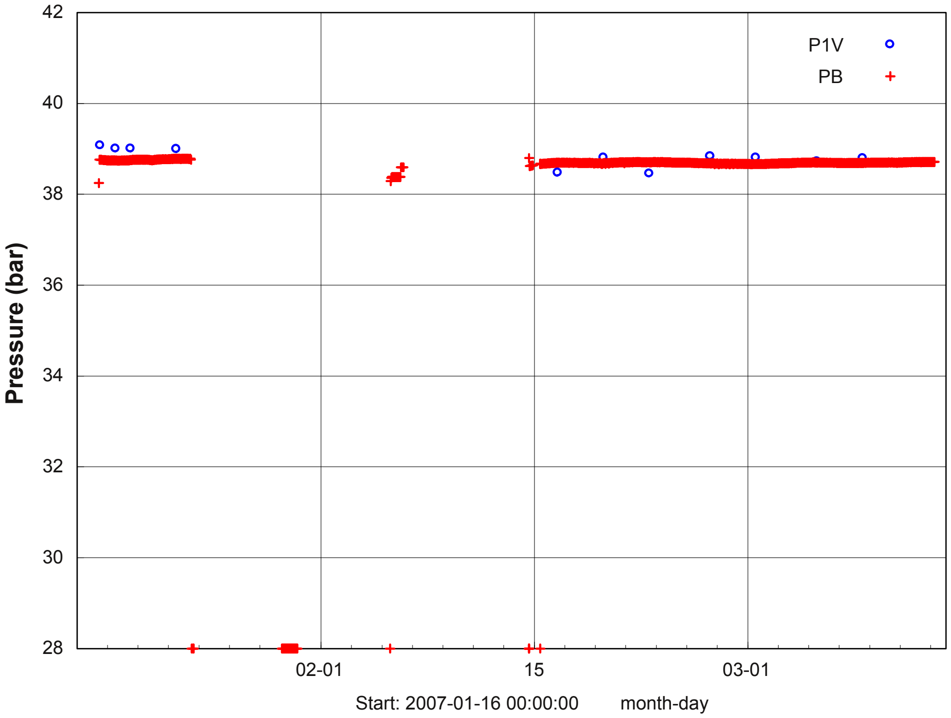


Figure A5-1. *Pressure measurements (P1V and PB) in section 447.5–454.6 m. The sensor P1V measures the pressure within the section and is placed in the in situ sampling unit. This value was manually recorded during the measurement period. The sensor PB, placed in the borehole Chemmac, measures the pressure above the section.*

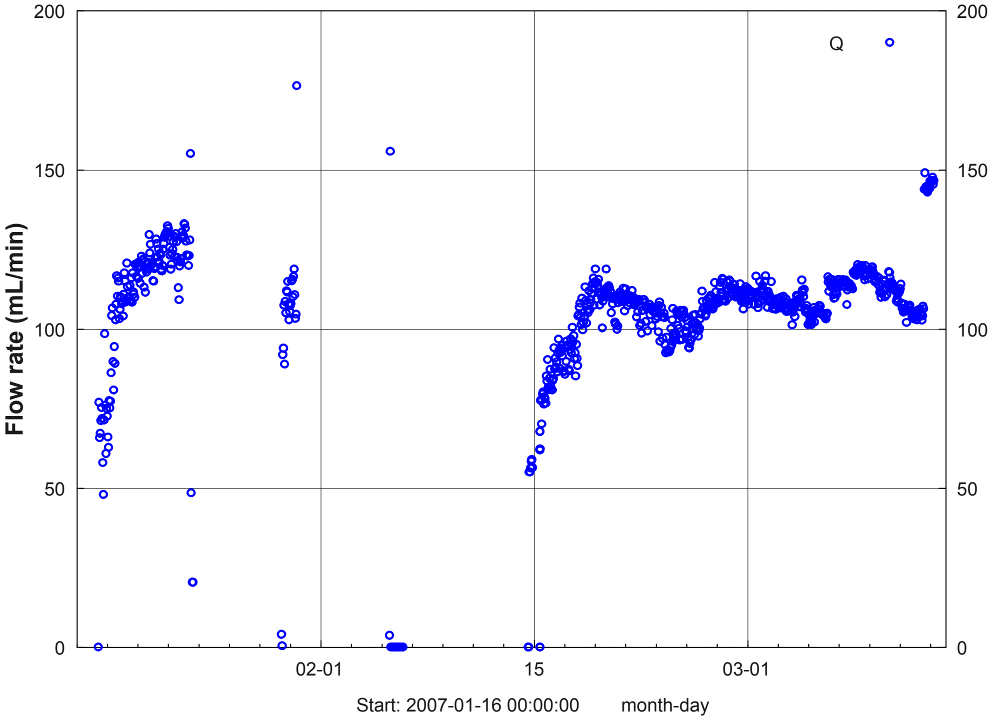


Figure A5-2. *Pumping flow rate (Q) in section 447.5–454.6 m.*

Appendix 6

Sampling and analytical methods

Table A6-1. Sample handling routines 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	No	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^-, SO_4, 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 (1 mL 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	Yes	Ev 1 mL 1 M NaOH+ 1 mL 1 M 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 (Acid washed)	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 (Acid washed)	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	Not critical (month)

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/ conservation*	Analysis method	Analysis within – or delivery time to lab
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
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	$\delta^{2}H$, $\delta^{18}O$	Plastic	100	No	–	MS	Not critical (month)
Tritium	^{3}H (enhanced.)	Plastic (dry bottle)	500	No	–	LSC	
Chlorine-37	^{37}Cl	Plastic	100	No	–	ICP MS	Not critical (month)
Carbon isotopes	^{13}C, pmC	Plastic (HDPE)	100×2	No	–	(A)MS	A few days
Sulphur isotopes	^{34}S	Plastic	500–1,000	No	–	Combustion, MS	No limit
Strontium-isotopes	$^{87}Sr/^{86}Sr$	Plastic	100	No	–	TIMS	Days or Week
Uranium and Thorium isotopes	^{234}U, ^{235}U, ^{238}U, ^{232}Th, ^{230}Th	Plastic	50 1,000	No	–	Chemical separat. Alfa/ gamma spectrometry	No limit
Boron isotopes	$^{10}B/^{11}B$	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP – MS	No limit
Radon and Radium isotopes	^{222}Rn, ^{226}Ra	Plastic	500–1,000	No	No	LSS	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	Polycarbonate filter	0.4, 0.2 and 0.05 µm	–	Ar atmosphere	ICP-AES ICP-MS	Immediate transport
Fractionation; Humic and fulvic acids, inorganic constituents	< 1,000 D > 1,000 D but < 5,000 D > 5,000 D	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

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/ conservation*	Analysis method	Analysis within – or delivery time to lab
Nutrient salt + silicate	NO_2, NO_3, NO_2+NO_3, NH_4, PO_4, SiO_4	Sample tubes, plastic	25×2 250	No	No, frozen immediately***	Spectrophotometry	Short transportation time
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.

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
LSS	Liquid Scintillation Spectrometry
(A)MS	(Accelerator) Mass Spectrometry
GC	Gas Chromatography

Table A6-2. 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^-	Mohr- titration	> 70	mg/L	5%	< 10%
Cl^-	IC	1–100		6%	10%
SO_4	IC	1	mg/L	10%	15%
Br^-	IC	0.2	mg/L	9%	20%
Br^-	ICP	0.001		15%	
F^-	IC	0.1	mg/L	10%	20%
F^-	Potentiometric	–		–	
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%

Component	Method	Reporting limits or range		Unit	Measurement uncertainty[3]	"Total" uncertainty[4]
SiO_4	Spectrophotometry	1		µg/L	3% (> 200 µg/L)	–
O_2	Iodometric 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%
δ^2H	MS	2		‰ SMOW[5]	1‰	–
$\delta^{18}O$	MS	0.1		‰ SMOW[5]	0.2‰	–
^3H	LSC	0.8 eller 0.1		TU[6]	0.8 eller 0.1	Correct order of size
^{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]	–	–
$\delta^{34}S$	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]	–	–
234U, 235U, 238U, 232Th, 230Th	Alfa spectr.	0.0005		Bq/L[12]	5%	–
222Rn, 226Rn	LSS	0.03		Bq/L	5%	–

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:
   $\text{pmC} = 100\times e^{((1950-y-1.03t)/8274)}$
   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 7

Quantification of colloids in natural groundwater from Forsmark boreholes KFM11A, section (447.5–454.64) m and KFM08D, sections (828.4–835.54) m and (669.7–676.84) m

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Introduction

Colloid analysis has been performed in groundwater samples collected during the site investigation program at Forsmark, close to Forsmark nuclear power station, Sweden. Samples from two boreholes and different sampling sections have been collected in stainless steel cylinders, preventing as much as possible the oxidation of the anoxic groundwater samples. 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 complete geochemical 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 background colloid concentration in these specific boreholes and to compare the data with those obtained from other sites.

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 in Figure A7-1. 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 (N/ml) are given relative to a calibration with polystyrene reference colloids. Mass concentrations are calculated by assuming an average colloid density of 2.7 g/cm^3 and spherical particle shape. A more detailed description of data evaluation is given in /1/.

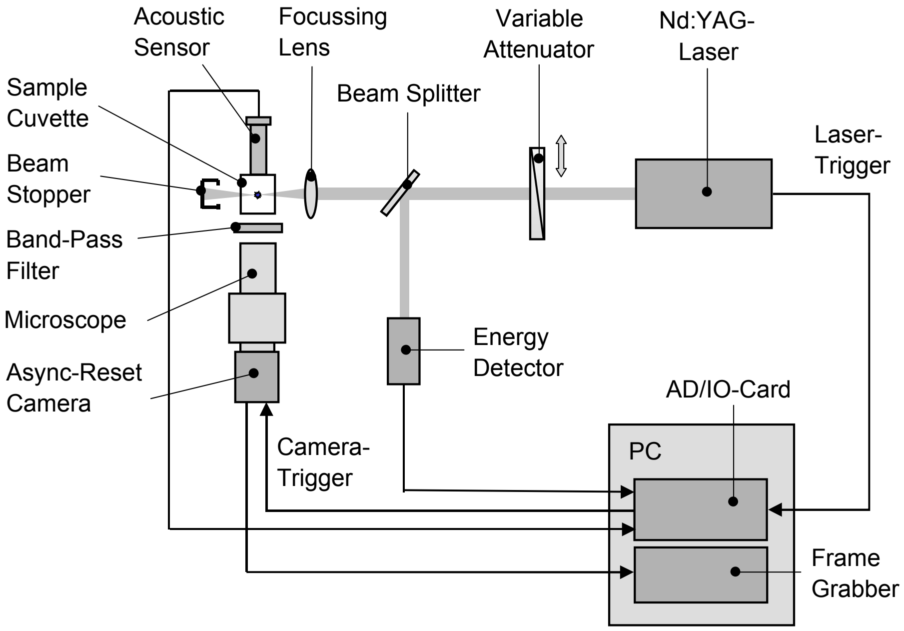


Figure A7-1. Schematic diagram of the mobile laser-induced breakdown detection system.

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.

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 groundwater colloids sampled at a natural analogue site (Ruprechtov, Czech Republic).

Figure A7-2 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 Figure A7-2). 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 groundwater 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.

Borehole sampling

Samples were taken

- At March 13, 2007 from Forsmark borehole KFM11A, section between (447.5–454.64) m. The vertical depth (inclined borehole) was approximately (387–393) m with a measured pressure in the borehole section of ~ 38 bar. The sample is filled in the SKB steel cylinder PVB 220.

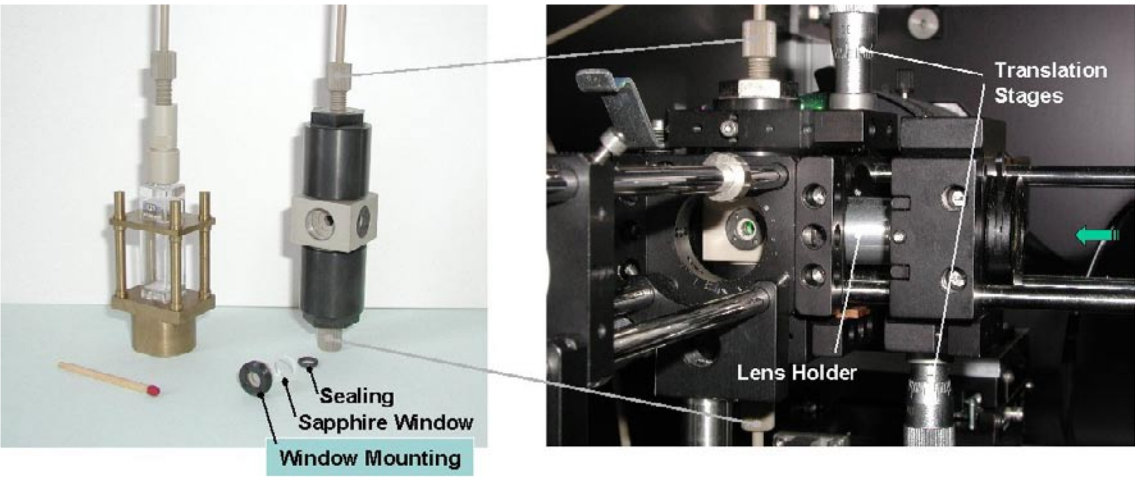


Figure A7-2. LIBD high-pressure flow-through detection cell (left: conventional flow-through silica detection cell).

- At May 2, 2007 from Forsmark borehole KFM08D, section between (828.4–835.54) m. The vertical depth was ~ (661.3–666.8) m with a measured pressure in the borehole section of 61.4 bar. The samples are filled in the SKB steel cylinders PVB 028 and PVB 9506-8.
- At June 26, 2007 from ForsmarK borehole KFM08D, section between (669.7–676.84) m. The vertical depth was ~ (537.8–543.4) m with a measured pressure in the borehole section of 50 bar. The samples are filled in the SKB steel cylinders PVB 203 and PVB 204.

The stainless steel cylinders (Figure A7-3) are groundwater 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 (SKB).

In general one day after sampling the cooled samples arrived at the INE where they have been stored in a fridge (Temp. about 10°C) until colloid detection several days later.

Configuration of laboratory experiments

Each sampling cylinder was connected with the LIBD detection cell and the detection cells for pH-, Eh-, electrical conductivity-, oxygen content-detection and for taking samples for chemical groundwater analysis. As far as possible pressure resistant versions of the sensors are selected. In the specifications of the Eh-/pH-electrodes (Hamilton POLILYTE PLUS/POLILYTE PRO) a maximum groundwater pressure of 50 bar is designated. The maximum pressure for the oxygen-detector (Mettler Toledo InPro 6900) is specified with 6 bar and the electrical conductivity-detector (InPro 7000-VP) is 34 bar.

A scheme of the corresponding laboratory setup is plotted in Figure A7-4 with an image of the experimental configuration in Figure A7-5.

Figure A7-3. SKB stainless steel sampling cylinder (left: piston side, right: mounting adapter side).

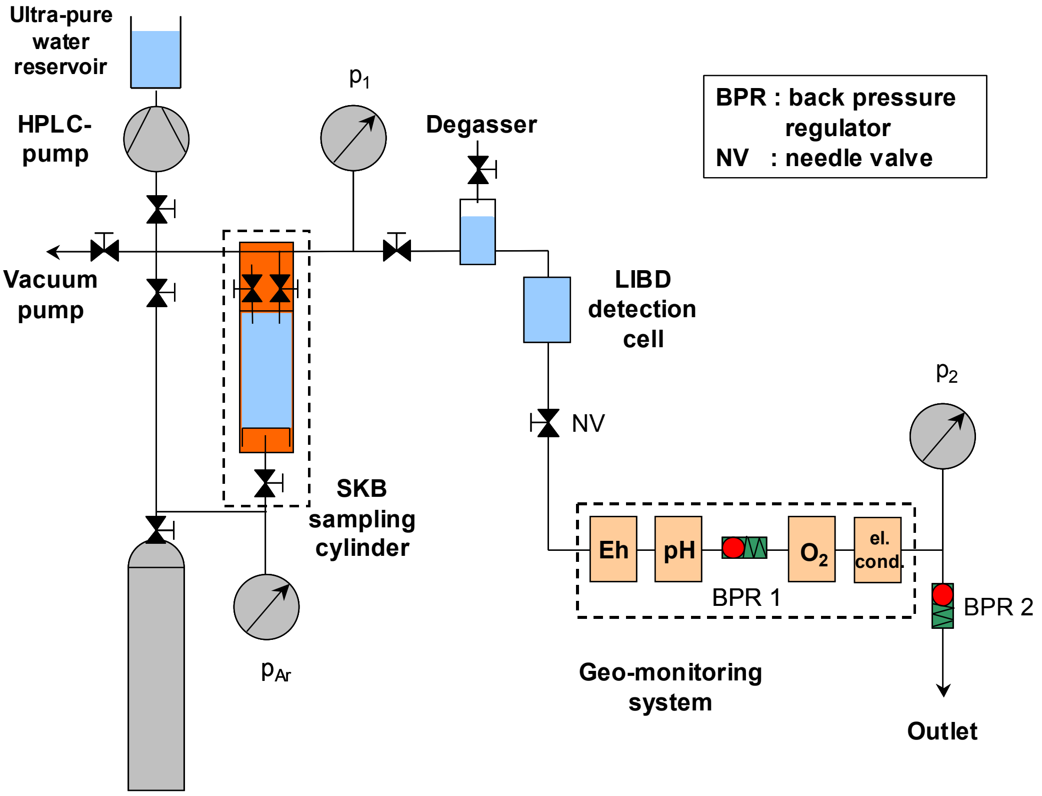


Figure A7-4. *Scheme of the laboratory setup for in-line LIBD colloid analysis and groundwater monitoring.*

Figure A7-5. *Experimental configuration.*

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 on the water side of the sampling cylinder with ultra-pure water and to set the water pressure according the hydrostatic pressure of the samples. This was the expected water pressure in the sampling cylinder. The gas side of the sampling cylinder is then filled with the corresponding Argon gas pressure.

Now one of the top valves of the sampling cylinder can be opened without contact of the sampled groundwater with atmospheric oxgen. With Argon gas the groundwater 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 for Eh, pH (back pressure regulator 1 set to 40 bar), Oxygen, a sensor for electrical conductivity and a sensor for the pressure detection are arranged downstream.

Before the sampling outlet an additional back pressure regulator, set to 5 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 do not contain the sampled groundwater, respectively.

Groundwater 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 SEM/EDX.

Results

Chemical analysis

Data from geo-monitoring as well as the chemical composition of five samples (two from the same groundwater) are displayed in Table A7-1.

The groundwater pH of (7.9–8.2) is equivalent to the pH detected so far in other Forsmark (7.3–8.4) and Äspö groundwater samples (7.3–7.8).

Additionally, the oxygen values (Table A7-1) demonstrate that geochemical conditions are maintained within all sampling containers during transport, storage and colloid detection. This indicates that a significant intrusion of atmosphere oxygen did not occur. In two groundwater containers an oxygen concentration of ~0.010 mg/l was detected. As these detected values are slightly higher than the sensors detection limit (0.001 mg/l) it might be caused by sensor instabilities (see logged raw data) during the measurement.

All three Forsmark groundwaters are determined by their relatively high Cl^--content of 3,300 mg/l to 7,900 mg/l. Whereas the chemical composition of Äspö and Forsmark groundwater is mainly characterized by the salinity from 3,000 to 14,000 mg/l chloride. The Forsmark DOC is considerably higher (~ 4 mg/l) than the DOC of the Äspö groundwater with the same salinity /4/.

Table A7-1. Monitored data of pH, Eh, el. conductivity, oxygen content and chemical analysis of the groundwater samples from Forsmark boreholes KFM11A, KFM08D.

Borehole ID		KFM11A	KFM08D		KFM08D	
Secup	m	447.5	828.4		669.7	
Seclow	m	454.64	835.54		676.84	
Sampling depth	m	387–393	661.3–666.8		537.8–543.4	
Hydr. pressure	bar	~ 38	~ 61.4		~ 50	
Container ID		**SKB PVB 220**	**SKB PVB 9506-8**	**SKB PVB 028**	**SKB PVB 204**	**SKB PVB 203**
Sample ID		**FOR09A**	**FOR10A**	**FOR11A**	**FOR12A**	**FOR13A**
pH		7.88	8.09	8	8.17	8.15
Redox (Ag/AgCl)	mV	166	–137	–96	18	23
Eh (SHE)	mV	380	77	118	232	237
el. cond.	mS/m	1,131	2,070	2,090	1,927	1,947
O_2 content	mg/l	0.004	0.188	0.098	0.316	0.14
Na^+	mg/l	1,194	1,825	1,782	1,747	1,620
K^+	mg/l	2.59	19.9	16	13.3	10.4
Ca^{2+}	mg/l	974	2,949	3,275	2,655	2,659
Mg^{2+}	mg/l	62.05	5.92	6.85	3.44	3.47
HCO_3^- (a)	mg/l	54.34	7.12	8	4.89	5.33
Cl^-	mg/l	3,293	7,954	7,780	7,077	7,381
SO_4^{2-}	mg/l	215.4	135.8	146.4	88.57	87.86
Br^-	mg/l	< 0.1	59	64.5	60.1	60.1
F^-	mg/l	< 0.1	1.27	1.19	1.34	1.35
Si^{4+}	mg/l	4.27		3.25	3.13	3.14
Fe-ICP	mg/l	3.17		1.5	2.2	2.96
Mn^{2+}	mg/l	0.44		0.066	0.05	0.06
Li^+	mg/l	0.07		0.031	0.025	0.025
Sr^{2+}	mg/l	16.5		37.9	26.7	26
DOC	mg/l	12.9	11.5	7.3	7.0	4.3
IC	mg/l	10.7	1.4	1.57	0.96	1.05

(a) calculated from IC.

Colloid analysis

Groundwater from KFM11A (447.5–454.64) m

Data determined with the laser-induced breakdown detection system are listed in Table A7-2. The volume of the samples was sufficient to perform four or five colloid measurements for each PVB container (see logged raw data). So temporal variations in the colloid concentration during the elution of the groundwater can be detected.

After evaluation of image processed data colloid size ditributions with two main average colloid fractions are derived. A 1st colloid fraction with diameters of 112–235 nm with corresponding mass concentrations of 3.3–20 µg/l are calculated.

590–850 nm particles with mass concentrations of 105–125 µg/l are the main part of the 2nd colloid fraction. This 2nd fraction contains more than 99% of the total particle mass, whereas the total colloid number density is determined of the 1st (smaller) colloid fraction.

Table A7-2. LIBD data with average colloid diameter and colloid concentration of the analyzed groundwater from Forsmark borehole KFM11A, (447.5–454.64) m.

Borehole ID		**KFM11A**			
Secup – Seclow	m	447.5–454.64			
Sampling depth	m	387–393			
Hydr. pressure	bar	~ 38			
Container ID		SKB PVB 220			
LIBD/det. ID		**FOR9B**	**FOR9D**	**FOR9F**	**FOR9G**
Trigger-pulses		2,500	2,700	3,000	3,000
1st coll. fraction (1):					
BD-events		514	306	547	336
BD-probability		0.2056	0.113	0.1823	0.112
coll. num. density	N/ml	2.7E+06	1.7E+06	1.1E+06	1.3E+06
coll. diam.	nm	126	112	235	131
coll. mass conc.	µg/l	7.7	3.3	20	4.2
2nd coll. fraction (2):					
BD-events		446	553	395	597
BD-probability		0.1784	0.2048	0.1317	0.199
coll. num. density	N/ml	2.7E+05	3.8E+05	1.4E+05	3.4E+05
coll. diam.	nm	673	587	849	613
coll. mass conc.	µg/l	116	107	125	112
Sum (1)+(2):					
coll. num. density	N/ml	3.0E+06	2.0E+06	1.2E+06	1.7E+06
coll. mass conc.	µg/l	124	110	145	116

Figure A7-6 shows the corresponding SEM images of groundwater KFM11A (447.5–454.64) m colloids. It is evident that two major colloid fractions exist. A 1st small colloid fraction has a size ~ 100 nm. This seems to be the component with the highest number density. The 2nd particle fraction (500–1,000) nm is the component with the lowest number density. Some particles seem to be agglomerates of the 1st fraction (Figure A7-6ab).

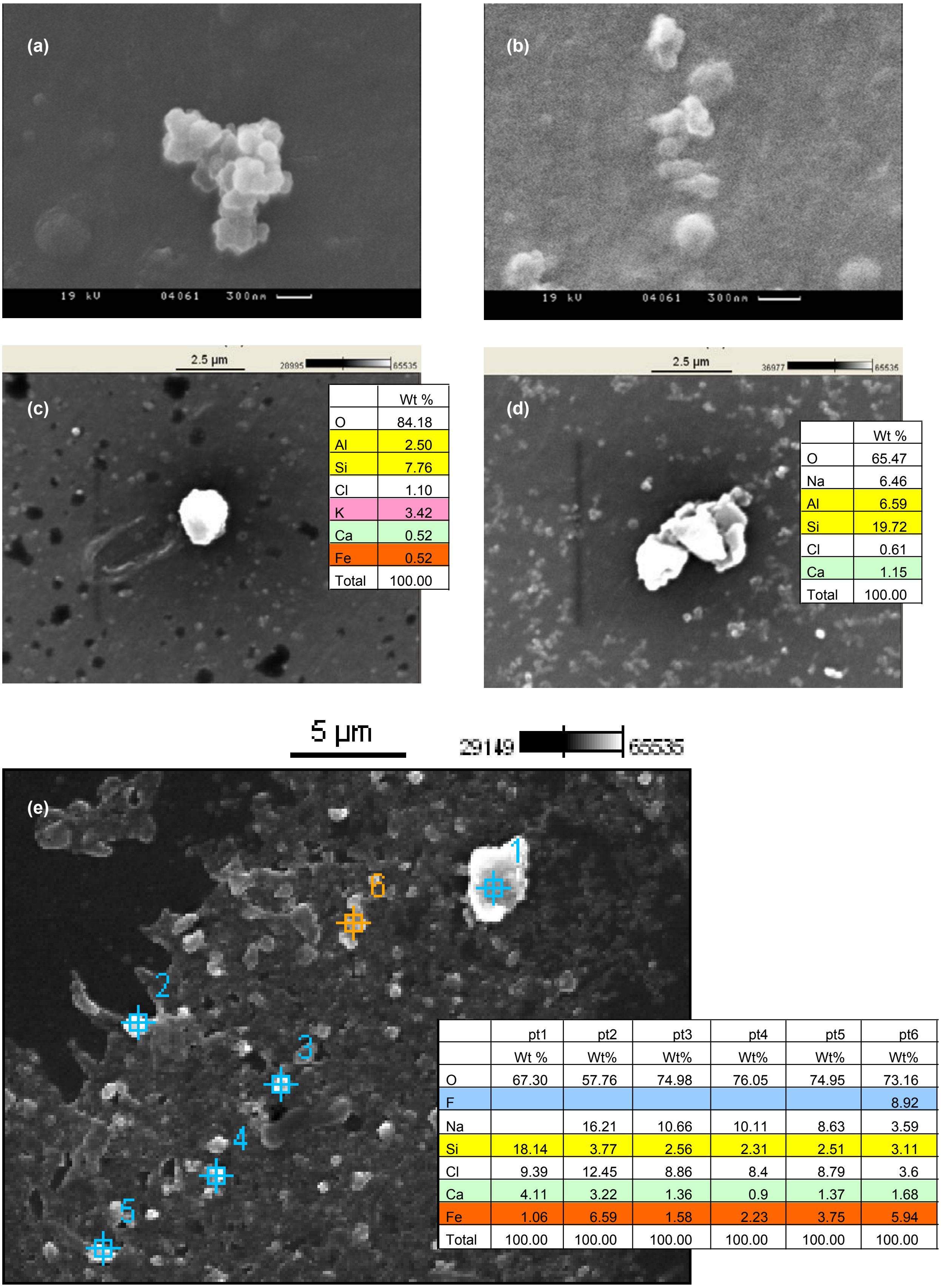
For the first fraction EDX element analysis was not possible because of the small quantities of colloidal material. The second colloid fraction consists of Al, Si, Ca, F, Fe (alumino-silicates, calcite, fluorite, Fe-oxihydroxides).

Groundwater from KFM08D (828.4–835.54) m

Table A7-3 shows the results for the elution of groundwater KFM08D (828.4–835.54) m. Only one colloid measurement (FOR10D) could be evaluated with one colloid fraction and an average diameter of 140 nm and 12 µg/l colloid mass concentration, respectively. In most cases, two colloid fractions must be considered. According the fluctuations during the groundwater elution, the smaller fraction consists of colloids with (20–80) nm diameter (concentration: (0.2–2.5) µg/l) or colloids with diameters < 20 nm with concentrations < 1 µg/l.

The larger colloid fraction consits of of colloids with (300–800) nm diameter and (20–120) µg/l colloid mass concentration, respectively.

The same effects occurred with the groundwater from both sampling cylinders PVB 9506-8 and PVB 028 (see logged raw data).



	Wt %
O	84.18
Al	2.50
Si	7.76
Cl	1.10
K	3.42
Ca	0.52
Fe	0.52
Total	100.00

	Wt %
O	65.47
Na	6.46
Al	6.59
Si	19.72
Cl	0.61
Ca	1.15
Total	100.00

	pt1	pt2	pt3	pt4	pt5	pt6
	Wt %	Wt%	Wt%	Wt%	Wt%	Wt%
O	67.30	57.76	74.98	76.05	74.95	73.16
F						8.92
Na		16.21	10.66	10.11	8.63	3.59
Si	18.14	3.77	2.56	2.31	2.51	3.11
Cl	9.39	12.45	8.86	8.4	8.79	3.6
Ca	4.11	3.22	1.36	0.9	1.37	1.68
Fe	1.06	6.59	1.58	2.23	3.75	5.94
Total	100.00	100.00	100.00	100.00	100.00	100.00

Figure A7-6. *SEM images of groundwater KFM11A (447.5–454.64) m colloids on a 50 nm track-etched Polycarbonate filter.*

Table A7-3. LIBD data with average colloid diameter and colloid concentration of the analyzed groundwater from Forsmark borehole KFM08D, (828.4–835.54) m.

Borehole ID		**KFM08D**					**KFM08D**				
Secup – Seclow	m	828.4–835.54					828.4–835.54				
Sampling depth	m	661.3–666.8					661.3–666.8				
Hydr. pressure	bar	~ 61.4					~ 61.4				
Container ID		SKB PVB 9506-8					SKB PVB 028				
LIBD/det. ID		**FOR10B**	**FOR10C**	**FOR10D**	**FOR10E**	**FOR10H**	**FOR11A**	**FOR11B**	**FOR11C**	**FOR11D**	**FOR11G**
Trigger-pulses		2,000	2,500	5,000	4,000	5,000	4,000	4,000	2,901	6,000	6,000
1st coll. fraction (1):											
BD-events		765	388	1,265	351	544	646	482	190	325	164
BD-probability		0.383	0.1552	0.2532	0.0878	0.1088	0.1615	0.1205	0.06549	0.05417	0.02733
coll. num. density	N/ml	2.3E+07	5.3E+06	3.0E+06			2.7E+07				6.3E+05
coll. diam.	nm	43	59	139	< 20	< 20	17	< 20	< 20	< 20	76
coll. mass conc.	µg/l	2.5	1.53	11.62	< 1	< 1	0.199	< 1	< 1	< 1	0.393
2nd coll. fraction (2):											
BD-events		233	226		582	586	680	686	588	834	680
BD-probability		0.1165	0.0904		0.1455	0.1172	0.17	0.1715	0.2027	0.139	0.1133
coll. num. density	N/ml	2.5E+05	2.2E+05		5.2E+05	4.6E+05	4.1E+05	3.9E+05	4.8E+05	1.7E+05	1.3E+05
coll. diam.	nm	491	441		342	311	465	488	479	790	834
coll. mass conc.	µg/l	43	27		29	20	58	64	75	117	103
Sum (1)+(2):											
coll. num. density	N/ml	2.3E+07	5.6E+08	3.0E+06			2.7E+07				7.5E+0.5
coll. mass conc.	µg/l	45	29	12	29	20	59	64	75	117	103

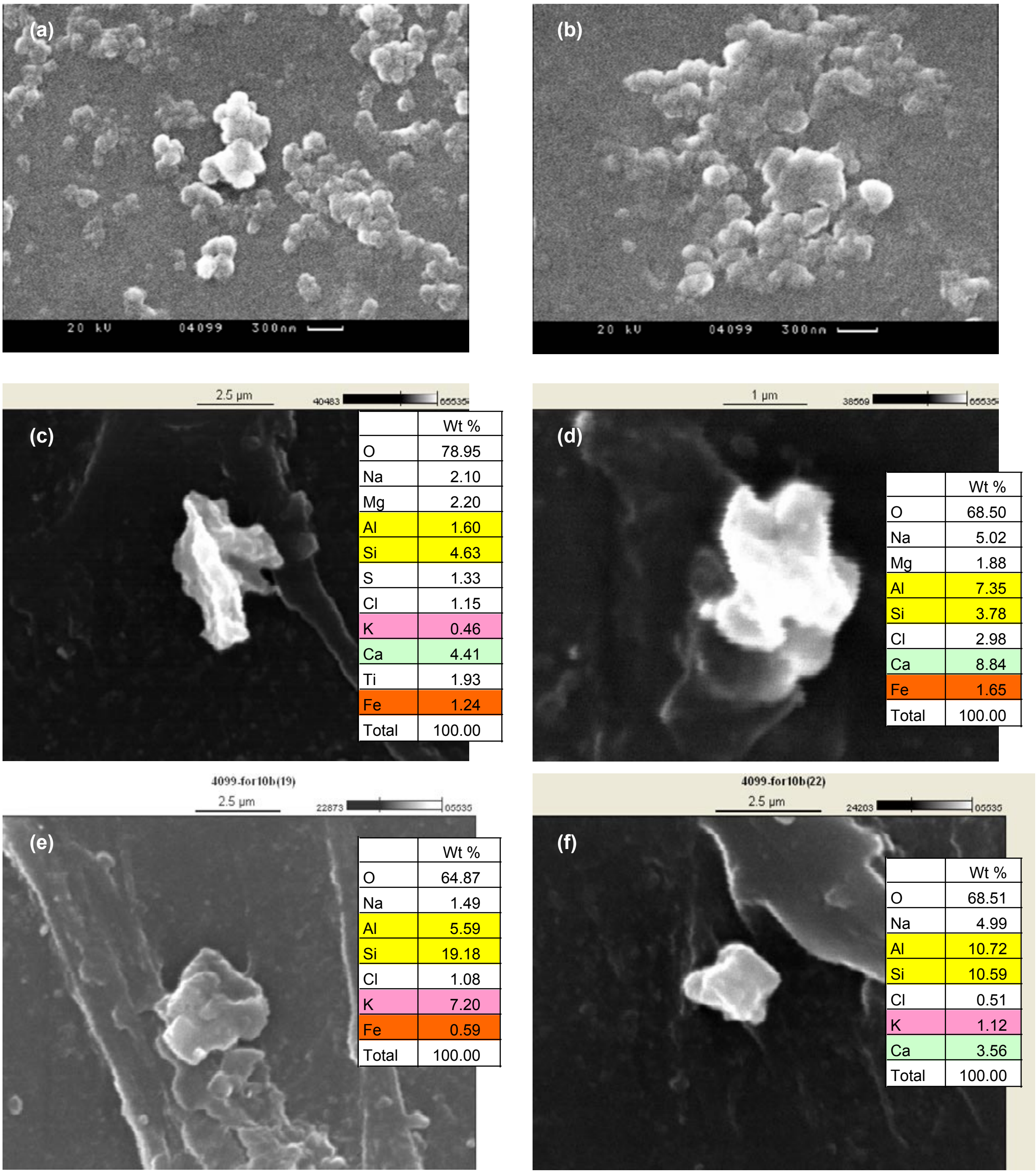
SEM images of this groundwater filter (Figure A7-7) show a big amount of colloids with diameters below 100 nm and a minor number of colloids with sizes around 1 µm. This means that the LIBD derived data including the existence of two main colloid fractions seem to be confirmed with the SEM.

Unfortunately, our SEM is not sensitive enough to allow a direct EDX element analysis of the 1st colloid fraction. With EDX analyzed elements of the 2nd larger colloid fraction are Al, Si (alumino-silicates, silicates), Fe, Ca.

Groundwater from KFM08D (669.7–676.84) m

The same borehole has been sampled again with two steel cylinders, but from a section 200 m higher in the borehole. With each groundwater sample 5 and 4 LIBD colloid measurements (Table A7-4) are performed, again to quantify temporal fluctuations caused by changing flow conditions.

During groundwater elution from both SKB steel cylinders PVB 204 and PVB 203 colloids with an average diameter of (< 20–30) nm (1st colloid fraction) and (620–1,300) nm (2nd colloid fraction) are detected. The corresponding mass concentrations for the 1st fraction are < 1 µg/l and for the 2nd fraction (800–4,500) µg/l.



(c)

	Wt %
O	78.95
Na	2.10
Mg	2.20
Al	1.60
Si	4.63
S	1.33
Cl	1.15
K	0.46
Ca	4.41
Ti	1.93
Fe	1.24
Total	100.00

(d)

	Wt %
O	68.50
Na	5.02
Mg	1.88
Al	7.35
Si	3.78
Cl	2.98
Ca	8.84
Fe	1.65
Total	100.00

(e)

	Wt %
O	64.87
Na	1.49
Al	5.59
Si	19.18
Cl	1.08
K	7.20
Fe	0.59
Total	100.00

(f)

	Wt %
O	68.51
Na	4.99
Al	10.72
Si	10.59
Cl	0.51
K	1.12
Ca	3.56
Total	100.00

Figure A7-7. *SEM images of groundwater KFM08D (828.4–835.54) m colloids on a 50 nm track-etched Polycarbonate filter.*

Table A7-4. LIBD data with average colloid diameter and colloid concentration of the analyzed groundwater from Forsmark borehole KFM08D (669.7–676.84) m.

Borehole ID		**KFM08D**					**KFM08D**			
Secup – Seclow	m	669.7–676.84					669.7–676.84			
Sampling depth	m	537.8–543.4					537.8–543.4			
Hydr. pressure	bar	~ 50					~ 50			
Container ID		SKB PVB 204					SKB PVB 203			
LIBD /det. ID		**FOR12A**	**FOR12B**	**FOR12C**	**FOR12D**	**FOR12E**	**FOR13A**	**FOR13B**	**FOR13C**	**FOR13D**
Trigger-pulses		1,111	954	947	1,250	1,453	962	844	858	469
1st coll. fraction (1):										
BD-events		251	263	237	111	131	132	195	124	110
BD-probability		0.226	0.276	0.25	0.089	0.09	0.168	0.231	0.144	0.23
Coll. num. density	N/ml			1.9E+07				1.7E+07	4.7E+08	7.1E+07
coll. diam.	nm	< 20	< 20	33	< 20	< 20	< 203	3	< 20	11
coll. mass conc.	µg/l	< 1	< 1	0.738	< 1	< 1	< 1	0.898	< 1	0.144
2nd coll. fraction (2):										
BD-events		860	691	710	1,139	1,322	800	649	734	359
BD-probability		0.774	0.724	0.75	0.911	0.91	0.832	0.769	0.855	0.765
coll. num. density	N/ml	1.5E+06	1.1E+06	9.3E+05	1.4E+06	1.9E+06	2.7E+06	1.6E+06	2.2E+06	2.1E+06
coll. diam.	nm	865	975	1,172	1,313	1,026	618	819	777	649
coll. mass conc.	µg/l	1,353.0	1,438	2,121	4,500	2,934	910	1,215	1,463	807
Sum (1)+(2):										
coll. num. density	N/ml			2.0E+07				1.9E+07	4.7E+08	7.3E+07
coll. mass conc.	µg/l	1,353	1,438	2,122	4,500	2,934	910	1,216	1,463	807

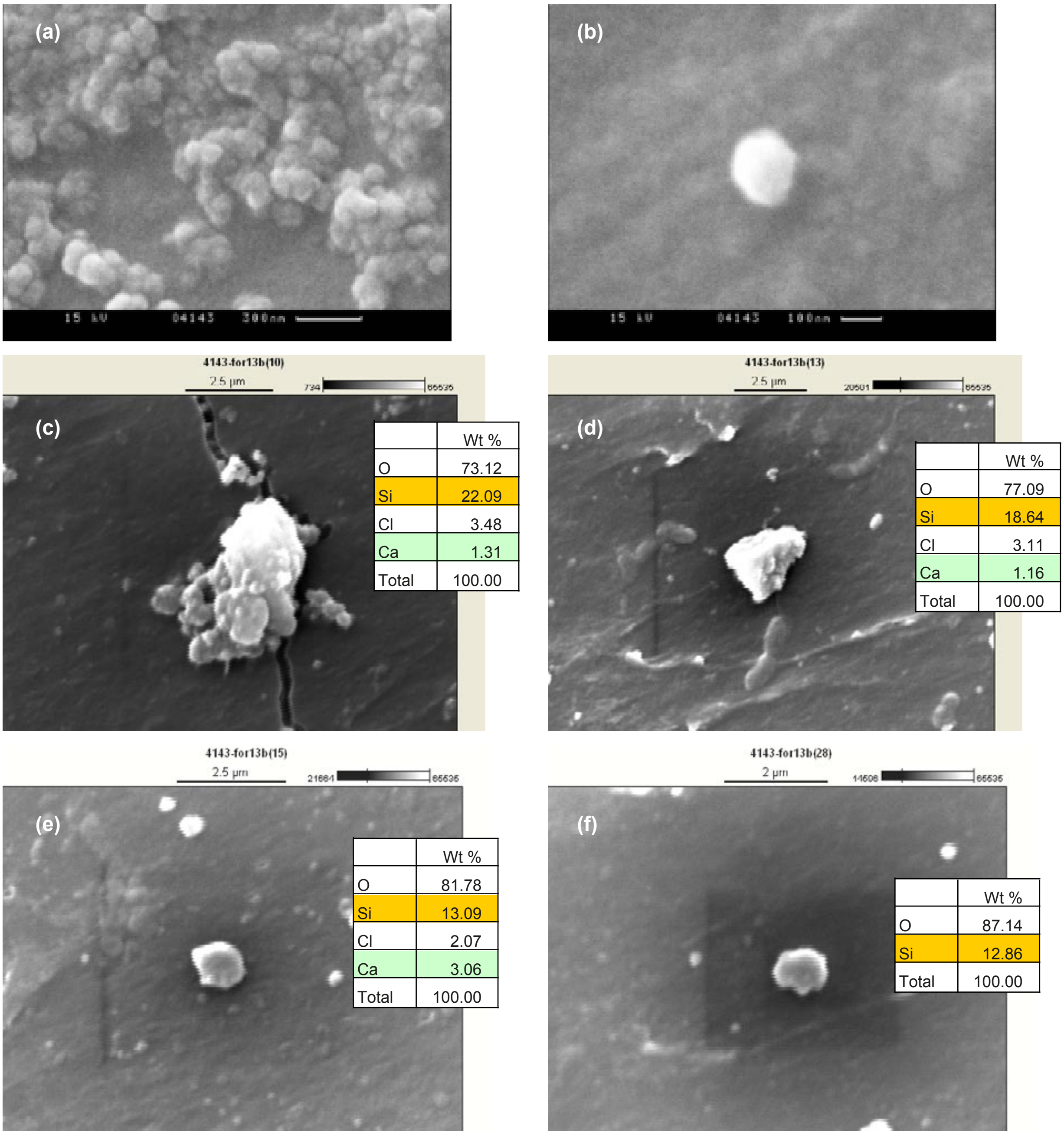
Corresponding SEM images in Figure A7-8 show colloids starting from a size around 100 nm (Figure A7-8b). They look like agglomerates (Figure A7-8a) of a basic form of colloids which was also found in other groundwater samples (Figure A7-6, Figure A7-7).

In this groundwater the larger particles (several µm) consisted of Si, Ca.

Comparison with Äspö and Laxemar data

In the Äspö colloid project /4/ a series of boreholes along the access tunnel have been sampled and their groundwater was directly analyzed with the mobile LIBD system. A correlation was drawn (Figure A7-9) between the colloid concentration and the Cl^- concentration of the groundwater. At a Cl^- concentration of about 4,000 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 KFM sample data from 307 m to 663 m sampling depth fits quite well into this correlation. But, according to the colloid concentration correlation with groundwater salinity we should expect lower colloid concentrations for samples KFM01D, KFM08A, and KFM08D from sampling depths deeper 430 m (Figure A7-9). Possible reasons for the somewhat high particle concentrations have been discussed in previous Forsmark reports.



(c)

	Wt %
O	73.12
Si	22.09
Cl	3.48
Ca	1.31
Total	100.00

(d)

	Wt %
O	77.09
Si	18.64
Cl	3.11
Ca	1.16
Total	100.00

(e)

	Wt %
O	81.78
Si	13.09
Cl	2.07
Ca	3.06
Total	100.00

(f)

	Wt %
O	87.14
Si	12.86
Total	100.00

Figure A7-8. *SEM images of groundwater KFM08D (669.7–676.84) m colloids on a 50 nm track-etched Polycarbonate filter.*

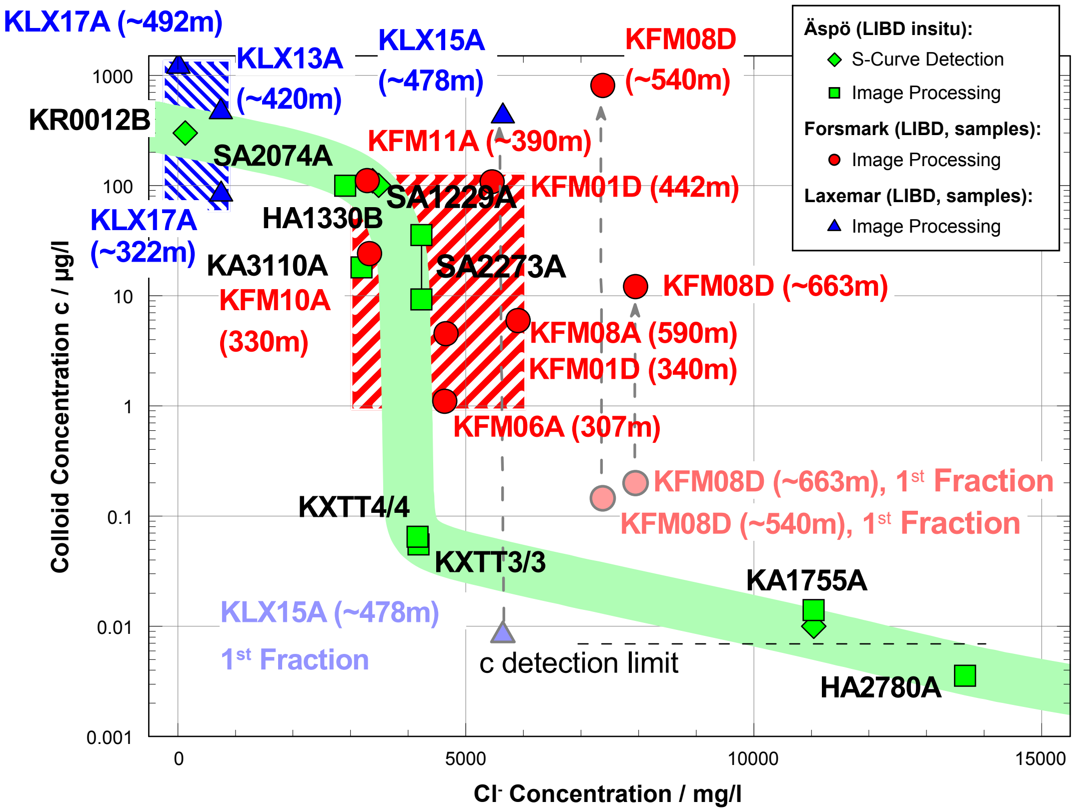


Figure A7-9. *Correlation between colloid concentration and chloride concentration in different groundwater from Äspö /2, 4/ and in Forsmark samples. ( ): sampling depths.*

For both groundwater from KFM08D, depth ~ 540 m and ~ 663 m, it was possible to perform a 2 fraction evaluation of the LIBD data. This evaluation of a small 1st colloid fraction with particle sizes around the detection limit (20 nm) agrees well with the data derived from the SEM images (Figure A7-7, Figure A7-8). If one postulates that the large 2nd colloid fraction (Calcite, Alumino-Silicates, Silicates, ..) are mainly mechanically erroded particles from borehole drilling, then the 1st colloid fraction may represent the undisturbed colloids of the natural groundwater in this borehole zone.

This new data come close to the Cl^- concentration dependency of the insitu-detected groundwater colloids in the Äspö-tunnel (Figure A7-9), especially for groundwater with Cl-concentrations > 5,000 mg/l.

References

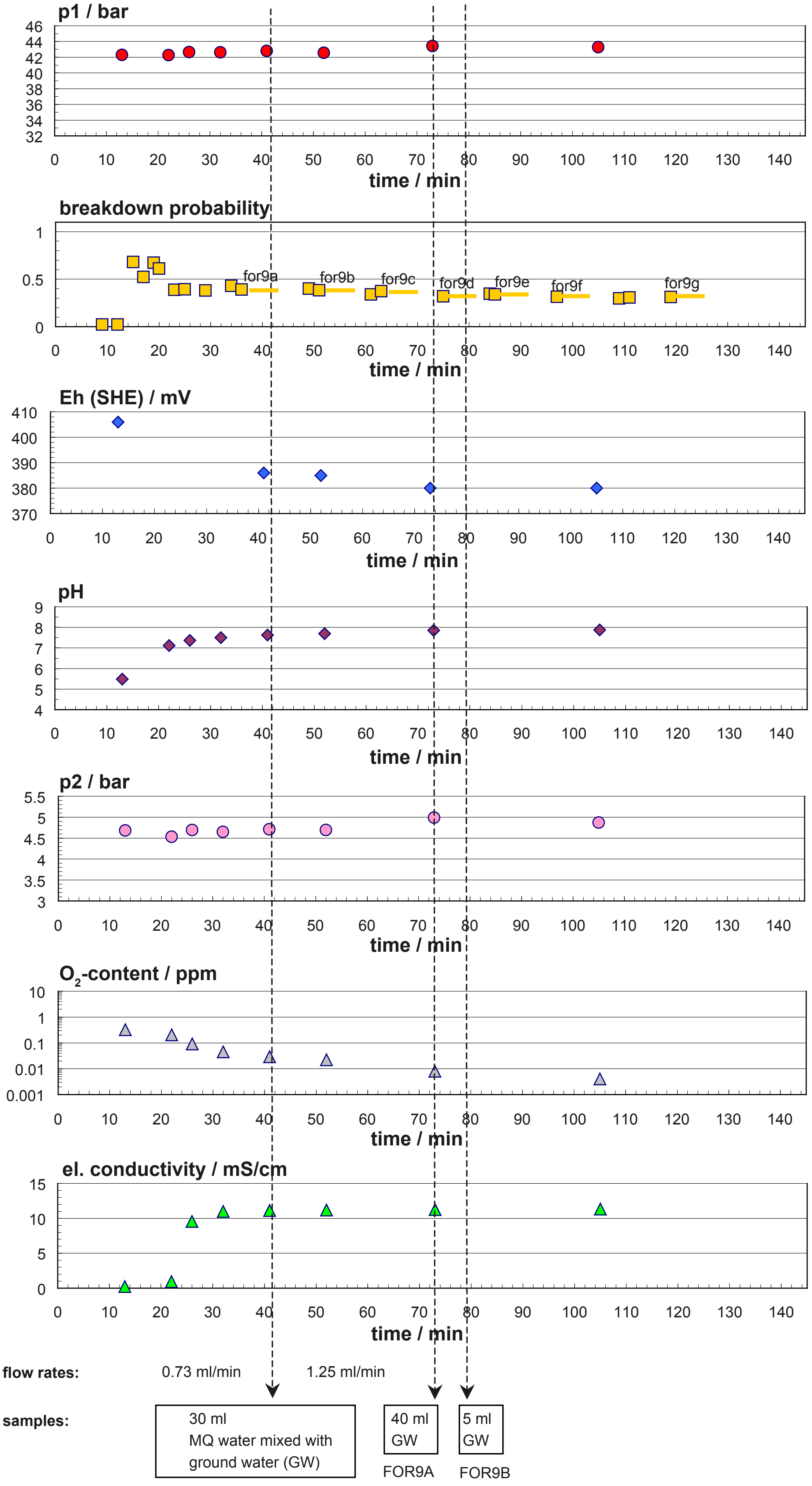
/1/ **Hauser W, Geckeis H, Kim J I, Fierz Th, 2002.** A mobile laser-induced breakdown detection system and its application for the in situ-monitoring of colloid migration, Coll. Surf. 203, 2002, 37–45

/2/ **Hauser W, Geckeis H, Götz R, 2003.** In situ determination of natural groundwater colloids in granite shear zones along the Äspö HRL Tunnel by LIBD, 27th Int. conf. on Scientific Basis for Nuclear Waste Management, Kalmar, S, June 15–18, 2003.

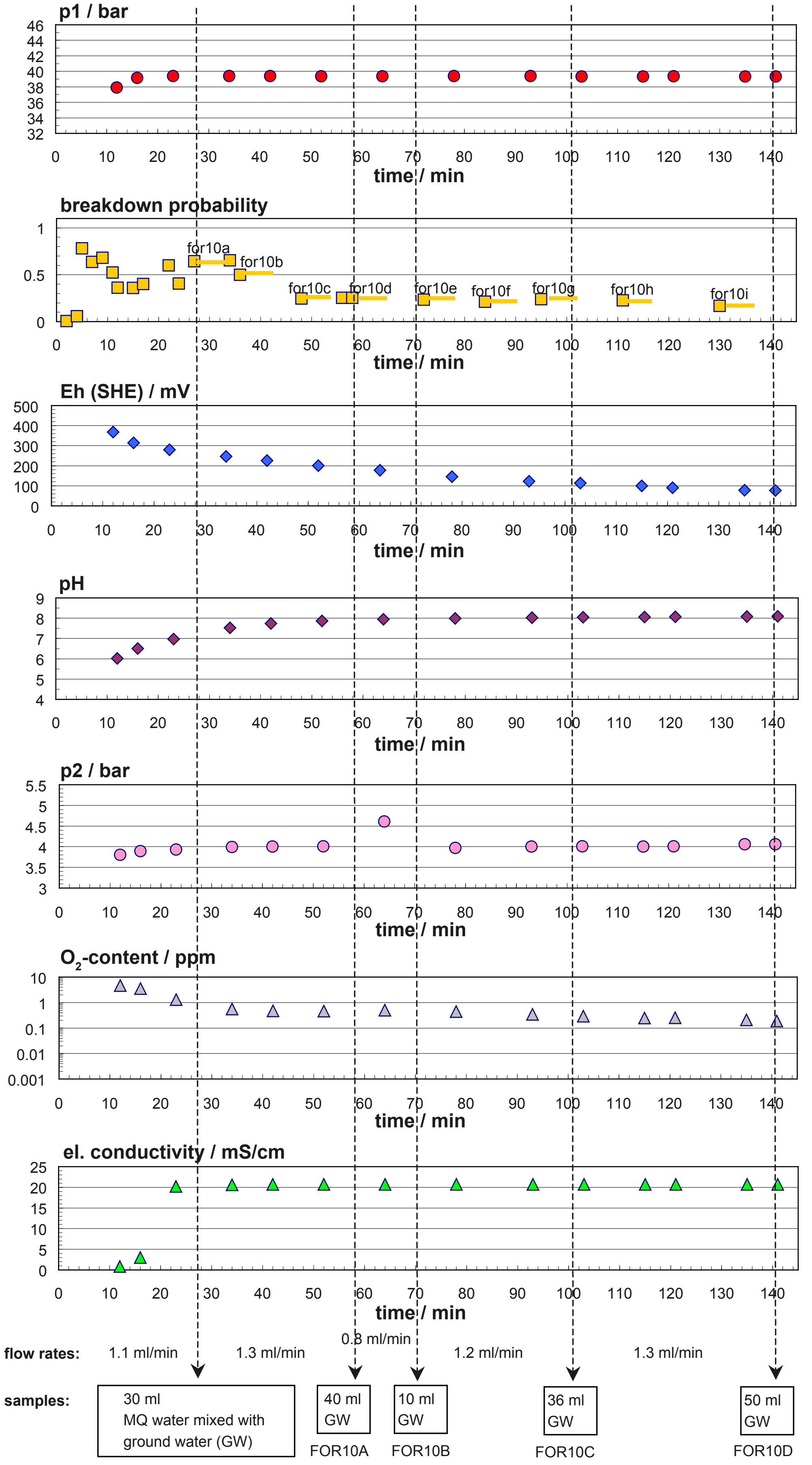
/3/ **Geckeis H, Schäfer T, Rabung T, Hauser W, Möri A, Missana T, Eikenberg J, Degueldre C, Fierz T, Alexander W R, 2003.** Inorganic colloid borne actinide migration studied under in-situ conditions at the Grimsel test site, 9th Int. conf. on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '03, Gyeongju, Korea, Sept. 21–26.

/4/ **Hauser W, Götz R, Geckeis H, Kienzler B, 2003.** In-situ colloid detection in granite groundwater along the Äspö Hard Rock Laboratory access tunnel, In Laaksoharju, M., Äspö Hard Rock Laboratory, Status report of the Colloid investigation conducted at the Äspö HRL during the years 2000–2003, SKB International Progress Report IPR-03-38, Stockholm.

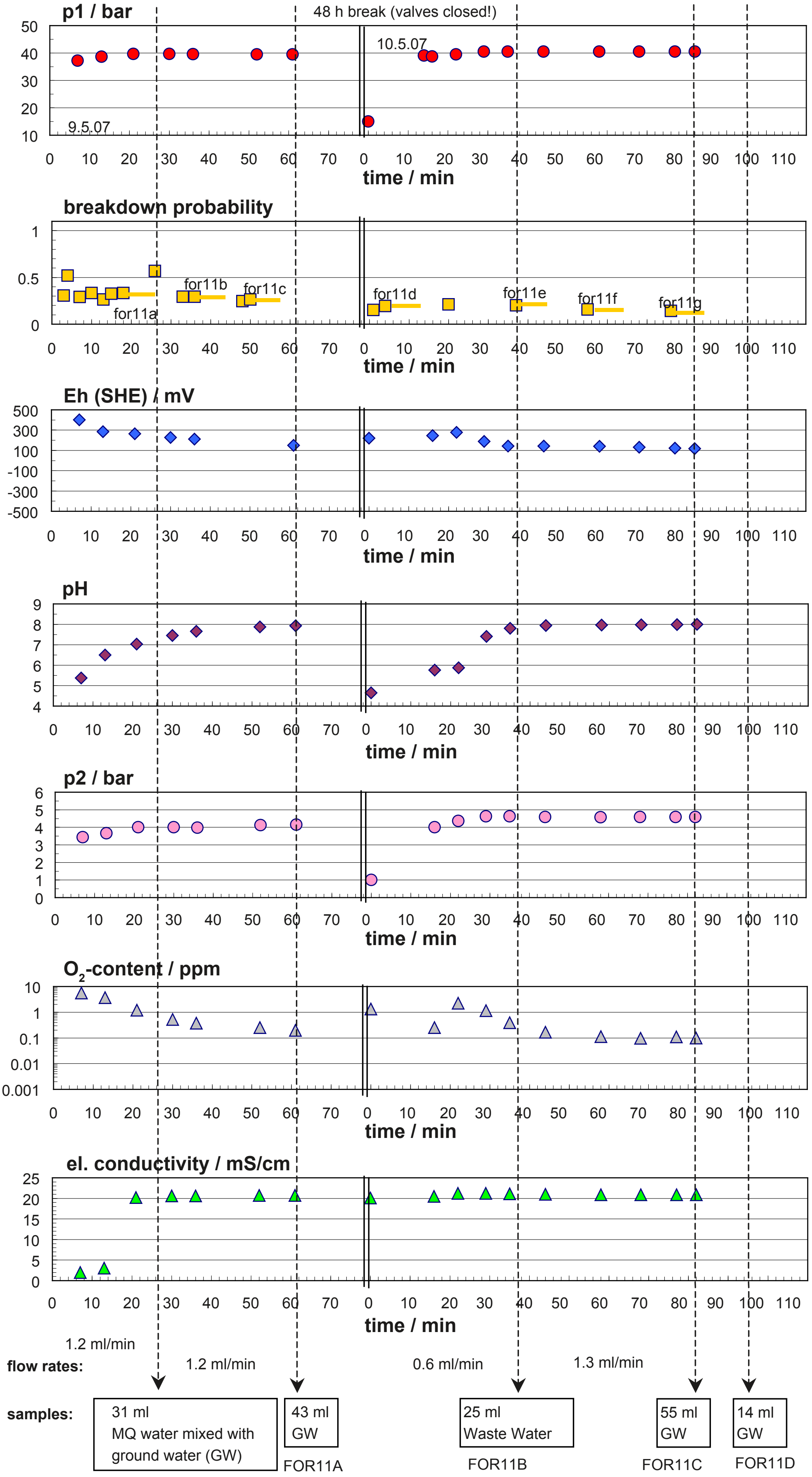
Logged raw data from elution of sampling container SKB PVB 220 (KFM11A (447.5-454.64 m))



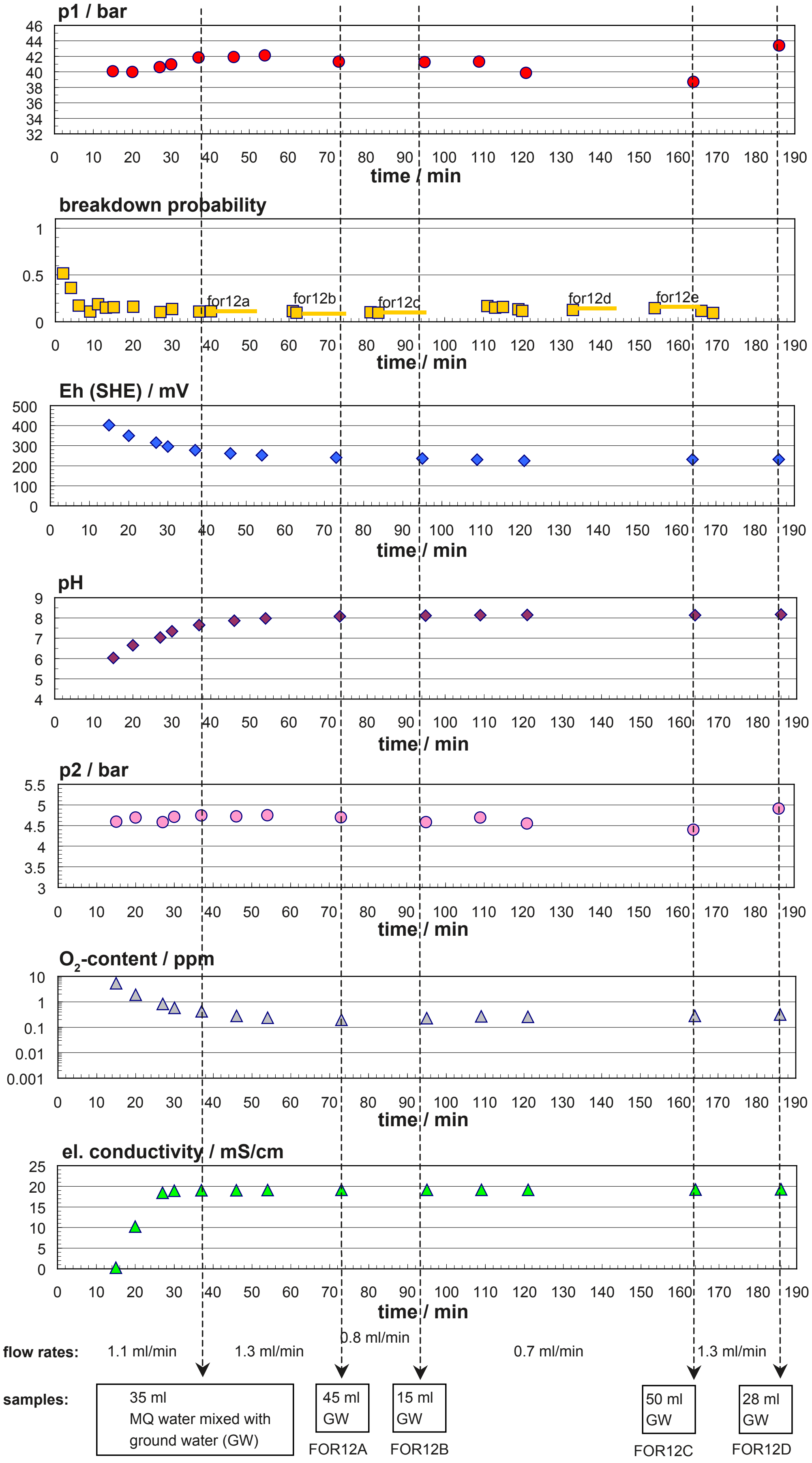
Logged raw data from elution of sampling container SKB PVB 9506-8 (KFM08D (828-835 m))



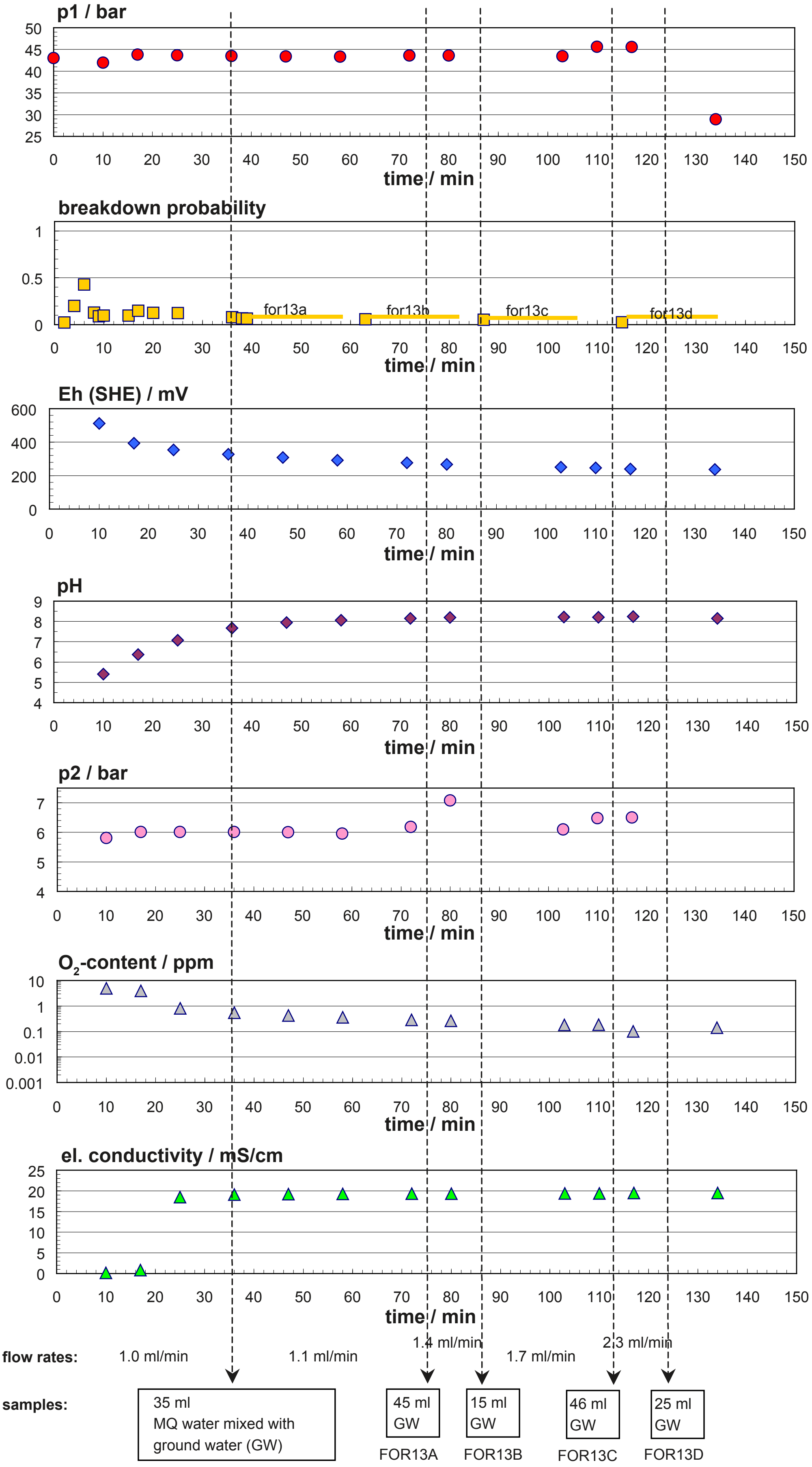
Logged raw data from elution of sampling container SKB PVB 028 (KFM08D (828-835 m))



Logged raw data from elution of sampling container SKB PVB 204 (KFM08D (670-677 m))



Logged raw data from elution of sampling container SKB PVB 203 (KFM08D (670-677 m))



Chemmac measurements in KFM11A, section 447.5–454.6 m

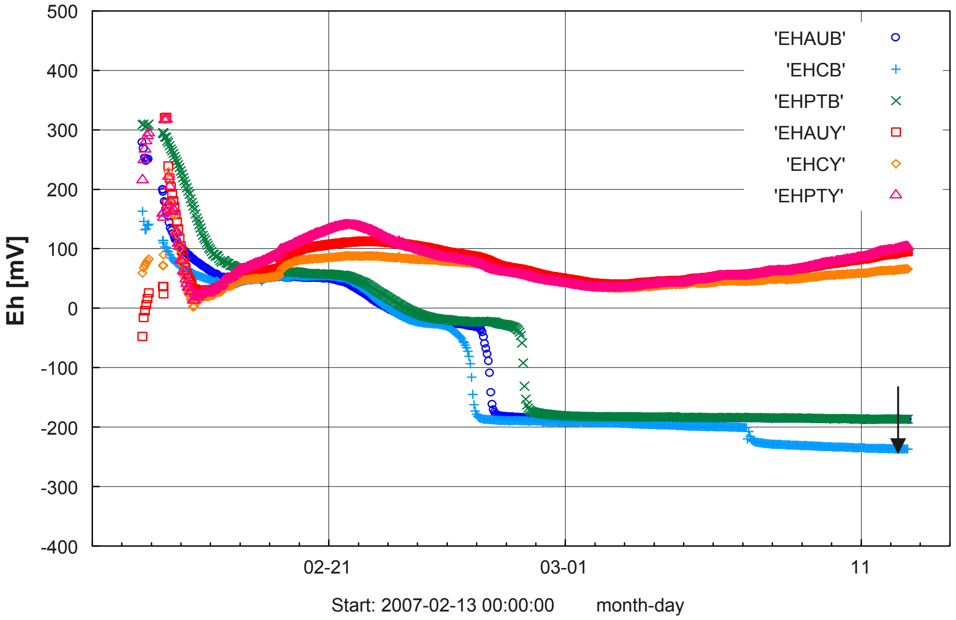


Figure A8-1. Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes in the borehole section (EHAUB, EHCB and EHPTB) and at the surface by gold, glassy carbon and platinum (EHAUY, EHCY and EHPTY). The arrow shows the chosen representative Eh values for the borehole section.

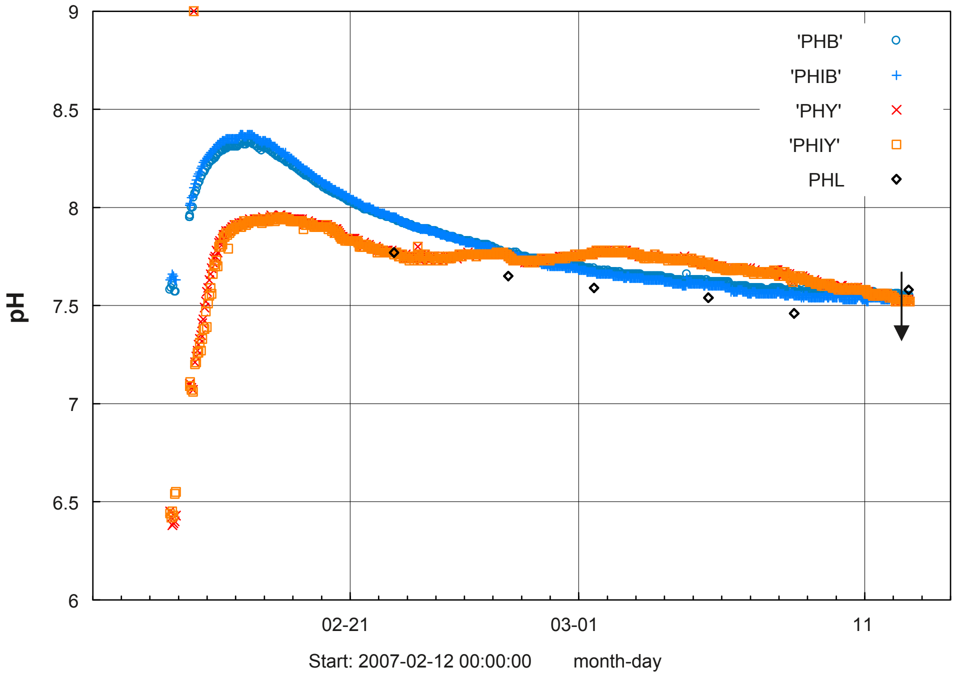


Figure A8-2. Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.

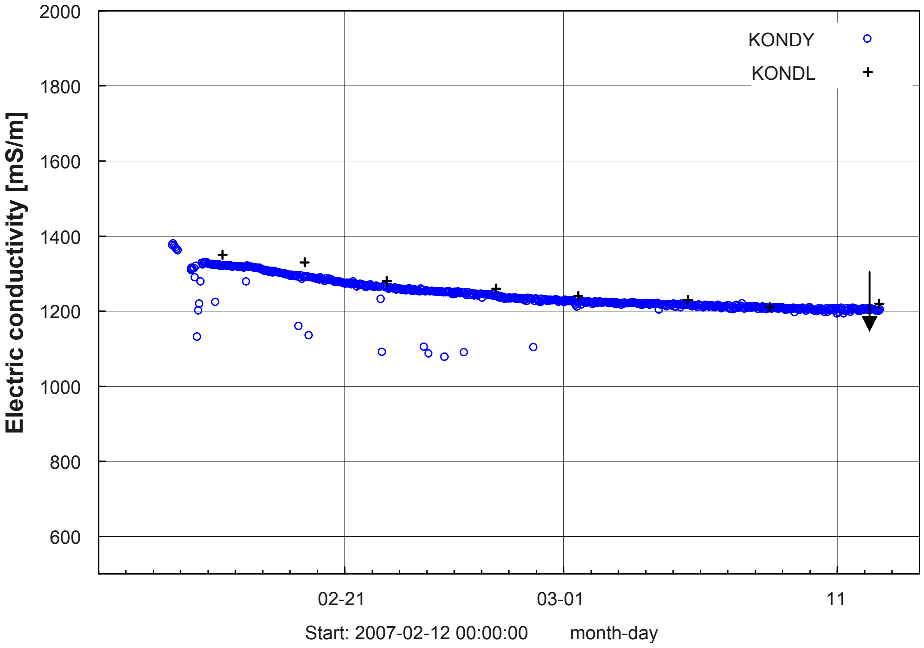


Figure A8-3. Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.

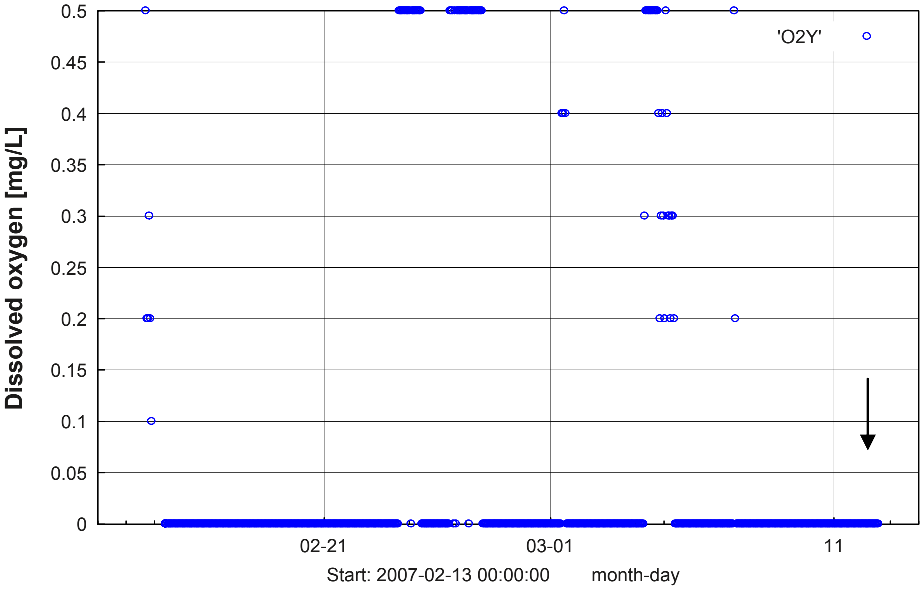


Figure A8-4. Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section.

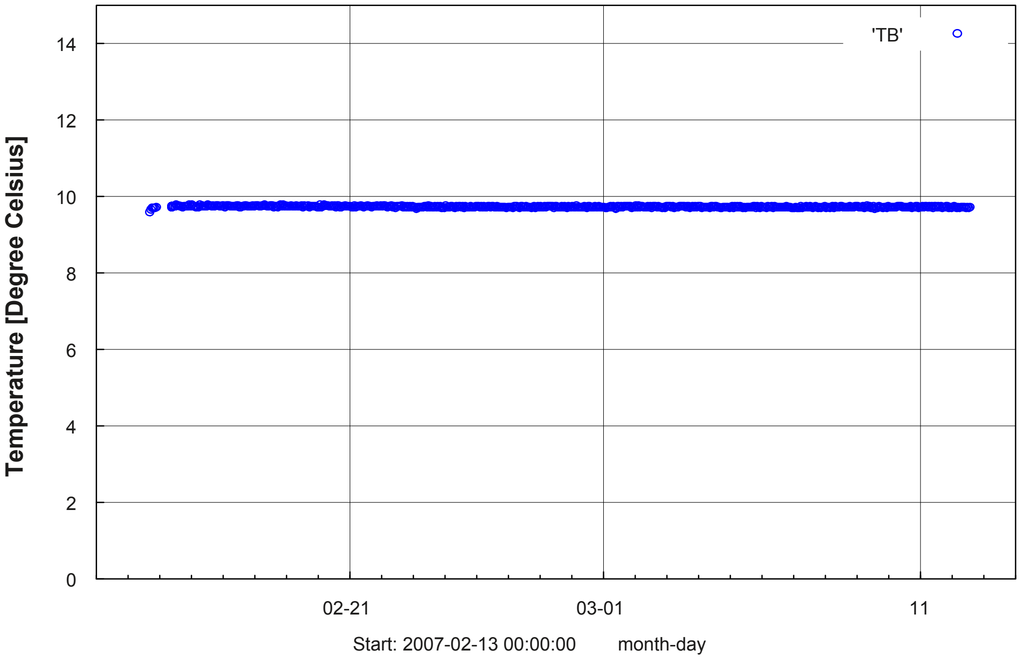


Figure A8-5. *Temperature of the groundwater in the borehole section (TB).*

Appendix 9

Compilation of water analysis data

Table A9-1. Water composition. Compilation September 2007.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	RCB (%)	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
KFM11A	447.50	454.64	12589	2007-01-18	–	–	–	–	–	8.64	4,690	–	–	–	–	–	–	–	–	–
KFM11A	447.50	454.64	12702	2007-02-16	–	–	–	–	–	8.79	4,770	–	–	–	–	–	–	–	–	–
KFM11A	447.50	454.64	12703	2007-02-19	0.20	1,280	6.73	1,520	25.1	8.42	4,550	213	76.7	24.2	1.27	4.72	<0.02	<0.02	0.005	0.098
KFM11A	447.50	454.64	12705	2007-02-22	–0.41	1,250	6.24	1,460	28.1	12.7	4,430	232	90.8	24.2	1.16	5.65	<0.02	0.02	0.003	0.101
KFM11A	447.50	454.64	12706	2007-02-26	–1.30	1,250	5.46	1,390	29.7	16.4	4,390	244	90.8	21.1	1.13	5.56	0.193	0.218	0.207	0.102
KFM11A	447.50	454.64	12707	2007-03-01	–0.79	1,250	5.61	1,350	30.8	19.4	4,270	250	92.0	21.5	1.12	5.73	0.418	0.452	0.453	0.105
KFM11A	447.50	454.64	12724	2007-03-05	–0.83	1,250	5.57	1,330	33.6	21.3	4,240	259	94.8	20.2	1.08	5.89	0.447	0.462	0.462	0.112
KFM11A	447.50	454.64	12725	2007-03-08	–2.02	1,250	5.65	1,280	34.9	22.5	4,260	255	93.9	19.3	1.06	5.83	0.392	0.421	0.413	0.114
KFM11A	447.50	454.64	12727	2007-03-12	–1.40	1,250	5.93	1,280	37.5	23.9	4,210	264	95.0	19.7	1.06	5.96	0.226	0.246	0.240	0.123
KFM11A	690.00	710.00	12843	2007-07-11	0.04	1,570	20.8	1,070	115	81.7	4,410	252	92.8	24.5	0.92	7.09	6.43	–	–	1.080
KFM11A	690.00	710.00	12844	2007-07-13	–1.34	1,590	19.0	1,240	103	78.0	4,850	231	90.8	28.9	0.99	6.52	5.13	–	–	0.885
KFM11A	690.00	710.00	12845	2007-07-16	–1.08	1,690	14.8	1,460	78.1	63.5	5,360	200	73.3	33.6	1.04	6.15	2.91	2.96	2.99	0.586

– = Not analysed

A = Results will be reported later

x = No result due to analytical problems

< value = below reporting limit

RCB (%) = Rel. charge balance error %

SICADA: water_composition

Table A9-1. Water composition (cont.). Compilation September 2007.

Idcode	Secup m	Seclow m	Sample no.	Li mg/L	Sr mg/L	I^- mg/L	pH	TOC mg/L	DOC mg/L	HS^- mg/L	Drill_ water %	ElCond mS/m	NH_4N mg/L	NO_2-N mg/L	NO_3-N mg/L	NO_2-N+NO_3-N mg/L	PO_4-P mg/L	P mg/L
KFM11A	447.50	454.64	12589	–	–	–	7.11	–	–	–	12.8	1,360	–	–	–	–	–	–
KFM11A	447.50	454.64	12702	–	–	–	x	–	–	–	9.59	1,350	–	–	–	–	–	–
KFM11A	447.50	454.64	12703	0.077	19.8	–	x	–	2.5	<0.006	8.47	1,330	0.063	–	–	–	–	–
KFM11A	447.50	454.64	12705	0.051	20.0	–	7.77	–	1.2	<0.006	7.71	1,280	0.065	–	–	–	–	–
KFM11A	447.50	454.64	12706	0.051	18.4	–	7.65	–	1.1	<0.006	7.12	1,260	0.088	–	–	–	–	–
KFM11A	447.50	454.64	12707	0.049	17.9	0.073	7.59	–	1.1	0.009	6.71	1,240	0.094	<0.0002	0.0003	0.0004	0.0005	<0.005
KFM11A	447.50	454.64	12724	0.049	17.6	0.073	7.54	–	1.0	0.013	6.00	1,230	0.109	<0.0002	<0.0003	<0.0003	0.0005	<0.005
KFM11A	447.50	454.64	12725	0.049	17.2	–	7.46	–	1.0	0.013	6.12	1,210	0.115	–	–	–	–	–
KFM11A	447.50	454.64	12727	0.047	17.1	0.059	7.58	1.1	1.3	0.012	5.88	1,220	0.049	<0.0002	0.0009	0.0009	0.0006	<0.005
KFM11A	690.00	710.00	12843	0.043	12.3	–	7.13	–	–	–	5.21	1,320	–	–	–	–	–	–
KFM11A	690.00	710.00	12844	0.044	15.7	–	7.34	–	–	–	4.15	1,410	–	–	–	–	–	–
KFM11A	690.00	710.00	12845	0.044	18.1	0.030	7.42	4.7	6.3	0.040	3.32	1,510	0.441	<0.0002	<0.0003	<0.0003	0.0012	<0.040

– = Not analysed

A = Results will be reported later

x = No result due to analytical problems

< value = below reporting limit

RCB (%) = Rel. charge balance error %

SICADA: water_composition

Table A9-2. Trace elements. Compilation September 2007. Compilation September 2007.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Al ug/L	As ug/L	B ug/L	Ba ug/L	Cd ug/L	Cr ug/L	Co ug/L	Hg ug/L	Ni ug/L	V ug/L	U ug/L	Th ug/L	Sc ug/L	Rb ug/L	Y ug/L	Zr ug/L	In ug/L
KFM11A	447.50	454.64	12707	2007-03-01	27.4	0.95	1,040	90.1	<0.02	0.09	0.038	<0.002	0.886	0.063	1.19	<0.2	<0.4	12.2	0.229	<0.1	<0.2
KFM11A	447.50	454.64	12724	2007-03-05	5.19	0.87	1,050	89.2	<0.02	0.37	0.037	<0.002	1.060	0.064	1.04	<0.2	<0.4	12.4	0.200	<0.1	<0.2
KFM11A	447.50	454.64	12727	2007-03-12	14.7	0.64	1,050	87.2	<0.02	0.38	0.099	<0.002	1.520	0.054	1.13	<0.2	<0.4	13.7	0.234	<0.1	<0.2
KFM11A	690.00	710.00	12845	2007-07-16	11.2	<1.0	817.0	174	<0.05	<0.1	0.224	<0.002	0.625	0.087	3.25	<0.2	0.594	25.4	0.995	<0.3	<0.5

Table A9-2. Trace elements (cont.). Compilation September 2007.

Idcode	Secup m	Seclow m	Sample no.	Sb ug/L	Cs ug/L	La ug/L	Hf ug/L	Tl ug/L	Ce ug/L	Pr ug/L	Nd ug/L	Sm ug/L	Eu ug/L	Gd ug/L	Tb ug/L	Dy ug/L	Ho ug/L	Er ug/L	Tm ug/L	Yb ug/L	Lu ug/L
KFM11A	447.50	454.64	12707	0.284	0.396	<0.02	<0.02	<0.03	0.022	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
KFM11A	447.50	454.64	12724	0.280	0.409	<0.02	<0.02	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
KFM11A	447.50	454.64	12727	0.258	0.532	<0.02	<0.02	<0.03	<0.02	<0.02	0.042	0.0394	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
KFM11A	690.00	710.00	12845	0.270	0.558	0.238	<0.05	<0.05	0.25	<0.05	0.117	<0.05	<0.05	0.0528	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

< value = below reporting limit

SICADA: trace_elements

Table A9-3. Isotopes I (H-, O-, B-, S-, Cl- and C-isotopes). Compilation September 2007.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	δ^2H ‰ SMOW	^3H TU	$\delta^{18}O$ ‰ SMOW	$^{10}B/^{11}B$ no unit	$\delta^{34}S$ ‰ CDT	$\delta^{13}C$ ‰ PDB	$^{87}Sr/^{86}Sr$ no unit	^{14}C pmC	$\delta^{37}Cl$ ‰ SMOC
KFM11A	447.50	454.64	12703	2007-02-19	–91.4	0.90	–12.2	–	–	–	–	–	–
KFM11A	447.50	454.64	12705	2007-02-22	–89.1	3.00	–11.9	–	–	–	–	–	–
KFM11A	447.50	454.64	12706	2007-02-26	–89.2	2.70	–11.6	–	–	–	–	–	–
KFM11A	447.50	454.64	12707	2007-03-01	–88.2	2.70	–11.5	–	25.1	–	0.716194	–	0.18
KFM11A	447.50	454.64	12724	2007-03-05	–87.4	3.20	–11.5	–	25.0	–	0.716192	–	0.19
KFM11A	447.50	454.64	12725	2007-03-08	–86.7	3.50	–11.4	–	–	–	–	–	–
KFM11A	447.50	454.64	12727	2007-03-12	–87.1	2.60	–11.2	0.2377	25.0	–11.60	0.716217	57.4	–0.03
KFM11A	690.00	710.00	12843	2007-07-11	–73.6	5.20	–10.0	–	–	–	–	–	–
KFM11A	690.00	710.00	12844	2007-07-13	–76.5	4.10	–10.3	–	–	–	–	–	–
KFM11A	690.00	710.00	12845	2007-07-16	–79.1	3.10	–10.7	0.2360	31.5	–12.4	0.717188	A	–0.4

– = Not analysed

A = Results will be reported later

< value = below reporting limit

SICADA: isotopes_1

Table A9-4. Isotopes II (U-, Th, Ra- and Rn-isotopes). Compilation September 2007.

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 mBq/L
KFM11A	447.50	454.64	12727	2007-03-12	14.00	0.40	35.00	0.70	1.00	<0.015

< value = below reporting limit

SICADA: isotopes_2

Table A9-5. Dissolved gases. Compilation September 2007.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Ar mL/L	He mL/L	N_2 mL/L	CO_2 mL/L	CH_4 mL/L	O_2 mL/L	H_2 µL/L	CO µL/L	C_2H_6 µL/L	C_2H_4 µL/L	C_2H_2 µL/L	C_3H_8 µL/L	C_3H_6 µL/L	DISS_GAS mL/L H_2O
KFM11A	447.50	454.64	12727	2007-03-13	0.88	3.400	99.0	0.420	0.100	0.028	34.0	<5.2	0.21	0.11	<0.05	0.11	0.11	104.00

< value = below reporting limit

> value = above reporting limit

SICADA: dissolved_gases