

Forsmark site investigation

Hydrochemical characterisation in borehole KFM08D

Results from two investigated borehole sections at 669.7–676.8 m and 828.4–835.5 m

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December 2007

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Abstract

Complete chemical characterisation is the most extensive chemical investigation method performed in core-drilled boreholes. The method comprehends 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 applied in two sections from borehole KFM08D, at 669.7–676.8 m borehole length (vertical depth 538 m) and 828.4–835.5 m borehole length (vertical depth 661 m), respectively. The results include on-line measurements of redox potential (Eh), pH, dissolved oxygen, electrical conductivity and water temperature in the borehole sections, together with chemical analyses of major constituents, trace metals and isotopes. In addition to the regular analytical protocol, determinations of the isotope Chlorine-36 were conducted. The contents of colloids were measured in groundwater from both sections by laser-induced breakdown colloid detection (LIBD). Furthermore, determinations of gas content and composition, and microbe content and their physiological characteristics were made. In section 669.7–676.8 m, organic and inorganic colloids were investigated by size fractionation and the amounts of inorganic colloids collected on filters were determined by chemical analyses.

The water composition was stable in both sections during the pumping and sampling periods. The chloride concentrations amounted to 7,460 mg/L and 8,160 mg/L while the flushing water contents were 5% and 4% in sections 669.7–676.8 m and 828.4–835.5 m, respectively. The Eh measurement in section 669.7–676.8 m was relatively successful and stabilised at approximately –260 mV, while in section 828.4–835.5 m the electrodes did not stabilise within the measurement period. The colloid contents measured by LIBD amounted to around 1 µg/L or less in both sections. The organic constituents were present mainly as fulvic acids and low molecular weight acids (citric acid, oxalic acid, etc).

The groundwaters observed in both investigated borehole sections are of old brackish, non-marine character, which is to be expected in low-fractured rock between deformation zones at the actual depths. The results from borehole KFM08D are of special interest, since they represent repository depth within the prioritised part of the Forsmark candidate area.

Sammanfattning

Fullständig kemikaraktisering är den mest omfattande kemiska undersökningsmetoden för kärnborrhål. Metoden innefattar 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 två sektioner av borrhålet KFM08D, vid 669,7–676,8 m borrhålslängd (vertikalt djup 538 m) och vid 828,4–835,5 m borrhålslängd (vertikalt djup 661 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. Förutom det ordinarie analysprogrammet utfördes bestämningar av isotopen klor-36. Kolloidinnehållet i grundvatten från båda sektionerna bestämdes med laser-inducerad nedbrytning (LIBD). Vidare fastställdes gasinnehåll och sammansättning samt antal mikroorganismer och deras fysiologi. I sektion 669,7–676,8 m undersöktes oorganiska och organiska kolloider (humus och fulvosyror) med fraktioneringsteknik och mängden oorganiska kolloider samlade på filter bestämdes med ICP-analyser.

Vattensammansättningen var stabil i båda sektionerna under pump-/provtagningsperioderna. Kloridkoncentrationerna uppgick till 7 460 mg/l respektive 8 160 mg/l och spolvattenhalterna till 5 % i sektionen 669,7–676,8 m respektive 4 % i sektionen 828,4–835,5 m. Redoxpotentialmätningarna var relativt lyckade i sektion 669,7–676,8 m och stabiliserade sig på ungefär –260 mV, men i sektion 828,4–835,5 m däremot, uppnåddes inte stabila potentialer under mätperioden. Kolloidkoncentrationen mätt med LIBD uppgick till runt 1 µg/L eller mindre i båda sektionerna. De organiska komponenterna förelåg huvudsakligen som fulvosyror eller andra lågmolekylära syror (citronsyra, oxalsyra etc).

Grundvattnen i båda undersökta borrhålssektionerna visade sig ha den gamla, icke-marina karaktär som kunde förväntas på de aktuella djupen i sprickigfattigt berg mellan deformationszoner. Resultaten från KFM08D är särskilt intressanta eftersom de representerar förvarsdjupet i den prioriterade delen av Forsmarks kandidat område.

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1 Introduction

This document reports performance and results of the activity Complete Chemical Characterisation in borehole KFM08D within the site investigation programme at Forsmark /1/. The work was conducted according to the activity plan AP PF 400-07-029 witch refers to SKB's method description MD 430.017. The present report includes hydrogeochemical data from field work carried out during April to June 2007. Also sampling for microbe studies, in compliance with activity plan AP PF 400-05-66, was performed within the present activity. The microbe investigations will, however, be reported in a separate primary data report /2/.

The controlling documents for the activity are listed in Table 1-1. The activity plan, the method descriptions and the measurement system descriptions constitute SKB's internal controlling documents.

Original data from the reported activity are stored in SKB's primary database Sicada, where data are traceable by the activity plan number (AP PF 400-07-029). Only data in SKB's 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 the normal procedure is that major data revisions entail a revision of the P-report. Minor revisions are normally presented as supplements, available at www.skb.se.

The telescopic borehole KFM08D at drill site 8 (DS8) /3/ is presented on the map in Figure 1-1 together with nearby situated core-drilled and percussion-drilled boreholes. Its location together with other current deep telescopic and conventional core-drilled boreholes within the investigation area is shown on the small inset in Figure 1-1. KFM08D is inclined at 55°, dipping east.

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

| Activity plan | Number | Version |
|--|--------------------|-----------------|
| Fullständig kemikaraktärisering med mobilt fältlaboratorium i KFM08D. | AP PF 400-07-029 | 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 borrhårustning 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 | 1.0 |
| | SKB MD 434.005 | 1.0 |
| | SKB MD 434.006 | 1.0 |
| | SKB MD 434.007 | 1.0 |
| | SKB MD 433.018 | 1.0 |
| Mätsystembeskrivning för fraktionering av humus- och fulvosyror. | SKB MD 431.043 | 1.0 |
| Mätsystembeskrivning för kolloidfiltreringssystem, handhavandedel. | SKB MD 431.045 | To be published |
| Provtagning och analyskemilaboratorium. | SKB MD 452.001–019 | – |

The borehole section between 0–59.0 m is percussion-drilled and has a stainless steel casing with an internal diameter of 200 mm, whereas the 59.0–942.3 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).

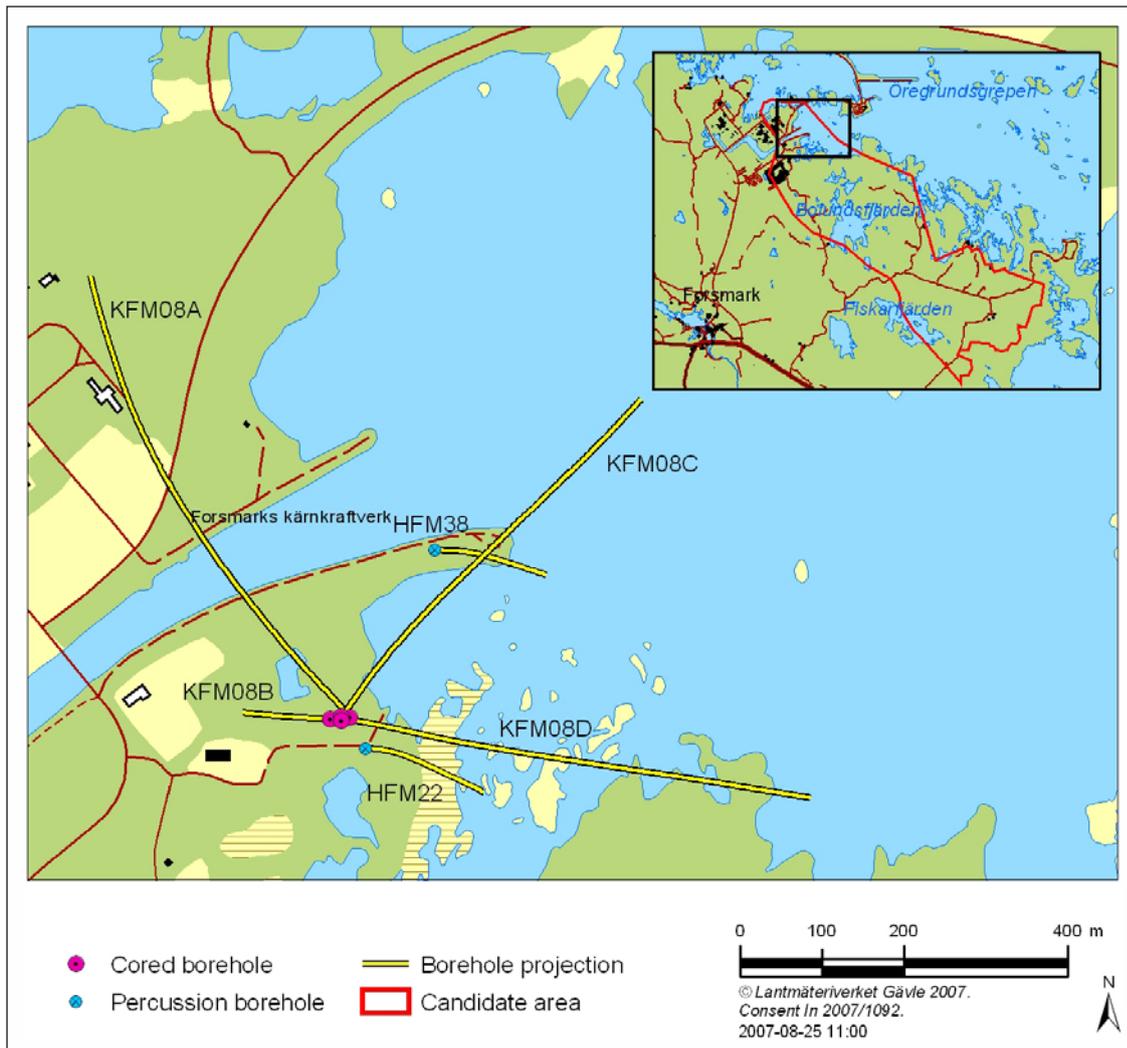


Figure 1-1. Locations and projections on the horizontal plane of the telescopic borehole KFM08D and nearby situated core-drilled and percussion-drilled boreholes, including the flushing water well HFM22, at drill site DS8. The inset in the upper right corner shows the location of DS8 within the investigation area at Forsmark.

2 Objectives and scope

Complete chemical characterisation is the most extensive chemical investigation method performed in core-drilled boreholes. The method is carried out in order to 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/. Hydrochemical investigations in borehole KFM08D are of special interest since it is located close to the centre of this prioritised part and hydrochemical data are very sparse at and below repository depth in this area due to the very limited amount of water-yielding fractures.

The analytical programme in sections at 669.7–676.8 m and 828.4–835.5 m borehole length was carried out according to SKB chemistry class 4 and class 5 including all options /1/. In addition, the isotope chlorine-36 was determined. Redox potential (Eh), pH, 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 collected in situ were used for determination of colloid content by LIBD technique, for determination of gas content and composition as well as for microbe studies. In section 669.7–676.8 m the colloid content was also determined by filtration followed by chemical analysis, and fractionations of organic acids and inorganic species were performed in order to investigate size distribution (DOC and ICP analyses). Furthermore, enrichment of organic acids was conducted in order to determine $\delta^{13}\text{C}$ and pmC in organic constituents.

3 Background

3.1 Flushing water history

The percussion-drilled borehole HFM22 /5/ served as a supply well for the flushing water used to drill borehole KFM08D. The chemical composition of the flushing water, which was checked twice before use /6/, appeared to be of marine character, thus deviating in origin and character from the deep groundwaters investigated in KFM08D. The drilling of the 942.3 m long borehole consumed 884 m³ of flushing water and the volume of returned water pumped from the borehole by air-lift pumping during drilling was 1,976 m³. After drilling, nitrogen flushing was carried out eight times from the bottom of the borehole, resulting in discharge of an additional volume of 14 m³ 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 return water was checked regularly and a total of 126 samples of each sample type were analysed. The Uranine concentrations in the flushing water and in the return 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 KFM08D via the flushing water and the amount recovered from air-lift pumping during core drilling.

| Uranine | (g) |
|---|-----|
| Added, according to the log book. | 197 |
| Added, calculated from the average Uranine concentration and the total volume of flushing water. | 179 |
| Recovered, estimated from the average Uranine concentration and the total volume of returned water. | 121 |

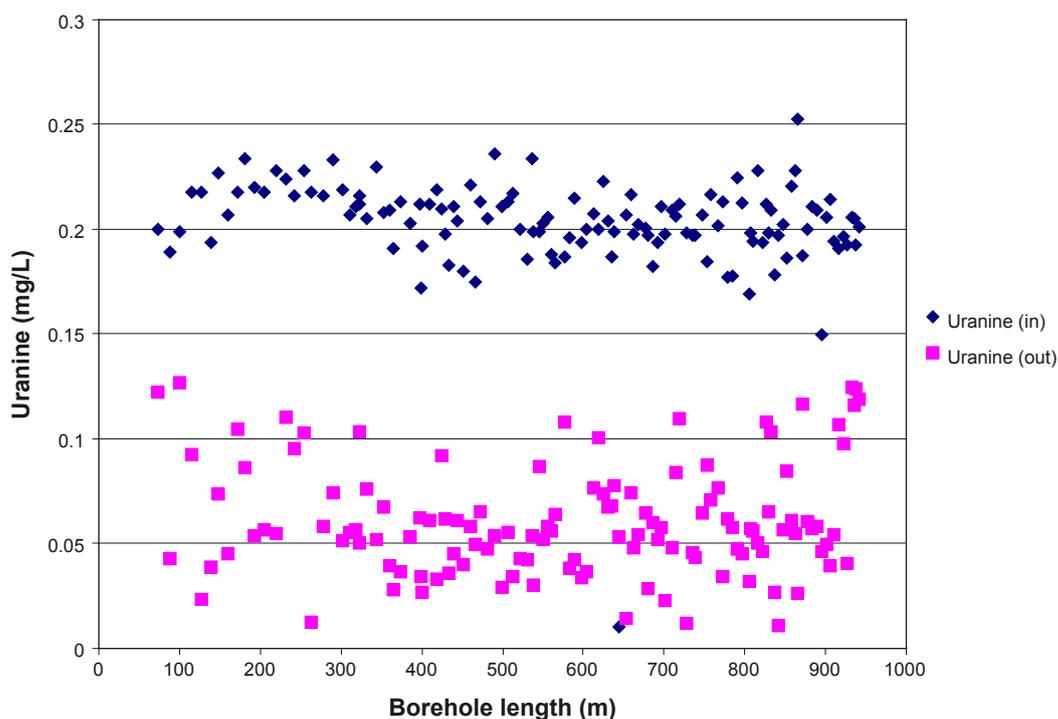


Figure 3-1. Uranine concentrations in the flushing water and in the recovered water versus borehole length.

The Uranine budget in Table 3-1 suggests that as much as about 380 m³ of the flushing water was lost to the borehole and the adjacent host bedrock during drilling. Additional cleaning was carried out by nitrogen flushing after drilling but no Uranine analyses were performed on the water discarded during this cleaning. The flushing water content was still very high, especially in section 669.7–676.8 m, at the start of the pumping/sampling period.

As borehole KFM08D 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 forced to bubble 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 3.1 and 3.3 mg/L. 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, which is applied during drilling of all telescopic boreholes, 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

KFM08D 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 effect on, for example, the in situ microbiological conditions. The activities/investigations performed in KFM08D prior to the chemistry campaign are listed in Table 3-2.

3.3 Choice of borehole sections

The differential flow logging /10/ of the borehole prior to the chemical investigation revealed relatively few water-bearing fractures. Figure 3-2 presents the hydraulic transmissivities along the borehole. The water-yielding fractures in KFM08D are located at 393 m, 676 m and 832 m borehole lengths. Hydrochemical data are very sparse from repository depth and below in the prioritised area, therefore the two deepest sections were selected.

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.

Table 3-2. Activities performed in KFM08D prior to and in connection with the chemical characterisation.

| Activities performed | Date of completion | Length or section (m) | Comment |
|---|--------------------|---------------------------------|---|
| Percussion drilling | 2006-12-04 | 0–59.0 | |
| Core drilling | 2007-02-10 | 0–942.3 | HFM22 was the source of flushing water for drilling the cored part of KFM08D. HFM22 is an SKB chemical-type borehole /3, 5, 6/. Flushing water volume = 884 m ³ . Return water volume 1,976 m ³ . |
| Flushing water treatment | – | – | Automatic dosing of Uranine was used during drilling of KFM08D. In this way there was no need for an in-line storage tank placed after the UV-system /3/. |
| Nitrogen flushing/lifting eight times from the bottom of the borehole | 2007-02-19 | 0–942.3 | Exchanged volume 14 m ³ . |
| Geophysical logging | 2007-02-22 | 59.0–935.0 | /8/ |
| BIPS-logging | 2007-05-09 | 59–928.0 | /9/ |
| Differential flow logging | 2007-03-22 | 50–933.0 | /10/ |
| Hydrochemical characterisation | 2007-07-20 | 669.7–676.8 m and 828.4–835.5 m | Presented in this report. |
| Microbe investigation | – | 669.7–676.8 m and 828.4–835.5 m | /2/ |

Table 3-3. Selected fractures for hydrochemical sampling and hydraulic transmissivity calculated from differential flow logging (T_D).

| Fracture (m) | Elevation (m.b.s.l.) | T_D (m ² /s) /10/ | Comments |
|--------------|----------------------|--------------------------------|--|
| 393.3 | 317 | 1.0E–7 | Not investigated |
| 676.2 | 543 | 1.8E–7 | T (fracture), hydrochemical characterisation |
| 832.2 | 664 | 2.9E–8 | T (fracture), hydrochemical characterisation |

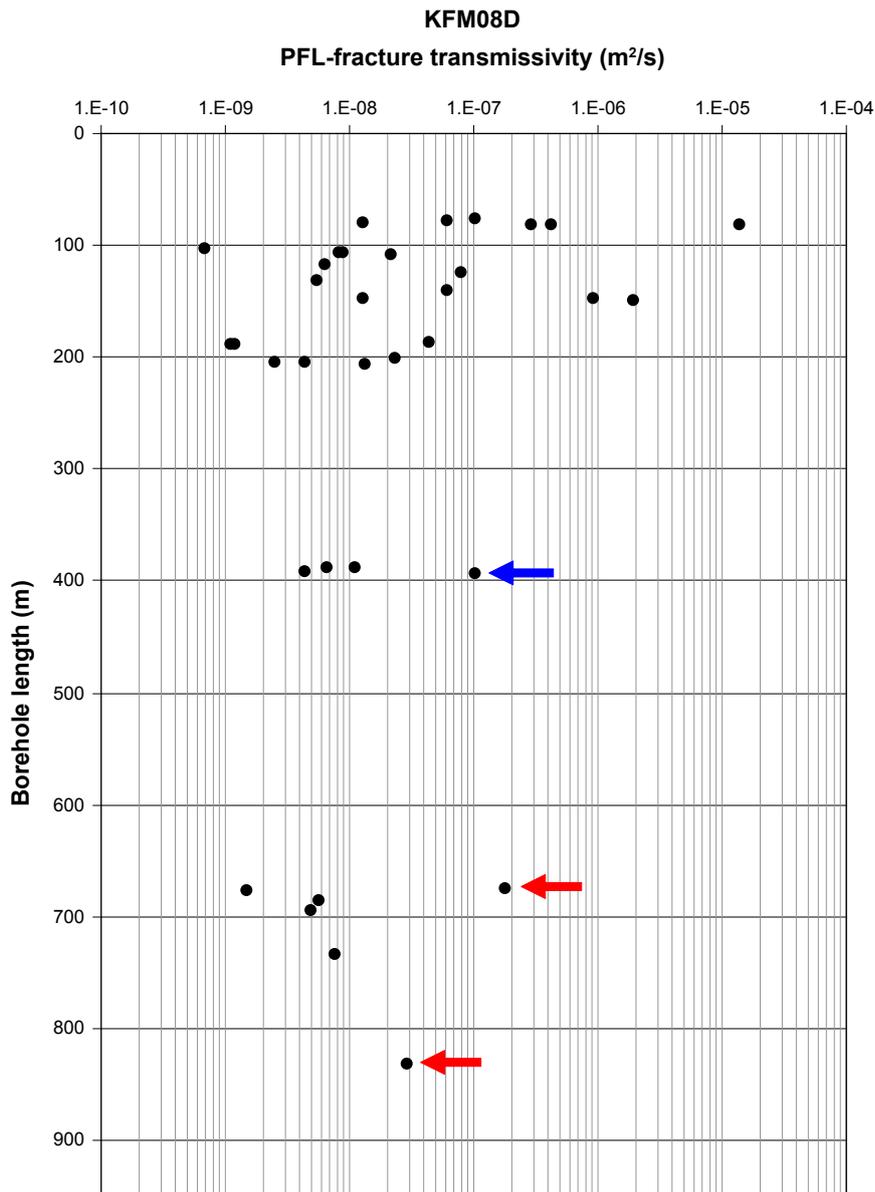


Figure 3-2. Hydraulic transmissivity along borehole KFM08D. Selected fractures planned to be investigated are indicated with arrows; red = hydrochemical characterisation, blue = short pumping period in order to obtain two or three water samples (not performed). The actual investigated flow anomaly above 676.2 m does not show on the diagram.

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), see Table 1-1.

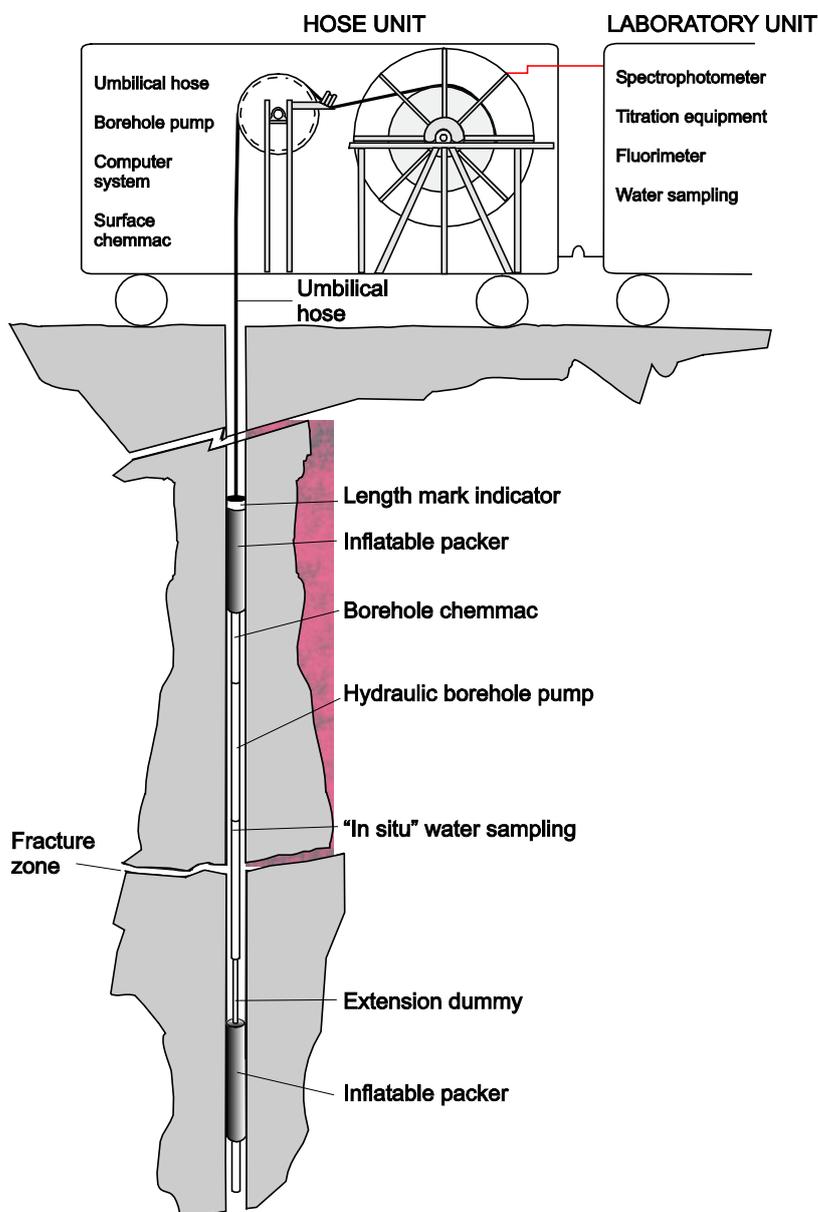


Figure 4-1. The mobile laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.

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

The downhole equipment comprises inflatable packers, pump, borehole Chemmac and the in situ sampling unit (PVP), allowing measurement (borehole Chemmac) and sampling in situ in the borehole section (PVP sampling unit). The four sampled 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 analyses and microbe investigations.

The mobile units used for the investigation of borehole KFM08D 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 Forsmark core mapping facility at and not at drill site DS8.

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 were 2.0, 2.0, 0.4, 0.2 and 0.05 μm in section 669.7–676.8 m. The equipment is described in SKB MD 431.045 (Mätsystembeskrivning för kolloidfiltrerings-system, handhavandedel, SKB internal controlling document to be published), see Table 1-1. Figure 4-2 shows the equipment set-up.

The major equipment features are:

- Filtering is performed in a closed system under an argon atmosphere, thus avoiding the risk of iron precipitation due to contact between the groundwater sample and air.
- Filtering is performed at a pressure similar to that of the groundwater in the borehole section. The system is adjusted to create a pressure difference between the inlet of the filter package and the outlet side. The pressure difference drives the sample water through the filters.
- The design of the sample containers, and the mounting with the outlet at the top, prevents migration of larger particles 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 modifications of the equipment later on, are:

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

When performing the filtration prior to a colloid study by SEM (Scanning Electron Microscopy), the equipment is supplemented with a portable glove-box filled with argon for handling the filters.

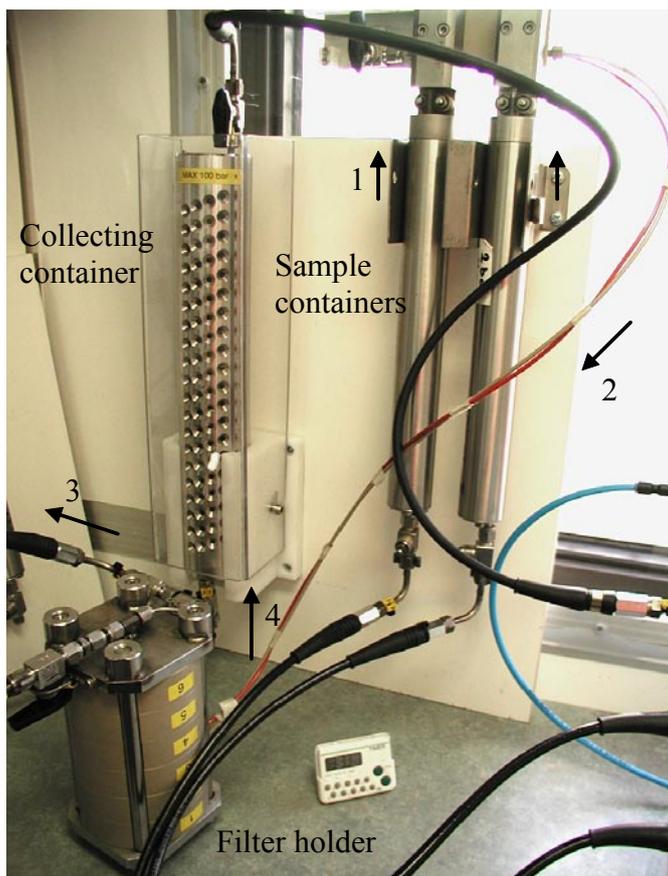


Figure 4-2. The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1 to 4, show the flow direction of the sample water through the system.

4.3 Equipment for enrichment of humic and fulvic acids

Enrichment of humic and fulvic acids is conducted in order to collect enough material to determine $\delta^{13}\text{C}$ and pmC (percent modern carbon) on organic constituents in the groundwater. The equipment for enrichment includes a porous column filled with an anion exchanger (DEAE-cellulose) and a textile filter with a well-defined pore size. The textile filter is placed inside the column in order to prevent the ion exchange resin from diffusing through the column. The equipment and performance is described in SKB MD 431.044 (Mätssystembeskrivning för uppkoncentrering av humus- och fulvosyror), see Table 1-1. Figure 4-3 shows the equipment setup. Since the ion exchange resin in the column creates a counter-pressure that disturbs the water flow through the surface Chemmac, a pump was used for pumping a portion of the outlet water through the column (approximately 1.8 L/hour).

4.4 Equipment for fractionation of humic and fulvic acids

The equipment consists of membrane filters with a defined cut-off (pore size), a membrane pump, flexible tubing and vessels. Generally, two sample portions from each section are filtered through filters with cut-offs of 1,000 D and 5,000 D, respectively (D = Dalton, 1 D = 1 g/mol). The equipment and performance are described in SKB MD 431.043 (Mätssystembeskrivning för fraktionering av humus- och fulvosyror), see Table 1-1. Figure 4-4 schematically describes the function of a membrane filter and Figure 4-5 shows the equipment set up.

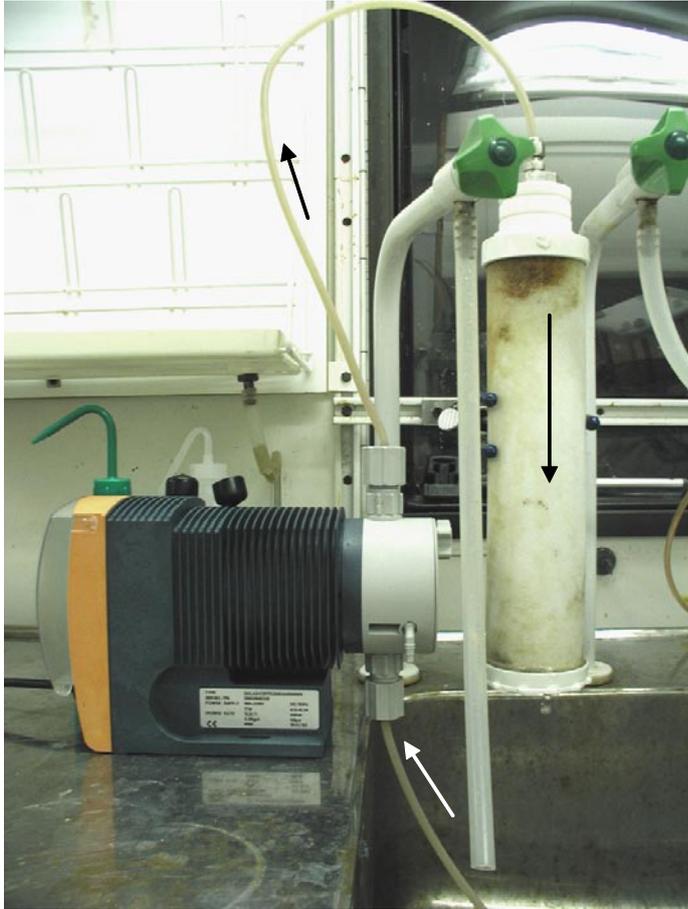


Figure 4-3. The ion exchange column. The arrows show the water flow direction.

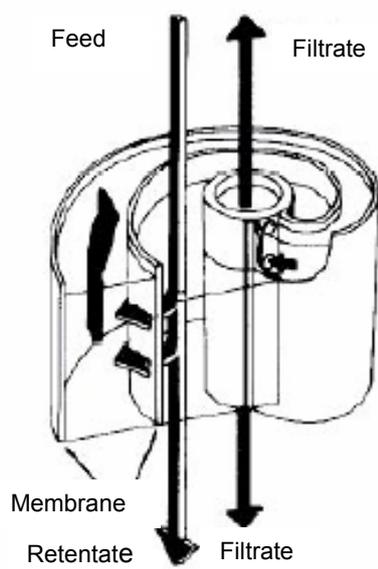


Figure 4-4. Outline of membrane filter with water flow directions.

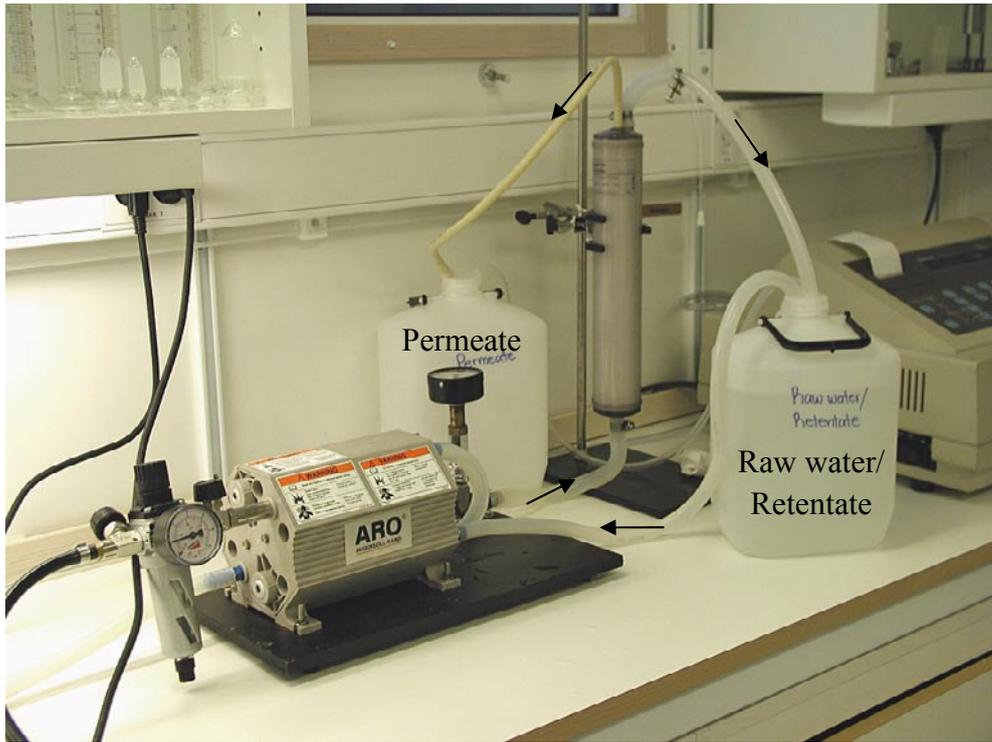


Figure 4-5. Equipment for fractionation of humic and fulvic acids.

5 Performance

5.1 General

The chemical characterisation of groundwater in borehole KFM08D was conducted according to activity plan AP PF 400-07-029 following the method described in SKB MD 430.017 (Metodbeskrivning för fullständig kemikaraktisering med mobilt fältlaboratorium), cf Table 1-1. Table 5-1 gives an overview of the investigation sequence in KFM08D.

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 before the downhole equipment is lowered in the borehole include:

- Cleaning 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 the present cases overpressures of 5 and 5.5 bars were applied.
- Calibration of the pH and redox electrodes in the downhole Chemmac equipment.

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 together with the regular downhole equipment. The length mark detector indicates length calibration marks milled into the borehole wall at almost every 50 m along the borehole /3/. At each indication, a reading is made of the corresponding length mark on the umbilical hose. The correct distance to each length mark is obtained from the Sicada database.

Table 5-1. Investigation sequence in KFM8D.

| Start date/Stop date | Investigation | Section (m) | Comment |
|---------------------------|---|-------------|--|
| 2007-05-02/ 2007-06-26 | Complete hydrochemical characterisation | 669.7–676.8 | Pumped volume = 6.7 m ³ . Flow rate approx. 90 mL/min. |
| 2007-04-02/ 2007-05-02 | Reduced hydrochemical characterisation | 828.4–835.5 | Pumped volume = 1.6 m ³ . Flow rate approx. 40 mL/min. |

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 of 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/fractures of interest. 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 $\delta^{13}\text{C}$ and pmC.
- Fractionation of humic and fulvic acids, as well as inorganic species to determine the size distribution, is performed at the end of the pumping period.
- A decision when to terminate the sampling work in the section is made during 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 all or most 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.
- Following stopping of the borehole pump and deflation of the packers, the equipment is lifted and the different downhole units are dismantled.
- Calibration of the electrodes in the downhole Chemmac and surface Chemmac.

5.2.2 Performance in section 669.7–676.8 m

For section 669.7–676.8 m there is some uncertainty about the flow anomaly concerned and its position, see Chapter 6.

The chemical characterisation was performed using the following configuration of the downhole equipment in the borehole. From the top: umbilical hose, length mark detector, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP), and lower packer, see Appendix 4. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping flow rate was about 90 mL/min and the drawdown approximately 40 m at the end of the measurement period. However, regular pressure variations of around 4 bars were observed within the section. These variations were not observed in manual registrations and are most probably due to an unsuitable combination of pump-piston return time and logging interval. Diagrams showing the pressures above and within the borehole section and the flow rate during the pumping/measurement period are 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 669.7–676.8 m.

| Date | Event | Sample no. |
|--------|---|------------|
| 070502 | Calibration of surface Chemmac, MYC3. | |
| 070503 | Calibration of borehole Chemmac. | |
| | Lowering of downhole equipment S3 (669.70–676.84 m). | |
| 070504 | Water sampling: Uranine. | |
| 070507 | Water sampling: Uranine. | |
| 070508 | Water sampling: Uranine. | |
| 070510 | Water sampling: Uranine. | |
| 070511 | Water sampling: Uranine. | |
| 070514 | Water sampling: SKB class 2. | 12790 |
| | Lowering of downhole equipment S3 (669.70+1–676.84+1 m). | |
| 070516 | Raising one metre (669.70–676.84 m). | |
| | Start of Chemmac measurements. | |
| 070521 | Water sampling: Uranine. | |
| 070523 | Water sampling: Uranine. | |
| 070528 | Water sampling: Uranine. | |
| 070529 | Water sampling: SKB class 4. | 12803 |
| 070531 | Water sampling: SKB class 4. | 12804 |
| 070604 | Water sampling: SKB class 5. | 12805 |
| 070607 | Water sampling: Uranine. | |
| 070608 | Humic and fulvic acids; enrichment start. | |
| | Water sampling: SKB class 4. | 12806 |
| 070611 | Water sampling: SKB class 5. | 12816 |
| 070614 | Water sampling: SKB class 4. | 12817 |
| 070618 | Water sampling: SKB class 5, all options. | 12818 |
| | PVP-sampler: raised pressure and opening of valve at 15:28. | |
| 070619 | PVP-sampler: closure of valve at 04:45. | |
| | Sampling for colloids (ICP), microbes and dissolved gases. | 12818 |
| | End of Chemmac measurements. | |
| | Raising equipment. | |
| | Lowering of downhole equipment S3 (669.70+1–676.84+1 m). | |
| 070620 | Raising one metre (669.70–676.84 m). | |
| | Raising ground water level indicator. | |
| | Measurement system failure. | |
| | Changing of opto switch. | |
| 070621 | Humic and fulvic acids; fractionation 1 kD. | 12818 |
| | Humic and fulvic acids; fractionation 5 kD. | 12818 |
| 070622 | Humic and fulvic acids; enrichment stop. | |
| | Measurement application failure. | |
| | Stop of borehole pump: a modification of the sampling method (PVP-sampler). | |
| 070626 | PVP-sampler: raised pressure and opening of valve at 06:57. | |
| | PVP-sampler: closure of valve at 08:12. | |
| | Sampling for colloids (ICP, SEM and LIBD). | |
| | End of Chemmac measurements. | |
| | Raising of equipment. | |
| | Calibration of surface Chemmac. | |
| | Calibration of borehole Chemmac. | |
| 070629 | Humic and fulvic acids; enrichment eluation. | 12818 |

Due to a request from the laboratory performing the LIBD investigation, see 5.2.5, the pump was stopped for four days prior to raising the downhole equipment and opening of the valves on the PVB containers.

5.2.3 Performance in section 828.4–835.5 m

The chemical characterisation in section 828.4–835.5 m was performed using the following configuration of the downhole equipment in the borehole. From the top: umbilical hose, length mark detector, 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 estimated average pumping flow rate was 40 mL/min and the drawdown approximately 55 m at the end of the measurement period. Diagrams showing the pressures above and within the borehole section and the flow rate during the pumping/measurement period are presented in Appendix 5. The events during the investigation are listed in Table 5-3.

5.2.4 Water sampling, sample treatment and analyses

The pumped water from the borehole section is led from the hose unit into a container furnished with a sink and a tank for collecting the outlet water. Filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. During the entire sampling,

Table 5-3. Events during the *hydrochemical characterisation* pumping/measurement period in section 828.4–835.5 m.

| Date | Event | Sample no. |
|--------|---|----------------|
| 070402 | Calibration of borehole Chemmac. Lowering of downhole equipment S3 (828.40–835.54 m). Loss of contact with the probes. | |
| 070403 | Raising equipment. Lowering of downhole equipment S3 (828.40–835.54 m). Start of Chemmac measurements. | |
| 070404 | Calibration of surface Chemmac. | |
| 070404 | Water sampling: SKB class 2. | 12752 |
| 070409 | Water sampling: SKB class 4. | 12753 |
| 070411 | Oxygen probe changed. | |
| 070412 | Water sampling: SKB class 5. | 12762 |
| 070416 | Water sampling: SKB class 5. | 12766 |
| 070418 | Water sampling: SKB class 4. | 12773 |
| 070423 | Water sampling: SKB class 5. | 12774 |
| 070426 | Water sampling: SKB class 4. | 12775 |
| 070430 | Water sampling: SKB class 5, all options. PVP-sampler: raised pressure and opening of valve at 13:55. | 12776 |
| 070502 | PVP-sampler: closure of valve at 06:54. Sampling for dissolved gases and microbes. Sampling for colloids (LIBD). | 12776 12776 |
| | End of Chemmac measurements. Raising equipment. Calibration of borehole Chemmac. Calibration of surface Chemmac. | |

laboratory gloves were used to minimize 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 sampling method or type of sampling object.

5.2.5 Collection of in situ water samples

The in situ water sampling was conducted successfully in both sections. The in situ sampling in section 669.7–676.8 m was repeated in order to increase the number of samples and allow three colloid determination methods, i.e. laser-induced colloid breakdown detection (LIBD, see Appendix 7) as well as colloid filtering for SEM and filter analyses (by ICP). The purpose of each sample portion is given in Table 5-4.

Occasionally, previous colloid studies using the LIBD technique have resulted in unreasonably high colloid contents. Therefore the procedure for the second in situ sampling in section 669.7–676.8 m was somewhat changed; the borehole pump was down for four days prior to opening the valves of the PVB-containers, in order to investigate possible effects on the colloid content.

All of the PVB containers were quality controlled before use; this procedure includes disassembling of the container, thorough cleaning, reassembling and measurement of piston friction. The filled PVB-containers were packed together with ice packs in insulated bags and sent to the laboratories by express delivery service immediately after sampling.

5.2.6 Colloid filtration

The method for sampling colloids in groundwater entails filtering the groundwater through a series of connected filters in a closed system under an argon atmosphere. The pressure in the system is maintained at the same level as the pressure in the sampled borehole section. The intention is that colloids should be collected on the different filters (descending pore sizes) according to their sizes. The general filtration method that is used regularly in order to obtain colloid samples for ICP-MS determinations was somewhat modified prior to the performance of the filtering intended for SEM studies. The modifications are documented in the activity plan AP PF 400-07-029. Data for the performance of the filtration runs are given in Table 5-5.

Each filtration run results in five filter samples (two 2.0 µm, one 0.4 µm, one 0.2 µm and one 0.05 µm filter pore sizes) and two water samples (water in and water out). The samples from filtration runs “Filtration – ICP” and “Filtration + rinsing – ICP” (see next page) were sent for ICP analyses (major constituents and common trace metals). The rinsing of the filters was performed with 50 mL of oxygen-free de-ionised water kept at borehole pressure and temperature. The rinsing water was from the Milli Q system at the Äspö Chemistry laboratory and was also used for washing the PVB container before use.

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

| Sample portion no. | Section 669.7–676.8 m 2007-06-19 | Section 669.7–676.8 m 2007-06-26 | Section 828.4–835.54 m 2007-05-02 |
|--------------------|-------------------------------------|--|--------------------------------------|
| 1 | Microbes | Colloids (Filtration + rinsing – ICP)* | Microbes |
| 2 | Colloids (Filtration – ICP)* | Colloids (LIBD) | Colloids (LIBD) |
| 3 | Dissolved gas | Colloids (Filtration + rinsing – SEM)* | Dissolved gas |
| 4 | Colloids (Filtration – ICP)* | Colloids (LIBD) | Colloids (LIBD) |

* See 5.2.6 Colloid filtration.

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

| Section/date/type | Entering pressure (bar) | Max. differential pressure over filter package (bar) | Temp. (°C) | Filtering time (min) | Filtered volume (mL) | Comments |
|--|-------------------------|--|------------|----------------------|--------------------------------|---|
| 669.7–676.8 m /20070619/ Filtration – ICP | ~ 52 | 3.8 | ~ 19 | 26 | 280.5 | Leakage test prior to filtration. No leakage was noticed. No broken filters. |
| 669.7–676.8 m /20070626/ Filtration + rinsing – SEM | ~ 52 | 4.2 | ~ 21 | 10 | 154.0 (246.5) ¹⁾ | No broken filters. |
| 669.7–676.8 m /20070627/ Filtration + rinsing – ICP | ~ 52 | 3.0 | ~ 19 | 13 | 155.0 (246.0) ¹⁾ | Leakage test prior to filtration. No leakage was noticed. No broken filters. The PVB container was stored in fridge for one day before performing the filtering. |

¹⁾ Sample water volume. Value within brackets is the total filtered volume including the de-ionised rinsing water.

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

The leaching of the filters at the consulting laboratory for ICP analyses was performed with nitric acid, which means that the silicon content on the filters may be underestimated.

The colloid filtration method was carried out three times in section 669.7–676.8 m with some variations:

- Filtration – ICP; The regularly used colloid filtering method including a leakage test.
- Filtration + rinsing – SEM; Colloid filtering intended for SEM-analysis of the filters according to AP PF 400-07-029. Only one of the two PVB containers in the experiment setup contained sample water. After filtration, the filters were rinsed with de-ionised, oxygen-free water from the second container. In this way the pressure was maintained through the entire filtering and rinsing procedure. No separate leakage test was performed.
- Filtration + rinsing – ICP; Colloid filtering performed as “Filtration + rinsing – SEM” above, but the filters were analysed using ICP. A leakage test was made.

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 (and drying to stable weight) of a suspension containing 0.1 mg of each pore size at a pressure of 10 bars. The weight increases 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 weights on the 0.2 µm and 0.05 µm filters were also somewhat too high, 0.17 and 0.20 mg, respectively. Despite the weight increase that may be due to a minor water uptake, the test indicates that the total amount of synthetic colloids that passed through the tubing and valve system were collected on the intended filters.

5.2.7 Enrichment of humic and fulvic acids

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

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

5.2.8 Fractionation of organic and inorganic species

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

Sampled water from the investigated section was first filtered through a 0.40 μm filter and then through special membrane filters with cut-off sizes of 1,000 D and 5,000 D, respectively. The initial water volume, prior to filtration, was approximately 5 litres. The final retentate and permeate volumes following the filtration runs were approximately 1 and 4 litres, respectively, which gave an enrichment factor of five in the retentate.

Water samples were collected from the retentate and permeate as well as from the untreated groundwater. Each sample was analysed for dissolved organic carbon (DOC), major constituents, common trace metals and uranium. The analyses of metal ions indicate if metals such as Al, Si, Mn, Fe and U exist as colloidal species.

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

| Borehole section (m) | Duration of enrichment (days) | Volume through ion exchanger (L) |
|----------------------|-------------------------------|----------------------------------|
| 669.7–676.8 | 11 | 650 |

6 Nonconformities

The hydrochemical characterisation in KFM08D has been conducted according to the SKB internal controlling documents AP PF 400-07-027 and SKB MD 430.017 with the following deviations and remarks:

- The planned short pumping/sampling in the fracture at 393 m was not performed due to time constraints.
- Some uncertainty exists concerning the positioning of the packer equipment and the location of the sampled flow anomaly at around 670 m. The flow log revealed a flow anomaly suitable for investigation at 676.2 m with $T = 1.8 \times 10^{-7}$. It was observed from pumping in the packed off section at 669.7–676.8 m, intended to incorporate this anomaly, that the obtained flow rate and drawdown did not correspond to the reported high T-value. The position of the section was lowered one metre and the expected flow rate and drawdown were obtained. However, due to the high flushing water content, the section was raised again to the first position. From this, it was concluded that the section position and/or the flow anomaly position was incorrect. Furthermore, it seems that a new water-yielding fracture, not revealed by the flow logging, became available due to pumping.
- A third, not planned, colloid filtration, “Filtration + rinsing – ICP”, was performed in section 669.7–676.8 m in order to check the effect of rinsing on the colloid content. This filtration was performed in order to facilitate comparison between the SEM and the ICP results.
- The SEM study in section 669.7–676.8 m was cancelled since the filters were lost by the courier service during transport to the institute performing the investigation.
- In section 828.4–835.5 m, some special sampling methods were cancelled and only one raising of the PVP unit was performed due to time constraints combined with a relatively high flushing water content.
- The allowed upper limit for flushing water content, 1%, was exceeded in both sections, 5% at 669.7–676.8 m and 4% at 828.4–835.5 m.
- The isotope chlorine-36 was determined in addition to the regular analytical protocol.

7 Data handling and interpretation

7.1 Chemmac measurement data

The processing of Chemmac data is described in SKB MD 434.007 version 2 (Mätssystembeskrivning för Chemmac mätsystem, SKB internal controlling document), see Table 1-1.

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* encompassing 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* with 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 when stabilisation has been achieved during 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 in the borehole section separately, since pH in the pumped water might differ from that in the borehole section. This is due to changes in gas pressure conditions which affect 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 $\pm 5\%$ are considered acceptable (in surface waters $\pm 10\%$).

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

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

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

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

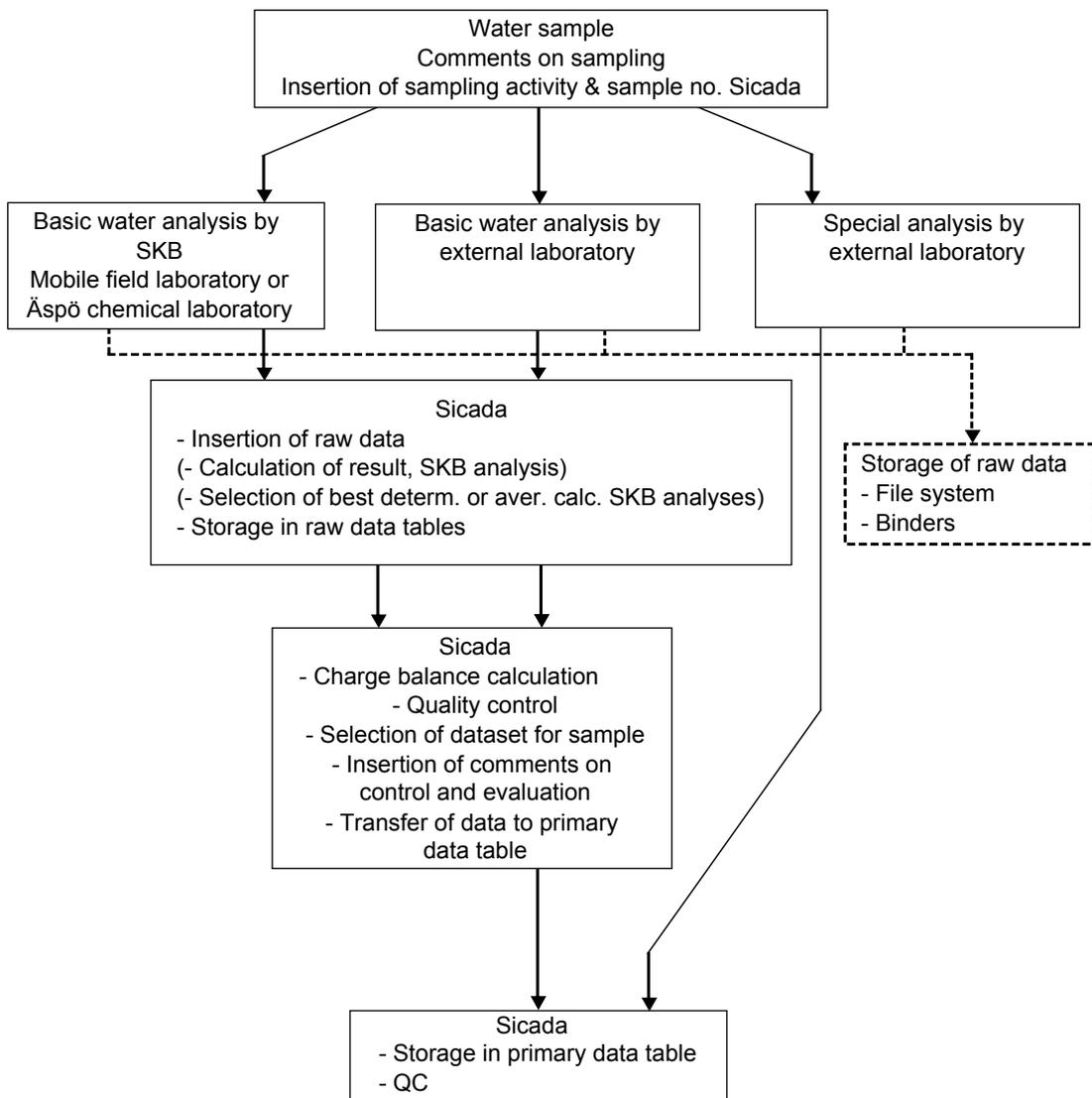


Figure 7-1. Overview of data management for hydrogeochemical data.

7.3 Data obtained using special sampling methods

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

Separate activities, methods and sample numbers are defined in Sicada for data on dissolved gases, colloids, fractions of humic and fulvic acids as well as $\delta^{13}\text{C}$ and pmC determined on organic constituents. All data are subjected to quality control.

7.3.1 Colloid filtration

The concentration of the colloid portion caught on each filter is calculated with the assumption that the water volume coming out in the collecting container is equal to the volume going into the system. This is not quite true as up to ten millilitres will be left in cavities in the filter holder package, in the tubing and in valves. A small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its content of the different elements is included in the analysis. The measurement uncertainty of each colloid concentration is calculated according to the equation below.

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

where

- U = measurement uncertainty ($\mu\text{g/L}$)
- V = water volume through the system (L)
- ΔV = estimated volume error, 0.010 L
- m = amount on filter (μg)
- Δm = measurement uncertainty of the filter analysis, 20% (μg)

The results of the colloid filtration (concentration and uncertainty) are stored in Sicada.

7.3.2 Dissolved gases

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

7.3.3 Enrichment of humic and fulvic acids

The pmC and $\delta^{13}\text{C}$ values for enriched organic acids are stored in a primary data table in Sicada without post processing or interpretation.

7.3.4 Fractionation of organic and inorganic species

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

8 Results

8.1 Chemmac measurements

The data sequences of pH, Eh, electrical conductivity, oxygen and temperature values from the Chemmac measurements in borehole sections 669.7–676.8 m and 828.4–835.5 m are plotted versus time in Appendices 8 and 9, respectively. The measured time series of data 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 Appendices 8 and 9. The selected values from the measurements in the investigated sections are given in Table 8-1 together with the corresponding results from the LIBD experiments.

In section 669.7–676.8 m, there was a fairly good agreement between the redox electrodes although the surface Chemmac electrodes stabilised at a higher level than the borehole Chemmac. Only the borehole electrodes were used for calculating a representative Eh value since, in general, redox measurements tend to be biased towards more positive redox potentials rather than the opposite. A possible reason is very small amounts of air/oxygen intruding somewhere along the sample water line at the surface. This is at times very difficult to avoid.

In section 828.4–835.5 m, the borehole electrode readings were negative but neither consistent nor stable and therefore it was not possible to select a representative value. The surface electrodes were still positive at the end of the measurement period.

The pH-electrodes in the borehole section and at the surface show an acceptable agreement in both borehole sections; minor discrepancies are likely to occur due to the effect of pressure decrease on the carbonate system.

Table 8-1. Evaluated results from the Chemmac measurements in KFM08D.

| Borehole section [m] | EC* [mS/m] | pH (surface Chemmac)** | pH (borehole Chemmac)** | Eh (Chemmac)** [mV] | Dissolved oxygen*** [mg/L] |
|-------------------------|------------|------------------------|-------------------------|------------------------|----------------------------|
| 669.7–676.8 | 1,990 ± 60 | 8.3 ± 0.1 | 8.4 ± 0.2 | –260 ± 50 ^B | 0.01 ± 0.01 |
| 669.7–676.8 LIBD(1)**** | 1,927 | 8.17 | – | 232 | < 0.316 |
| 669.7–676.8 LIBD(2)**** | 1,947 | 8.15 | – | 237 | < 0.14 |
| 828.4–835.4 | 2,150 ± 60 | 8.0 ± 0.1 | 8.2 ± 0.4 | ***** | 0.00 ± 0.01 |
| 828.4–835.4 LIBD(1)**** | 2,070 | 8.09 | – | 77 | < 0.188 |
| 828.4–835.4 LIBD(2)**** | 2,090 | 8.00 | – | 118 | < 0.098 |

* 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.

***** = No representative Eh value was selected due to unstable and inconsistent values.

^B = Only values from the borehole Chemmac have been used in the calculation.

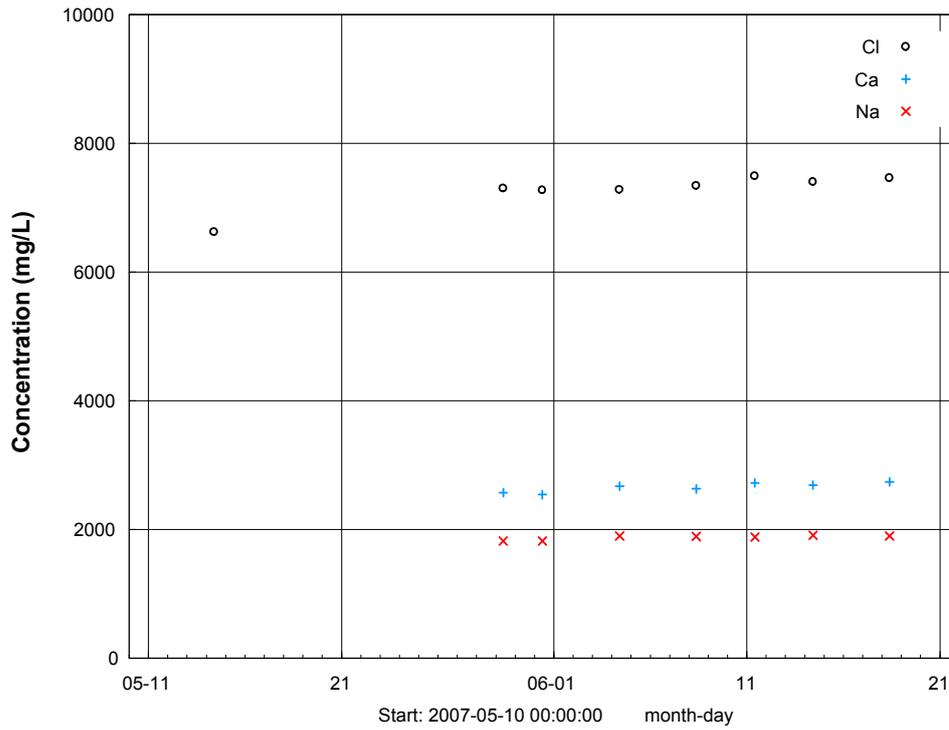


Figure 8-2. Chloride, calcium and sodium concentration from sample series at 669.7–676.8 m.

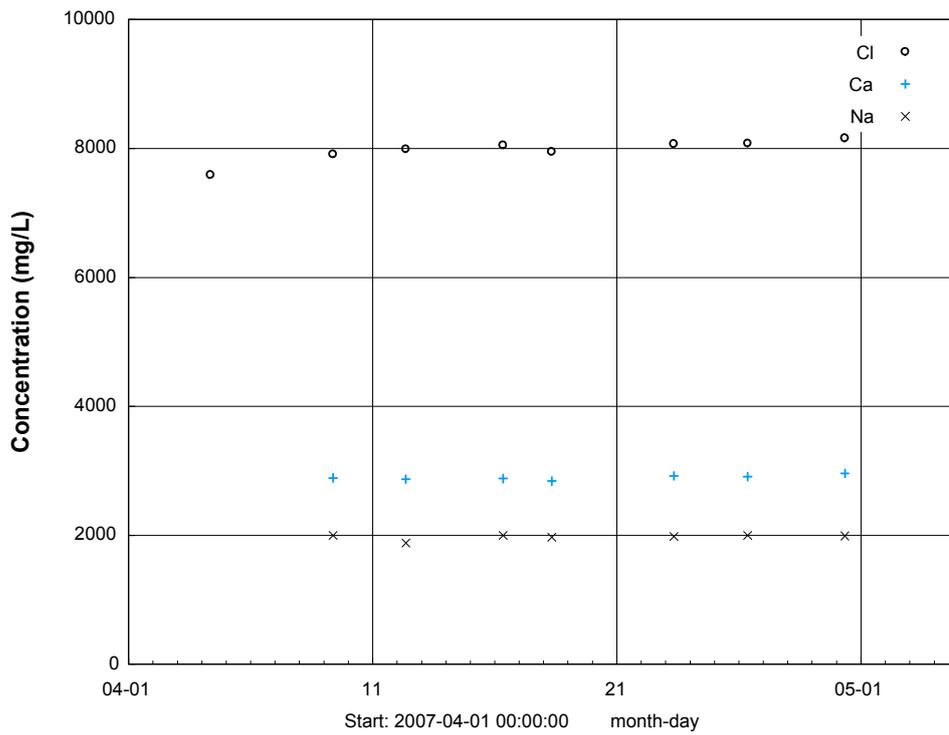


Figure 8-3. Chloride, calcium and sodium concentration from sample series at 828.4–835.5 m.

The iron concentrations are compared in Figures 8-4 and 8-5. The determinations by ICP-AES (total Fe) and spectrophotometry (Fe(II) and Fe-tot) agree well. The iron concentrations are low in both sections, although in section 669.7–676.8 m the concentration was higher at the start of the pumping/sampling period. In section 828.4–835.5 m, the iron concentrations increased slightly by the end of the period.

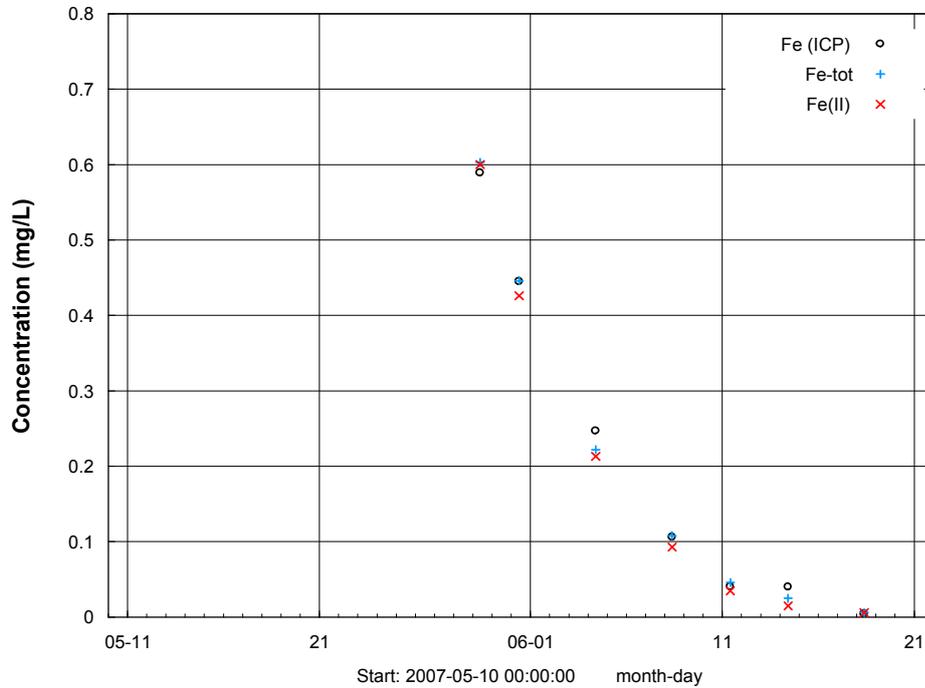


Figure 8-4. Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole section 669.7–676.8 m. Results below the detection limits, 0.04 for Fe(ICP) and 0.006 for Fe-tot and Fe(II), are plotted as the respective value.

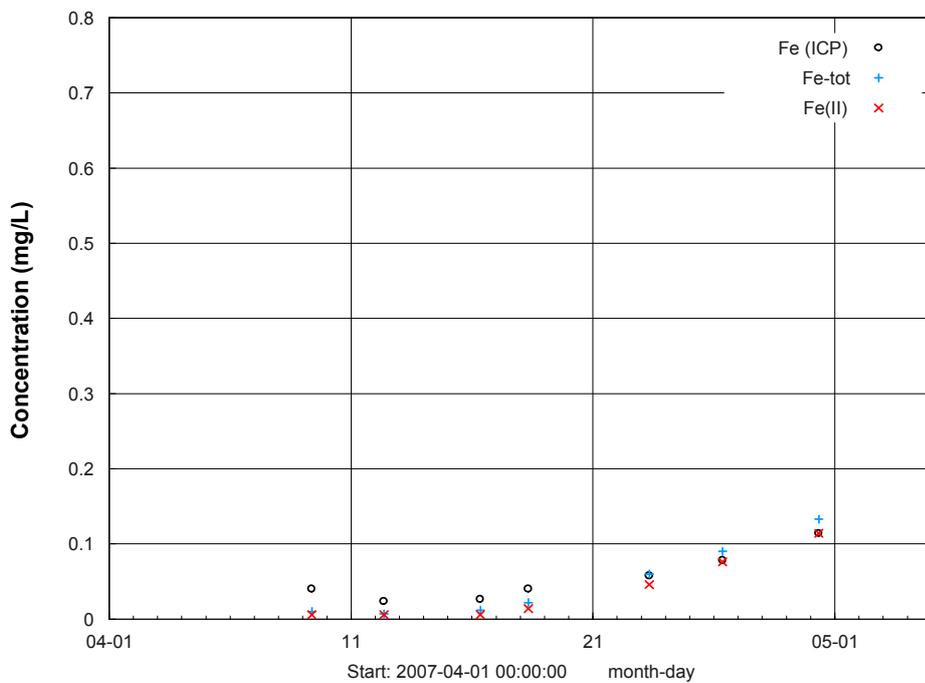


Figure 8-5. Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole section 828.4–835.5 m. Results below the detection limits, 0.04 for Fe(ICP) and 0.006 for Fe-tot and Fe(II), are plotted as the respective value.

Sulphate analysed by ion chromatography (IC) is compared with sulphate determined as total sulphur by ICP-AES for sections 669.7–676.8 m and 828.4–835.5 m in Figures 8-6 and 8-7, respectively. The agreement between the two analytical methods (IC and ICP-AES) is rather good although the discrepancies are somewhat larger than the reported analytical error for both of the sections. The results from the ICP measurements are considered to be more reliable, by experience, since the variations in time series usually are smaller. The sulphate concentrations are quite stable during the sampling periods.

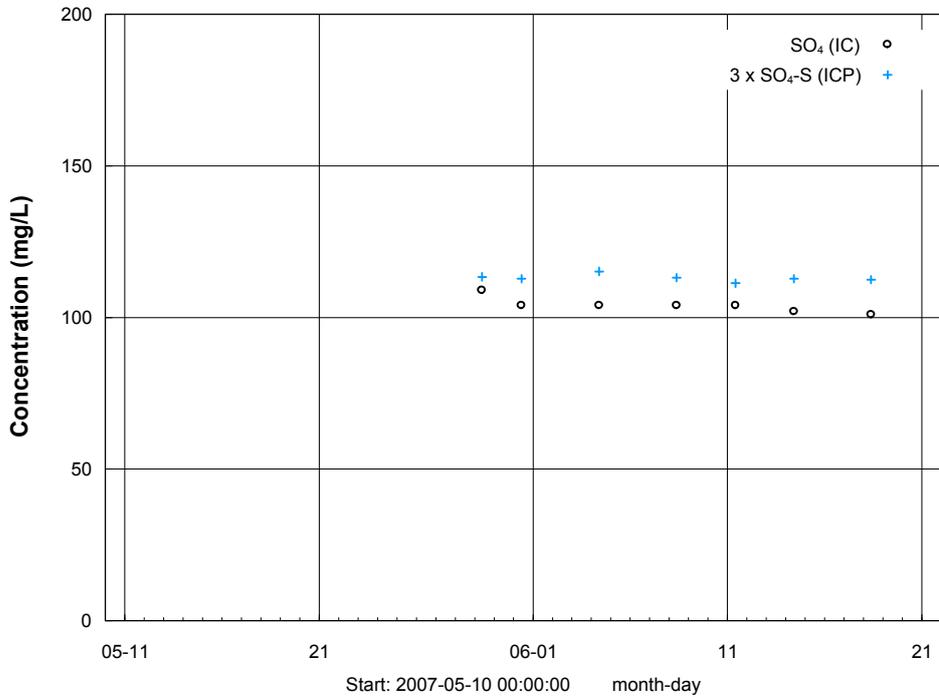


Figure 8-6. Sulphate (SO_4 by IC) to total sulphate calculated from total sulphur ($3 \times SO_4-S$ by ICP) versus date, borehole section 669.7–676.8 m.

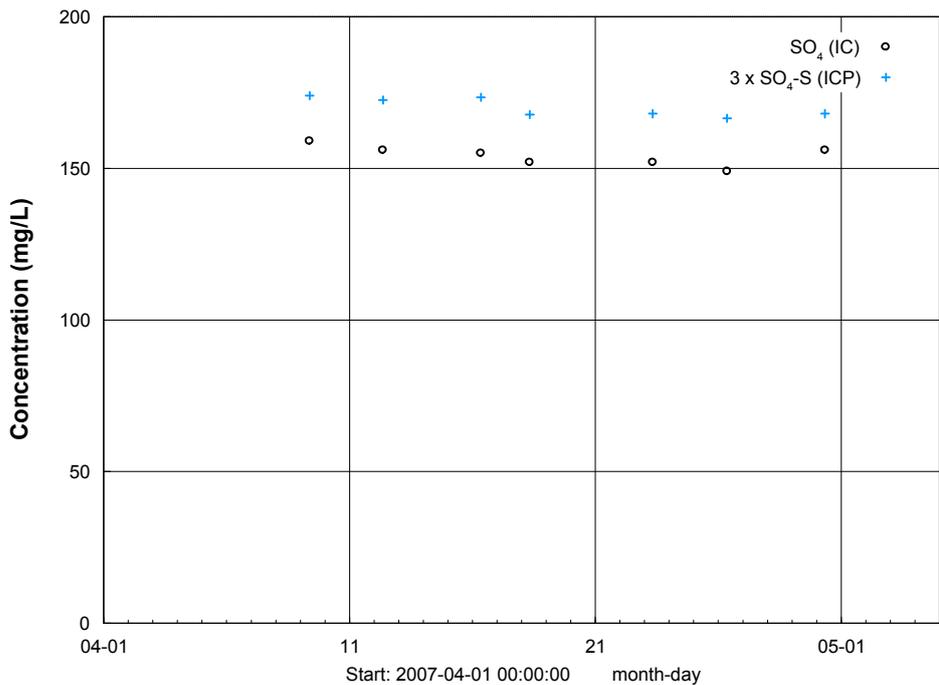


Figure 8-7. Sulphate (SO_4 by IC) to total sulphate calculated from total sulphur ($3 \times SO_4-S$ by ICP) versus date, borehole section 828.4–835.5 m.

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 KFM08D 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 the bromide concentration versus the chloride concentration provides a check if the measured values are within reason, see Figure 9-2.

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 but the aluminium concentration is still reported due to its importance for the modelling work. The trace element data are compiled in Appendix 10, Table A10-2.

8.2.3 Stable and radioactive isotopes

The regular isotope determinations include the stable isotopes ^2H , $\delta^{18}\text{O}$, $^{10}\text{B}/^{11}\text{B}^*$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$, ^{37}Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ as well as the radioactive isotopes ^3H (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, including the additional isotope ^{36}Cl , are compiled in Appendix 10, Tables A10-3 and A10-4.

Determinations of uranium-238 are compared with analyses of the element uranium by ICP MS in Table 8-2. The ^3H and $\delta^{18}\text{O}$ results are presented in Figures 8-9 and 8-10.

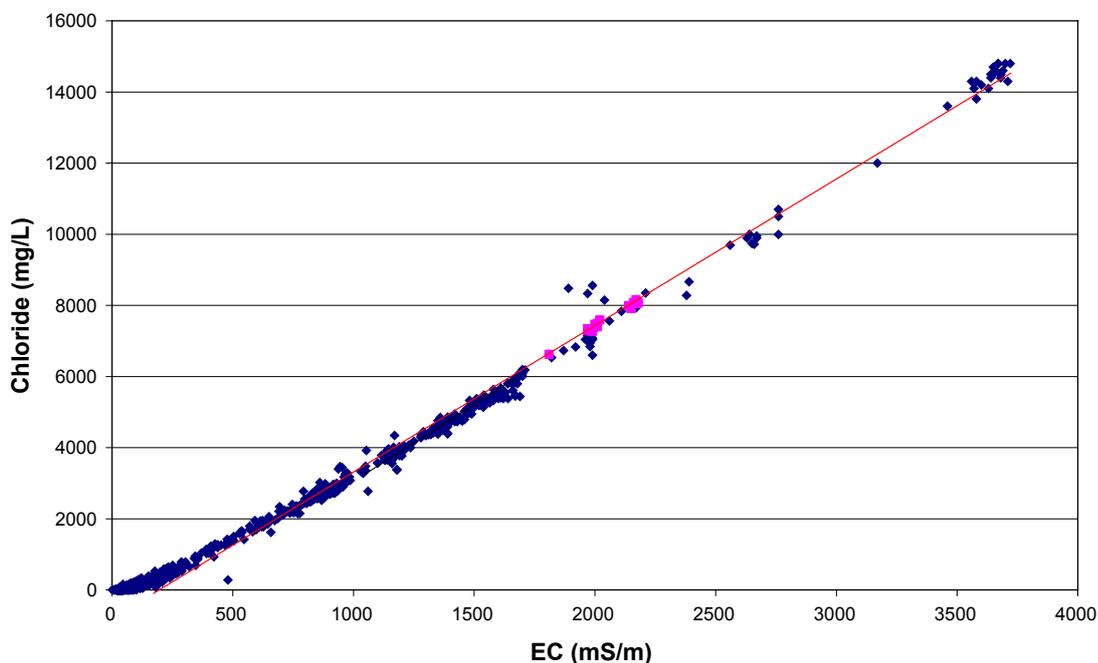


Figure 8-8. Chloride concentration versus electrical conductivity. Data from previous investigations at Forsmark are used to show the linear trend. Data from KFM08D are shown in pink.

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

Table 8-2. Comparison of uranium results. Uranium-238 (mBq/kg) is converted to U ($\mu\text{g/L}$). The expression used is given in Appendix 6.

| Section (m) | ^{238}U (mBq/kg) | ^{238}U converted to U ($\mu\text{g/L}$) | U ($\mu\text{g/L}$) by ICP |
|-------------|---------------------------|---|------------------------------|
| 669.7–676.8 | 20.0 | 1.61 | 1.57 |
| 828.4–835.5 | 2.0 | 0.161 | 0.219 |

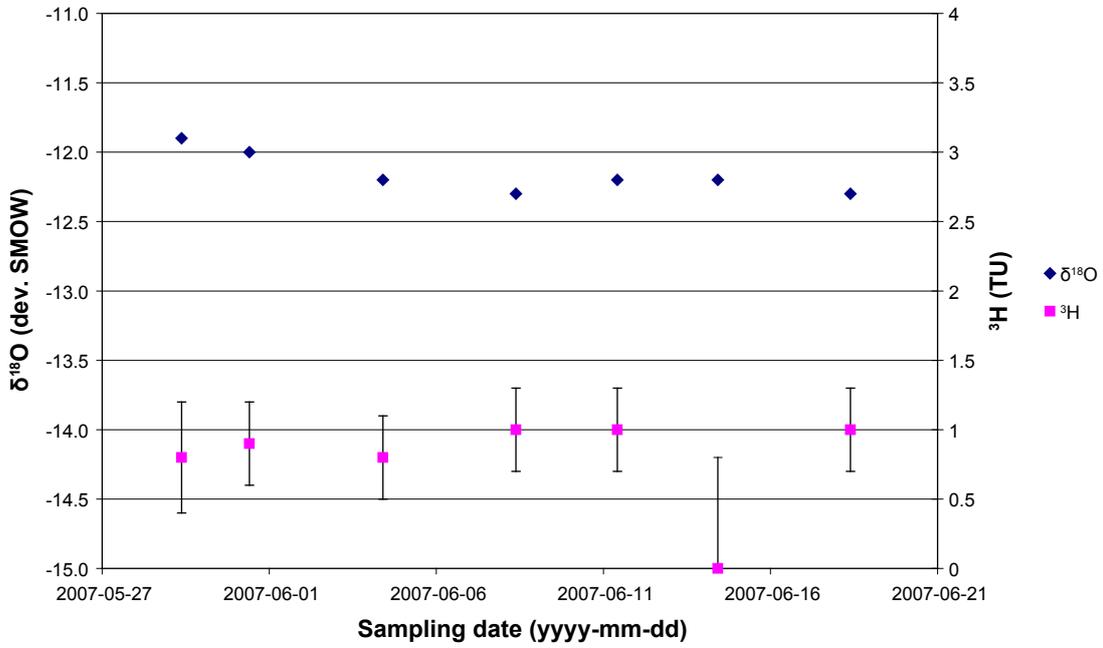


Figure 8-9. $\delta^{18}\text{O}$ and ^3H data versus sampling date, section 669.7–676.8 m.

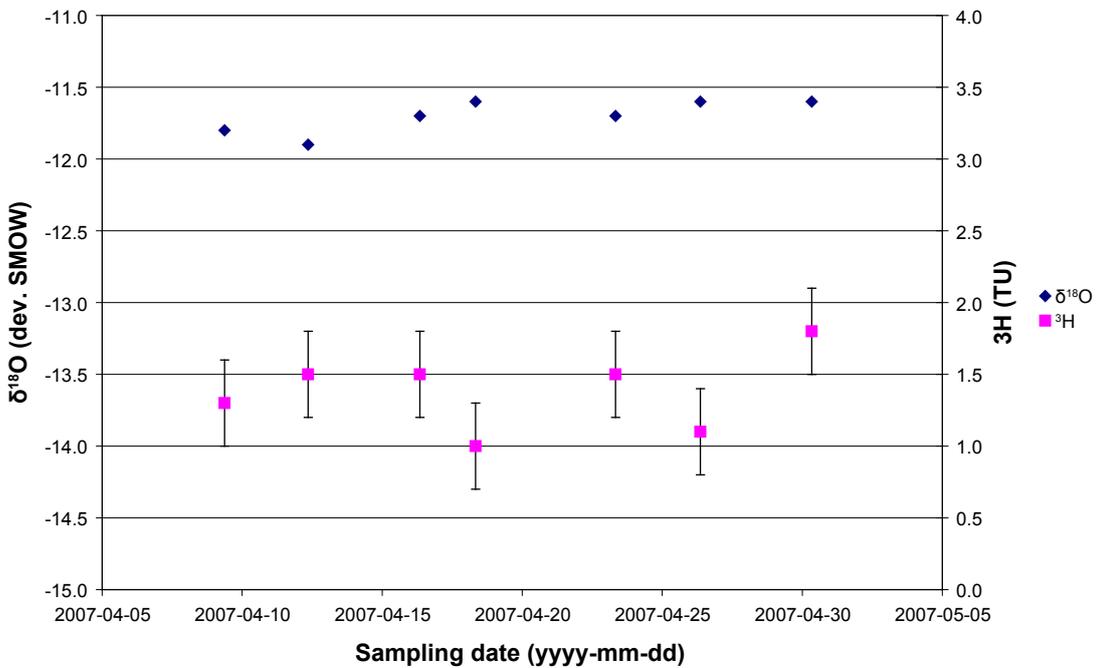


Figure 8-10. $\delta^{18}\text{O}$ and ^3H data versus sampling date, section 828.4–835.5 m.

In section 669.7–676.8 m, the carbon isotopes ($\delta^{13}\text{C}$ and pmC) were determined both in inorganic carbon (hydrogen carbonate) and in organic constituents (enriched samples). The organic pmC amounted to 35.8% in the enriched sample.

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 10, Table A10-5.

Total gas content in the groundwater as well as the detected oxygen contamination is given in Table 8-3. The effects of air leakage may be corrected for, assuming that the oxygen content is zero, by removing the air effect (nitrogen, oxygen and argon). The total gas content is somewhat higher in section 828.4–835.5 m than in section 669.7–676.8 m and it is mainly the nitrogen content that contributes to the difference. It cannot be excluded that some leakage of nitrogen into the PVB-container 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 compositions of the groundwater are presented in Figures 8-11 and 8-12.

Table 8-3. Total content of dissolved gas.

| | Section 669.7–676.8 m | Section 828.4–835.5 m |
|--------------------------|-----------------------|-----------------------|
| Total gas content (mL/L) | 98 | 110 |
| Oxygen content (mL/L) | 0.035 | < 0.01 |

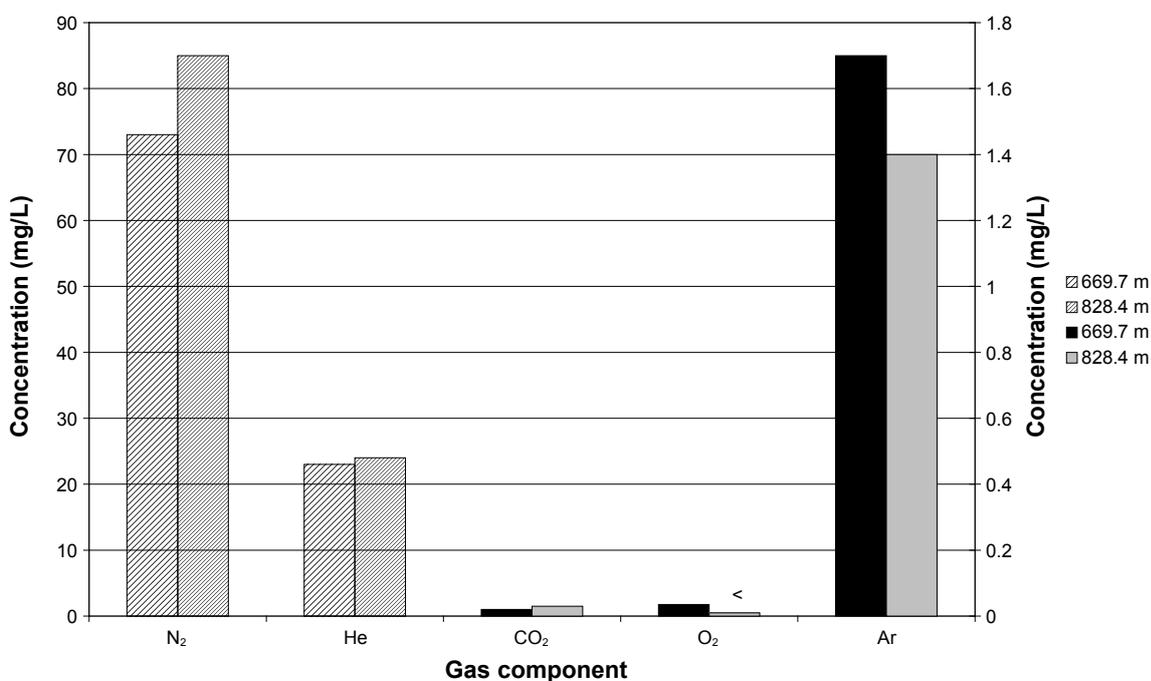


Figure 8-11. Gas components of high concentrations (N_2 , He, Ar, CO_2 , and O_2) in the samples collected in sections 669.7–676.8 m and 828.4–835.5 m using the in situ sampling equipment. Bars with diagonally striped and solid colour filled patterns refer to left and right hand axis, respectively.

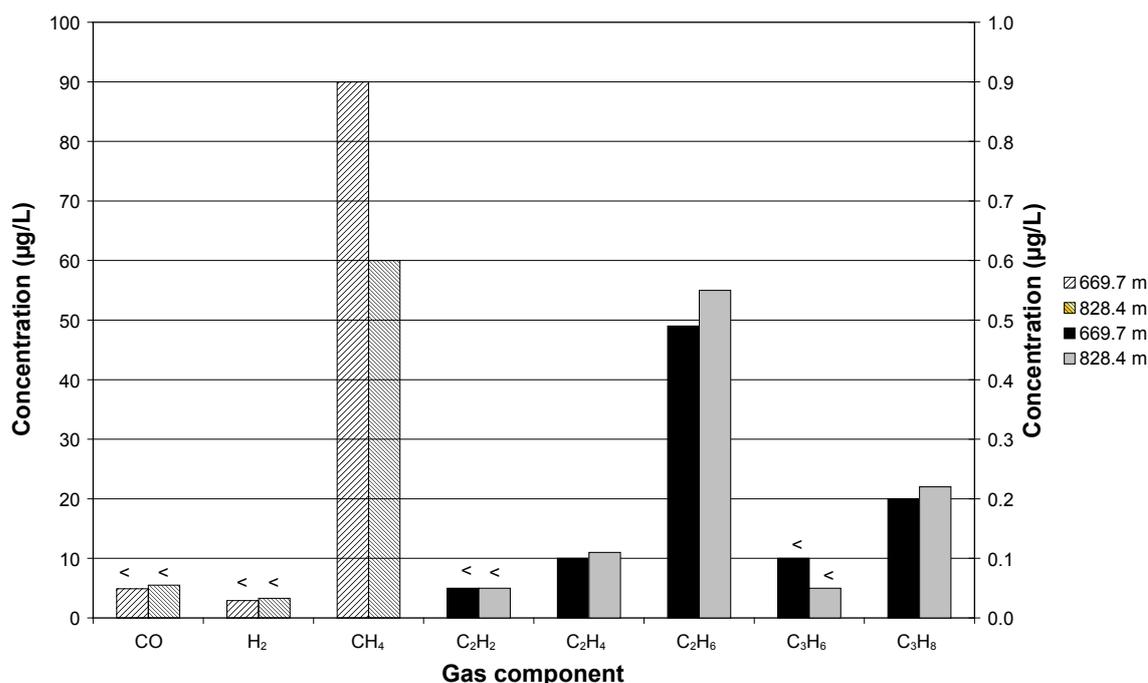


Figure 8-12. Gas components of low concentrations (CO , H_2 , CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 and C_3H_6), in the samples collected in sections 669.7–676.8 m and 828.4–835.5 m using the in situ sampling equipment. Bars with diagonally striped and solid colour filled patterns refer to left and right hand axis, respectively.

8.4 Colloids

The presence of colloids in the groundwater in section 669.7–676.8 m was investigated using three methods, 1) filtration through a series of connected filters in an argon atmosphere (three variations, see 5.2.6), 2) fractionation/ultra filtration using two cylindrical filters with cut-offs of 1,000 D and 5,000 D and 3) Laser-Induced Breakdown Detection, LIBD, Appendix 7. LIBD was used also in section 828.4–835.5 m.

8.4.1 Inorganic colloids – colloid filtration

The results from “Filtration – ICP” and “Filtration + rinsing – ICP” are presented in Figures 8-13 to 8-20. Note that the volume of sample water filtrated in “Filtration + rinsing – ICP” is only about half as much as in “Filtration – ICP” (see Table 5-5).

The diagrams present the amounts per litre of aluminium, iron, silicon, manganese, calcium (in mg), sulphur and uranium calculated from the amounts collected on each filter. The amounts of silicon on the filters may be underestimated due to the filter leachate method used (nitric acid). This assumption is supported by the LIBD-report, Appendix 7. The sodium diagram in Figure 8-13 is included in order to illustrate the presence of remaining sample water in the non-rinsed filters. The sodium contents in the rinsed filters were, all of them, below the detection limit. Analysis of blank filters showed that the contributions of iron, manganese and silica from filters were insignificant. The amounts of aluminium, iron and uranium were, however, of the same magnitude or just somewhat lower than in the filtration test. The following conclusions may be drawn from the colloid filtration results:

- The contents of sodium and calcium contained in the filters were significant for the non-rinsed filters but below the detection limits for the rinsed filters. Calcium from remaining water in the non-rinsed filters is therefore likely to contribute to the colloid content. In order to improve the estimation of the colloid content, the sample water volume in each non-rinsed filter and the corresponding calcium addition to the filters needs to be calculated and subtracted.

- The silicon, manganese and sulphur contents were all below the detection limits. Some filters showed aluminium, iron and uranium contents above the detection limits. However, the contents in the rinsed filters were often higher than in the non-rinsed filters, probably due to contamination and/or impact of analytical errors.
- Despite the experimental – and interpretation difficulties due to the extreme sensitivity for contamination, possible undesired precipitation and adsorption processes as well as the large impact of the analytical errors at the very low concentrations considered, the results indicate a very low colloid content in the order of a few $\mu\text{g/L}$. This is in agreement with the LIBD method and the result from fractionation, see below.

Results of colloid filtering experiments, section 669.7–676.8 m

Comparison between “Filtration + ICP” and “Filtration + rinsing – ICP”

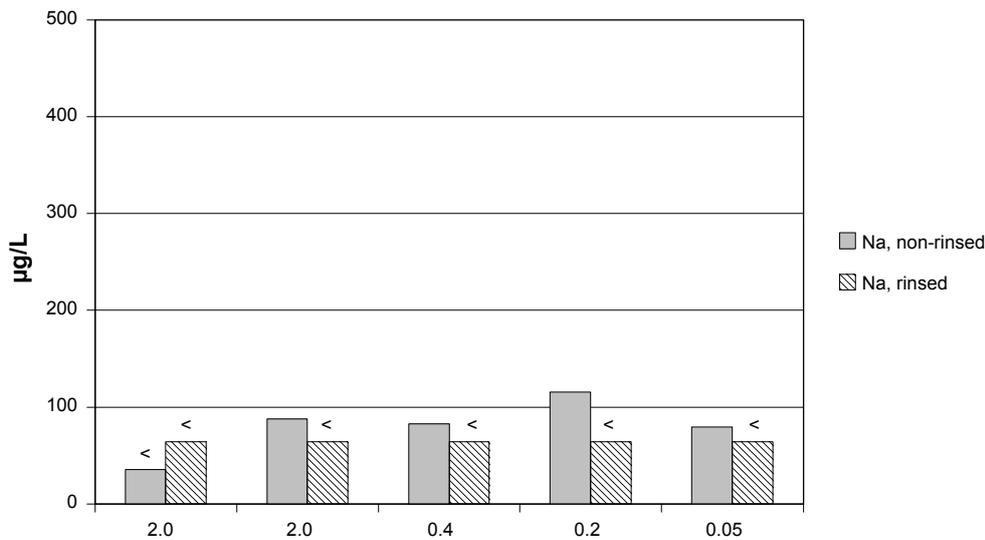


Figure 8-13. Concentration of sodium derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

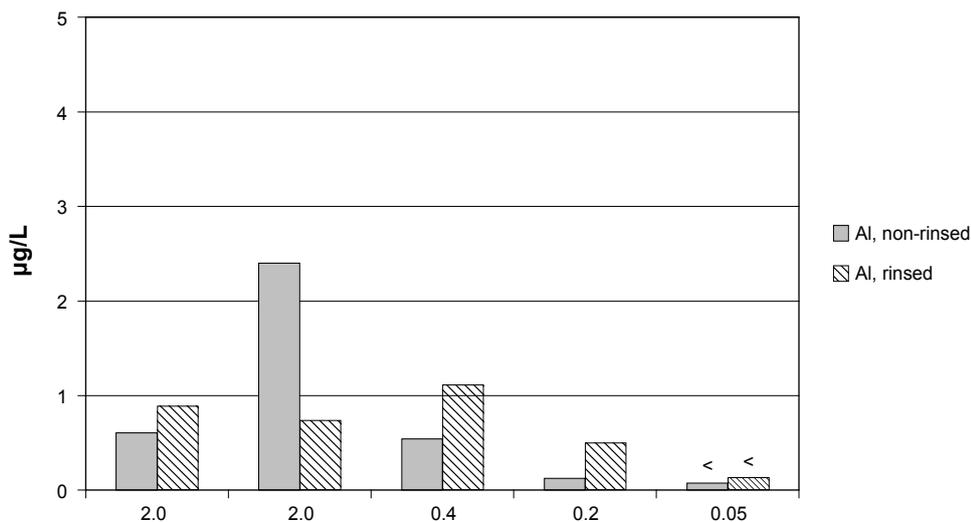


Figure 8-14. Concentration of aluminium derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

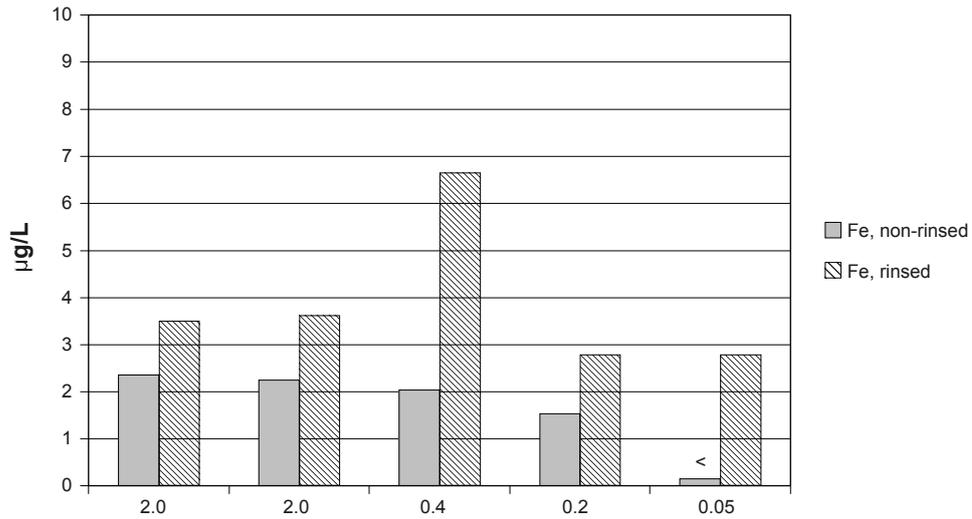


Figure 8-15. Concentration of iron derived from the amounts on the various non-rinsed or rinsed filters.

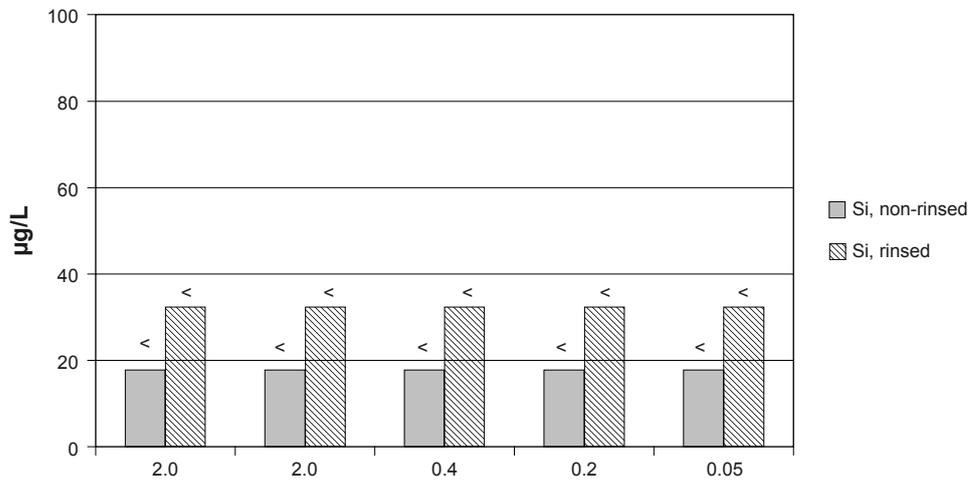


Figure 8-16. Concentration of silicon derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

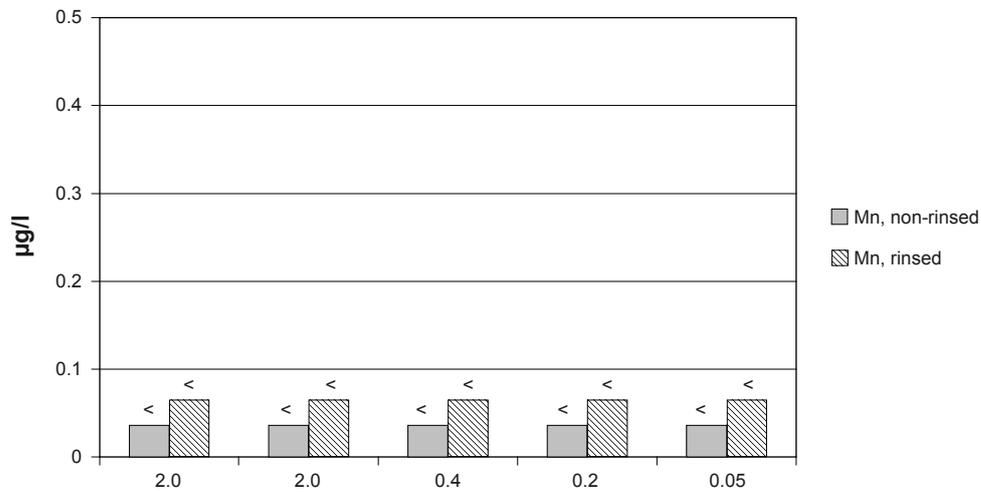


Figure 8-17. Concentration of manganese derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

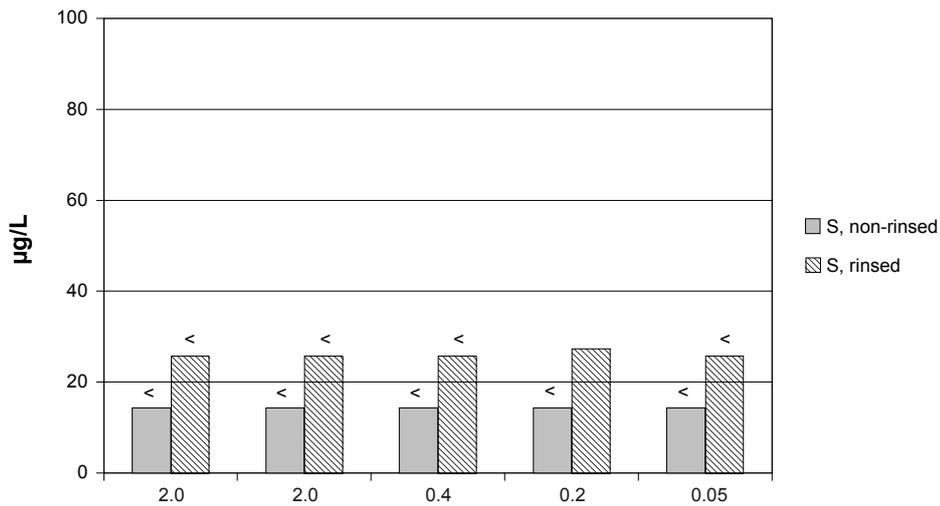


Figure 8-18. Concentration of sulphur derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

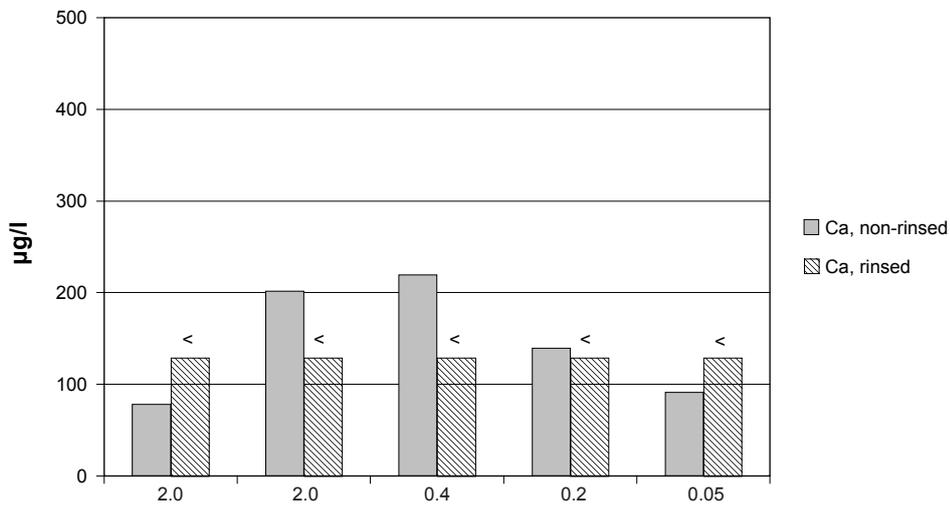


Figure 8-19. Concentration of calcium derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

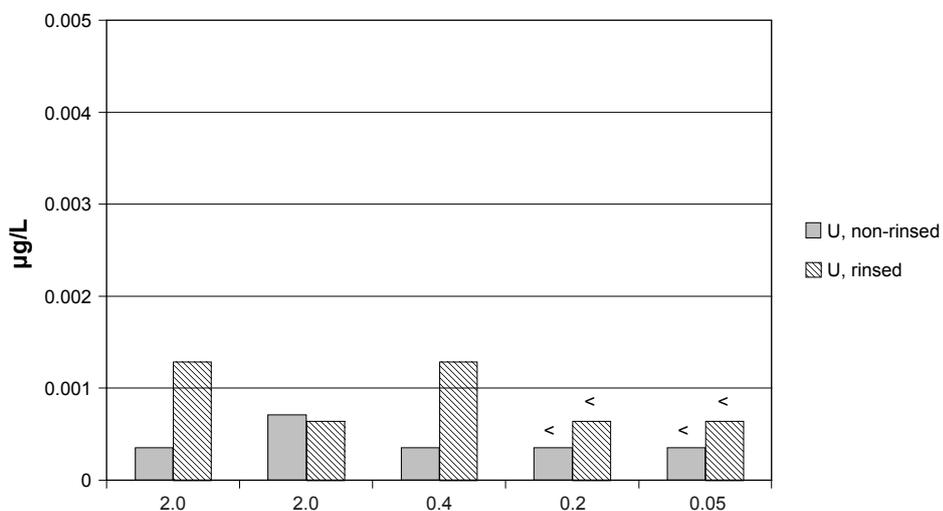


Figure 8-20. Concentration of uranium derived from the amounts on the various non-rinsed or rinsed filters. The lower detection limit is an effect of a larger filtered volume.

8.4.2 Inorganic colloids – fractionation

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

The fractionation results (see Table 8-4) indicate that Si, Ca, S and Mn exist solely as species with a molecular weight less than 1,000 g/mol. Such species are too small to be referred to as colloids. No calcite precipitation was detected. A small fraction of uranium with molecular weight more than 1,000 D and less than 5,000 D was observed in addition to the main fraction with molecular weight < 1,000 D.

The results for iron and aluminium were omitted due to inconsistent analytical results. In the iron case, this is due to very low concentrations close to or below the detection limit and the large impact of analytical errors. Aluminium, on the other hand, is very sensitive to contamination, although analytical errors may have an impact also here.

The blank samples (de-ionised water after passing through the washed filters) showed insignificant concentrations of silicon, calcium, sulphur, manganese and uranium.

8.4.3 Humic and fulvic acids – fractionation

The content of organic carbon in the borehole water in section 669.7–676.8 m, see Table 5-5, was below 1 mg/L and consists mainly of organic acids with molecular weights below 1,000 D. The fractionation in section 828.4–835.5 m was cancelled due to high contents of flushing water.

Table 8-4. Inorganic fractions (< 1,000 D, 1,000 D to 5,000 D and > 5,000 D) in section 669.7–676.8 m.

| Fraction | Si (mg/L) | Ca (mg/L) | S (mg/L) | Mn (µg/L) | U (µg/L) |
|-------------------------|-------------|-------------|------------|------------|-------------|
| < 1,000 D | 4.30 ± 0.62 | 2,450 ± 293 | 34.1 ± 4.2 | 60.6 ± 7.4 | 1.78 ± 0.30 |
| < 5,000 D | 4.26 ± 0.62 | 2,420 ± 291 | 34.4 ± 4.2 | 54.0 ± 6.6 | 2.13 ± 0.34 |
| > 1,000 D but < 5,000 D | < 0.1 | < 65.0 | < 2 | < 2 | 0.24 ± 0.08 |
| > 5,000 D | < 0.2 | < 140 | < 2 | < 3 | < 0.15 |
| Adsorption 1,000 D | < 1.5 | < 570 | < 9 | < 13 | 1.10 ± 0.60 |
| Adsorption 5,000 D | < 1.5 | < 530 | < 10 | < 14 | < 1.0 |

Table 8-5. Summary of fractionation results in KFM08D.

| Fraction | Section 669.7–676.8 m DOC (mg/L) |
|-----------|-------------------------------------|
| < 1,000 D | < 1.0 |
| < 5,000 D | < 1.0 |

9 Summary and discussion

The results from the hydrochemical investigation in KFM08D add important information about the groundwater compositions in the prioritised area for a planned repository. Furthermore, the borehole yields relatively little water and intersects a bedrock volume relatively free from large fractures and fracture zones, i.e. the type of bedrock conditions that will prevail at the location of a future repository for spent nuclear fuel.

The diagrams in Figures 9-1 to 9-3 display chloride and bromide concentrations versus depth as well as magnesium against chloride concentrations. Data from KFM08D are presented together with corresponding data from other boreholes at Forsmark. The chloride and magnesium concentrations in both of the borehole sections suggest brackish groundwaters of mainly old, non-marine origin. Two somewhat different trends (mixing lines) can be observed in Figure 9-2. The trend with low bromide to chloride ratios represents the marine mixing line, while the high ratio represents the non-marine mixing line. The ratios in both of the sections approach the steeper mixing line, corresponding to non-marine groundwaters.

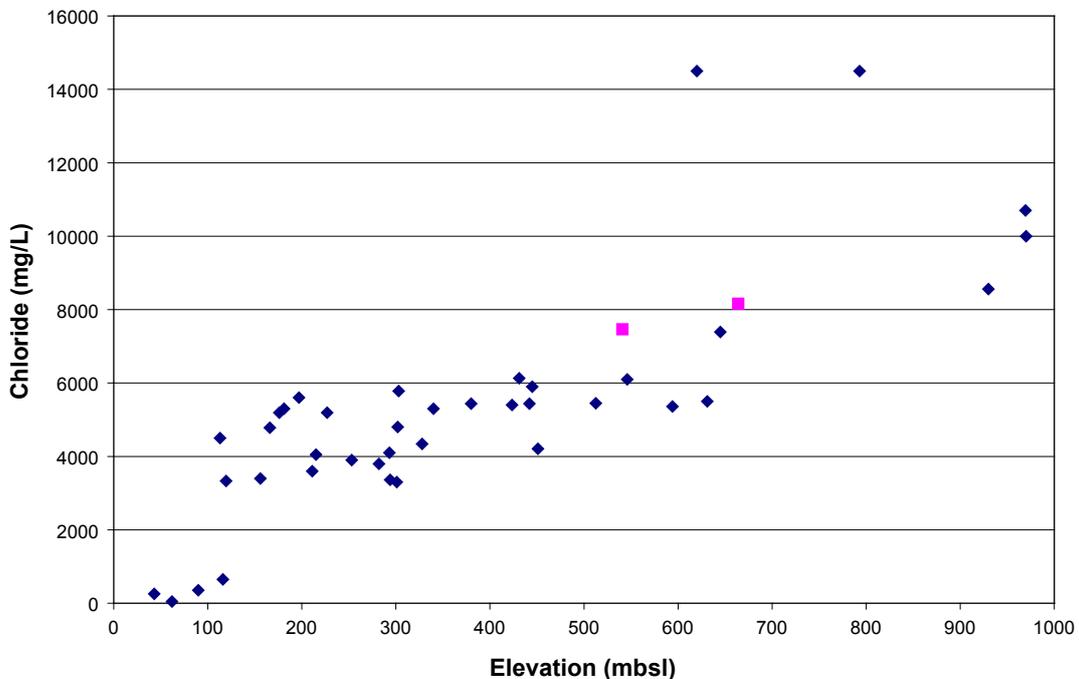


Figure 9-1. Chloride concentrations versus depth (m) at the Forsmark site. The values from KFM08D are shown in pink.

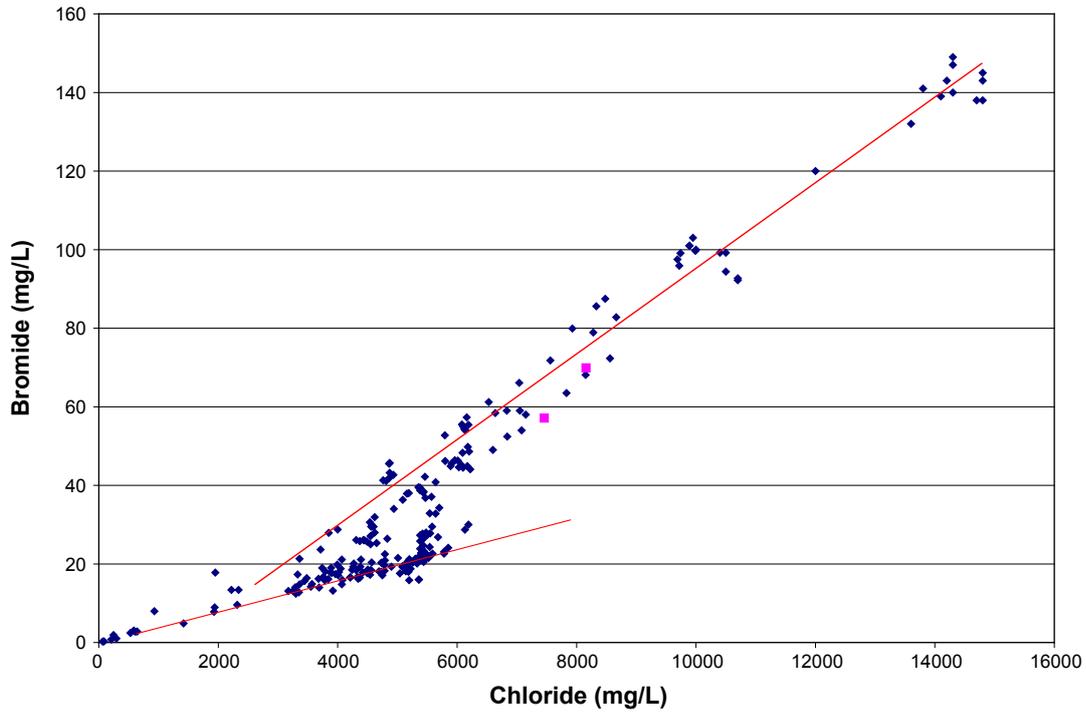


Figure 9-2. Bromide concentrations versus chloride concentrations at the Forsmark site. The values from KFM08D are shown in pink.

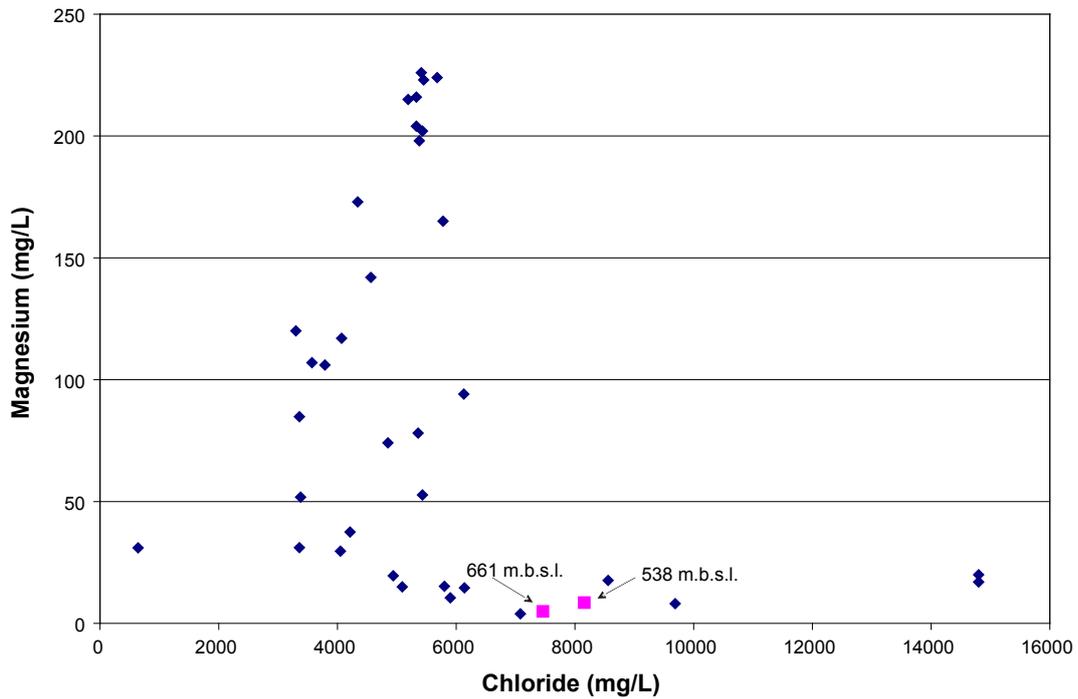


Figure 9-3. Magnesium concentrations versus chloride concentrations at the Forsmark site. The values from KFM08D are shown in pink.

The main conclusions from the hydrochemical characterisation in KFM08D are:

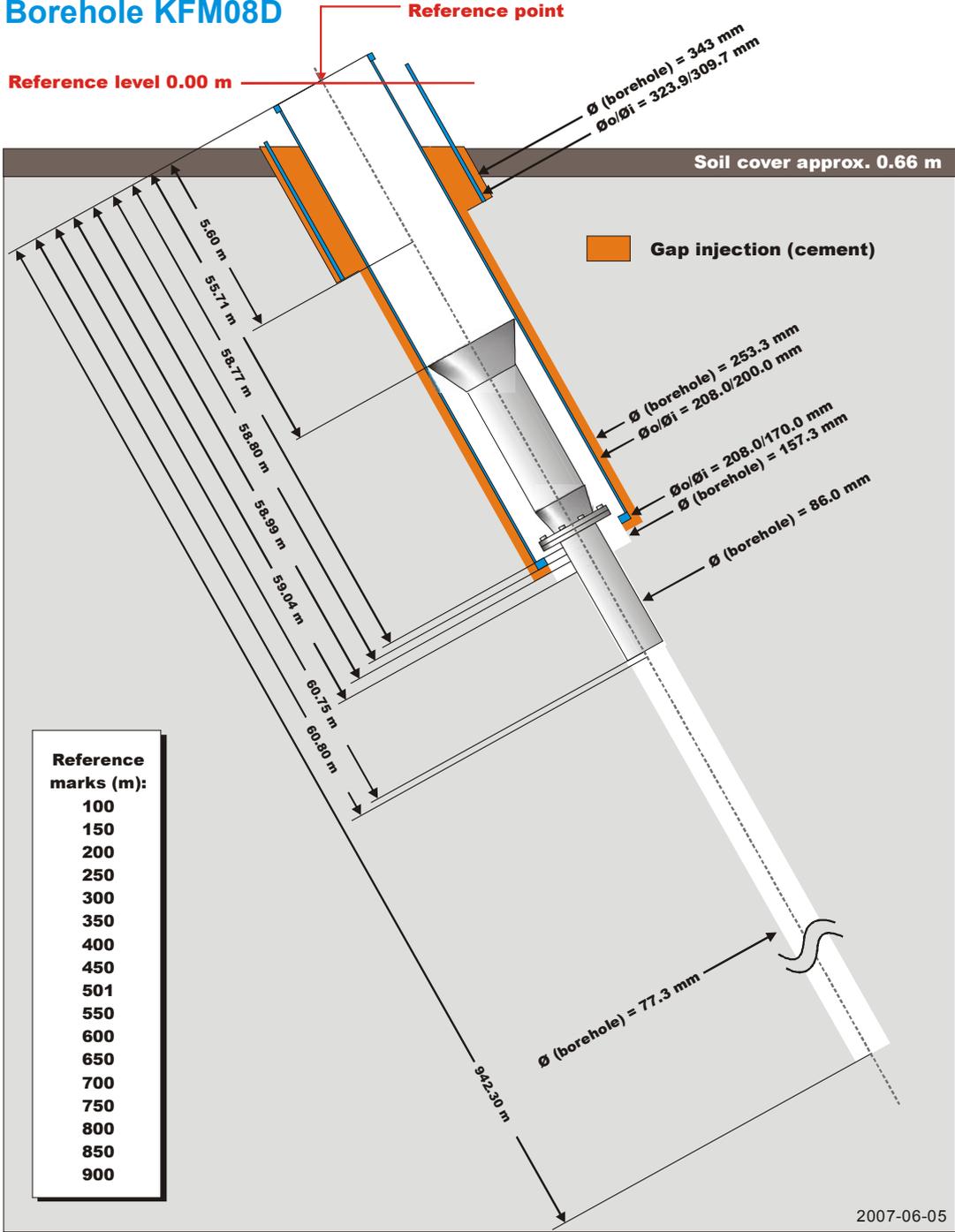
- In both of the sections, 669.7–676.8 m and 828.4–835.5 m, the low magnesium concentrations, the high chloride concentrations and the bromide to chloride ratios confirm groundwater compositions of a non-marine, deeper saline origin. This, together with a stable time series of main component concentrations, indicates that the bedrock is, in principle, impermeable above the investigated sections and that the groundwater has been isolated during several thousands of years. When comparing the previously investigated boreholes in the near vicinity, the composition is strongly similar to borehole KFM06A (section 768.0–775.1 m, /11/), borehole KFM08A (section 683.5–690.6 (690.8) m /12/) and borehole KFM01D (sections 428.5–435.6 m and 568.0–575.1 m /13/).
- The redox measurement in section 669.7–676.8 m performed quite well and the borehole electrodes stabilised at about –260 mV. In section 828.4–835.5 m the electrodes did not stabilise within the measurement period.
- The flushing water content at the beginning of the pumping/sampling period in section 669.7–676.8 m was especially high, although there was a significant decrease after some weeks of pumping. By the end of the pumping periods, the flushing water contents in sections 669.7–676.8 m and 828.4–835.5 m were still somewhat high, reaching 5% and 4%, respectively.
- In both of the sections, the major constituents showed stable concentrations during the pumping/sampling periods, indicating that no mixing occurred with water from other fracture systems with a different water composition.
- The quality of the water analyses is generally high, based on a comparison between results from different laboratories and methods as well as acceptable charge balance errors. The relative charge balance errors are within $\pm 5\%$.
- The uranium concentrations in the groundwater from KFM08D are reasonably low (0.2–4.5 $\mu\text{g/L}$) compared with the extremely high concentrations (80–120 $\mu\text{g/L}$) obtained in some of the other investigated boreholes and borehole sections in Forsmark.
- The colloid contents measured by LIBD amounted to less than or around 1 $\mu\text{g/L}$ in both sections, which is in agreement with a rough estimation from the colloid filtration study in section 669.7–676.8 m.
- If organic constituents exist in the groundwater, they are mostly present as low molecular weight fulvic acids and other low molecular weight organic acids such as citric acid and oxalic acid with a molecular weight less than 1,000 D.

10 References

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- /10/ **Kristiansson S, 2007.** Forsmark site investigation. Difference flow logging in borehole KFM08D. SKB P-07-84, Svensk Kärnbränslehantering AB.
- /11/ **Berg C, Wacker P, Nilsson A-C, 2005.** Forsmark site investigation. Chemical characterisation in borehole KFM06A. SKB P-05-178. Svensk Kärnbränslehantering AB.
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Design of cored borehole KFM08D

Technical data
Borehole KFM08D



Drilling reference point

Northing: 6700491.68 (m), RT90 2,5 gon V 0:-15
Easting: 1631199.16 (m), RT90 2,5 gon V 0:-15
Elevation: 2.61 (m), RHB 70

Orientation

Bearing (degrees): 99.98°
Inclination (degrees): -55.00°

Borehole

Length: 942.30 m

Percussion drilling period

Drilling start date: 2006-11-23
Drilling stop date: 2006-12-04

Core drilling period

Drilling start date: 2006-12-13
Drilling stop date: 2007-02-10

Selected results from differential flow logging, KFM08D

Forsmark, borehole KFM08D

Flow rate, caliper and single point resistance

- △ Without pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- ▽ Without pumping (L=5 m, dL=5 m), (Flow direction = into the bedrock)
- △ With pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- Without pumping (L=5 m, dL=0.5 m), 2007-03-15 - 2007-03-17
- With pumping (Drawdown 5 m, L=5 m, dL=0.5 m), 2007-03-18 - 2007-03-20
- With pumping (Drawdown 5 m, L=1 m, dL=0.1 m), 2007-03-20 - 2007-03-22
- With pumping during fracture-EC (Drawdown 5 m, L=0.5 m, dL=0.1 m), 2007-03-22 - 2007-03-23
- Lower limit of flow rate

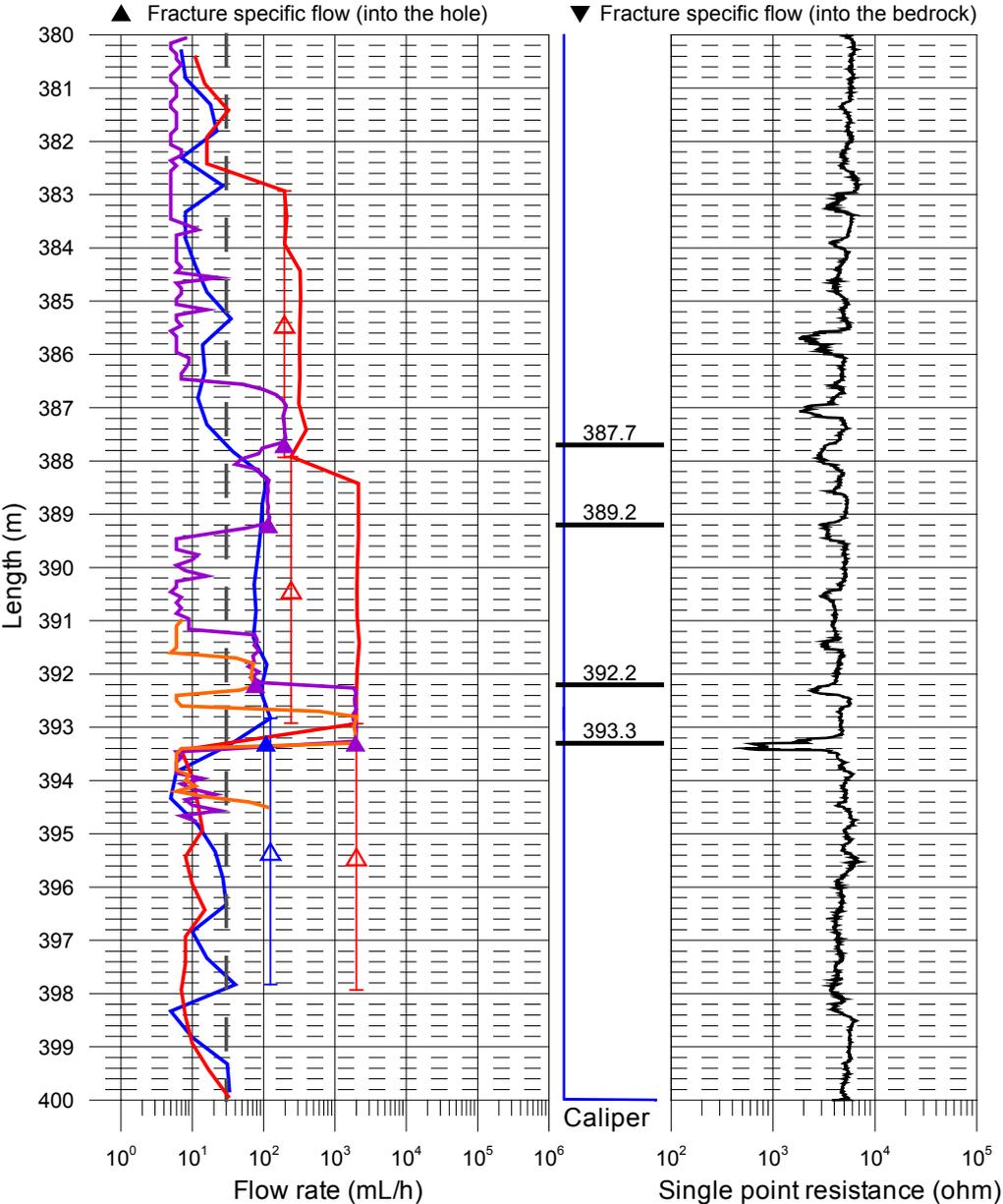


Figure A2-1. Borehole KFM08D: differential flow measurements from 380–400 m including the water bearing fracture zone at 393 m /10/.

Forsmark, borehole KFM08D

Flow rate, caliper and single point resistance

- ▲ Without pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- ▼ Without pumping (L=5 m, dL=5 m), (Flow direction = into the bedrock)
- ▲ With pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- Without pumping (L=5 m, dL=0.5 m), 2007-03-15 - 2007-03-17
- With pumping (Drawdown 5 m, L=5 m, dL=0.5 m), 2007-03-18 - 2007-03-20
- With pumping (Drawdown 5 m, L=1 m, dL=0.1 m), 2007-03-20 - 2007-03-22
- With pumping during fracture-EC (Drawdown 5 m, L=0.5 m, dL=0.1 m), 2007-03-22 - 2007-03-23
- Lower limit of flow rate

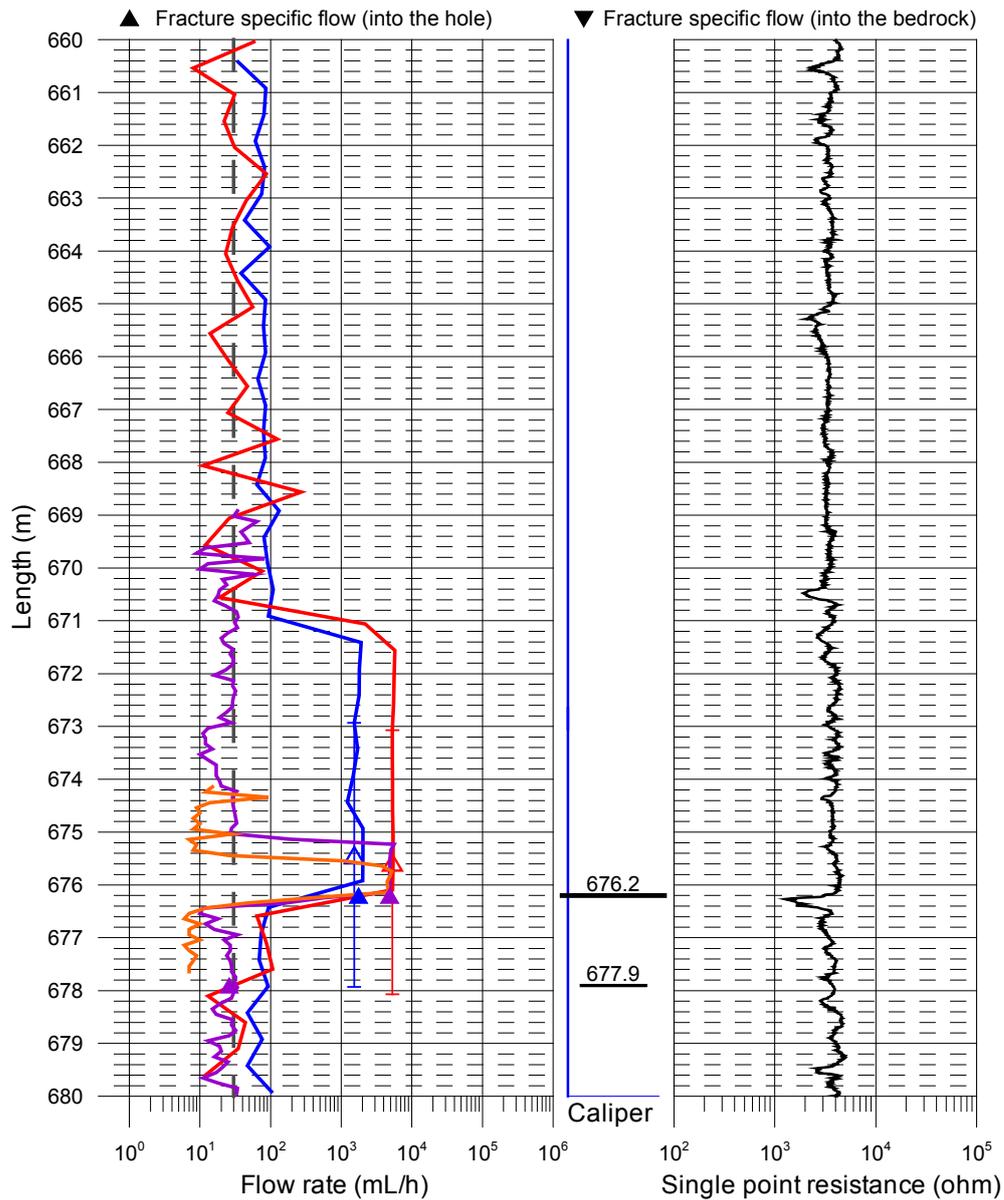


Figure A2-2. Borehole KFM08D: differential flow measurements from 660–680 m including the water bearing fracture zone at 676 m /10/. The flow log gives no indication of a flow anomaly located in the vicinity above 676.2 m which fits to the sampled section 669.7–676.8 m, see Chapter 6.

Forsmark, borehole KFM08D

Flow rate, caliper and single point resistance

- △ Without pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- ▽ Without pumping (L=5 m, dL=5 m), (Flow direction = into the bedrock)
- △ With pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- Without pumping (L=5 m, dL=0.5 m), 2007-03-15 - 2007-03-17
- With pumping (Drawdown 5 m, L=5 m, dL=0.5 m), 2007-03-18 - 2007-03-20
- With pumping (Drawdown 5 m, L=1 m, dL=0.1 m), 2007-03-20 - 2007-03-22
- With pumping during fracture-EC (Drawdown 5 m, L=0.5 m, dL=0.1 m), 2007-03-22 - 2007-03-23
- Lower limit of flow rate

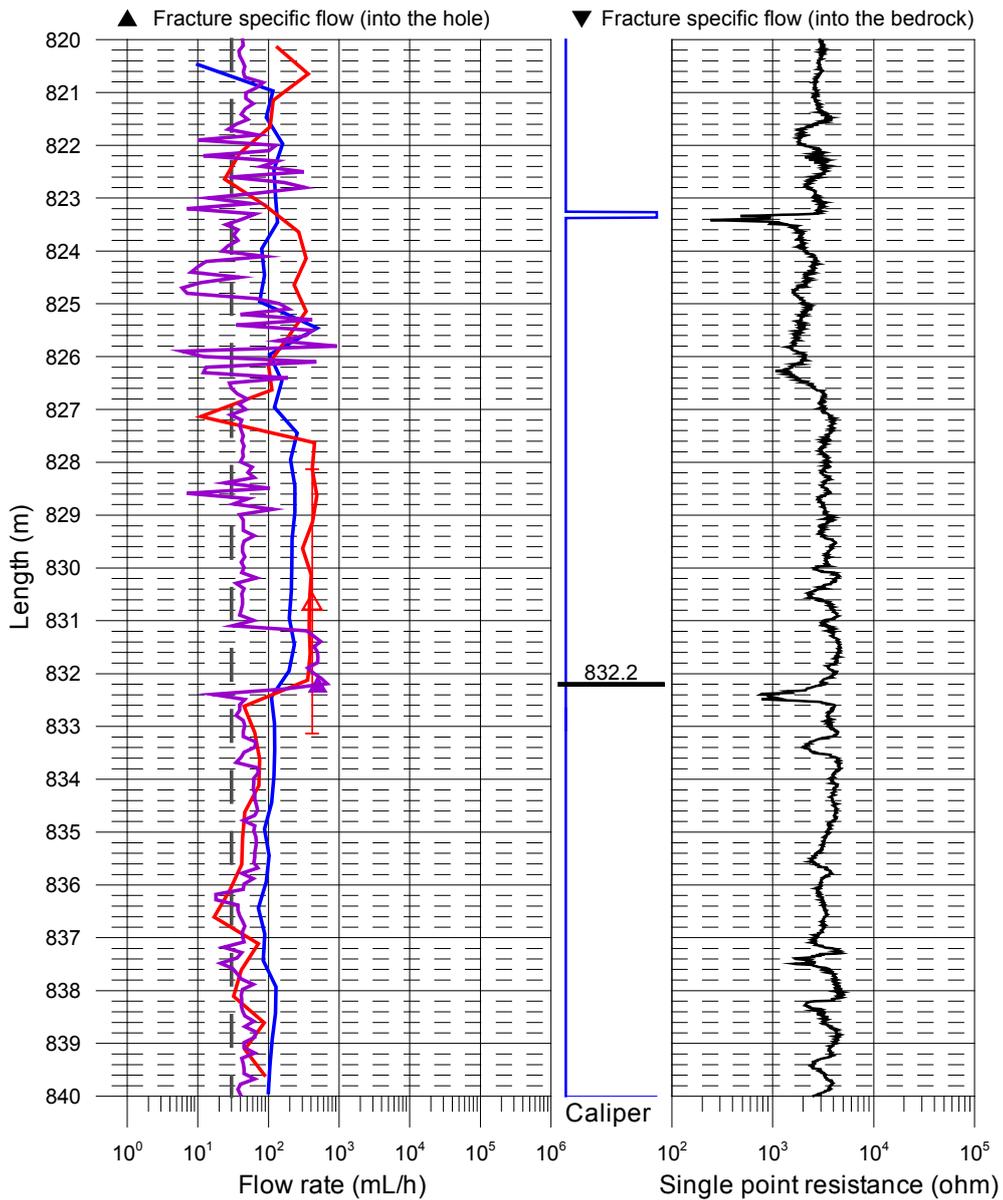


Figure A2-3. Borehole KFM08D: differential flow measurements from 820–840 m including the water bearing fracture zone at 832 m /10/.

Selected BIPS logging images, KFM08D

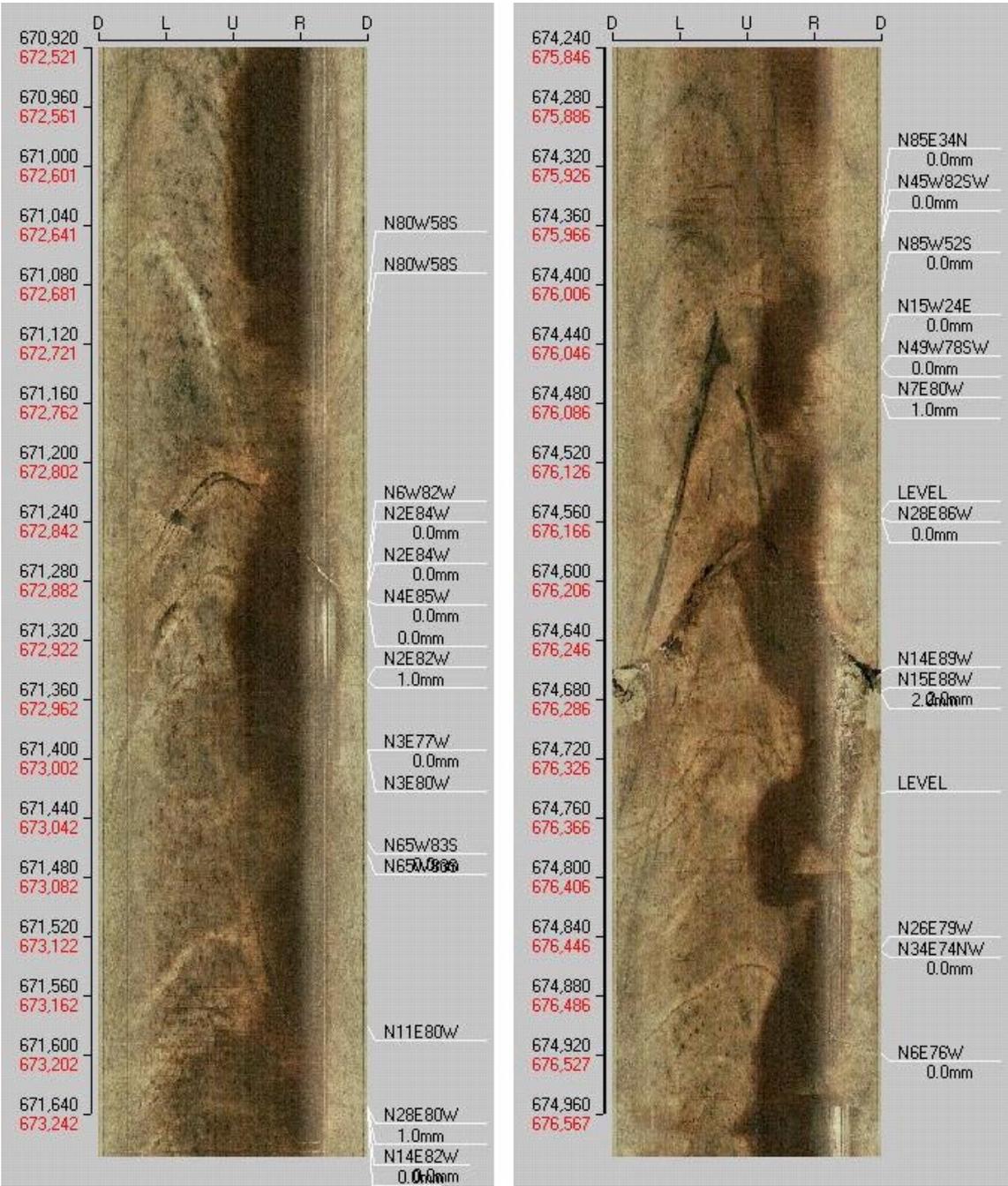


Figure A3-1. Borehole KFM08D: selected BIPS logging images from 672.5 to 676.6 m borehole length, including possible water bearing fractures in section 669.7–676.8 m (first image) and the abandoned section 670.7–677.8 m (both images), see Chapter 6 for explanation. The non-adjusted length is marked with black and the adjusted true length is marked with red /9/.

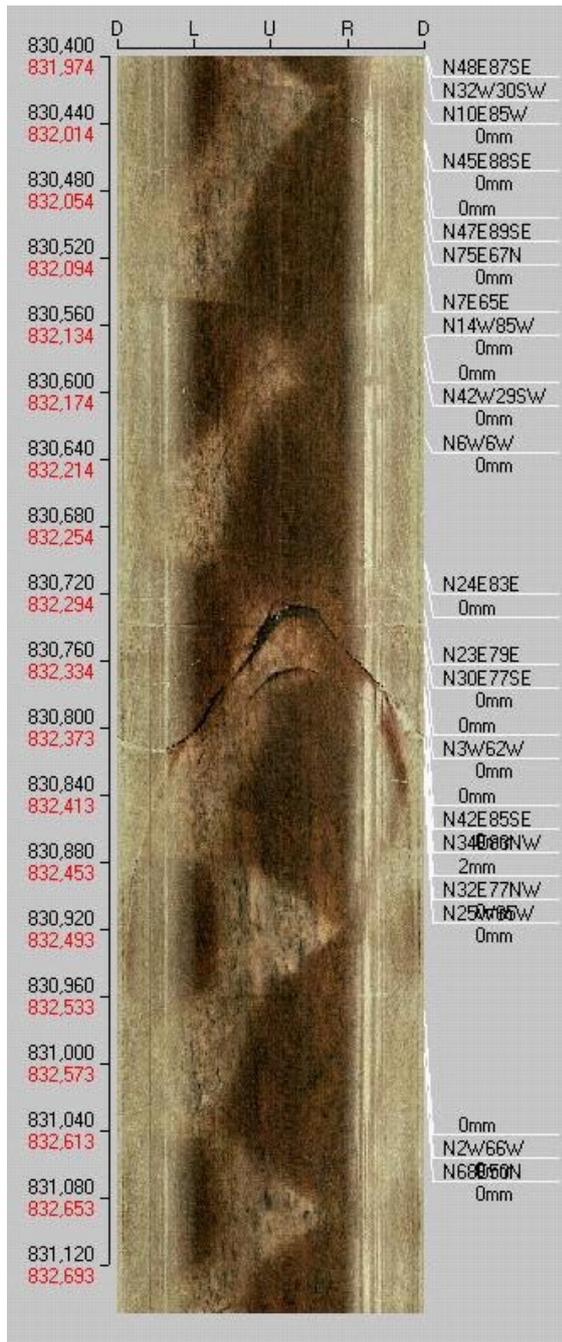


Figure A3-2. Borehole KFM08D: selected BIPS logging image from 832.0 to 832.7 m borehole length, including the water bearing fracture at 832 m. The non-adjusted length is marked with black and the adjusted true length is marked with red /9/.

Measurement information, KFM08D

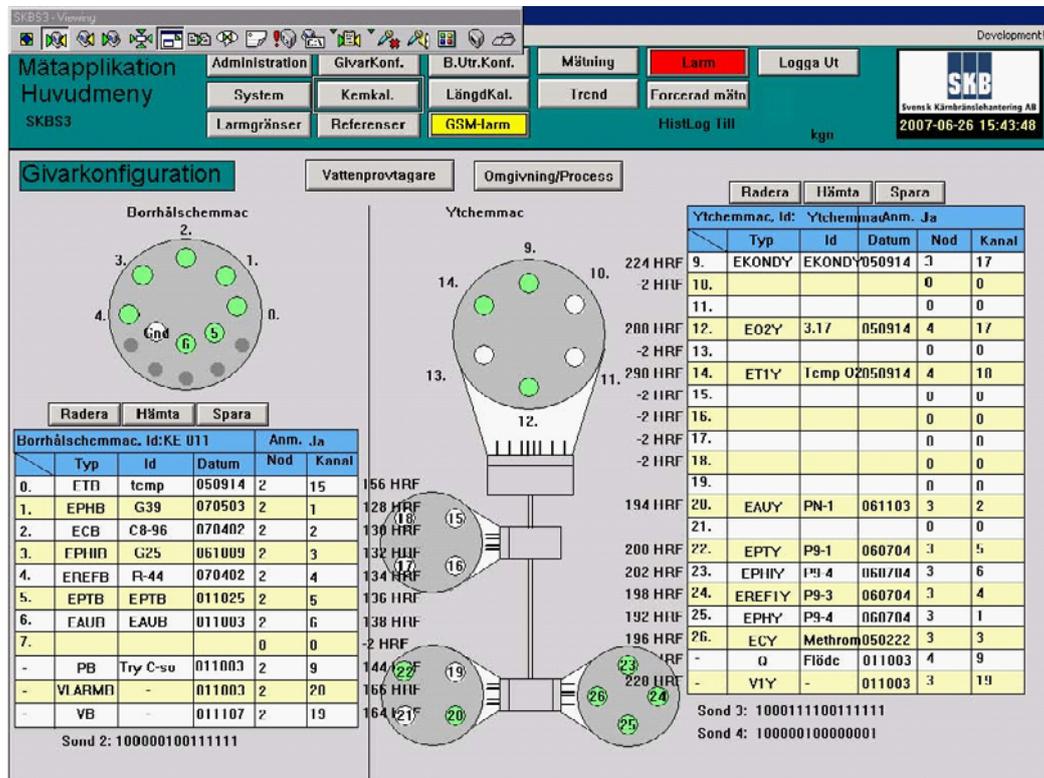


Figure A4-1. Electrode configuration, section 669.7–676.8 m.

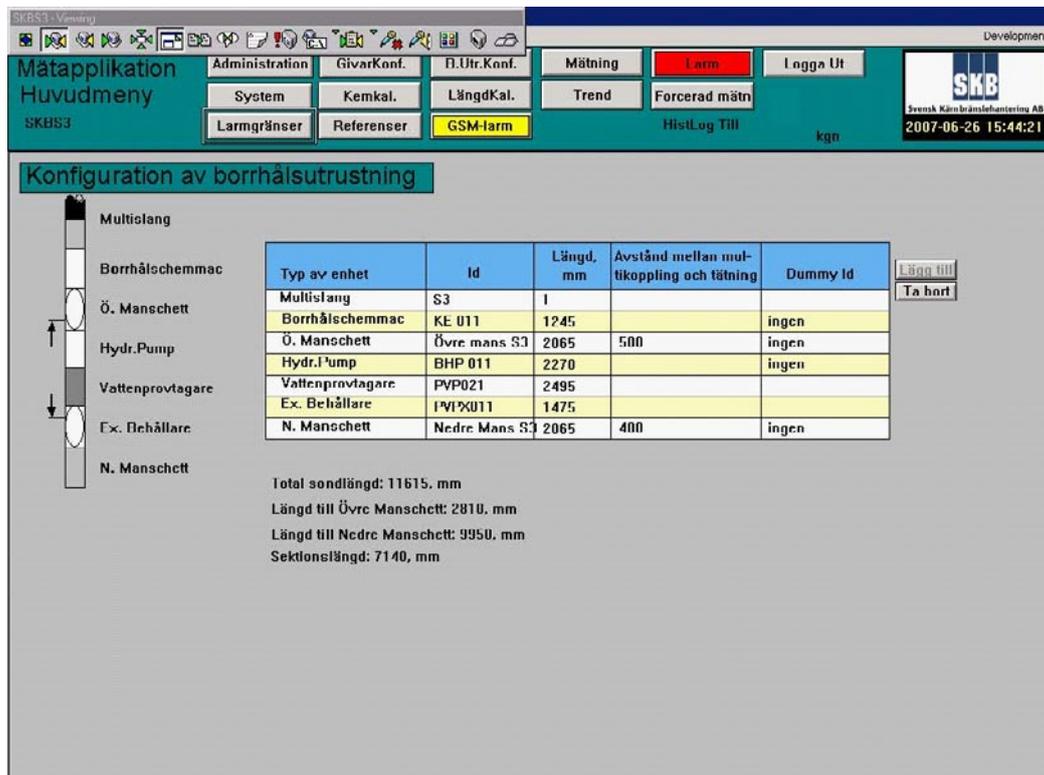


Figure A4-2. Configuration of downhole equipment, section 669.7–676.8 m.

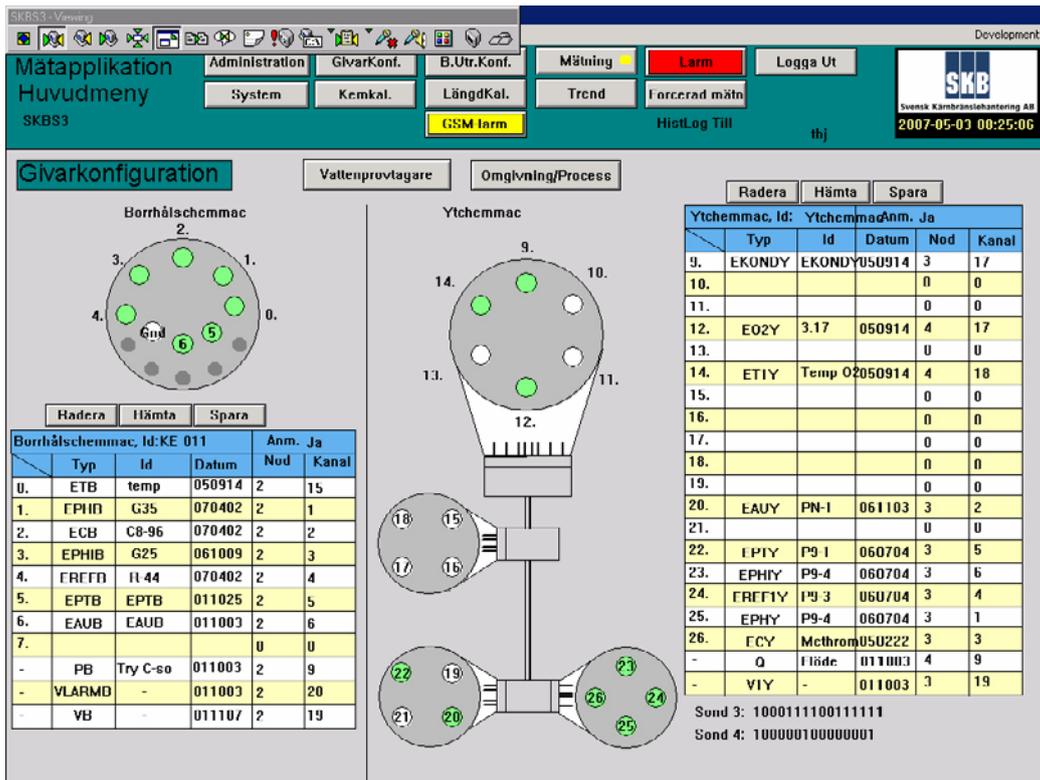


Figure A4-5. Electrode configuration, section 828.4–835.5 m.

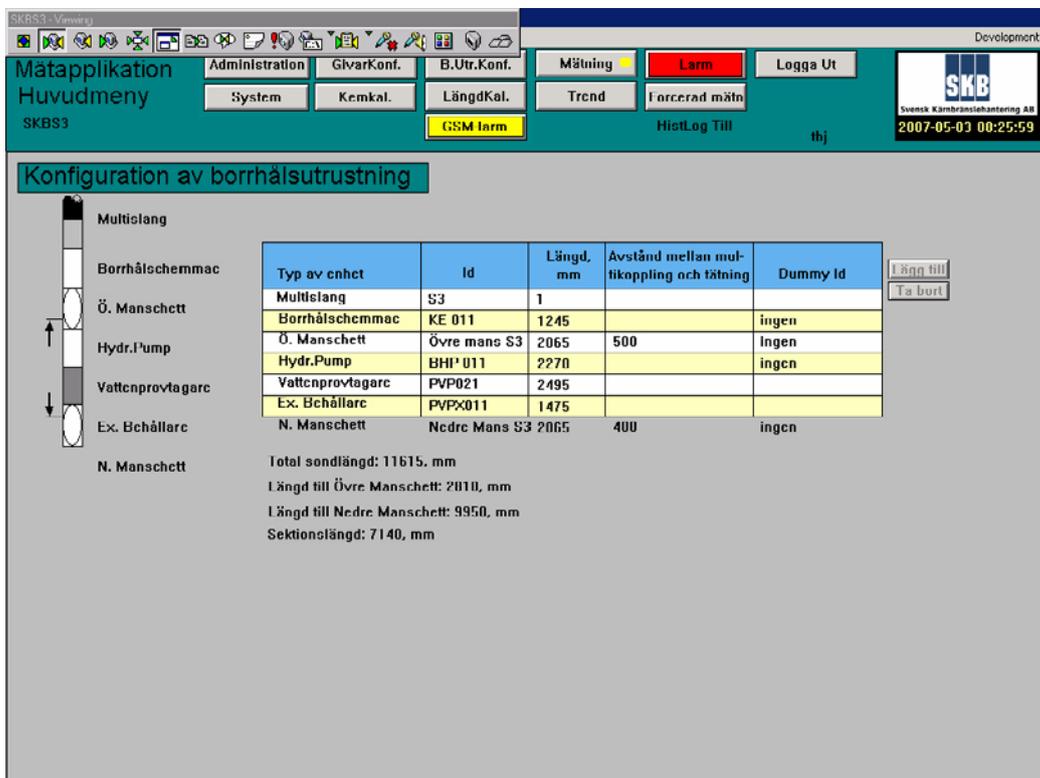


Figure A4-6. Configuration of downhole equipment, section 828.4–835.5 m.

Flow and pressure measurements, KFM08D

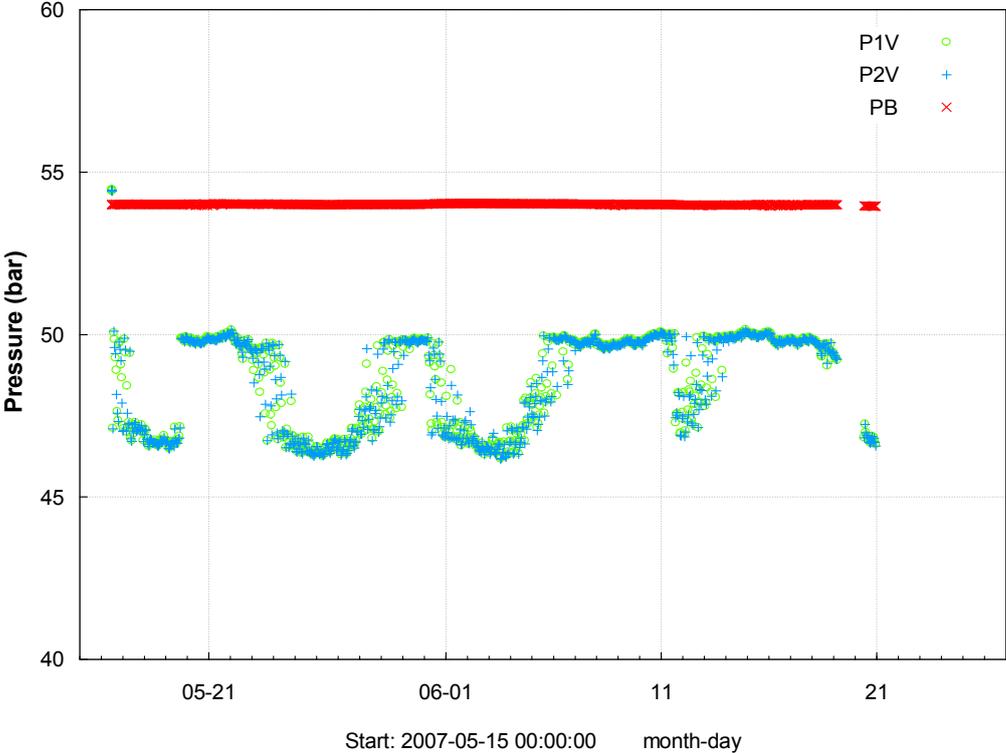


Figure A5-1. Pressure measurements (P1V, P2V and PB), section 669.7–676.8 m. The sensors P1V and P2V measure the pressure within the section and are both placed in the in situ sampling unit. The sensor PB, placed in the borehole Chemmac, measures the pressure above the section.

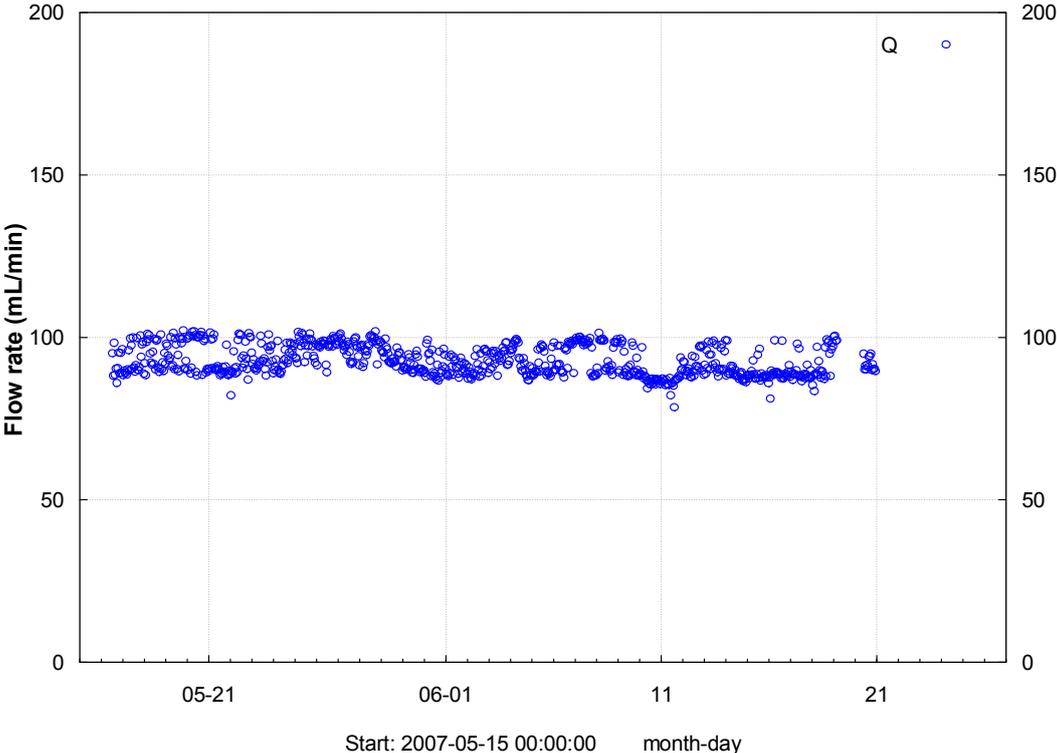


Figure A5-2. Pumping flow rate (Q), section 669.7–676.8 m.

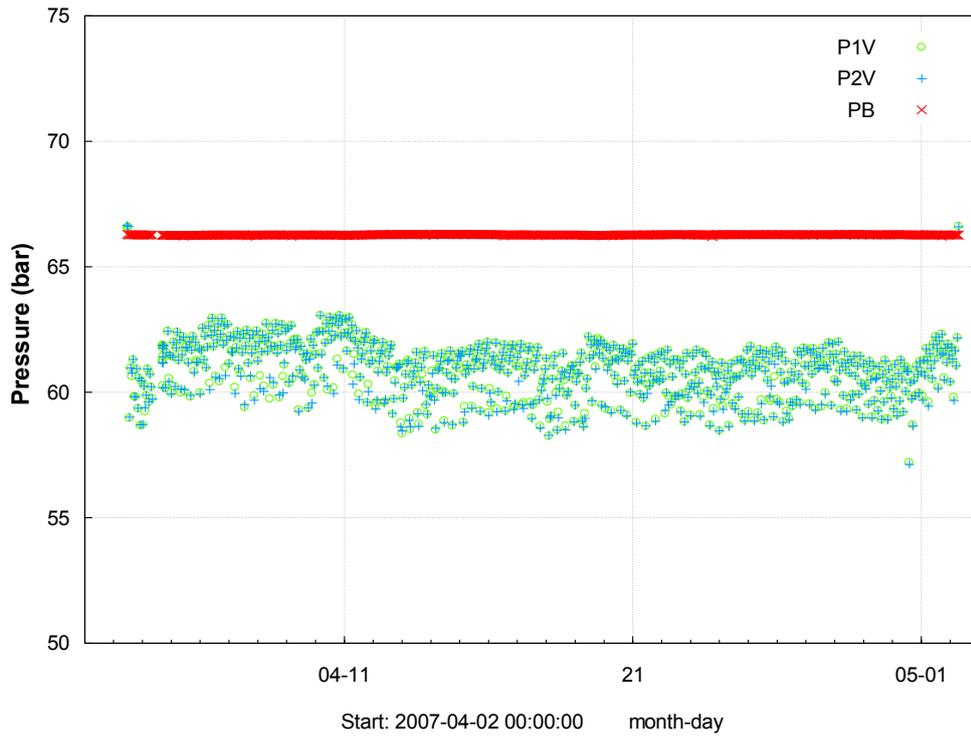


Figure A5-3. Pressure measurements (P1V, P2V and PB), section 828.4–835.5 m. The sensors P1V and P2V measure the pressure within the section and are both placed in the in situ sampling unit. The sensor PB, placed in the borehole Chemmac, measures the pressure above the section.

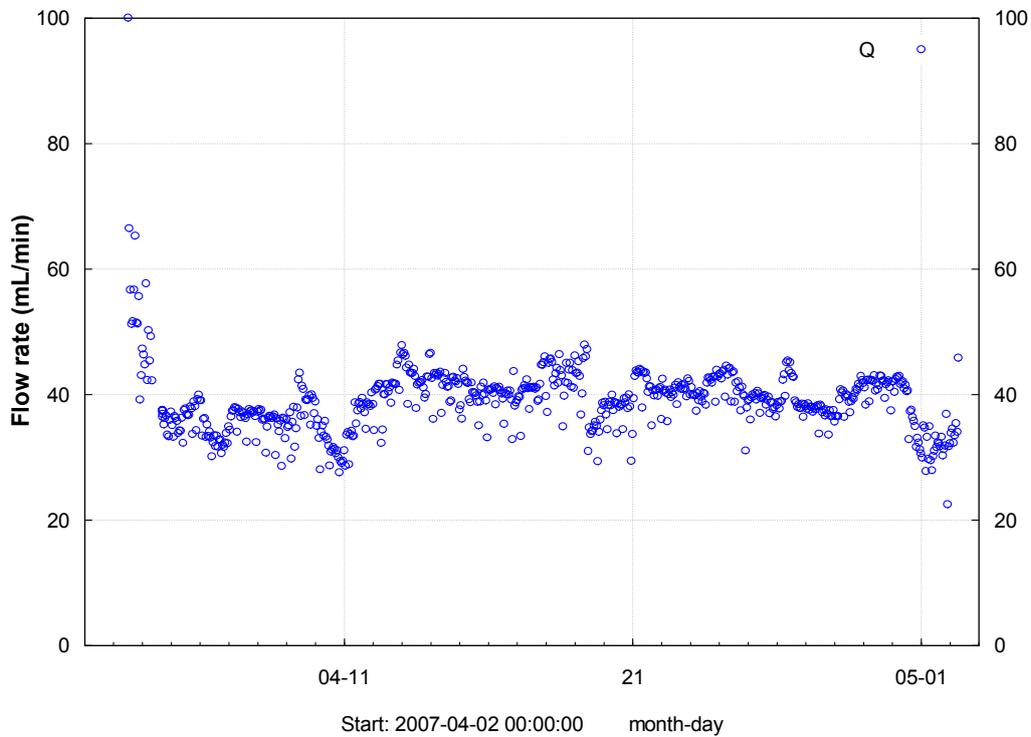


Figure A5-4. Pumping flow rate (Q), section 828.4–835.5 m.

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) |
| Dissolved organic Carbon, dissolved inorganic Carbon | DOC, DIC | Plastic | 250 25 | Yes | Frozen, transported in isolated bag | UV oxidation, IR Carbon analysator Shimadzu TOC5000 | Short transportation time |

| Component group | Component/element | Sample container (material) | Volume (mL) | Filtering | Preparation/ Conservation* | Analysis method | Analysis within – or delivery time to lab. |
|---|--|--|---------------------------------|-----------|-------------------------------------|---|--|
| Total organic Carbon | TOC | Plastic | 250 25 | No | Frozen, transported in isolated bag | UV oxidation, IR Carbon analysator Shimadzu TOC5000 | Short transportation time |
| Environmental isotopes | $\delta^2\text{H}$, $\delta^{18}\text{O}$ | Plastic | 100 | No | – | MS | Not critical (month) |
| Tritium | ^3H (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 | $^{87}\text{Sr}/^{86}\text{Sr}$ | 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 | $^{10}\text{B}/^{11}\text{B}$ | 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 |
| 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 |

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

* Suprapur acid is used for conservation of samples.

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

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

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 | ICP | 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 ² H | MS | 2 | | ‰ SMOW ⁵ | 1‰ | – |
| δ ¹⁸ O | MS | 0.1 | | ‰ SMOW ⁵ | 0.2‰ | – |
| ³ H | LSC | 0.8 | | TU ⁶ | 0.8 | – |
| ³⁷ Cl | ICP MS | 0.2‰ (20 mg/L) | | ‰ SMOC ⁷ | – | – |
| δ ¹³ C | A (MS) | – | | ‰ PDB ⁸ | – | – |
| ¹⁴ C pmc | A (MS) | – | | PMC ⁹ | – | – |
| δ 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 | – | – |
| ²³⁴ U, ²³⁵ U, ²³⁸ U, ²³² Th, ²³⁰ Th | Alfa spectr. | 0.0005 | | Bq/L ¹² | 5% | – |
| ²²² Rn, ²²⁶ Rn | LSS | 0.03 | | Bq/L | 5% | – |

1. Reporting limits at salinity $\leq 0.4\%$ (520 mS/m) and $\leq 3.5\%$ (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 deviation¹³ 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 deviation¹³ from SMOC (Standard Mean Oceanic Chloride).
8. Per mille deviation¹³ 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 deviation¹³ 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/kg²³⁸U, 1 ppm Th = 3.93 Bq/kg²³²Th.
13. Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:

$$\delta\text{‰} = 1,000 \times (K_{\text{sample}} - K_{\text{standard}}) / K_{\text{standard}}$$
 where K= the isotope ratio and $\text{‰} = {}^2\text{H}$, ${}^{18}\text{O}$, ${}^{37}\text{Cl}$, ${}^{13}\text{C}$ or ${}^{34}\text{S}$ etc.

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/cm³ and spherical particle shape. A more detailed description of data evaluation is given in /1/.

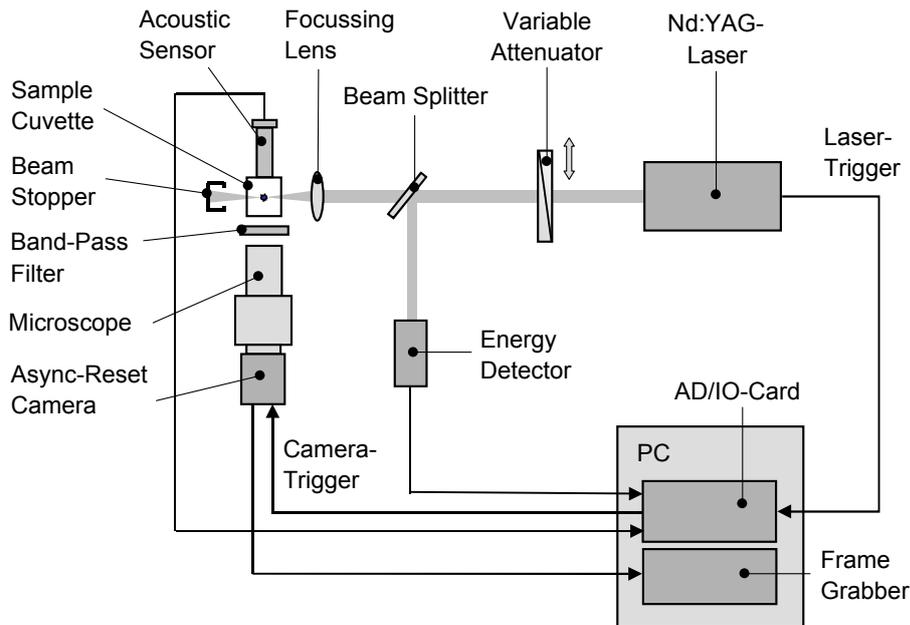


Figure A7-1. Schematic diagram of the mobile laser-induced breakdown detection system.

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.

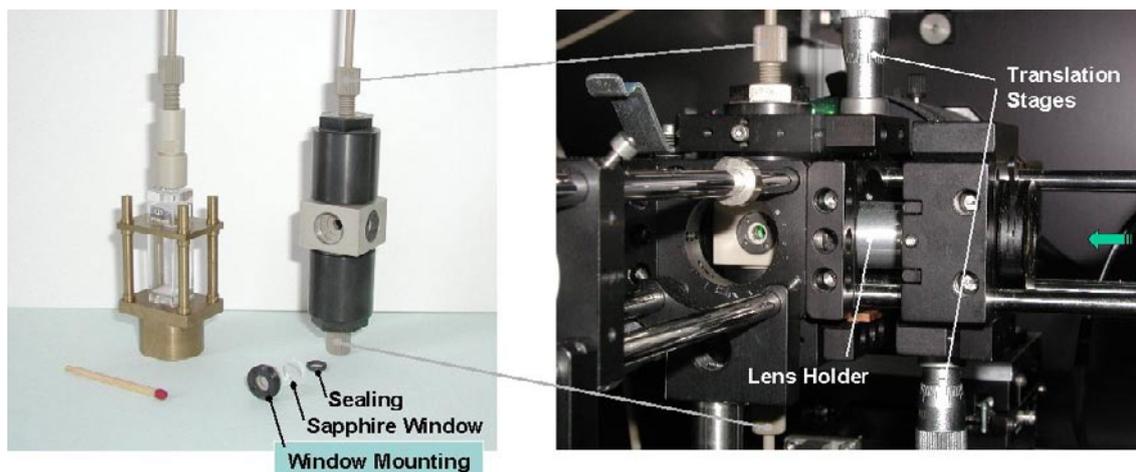


Figure A7-2. LIBD high-pressure flow-through detection cell (left: conventional flow-through silica detection cell).

- 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 elsewhere (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).

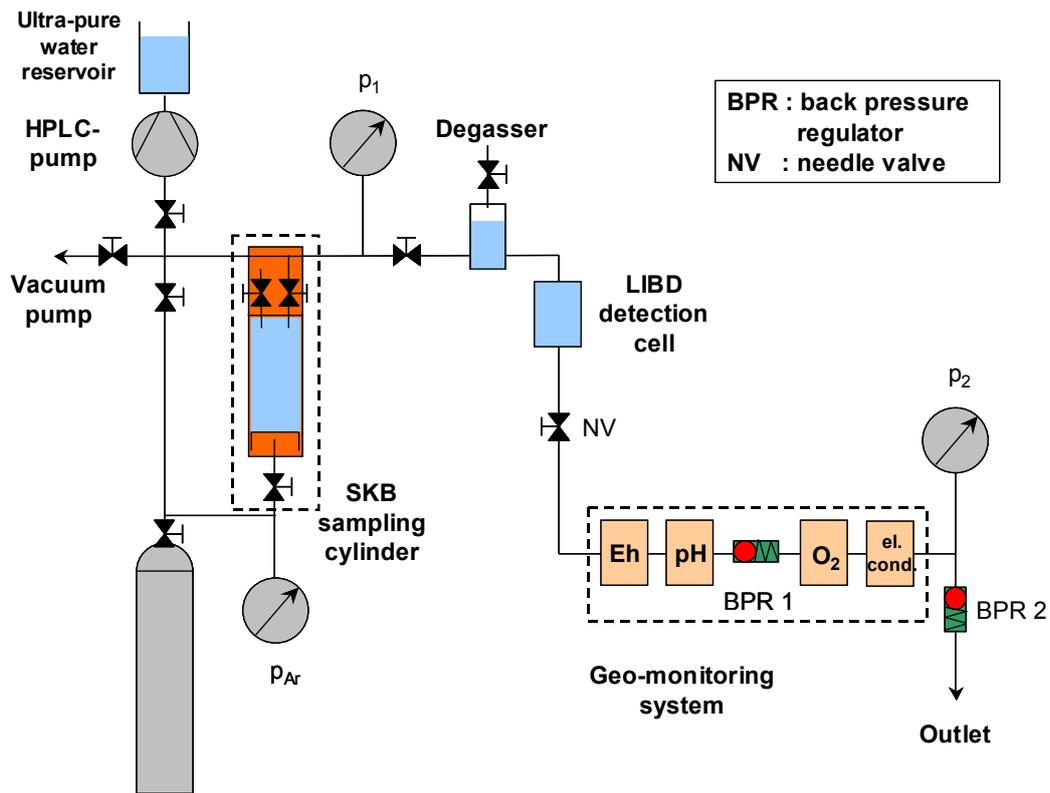


Figure A7-4. Scheme of the laboratory setup for in-line LIBD colloid analysis and groundwater monitoring.



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 oxygen. 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 distributions 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 consists 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).

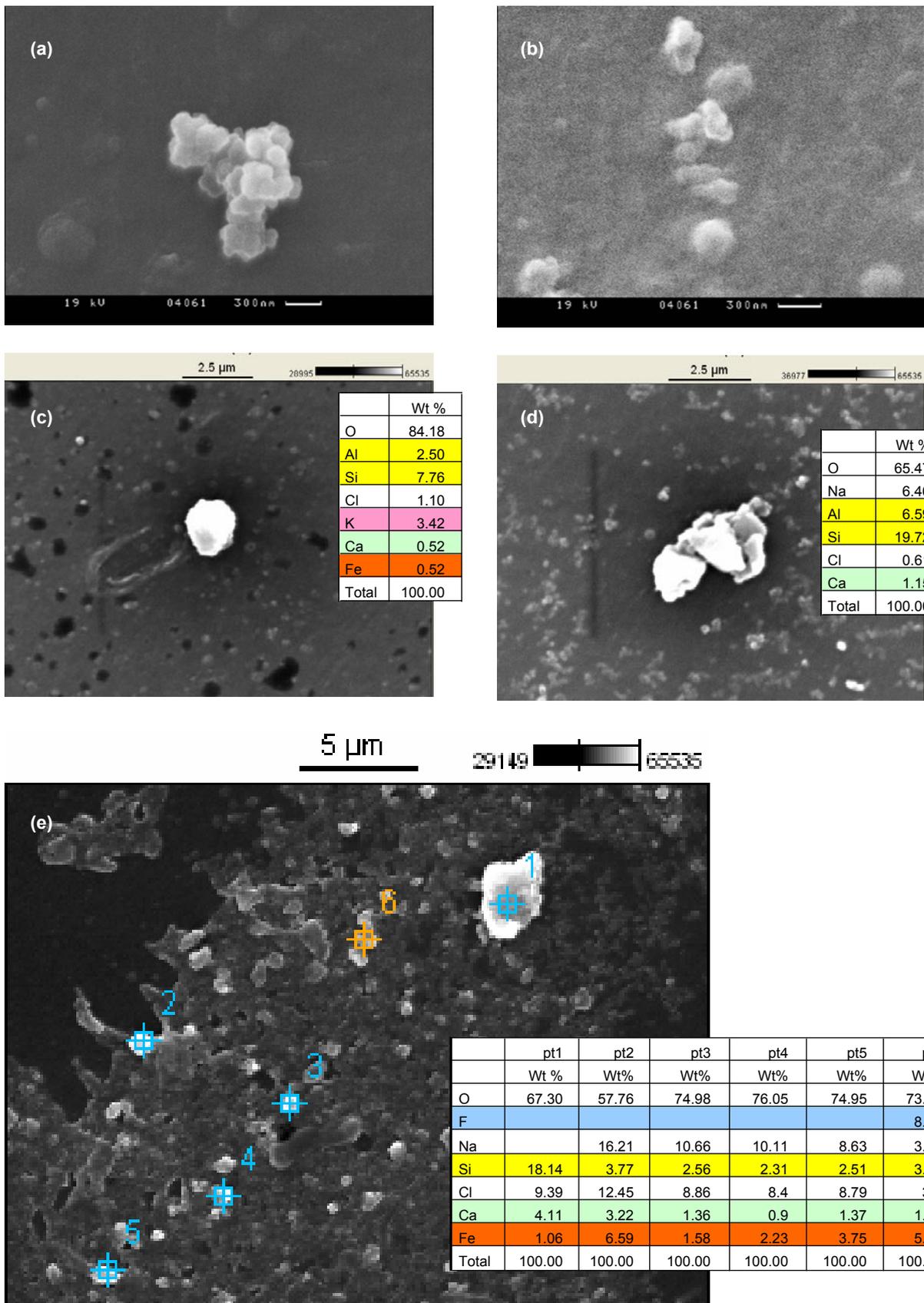


Figure A7-6. SEM images of groundwater KFM11A (447.5–454.64) m colloids on a 50 nm track-etched Polycarbonate filter.

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+05 |
| 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.

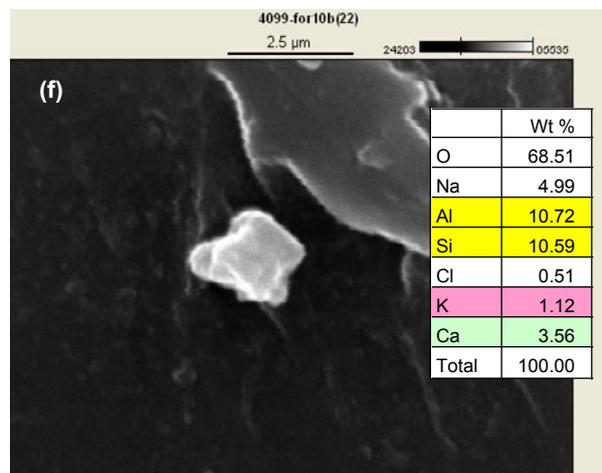
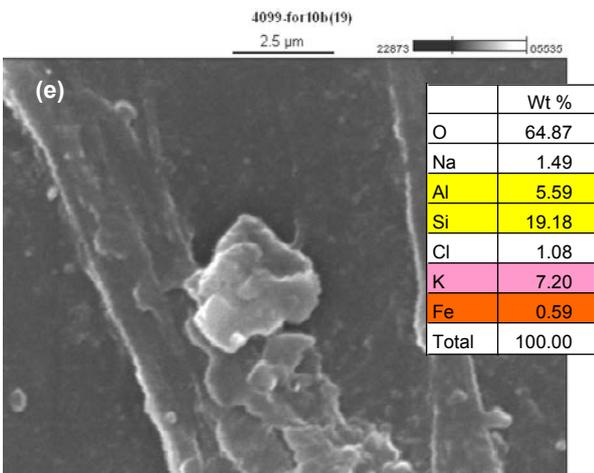
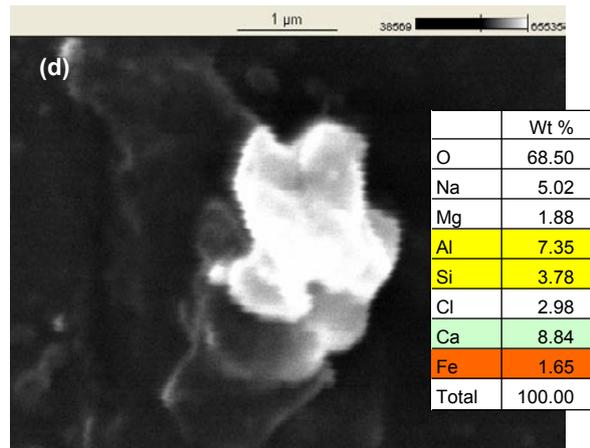
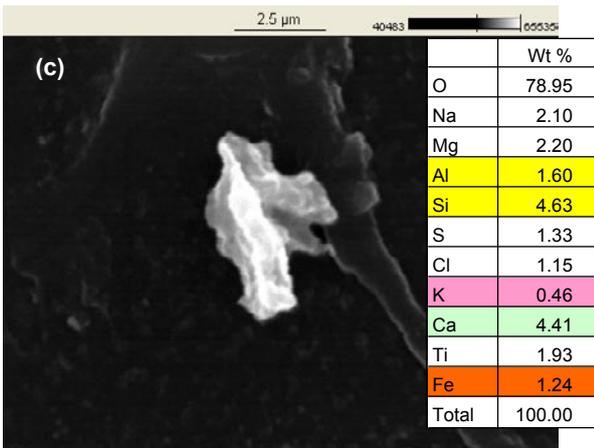
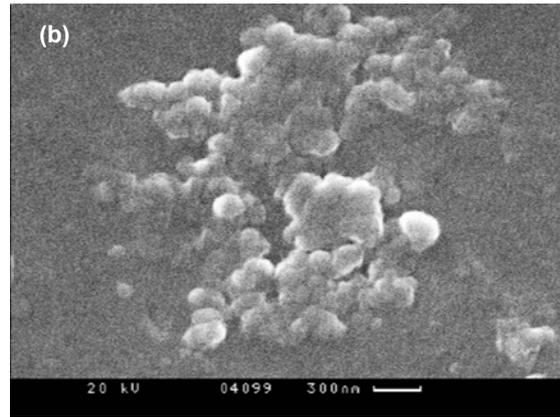
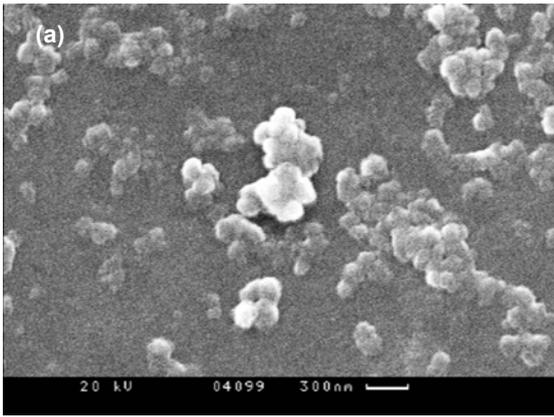


Figure A7-7. SEM images of groundwater KFM08D (828.4–835.54) m colloids on a 50 nm track-etched Polycarbonate filter.

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.

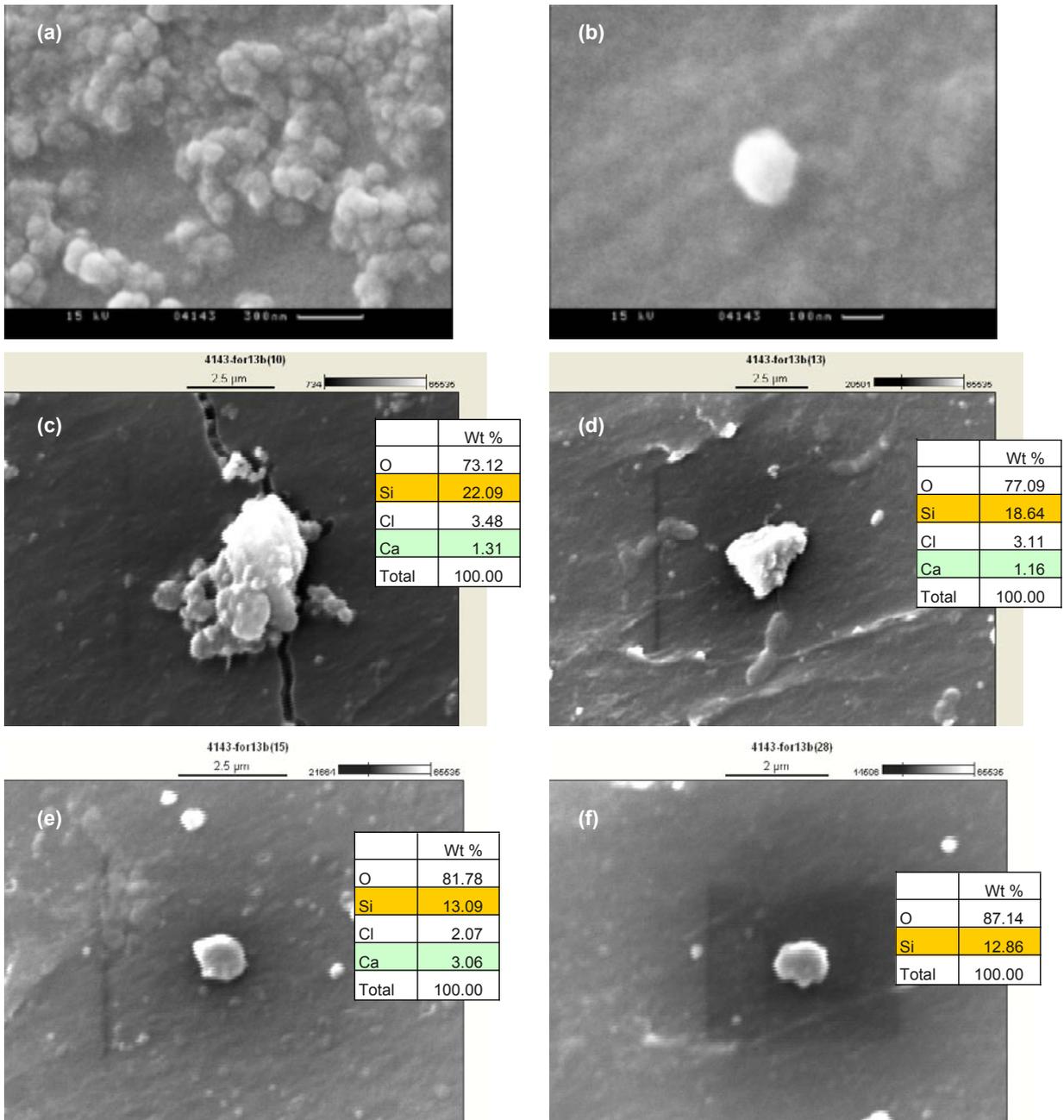


Figure A7-8. SEM images of groundwater KFM08D (669.7–676.84) m colloids on a 50 nm track-etched Polycarbonate filter.

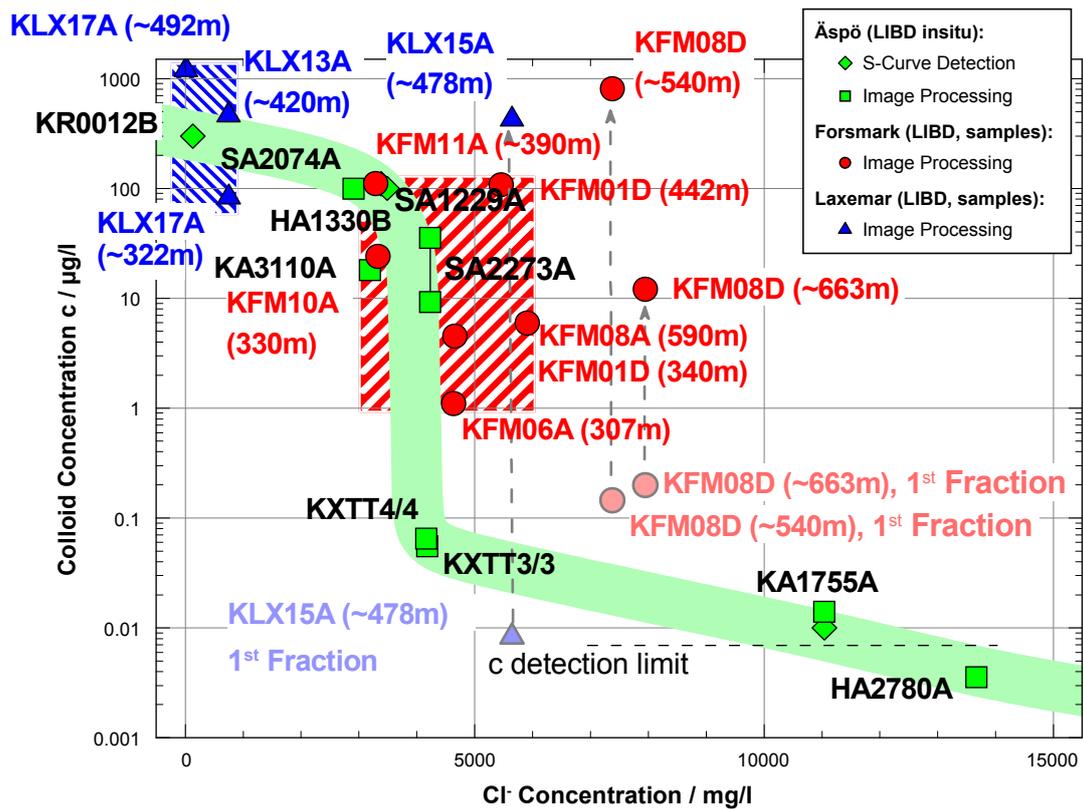


Figure A7-9. Correlation between colloid concentration and chloride concentration in different groundwater from Äspö /2, 4/ and in Forsmark samples. (): sampling depths.

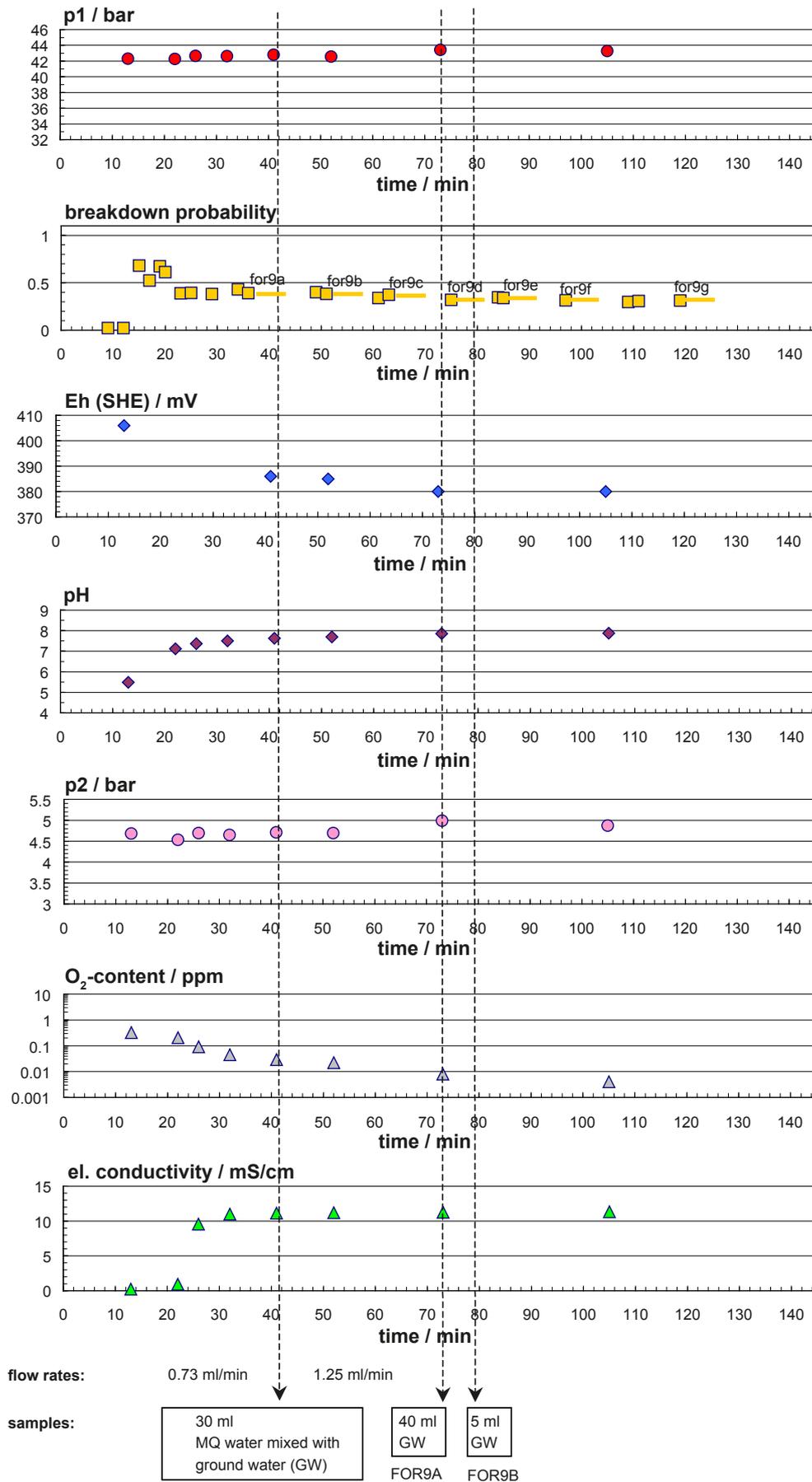
For both groundwater from KFM08D, depth ~ 540 m and ~ 663 m, it was possible to perform a 2 fraction evaluation of the LIBD data. This evaluation of a small 1st colloid fraction with particle sizes around the detection limit (20 nm) agrees well with the data derived from the SEM images (Figure A7-7,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

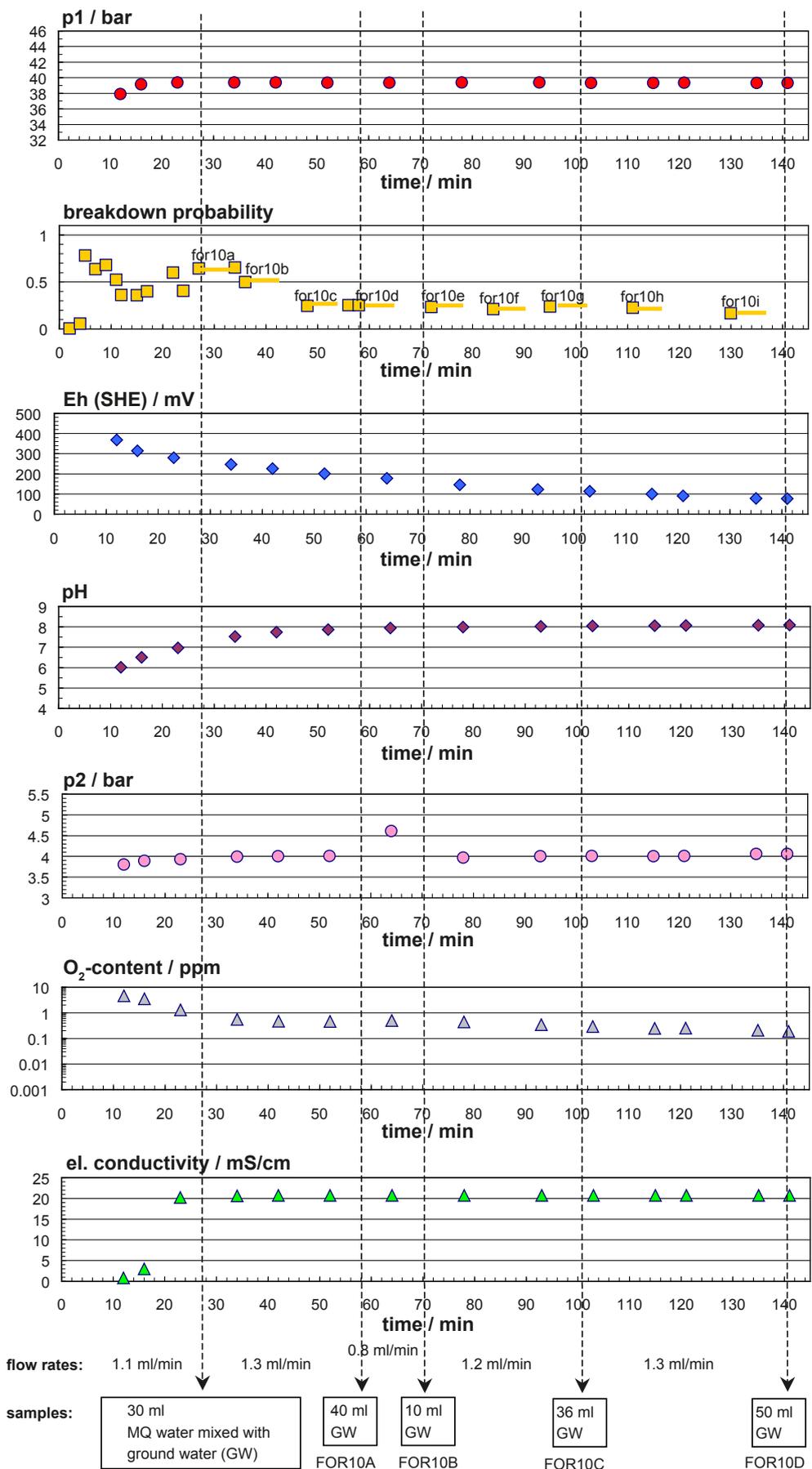
References

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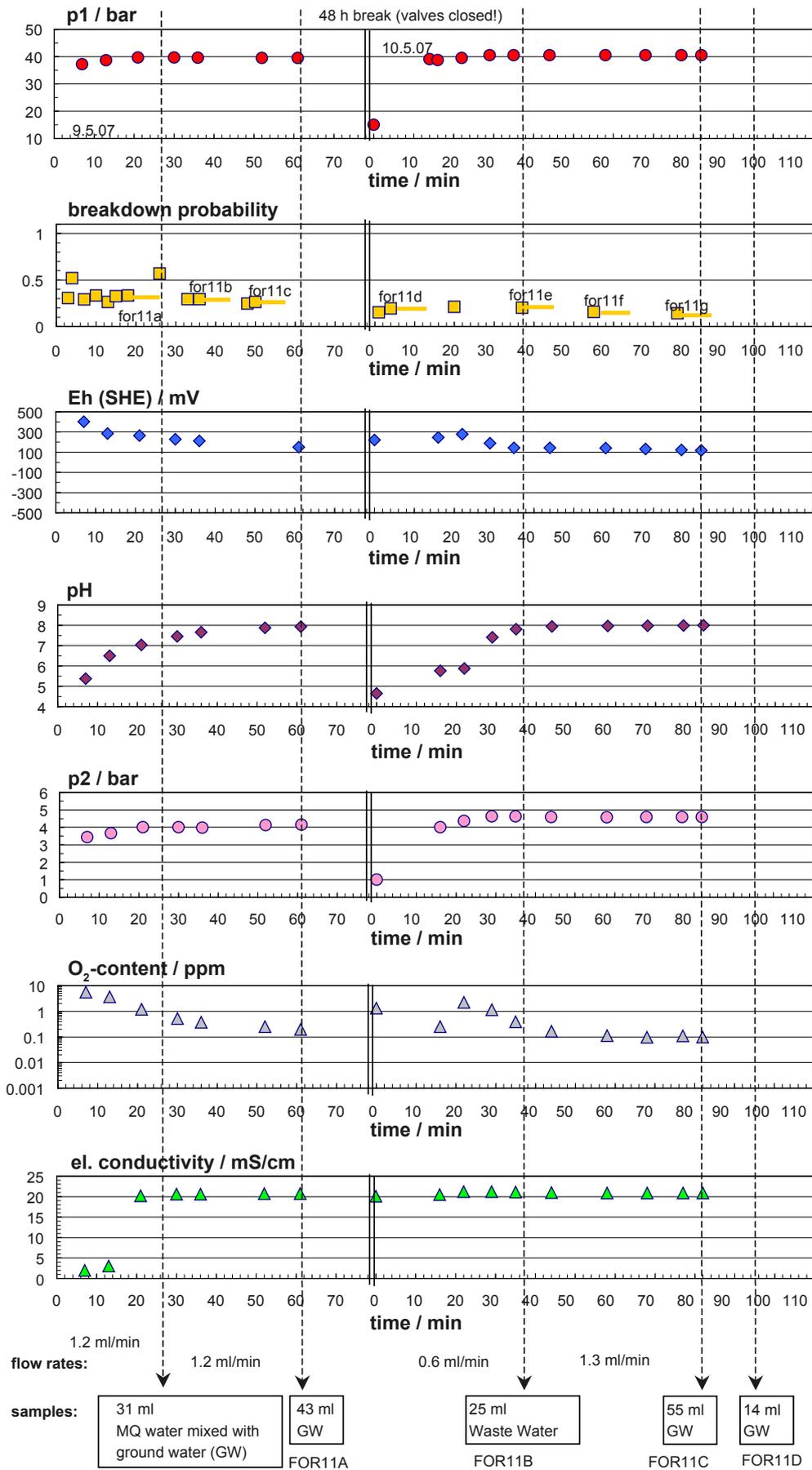
Logged raw data from elution of sampling container SKB PVB 220 (KFM11A (447.5-454.64 m))



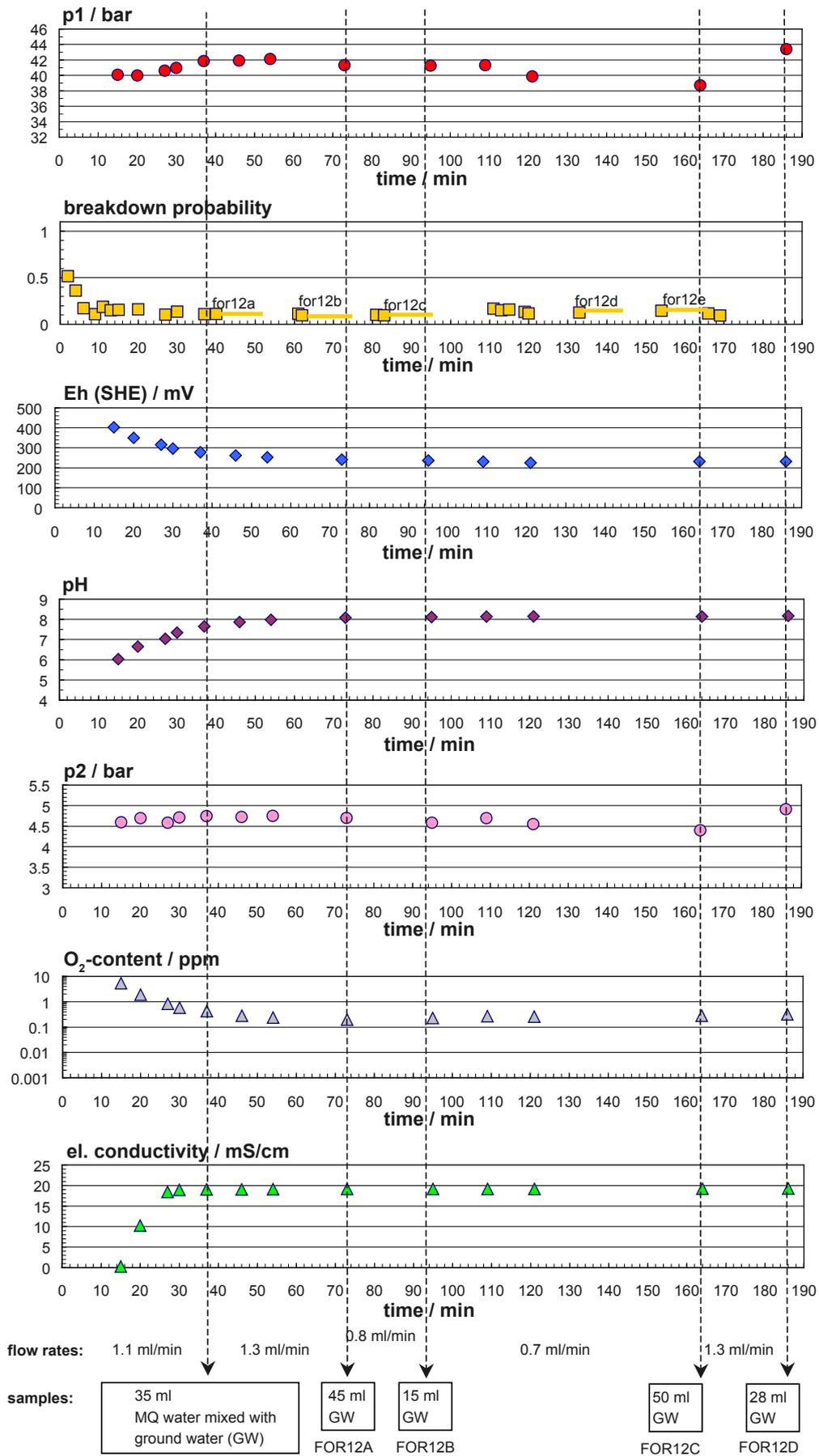
Logged raw data from elution of sampling container SKB PVB 9506-8 (KFM08D (828-835 m))



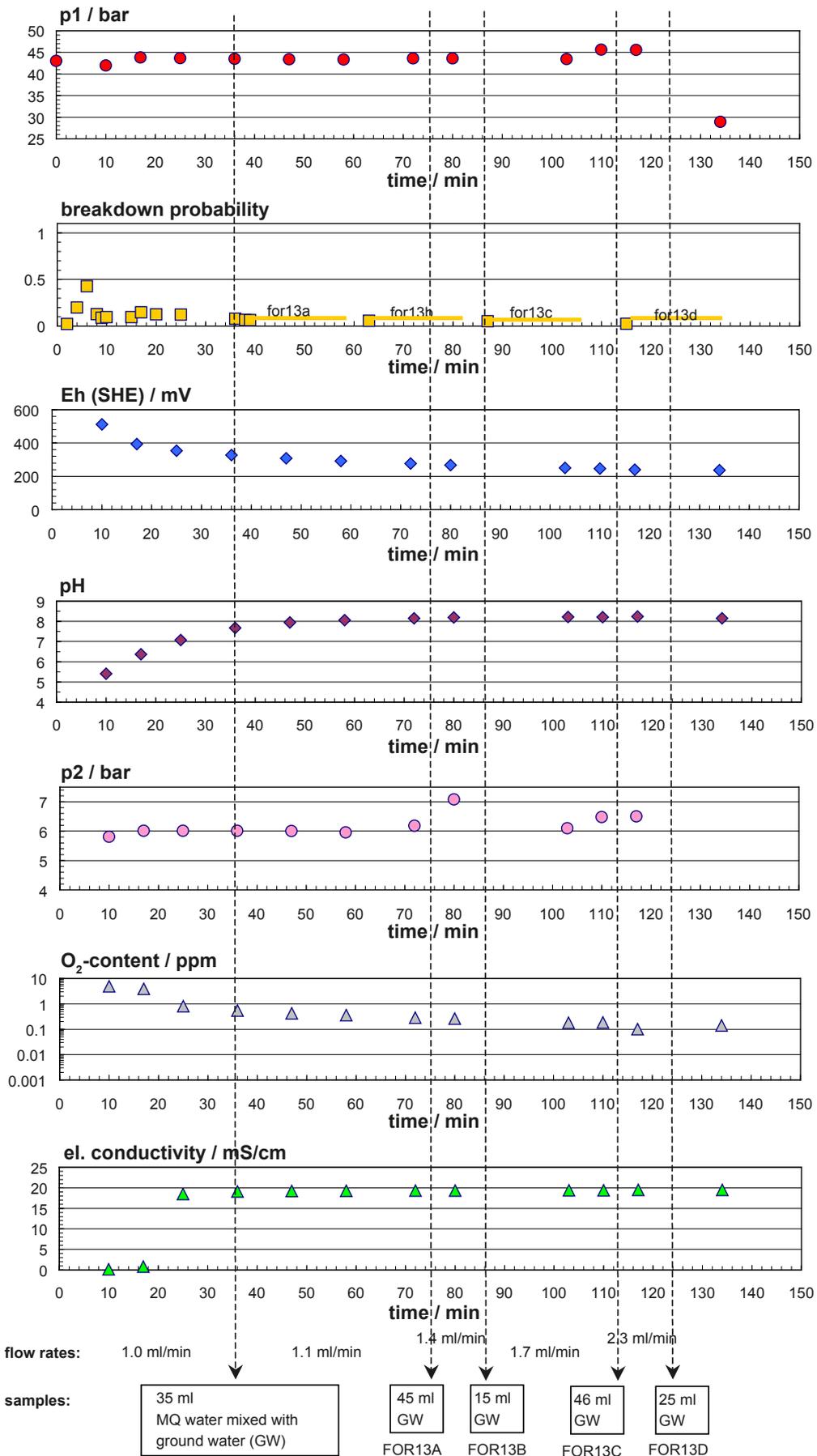
Logged raw data from elution of sampling container SKB PVB 028 (KFM08D (828-835 m))



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 KFM08D, section 669.7–676.8 m

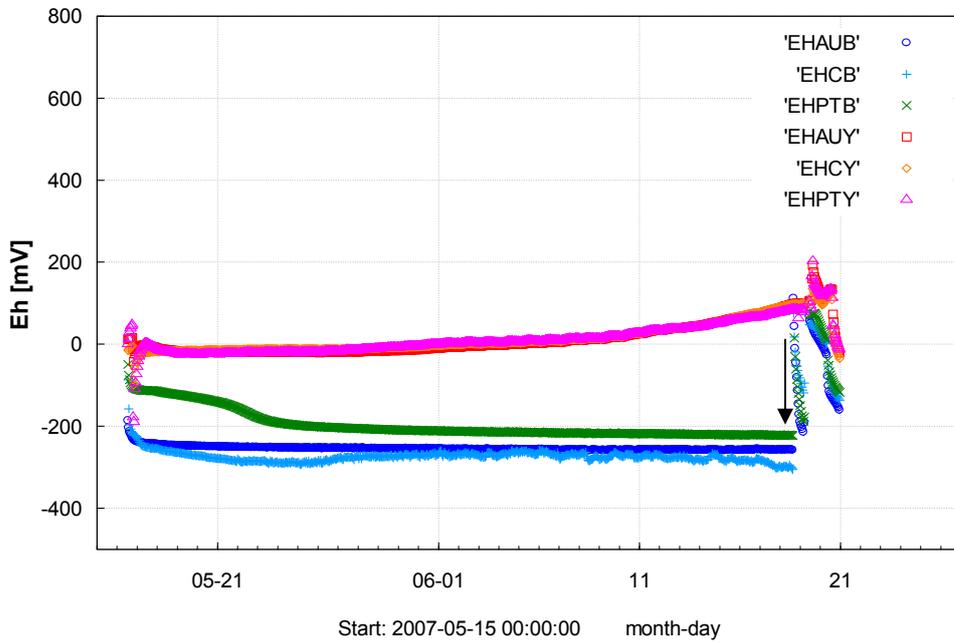


Figure A8-1. Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes in the borehole section (EHAUB, EHCB and EHPTB) and at the surface by gold, glassy carbon and platinum (EHAUY, EHCY and EHPTY). The arrow shows the chosen representative Eh values for the borehole section.

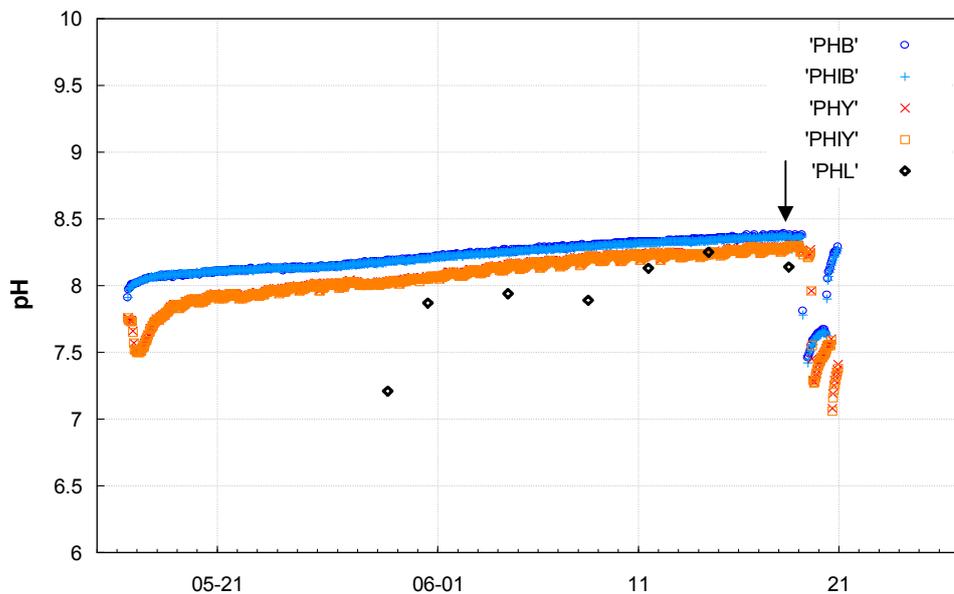


Figure A8-2. Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.

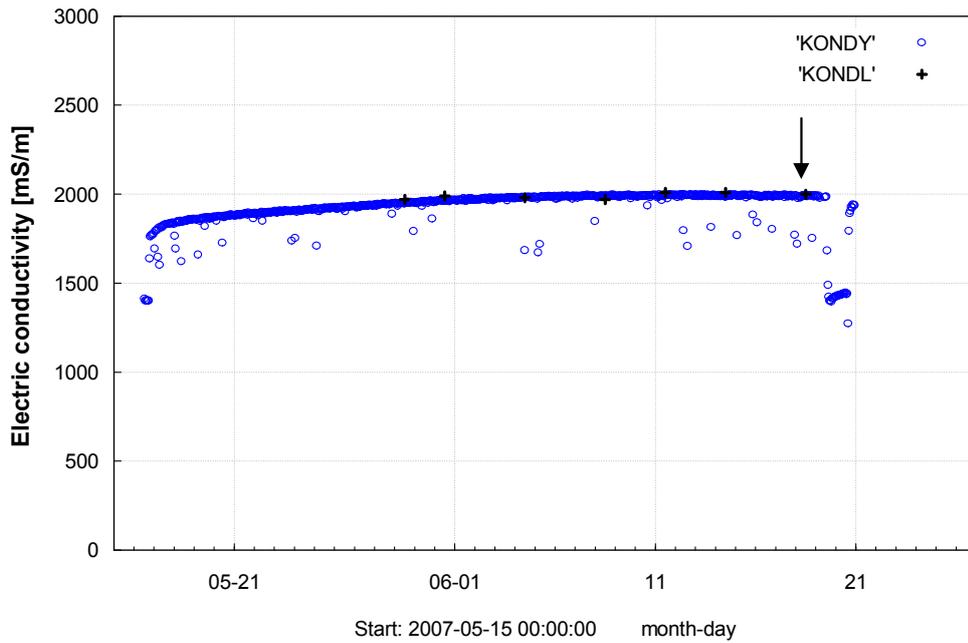


Figure A8-3. Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.

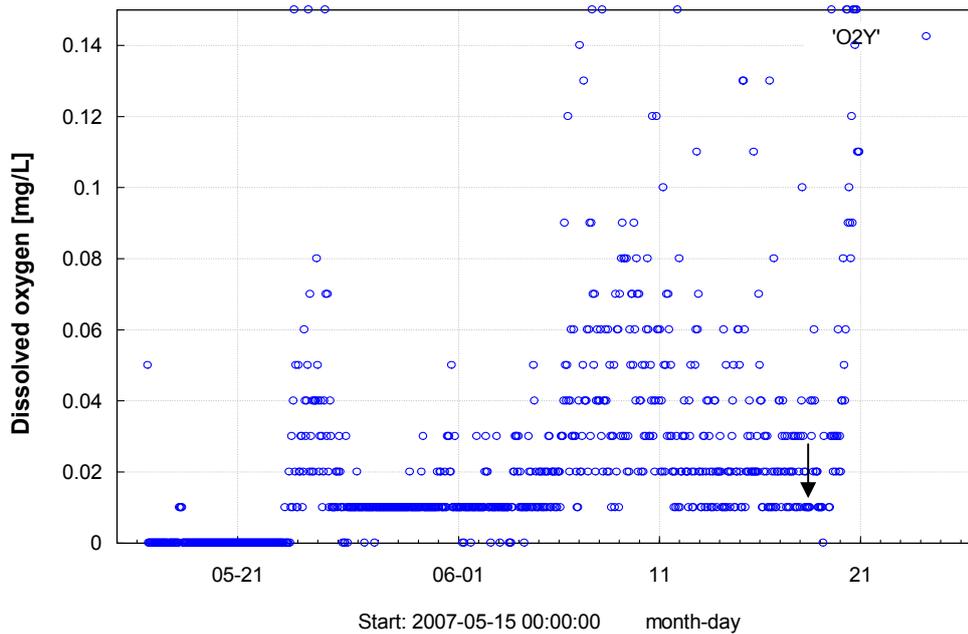


Figure A8-4. Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section. The scattered readings suggest minor intrusion of air somewhere in the sample water line at the surface or electric noise.

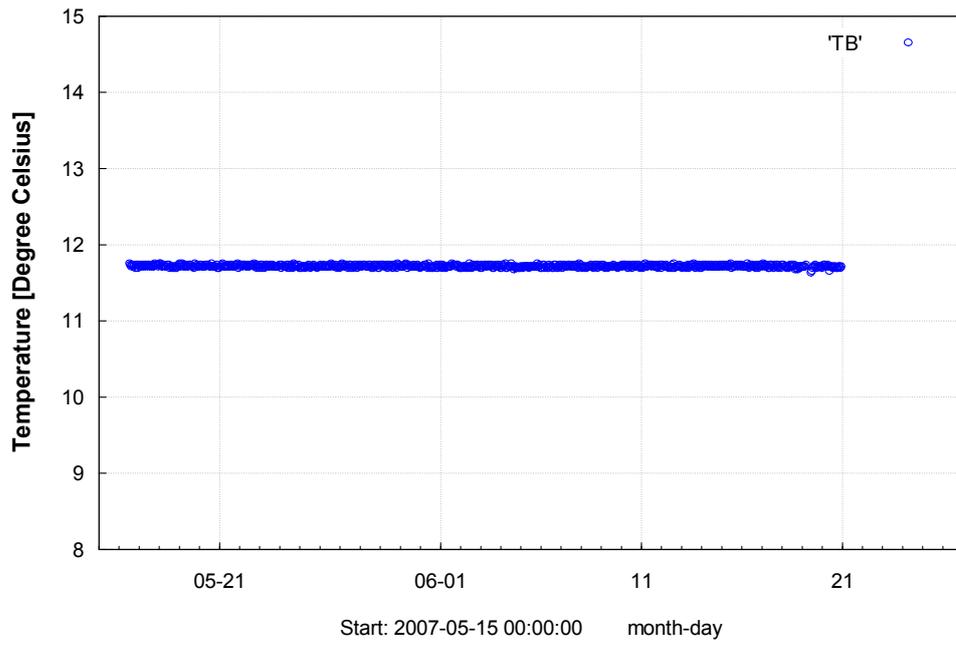


Figure A8-5. Temperature of the groundwater in the borehole section (TB).

Chemmac measurements in KFM08D, section 828.4–835.5 m

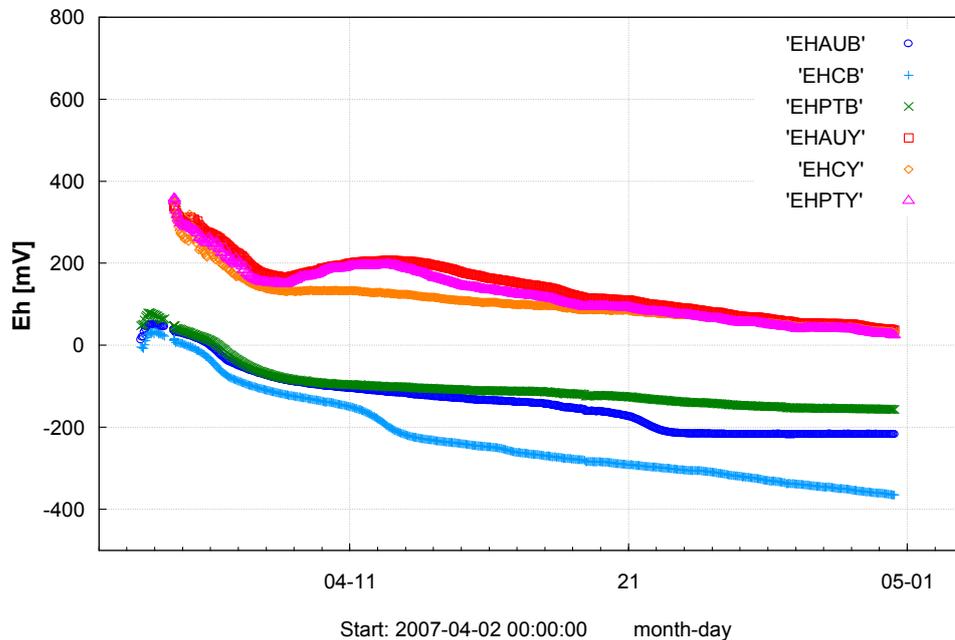


Figure A9-1. Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes in the borehole section (EHAUB, EHCB and EHPTB) and at the surface by gold, glassy carbon and platinum (EHAUY, EHCY and EHPTY). A representative Eh value for the borehole section was not chosen since the recorded redox potentials did not reach stable and agreeing values.

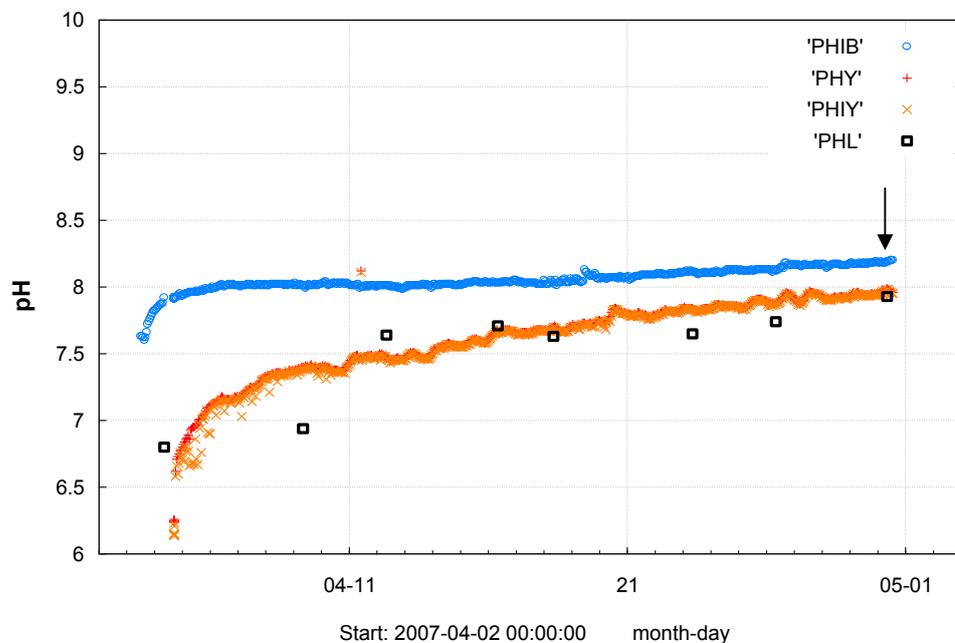


Figure A9-2. Measurements of pH by one glass electrode in the borehole section (PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. PHB was omitted due to unreliable values. The arrow shows the chosen representative pH values for the borehole section.

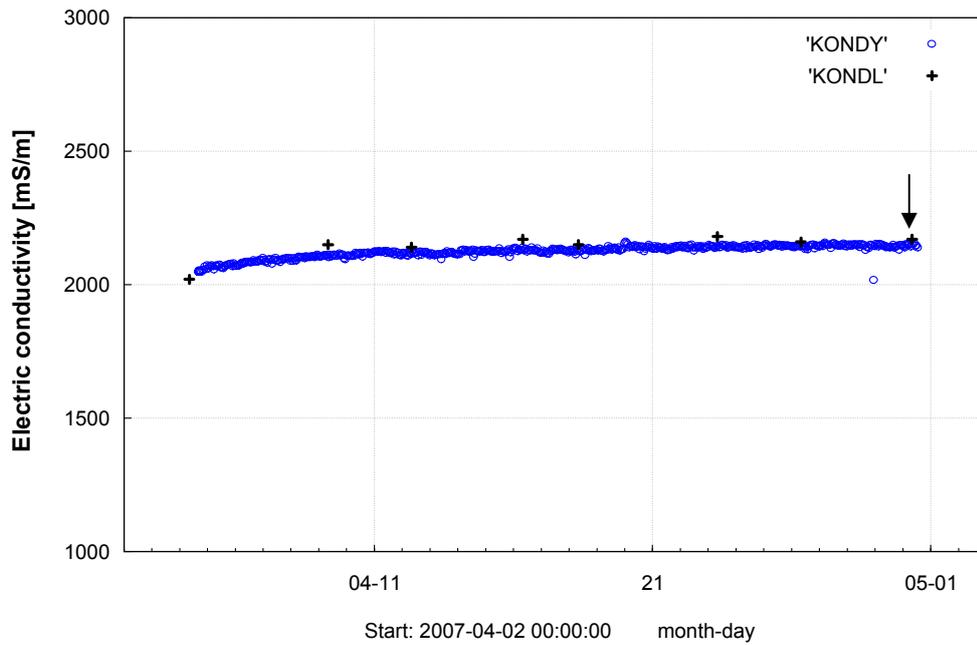


Figure A9-3. Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.

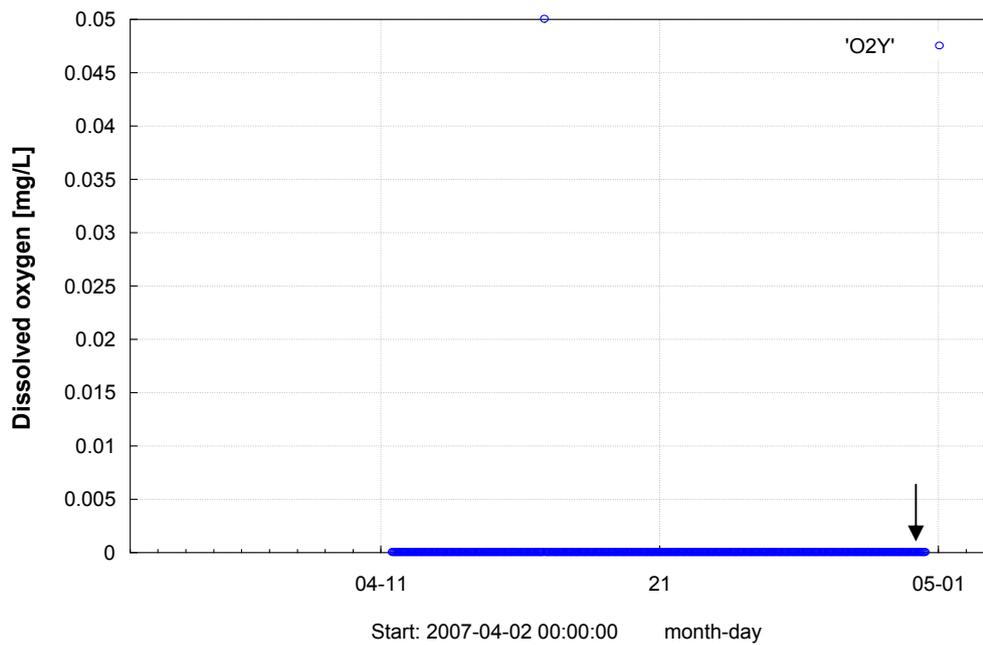


Figure A9-4. Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section.

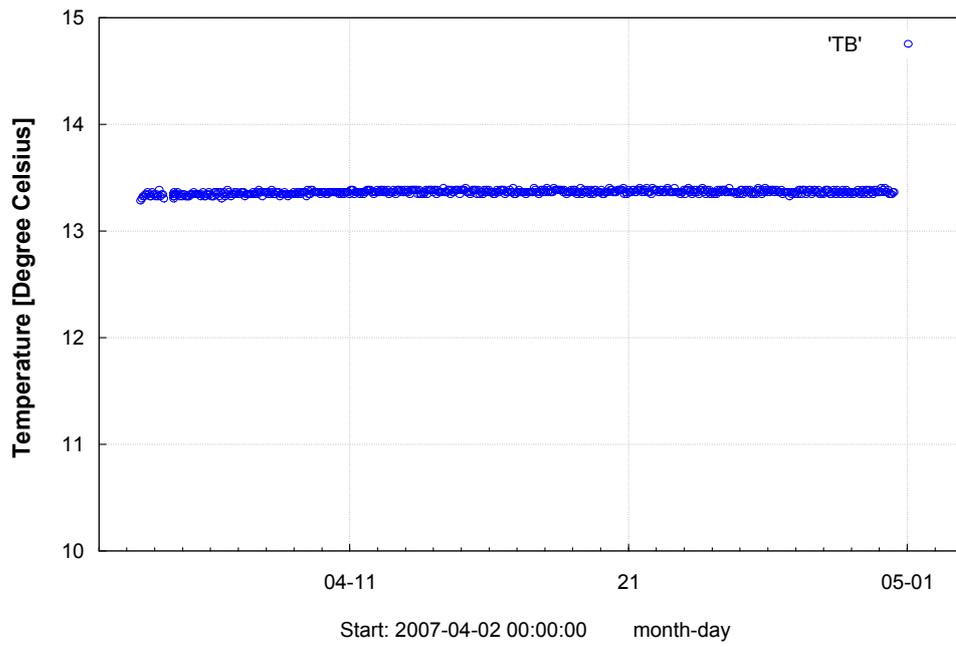


Figure A9-5. Temperature of the groundwater in the borehole section (TB).

Compilation of groundwater analysis data

Table A10-1. 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 | Fell mg/L | Mn mg/L | Li mg/L |
|--------|------------|-------------|---------------|------------------|------------|------------|-----------|------------|------------|---------------------------------------|-------------------------|---------------------------------------|----------------------------|------------|------------------------|------------|------------|----------------|--------------|------------|------------|
| KFM08D | 669.70 | 676.84 | 12790 | 2007-05-14 | - | - | - | - | - | 20.1 | 6,620 | - | - | - | - | - | - | - | - | - | - |
| KFM08D | 669.70 | 676.84 | 12803 | 2007-05-29 | -0.07 | 1,820 | 7.19 | 2,570 | 8.8 | 10.1 | 7,300 | 109 | 37.8 | 59.2 | 1.60 | 4.97 | 0.5890 | 0.603 | 0.600 | 0.1070 | 0.022 |
| KFM08D | 669.70 | 676.84 | 12804 | 2007-05-31 | -0.24 | 1,820 | 7.19 | 2,540 | 7.8 | 8.98 | 7,270 | 104 | 37.6 | 59.3 | 1.70 | 4.82 | 0.4450 | 0.446 | 0.426 | 0.1030 | 0.024 |
| KFM08D | 669.70 | 676.84 | 12805 | 2007-06-04 | 2.02 | 1,900 | 6.36 | 2,670 | 6.9 | 7.74 | 7,280 | 104 | 38.4 | 58.1 | 1.68 | 4.98 | 0.2470 | 0.222 | 0.213 | 0.0835 | 0.026 |
| KFM08D | 669.70 | 676.84 | 12806 | 2007-06-08 | 1.02 | 1,890 | 5.37 | 2,630 | 5.8 | 6.61 | 7,340 | 104 | 37.7 | 61.9 | 1.75 | 4.92 | 0.1060 | 0.108 | 0.093 | 0.0655 | 0.024 |
| KFM08D | 669.70 | 676.84 | 12816 | 2007-06-11 | 0.97 | 1,880 | 5.66 | 2,720 | 5.4 | 6.90 | 7,490 | 104 | 37.1 | 58.7 | 1.77 | 4.82 | 0.0405 | 0.046 | 0.035 | 0.0590 | 0.022 |
| KFM08D | 669.70 | 676.84 | 12817 | 2007-06-14 | 1.51 | 1,910 | 5.59 | 2,690 | 5.1 | 7.86 | 7,400 | 102 | 37.6 | 59.4 | 1.50 | 4.88 | <0.04 | 0.025 | 0.015 | 0.0544 | 0.025 |
| KFM08D | 669.70 | 676.84 | 12818 | 2007-06-18 | 1.59 | 1,900 | 5.42 | 2,740 | 4.9 | 6.98 | 7,460 | 101 | 37.5 | 57.1 | 1.48 | 4.92 | 0.0044 | <0.006 | <0.006 | 0.0498 | 0.027 |
| KFM08D | 828.40 | 835.54 | 12752 | 2007-04-04 | - | - | - | - | - | 12.9 | 7,590 | - | - | - | - | - | - | - | - | - | - |
| KFM08D | 828.40 | 835.54 | 12753 | 2007-04-09 | 1.12 | 2,000 | 6.96 | 2,890 | 10.7 | 9.01 | 7,910 | 159 | 58.0 | 64.4 | 1.41 | 4.48 | <0.04 | 0.010 | <0.006 | 0.0936 | 0.029 |
| KFM08D | 828.40 | 835.54 | 12762 | 2007-04-12 | -0.71 | 1,880 | 7.36 | 2,870 | 10.1 | 9.85 | 7,990 | 156 | 57.5 | 60.9 | 1.42 | 4.46 | 0.0235 | 0.007 | <0.006 | 0.0920 | 0.032 |
| KFM08D | 828.40 | 835.54 | 12766 | 2007-04-16 | 0.13 | 2,000 | 6.66 | 2,880 | 9.7 | 9.65 | 8,050 | 155 | 57.8 | 72.4 | 1.46 | 4.57 | 0.0263 | 0.012 | <0.006 | 0.0847 | 0.030 |
| KFM08D | 828.40 | 835.54 | 12773 | 2007-04-18 | 0.08 | 1,970 | 6.46 | 2,840 | 10.0 | 10.2 | 7,950 | 152 | 55.9 | 64.4 | 1.48 | 4.48 | <0.04 | 0.022 | 0.014 | 0.0900 | 0.032 |
| KFM08D | 828.40 | 835.54 | 12774 | 2007-04-23 | 0.26 | 1,980 | 6.37 | 2,920 | 8.9 | 9.37 | 8,070 | 152 | 56.0 | 74.0 | 1.41 | 4.44 | 0.0575 | 0.060 | 0.046 | 0.0770 | 0.033 |
| KFM08D | 828.40 | 835.54 | 12775 | 2007-04-26 | 0.30 | 2,000 | 6.10 | 2,910 | 8.7 | 8.87 | 8,080 | 149 | 55.5 | 65.4 | 1.47 | 4.46 | 0.0780 | 0.090 | 0.076 | 0.0752 | 0.034 |
| KFM08D | 828.40 | 835.54 | 12776 | 2007-04-30 | 0.23 | 1,990 | 6.26 | 2,960 | 8.5 | 9.07 | 8,160 | 156 | 56.0 | 69.9 | 1.49 | 4.50 | 0.1140 | 0.133 | 0.114 | 0.0725 | 0.033 |

- = Not analysed

< value = below reporting limit

RCB (%) = Rel. charge balance error %

pH_L = pH, laboratory measurement in batch sample

EC_L = Electrical conductivity, laboratory measurement in batch sample

SICADA: water_composition.

Table A10-1. Water composition (cont.). Compilation September 2007.

| Idcode | Secup m | Seclow m | Sample no. | Sr mg/L | F mg/L | pH_L | TOC mg/L | DOC mg/L | HS ⁻ mg/L | Drill_water % | EC_L mS/m | NH ₄ N 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 |
|--------|------------|-------------|---------------|------------|-----------|------|-------------|-------------|-------------------------|------------------|--------------|---------------------------|----------------------------|----------------------------|---|----------------------------|-----------|
| KFM08D | 669.70 | 676.84 | 12790 | – | – | 7.47 | – | – | – | 20.1 | 1,810 | – | – | – | – | – | – |
| KFM08D | 669.70 | 676.84 | 12803 | 27.5 | – | 7.21 | – | <1 | <0.006 | 8.90 | 1,970 | 0.0814 | – | – | – | – | – |
| KFM08D | 669.70 | 676.84 | 12804 | 27.7 | – | 7.87 | – | 1.1 | 0.006 | 8.20 | 1,990 | 0.0728 | – | – | – | – | – |
| KFM08D | 669.70 | 676.84 | 12805 | 29.3 | 0.216 | 7.94 | – | <1 | 0.009 | 6.95 | 1,980 | 0.0579 | <0.0002 | <0.0003 | <0.0003 | <0.0005 | <0.04 |
| KFM08D | 669.70 | 676.84 | 12806 | 29.0 | – | 7.89 | – | <1 | <0.006 | 6.15 | 1,970 | 0.0504 | – | – | – | – | – |
| KFM08D | 669.70 | 676.84 | 12816 | 29.0 | 0.221 | 8.13 | – | <1 | 0.010 | 5.70 | 2,010 | 0.0477 | 0.0002 | 0.0004 | 0.0006 | <0.0005 | <0.04 |
| KFM08D | 669.70 | 676.84 | 12817 | 29.6 | – | 8.25 | – | <1 | 0.009 | 5.65 | 2,010 | 0.0443 | – | – | – | – | – |
| KFM08D | 669.70 | 676.84 | 12818 | 29.3 | 0.228 | 8.14 | <1 | <1 | <0.006 | 5.40 | 2,000 | 0.0408 | <0.0002 | 0.0003 | 0.0004 | <0.0005 | <0.04 |
| KFM08D | 828.40 | 835.54 | 12752 | – | – | 6.80 | – | – | – | 15.4 | 2,020 | – | – | – | – | – | – |
| KFM08D | 828.40 | 835.54 | 12753 | 30.3 | – | 6.94 | – | 2.2 | <0.006 | 8.15 | 2,150 | 0.1110 | – | – | – | – | – |
| KFM08D | 828.40 | 835.54 | 12762 | 30.6 | 0.186 | 7.64 | – | 2.6 | <0.006 | 7.25 | 2,140 | 0.0833 | <0.0002 | 0.0089 | 0.0090 | 0.0054 | <0.04 |
| KFM08D | 828.40 | 835.54 | 12766 | 33.1 | 0.232 | 7.71 | – | 2.0 | 0.067 | 6.30 | 2,170 | 0.0750 | <0.0002 | 0.0028 | 0.0029 | <0.0005 | <0.04 |
| KFM08D | 828.40 | 835.54 | 12773 | 32.6 | – | 7.63 | – | 1.2 | 0.052 | 6.30 | 2,150 | 0.0718 | – | – | – | – | – |
| KFM08D | 828.40 | 835.54 | 12774 | 33.2 | 0.230 | 7.65 | – | 1.2 | 0.054 | 4.85 | 2,180 | 0.0621 | <0.0002 | 0.0020 | 0.0021 | 0.0005 | <0.04 |
| KFM08D | 828.40 | 835.54 | 12775 | 33.1 | – | 7.74 | – | 1.2 | 0.082 | 4.45 | 2,160 | 0.0688 | – | – | – | – | – |
| KFM08D | 828.40 | 835.54 | 12776 | 33.1 | 0.227 | 7.93 | 1.0 | <1 | 0.068 | 4.25 | 2,170 | 0.0596 | <0.0002 | 0.0119 | 0.0119 | <0.0005 | <0.04 |

– = Not analysed

< value = below reporting limit

RCB (%) = Rel. charge balance error %

pH_L = pH, laboratory measurement in batch sample

EC_L = Electrical conductivity, laboratory measurement in batch sample

SICADA: water_composition.

Table A10-2. Trace elements. 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 | Sb ug/L |
|--------|------------|-------------|---------------|------------------|------------|------------|-----------|------------|------------|------------|------------|------------|------------|-----------|-----------|------------|------------|------------|-----------|------------|------------|------------|
| KFM08D | 669.70 | 676.84 | 12805 | 2007-06-04 | 98.5 | <1 | 727 | 471 | <0.05 | 1.97 | 0.180 | <0.002 | 16.1 | 0.128 | 1.01 | <0.2 | <0.5 | 14.7 | 0.292 | <0.3 | <0.5 | 0.170 |
| KFM08D | 669.70 | 676.84 | 12816 | 2007-06-11 | 108.0 | <1 | 729 | 458 | <0.05 | 0.386 | 0.091 | <0.002 | 1.10 | 0.101 | 0.415 | <0.2 | <0.5 | 13.9 | 0.298 | <0.3 | <0.5 | 0.120 |
| KFM08D | 669.70 | 676.84 | 12818 | 2007-06-18 | 22.7 | <1 | 729 | 413 | <0.05 | <0.1 | <0.05 | <0.002 | 0.704 | 0.0749 | 0.219 | <0.2 | <0.5 | 14.0 | 0.273 | <0.3 | <0.5 | 0.117 |
| KFM08D | 828.40 | 835.54 | 12762 | 2007-04-12 | 10.5 | <1 | 690 | 205 | <0.05 | 0.677 | 0.156 | 0.0041 | 2.97 | 0.0514 | 4.54 | <0.2 | <0.5 | 17.3 | 0.365 | <0.3 | <0.5 | 0.164 |
| KFM08D | 828.40 | 835.54 | 12766 | 2007-04-16 | 14.1 | <1 | 703 | 215 | <0.05 | 1.28 | <0.05 | 0.0026 | 1.76 | 0.141 | 3.34 | <0.2 | <0.5 | 16.6 | 0.418 | 1.55 | <0.5 | 0.285 |
| KFM08D | 828.40 | 835.54 | 12774 | 2007-04-23 | 13.3 | <1 | 713 | 215 | <0.05 | 0.301 | <0.05 | <0.002 | 0.994 | 0.153 | 2.06 | <0.2 | <0.5 | 15.2 | 0.264 | 1.29 | <0.5 | 0.268 |
| KFM08D | 828.40 | 835.54 | 12776 | 2007-04-30 | 21.7 | <1 | 726 | 217 | <0.05 | 0.534 | <0.05 | <0.002 | 1.72 | 0.109 | 1.57 | <0.2 | <0.5 | 15.4 | 0.241 | 1.17 | <0.5 | 0.273 |

< value = below reporting limit

SICADA: trace_elements

Table A10-2. Trace elements (cont.). Compilation September 2007.

| Idcode | Secup m | Seclow m | Sample no. | Sampling date | 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 | |
|--------|------------|-------------|---------------|------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------|
| KFM08D | 669.70 | 676.84 | 12805 | 2007-06-04 | 0.305 | <0.05 | <0.05 | <0.05 | 0.0635 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| KFM08D | 669.70 | 676.84 | 12816 | 2007-06-11 | 0.287 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| KFM08D | 669.70 | 676.84 | 12818 | 2007-06-18 | 0.302 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| KFM08D | 828.40 | 835.54 | 12762 | 2007-04-12 | 0.384 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| KFM08D | 828.40 | 835.54 | 12766 | 2007-04-16 | 0.442 | <0.05 | 0.320 | <0.05 | 0.0835 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| KFM08D | 828.40 | 835.54 | 12774 | 2007-04-23 | 0.401 | <0.05 | 0.320 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |
| KFM08D | 828.40 | 835.54 | 12776 | 2007-04-30 | 0.394 | <0.05 | 0.396 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 | <0.05 |

< value = below reporting limit

SICADA: trace_elements

Table A10-3. Isotopes I (H-, O-, B-, S-, Cl- and C-isotopes). Compilation October 2007.

| Idcode | Secup m | Seclow m | Sample no | Sampling date | δ²H ‰ SMOW | ³H TU | δ¹⁸O ‰ SMOW | ¹⁰B/¹¹B no unit | δ³⁴S ‰ CDT | δ¹³C ‰ PDB | ⁸⁷Sr/⁸⁶Sr no unit | ¹⁴C pmC | δ³⁷Cl ‰ SMOC | ³⁶Cl/(³⁵Cl+³⁷Cl)(E-15) no unit |
|---------------|--------------------|---------------------|----------------------|--------------------------|----------------------------------|-----------------------------|-----------------------------------|--|----------------------------------|----------------------------------|--|-------------------------------|------------------------------------|--|
| KFM08D | 669.70 | 676.84 | 12803 | 2007-05-29 | -84.3 | 0.8 | -11.9 | - | - | - | - | - | - | - |
| KFM08D | 669.70 | 676.84 | 12804 | 2007-05-31 | -84.2 | 0.9 | -12.0 | - | - | - | - | - | - | - |
| KFM08D | 669.70 | 676.84 | 12805 | 2007-06-04 | -83.9 | 0.8 | -12.2 | 0.2387 | 31.2 | - | 0.717558 | - | 0.51 | - |
| KFM08D | 669.70 | 676.84 | 12806 | 2007-06-08 | -85.1 | 1.0 | -12.3 | - | - | - | - | - | - | - |
| KFM08D | 669.70 | 676.84 | 12816 | 2007-06-11 | -84.5 | 1.0 | -12.2 | 0.2403 | 31.4 | - | 0.717537 | - | 0.29 | - |
| KFM08D | 669.70 | 676.84 | 12817 | 2007-06-14 | -84.6 | <0.8 | -12.2 | - | - | - | - | - | - | - |
| KFM08D | 669.70 | 676.84 | 12818 | 2007-06-18 | -84.0 | 1.0 | -12.3 | 0.2395 | 31.6 | A | 0.717523 | A | 0.42 | 36 ± 6 |
| KFM08D | 828.40 | 835.54 | 12753 | 2007-04-09 | -83.8 | 1.3 | -11.8 | - | - | - | - | - | - | - |
| KFM08D | 828.40 | 835.54 | 12762 | 2007-04-12 | -84.3 | 1.5 | -11.9 | 0.2428 | 26.4 | - | 0.717519 | - | -0.02 | - |
| KFM08D | 828.40 | 835.54 | 12766 | 2007-04-16 | -83.0 | 1.5 | -11.7 | 0.2382 | 27.3 | - | 0.717536 | - | -0.05 | - |
| KFM08D | 828.40 | 835.54 | 12773 | 2007-04-18 | -82.8 | 1.0 | -11.6 | - | - | - | - | - | - | - |
| KFM08D | 828.40 | 835.54 | 12774 | 2007-04-23 | -82.7 | 1.5 | -11.7 | 0.2389 | 26.8 | - | 0.717528 | - | -0.02 | - |
| KFM08D | 828.40 | 835.54 | 12775 | 2007-04-26 | -85.0 | 1.1 | -11.6 | - | - | - | - | - | - | - |
| KFM08D | 828.40 | 835.54 | 12776 | 2007-04-30 | -82.5 | 1.8 | -11.6 | 0.2373 | 26.6 | A | 0.717524 | A | -0.08 | 34 ± 3 |

A = Results will be reported later

- = Not analysed

SICADA: Isotopes I.

Table A10-4. 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 Bq/L | ²²² Rn | ²²² Rn |
|--------|------------|-------------|---------------|------------------|---------------------------|---------------------------|---------------------------|----------------------------|----------------------------|---------------------------|------------------------|--------------------------|
| | | | | | | | | | | | Bq/L | Bq/L |
| | | | | | | | | | | | At time of analysis | At time of collection |
| KFM08D | 669.70 | 676.84 | 12818 | 2007-06-18 | 2.8 | 0.14 | 8.8 | 0.28 | | 0.05 | 296 | 567 |
| KFM08D | 828.40 | 835.54 | 12776 | 2007-04-30 | 20 | 1.1 | 67 | 0.2 | 0.4 | <0.015 | 260 | 492 |

A = Results will be reported later

< value = below reporting limit

SICADA: u_th_isotope_t, ra_rn_isotope_t

Table A10-5. Dissolved gases. Compilation October 2007.

| Idcode | Secup m | Seclow m | Sample no. | Sampling date | Ar | He | N ₂ | CO ₂ | CH ₄ | O ₂ | H ₂ | CO | C ₂ H ₆ | C ₂ H ₄ | C ₂ H ₂ | C ₃ H ₈ | C ₃ H ₆ | DISS_GAS |
|--------|------------|-------------|---------------|------------------|------|------|----------------|-----------------|-----------------|----------------|----------------|------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|----------|
| | | | | | mL/L | mL/L | mL/L | mL/L | mL/L | mL/L | μL/L | μL/L | μL/L | μL/L | μL/L | μL/L | μL/L | μL/L |
| KFM08D | 669.70 | 676.84 | 12818 | 2007-06-19 | 1.7 | 23 | 73 | 0.02 | 0.09 | 0.035 | <2.9 | <4.9 | 0.49 | 0.10 | <0.05 | 0.20 | <0.1 | 98 |
| KFM08D | 828.40 | 835.54 | 12776 | 2007-05-02 | 1.4 | 24 | 85 | 0.03 | 0.06 | <0.01 | <3.3 | <5.5 | 0.55 | 0.11 | <0.05 | 0.22 | <0.05 | 110 |

< value = below reporting limit

SICADA: Dissolved_gases