

Forsmark site investigation

Hydrochemical characterisation in KFM02A

**Results from three investigated borehole
sections; 106.5–126.5,
413.5–433.5 and 509.0–516.1 m**

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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

Chemical characterisation of groundwater has been conducted in the three sections 106.5–126.5 m, 413.5–433.5 m and 509.0–516.1 m of borehole KFM02A. The characterisation has been performed using two slightly different investigation methods, *complete chemical characterisation* and *sampling during pumping test*.

Complete chemical characterisation is the most extensive chemical investigation method performed in core drilled boreholes. The method entails pumping, measurements *on-line* and regular water sampling for chemical analyses in isolated borehole sections during approximately three weeks per section at a flow rate of between 50 and 200 mL/min.

Sampling during pumping tests in core drilled boreholes implies that the pumping is performed at a flow rate of several litres per minute and that the collected water samples represent a larger bedrock volume and/or a more dominating hydraulic structure than the samples that are collected during *Complete chemical characterisation*. The pumping/ measurement period is shorter and fewer samples are collected than in the method above.

The results obtained from the *complete chemical characterisation* of section 509.0–516.1 m include on-line measurements of redox potential, pH, dissolved oxygen, electric conductivity and water temperature in the borehole section as well as chemical analyses of major constituents, trace metals and isotopes. Furthermore, gas content and composition, inorganic colloids as well as humic and fulvic acids were investigated in the groundwater. The results from the pumping test method performed in the two other sections, 106.5–126.5 m and 413.5–433.5 m, do not include redox potential, gas determinations and inorganic colloids by filtration technique.

The water composition was stable during the entire pumping and sampling period in the borehole sections 413.5–433.5 m and 509.0–516.1 m. In the section 106.5–126.5 m there was a slight increase in the salinity during the pumping period. The chloride concentrations amounted to approx. 640 mg/L (106.5–126.5 m) and 5400 mg/L (413.5–433.5 m and 509.0–516.1 m). The redox potential measurements are reported only for section 509.0–516.1 m where the electrodes stabilised at approximately –140 mV. The reducing conditions in the groundwater of this section were also verified by the presence of ferrous iron Fe (+II) at relatively high concentrations. The content of inorganic colloids was very low or nonexistent and the organic constituents were present mainly as fulvic acids and possibly other low molecular weight organic acids (citric acid, oxalic acid etc).

Sammanfattning

Kemisk karakterisering av grundvatten har utförts i de tre borrhålssektionerna 106.5–126.5 m, 413.5–433.5 m och 509.0–516.1 m av borrhålet KFM02A. Karakteriseringen har gjorts med två något olika undersökningsmetoder, *fullständig kemikarakterisering* och *provtagning under pumptester*.

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

Metoden *Provtagning under pumptester i kärnborrhål* innebär att pumpningen utförs med ett flöde på flera liter per minut och att de uttagna vattenproven representerar en större bergvolym och/eller en mer dominerande hydraulisk struktur än proven som tas ut vid *Fullständig kemikarakterisering*. Pump/mätperioden är kortare och färre prov tas ut än i ovanstående metod.

Resultaten som erhöles från den fullständiga kemikarakteriseringen av sektionen 509.0–516.1 m omfattar mätningar *on-line* av redoxpotential, pH, löst syre, elektrisk konduktivitet och vattentemperatur i borrhålssektionen liksom kemiska analyser av huvudkomponenter, spårelement och isotoper. Vidare undersöktes gasmängd och sammansättning, oorganiska kolloider samt humus- och fulvosyror i grundvattnet. Resultaten från pumptestmetoden som utförts i de andra två sektionerna, 106.5–126.5 och 413.5–433.5 m, inkluderar inte redoxpotential, gasbestämningar och oorganiska kolloider genom filtrering av *in situ* prov.

Vattensammansättningen var stabil under pump/provtagningsperioderna i borrhålssektionerna 413.5–433.5 m och 509.0–516.1 m. I sektionen 106.5–126.5 m ökade salthalten något under pumpperioden. Kloridkoncentrationerna uppgick till cirka 640 mg/L (106.5–126.5 m) och 5400 mg/L (413.5–433.5 m och 509.0–516.1 m). Redoxpotentialen rapporteras endast för sektionen 509.0–516.1 m där värdena stabiliserade sig på ca –140 mV. De reducerande förhållandena i grundvattnet i denna sektion bevisades också av närvaron av tvåvärt järn i relativt höga koncentrationer. Innehållet av oorganiska kolloider var mycket lågt eller obefintligt och de organiska komponenterna förelåg huvudsakligen som fulvosyror eller andra lågmolekylära syror (citronsyra, oxalsyra etc).

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1 Introduction

This document reports the performance and results from the two activities: “Complete chemical characterisation” and “Sampling during pumping tests in core drilled boreholes” performed in the cored borehole KFM02A within the site investigation programme at Forsmark /1/. The work was conducted according to the activity plan AP PF 400-03-38 (SKB internal controlling document). The report presents hydrogeochemical data from the following three borehole sections:

- 106.5–126.5 m (Sampling and analyses during pumping tests in core drilled boreholes, modified method, conducted by Geosigma AB)
- 413.5–433.5 m (Sampling and analyses during pumping tests in core drilled boreholes, modified method, conducted by Geosigma AB)
- 509.0–516.1 m (Complete chemical characterisation, conducted by ÅF Energi och Miljö AB)

The fieldwork was carried out during the period June 2003–Feb 2004. Sampling for microbe studies, based on the activity plan AP PF 400-03-09 (SKB internal controlling document) was also performed within the present activity (only at 509–516 m). The microbe investigations and results are reported in /2/.

Borehole KFM02A is the second deep telescopic borehole drilled at Forsmark /3/. The location of the borehole and the current drilling sites for deep telescopic boreholes within the investigation area are shown in Figure 1-1, whereas Figure 1-2 is a detailed map of drilling site DS2 with KFM02A and nearby situated percussion drilled boreholes in rock and soil. The borehole section between 0–100 m is percussion drilled and has a stainless steel casing with an internal diameter of 200 mm, whereas the 100–1002.4 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 method descriptions MD 620.003 (Method description for drilling cored boreholes) and MD 610.003 (Method description for percussion drilling). A SKB chemical-type borehole requires cleaning procedures to be carried out on all downhole equipment to be used in the borehole, both during and after drilling, according to level 2 in the cleaning instructions outlined in MD 600.004 (Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning). All method descriptions and instructions are SKB internal controlling documents.

The data reference to the present activity is given in Table 1-1.

Table 1-1. Data reference.

Activity	Database	Identity number
Hydrochemical characterisation in KFM02A	SICADA	Field note no Forsmark 203

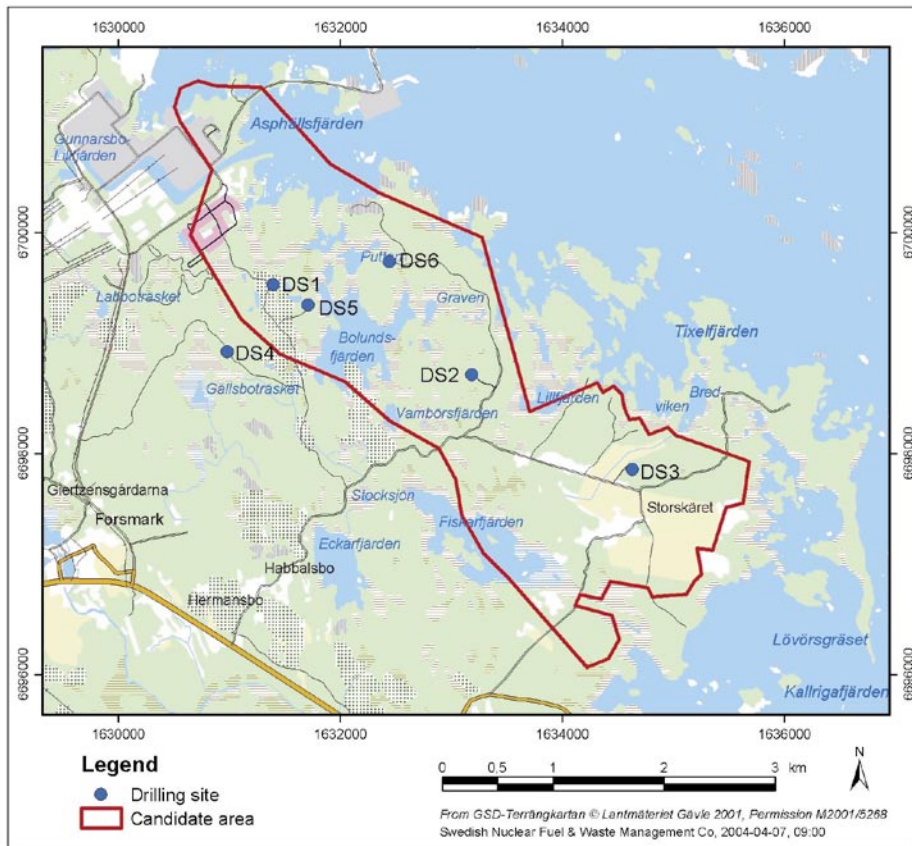


Figure 1-1. The investigation area at Forsmark (approximately the area inside the black square) including the candidate area selected for more detailed investigations. The six drilling sites for deep boreholes, DS1-6, are marked with blue circles. Borehole KFM02A is situated at drilling site DS2.

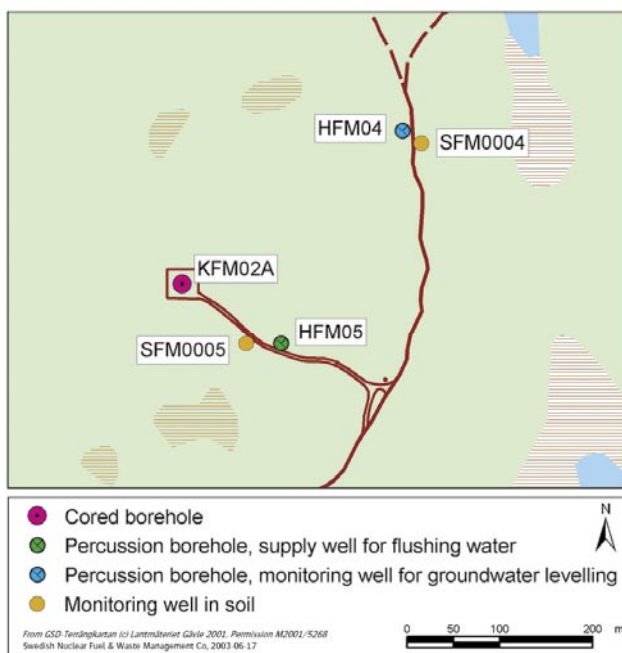


Figure 1-2. Location of the cored borehole KFM02A, the percussion boreholes and the monitoring wells in soil at drilling site DS2.

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 get as complete information as possible about the groundwater chemical conditions in individual water bearing fractures or local minor fracture zones. Considerable effort is put on obtaining representative samples from a limited rock volume. Careful pumping and continuous control of the pressure in the sampled borehole section, as well as above the section, is maintained in order to minimise the risk of mixing with water from other fracture systems.

The method “Sampling during pumping tests in core drilled boreholes” is primarily performed as a complementary study in order to increase the volume of hydrochemical data. The method is often used in borehole sections with a large yield of water. The water samples collected during pumping tests often represent a larger bedrock volume and/or a more dominating hydraulic structure than the samples that are collected during “Complete chemical characterisation”. Pumping is performed using equipment for hydraulic tests (PSS). The use of this method/equipment in KFM02A, instead of “Complete chemical characterisation”, allowed investigations in two boreholes to be carried out in parallel. Further, the possibility of using a high pumping flow rate was favourable due to the high content of remaining flushing water in this borehole.

The difference between the two methods regarding sampling and measurement activities is shown in Table 2-1 below.

Table 2-1. List of sampling and measurement activities included in the two investigation methods.

Sampling or measurement activity	“Complete chemical characterisation”	“Sampling during pumping tests in core drilled boreholes”
Water sampling series including class 4 and class 5 samples.	Yes	Yes
Surface Chemmac measurement.	Yes	Yes (redox potential measurements are difficult due to heavy pumping through a pipe string and are seldom successful)
Borehole Chemmac measurement.	Yes	No
Collection of in situ samples for gas, colloids and microbes.	Yes	No
Fractionation of humic and fulvic acids as well as inorganic species.	Yes	Yes
Enrichment of organic acids, determ of $\delta^{13}\text{C}$ and pmC (percent modern carbon).	Yes	Yes

3 Background

3.1 Flushing water history

The percussion drilled borehole HFM05 served as a supply well for the flushing water used to drill borehole KFM02A /4/. The chemical composition of the flushing water was checked before and during use. The analytical data from the supply well HFM05 are reported in /5/. The core drilling of the 1000 m long borehole consumed 1130 m³ of flushing water and the volume of returned water pumped from the borehole during drilling was 2003 m³. The nominal concentration of the dye Uranine, added as a tracer to mark the flushing water, was 0.2 mg/L. Automatic dosing equipment to introduce Uranine was installed in the flushing water line to supply flushing water to the drilling of KFM02A. The Uranine concentration in the flushing water was checked regularly during drilling and a total of 61 samples were analysed. The average Uranine concentration in the entire sample series was 0.22 ± 0.11 mg/L. The average value for the last thirty samples (when the new dosing system started to work satisfactory) was 0.26 ± 0.02 mg/L. The Uranine concentrations in the sample series of flushing water as well as of the return water are presented in Figure 3-1. Further, the amount of Uranine added to the borehole via the flushing water and the estimated amount recovered in the return water is given in Table 3-1.

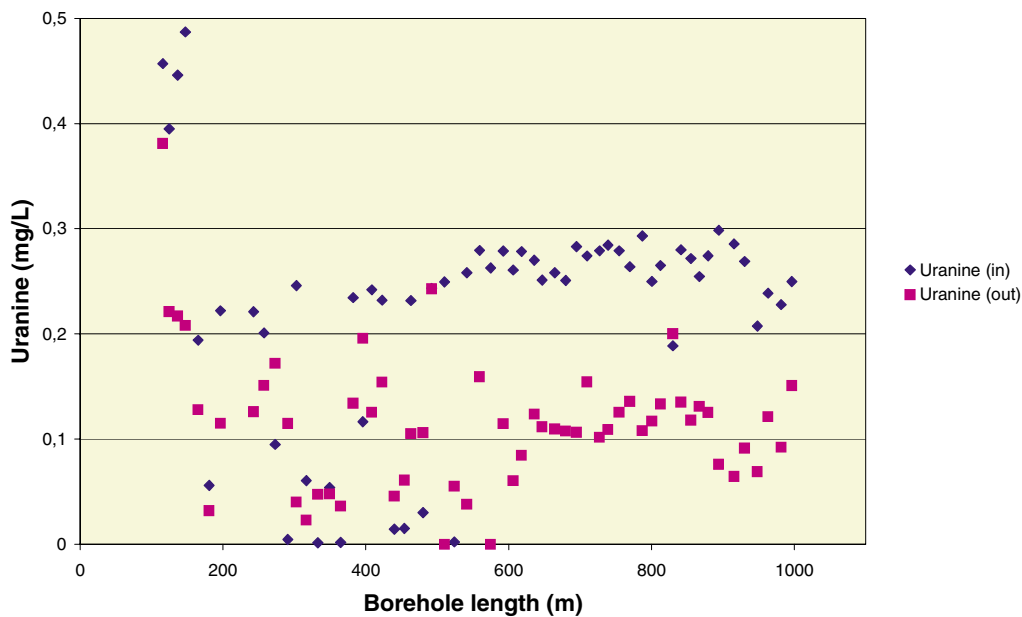


Figure 3-1. Uranine concentrations in the flushing water and in the return water versus borehole length. The addition of Uranine was done using the automatic dosing equipment which is controlled by a flow meter. After some initial problems the concentration was sufficiently constant although somewhat higher than the nominal value of 0.2 mg/L.

Table 3-1. Amount of Uranine added to KFM02A via the flushing water during core drilling and the amount recovered from the contemporary mammoth pumping.

Uranine	(g)
Added, according to the log book.	250
Added, calculated from the average Uranine concentration and the total volume of flushing water.	252
Recovered, estimated from the average Uranine concentration and the total volume of return water.	230

The Uranine budget in Table 3-1 suggests that approximately 100 m³ of the flushing water was lost to the borehole and the adjacent host bedrock. It became clear later on /6/ that the remaining flushing water was going to be a major problem and that extra pumping was going to be required. As shown in Figure 3-2, the cumulative volume of flushing water exceeds the volume of return water during the first part of the drilling. Two other factors may contribute to the more problematic flushing water situation in this borehole compared to the boreholes KFM01A and KFM03A namely:

- There is one very dominant water bearing fracture zone at about 120 m along the borehole (just below the casing). Consequently, the pumping performed in the upper part of the borehole during drilling was less efficient, especially at depth, since a major part of the pumped water originated from this fracture.
- Water bearing fracture zones exist only to a depth of about 520 m and they tend to be less conductive compared to the shallow zone at 120 m. Flushing water was presumably pressed into these few and minor zones since the water pressure during drilling was quite large, causing high flow gradients into these fractures.

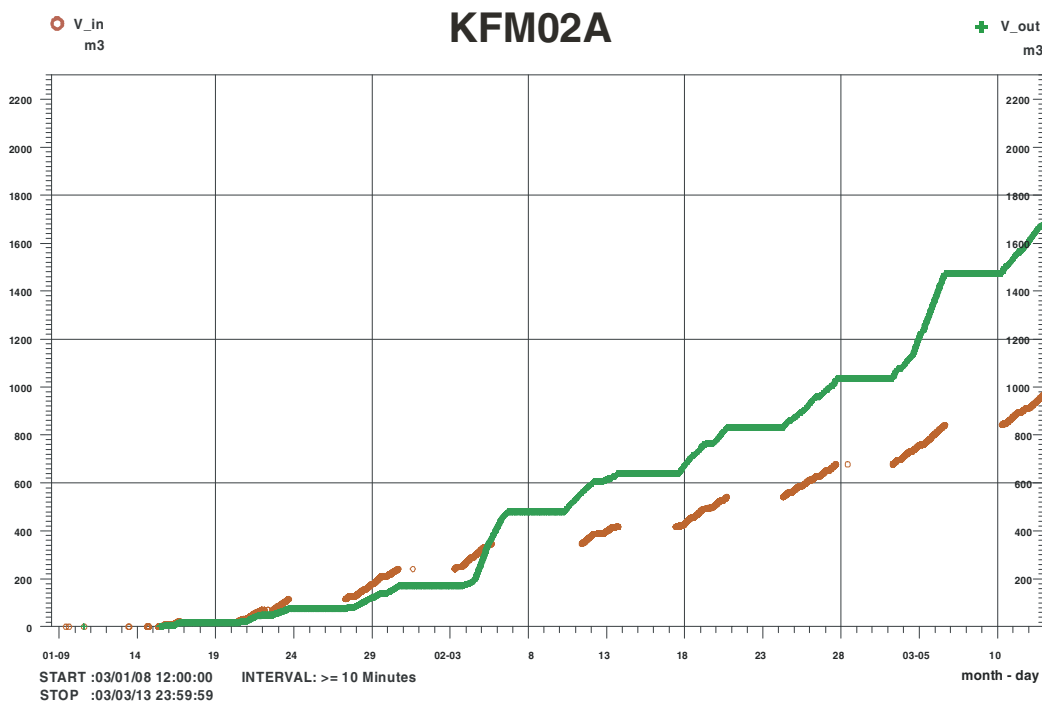


Figure 3-2. Cumulative volume of flushing water (in) and return water (out) plotted versus date.

As borehole KFM02A is of SKB chemical-type, the following special precautions were taken in order to minimise contamination via the flushing water:

- The supply well was also of SKB chemical-type.
- Borehole HFM05 was selected to supply flushing water because the dominant water bearing fractures were situated at about 150 m depth. The flushing water had therefore a low concentration of total organic carbon (TOC). The concentration should preferably be below 5 mg/L and the concentration in the samples collected in HFM05 was in the range 2.3–2.6 mg/L.
- New dosing equipment for Uranine was installed, thereby removing the need for an in-line flushing water storage tank after the UV-system.

Analyses of the microbe content in the flushing water, before and after the UV-system, was performed during drilling /7/. The results showed that the amounts of algae and bacteria in the flushing water entering the borehole were reduced compared to KFM01A, probably due to the absence of the in-line storage tank after the UV-system. However, the microbe content was still too high to be satisfactory and further measures need to be taken in order to avoid microbial growth in the flushing water in future drilling activities.

3.2 Previous events and activities in the borehole

KFM02A is a SKB chemical-type core borehole and thus specially intended for complete hydrochemical characterisation. Only those investigations that are necessary in order to select borehole sections are carried out in the borehole prior to the chemistry campaign. The more downhole equipment used in the borehole, the greater is the risk of contamination and effects on the *in situ* microbiological conditions. The activities/investigations performed in KFM02A prior to the chemistry campaign are listed in Table 3-2 below.

Table 3-2. Activities performed in borehole KFM02A prior to the chemical characterisation.

Activities performed	Date of completion	Length or section (m)	Comment
Percussion drilling	2002-11-26	0–100	
Pumping tests and water sampling	2002-11-29	18.0–100.4	/4, 5/ Water samples: SKB no 4398 (pumped volume 1.95 m ³) SKB no 4397 (pumped volume 24.8 m ³)
Geophysical logging and BIPS logging	2002-12-03	0–100	–
Casing installed	2002-12-10	0–100	After the hydraulic tests, a casing was installed and gap grouted, sealing off water inflow to this part of the borehole.
Core drilling	2003-03-12	100.4–1002.4	HFM05 was the source of flushing water for drilling the cored part of KFM02A. HFM05 is a SKB chemical-type borehole /3, 5/.
Water sampling, Wireline sond	2003-01-20	105–159	WL-sond water samples (Uranine conc within brackets). SKB no 4462 (43%)
	2003-01-27	250–290	SKB no 4468 (20%)
	2003-01-29	249–396	SKB no 44469 (89%)
Flushing water treatment	–	–	Automatic dosing of Uranine was introduced during drilling of KFM02A. In this way no inline storage tank was needed after the UV-system /3/.
BIPS-logging	2003-02-13	100–635	–
Geophysical logging	2003-02-14	100–634	
Microbe control	2003-03-04	–	Check of microbe content in flushing water /7/.
Hydrochemical logging	2003-03-31	994	High flushing water content along the borehole (about 40–50% below 200 m and c 80% below 600 m depth) /6/.
Difference flow logging	2003-05-08	101–997	/8/
Hydrogeochemical characterisation including sampling for microbe investigation in section 509–516 m	2004-02-24	–	Presented in this report.
Microbe investigation	–	–	/2/

3.3 Choice of borehole sections

A very dominant water bearing zone (109–121 m) was identified early during core drilling of borehole KFM02A. The water yield was very large which made it difficult to identify additional inflow zones further down in the borehole. However, results from the subsequent difference flow logging showed a number of minor water bearing zones that were possible to investigate down to about 513 m, see Appendix 2. Below this depth, no water yielding fractures were observed. The identified zones of sufficient importance to be selected are listed in Table 3-3.

Table 3-3. Significant water yielding fractures/fracture zones identified from difference flow logging of KFM02A /8/. Selected fractures/fracture zones are given in bold text.

Borehole length (m)	Approximate flow (L/h), pumping in 1 m sections, drawdown c 10 m
109 –121	Several fractures, giving about 200 L/h each
162–182.5	Several fractures, giving about 2–30 L/h each
216.5	10
227.5	2
265.5–299.5	Several fractures, giving about 10–20 L/h each
301	2
416–427	Two fractures, giving about 20 L/h each
436.5	4
449.5	3
453.5	30
478–486	Several fractures, giving about 1–9 L/h each
513	Discreet and well defined fracture, 90 L/h

Section 106.5–126.5 m was selected in order to investigate the most dominant water inflow into the borehole and also to allow comparison between groundwater data obtained at the same depth in KFM01A and KFM02A. The 20 m long section was necessary in order to ensure fracture-free rock beneath the inflatable packers as the fracture zone is quite extensive. Pumping/sampling using the hydraulic test equipment at a high pumping flow rate was preferred as the water yield was large. Further, groundwater at the same depth was studied also in KFM01A, therefore there was no real need for *in situ* sampling and Eh-measurements at the actual depth. The calculated hydraulic transmissivity (T) for the borehole section was $1.1 \cdot 10^{-4} \text{ m}^2/\text{s}$ ($T > 10^{-6} \text{ m}^2/\text{s}$ is optimal). The recorded flow logging of the section is given in Appendix 2.

Between 126.5 and 413.5 m, the water bearing zones were of less interest due to complicated fracture patterns and the need for a long section or a low flow yield. Possible deeper sections were considered more important to investigate and section 413.5–433.5 m was selected next. The flow yield at this section was large enough for the hydraulic test equipment (PSS) and a similar section length of 20 m was used as before. A high content of remaining flushing water was anticipated from the results of previous activities /3, 6/ and the hydraulic test equipment was suitable also for this reason since it allows a high pumping flow rate. The calculated hydraulic transmissivity (T) for the borehole section was $2.7 \cdot 10^{-6} \text{ m}^2/\text{s}$. The recorded flow logging of the section is given in Appendix 2.

The well defined fracture at 513 m (repository depth) was considered very important to investigate and therefore selected for complete hydrochemical characterisation. There is solid bedrock above and below the fracture and a section length of 7 m could be used with a suitable section at 509.0 to 516.1 m. The calculated hydraulic transmissivity (T) for the borehole section was $3.9 \cdot 10^{-6} \text{ m}^2/\text{s}$ (the range $T = 10^{-8}$ to $T = 10^{-6} \text{ m}^2/\text{s}$ is optimal). The recorded flow logging of the section is given in Appendix 2.

4 Equipment

4.1 The Pipe String System (PSS)

The SKB pipe string system (PSS) consists of a measurement container and a set up of downhole equipment. The system is normally used for hydraulic pumping tests and hydraulic injection tests but was in this case applied for pumping and chemical sampling. The equipment is described in SKB MD 345.100–124 (Pipe String System, SKB internal controlling document). The PSS unit was combined with a separate chemistry unit for computer work and Chemmac measurements (MYC). This unit is described in SKB MD 434.007 (Mätssystembeskrivning för mobil ytChemmac, SKB internal controlling document) and SKB MD 433.018 (Mätssystembeskrivning för data-applikation, SKB internal controlling document). The Chemmac measurement system in the MYC-unit includes communication system, a measurement application and a flow-through cell with electrodes and sensors at ground level.

The PSS3 equipment is designed for flow rates between 5 and 30–40 L/min. In order to pump at lower flow rates (down to 1 L/min), it is necessary to re-circulate the pumped water back to the pump.

The units used in borehole KFM02A consisted of the hydrotest unit PSS3 and the MYC3 unit for computer work and surface Chemmac measurements. The laboratory unit L3 was used for analysis work. However, the laboratory unit was not placed at the drilling site and thus not directly connected to the outlet of the pumped water during pumping of section 413.5–433.5 m.

4.1.1 Measurement container

The PSS is primarily designed for pumping and injection tests in packed off borehole sections. All equipment needed to perform the tests is located in a steel container placed on pallets to adjust to a suitable working level in relation to the borehole casing. The container is divided into a data and a workshop compartment, see Figure 4-1.

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

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

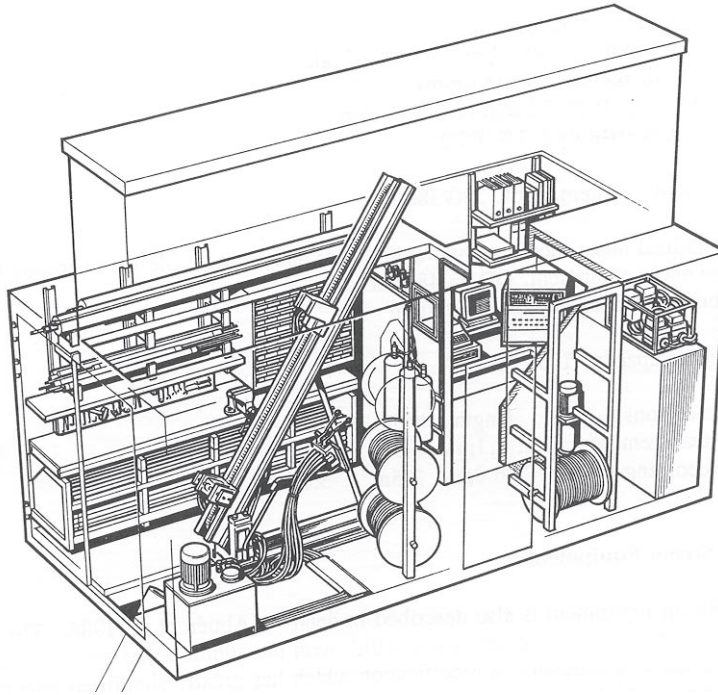


Figure 4-1. Outline of the PSS3 container with equipment.

4.1.2 Downhole equipment

A schematic drawing of the downhole equipment is shown in Figure 4-2. The pipe string consists of aluminium pipes 3 m in length with an inner diameter of 21 mm connected by stainless steel taps sealed with double o-rings. The length of the test section comprises pipes of 5 m which can be varied to investigate 5, 20 or 100 m sections, the electric cable is also prepared for these lengths. Pressure is measured above (P_a), within (P) and below the test section (P_b), which is isolated by two packers. The groundwater temperature in the test section is also measured. The hydraulic connection between the pipe string and the test section can be closed or opened by a test valve operated by the measurement system.

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

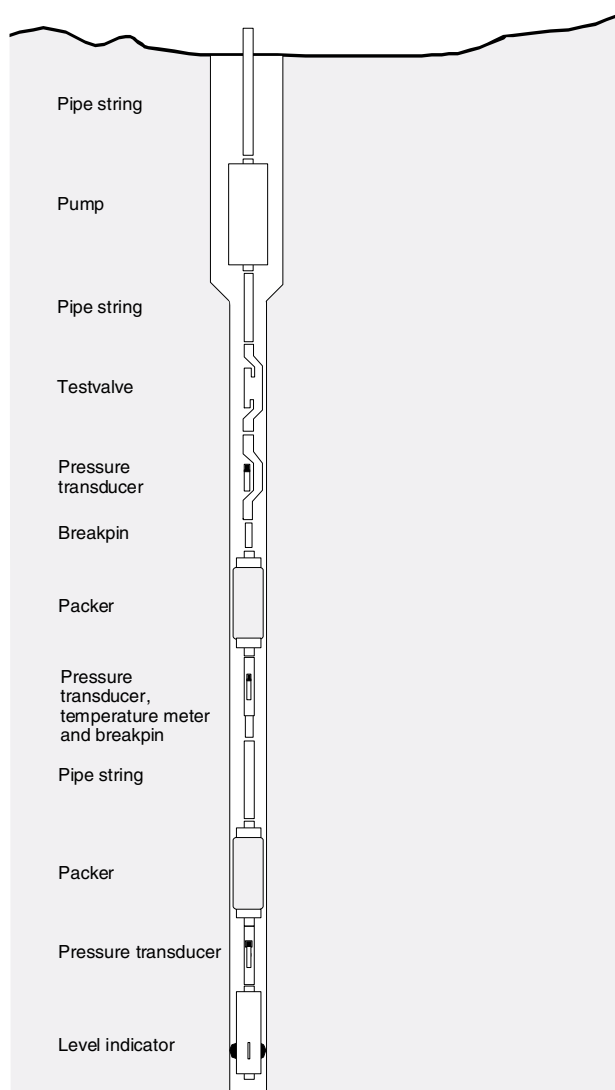


Figure 4-2. Schematic drawing of the downhole equipment in the PSS3 system.

4.2 The mobile field laboratory (MFL)

The mobile field laboratories used by SKB for water sampling and downhole measurements consist of a laboratory unit, a hose unit with downhole equipment and a Chemmac measurement system; the system is presented schematically in Figure 4-3. It is also possible to include a separate computer unit (MYC). The different parts of the system are described in the SKB internal controlling documents SKB MD 434.004, 434.005, 434.006, 434.007 and SKB MD 433.018 (Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation).

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

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

The mobile units used in borehole KFM02A, section 509.0–516.1 m, consisted of the hose unit S3, the laboratory unit L3 and the MYC 3 unit for computer work. The equipment used for colloid filtration, enrichment of humic and fulvic acids and fractionation of humic and fulvic acids are described below.

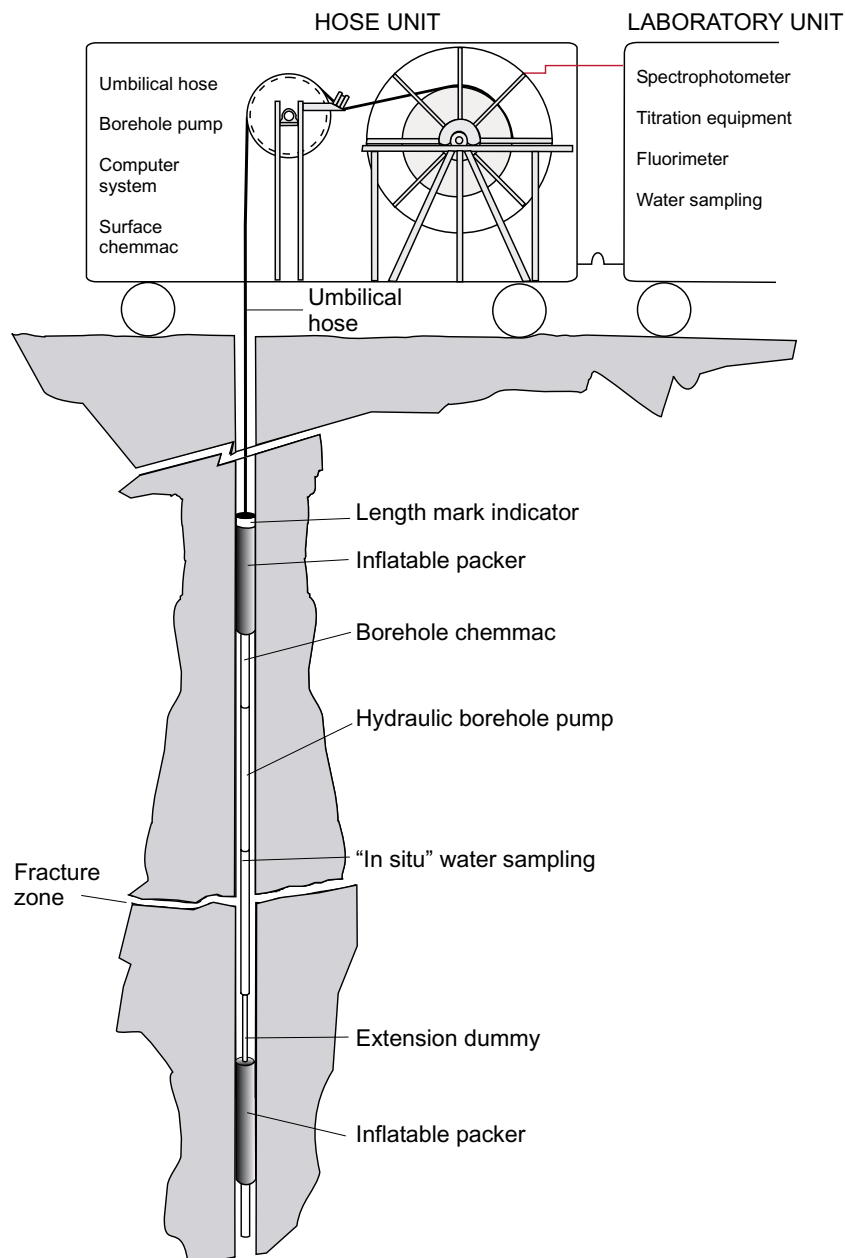


Figure 4-3. The mobile chemistry laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the *in situ* water sampler must always be positioned first in the sample water path.

Some crucial differences between the PSS and the MFL equipment need to be pointed out;

- The sample water channel/tube of the umbilical hose in the hose unit of the mobile field laboratory has an inner diameter of 4 mm. The pipe string in the PSS3 equipment is wider at 21 mm.
- The pipe string is made of aluminium, while the sample water channel/tubing is made of polyamide.
- The maximum flow rate by the hose unit pump is in the range of 200–250 mL/min, while the pipe string system has a maximum flow rate of 30–40 L/min (only about 200 mL/min is led through the surface Chemmac).
- At low flow rates it is necessary to re-circulate the pumped water to the PSS pump.

4.3 Colloid filtering equipment

The colloid filtering system is still at the development stage. The equipment is adapted to the sample containers (PVB) from the PVP water sampling unit. The colloid filtering equipment consists of holders for two PVB-containers, a separated tube and valve system for water and gas, a filter holder package for five filters, and a collecting container. The pore sizes of the five connected filters are 0.4, 0.4, 0.2, 0.05 and 0.05 μm . The equipment is described in SKB MD 431.045 (Mätsystembeskrivning för kolloidfiltreringssystem, handhavandedel SKB internal controlling document to be published). Figure 4-4 shows the equipment setup.

The major equipment features are:

- Filtering is performed in a closed system under argon atmosphere, thus avoiding the risk of iron precipitation due to contact between the groundwater sample and air.
- Filtering is performed at a pressure similar to that of the groundwater in the borehole section. The system is adjusted to create a pressure difference between the inlet of the filter package and the outlet side. The pressure difference drives the sample water through the filters.
- The design of the sample containers, and the mounting with the outlet at the top, prevents migration of larger particles which may clog the filters. Furthermore, clogging is prevented also by the first two filters with pore size 0.4 μm which are mounted parallel to each other.

Disadvantages/drawbacks, which may result in later modifications of the equipment, are:

- The sample volume is limited to a maximum of 2·190 mL.
- The PVB sample containers are made of stainless steel which may contaminate the samples. If the method proves to be successful, an improvement could include the use of Teflon coating on the inside of the cylindrical containers.

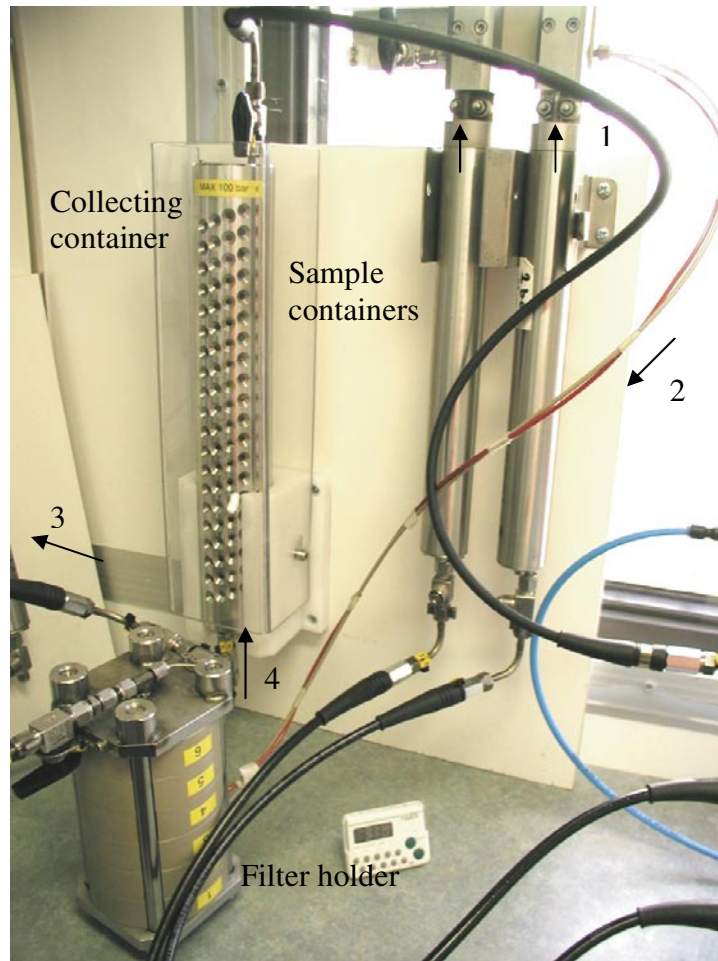


Figure 4-4. The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1 to 4, show the flow direction of the sample water through the system.

4.4 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 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 are described in SKB MD 431.044 (Mätssystembeskrivning för uppkoncentrering av humus- och fulvosyror, SKB internal controlling document). Figure 4-5 shows the equipment setup. Since the ion exchange resin in the column creates a counter-pressure, which disturbs the water flow through the surface Chemmac, a pump was used in sections 106.5–126.5 and 413.5–433.5 m for pumping a portion of the outlet water through the column (approximately 2.4 L/hour).



Figure 4-5. *The ion exchange column mounted to the outlet of pumped groundwater from the borehole section.*

4.5 Equipment for fractionation of humic and fulvic acids

The equipment consists of membrane filters with a defined cut-off (pore size), a membrane pump, flexible tubing and vessels. Generally, one water sample from each section is filtered through two filters with different pore sizes (1000 D and 5000 D, D = Dalton, 1D = 1 g/mol). The equipment and performance are described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror, SKB internal controlling document). Figure 4-6 shows the equipment setup.

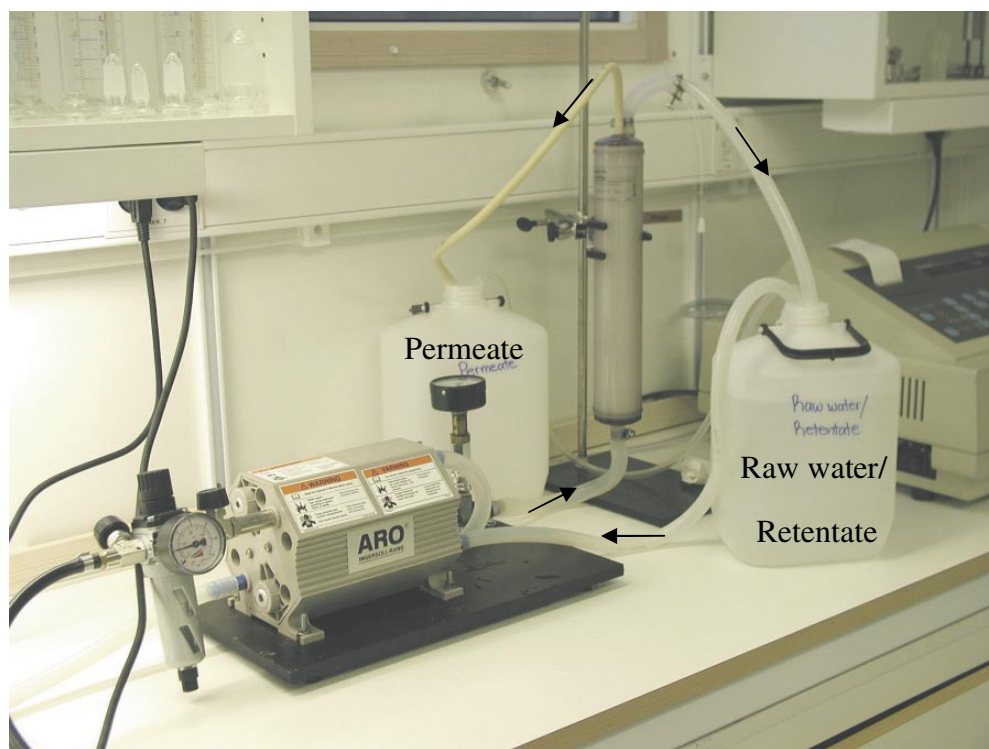


Figure 4-6. Equipment for fractionation of humic and fulvic acids.

5 Performance

Chemical characterisation of the three sections in borehole KFM02A was performed according to activity plan AP PF 400-03-38 following the methods described in SKB MD 430.017 and SKB 430.018 (Metodbeskrivning för fullständig kemikaraktisering med mobilt fältlaboratorium and Metodbeskrivning för provtagning under pumpster i kärnbrorrhål, both are SKB internal controlling documents). The investigations in the sections 106.5–126.5 and 413.5–433.5 m were conducted mainly according to SKB MD 430.018 (sampling during pumping tests in cored boreholes). As no actual pumping tests were made, there was no need to follow standard pumping test procedures. Therefore, the pumping time could be prolonged and the sampling was more extended compared to the method description.

Planning of the chemical investigation in the borehole was modified several times, due to large amounts of remaining flushing water in the borehole sections and also to allow an opportunity to conduct geophysical logging. An overview of the final investigation sequence is given in Table 5-1.

Table 5-1. Investigation sequence in KFM02A.

Start date/ Stop date	Investigation	Section (m)	Comment
2003-06-04/ 2003-06-12	Interrupted test Complete chemical characterisation	417.0–426.5	High flushing water content. Slow decrease. Doubt whether there is leakage from the water column in the borehole or not. Pumped volume ~ 2 m ³ .
2003-06-13/ 2003-06-26	Interrupted test Complete chemical characterisation	509.0–516.1	High flushing water content. Slow decrease. Pumped volume = 3.8 m ³ . (2003-06-11–2003-06-26)
2003-07-03/ 2003-08-04	Clean-up pumping using PSS3	505–520	Initial flushing water content = 14.5%. Final flushing water content = 7.5%.
2003-08-04/ 2003-08-10	Geophysical logging	0 –1000	The pumping was interrupted for one week.
2003-08-12/ 2003-08-25	Continued clean-up pumping using PSS3	505–520	Initial flushing water content = 7.7%. Final flushing water content = 6.0%. Total pumped volume, clean up pumping (505–520 m) = 205 m ³ .
2003-08-28/ 2003-08-31	Pumping the entire borehole	0–1002.4	Pumped volume = 163.4 m ³ .
2003-09-01/ 2003-10-21	Complete chemical characterisation	509.0–516.1	Pumped volume = 10.0 m ³ .
2003-10-31/ 2003-11-19	Sampling during pumping tests, PSS3	106.5–126.5	Pumped volume = 930.4 m ³ .
2003-11-19/ 2003-12-17	Clean-up pumping using PSS3	413.5–433.5	Pumped volume = 96.6 m ³ .
2004-01-27/ 2004-02-23	Sampling during pumping tests, PSS3	413.5–433.5	Pumped volume = 95.9 m ³ .

5.1 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. The procedure for the method *Sampling during pumping tests* is basically the same as for *Complete chemical characterisation*, except that no downhole measurements or *in situ* sampling can be conducted. The points below that are valid only for the complete chemical characterisation of the section 509.0–516.1 m, and not for the pumping/measurements in sections 106.5–126.5 and 413.5–433.5 m, are given in italic text.

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

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

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

- The outside of the umbilical hose/pipe string 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, a length mark detector unit (caliper) is mounted together with the ordinary downhole equipment. The length mark detector indicates length calibration marks milled into the borehole wall at almost every 50 m along the borehole /3/. At each indication, a reading is made of the corresponding length mark on the umbilical hose. The length calibration for the pipes in the PSS equipment is made at each section. At the lower end of the borehole equipment, a calliper type of level indicator gives a signal when passing a reference depth mark. The correct distance to each length mark is obtained from the SICADA database.*

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

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

- Careful attention is paid in order to make sure that the packed off section is well isolated from the rest of the borehole. A significant drawdown in the section during pumping is one indication that the section is isolated. Leakage would cause pumping of water from the borehole column above and/or below the packers and not only from the fracture zone of interest. However, the drawdown in the borehole section must not be too large since the greater the drawdown, the larger the bedrock volume affected by the pumping and the risk of mixing with water from other fracture systems increases. The pumping flow rate is adjusted depending on the flow yield from the fracture or fracture zone (to between 50 and 300 mL/min using MFL, or as high as possible using PSS) 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 at the site.
- Enrichment of humic and fulvic acids is conducted for as long time as possible in each section. The time needed depends on the carbon concentration in the water and the flow rate through the ion-exchanger. Generally, a period of at least two weeks is needed to collect the amount of carbon required to determine $\delta^{13}\text{C}$ 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 at 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 options is collected the day before termination.

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

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

5.2 Performance in section 106.5–126.5 (PSS3)

The pumping/measurements and water sampling in section 106.5–126.5 m was performed using the PSS3 unit in combination with the MYC3 unit and the L3 unit.

The pumping was carried out at a flow rate of about 33 L/min with a drawdown in the borehole section of about 1.9 m. Diagrams showing flow rate and pressures during the pumping/measurement period are given in Appendix 4, Figures A4-1 and A4-2. The events during the investigation are listed in Table 5-2.

Table 5-2. Events during the pumping/measurement period with PSS3 in section 106.5–126.5 m.

Date	Events <i>Improvement/deviation</i>	SKB sample no
031105	Calibration of surface Chemmac.	
031106	<u>Start of Chemmac measurements.</u>	
031106–07	Identified pressure response from the drilling of HFM16, see Appendix 4, Figure A4-2. The response is further discussed in /11/.	
031107	<u>Sampling during pumping tests (PSS3) (106.5–126.5 m).</u>	
031107	Water sampling: SKB class 4. <i>No contact with conductivity meter and oxygen electrode.</i>	8097
031110	Humic and fulvic acids; enrichment start. Humic and fulvic acids, fractionation, 1 kD.	8100
031111	Humic and fulvic acids; fractionation, 5 kD. Identified pressure response from the drilling of HFM16, see Appendix 4, Figure A4-2. The response is further discussed in /11/.	8100
031112	Humic and fulvic acids; fractionation, 1 kD.	8100
031113	Water sampling: SKB class 4. Humic and fulvic acids; fractionation, 1 kD.	8099 8100
031117	Humic and fulvic acids; enrichment stop. Restart of measurement and masternode. Regained contact with conductivity meter and oxygen electrode.	
031118	Water sampling: SKB class 5. Humic and fulvic acids; enrichment elution.	8100 8100
031119	<u>End of Chemmac measurements. Lifting.</u>	
031120	Calibration of surface Chemmac.	

5.3 Performance in section 413.5–433.5 m (PSS3)

The pumping/measurements and water sampling in section 413.5–433.5 m were performed using the PSS3 unit in combination with the MYC3 unit.

The pumping was carried out at a flow rate of about 2.4 L/min during the period 2003-11-19 to 2003-12-17 with a drawdown in the borehole section of about 31.6 m. During the pumping period 2004-01-27 to 2004-12-17, the flow rate was about 2.5 L/min with a drawdown in the section of about 31.1 m. Diagrams showing flow rate and pressures during the pumping/measurement period are given in Appendix 4, Figures A4-3 to A4-6. The events during the investigation are listed in Table 5-3.

Table 5-3. Events during the pumping/measurement period with PSS3 in section 413.5–433.5 m.

Date	Events <i>Improvement/deviation</i>	SKB sample no
031119	<i>During the re-establishment of the PSS3, a metal tool was accidentally dropped in the borehole and it probably fell to the bottom.</i>	
031218	<i>Interruption of pumping (Christmas break). Equipment insulated from frost.</i>	
040109	<i>By lifting the PSS3 equipment to perform radar measurements in the borehole, the cone placed between the spaced and the narrow part of the borehole was found to be loose. The PSS3 equipment had to be removed from the borehole to adjust the cone.</i>	
040127	<i>The PSS3 equipment was re-assembled and lowered to the section (413.5–433.5 m) to be investigated. Pumping was started.</i>	
040204	Calibration of surface Chemmac. <u>Start of Chemmac measurements.</u> Calibration of surface Chemmac.	
040205	Water sampling: SKB class 4.	8159
040209	<i>Outgoing tecalan tubes from surface Chemmac were frozen during the weekend. Therefore, the flow to surface Chemmac was turned off until a heating cable was installed.</i>	
040210	<i>Heating cable in place, flow through surface Chemmac resumed.</i>	
	Water sampling: SKB class 4.	8266
040213	<i>One electrode in the surface Chemmac was loose, later replaced.</i>	
040216	Humic and fulvic acids; enrichment start.	
040217	Humic and fulvic acids; fractionation 5 kD.	8272
040218	Humic and fulvic acids; fractionation 1 kD.	8272
040223	Water sampling: SKB class 5. Humic and fulvic acids; enrichment stop. <u>End of Chemmac measurements. Lifting.</u>	8272
	Calibration of surface Chemmac.	
040224	Humic and fulvic acids; enrichment eluation.	8272

5.4 Performance in section 509.0–516.1 m (MFL)

The investigations in section 509.0–516.1 m were performed using the mobile field laboratory units. The configuration of the downhole equipment in the borehole was, from the top: umbilical hose, borehole Chemmac, upper packer, borehole pump, *in situ* water sampler (PVP), extension dummy and lower packer. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping was performed at a flow rate of about 140 mL/min and the drawdown could not be recognised. On the contrary, during pumping, the pressure in the packed off section was 0.3 to 0.4 bar higher than above the section. This is probably due to a high natural pressure caused by a heavy flow into this part of the borehole. Diagrams showing the pressures within and above the borehole section and the flow rate during the pumping/measurement period are given in Appendix 4, Figures A3-7 and A3-8.

The events during the investigation are listed in Table 5-4.

Table 5-4. Events during the pumping/measurement period with MFL in section 509.0–516.1 m.

Date	Events <i>Improvement/deviation</i>	SKB sample no
030827	Calibration of borehole Chemmac.	
030901	<u>Lowering of downhole equipment (509.00–516.08 m)</u>	
030902	Water sampling: Uranine.	
030902	Calibration of surface Chemmac.	
	Water sampling: SKB class 2.	4978
030904	Water sampling: SKB class 4.	4979
	<i>Change of membrane in oxygen probe, re-calibration of oxygen meter.</i>	
030908	Humic and fulvic acids; enrichment start.	
	Water sampling: SKB class 5.	4980
030909	<i>Restart of measurements following communication problem between hose unit (S3) and MYC-wagon (MYC3).</i>	
030910	<i>Restart of measurements after moving MYC3.</i>	
030912	Water sampling: SKB class 4.	4981
030915	Water sampling: SKB class 5.	4982
030918	Water sampling: SKB class 4.	4984
030922	Water sampling: SKB class 5.	4985
030924	<i>Humic and fulvic acids; enrichment stop; no ion exchanger left in the column. New enrichment started.</i>	
030925	Water sampling: SKB class 4.	8009
030929	Humic and fulvic acids; fractionation 1 kD and 5 kD.	8010
030929	Water sampling: SKB class 5.	8010
	PVP-sampler; opening of valve at 16:05.	
030930	PVP-sampler; closure of valve at 07:00.	8010
	<u>Lifting.</u>	
	Dismounting of PVP unit, check of closing valve.	
	Calibration of borehole Chemmac.	
031001	Calibration of surface Chemmac.	
031002	<u>Lowering of downhole equipment (509.00–516.08 m).</u>	
	Calibration of borehole and surface Chemmac.	
031007	Node 3 out of function.	
	Calibration of surface Chemmac.	
031008	Water sampling: SKB class 4.	8013
	<i>Changed prom at nod 3 and 4.</i>	
031016	Water sampling: SKB class 4.	8014
031016	Humic and fulvic acids: fractionation, 5 kD.	8016
031017	Humic and fulvic acids: fractionation, 1 kD.	8016
031020	Humic and fulvic acids; enrichment stop and eluation.	8016
	Water sampling: SKB class 5.	8016
	PVP-sampler; opening of valve at 17:10	
031021	PVP-sampler; "closure" of valve at 07:35 (<i>problem with the PVP-sampler, valve will not open despite a pressure of 58 bars</i>).	
	<u>Lifting.</u>	
031022	<u>Lowering of downhole equipment (509.00–516.08 m).</u>	
031024	PVP-sampler; opening of valve at 10:50	
031027	PVP-sampler; closure.	8016
	<u>Lifting.</u>	
	Colloid filtration	

5.5 Water sampling, sample treatment and analyses

The pumped water from the borehole section is led into the laboratory unit where sampling and sample filtration is carried out. When the laboratory unit is not available at the drilling site, as was the case for section 413.5–433.5 m, the pumped borehole water is led into the MYC-unit instead. In either case, filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. A water sample is defined as water collected during one day and consists of several sample portions, labelled with the same sample number.

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

5.6 Collection of *in situ* water samples

The *in situ* water sampling was conducted only in section 509.0–516.1 m where it was repeated three times. This was due to the following reasons:

- At the first lift of the borehole equipment on September 30th, there was uncertainty if the packers were leaking or not. It was decided to cancel the microbe determination and the colloid filtration. The sample water was allowed to flow through and rinse the PVP-system and its four sample containers (PVB) for 15 hours before the valves were closed.
- At the second sampling occasion on October 21st, the collection of the *in situ* water samples failed since a valve in the PVP equipment did not open.
- At the third run on October 27th, the *in situ* water sampling was conducted successfully. The sample water was allowed to flow through and rinse the PVP-system and its four sample containers (PVB) for 68 hours before the valves were closed.

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

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

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

Sample portion no	Section 509.0–516.1 m 2003-09-30	Section 509.0–516.1 m 2003-10-21	Section 509.0–516.1 m 2003-10-27
1	Dissolved gas	–	Dissolved gas
2	Microbes (not performed)	–	Microbes
3	Colloid filtration (not performed)	–	Colloid filtration
4	Colloid filtration (not performed)	–	Colloid filtration

– = collection of *in situ* water sample failed.

The two PVB-containers for colloid filtration were filtered the same day. The PVB-containers for dissolved gases and microbes were packed together with ice packs in insulated bags and sent by express delivery service immediately after sampling. The microbe sample arrived at the laboratory in Gothenburg before three o'clock the same day and the gas sample arrived at the laboratory in Finland the following morning.

5.7 Colloid filtration

Colloid filtration was performed only in section 509.0–516.1 m. 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 size. Two of the four sample portions (PVB) collected *in situ* in the borehole section are used for colloid filtration. Data on performance of the filtration run are given in Table 5-6. A leak test at 10 bars was also done prior to the sampling in order to eliminate the risk of leakage. Thereafter, if no leakage was noticed, the system was dried and assembled.

Each filtration results in five filter samples (two 0.4 µm, one 0.2 µm and two 0.05 µm filter pore sizes) and two water samples (water in and water out). All samples were sent for ICP analyses (major constituents and common trace metals).

Table 5-6. Colloid filtration; performance.

Section/date	Entering pressure (bar)	Max diff pressure (bar)	Temp. (°C)	Filtering time (min)	Filtered volume (mL)	Comments
509.0–516.1 m/ 20031027	~ 53	5.1	~ 5	61	148.1	Broken filters: 0,2 and both 0,05 µm

5.8 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 of the organic constituents in the groundwater. The enrichment method entails collection of organic acids on an ion exchanger, elution of the resin and evaporation of the resulting solution. The method is described in SKB MD 431.044 (Mätsystembeskrivning för uppkoncentrering av humus- och fulvosyror). The dry residue is used for isotope determination; a minimum amount of 10 mg organic carbon is needed. In addition to organic material, the residue also contains sodium hydroxide from the elution. The sample is acidified at the analytical laboratory prior to analysis in order to prevent the formation of carbon dioxide.

The water was allowed to flow through the ion exchanger for 10 days in section 106.5–126.5 m, 6 days in section 413.5–433.5 m and 17 days in section 509.0–516.1. The total water volume is estimated to about 500 L, 330 L and 900 L, respectively. Theoretically, assuming a 50% capacity of the ion exchange resin, the resin would adsorb 100 mg carbon (10 mg is needed for the isotope analyses).

5.9 Fractionation of humic and fulvic acids

Humic and fulvic acids were fractionated with respect to molecular weight using an ultra-filtration technique. The method is described in SKB MD 431.043 (Mätsystembeskrivning för fraktionering av humus- och fulvosyror). Sampled water from the three sections at 106.5–126.5 m, 413.5–433.5 m and 509.0–516.1 m were filtered through membrane filters with cut-off sizes of 1000 D and 5000 D, respectively. The reproducibility was verified in sections 106.5–126.5 m (filtering three times with the 1000 D filter) and 509.0–516.1 m (filtering twice with each one of the 1000 D and 5000 D filters). The initial water volumes, prior to filtration, were approximately 5 litres. The final retentate and permeate volumes following the filtration runs were approximately 1 and 4 litres, respectively, which gave an enrichment factor of five in the retentate. Water samples were collected from the retentate and the permeate as well as from the untreated groundwater in the borehole section. Each sample was analysed for dissolved organic carbon (DOC), major constituents and common trace metals. The analyses of metal ions are conducted in order to detect any precipitation of metals that could possibly lead to co-precipitation of the humic and fulvic acids. Furthermore, the analyses of metal ions should indicate if metals such as Al, Si, Mn and Fe exist as colloidal species.

6 Nonconformities

The hydrochemical characterisation of the three sections in KFM02A has been conducted according to the SKB internal controlling documents AP PF 400-03-38 and SKB MD 430.017 and 430.018. Some equipment malfunctions have occurred during the pumping/measurement periods. The equipment malfunctions are listed in Tables 5-2 to 5-4. Furthermore, the surface Chemmac redox measurements in the sections 106.5–126.5 and 413.5–433.5 m were considered unreliable and are therefore omitted/not reported, see Chapter 8.1. This was expected since earlier experiences from the pre-investigations at Äspö /10/ also showed difficulties in measuring redox parameters when sample water is pumped at a high flow rate through a pipe string. Electric conductivity in section 106.5–126.5 m was not measured due to an inadequate conductivity meter. Electrical noise caused scattered electrical conductivity and dissolved oxygen data in section 413.5–433.5 m, and these measurements were omitted.

The colloid filtering experiment was less successful as three out of five filters were broken by the pressure increase needed to push the water through the filter system. Therefore, the data from the colloid filtering are less useful.

The allowed upper limit for flushing water content, 1%, was exceeded in sections 413.5–433.5 m (3%) and 509.0–516.1 m (6%). This condition has not been reported in any deviation report.

7 Data handling and interpretation

7.1 Chemmac measurement data

Processing of the Chemmac data is described in SKB MD 434.007-02 (Mätssystem-beskrivning för Chemmac mätsystem, SKB internal controlling document, in progress).

7.1.1 Data file types and calculation software

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

- Calibration files from calibration measurements (*.CRB) and corresponding comment files (*.CI). The files are used for calculation of calibration constants (pH and Eh) and the calibration factor (electric conductivity). For surface Chemmac ten *.CRB and ten *.CI files, 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 as 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 electric conductivity values using the specially designed calculation software (Hilda). The resulting files containing calculated and evaluated values as well as comments on the performance are:

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

7.1.2 Calculations and evaluation of pH and redox potential

The redox potential is measured by three electrodes at the surface and also in the downhole borehole section. In addition, pH is measured by two electrodes at the surface and also in the borehole section. In sections 106.5–126.5 m and 413.5–433.5 m, only the surface electrodes were used. Furthermore, the registrations by the redox and the pH electrodes are logged each hour during a measurement period of approximately three weeks and a calibration is performed before and after the measurement period. The treatment of the raw data includes the following steps:

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

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

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

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

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

7.2 Water analysis data

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

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

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

- Comparison of the results from different laboratories and/or methods. The analyses are repeated if a large disparity is noted (generally more than 10%).
- Calculation of charge balance errors, equation (1). Relative errors within $\pm 5\%$ are considered acceptable (in surface waters $\pm 10\%$).

$$\text{Relative error (\%)} = 100 \times \frac{\sum \text{cations}(\text{equivalents}) - \sum \text{anions}(\text{equivalents})}{\sum \text{cations}(\text{equivalents}) + \sum \text{anions}(\text{equivalents})} \quad (1)$$

- 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 which are considered most reliable.

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

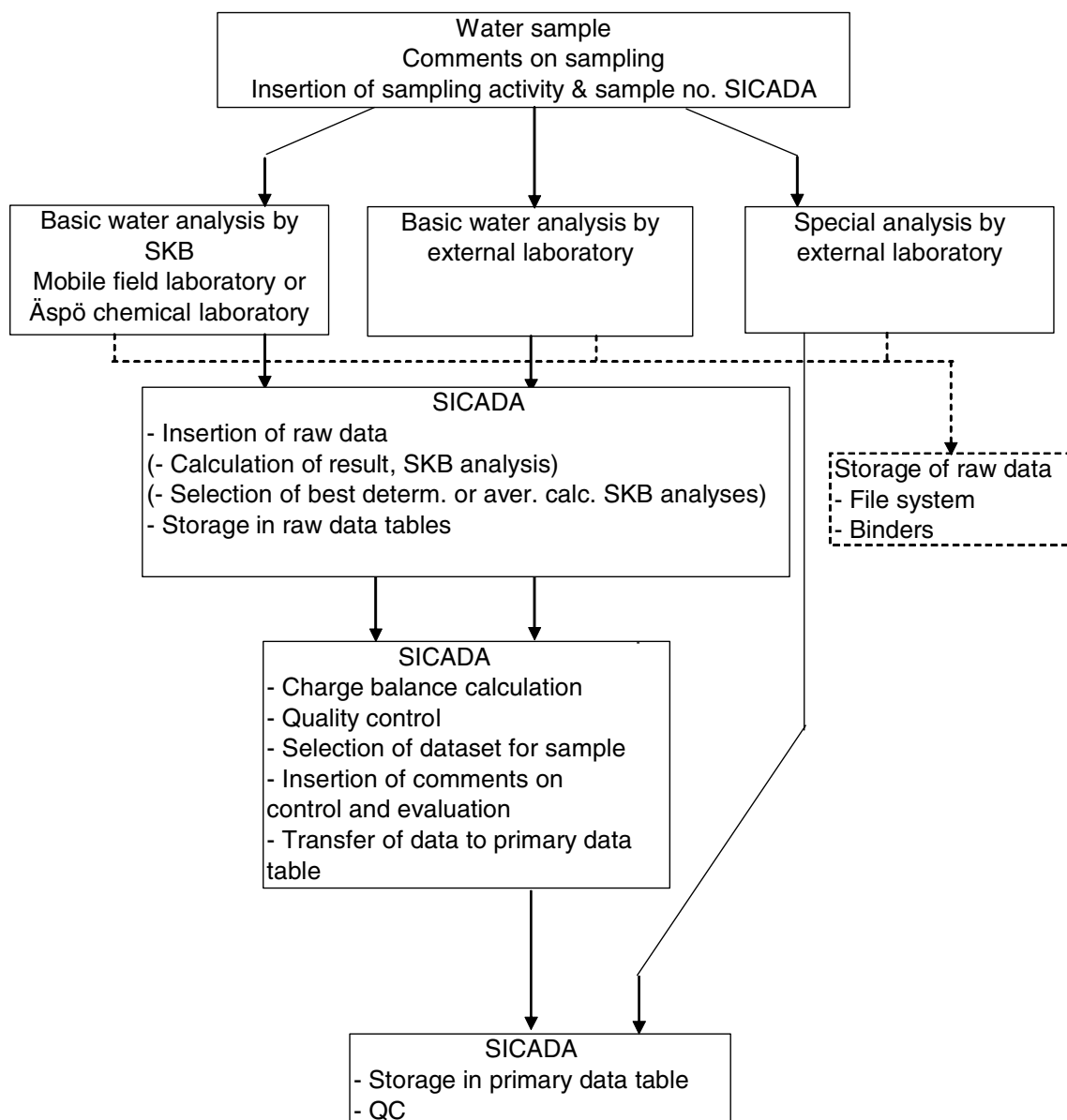


Figure 7-1. Overview of data management for hydrogeochemical data.

7.3 Data from special sampling methods

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

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

7.3.1 Colloid filtration

The concentration of the colloid portion caught on each filter is calculated with the assumption that the water volume entering the collecting container is equal to the volume going into the system. This is not quite true as up to ten millilitres will remain 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 following filtration and its content of the different elements is included in the analysis. The measurement uncertainty of each colloid concentration is calculated from the “sum” of the measurement uncertainties of the filter analyses and estimated volume error (volume passing through the filters) according to equation (2).

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

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 calculated results from the colloid filtration filters are stored in SICADA. The results from water samples are directly inserted into the primary data tables in SICADA.

7.3.2 Dissolved gases

The results of the gas analyses are stored in the primary data tables in SICADA without 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 SICADA without processing or interpretation.

7.3.4 Fractionation of humic and fulvic acids

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 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. < 1000 D, 1000–5000 D and > 5000 D.

8 Results

8.1 Chemmac measurements

Sections 106.5–126.5 m and 413.5–433.5 m were investigated using the PSS3 equipment combined with the surface Chemmac in the MYC3 unit. In such cases, however, it is usually difficult to measure reliable redox potentials using pipe string systems and heavy pumping. The redox potential values are therefore rejected. Besides, measurement of electric conductivity in section 106.5–126.5 m was omitted due to a defective conductivity meter. Electrical noise caused scattered electric conductivity and dissolved oxygen data in section 413.5–433.5 m and these measurements are therefore rejected. The measurement sequences of pH, dissolved oxygen and water temperature for section 106.5–126.5 are plotted versus time in Appendix 5 and for section 413.5–433.5 m in Appendix 6.

Section 509.0–516.1 m was investigated using the complete chemical characterisation method and the Chemmac measurement in the section was on the whole successful, despite some interruptions. However, the redox electrodes of the surface Chemmac did not stabilise at a reasonable value within the measurement period. It is possible that air was entering into the surface cell or that released gas caused small bubbles on the electrode surfaces. The measurement sequences of pH, Eh, electric conductivity, dissolved oxygen and water temperature are plotted versus time in Appendix 7. The pH and redox potential data measured by the downhole Chemmac electrodes were calculated using a linear drift correction. The redox electrode values of the surface Chemmac were omitted from the calculation of the representative Eh value presented in Table 8-1.

The measurement data sequences were evaluated in order to obtain one representative value of Eh, pH, electric conductivity and dissolved oxygen for the borehole section as described in Section 7.1. Data were selected from a part of the measurement sequences where the electrodes have stabilised. The evaluated results from the measurements in the three sections are given in Table 8-1.

Table 8-1. Evaluated results from the Chemmac measurements in KFM02A.

Borehole section (m)	Electric conductivity* (mS/m)	pH (surface Chemmac)**	pH (borehole Chemmac)**	Eh (borehole Chemmac)** (mV)	Dissolved oxygen*** (mg/L)
106.5–126.5	–	7.53 ± 0.09	–	–	0.00 ± 0.01
413.5–433.5	–	7.11 ± 0.18	–	–	–
509.0–516.1	1613 ± 20	6.93 ± 0.24	6.83 ± 0.15	–143 ± 30	0.01 ± 0.01

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

** Evaluated result and measurement uncertainty calculated as described in Section 7.1.2.

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

8.2 Water analyses

8.2.1 Basic water analyses

The basic water analyses include the major constituents Na, K, Ca, Mg, S, SO_4^{2-} , Cl^- , Si and HCO_3^- as well as the minor constituents Fe, Li, Mn, DOC, Br, F, HS^- and NH_4^+ . Furthermore, batch measurements of pH and electric conductivity are included. Another important parameter is the flushing water content in each sample. The basic water analysis data and relative charge balance errors are compiled in Appendix 9, Table A9-1. Existing batch measurement values of pH and/or electric conductivity are compared to the corresponding on-line Chemmac measurement values in Appendices 5, 6 and 7.

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

The flushing water contents in the sample series collected in the borehole sections are presented in Figure 8-1. The flushing water content should not exceed 1% in a sample considered representative for the groundwater of the sampled fracture zone. This condition was met for the samples collected in the section 106.5–126.5 m. However, in the sections 413.5–433.5 m and 509.0–516.1 m, the flushing water content was 3% and 6%, respectively, in the final water sample. These conditions prevailed despite that the PSS3 equipment had been used for “clean-up” pumping (417.0–426.5 and 505.0–520.0 m) before the hydrochemical characterisation took place (Table 5-1).

The concentration levels of sodium, calcium and chloride are presented in Figures 8-2 to 8-4. The concentrations of all major constituents remained practically constant during the pumping and sampling periods except for section 106.5–126.5 m, where a slightly increasing concentration trend could be noted.

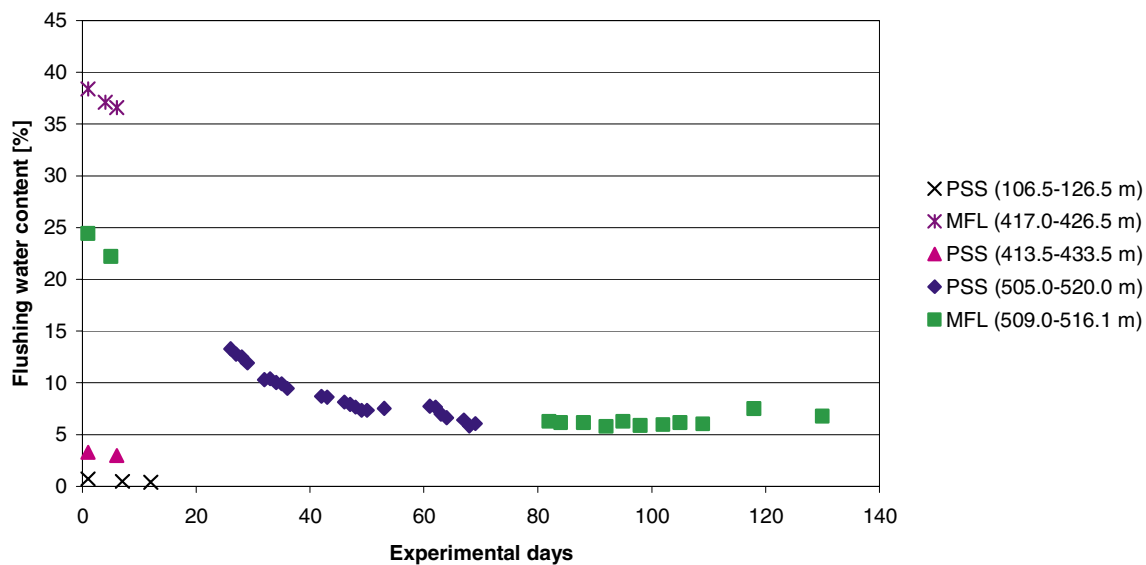


Figure 8-1. Flushing water content versus numbers of experimental days.

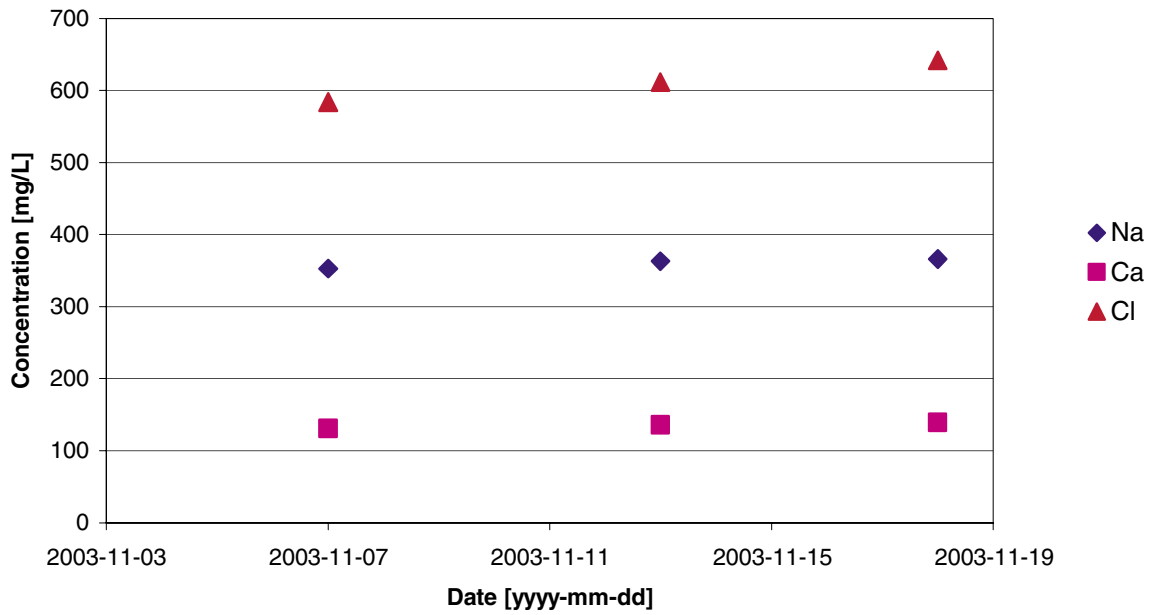


Figure 8-2. Sodium, calcium and chloride concentration trends from sample series at 106.5–126.5 m.

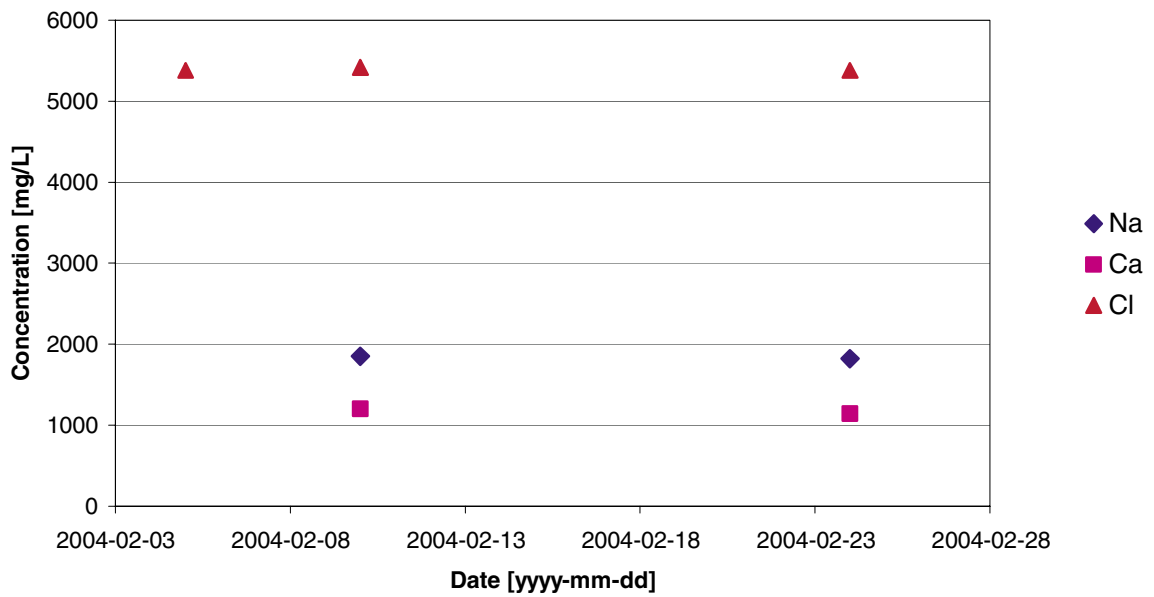


Figure 8-3. Sodium, calcium and chloride concentration trends from sample series at 413.5–433.5 m.

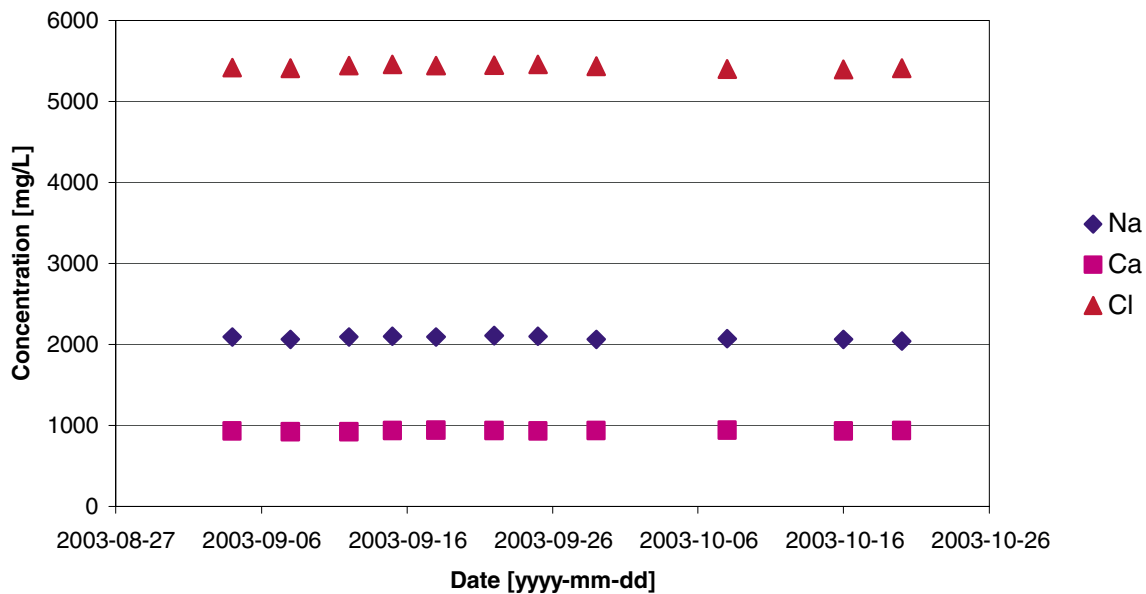


Figure 8-4. Sodium, calcium and chloride concentration trends from sample series at 509.0–516.1 m.

The iron concentrations determined by ICP-AES (total Fe) and by spectrophotometry (Fe(+II) and Fe-tot) are compared in Figures 8-5, 8-6 and 8-7. The iron analyses for section 106.5–126.5 m show low Fe(+II) concentrations compared to total iron concentrations. It is not likely that the difference represents the Fe(+III) concentration in a groundwater representative of the borehole section, therefore Fe(+II) data are omitted in SICADA.

The discrepancy may be caused by:

- Oxidation of Fe(+II) prior to the analyses due to time delays between sampling and reagent addition. According to the field laboratory staff, this was however, not the case.
- Contamination by rust or Fe(+III) precipitate from equipment prior to sampling.
- Intrusion of air somewhere in the water sampling line and oxidation of Fe(+II). This is the most likely explanation, although the oxygen measurement shows zero concentration.

The iron concentrations in the other two sections are more consistent and remain constant during the investigation periods except for the increase after the interruption in section 509.0–516.1 m. Furthermore, the ICP-results in both sections are similar to, or in a few samples somewhat lower than, the results obtained by spectrophotometry. Any colloidal iron present in a sample would give the opposite effect, as the spectrophotometric method excludes (or only partly includes) colloids, while the ICP technique makes no distinction between different iron-containing species.

The DOC results from three borehole sections, 106.5–126.5, 413.5–433.5 and 509.0–516.1 m, are plotted versus experimental day in Figure 8-8. DOC analyses in saline waters are, by experience, considered less reliable than in fresh waters. However, in this case the concentrations appear to be quite consistent.

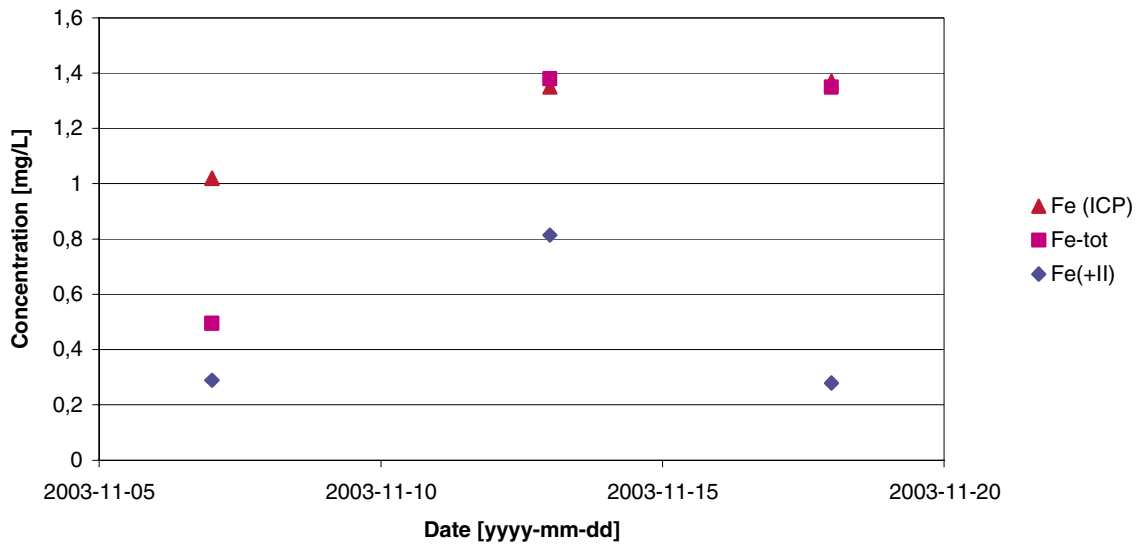


Figure 8-5. Comparison of iron concentrations obtained by ICP-AES and spectrophotometry from borehole section 106.5–126.5 m.

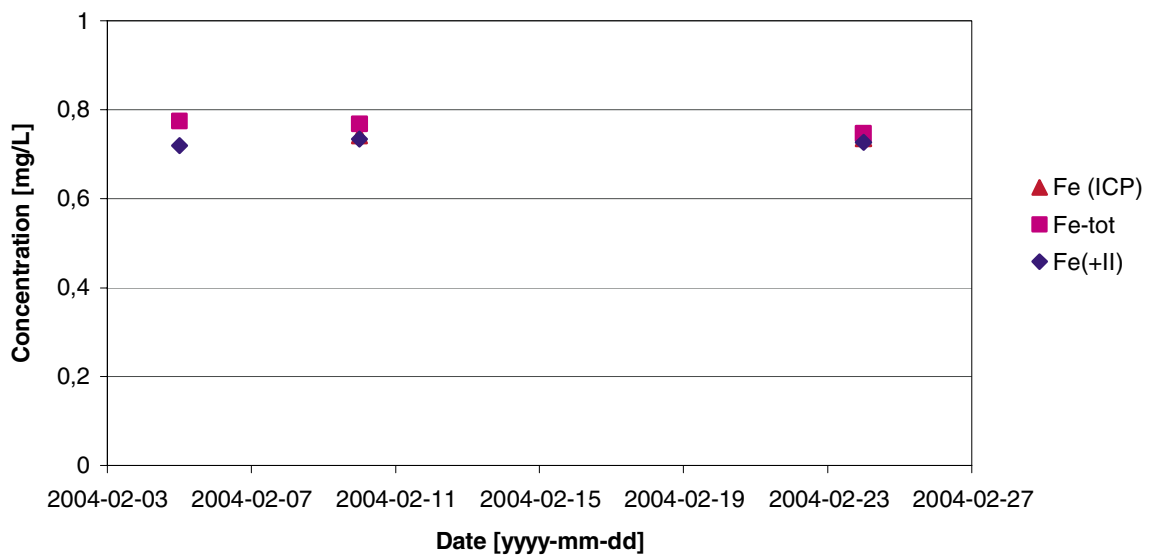


Figure 8-6. Comparison of iron concentrations obtained by ICP-AES and spectrophotometry from borehole section 413.5–433.5 m.

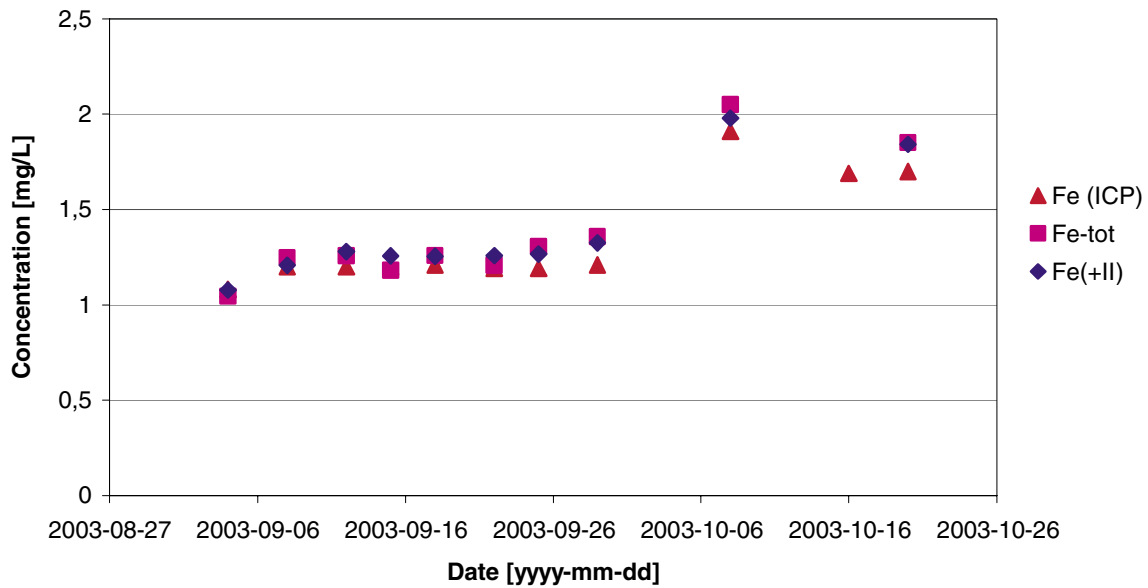


Figure 8-7. Comparison of iron concentrations obtained by ICP-AES and spectrophotometry from borehole section 509.0–516.1 m.

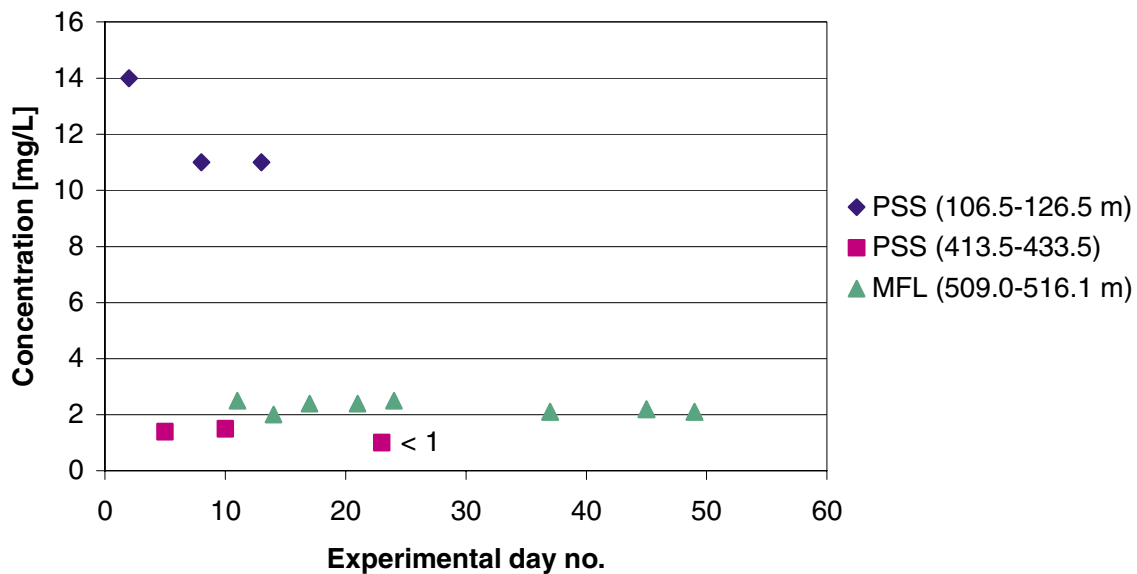


Figure 8-8. DOC concentrations versus experimental day number from sections 106.5–126.5 m and 509.0–516.1 m.

Sulphate analysed by ion chromatography (IC) is compared to sulphate determined as total sulphur by ICP-AES in Figures 8-9 to 8-11. As shown, there is a satisfactory agreement, especially in section 106.5–126.5 m. However, the results from the ICP measurements are considered more reliable, by experience, since the variation between the samples in a time series is often less when using this method.

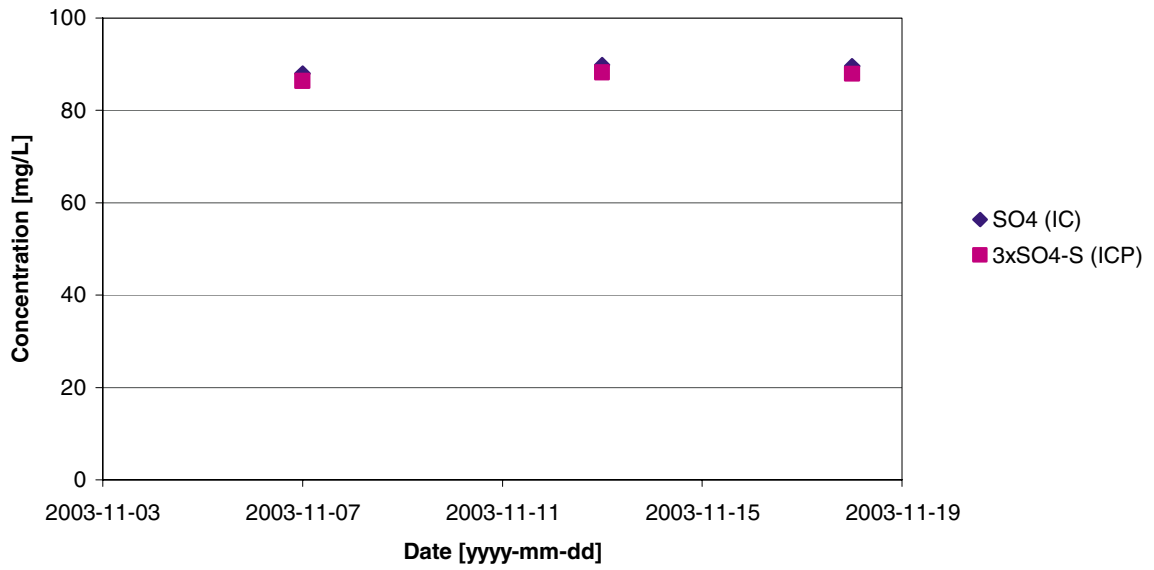


Figure 8-9. Sulphate (SO_4 by IC) compared to sulphate calculated from total sulphur ($3 \cdot SO_4-S$ by ICP) versus date. Samples collected in section 106.5–126.5 m.

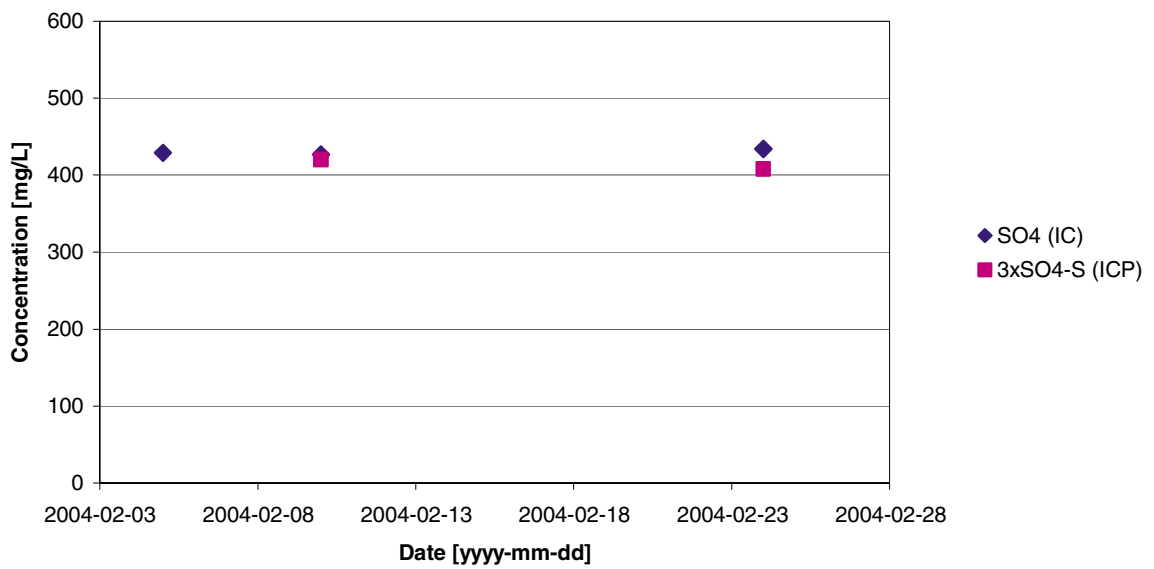


Figure 8-10. Sulphate (SO_4 by IC) compared to sulphate calculated from total sulphur ($3 \cdot SO_4-S$ by ICP) versus date. Samples collected in section 413.5–433.5 m.

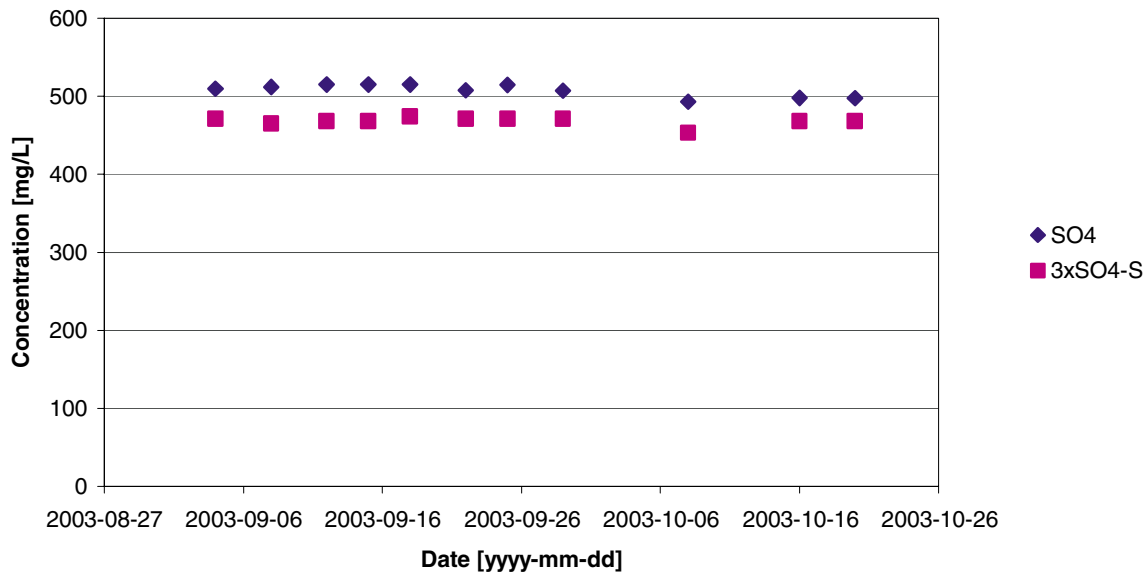


Figure 8-11. Sulphate (SO_4 by IC) compared to sulphate calculated from total sulphur ($3 \cdot SO_4-S$ by ICP) versus date. Samples collected in section 509.0–516.1 m.

The chloride concentrations are plotted versus the corresponding electric conductivity values in Figure 8-12. The plot gives an approximate indication that the values are reasonable. The data from the borehole sections agree well with the line obtained by earlier data from the Äspö Hard Rock Laboratory.

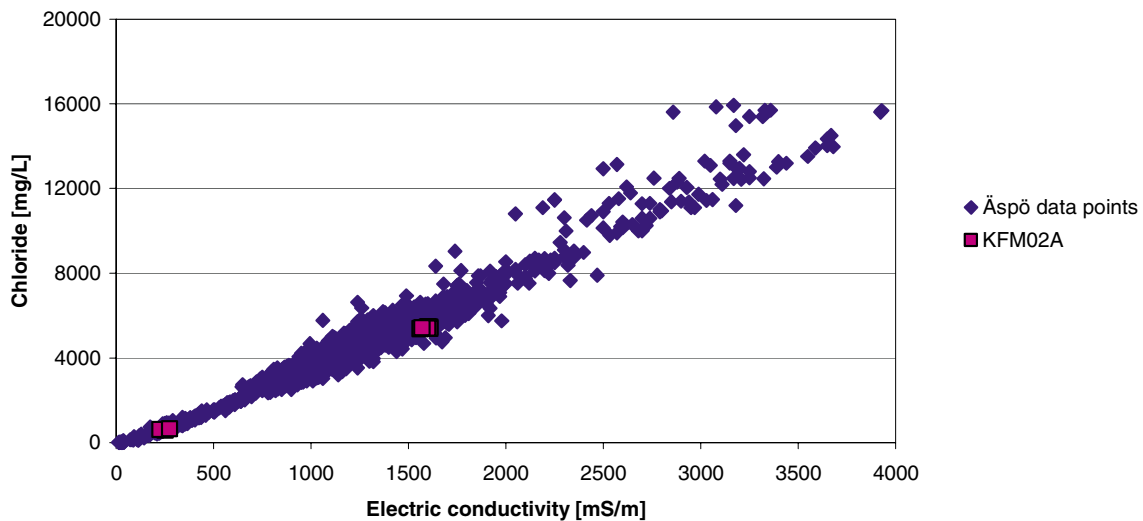


Figure 8-12. Chloride concentration versus electric conductivity. Data from earlier investigations at the Äspö Hard Rock Laboratory are used to show the linear trend. Data from KFM02A agree with a regression line.

8.2.2 Trace elements (rare earth metals and others)

The analyses of trace and rare earth metals include U, Th, Sc, Rb, Y, Zr, In, Sb, Cs, 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 trace element data are compiled in Appendix 9, Table A9-3.

8.2.3 Stable and radioactive isotopes

The isotope determinations include the stable isotopes δD , $\delta^{18}O$, $^{10}B/^{11}B$, $\delta^{34}S$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ as well as the radioactive isotopes Tr (TU), ^{14}C (pmC), ^{238}U , ^{235}U , ^{234}U , ^{232}Th , ^{230}Th , ^{226}Ra and ^{222}Rn . The isotope data are compiled in Appendix 9, Table A9-2 and Table A9-4. Some of the isotope results were not available at the printing date and will be included in a version no 2 of this report.

The tritium and $\delta^{18}O$ results from section 509.0–516.1 m are presented in Figure 8-13. The tritium content was below the detection limit (0.8 Tritium Units) in all samples except one. The $\delta^{18}O$ ratios remained stable during the sampling period.

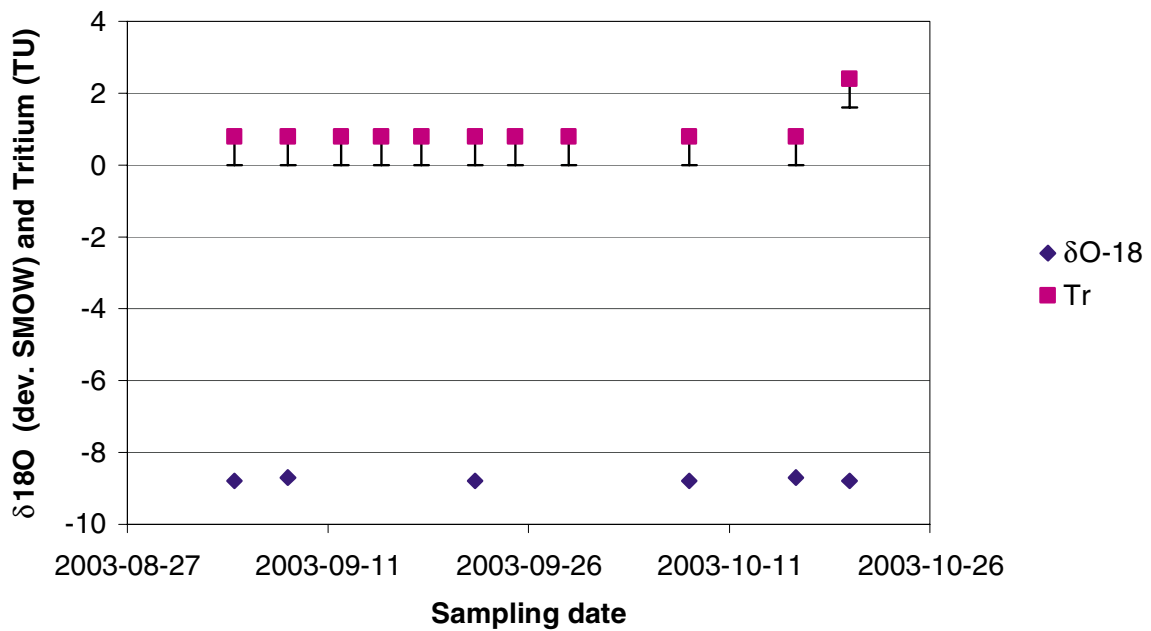


Figure 8-13. Tritium and $\delta^{18}O$ data from samples collected in section 509.0–516.1 m.

The carbon isotopes ($\delta^{13}\text{C}$ and pmC) were determined both in inorganic carbon (hydrogen carbonate) and in organic constituents. The results are compared in Table 8-2 below. Enrichment of organic carbon was necessary in order to obtain enough organic material, see Section 5.8.

The pmC values obtained from the organic carbon are approximately 30% higher than the corresponding values for inorganic carbon. This discrepancy is common and is explained by the different origins of the carbon and by substitution reactions that occur between dissolved carbonates in the water and carbonate minerals, which alter the isotope signature of the inorganic carbon in the water.

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

Borehole section (m)	Inorg. $\delta^{13}\text{C}$ (dev PDB)	Org. $\delta^{13}\text{C}$ (dev PDB)	Inorg. pmC	Org. pmC
106.5–126.5	-12.9	-26.7	64.50	89.3
413.5–433.5	x	x	x	x
509.0–516.1	-9.1	-27.7	15.80	45.1

x = Not yet analysed.

8.3 Dissolved gases

Sampling for gas analyses was performed in section 509.0–516.1 m. The analyses of dissolved gases include argon (Ar), helium (He), nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), oxygen (O_2), hydrogen (H_2), carbon monoxide (CO), ethane (C_2H_6), ethene (C_2H_4), ethyne (C_2H_2), propane (C_3H_8) and propene (C_3H_6). The gas data are compiled in Appendix 9, Table A9-5. Two in situ gas samples were collected (2003-09-30 and 2003-10-27) and the results are compared in Figures 8-14 and 8-15. The total gas contents were 83.2 mL/L and 73.6 mL/L respectively. The oxygen contents of 0.04 mL/L and 0.12 mL/L indicate that there was an air leakage into the purging system at the laboratory. The results can be corrected by removing the air effect (nitrogen, oxygen and argon) assuming that the oxygen content is zero. The two analysed samples from the 509.0–516.1 m section show reasonable agreement. A notable difference between the two analysis results is that the proportion of argon compared to nitrogen is higher in the last sample.

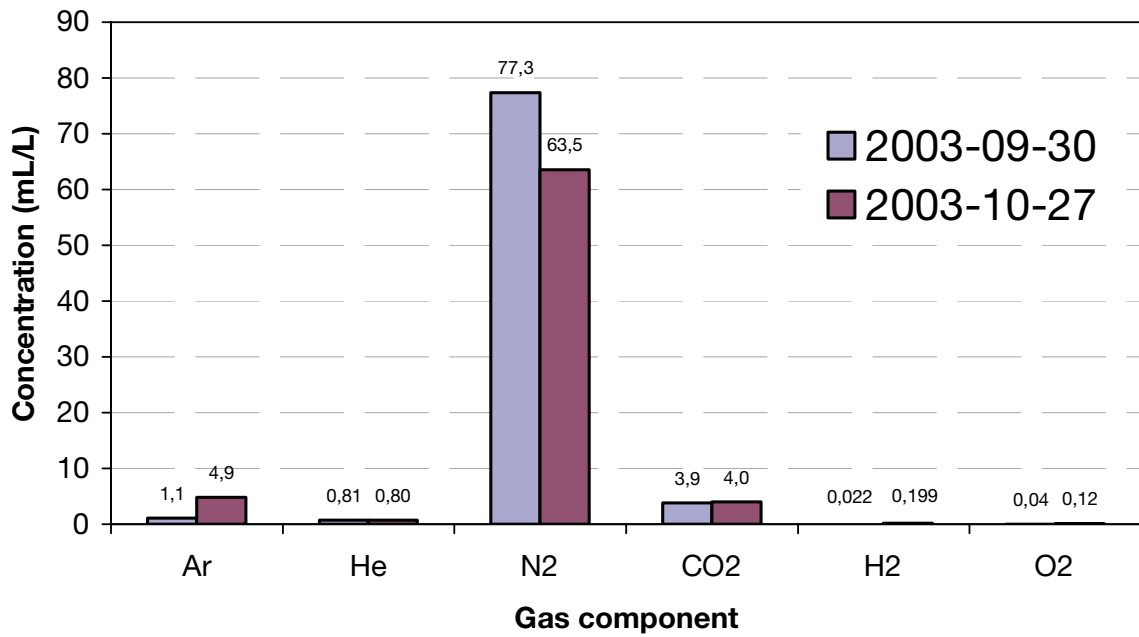


Figure 8-14. Gas components of high concentrations (Ar, He, N₂, CO₂, H₂ and O₂) in samples collected 2003-09-30 and 2003-10-27 using the in situ sampling equipment.

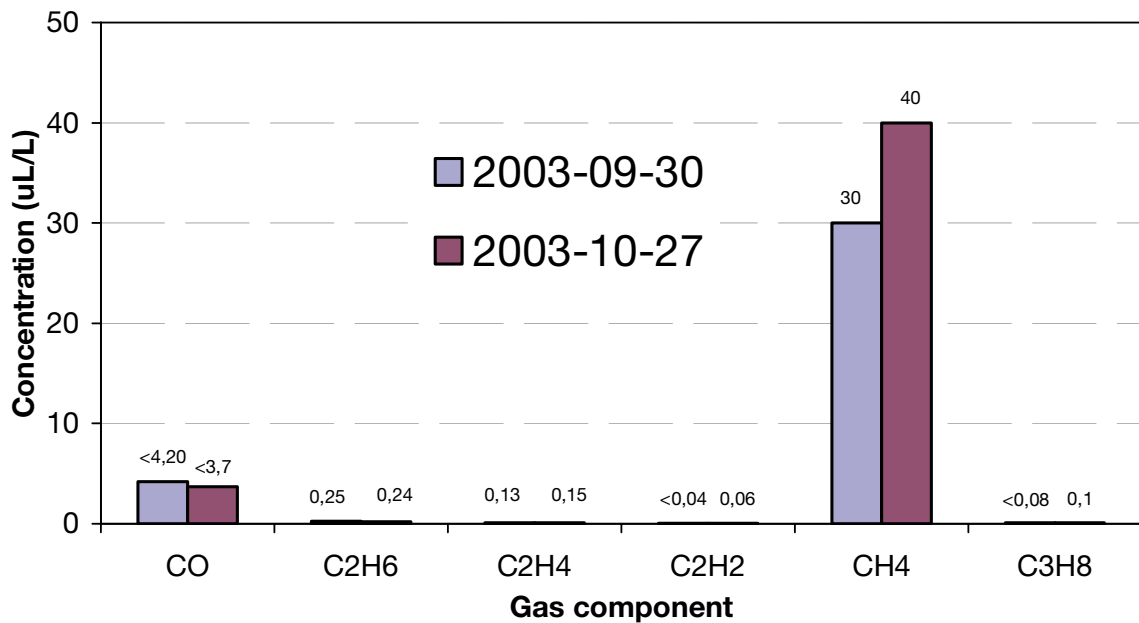


Figure 8-15. Gas components of low concentrations (CO, C₂H₆, C₂H₄, C₂H₂, CH₄ and C₃H₈) in samples collected 2003-09-30 and 2003-10-27 using the in situ sampling equipment.

8.4 Inorganic colloids

The presence of inorganic colloids was investigated by two different methods. One method was colloid filtration through a series of connected filters of different pore sizes. A second method was fractionation/ultra filtration using cylindrical membrane filters with a cut-off of 1000 D and 5000 D, respectively. The results of the two methods are difficult to compare quantitatively but a qualitative agreement may be identified.

8.4.1 Inorganic colloids – colloid filtration

The colloid filtering system is still at the development stage. The results from the colloid filtration method conducted in the section 509.0–516.1 m are presented in Figures 8-16 to 8-19. Evaluation of the method tests is reported in a final method evaluation report /9/.

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

Comments and conclusions regarding the results presented in Figures 8-16 to 8-19 follow below:

- The input sample is collected after filtration from the small residual volume in the PVB-container. A possible explanation to the high input concentrations of aluminium, when comparing with the concentration in the pumped water, is that the sample water when poured from the PVB-container contacts contaminated surfaces on the outlet. The contamination source is probably dirt from the borehole section.
- The differences between the output concentrations from the filter package of aluminium, silicon and manganese, and the concentration in the pumped borehole water, are small (discrepancy less than 10%), except for iron.
- The concentrations of aluminium, iron, silica and manganese in filter sample blanks, taken from their boxes without any preparation, were insignificant.
- The results from the three sections show that calcite was not precipitated to any significant extent during the colloid filtrations.
- The relevant filters for collection of colloids were broken. Therefore, the data from the colloid filtering are less useful. Analytical results from broken filters are given within brackets in Figures 8-16 to 8-19.

8.4.2 Inorganic colloids – fractionation

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

The results presented in Tables 8-3, 8-4 and 8-5 were calculated using mass balance equations (SKB MD 431.043). As shown, Fe, Si, Al and Mn exist as species (associated or non-associated with humic and fulvic acids) with a molecular weight less than 1000 g/mol. Such species are too small to be referred to as colloids. Iron and aluminium was partly precipitated during the fractionation, since oxygen is present in the filtering system (pump, filter, hose etc). Although unlikely, the presence of iron and aluminium containing species of a larger fraction cannot be completely excluded.

Table 8-3. Inorganic fractions (1000 D and 5000 D filters) in section 106.5–126.5 m.

Fraction	Fe (mg/L)	Si (mg/L)	Al (µg/L)	Mn (mg/L)
< 1000 D (1)*	0.038 ± 0.004	5.5 ± 0.8	2.1 ± 0.4	0.27 ± 0.03
< 1000 D (2)*	0.041 ± 0.004	5.5 ± 0.8	1.9 ± 0.4	0.27 ± 0.03
< 1000 D (3)*	0.040 ± 0.004	5.5 ± 0.8	2.0 ± 0.4	0.28 ± 0.03
< 5000 D	0.70 ± 0.07	5.6 ± 0.8	2.8 ± 0.6	0.28 ± 0.03
> 1000 D but < 5000 D	–	–	–	–
> 5000 D	–	–	–	–
Adsorption 1000 D (1)	0.81 ± 0.13	–	–	–
Adsorption 1000 D (2)	0.95 ± 0.14	–	1.6 ± 1.1	–
Adsorption 1000 D (3)	1.01 ± 0.13	–	1.6 ± 1.1	–
Adsorption 5000 D	0.46 ± 0.15	–	1.3 ± 1.1	–

* The fractionation was repeated three times with the 1000 D filter in order to verify the reproducibility of the method.

– = Not found.

Table 8-4. Inorganic fractions (1000 D and 5000 D filters) in section 413.5–433.5 m.

Fraction	Fe (mg/L)	Si (mg/L)	Al (µg/L)	Mn (mg/L)
< 1000 D	0.29 ± 0.03	7.16 ± 1.07	3.5 ± 0.7	1.77 ± 0.18
< 5000 D	0.13 ± 0.01	7.19 ± 1.08	2.9 ± 0.6	1.78 ± 0.18
> 1000 D but < 5000 D	–	–	–	–
> 5000 D	–	–	–	–
Adsorption 1000 D	0.26 ± 0.07	–	3.2 ± 1.7	–
Adsorption 5000 D	0.41 ± 0.06	–	2.7 ± 1.4	–

– = Not found.

Result of colloid filtering experiment using water sample from section 509.0–516.1 m.

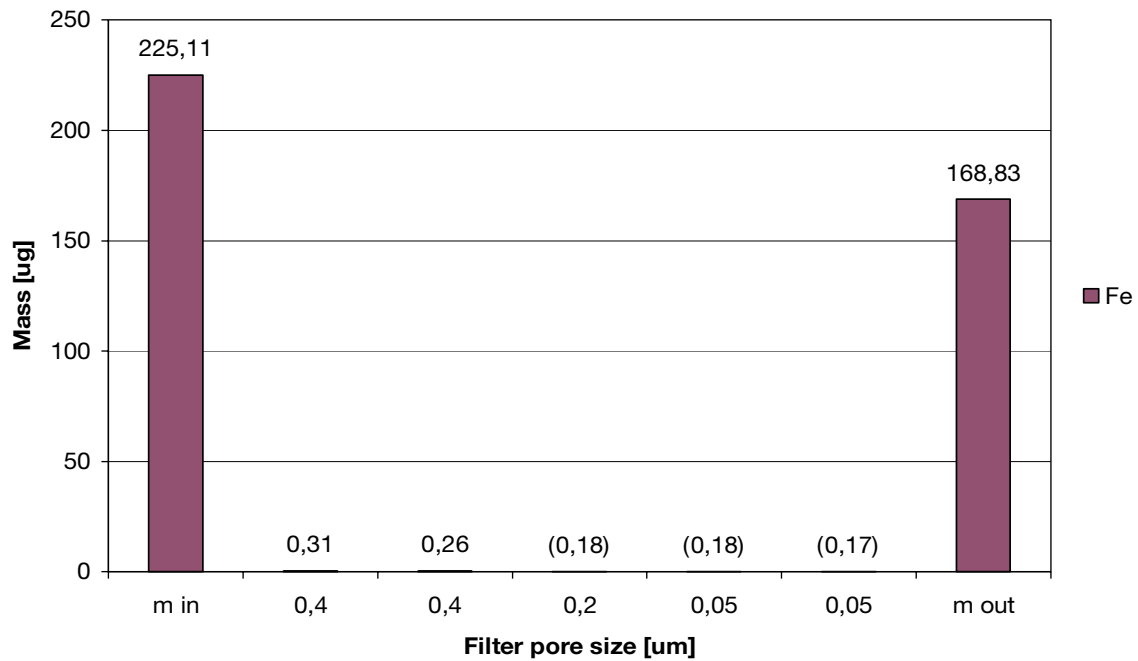


Figure 8-16. Amount of aluminium entering the filter system (*m in*), in the filters and in the collecting container (*m out*). Zero value = below detection limit.

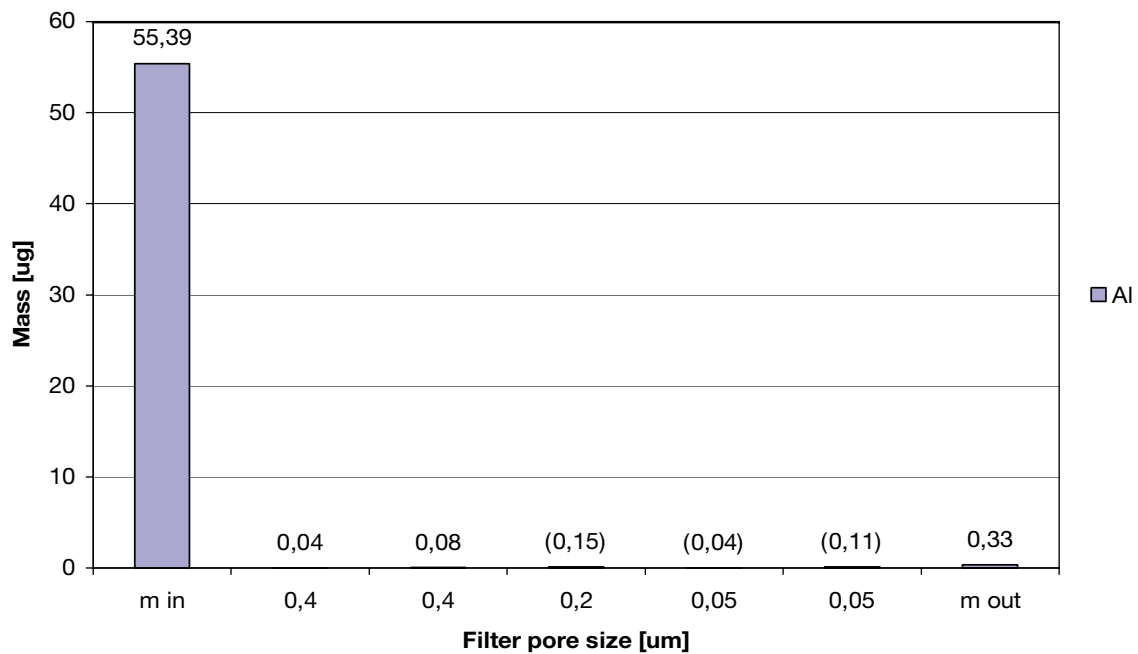


Figure 8-17. Amount of iron entering the filter system (*m in*), in the filters and in the collecting container (*m out*). Zero value=below detection limit.

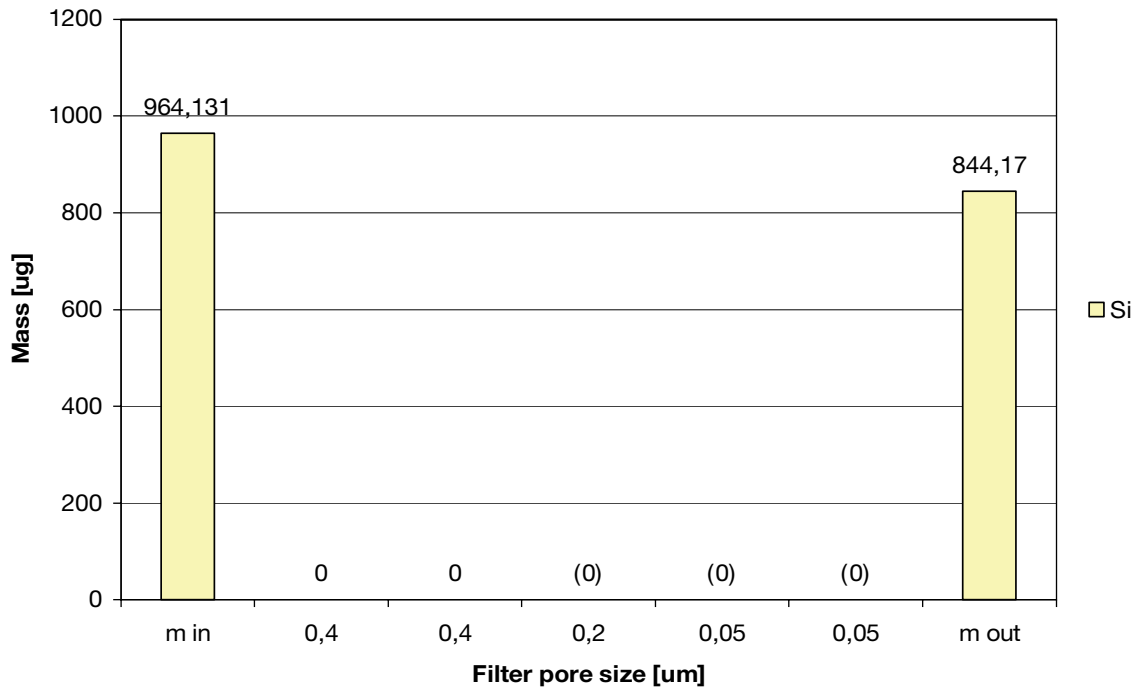


Figure 8-18. Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out). Zero value = below detection limit.

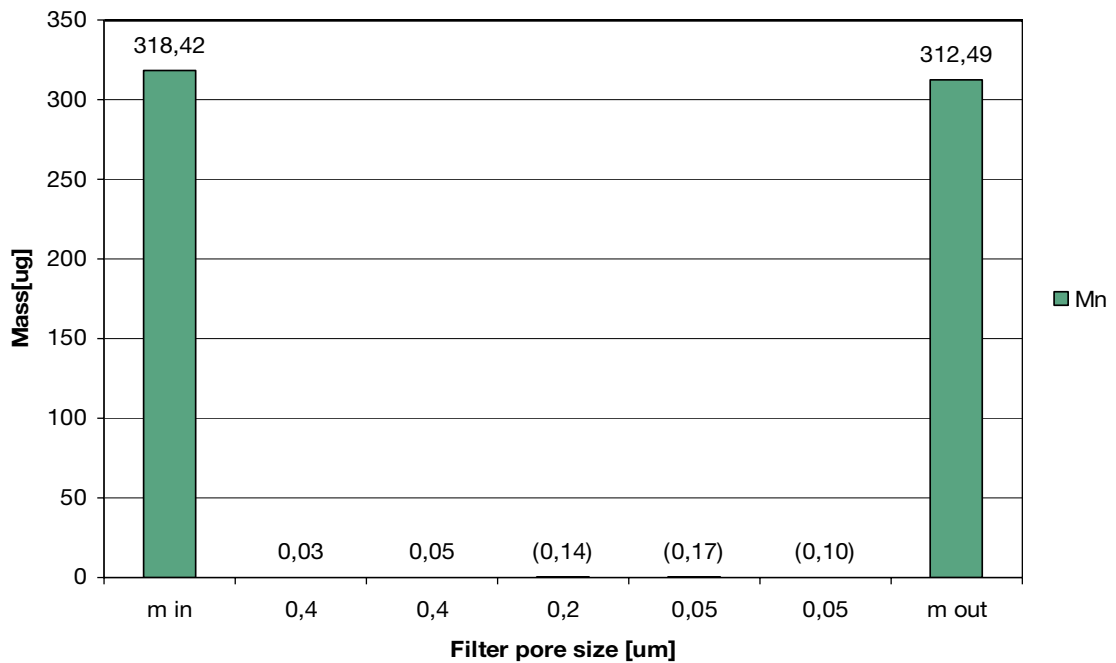


Figure 8-19. Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out). Zero value=below detection limit.

Table 8-5. Inorganic fractions (1000 D and 5000 D filters) in section 509.0–516.1 m.

Fraction	Fe (mg/L)	Si (mg/L)	Mn (mg/L)
< 1000 D (1)*	0.86 ± 0.09	4.5 ± 0.7	1.88 ± 0.18
< 1000 D (2)*	1.5 ± 0.15	4.7 ± 0.7	2.04 ± 0.20
< 5000 D (1)*	0.89 ± 0.09	4.6 ± 0.7	1.95 ± 0.20
< 5000 D (2)*	1.5 ± 0.15	4.7 ± 0.7	2.03 ± 0.20
> 1000 D but < 5000 D (1)	–	–	–
> 1000 D but < 5000 D (2)	–	–	–
> 5000 D (1)	–	–	–
> 5000 D (2)	–	–	–
Adsorption 1000 D (1)	0.36 ± 0.15	–	–
Adsorption 1000 D (2)	–	–	–
Adsorption 5000 D (1)	0.34 ± 0.15	–	–
Adsorption 5000 D (2)	–	–	–

* The fractionation was repeated twice with each filter in order to verify the reproducibility of the method.
 – = Not found.

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

In section 509.0–516.1 m additional aluminium was present in the system, probably originating from the filter itself or from contamination in the filtering equipment. Therefore, it was not possible to draw any conclusions regarding fractions of aluminium.

8.5 Humic and fulvic acids

The results from fractionation of organic acids in the sections at 106.5–126.5 m, 413.5–433.5 m and 509.0–516.1 m are summarised in Table 8-6. The fractionation in section 106.5–126.5 m was repeated three times with the 1000 D filter and conducted once with the 5000 D filter, Table 8-7. In section 413.5–433.5 m the fractionation was made once, Table 8-8, and in section 509.0–516.1 m twice with each filter, Table 8-9.

As shown in Table 8-6, about half the amount of the organic acids in the water in section 106.5–126.5 m has a molecular weight less than 1000 D, e.g. low molecular weight fulvic acids and possibly other low molecular weight organic acids (citric acid, oxalic acid etc). A fraction of high molecular species, humic acids, with a molecular weight exceeding 5000 D is also present. A smaller fraction has a molecular weight > 1000 D but < 5000 D. The majority of the organic acids in sections 413.5–433.5 and 509.0–516.1 m have molecular weights less than 1000 D while there are smaller fractions with molecular weights > 1000 D but < 5000 D and > 5000 D. Additional organic material was present in the first fractionation sequence in section 509.0–518.5 m, possibly due to contamination, and therefore the results in Table 8-6 consist of the second fractionation sequence.

The reproducibility of the fractionation in section 106.5–126.5 m was satisfactory, cf Table 8-7. For section 509.0–516.1 m, Table 8-9, carbon was added during the performance. Both filters were unused and the most probable source of contamination (despite extensive washing) is the solution in which the filters are stored when delivered from the manufacturer. There is a possibility that flushing water might have an effect on the fractionation results in the sense that high flushing water content could give an increased concentration of high molecular weight organic acids. However, in KFM02A there was no obvious connection between the flushing water content and the presence of organic acids with high molecular weight (Figure 8-1 and Table 8-6).

Table 8-6. Summary of fractionation results.

Fraction	Section 106.5–126.5 m DOC [mg/L]	413.5–433.5 m DOC [mg/L]	509.0–516.1 m DOC [mg/L]
< 1000 D	4.6 ± 0.6	1.1 ± 0.1	1.7 ± 0.2
> 1000 D but < 5000 D	1.5 ± 0.4	–	0.5 ± 0.1
> 5000 D	3.7 ± 0.7	0.11 ± 0.04	–

– = Not found.

The results above are based on data from fractionation with 1000 D and 5000 D filters; see Table 8-8 to 8-10.

Table 8-7. Results from fractionation with 1000 D and 5000 D filters in section 106.5–126.5 m.

Fraction (mg/L)	DOC concentration	Fraction (mg/L)	DOC concentration
< 1000 D (1)	4.6 ± 0.5	< 5000 D	6.1 ± 0.5
> 1000 D (1)	5.2 ± 0.7	> 5000 D	3.7 ± 0.7
Adsorption (1)	–	Adsorption	–
< 1000 D (2)	4.3 ± 0.5		
> 1000 D (2)	4.9 ± 0.7		
Adsorption (2)	–		
< 1000 D (3)	4.4 ± 0.5		
> 1000 D (3)	5.6 ± 0.7		
Adsorption (3)	–		

– = Not found.

Table 8-8. Results from fractionations with 1000 D and 5000 D filters in section 413.5–433.5 m.

Fraction	DOC concentration (mg/L)	Fraction	DOC concentration (mg/L)
< 1000 D	1.1 ± 0.1	< 5000 D	1.2 ± 0.1
> 1000 D	0.24 ± 0.06	> 5000 D	0.11 ± 0.04
Adsorption	–	Adsorption	–

– = Not found.

Table 8-9. Results from fractionations with 1000 D and 5000 D filters in section 509.0–516.1 m.

Fraction	DOC concentration (mg/L)	Fraction	DOC concentration (mg/L)
< 1000 D (1)	3.0 ± 0.3	< 5000 D (1)	3.1 ± 0.3
> 1000 D (1)	–	> 5000 D (1)	–
Additional material (1)	0.8 ± 0.4	Additional material (1)	0.8 ± 0.4
< 1000 D (2)	1.7 ± 0.2	< 5000 D (2)	2.0 ± 0.2
> 1000 D (2)	0.5 ± 0.1	> 5000 D (2)	–
Adsorption (2)	–	Adsorption (2)	–

– = Not found.

9 Summary and discussion

The complete chemical characterisation using the MFL units and the pumping/sampling using hydraulic test equipment (PSS3) in KFM02A were, on the whole, performed quite successfully.

High contents of remaining flushing water caused prolonged pumping periods and planning problems as it was difficult to foresee the pumping times needed to reduce these contents. Due to equipment malfunctions, electric conductivity and oxygen measurement data are missing from sections 106.5–126.5 m (EC) and 413.5–433.5 m (O₂ and EC). The main conclusions from the experimental results are:

- It is usually difficult to measure reliable redox potentials using pipe string systems and heavy pumping. This was also the case in sections 106.5–126.5 m and 413.5–433.5 m where the PSS3 equipment was used. These redox measurement data were rejected.
- The redox potential measurement by the borehole Chemmac in section 509.0–516.1 m appears to be of good quality. The three downhole electrodes (gold, glassy carbon and platinum) stabilised at practically the same level (–143 mV). However, the electrodes of the surface Chemmac did not measure credible values except for shorter periods towards the end of the measurement period. Possible reasons are air intrusion or gas bubbles on electrode surfaces.
- An upper limit for the allowed flushing water content in a representative water sample is set to 1%. This condition was met in section 106.5–126.5 m, but not in sections 413.5–433.5 m (3%) and 509.0–516.1 m (6%).
- The salinity was stable during the pumping and sampling periods, except for section 106.5–126.5 m where a slightly increasing concentration trend was recognised. A stable salinity indicates that there was no contribution of water from more distant fracture systems with a different water composition.
- The iron analyses from section 106.5–126.5 m showed low Fe(+II) concentrations compared to total iron concentrations. It is not likely that the difference represents the Fe(+III) concentration of the groundwater. Further, more iron precipitate than usual was adsorbed on the membrane filters during the three fractionation experiments. It appears as if very small amounts of air entered somewhere along the water sampling line and caused oxidation of Fe(+II) prior to or at the sampling moment.
- Some of the special sampling experiments were repeated in order to test the reproducibility of the sampling methods. The fractionation was repeated three times with the 1000 D filter in section 106.5–126.5 m and twice with each filter (1000 D and 5000 D) in section 509.0–516.6 m. The results agreed as well as could be expected considering the size of the analytical errors. The *in situ* sampling for determination of dissolved gases was repeated in the section 509.0–516.6 m. The gas constituents agreed well except for argon and hydrogen where the difference between the two results were in the range 11–22%.
- The content of colloidal components of the groundwater in section 509.0–516.6 m is very low according to the results of the fractionation experiment and far below the recommended upper limit of 0.5 mg/L (safety assessment criterion).

- The organic constituents in the groundwater in section 106.5–126.5 m are both of low (< 1000 D) and high molecular weight (> 5000 D). The predominant fraction in sections 413.5–433.5 and 509.0–518.5 m are low molecular weight fulvic acids and possibly other low molecular weight organic acids (citric acid, oxalic acid etc) with a molecular weight less than 1000 D.

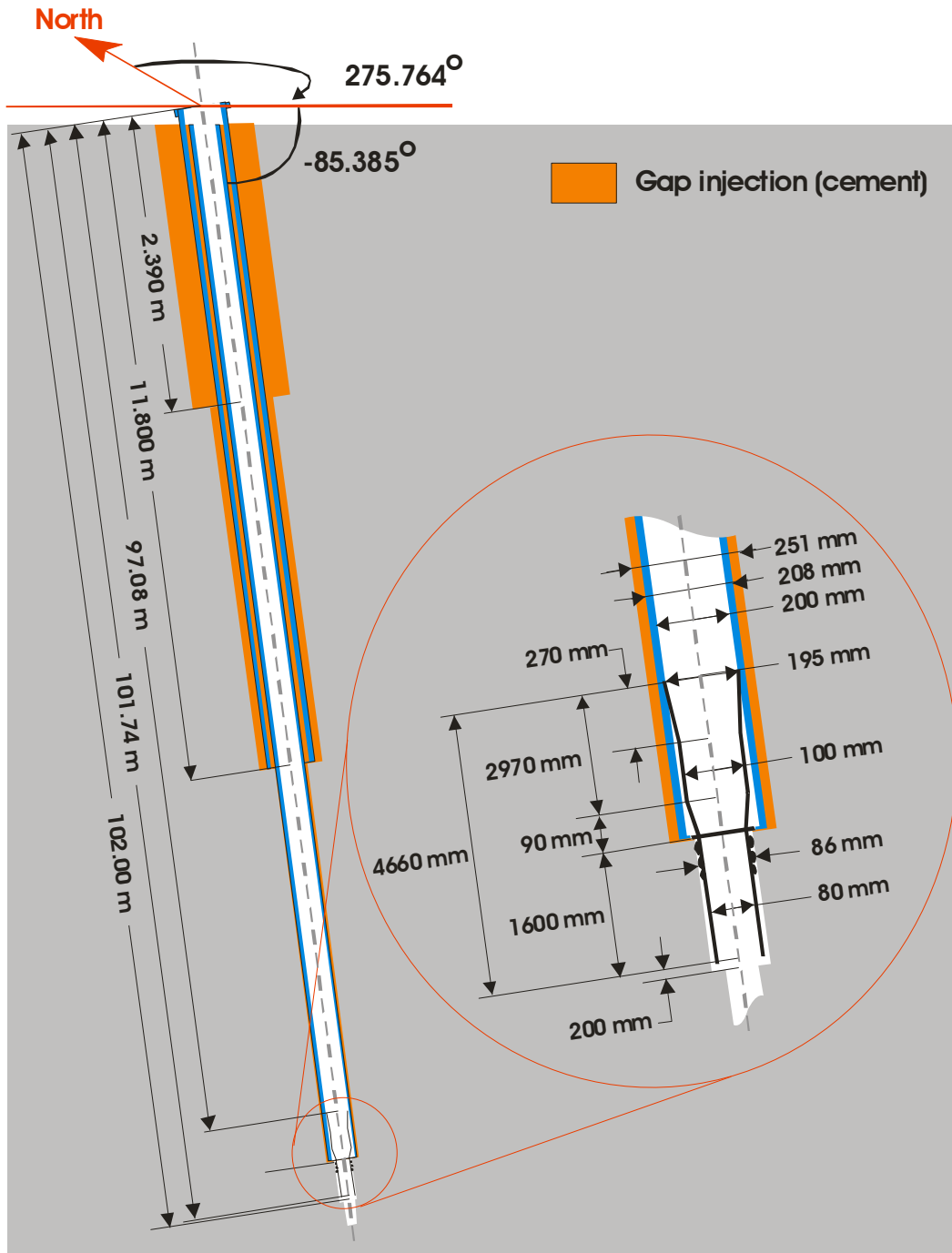
10 References

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- /2/ **Pedersen K, Kalmus A, 2004.** Forsmark site investigation. Total numbers and metabolic diversity of microorganisms in borehole KFM01A and KFM02A. Results from three investigated sections, 110–120.67 m and 176.8–183.9 m in KFM01A and section 509.0–516.1 m in KFM02A. SKB P-03-91, Svensk Kärnbränslehantering AB.
- /3/ **Claesson L-Å, Nilsson G, 2003.** Forsmark site investigation. Drilling of the telescopic borehole KFM02A at drilling site DS2. SKB P-03-52, Svensk Kärnbränslehantering AB.
- /4/ **Claesson L-Å, Nilsson G, 2003.** Forsmark site investigation. Drilling of a flushing water well, HFM05 and a monitoring well, HFM04, at drilling site DS2. SKB P-03-51, Svensk Kärnbränslehantering AB.
- /5/ **Nilsson A-C, 2003.** Forsmark site investigation. Sampling and analyses of groundwater in percussion drilled boreholes and shallow monitoring wells at drillsite DS2. Results from the percussion boreholes HFM04, HFM05, KFM02A (borehole section 0–100 m) and the monitoring wells SFM0004 and SFM0005. SKB P-03-48, Svensk Kärnbränslehantering AB.
- /6/ **Wacker P, Nilsson A-C, 2003.** Forsmark site investigation. Hydrochemical logging and “clean up” pumping in KFM02A. SKB P-03-95, Svensk Kärnbränslehantering AB.
- /7/ **Pedersen K, Kalmus A, 2003.** Forsmark site investigation. Control of microorganism content in flushing water used for drilling of KFM02A and KFM04A. SKB P-03-92, Svensk Kärnbränslehantering AB.
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Design of cored borehole KFM02A

Technical data

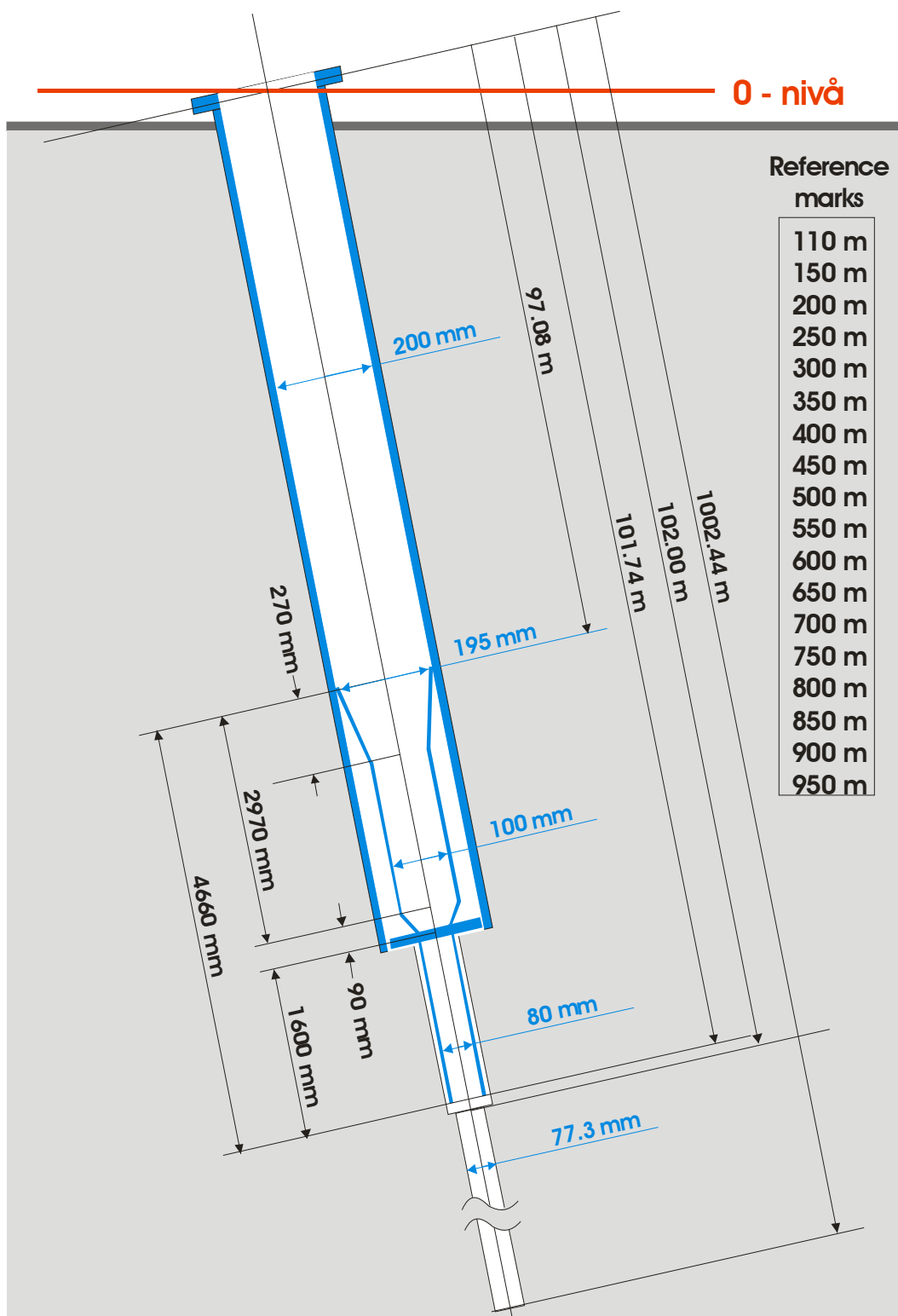
Borehole KFM02A



Drilling reference point

Northing: 6698712.501 (m), RT90 2,5 gon V 0:-15
 Easting: 1633182.863 (m), RT90 2,5 gon V 0:-15
 Elevation: 7.353 (m), RHB 70

KFM02A



Drilling period

Drilling start date: 2002-11-20
 Drilling stop date: 2003-03-26

Drilling reference point

Northing: 6698712.501 (m), RT90 2,5 gon V 0:-15
 Easting: 1633182.863 (m), RT90 2,5 gon V 0:-15
 Elevation: 7.353 (m), RHB 70

Results of difference flow logging in KFM02A

Forsmark, Borehole KFM02A

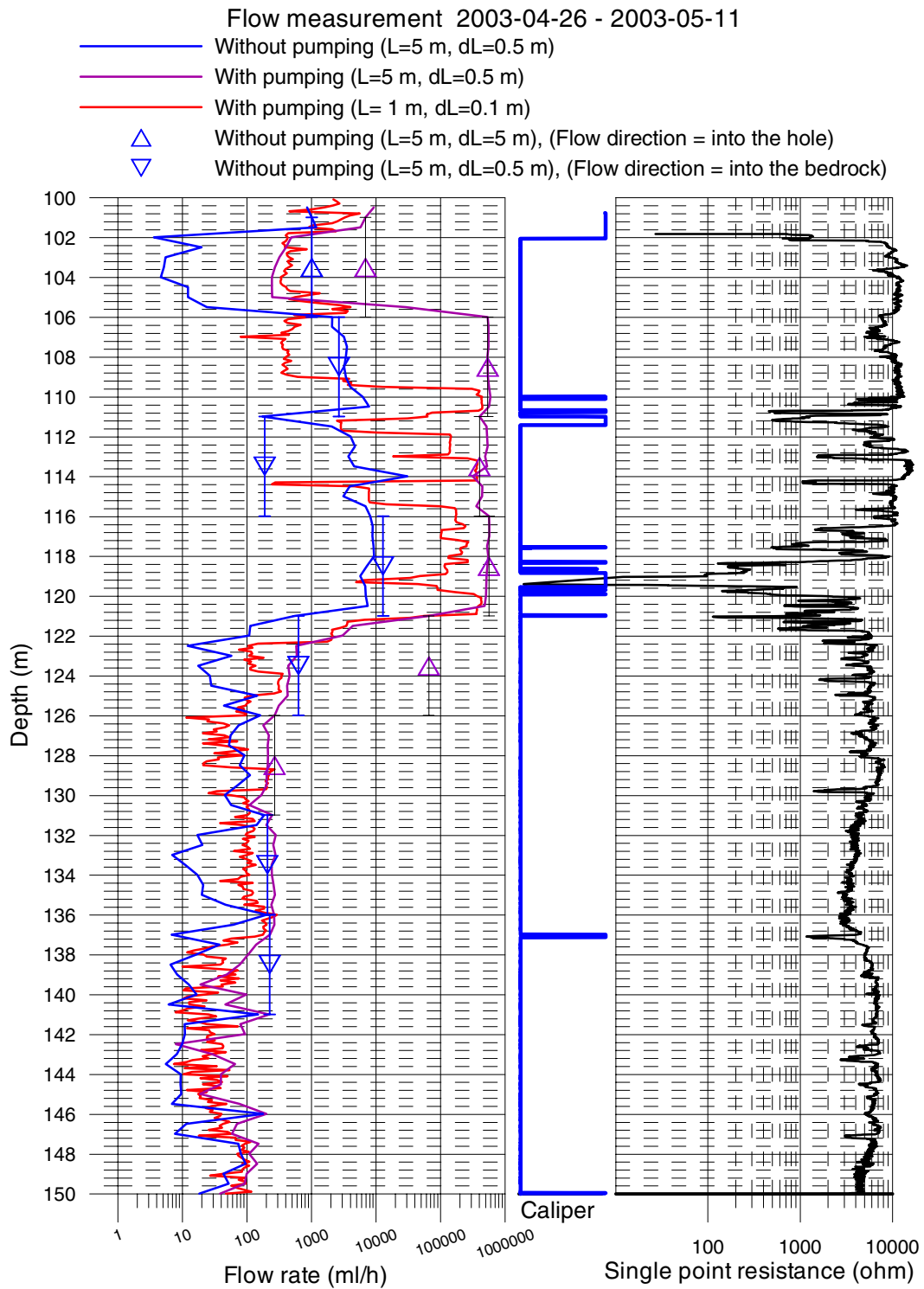


Figure A2-1. Borehole KFM02A: Differential flow measurements from 100–150 m including the water bearing fracture zone at 109–121 m /8/.

Forsmark, Borehole KFM02A

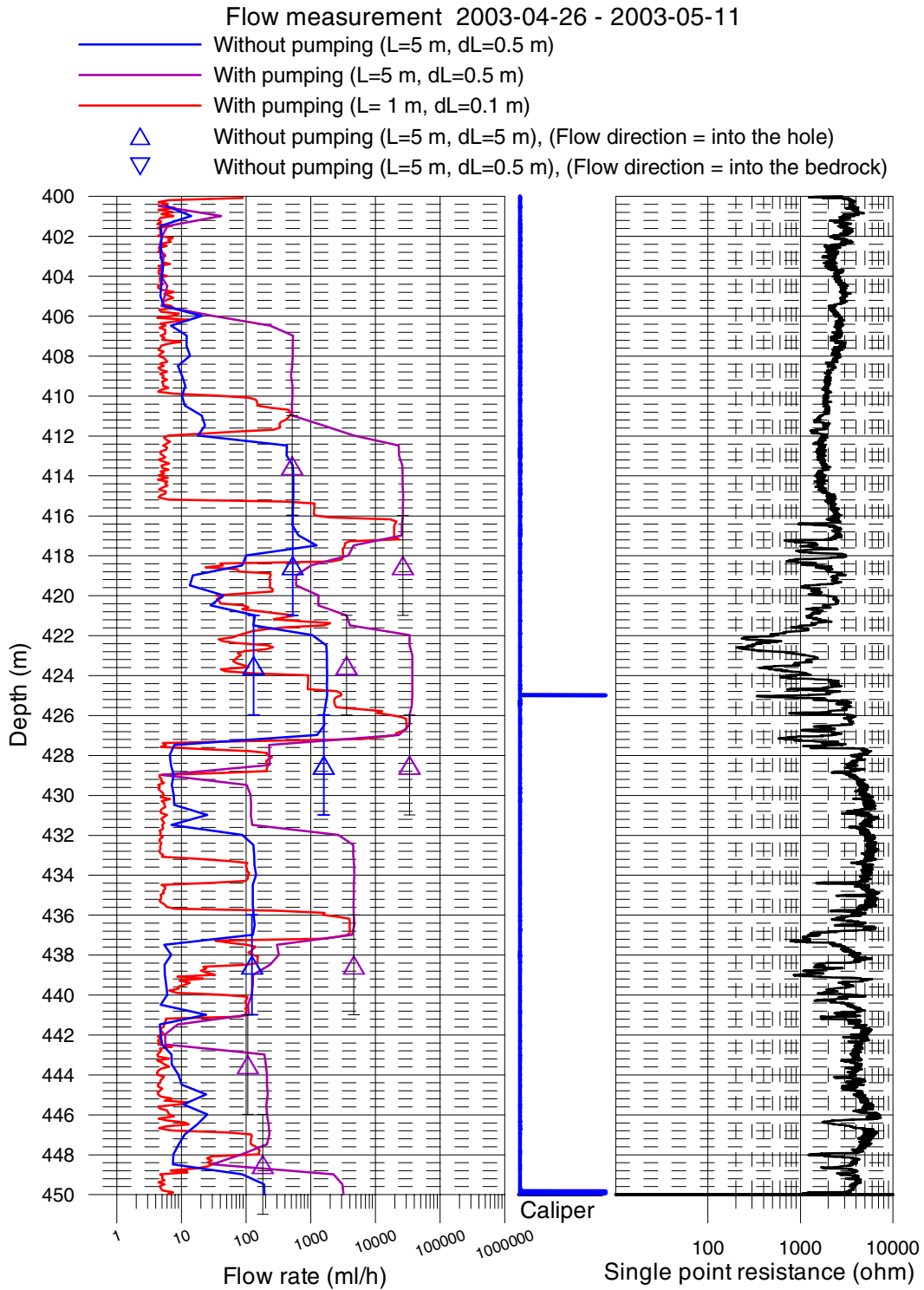


Figure A2-2. Borehole KFM02A: Differential flow measurements from 400–450 m including the water bearing fracture zone at 415 to 427 m /8/.

Forsmark, Borehole KFM02A

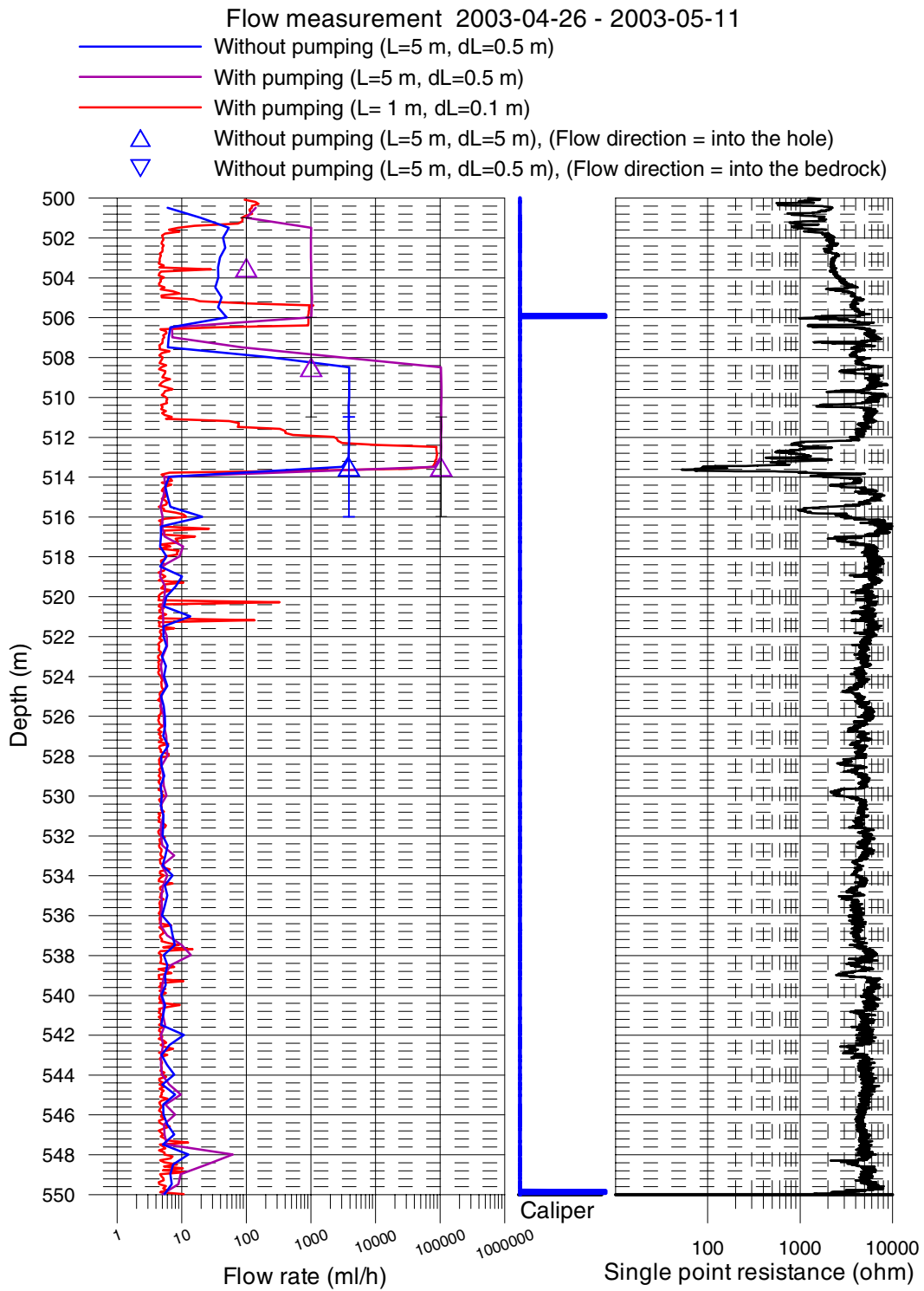


Figure A2-3. Borehole KFM02A: Differential flow measurements from 500–550 m including the water bearing fracture at 513 m /8/.

Measurement information, section 509.0–516.1 m

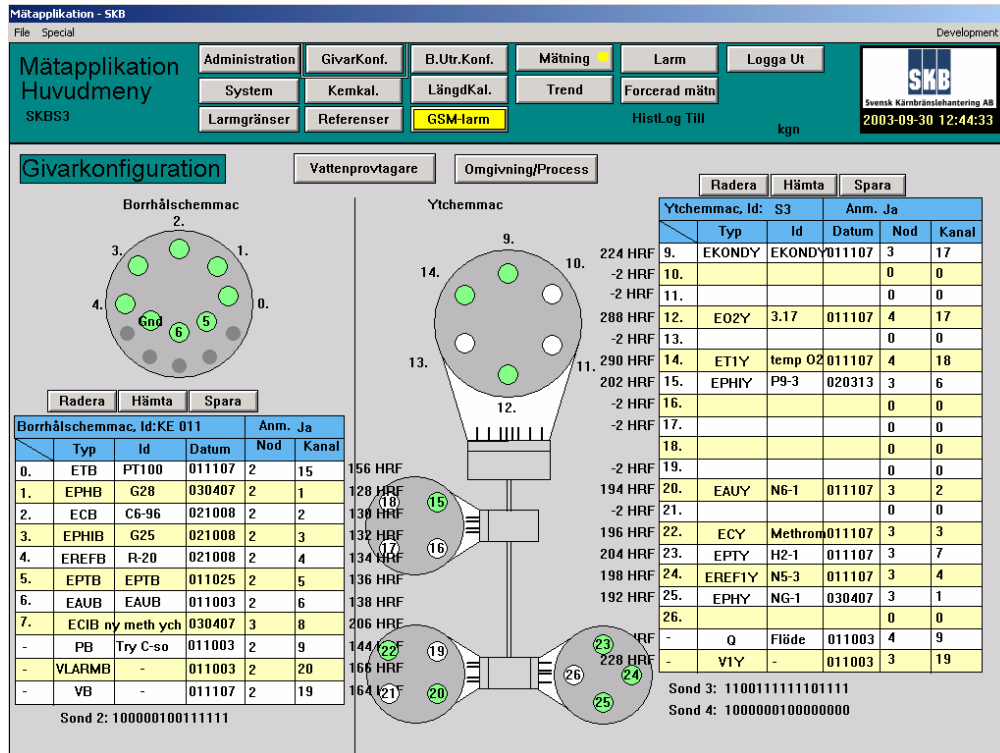


Figure A3-1. Electrode configuration.

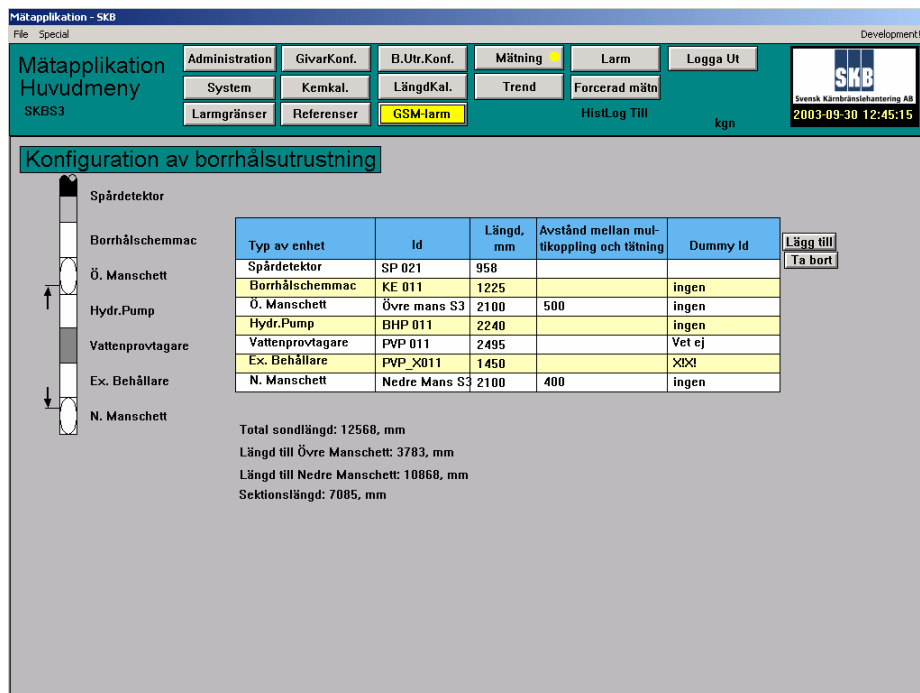


Figure A3-2. Configuration of downhole equipment.

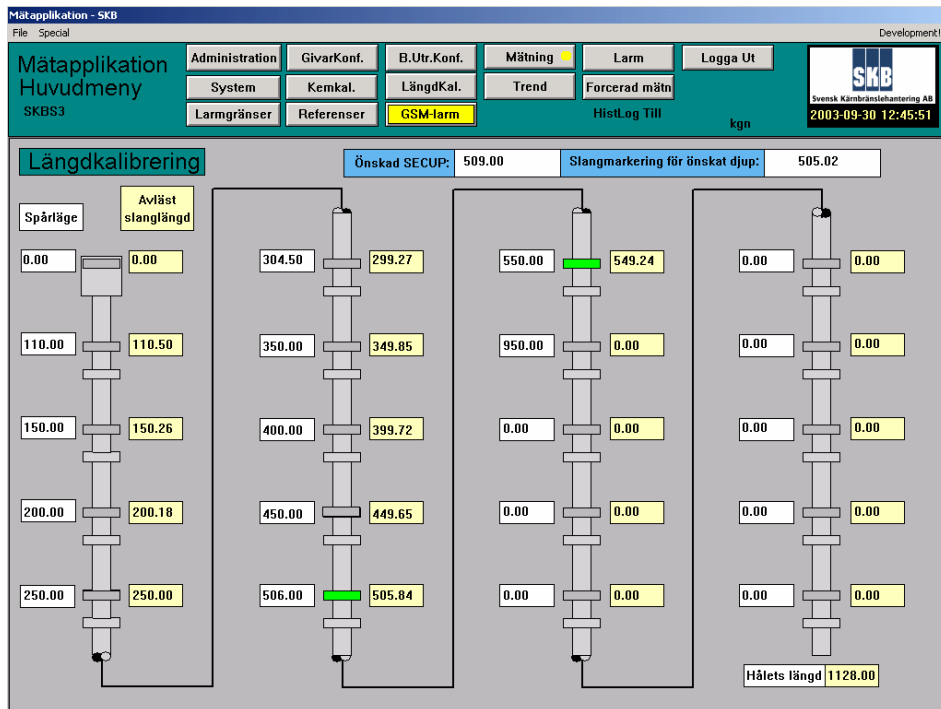


Figure A3-3. Length calibration

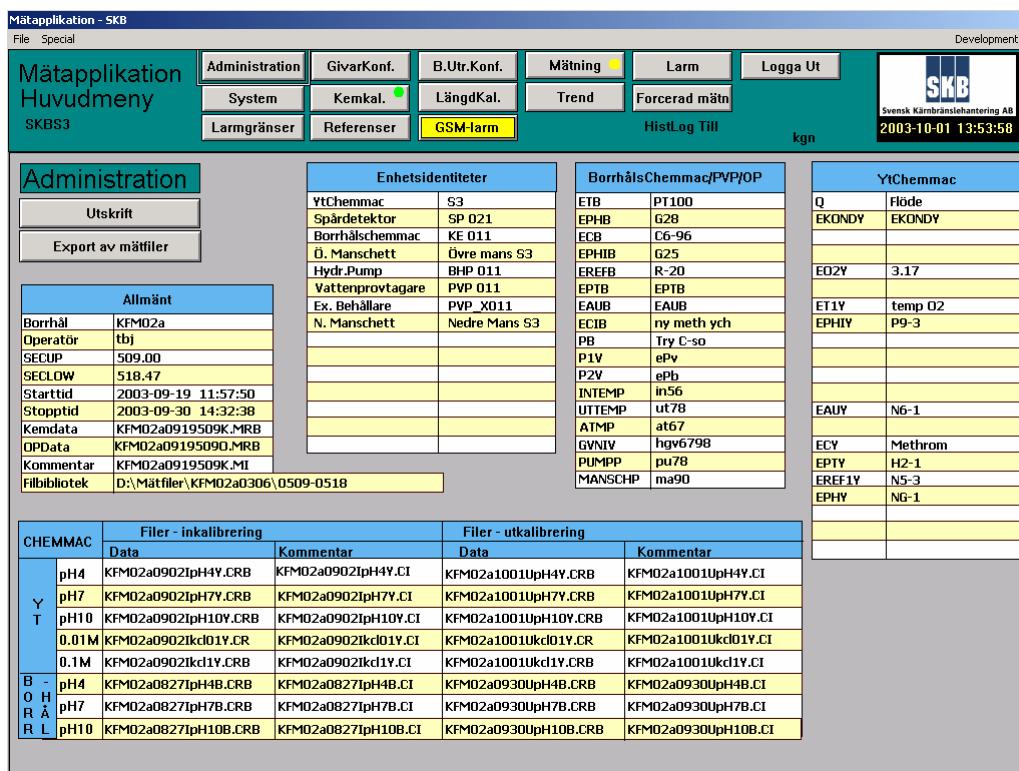


Figure A3-4. Administration (031001), erroneous section length (SECLOW).

Flow and pressure measurements

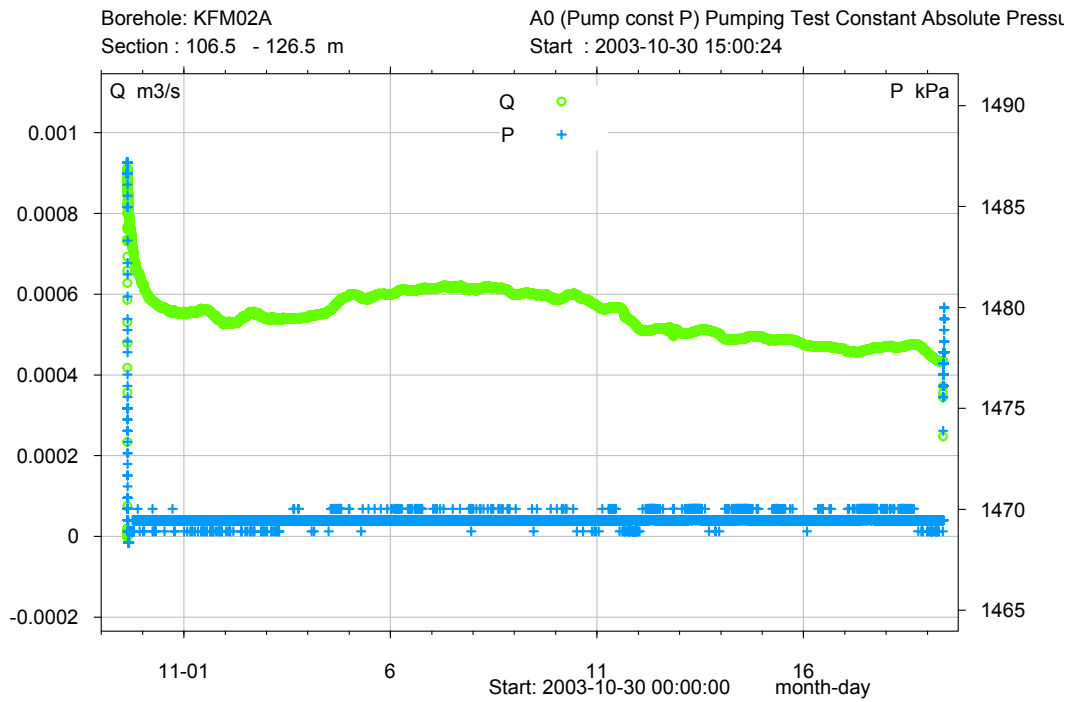


Figure A4-1. Pressure (P) within the borehole section and flow rate (Q) measurements from the borehole section 106.5-126.5 m. The variations in flow rate are due to the automatic control system which is set to keep a constant pressure in the section. When the pressure is altered the system will change the flow rate to keep the pressure at a constant level.

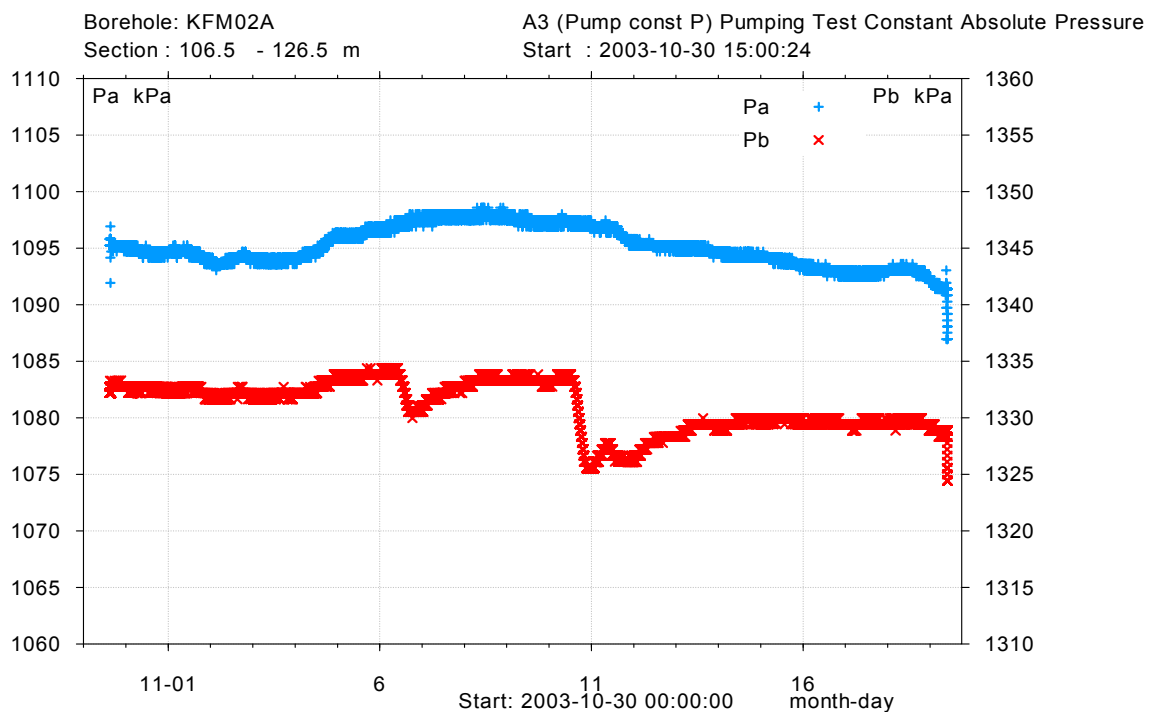


Figure A4-2. Pressures above (P_a) and below (P_b) the borehole section 106.5-126.5 m. Pressure responses from drilling of the percussion borehole HFM16 were identified 2003-11-06 to 2003-11-07 and 2003-11-11.

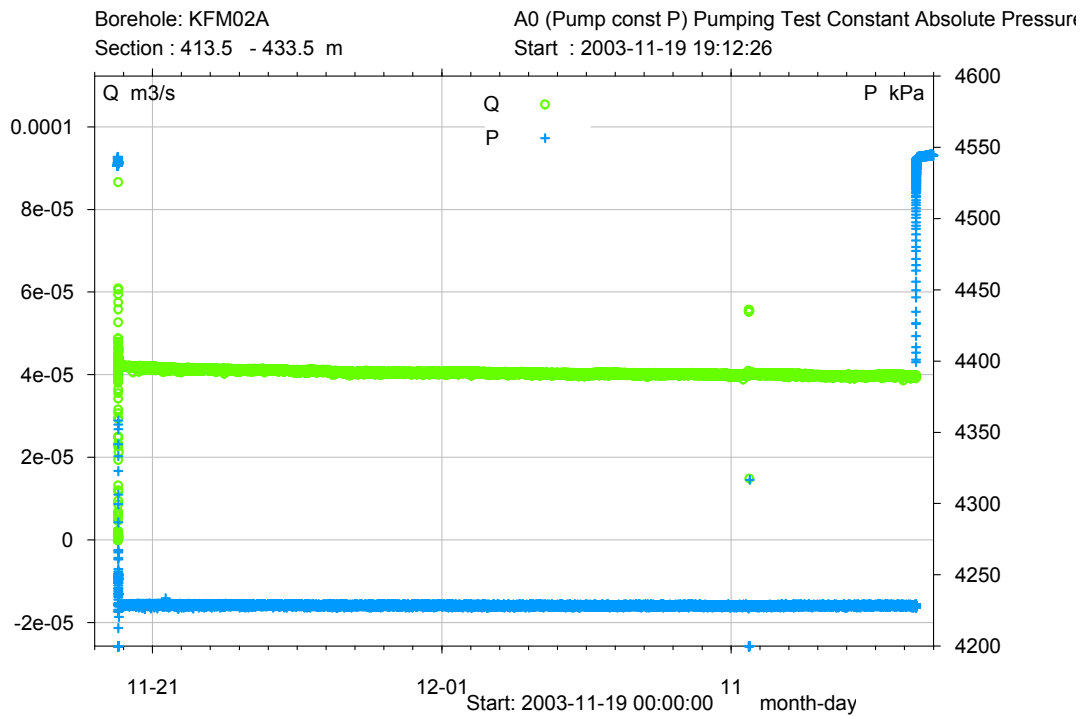


Figure A4-3. Pressure (P) within the borehole section and flow rate (Q) measurements from the borehole section 413.5-433.5 m during the period 2003-11-19 to 2003-12-17.

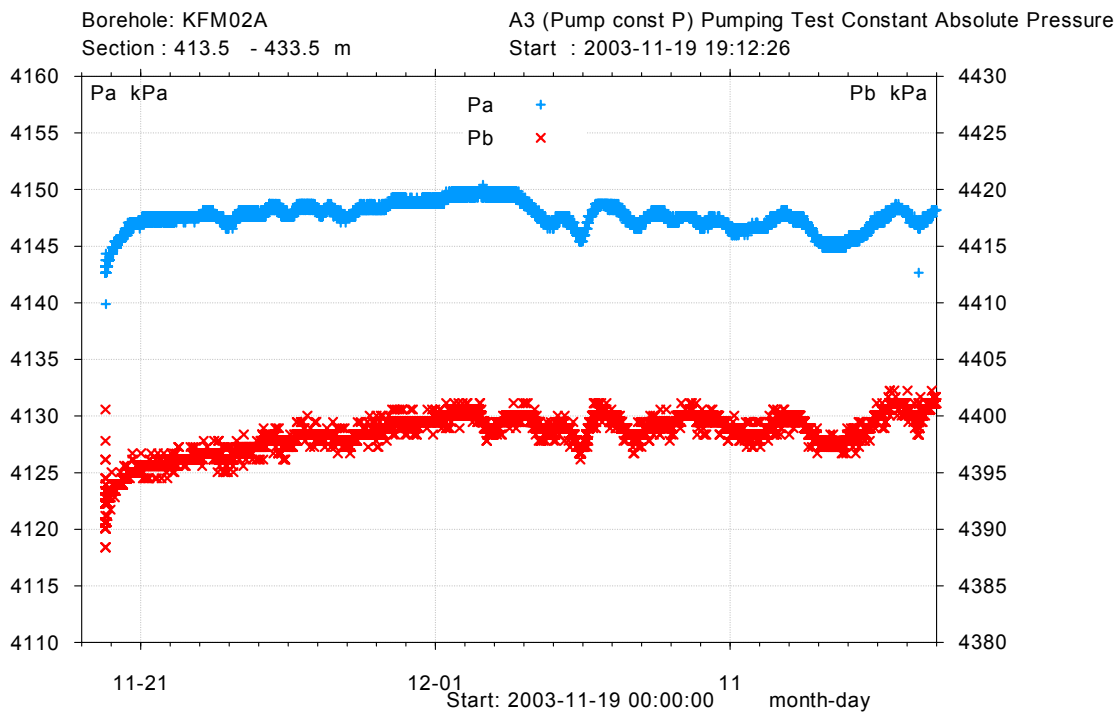


Figure A4-4. Pressures above (P_a) and below (P_b) the borehole section 413.5-433.5 m during the period 2003-11-19 to 2003-12-17.

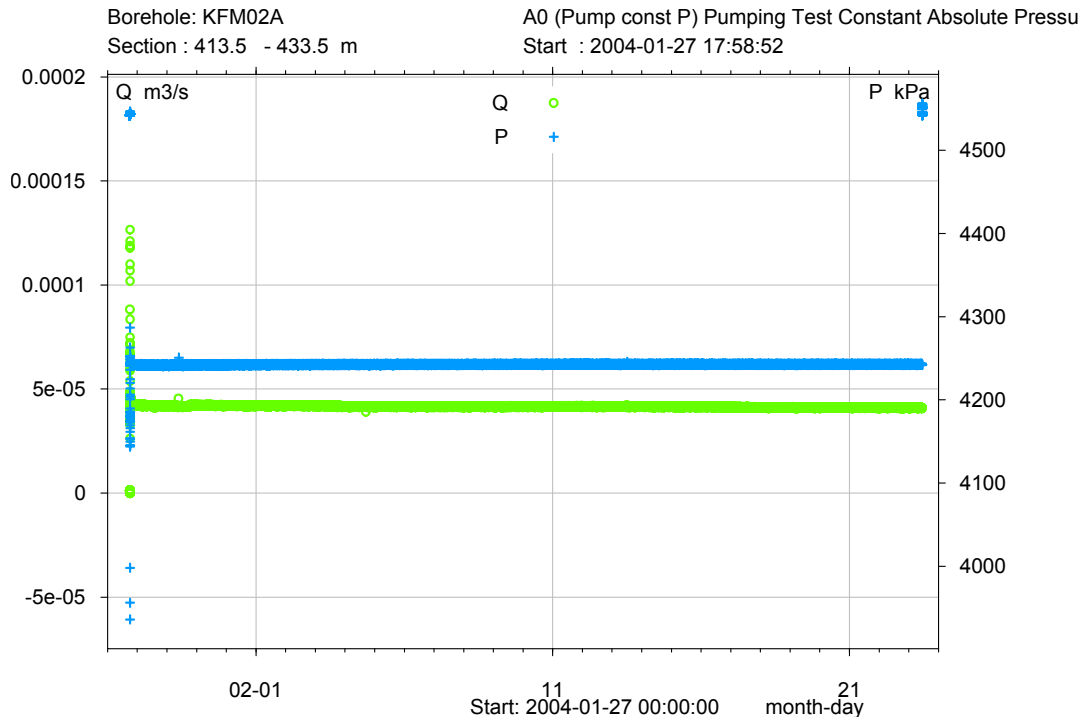


Figure A4-5. Pressure (P) within the borehole section and flow rate (Q) measurements from the borehole section 413.5-433.5 m during the period 2004-01-27 to 2004-02-23

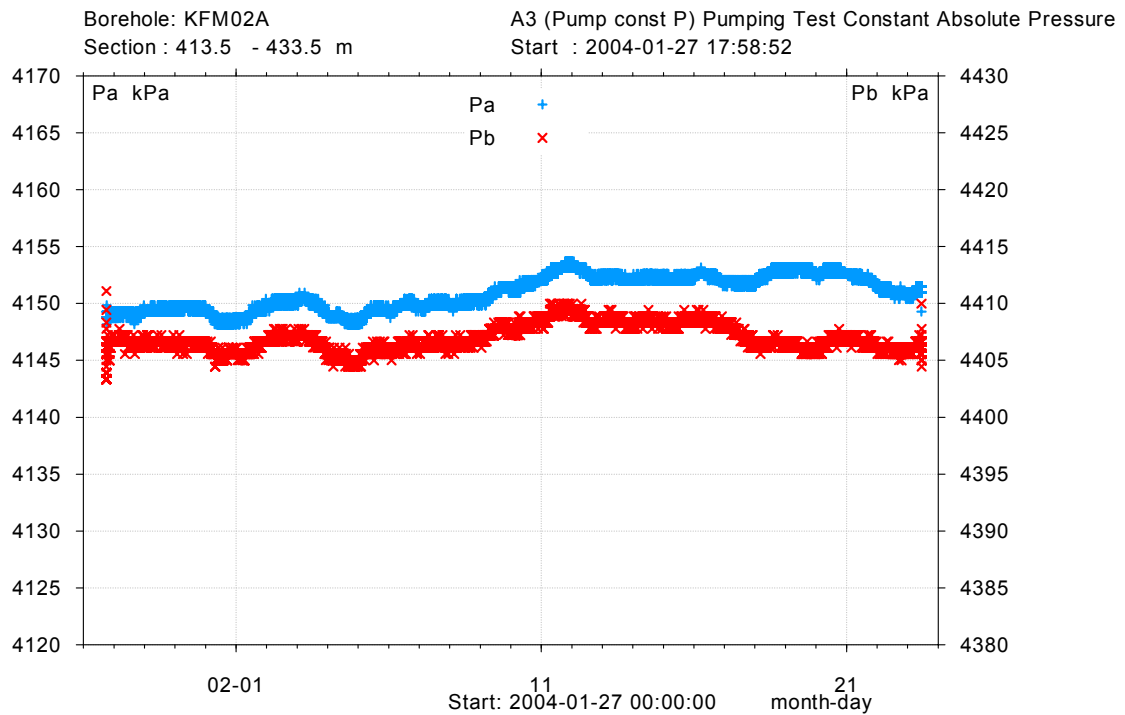


Figure A4-6. Pressures above (P_a) and below (P_b) the borehole section 413.5-433.5 m during the period 2004-01-27 to 2004-02-23.

Chemmac measurement, section 106.5–126.5 m

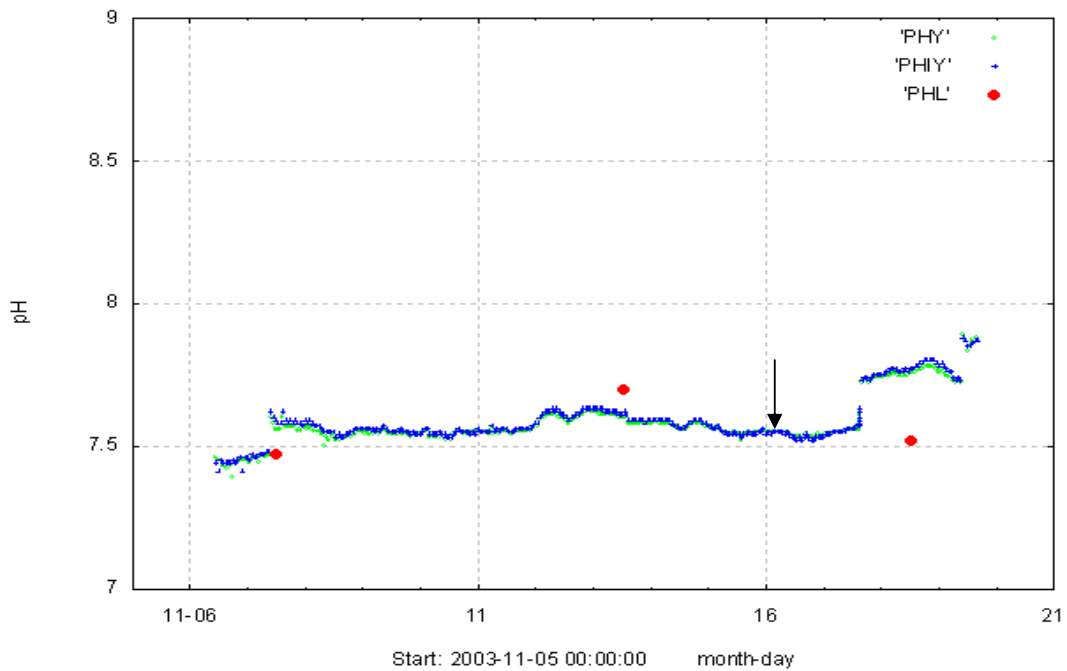


Figure A5-1. Measurements of pH by two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.

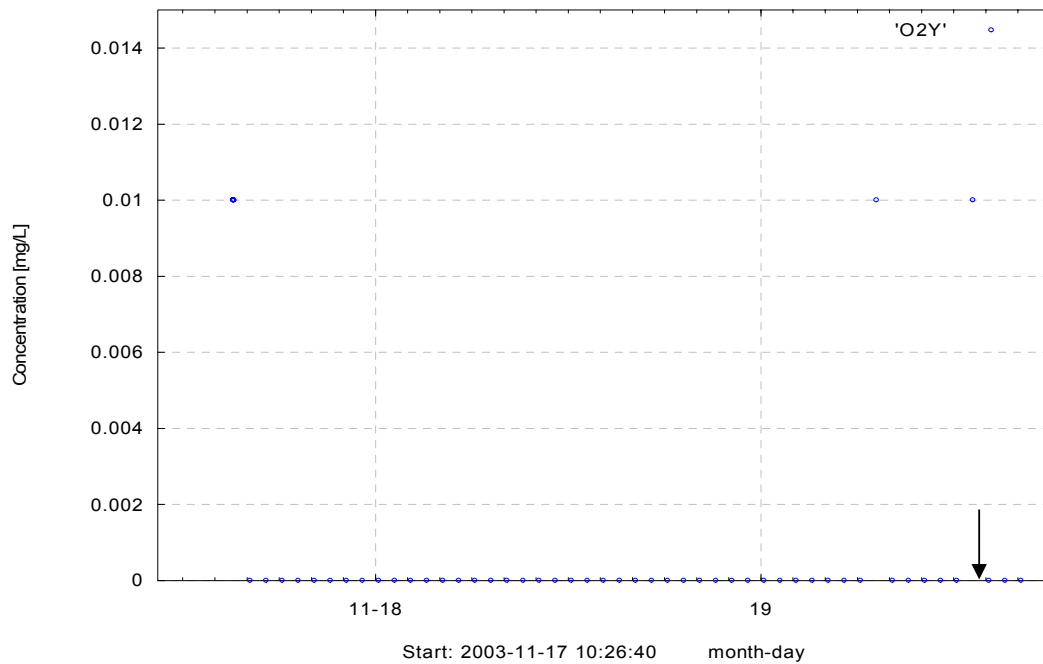


Figure A5-2. Dissolved oxygen measurements in the surface measurement cell (O2Y). There was no connection with the oxygen electrode until the last few days of the measurement. The arrow shows the chosen representative value for dissolved oxygen in the borehole section.

Borehole: KFM02A
Section : 106.5 - 126.5 m
A4 (Pump const P) Pumping Test Constant Absolute Pressure
Start : 2003-10-30 15:00:24

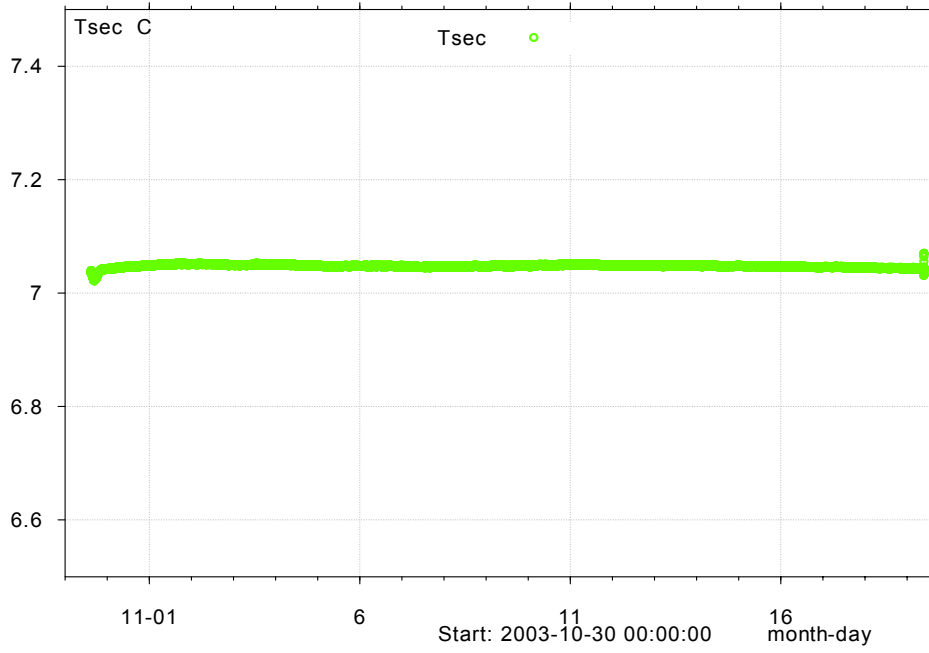


Figure A5-2. Temperature of the groundwater in section 106.5-126.5 m. The measurements were performed by equipment in the PSS3 unit.

Chemmac measurement, section 413.5–433.5 m

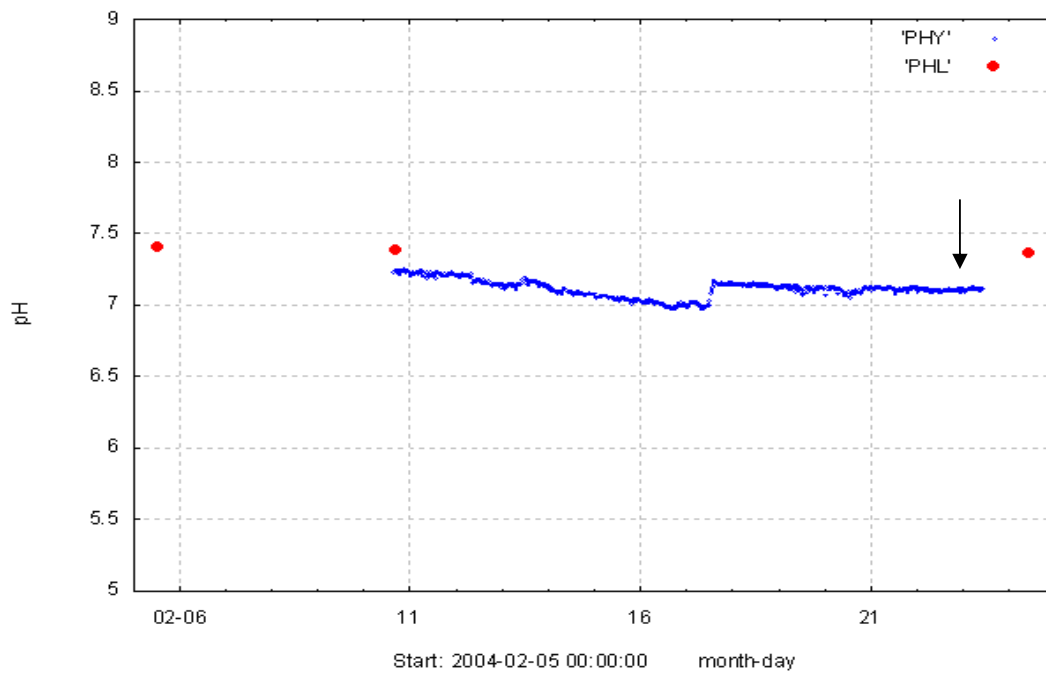


Figure A6-1. Measurements of pH by a glass electrodes at the surface (PHY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH value for the borehole section.

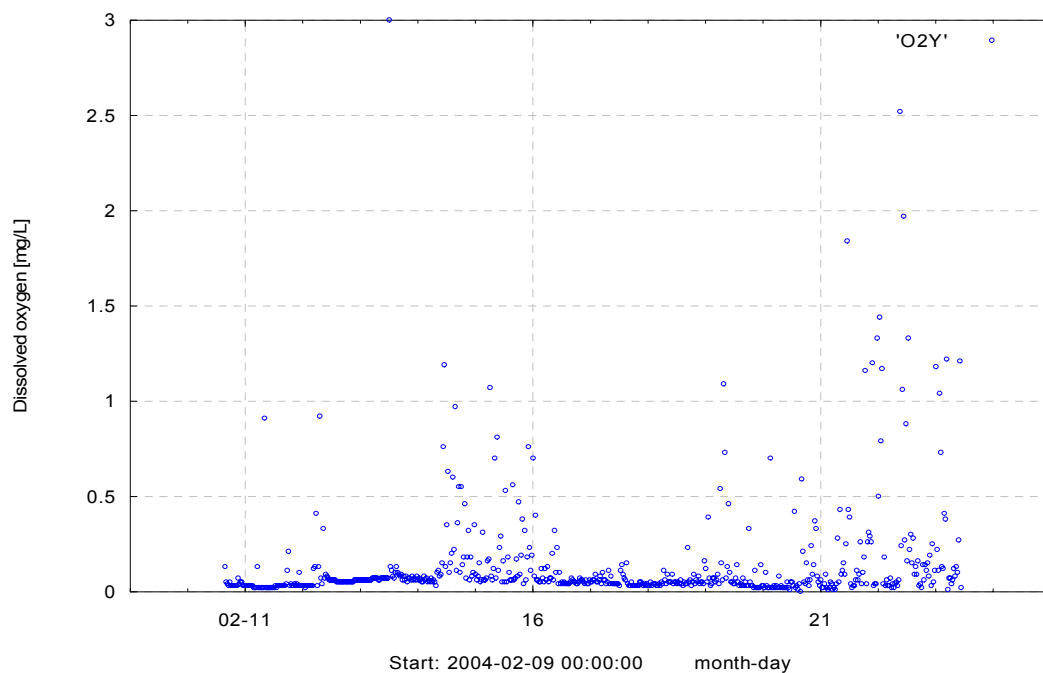


Figure A6-2. Dissolved oxygen measurements in the surface measurement cell (O2Y). The scatter in the measurement values is probably due to electrical noise.

Borehole: KFM02A
Section : 413.5 - 433.5 m

A4 (Pump const P) Pumping Test Constant Absolute Pressure
Start : 2004-01-27 17:58:52

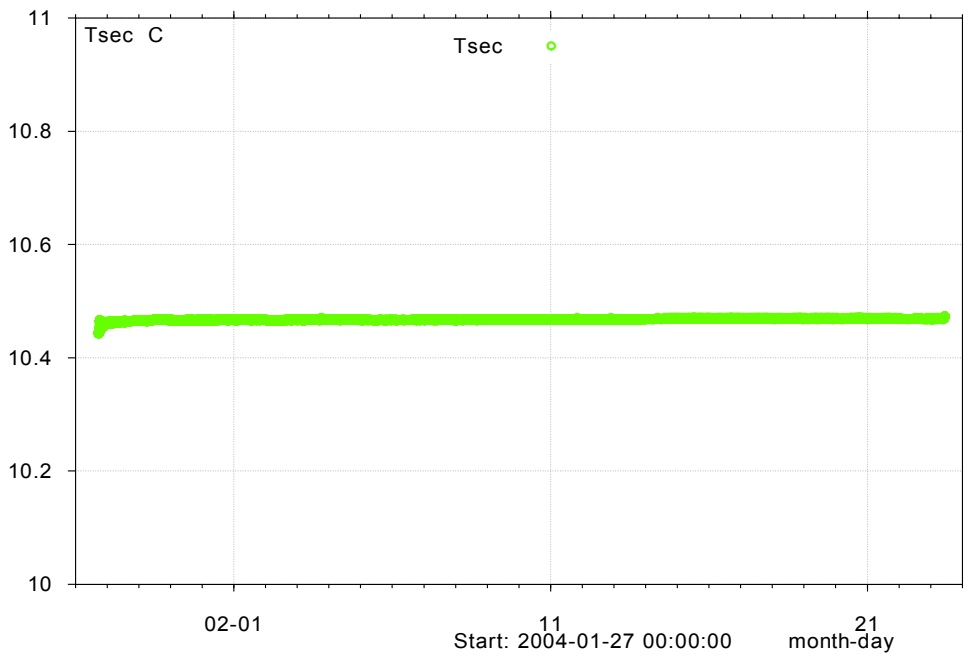


Figure A6-3. Temperature of the groundwater in section 413.5-433.5 m. The measurements were performed by equipment in the PSS3 unit.

Chemmac measurement, section 509.0–516.1 m

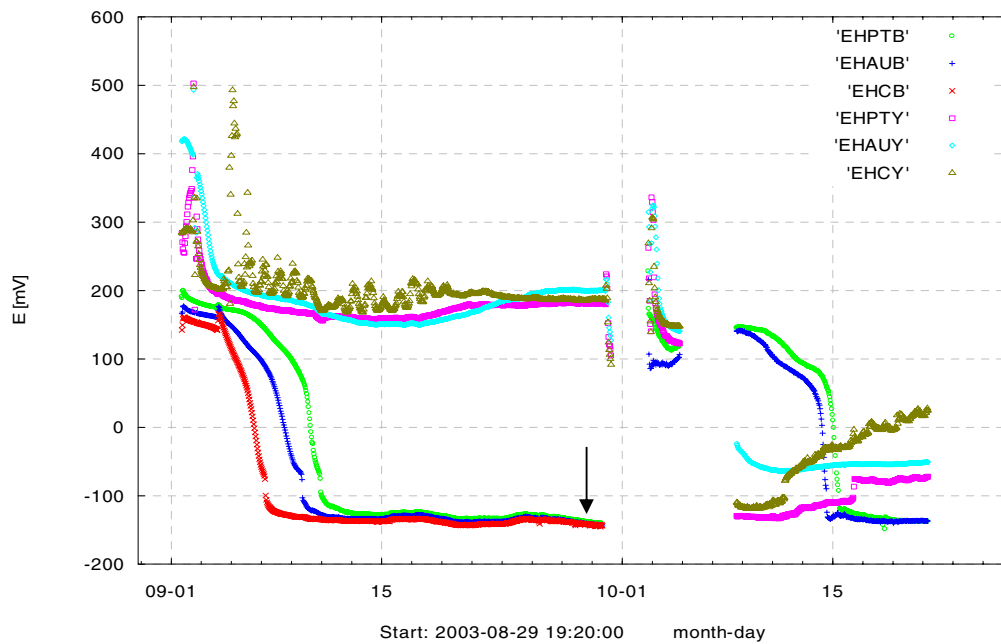


Figure A7-1. Redox potential measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCY). The arrow shows the chosen representative Eh values for the borehole section.

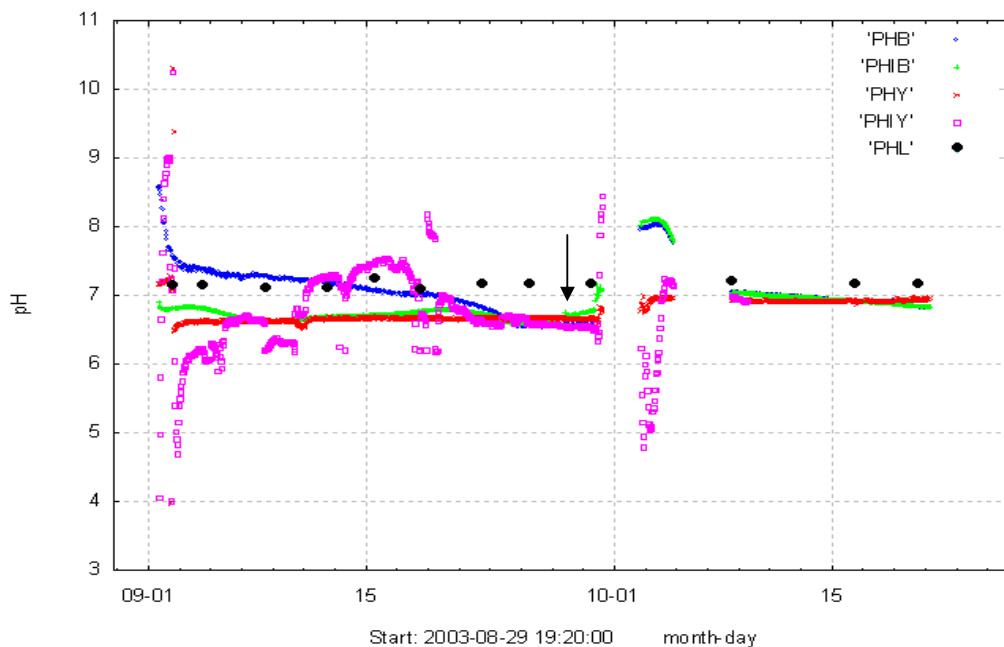


Figure A7-2. Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrode at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrows show the chosen representative pH values for the borehole section).

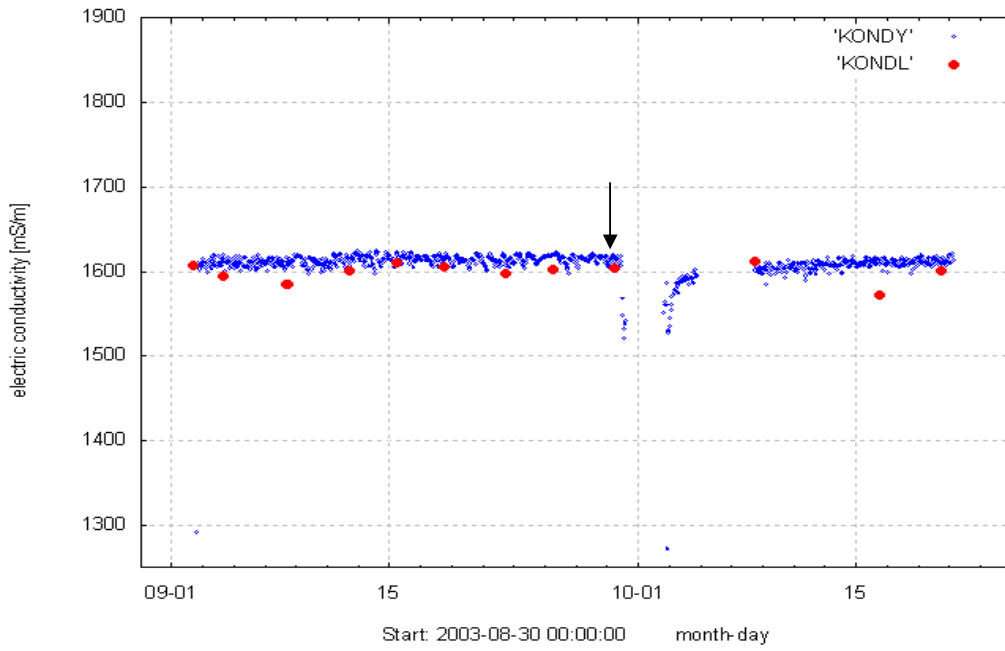


Figure A7-3. Electric conductivity measurements in the surface measurement cell (KONDY). The electric conductivity measured in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.

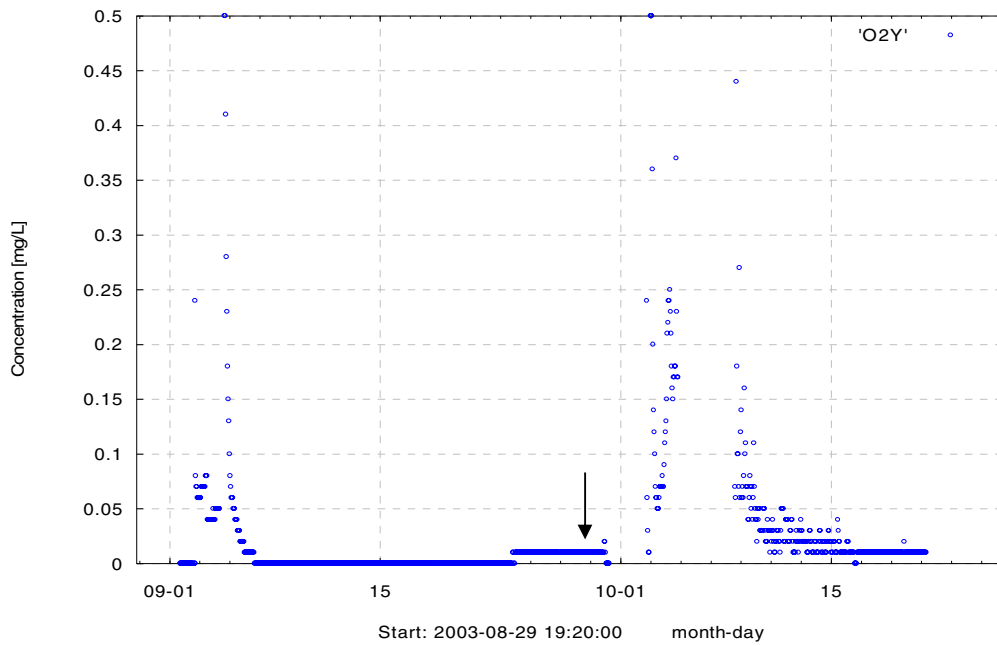


Figure A7-4. Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative value for dissolved oxygen in the borehole section.

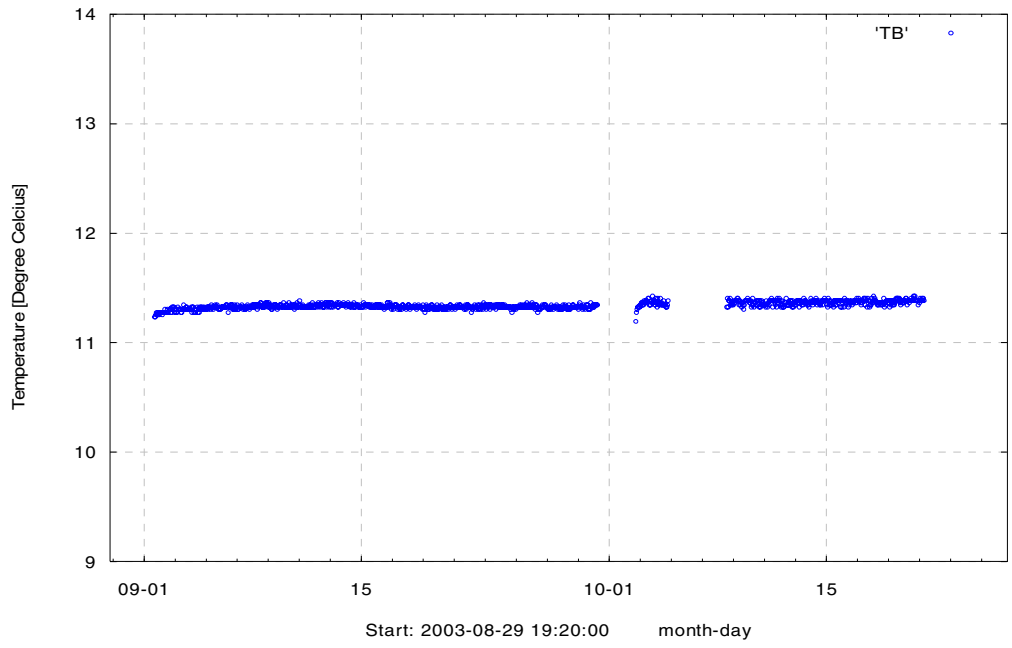


Figure A7-5. Temperature of the groundwater in the borehole section (TB).

Sampling and analysis methods

Table A8-1. Sample handling routines and analysis methods

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Anions 1.	HCO ₃ pH(lab) cond (lab)	Plastic	250	Yes (not in the field)	No	Titration Pot. meas, Cond. meas	Mobile field lab. AnalyCen	The same day – maximum 24 hours
Anions 2	Cl, SO ₄ , Br ⁻ , F ⁻ , I ⁻	Plastic	100	Yes (not in the field)	No	Titration (Cl ⁻) IC (Cl ⁻ , SO ₄ , Br ⁻ , F ⁻) ISE (F ⁻)	Åspö:s chemistry lab. AnalyCen	Not critical (month)
	Br, I	Plastic	100	Yes (not in the field)	No	ICP-MS	Paavo Ristola OY Analytica AB,	Not critical (month)
Cations, Si and S according to SKB class 3	Na, K, Ca, Mg, S(tot), Si(tot), Li, Sr	Plastic (at low conc. acid washed bottles)	100	Yes (not in the field)	Yes (not in the field, 1 mL HNO ₃)	ICP-AES ICP-MS	Analytica AB, AnalyCen	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	Analytica AB, AnalyCen	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic (Acid washed)	500	Yes	Yes (5 mL HCl)	Spectrophotometry Ferrozine method	Mobile field lab.	As soon as possible the same day
Hydrogen sulphide	HS ⁻	Glass (Winkler)	About 120x2	No	Ev 1 mL 1 M NaOH+ 1 mL 1M ZnAc	Spectrophotometry	AnalyCen Åspö:s chemistry lab.	Immediately or if conserved, a few days
Nutrient salts	NO ₂ , NO ₃ +NO ₂ , NH ₄ , PO ₄	Plastic	250	No	No	Spectrophotometry	Åspö:s chemistry lab. AnalyCen	Maximum 24 hours
Environmental metals	Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP-AES ICP-MS	Analytica AB, AnalyCen	Not critical (month)
Lantanoids, U, Th and so on.	Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP-AES ICP-MS	SGAB Analytica, AnalyCen	Not critical (month)

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Dissolved organic Carbon, dissolved inorganic Carbon	DOC, DIC	Plastic	250 25	Yes	Frozen, transported in isolated bag	UV oxidation, IR Carbon analyser Shimadzu TOC5000	Paavo Ristola OY Dept. of System ecology, SU	Short transportation time
	TOC	Plastic	250 25	No	Frozen, transported in isolated bag	UV oxidation, IR Carbon analyser Shimadzu TOC5000	Paavo Ristola OY Dept. of System ecology, SU	Short transportation time
Environmental isotopes	$\delta^2\text{H}$, $\delta^{18}\text{O}$	Plastic	100	No	-	MS	IFE	Not critical (month)
Tritium,	^3H (enhanced.)	Plastic (dry bottle)	500	No	-	LSC	Univ. of Waterloo	Not critical (month)
Chlorine-37	$\delta^{37}\text{Cl}$	Plastic	100	No	-	ICP MS		
Carbon isotopes	$\delta^{13}\text{C}$, pmC (^{14}C)	Glass (brown)	100x2	No	-	(A)MS	Univ. of Waterloo	A few days
Sulphur isotopes	$\delta^{34}\text{S}$	Plastic	500 –1000	Yes	-	Combustion, ICP MS	IFE	No limit
Strontium-isotopes	$^{87}\text{Sr}/^{86}\text{Sr}$	Plastic	100	Yes	-	TIMS	IFE	Days or Week
Uranium and Thorium isotopes	^{234}U , ^{235}U , ^{238}U , ^{232}Th , ^{230}Th ,	Plastic	50	No	-	Chemical separat. Alfa/gamma spectrometry	IFE SUERC	No limit
Boron isotopes	$^{10}\text{B}/^{11}\text{B}$	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP – MS	Analytica AB	No limit
Radon and Radium isotopes	^{222}Rn , ^{226}Ra	Plastic	500	No	No	EDA, RD-200	IFE SUERC	Immediate transport
Dissolved gas (content and composition)	Ar, N ₂ , CO ₂ , O ₂ , CH ₄ , H ₂ , CO, C ₂ H ₂ , C ₂ H ₄ , C ₃ H ₆ , C ₃ H ₈	Cylinder of stainless steel	200	No	No	GC	Paavo Ristola OY	Immediate transport
Colloids	Filter series and fractionation (see below)	Polycarbonate filter	0.45, 0.2 and 0.05 μm	-	N ₂ atmosphere	ICP-AES ICP-MS	Analytica AB	Immediate transport
Humic and fulvic acids	Fractionation	Fractions are collected in plastic bottles	250	-	N ₂ atmosphere	UV oxidation, IR (DOC)	Paavo Ristola OY	Immediate transport
Archive samples with acid	-	Plast (washed in acid)	100x2 **	Yes	Yes (1 mL HNO_3)	-	-	Storage in freeze container
Archive samples without acid	-	Plastic	250x2 **	Yes	No	-	-	Storage in freeze container

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Carbon isotopes in humic and fulvic acids	$\delta^{13}\text{C}$, pmC (^{14}C)	DEAE cellulose (anion exchanger)	-	-	-	(A)MS	The Ångström laboratory, Uppsala	A few days

* Suprapur acid is used for conservation of samples.

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

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

Abbreviations and definitions:

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

Table A8-2. Reporting limits and measurement uncertainties

Component	Method	Detection limit	Reporting limit or range	Unit	Measurement uncertainty ²	"Total" uncertainty ³
HCO ₃	Alkalinity titration	0.2	1	mg/L	4 %	<10 %
Cl ⁻	Mohr titration	5	70	mg/L	5 %	<10 %
Cl ⁻	IC	0.2	0.5		6 %	10 %
SO ₄	IC	0.2	0.5	mg/L	6 %	15 %
Br ⁻	IC	0.2	0.7	mg/L	9 %	20 %
Br ⁻	ICP	-	0.001 – 0.010 ¹		15 %	
F ⁻	IC	0.2	0.6	mg/L	10 %	20 %
F ⁻	Potentiometry	-	-		-	-
I ⁻	ICP	-	0.001 – 0.010 ¹	mg/L	15 %	20 %
Na	ICP	-	0.1	mg/L	4 %	10 %
K	ICP	-	0.4	mg/L	6 %	15 %
Ca	ICP	-	0.1	mg/L	4 %	10 %
Mg	ICP	-	0.09	mg/L	4 %	10 %
S(tot)	ICP	-	0.160	mg/L	10 %	15 %
Si(tot)	ICP	-	0.03	mg/L	4 %	15 %
Sr	ICP	-	0.002	mg/L	4 %	15 %
Li	ICP	-	0.2 - 2 ¹	µg/L	10 %	20 %
Fe	ICP	-	0.4-4 ¹	µg/L	6 %	10 %
Mn	ICP	-	0.03-0.1 ¹	µg/L	8 %	10 %
Fe (II), Fe(tot)	Spectrophotometry	5	20	µg/L	15 % (>30 µg/L)	20 %
DOC	See tab. 1	-	0.5	mg/L	8 %	30 %
HS ⁻	Spectrophotometry	0.02	0.03	mg/L	± 0.03 mg/L <0.2 mg/L	-
TOC	See tab. 1	-	0.5	mg/L	10 %	30 %
δ ² H	MS	-	2	‰ SMOW ⁴	1.0 ‰	-

Component	Method	Detection limit	Reporting limit or range	Unit	Measurement uncertainties ²	"Total" uncertainties ³
$\delta^{18}\text{O}$	MS	-	0.1	‰ SMOW ⁴	0.2 ‰	-
$\delta^{37}\text{Cl}$	ICP MS	-	0.2 ‰ (20 mg/L)	‰ SMOC ⁶	-	-
$\delta^{13}\text{C}$	A (MS)	-	>20 mg Carbon	‰ PDB ⁷	-	-
pmC (¹⁴ C)	A (MS)	-	>20 mg Carbon	pmC ⁸	-	-
$\delta^{34}\text{S}$	ICP MS	-	0.2 ‰	‰ CDT ⁹	0.2 ‰	-
⁸⁷ Sr/ ⁸⁶ Sr	MS	-	-	No unit (ratio) ¹⁰	0.000020	-
¹⁰ B/ ¹¹ B	ICP MS	-	-	No unit (ratio) ¹⁰	0,0020	-
²³⁴ U, ²³⁵ U, ²³⁸ U, ²³² Th, ²³⁰ Th	Alfa spectr.	-	0.05 (0.0005 ¹³)	Bq/L ¹²	0.05 Bq/L	Right order of magnitude
²²² Rn, ²²⁶ Rn	LSC	-	0.1 (0.0005 ¹³)	Bq/L	0.05 Bq/L	

- Reporting limits at salinity ≤ 0.4 ‰ (520 mS/m) and ≤ 3.5 ‰ (3810 mS/m) respectively.
- Measurement uncertainty reported by consulted laboratory, generally 95 % confidence interval.
- Estimated total uncertainty by experience (includes effects of sampling and sample handling).
- Per mille deviation¹¹ from SMOW (Standard Mean Oceanic Water).
- TU=Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10^{-18} (1 Bq/L Tritium = 8.45 TU).
- Per mille deviation¹¹ from SMOC (Standard Mean Oceanic Chloride).
- Per mille deviation¹¹ from PDB (the standard PeeDee Belemnite).
- 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
- Per mille deviation¹¹ from CDT (the standard Canyon Diablo Troilite).
- Isotope ratio without unit.
- Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:
 $\delta^y\text{I} = 1000 \times (K_{\text{sample}} - K_{\text{standard}}) / K_{\text{standard}}$, where K= the isotope ratio and $y\text{I} = {}^2\text{H}, {}^{18}\text{O}, {}^{37}\text{Cl}, {}^{13}\text{C}$ or ${}^{34}\text{S}$ etc.
- 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
- The consulted laboratory is changed recently and the new laboratory reports lower detection limits.

Table A8-3. Participant laboratories

Äspö water chemical laboratory (SKB) Mobile field laboratory, Forsmark (SKB)
Inainöörtoimisto Paavo Ristola Oy Teollisuus-ja Voimalaitoskemia Rajantorpantie 8, C-talo 01600 Vantaa FINLAND
Dept. of System ecology Stockholm University 10691 Stockholm
Analytica AB Aurorum 10 977 75 Luleå (Nytorpsvägen 16 Box 511 183 25 Täby)
Environmental Isotope Laboratory Dep. Of earth sciences University of Waterloo Waterloo, Ontario N2L 3G1 CANADA
Institutt for energiteknik (IFE) Insituttveien 18 P.O Box 40 2027 Kjeller NORGE
AnalyCen Nordic AB Box 905 531 19 Lidköping
The Ångström laboratory Box 534 Se-751 21 Uppsala
Scottish Universities Environmental Research Centre (SUERC) Rankin Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, Scotland, UK.

Compilation of water analysis data

Compilation June 2004

Table A9-1. Water Composition

Idcode	Secup	Seclow	Sample	Sample	Charge	Na	K	Ca	Mg	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	SO ₄ -S	Br	F ⁻	Si	Fe	Fe-tot	Fell	Mn	Li
m	m	m	no	date	Bal %	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/l	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
KFM02A	106.5	126.5	8097	2003-11-07	0.1	353	9.4	131	28.5	359	584	88.0	28.8	3.02	1.13	7.1	1.02	0.495	x	0.28	0.015
KFM02A	106.5	126.5	8099	2003-11-13	-1.8	363	9.6	136	30.3	419	612	89.8	29.4	2.76	1.28	7.1	1.35	1.38	x	0.29	0.015
KFM02A	106.5	126.5	8100	2003-11-18	-0.7	366	9.7	139	31.0	353	642	89.6	29.3	2.79	1.32	7.1	1.37	1.35	x	0.25	0.014
KFM02A	413.5	433.5	8159	2004-02-05	-	-	-	-	-	-	5380	429	-	27.3	-	-	-	0.775	0.720	-	-
KFM02A	413.5	433.5	8266	2004-02-10	-2.4	1850	21.6	1200	195	93.0	5420	427	140	27.7	<0.2	7.8	0.742	0.768	0.734	1.88	0.054
KFM02A	413.5	433.5	8272	2004-02-24	-3.3	1820	21.4	1140	198	93.0	5380	434	136	25.8	<0.2	7.8	0.736	0.747	0.727	1.81	0.057
KFM02A	417.0	426.47	4831	2003-06-04	-	-	-	-	-	132	4400	-	-	-	-	-	-	-	-	-	-
KFM02A	417.0	426.47	4832	2003-06-06	-	-	-	-	-	135	4390	-	-	-	-	-	-	-	-	-	-
KFM02A	417.0	426.47	4833	2003-06-12	-	-	-	-	-	144	4790	-	-	-	-	-	-	-	-	-	-
KFM02A	509.0	516.08	4834	2003-06-13	-	-	-	-	-	143	-	-	-	-	-	-	-	-	-	-	-
KFM02A	509.0	516.08	4835	2003-06-16	-	-	-	-	-	136	-	-	-	-	-	-	-	-	-	-	-
KFM02A	509.0	516.08	4836	2003-06-19	-	-	-	-	-	132	-	-	-	-	-	-	-	-	-	-	-
KFM02A	509.0	516.08	4837	2003-06-24	-	-	-	-	-	132	-	-	-	-	-	-	-	-	-	-	-
KFM02A	509.0	516.08	4978	2003-09-02	-	-	-	-	-	123	-	-	-	-	-	-	-	-	-	-	-
KFM02A	509.0	516.08	4979	2003-09-04	-2.9	2090	33.7	929	231	123	5420	510	157	22.7	1.11	5.3	1.08	1.04	1.08	2.14	0.051
KFM02A	509.0	516.08	4980	2003-09-08	-3.3	2060	33.3	921	231	124	5410	512	155	22.0	0.90	5.2	1.20	1.25	1.21	2.12	0.051
KFM02A	509.0	516.08	4981	2003-09-12	-3.1	2090	33.7	923	232	123	5440	515	156	22.0	1.08	5.3	1.20	1.26	1.28	2.14	0.051
KFM02A	509.0	516.08	4982	2003-09-15	-2.9	2100	33.8	932	233	122	5460	515	156	21.5	0.98	5.2	1.20	1.18	1.26	2.15	0.051
KFM02A	509.0	516.08	4984	2003-09-18	-2.9	2090	34.1	938	232	124	5450	515	158	22.0	0.93	5.3	1.21	1.26	1.26	2.17	0.052
KFM02A	509.0	516.08	4985	2003-09-22	-2.7	2110	33.9	933	234	124	5450	507	157	21.1	0.90	5.2	1.19	1.21	1.26	2.16	0.051
KFM02A	509.0	516.08	8009	2003-09-25	-3.0	2100	33.8	930	232	123	5460	514	157	22.6	0.99	5.2	1.19	1.31	1.27	2.15	0.051
KFM02A	509.0	516.08	8010	2003-09-29	-3.4	2060	34.1	933	229	124	5440	507	157	21.9	1.04	5.3	1.21	1.36	1.33	2.15	0.051
KFM02A	509.0	516.08	8013	2003-10-08	-2.5	2070	35.4	939	239	128	5400	493	151	22.8	0.89	6.2	1.91	2.05	1.98	2.17	0.049
KFM02A	509.0	516.08	8014	2003-10-16	-3.2	2060	33.1	928	228	126	5400	498	156	22.8	0.89	5.2	1.69	-	-	2.15	0.031
KFM02A	509.0	516.08	8016	2003-10-20	-3.5	2040	34.2	934	226	125	5410	498	156	23.8	0.84	5.2	1.70	1.85	1.84	2.16	0.051

-- Not analysed

x = No result due to sampling problems

xx = No result due to analytical problems

< "value" = result below detection limit

ChargeBal % = Relative charge balance error %

SICADA: water_composition

Idcode	Secup m	Seclow m	Sample no	Sr mg/L	pH	DOC mg/L	HS ⁻ mg/L	Flush_water %	EiCond mS/m	NH ₄ N mg/L
KFM02A	106,5	126,5	8097	0,99	7,47	14,0	<0,01	0,7	253	0,202
KFM02A	106,5	126,5	8099	1,00	7,70	11,0	0,01	0,5	227	0,372
KFM02A	106,5	126,5	8100	1,01	7,52	11,0	<0,01	0,4	274	0,509
KFM02A	413,5	433,5	8159	-	7,40	1,4	-	3,3	1560	0,821
KFM02A	413,5	433,5	8266	11,3	7,37	1,5	-	3,0	1570	1,91
KFM02A	413,5	433,5	8272	11,2	7,37	<1,0	-	2,2	1640	1,88
KFM02A	417,0	426,47	4831	-	7,38	-	-	38	1390	-
KFM02A	417,0	426,47	4832	-	7,42	-	-	37	1390	-
KFM02A	417,0	426,47	4833	-	7,35	-	-	37	1360	-
KFM02A	509,0	516,08	4834	-	7,45	-	-	24	1450	-
KFM02A	509,0	516,08	4835	-	7,36	-	-	22	1440	-
KFM02A	509,0	516,08	4836	-	7,37	-	-	-	1520	-
KFM02A	509,0	516,08	4837	-	7,32	-	-	-	1480	-
KFM02A	509,0	516,08	4978	-	7,17	-	-	6,3	1600	-
KFM02A	509,0	516,08	4979	8,02	7,17	-	<0,03	6,1	1590	2,02
KFM02A	509,0	516,08	4980	7,95	7,10	-	-	6,1	1580	2,70
KFM02A	509,0	516,08	4981	7,98	7,13	2,5	<0,03	5,8	1600	2,71
KFM02A	509,0	516,08	4982	7,98	7,27	2,0	-	6,3	1610	2,95
KFM02A	509,0	516,08	4984	8,11	7,10	2,4	<0,03	5,9	1600	2,97
KFM02A	509,0	516,08	4985	8,03	7,18	2,4	<0,03	6,0	1600	3,06
KFM02A	509,0	516,08	8009	8,05	7,16	2,5	<0,03	6,1	1600	2,95
KFM02A	509,0	516,08	8010	8,02	7,19	-	<0,03	6,0	1600	2,95
KFM02A	509,0	516,08	8013	8,09	7,22	2,1	<0,03	7,5	1610	2,93
KFM02A	509,0	516,08	8014	8,04	7,18	2,2	-	-	1570	2,63
KFM02A	509,0	516,08	8016	8,04	7,18	2,1	<0,03	6,8	1600	2,30

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

SICADA: water_composition

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

Idcode	Secup m	Seclow m	Sample no	Sampling date	$\delta^2\text{Hd}$ dev SMOW	^3H TU	$\delta^{18}\text{O}$ dev SMOW	$^{10}\text{B}/^{11}\text{B}$ no unit	$\delta^{34}\text{S}$ dev CDT	$\delta^{13}\text{C}$ dev PDB	$^{87}\text{Sr}/^{86}\text{Sr}$ no unit	^{14}C pmC	AGE_BP years	$\delta^{37}\text{Cl}$ dev SMOC
KFM02A	106,5	126,5	8097	2003-11-07	-82,1	<0,8	-11,7	0,2379	-	-	-	-	-	-
KFM02A	106,5	126,5	8099	2003-11-13	-82,2	<0,8	-11,7	0,2367	-	-	-	-	-	-
KFM02A	106,5	126,5	8100	2003-11-18	-80,9	<0,8	-11,6	0,2371	20,8	-12,9	0,719362	64,5	3470	A
KFM02A	413,5	433,5	8159	2004-02-05	-78,6	<0,8	-10,1	-	-	-	-	-	-	-
KFM02A	413,5	433,5	8266	2004-02-10	-77,7	<0,8	-10,1	-	-	-	-	-	-	-
KFM02A	413,5	433,5	8272	2004-02-24	-75,6	<0,8	-10,2	0,2424	A	A	A	A	A	A
KFM02A	509,0	516,08	4979	2003-09-04	-68,5	<0,8	-8,8	0,2363	-	-	-	-	-	-
KFM02A	509,0	516,08	4980	2003-09-08	-68,1	<0,8	-8,7	0,2370	27,3	-	0,718238	-	-	-
KFM02A	509,0	516,08	4981	2003-09-12	-	<0,8	-	0,2364	-	-	-	-	-	-
KFM02A	509,0	516,08	4982	2003-09-15	-	<0,8	-	0,2365	-	-	-	-	-	-
KFM02A	509,0	516,08	4984	2003-09-18	-	<0,8	-	0,2365	-	-	-	-	-	-
KFM02A	509,0	516,08	4985	2003-09-22	-68,4	<0,8	-8,8	0,2366	24,8	-	0,718269	-	-	-
KFM02A	509,0	516,08	8009	2003-09-25	-	<0,8	-	0,2370	-	-	-	-	-	-
KFM02A	509,0	516,08	8010	2003-09-29	-	<0,8	-	0,2373	24,5	-	0,718358	-	-	-
KFM02A	509,0	516,08	8013	2003-10-08	-66,5	<0,8	-8,8	0,2392	-	-	-	-	-	-
KFM02A	509,0	516,08	8014	2003-10-16	-66,5	<0,8	-8,7	0,2359	-	-	-	-	-	-
KFM02A	509,0	516,08	8016	2003-10-20	-67,0	2,4	-8,8	0,2374	24,9	-9,1	0,718247	15,8	14785	A

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
<"value" = result below detection limit
SICADA: h_o_isotopes, b_s_cl_sr_isotopes, c_s_isotopes

Table A9-3. Trace elements

Idcode	Secup m	Seclow m	Sample no	Sampling date	U µg/L	Th µg/L	Sc µg/L	Rb µg/L	Y µg/L	Zr µg/L	Sb µg/L	Cs µg/L	La µg/L	Hf µg/L	Tl µg/L	Ce µg/L	Pr µg/L	Nd µg/L	Sm µg/L	Eu µg/L
KFM02A	106,5	126,5	8100	2003-11-18	5,4	0,03	0,099	15,2	2,57	4,97	0,033	0,43	0,100	0,09	<0,03	0,180	0,030	0,120	0,044	0,009
KFM02A	413,5	433,5	8272	2004-02-24	13,9	<0,2	<0,5	58,3	5,91	<0,3	<0,1	1,9	0,427	<0,05	<0,3	0,561	0,075	0,353	0,100	<0,05
KFM02A	509,0	516,08	4980	2003-09-08	65,1	<0,2	<0,5	62,8	1,23	<0,3	<0,1	1,83	<0,05	<0,05	<0,3	<0,05	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	4982	2003-09-15	73,2	<0,2	<0,5	60,9	1,54	<0,3	<0,1	1,8	0,09	<0,05	<0,3	<0,05	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	4985	2003-09-22	76,4	<0,2	<0,5	61,9	1,58	<0,3	<0,1	1,76	0,174	<0,05	<0,3	0,06	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	8010	2003-09-29	84,3	<0,2	<0,5	63,3	1,58	<0,3	<0,1	1,78	0,194	<0,05	<0,3	0,102	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	8016	2003-10-20	88,6	<0,2	<0,5	62,7	1,40	<0,3	<0,1	1,74	0,183	<0,05	<0,3	0,140	<0,05	<0,05	<0,05	<0,05

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

Table A9-3. Trace elements

Idcode	Secup m	Seclow m	Sample no	Gd µg/L	Tb µg/L	Dy µg/L	Ho µg/L	Er µg/L	Tm µg/L	Yb µg/L	Lu µg/L
KFM02A	106,5	126,5	8100	0,110	0,021	0,21	0,060	0,220	0,03	0,220	0,04
KFM02A	413,5	433,5	8272	0,235	<0,05	0,31	0,089	0,252	<0,05	0,174	<0,05
KFM02A	509,0	516,08	4980	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	4982	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	4985	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	8010	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
KFM02A	509,0	516,08	8016	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05

- = Not analysed

x = No result due to sampling problems

xx = No result due to analytical problems

< "value" = result below detection limit

SICADA: trace_elements

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

Idcode	Secup m	Seclow m	Sample no*	Sampling date	²³⁸ U mBq/L	²³⁵ U mBq/L	²³⁴ U mBq/L	²³² Th mBq/L	²³⁰ Th mBq/L	²²⁶ Ra Bq/L	²²² Rn Bq/L
KFM02A	106,5	126,5	8100	2003-11-18	A	A	A	A	A	0,3	168
KFM02A	413,5	433,5	8272	2004-02-24	A	A	A	A	A	2,2	363
KFM02A	509,0	516,08	4980	2003-09-08	-	-	-	-	-	3,5	1200
KFM02A	509,0	516,08	4982	2003-09-15	-	-	-	-	-	-	-
KFM02A	509,0	516,08	4985	2003-09-22	-	-	-	-	-	-	-
KFM02A	509,0	516,08	8010	2003-09-29	-	-	-	-	-	-	-
KFM02A	509,0	516,08	8016	2003-10-20	A	A	A	A	A	3,1	563

- = Not analysed

A = Results will be reported later

x = No result due to sampling problems

xx = No result due to analytical problems

- "value" = result below detection limit

SICADA: u_th_isotope_t, ra_rn_isotope_t

Table A9-5. Dissolved gases

Idcode	Secup m	Seclow m	Sample no*	Sampling date	Ar mL/L	He mL/L	N ₂ mL/L	CO ₂ mL/L	CH ₄ mL/L	O ₂ mL/L	H ₂ µL/L	CO µL/L	C ₂ H ₆ µL/L	C ₂ H ₄ µL/L	C ₂ H ₂ µL/L	C ₃ H ₈ µL/L	C ₃ H ₆ µL/L	DISS_GAS mL/L
KFM02A	509,0	516,08	8010	2003-09-30	1,1	0,81	77,3	3,9	0,03	0,04	22,4	<4,2	0,25	0,13	<0,04	<0,08	0,14	83,2
KFM02A	509,0	516,08	8016	2003-10-27	4,9	0,80	63,5	4,0	0,04	0,12	199	<3,7	0,24	0,15	0,06	0,1	0,16	73,6

* Corresponding water sample no.

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