

Oskarshamn site investigation

Complete chemical characterisation in KLX15A

Results from the investigated borehole section: 623.0 to 634.5 m

Anette Bergelin, Kersti Nilsson, Anna Lindquist, Pia Wacker
Geosigma AB

December 2008

Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel
and Waste Management Co

Box 250, SE-101 24 Stockholm
Phone +46 8 459 84 00



Oskarshamn site investigation

Complete chemical characterisation in KLX15A

Results from the investigated borehole section: 623.0 to 634.5 m

Anette Bergelin, Kersti Nilsson, Anna Lindquist, Pia Wacker
Geosigma AB

December 2008

Keywords: Groundwater, Measurements on line, *In situ* sampling, Measurements *in situ*, Redox potential, Dissolved gas, Chemical analyses, Isotope determinations, Humic and fulvic acids, Colloids, Laser induced breakdown colloid detection, Scanning electron microscopy, Microbes, AP PS 400-07-053.

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.

Data in SKB's database can be changed for different reasons. Minor changes in SKB's database will not necessarily result in a revised report. Data revisions may also be presented as supplements, available at www.skb.se.

A pdf version of this document can be downloaded from www.skb.se

Abstract

Complete chemical characterisation is the most extensive chemical investigation method performed in core drilled boreholes. The method entails pumping, measurements on-line and regular water sampling for chemical analyses in isolated borehole sections during approximately three weeks per section at a flow rate of between 50 and 250 mL/min.

This report presents results from one section in borehole KLX15A at 623.0 to 634.5 m borehole length (vertical depth 478 to 485 m). The results obtained include on-line measurements of redox potential, pH, dissolved oxygen, electrical conductivity and water temperature together with chemical analyses of major constituents, trace metals and isotopes as well as gas content and composition. Furthermore, inorganic and organic colloids were investigated by fractionation, laser-induced breakdown colloid detection (LIBD) and scanning electron microscopy (SEM).

The water composition in the section was stable at the end of the pumping and sampling period. The chloride concentrations amounted to approximately 5,900 mg/l in the section while the flushing water content was 4.4%. The redox potentials from the electrodes were inconsistent and unstable due to several interruptions during the measurement and slow response of the electrodes.

The organic constituents were present mainly as acids with molecular weight less than 1,000 D.

The colloid content measured by LIBD and SEM was in the same order of magnitude; 0.008–5 µg/l and less than 1–20 µg/l, respectively, while the colloid concentration from the Filtration-ICP sample was 140 µg/l.

Sammanfattning

Fullständig kemikaraktisering 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 250 mL/min.

Denna rapport presenterar resultat från en sektion i borrhålet KLX15A vid 623,0 till 634,5 m borrhålslängd (vertikalt djup 478 till 485 m). Resultaten omfattar mätningar on-line av redox potential, pH, löst syre, elektrisk konduktivitet och vattentemperatur liksom kemiska analyser av huvudkomponenter, spårelement och samt bestämning av gasinnehåll och sammansättning. Vidare undersöktes sektion oorganiska och organiska kolloider (humus och fulvosyror) med fraktioneringsteknik, detektering genom laserinducerad nedbrytning (LIBD) och svepelektron mikroskopi (SEM).

Vattensammansättningen i sektionen var stabil under den senare delen av pump/provtagningsperioden. Kloridkoncentrationen uppgick till ca 5 900 mg/l medan spolvattenhalten var 4,4%. Redoxpotentialerna för elektroderna var inte stabila eller samstämmiga beroende på flera avbrott under mätningen och långsam elektrod respons.

De organiska föreningarna förekommer främst som enkla syror med molekylvikt mindre än 1 000 Dalton.

Koncentrationen av kolloider mätt med LIBD och SEM var i samma storleksordning och uppgick till mellan 0,008 och 5 µg/l respektive mindre än 1 µg/l till 20 µg/l, medan resultatet från Filtrering-ICP gav en koncentration på 140 µg/l.

Contents

1	Introduction	7
2	Objectives and scope	9
3	Background	11
3.1	Flushing water history	11
3.2	Previous activities in the borehole	12
3.3	Choice of borehole sections	12
4	Equipment	13
4.1	The mobile field laboratory	13
4.2	Colloid filtering equipment	14
4.3	Equipment for enrichment of humic and fulvic acids	16
4.4	Equipment for fractionation of humic and fulvic acids	17
5	Performance	19
5.1	General	19
5.2	Chemical characterisation	20
	5.2.1 Overview of field work procedure	20
	5.2.2 Performance in section 623.0 to 634.5 m	21
5.3	Water sampling, sample treatment and analyses	23
5.4	Collection of <i>in situ</i> water samples	23
5.5	Colloid filtration	24
5.6	Enrichment of humic and fulvic acids	25
5.7	Fractionation of humic and fulvic acids	25
5.8	Nonconformities	25
6	Data handling and interpretation	27
6.1	Chemmac measurement data	27
	6.1.1 Data file types and calculation software	27
	6.1.2 Calculations and evaluation of pH and redox potential	27
6.2	Water analysis data	28
6.3	Data from special sampling methods	30
	6.3.1 Colloid filtration	30
	6.3.2 Dissolved gases	30
	6.3.3 Enrichment of humic and fulvic acids	30
	6.3.4 Fractionation of humic and fulvic acids	30
7	Results	31
7.1	Chemmac measurements	31
7.2	Water analyses	32
	7.2.1 Basic water analyses	32
	7.2.2 Trace elements (rare earth metals and others)	35
	7.2.3 Stable and radioactive isotopes	35
7.3	Dissolved gas	36
7.4	Inorganic colloids	37
	7.4.1 Inorganic colloids – colloid filtration	38
	7.4.2 Inorganic colloids – fractionation	42
7.5	Humic and fulvic acids – fractionation	42
8	Summary	43
9	References	45

Appendix 1	Design of cored borehole KLX15A	47
Appendix 2	Selected results of differential flow logging in KLX15A	49
Appendix 3	Selected images from BIPS logging in KLX15A	51
Appendix 4	Measurement information, KLX15A	53
Appendix 5	Flow and pressure measurements, KLX15A	57
Appendix 6	Chemmac measurements in KLX15A, section 623.0 to 634.5 m	59
Appendix 7	Quantification of Colloids in Natural Groundwater from Laxemar Borehole KLX15A, Section (623–634.5) m	63
Appendix 8	Sampling and analysis methods	75
Appendix 9	Compilation of water analysis data	81

1 Introduction

This document reports performance of and results from the activity *Complete chemical characterisation* in the cored borehole KLX15A performed within the site investigation at Oskarshamn /1/. The work was conducted according to activity plan AP PS 400-07-053, SKB internal document, Table 1-1. The report presents hydrogeochemical data from field work carried out during the period of June 2007 to August 2007.

The controlling documents for the activity are listed in Table 1-1. The activity plan, the method description and the measurement system descriptions constitute SKB's internal controlling documents. The obtained data from the activity are reported to the SICADA database and are traceable by the activity plan number. Sampling for microbe studies was also performed within the present activity in the borehole section. The microbe investigations will be reported in a separate primary data report /2/.

Borehole KLX15A is a 1,000.4 m long telescopic borehole drilled at Laxemar subarea and inclined 54° from the horizontal plane. The interval 0–76 m is percussion-drilled with a diameter of approximately 200 mm and the interval 76–1,000 m is core-drilled with a diameter of 76 mm. The percussion borehole HLX14 served as the source of flushing water for the drilling of KLX15A. The locations of KLX15A and HLX14 are shown in Figure 1-1. The borehole design of KLX15A 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). Equipment used in the borehole after the drilling were cleaned according to level 1 in the cleaning instructions outlined in MD 600.004 (Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning). A SKB chemical-type borehole requires that cleaning procedures are 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).

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

Activity plan	Number	Version
Fullständig kemikaraktärisering i KLX15A.	AP PS 400-07-053	1.0
Method description	Number	Version
Metodbeskrivning för fullständig kemikaraktärisering med mobilt fältlaboratorium.	SKB MD 430.017	2.0
Measurement system descriptions		
Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning.	SKB MD 600.004	1.0
Mätssystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation.	SKB MD 434.004	1.0
	SKB MD 434.005	1.0
	SKB MD 434.006	1.0
	SKB MD 434.007	1.0
	SKB MD 434.018	
Mätssystembeskrivning för fraktionering av humus- och fulvosyror med membranfiltrering.	SKB MD 431.043	1.0
Mätssystembeskrivning för uppkoncentrering av humus- och fulvosyror för kol-13 och kol-14 bestämning.	SKB MD 431-044	1.0
Mätssystembeskrivning för kolloidfiltreringssystem.	SKB MD 431.045	In progress
Instructions		
Provtagning och analys-kemilaboratorium.	SKB MD 452.001-019	–

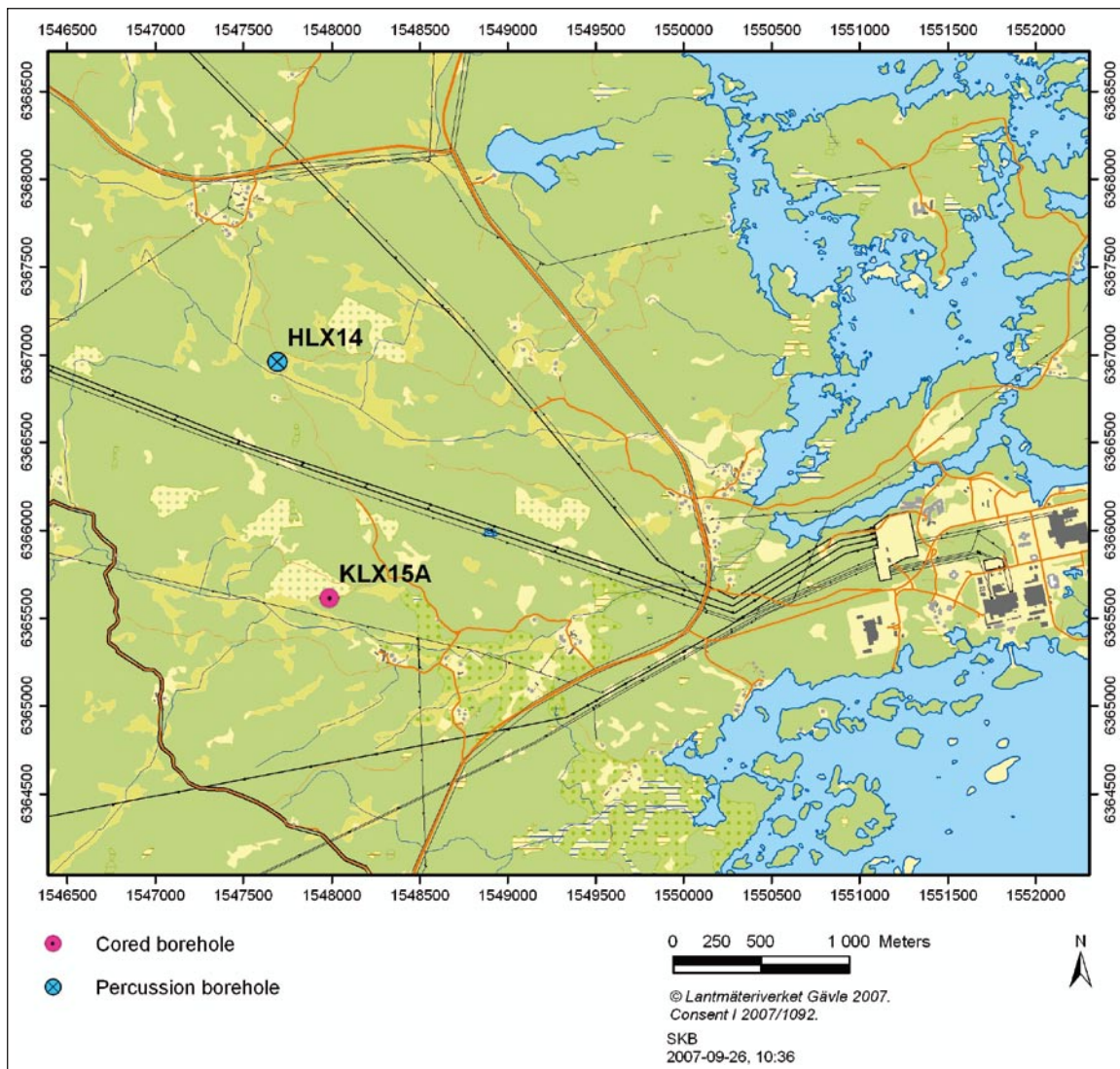


Figure 1-1. Locations of the core drilled borehole KLX15A and the percussion borehole HLX14 within the Oskarshamn site investigation area.

2 Objectives and scope

Complete chemical characterisation is the most extensive chemical investigation method performed in core-drilled boreholes. The method is employed in order to obtain as complete information as possible about the groundwater chemical conditions in individual water-bearing fractures or local minor fracture zones. Considerable effort is made to obtain 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 ground waters from other fracture systems.

The analytical programme was carried out according to SKB chemistry class 4 and class 5 including all options /1/. Furthermore, pH, redox potential (Eh) and water temperature were measured in flow-through cells downhole as well as at the ground surface. The flow-through cell at the surface also measured electrical conductivity and dissolved oxygen. In addition, samples were collected *in situ* in the section for determination of gas content and composition, microbe content and their characterisation as well as for determination of colloid content by fractionation, ICP, LIBD and SEM techniques.

3 Background

3.1 Flushing water history

The core drilling of the 1,000.4 m long borehole consumed 1,057 m³ of flushing water and the volume of returned water pumped from the borehole by air-lift pumping during drilling was 1,710 m³.

Uranine was added automatically to the tank with flushing water that supplies flushing water to the drilling head. The uranine concentration in the flushing water and returned water was checked regularly and a total of 133 samples of each sample type were analysed. The uranine concentrations in the flushing water and in the returned water are presented in Figure 3-1. A water budget, presenting the amount of uranine added to the borehole via the flushing water and the estimated amount recovered in the return water, is given in Table 3-1.

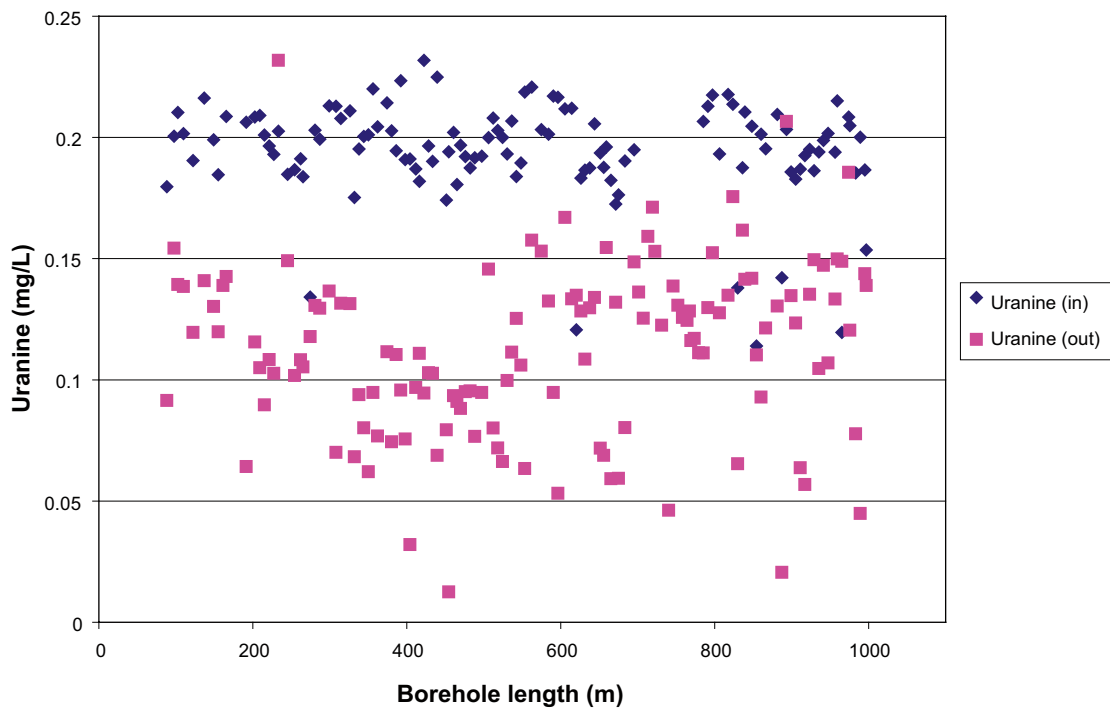


Figure 3-1. Uranine concentrations in the flushing water and in the recovered water versus borehole length.

Table 3-1. Amount of uranine added to KLX15A via the flushing water during core drilling and the amount recovered from the air-lift pumping.

Uranine	(g)
Added, calculated from the average uranine concentration added and the total volume of flushing water.	207
Recovered, estimated from the average uranine concentration recovered and the total volume of returned water.	193

The uranium budget in Table 3-1 suggests that flushing water has been lost to the borehole and the adjacent host bedrock during drilling.

Detailed information on the flushing water and drilling of the borehole can be obtained from the drilling report /3/.

3.2 Previous activities in the borehole

KLX15A is drilled as a so-called SKB chemical-type borehole even though the borehole was not intended for *Complete chemical characterisation*. Only activities that are necessary in order to select borehole sections are usually 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 affects on, for example, the *in situ* microbiological conditions. The activities/investigations performed in KLX15A prior to the chemistry characterisation are listed in Table 3-2 below.

3.3 Choice of borehole sections

The main objective for the *Complete chemical characterisation* in KLX15A was to investigate one section at repository depth (c. 410 to 550 m). The differential flow logging /5/ revealed two water-bearing zones (> 10,000 mL/h) within this borehole interval. Furthermore, two sections with water yield just below 10,000 mL/h were identified.

The section at 623.0 to 634.5 m was selected since it fulfilled all requirements (flow yield more than 10,000 mL/h, near repository depth and suitable for packer positioning, see Table 3-3. The pumping was carried out without any significant drawdown.

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

Table 3-2. Activities performed in KLX15A prior and in connection to the chemical characterisation.

Activity	Date of completion	Length or section (m)	Comment
Percussion drilling	2006-12-29	0.3–76.13	
Core drilling	2007-02-25	76.13–1,000.43	
Nitrogen lifting of water column	2007-03-12– 2007-03-13	0–1,000.43	
BIPS-logging	2007-03-29	11–979.3	/4/
Injection test	2007-04-28	80–1,000.43	
Differential flow logging	2007-05-02– 2007-05-18	15.13–973.85	/5/
Geophysical logging	2007-04-02	75–986	/6/

Table 3-3. Selected fractured/fracture zones identified from the differential flow logging of KLX15A.

Section	Borehole length (m)	Flow (mL/h)	Comments
1	630	> 10,000	
2	503	~ 3,000	Optional section

4 Equipment

4.1 The mobile field laboratory

The mobile field laboratories used by SKB for water sampling and downhole measurements consist of a laboratory unit, a hose unit with downhole equipment and a Chemmac measurement system, Figure 4-1; the system is presented schematically in Figure 4-2. It is also possible to include a separate unit for computer work (MYC). The different parts of the system are described in the SKB internal controlling documents SKB MD 434.004, 434.005, 434.006, 434.007 and SKB MD 433.018 (Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation).

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

The downhole equipment comprises inflatable packers, pump, borehole Chemmac and the *in situ* sampling unit (PVP), allowing measurement (borehole Chemmac) and sampling *in situ* in the borehole section (PVP sampling unit). The four sampled portions of ground-water collected with the PVP sampling unit maintain the pressure from the borehole section when raised to the surface. The portions are used for colloid and gas analysis and microbe investigations.

The mobile units used for the investigation of borehole KLX15A consisted of the hose unit S2, the laboratory unit L2 and the computer unit MYC 2 including surface Chemmac.



Figure 4-1. The mobile units used at KLX15A; from left hose unit with downhole equipment, a unit for computer work and laboratory unit.

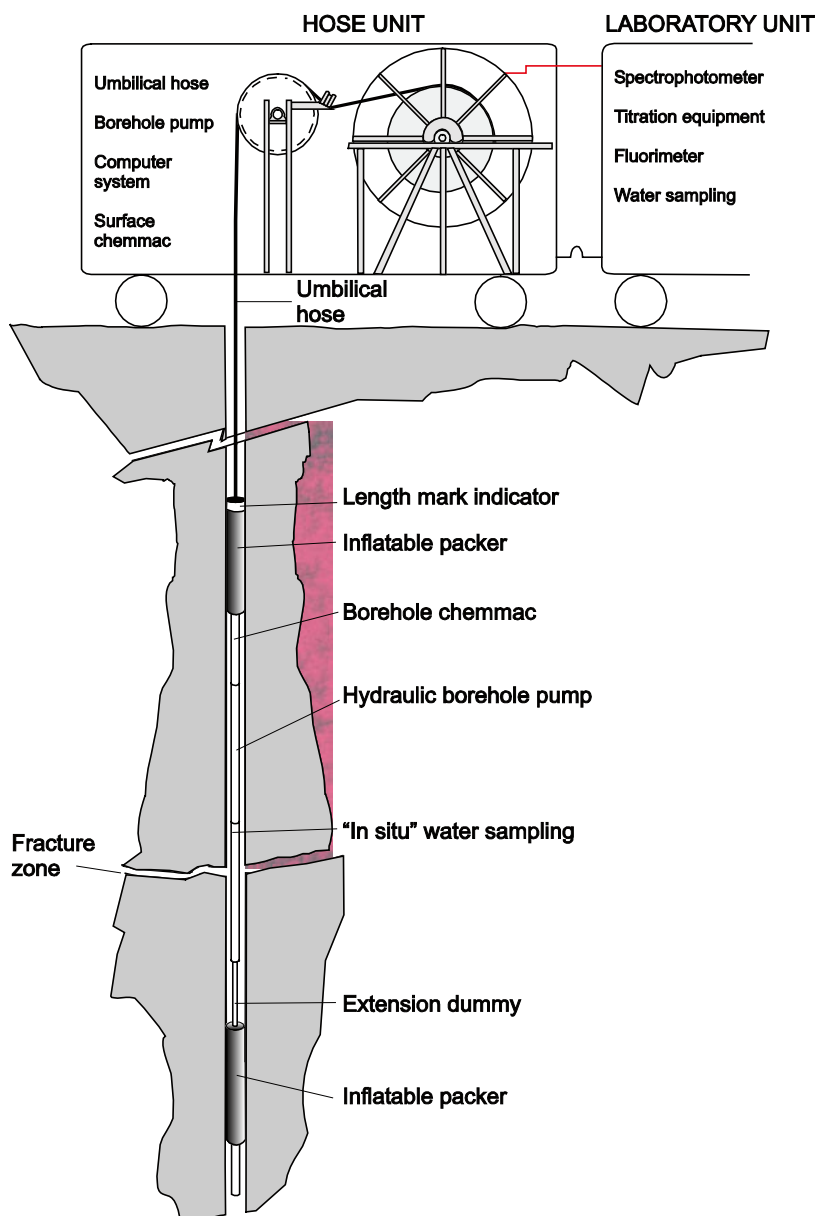


Figure 4-2. The mobile laboratory including laboratory unit, hose unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.

4.2 Colloid filtering equipment

The colloid filtering equipment is adapted to the sample containers (PVB) from the PVP water sampling unit and consists of holders for two PVB-containers, a separate tube and valve system for water and gas, a filter holder package for five filters, and a collecting container. The pore sizes of the five connected filters were 2.0, 2.0, 0.4, 0.2 and 0.05 μm in section 669.7 to 676.8 m. The equipment is described in SKB MD 431.045 (Mätssystembeskrivning för kolloidfiltreringssystem, handhavandedel, SKB internal controlling document to be published). Figure 4-3 shows the equipment set-up.

The major equipment features are:

- Filtering is performed in a closed system under an argon atmosphere, thus avoiding the risk of iron precipitation due to contact between the groundwater sample and air.
- Filtering is performed at a pressure similar to that of the groundwater in the borehole section. The system is adjusted to create a pressure difference between the inlet of the filter package and the outlet side. The pressure difference drives the sample water through the filters.
- The design of the sample containers, and the mounting with the outlet at the top, prevents migration of larger particles that may clog the filters. Furthermore, clogging is prevented by the first two filters with pore sizes 2.0 μm which are mounted parallel to each other.

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

The sample volume is limited to a maximum of 2×190 mL.

The PVB sample containers are made of stainless steel which may contaminate the samples. An improvement could be to use Teflon coating on the insides of the cylindrical containers.

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

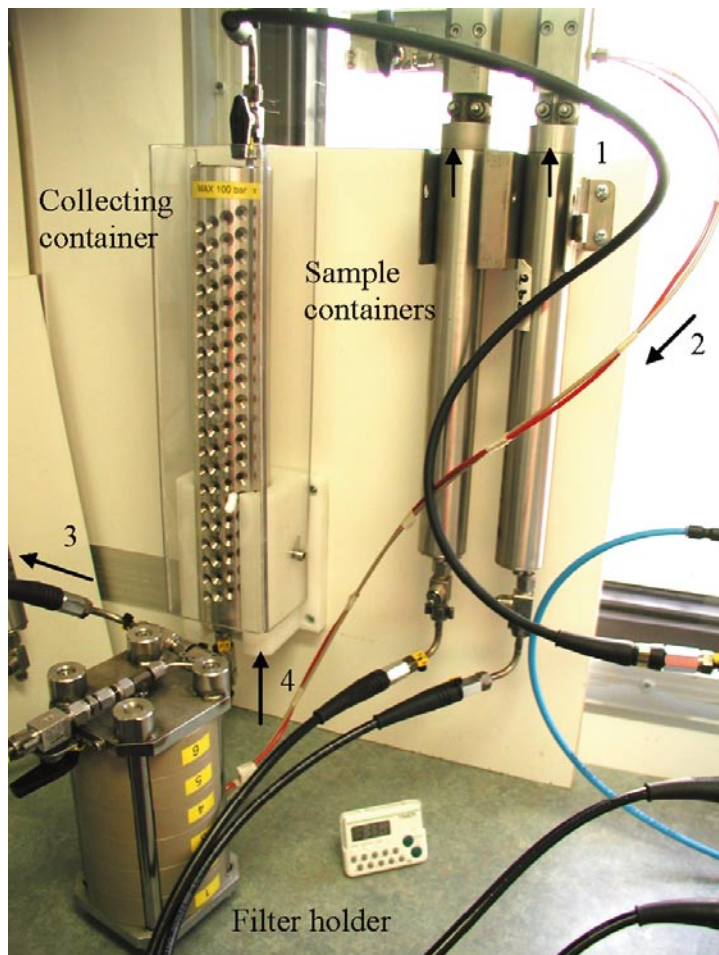


Figure 4-3. The colloid filtering equipment including the sample containers, the filter holder package and the collecting container. The black arrows, 1 to 4, show the flow direction of the sample water through the system.

4.3 Equipment for enrichment of humic and fulvic acids

Enrichment of humic and fulvic acids is conducted in order to collect enough material to determine $\delta^{13}\text{C}$ and pmC (percent modern carbon) on organic constituents in the groundwater. The equipment for enrichment includes a porous column filled with an anion exchanger (DEAE-cellulose) and a textile filter with a well-defined pore size. The textile filter is placed inside the column in order to prevent the ion exchange resin from diffusing through the column. The equipment and performance is described in SKB MD 431.044 (Mätssystembeskrivning för uppkoncentrering av humus- och fulvosyror, SKB internal controlling document). Figure 4-4 shows the equipment setup. Since the ion exchange resin in the column creates a counter-pressure, which disturbs the water flow through the surface Chemmac, a pump was used for pumping a portion of the outlet water through the column (approximately 2.4 L/hour).

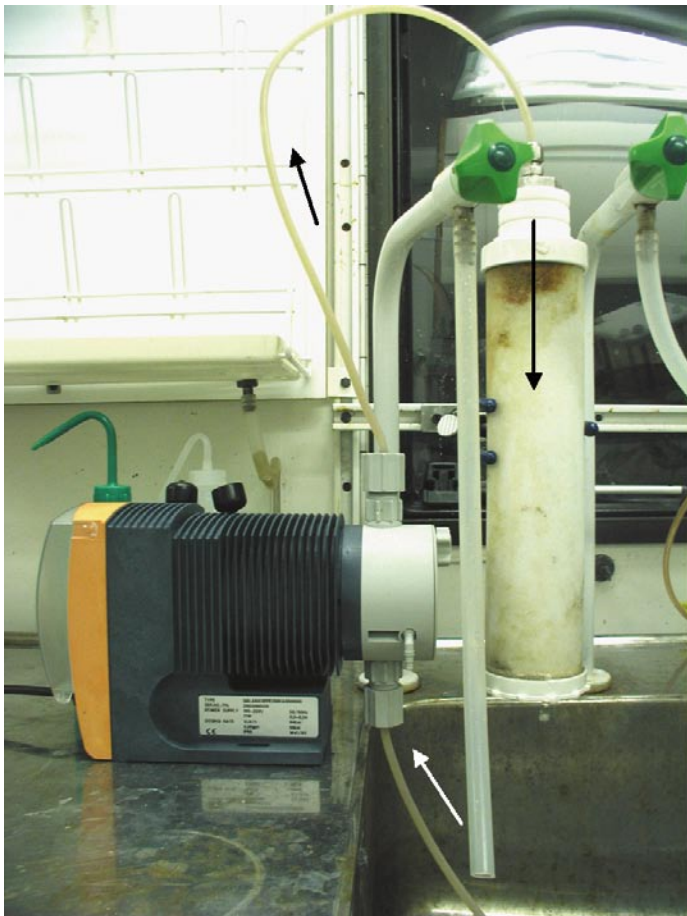


Figure 4-4. The ion exchange column. The arrows show the water flow direction.

4.4 Equipment for fractionation of humic and fulvic acids

The equipment consists of membrane filters with a defined cut-off (pore size), a membrane pump, flexible tubing and vessels. Generally, one water sample from each section is filtered through two filters with different pore sizes (1,000 D and 5,000 D, D=Dalton, 1D=1 g/mol). The equipment and performance are described in SKB MD 431.043 (Mätssystembeskrivning för fraktionering av humus- och fulvosyror, SKB internal controlling document). Figure 4-5 shows the equipment setup and Figure 4-6 schematically describes the function of a membrane.

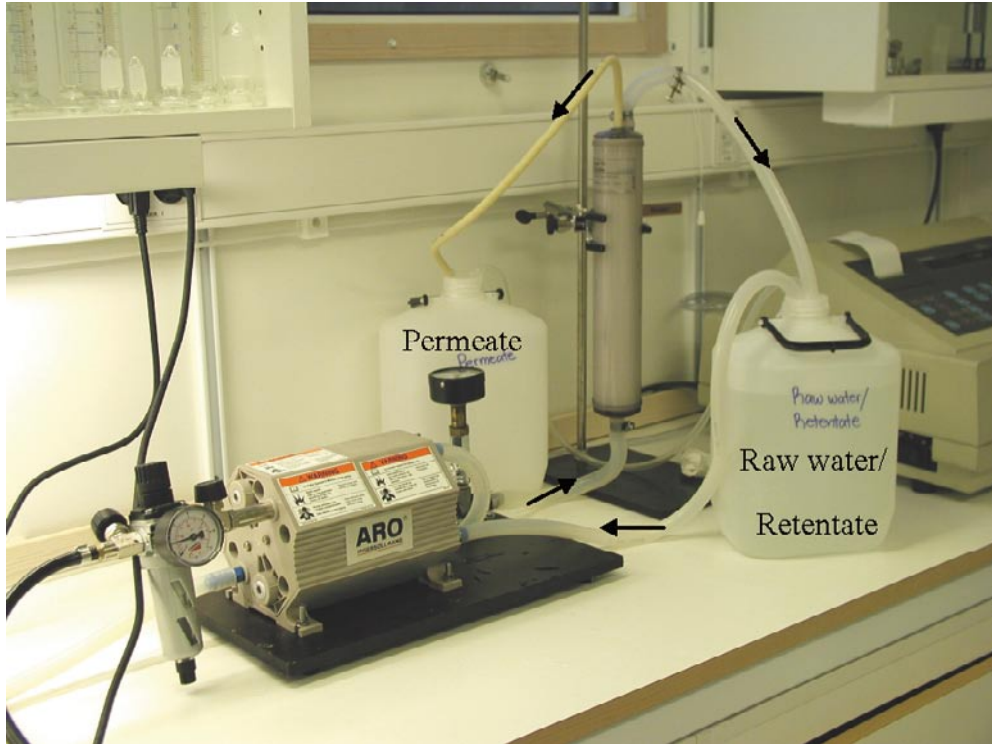


Figure 4-5. Equipment for fractionation of humic and fulvic acids.

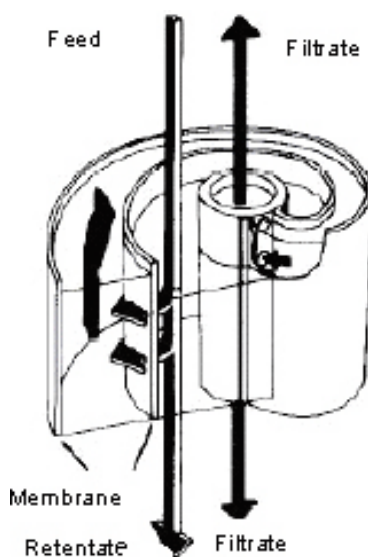


Figure 4-6. Outline of membrane filter with water flow directions.

5 Performance

5.1 General

Chemical characterisation in borehole KLX15A was conducted according to activity plan AP PS 400-07-053, SKB internal document, Table 1-1, following the method described in SKB MD 430.017 (Metodbeskrivning för fullständig karakterisering med mobilt fältlaboratorium). Table 5-1 gives an overview of the investigation sequence in KLX15A.

Table 5-1. Investigation sequence in KLX15A.

Start date/Stop date	Section (m)	Comment
2007-06-13/2007-08-07	623.00–634.5	Pumped volume = 14.6 m ³ Flow rate approx. 150–270 mL/min

5.2 Chemical characterisation

5.2.1 Overview of field work procedure

A short chronological summary of the different steps that constitute chemical characterisation of groundwater in a borehole section is given below. Preparations before the downhole equipment is lowered in the borehole include:

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

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

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

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

- Calibration of the pH and redox electrodes as well as the electrical conductivity and oxygen sensors in the surface Chemmac is conducted when the pumped water from the borehole section has reached the surface.
- Careful attention is paid to ensure that the packed-off section is well isolated from the rest of the borehole. A significant drawdown in the section during pumping is one indication that the section is properly sealed off. Leakage would cause pumping of water from the borehole column above and/or below the packers and not only from the fracture zone of interest. However, the drawdown in the borehole section must not be too large, because the greater the drawdown, the larger the bedrock volume affected by the pumping and the risk of mixing with groundwater from other shallower and/or deeper fracture systems increases. The pumping flow rate is adjusted depending on the flow yield from the fracture or fracture zone (to between 50 and 300 mL/min) and maintained more or less constant during the pumping and measurement period.
- Water samples are collected regularly once or twice a week during the pumping period. Changes in water composition are monitored by pH and conductivity measurements and by immediate analyses (pH, uranine, chloride, alkalinity, ammonium, ferrous and total iron).
- A decision when to terminate the sampling work in the section is made during a suitable stage of the pumping and measurement period. The investigation might be prolonged if the concentration of flushing water exceeds 1% or if the redox potential measurements have not reached stable values. A final SKB Class 5 sample including all options is collected the day before termination.

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

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

The following section (5.2.2) shortly describes the performance in the section 623.0 to 634.5 m. The main activities are presented in the events tables together with SKB sample numbers of the corresponding water samples.

5.2.2 Performance in section 623.0 to 634.5 m

The chemical characterisation in section 623.0 to 634.5 m was performed using the following configuration of the downhole equipment in the borehole. From the top: umbilical hose, length mark detector, borehole Chemmac, upper packer, borehole pump, *in situ* water sampler (PVP), and lower packer, see Appendix 4. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping flow rate varied between 150 and 250 mL/min and the drawdown was negligible during the entire measurement period. Diagrams showing the pressures above and within the borehole section and the flow rate during the pumping/measurement period are presented in Appendix 5. The events during the investigation are listed in Table 5-2.

Table 5-2. Events during the pumping/measurement period in section 623.0 to 634.5 m.

Date	Event	Sample no.
070613	Calibration of borehole Chemmac	
070614	Lowering of downhole equipment S2 (623.0 to 634.5 m) Start of borehole pump and Chemmac measurements Calibration of surface Chemmac	
070615	Water sampling: uranine	11925
070617	No measurement values.	
070618	Water sampling: SKB class 2	11926
070619	Restart of measurement system. No contact with borehole Chemmac	
070620	Regained contact with borehole Chemmac after de mounted opto switch. Lifting. No contact with borehole Chemmac. Borehole Chemmac changed and calibrated. Borehole pump changed. Lowering of downhole equipment S2 (623.0 to 634.5 m) Start of borehole pump and Chemmac measurements	
070625	Water sampling: SKB class 2	11927
070626	No temperature and pressure measurement in borehole. Restart of measurement application. Pressure and temperature logging.	
070628	Water sampling: SKB class 5	11928
070630	Power failure due to thunderstorm.	
070701	Restart of measurement application.	
070702	Water sampling: SKB class 5	11929
070704	Water sampling: SKB class 5 Pumping interrupted due to broken spring in the borehole pump.	11930

Date	Event	Sample no.
070705	Lifting of equipment and repair of borehole pump. Lowering of downhole equipment S2 (623.0 to 634.5 m) Lifting due to high power consumption. Lowering of downhole equipment S2 (623.0 to 634.5 m) Start of borehole pump and Chemmac measurements Calibration of oxygen meter.	
070706	Water sampling: SKB class 4	11931
070709	Water sampling: SKB class 5	11932
070711	Water sampling: SKB class 4	11933
070712	High power consumption. Loss of water in water tank supplying the driving pump and borehole pump. High power consumption.	
070713	Water sampling: SKB class 4	11934
070715	PVP-sampler: opening of valve at 17:27	
070716	Water sampling: SKB class 4 (except pH, conductivity, alkalinity, Fe ²⁺ , Fe _{tot} , NH ₄ ⁺ , HS ⁻). PVP-sampler: closure of valve at 06:31 Sampling for microbes and dissolved gases Stop of pump and end of Chemmac measurements	11935 15008
	Lifting Calibration of borehole Chemmac High power consumption, malfunction of length mark detector. Length mark detector de mounted. Lowering of downhole equipment S2 (623.0 to 634.5 m) Start of Chemmac measurements and borehole pump	
070717	Calibration of surface Chemmac Humic and fulvic acids; fractionation 1,000 D and 5,000 D	15008
070724	Stop of pump, pump spring broken.	
070725	Lifting Changing of pump spring Lowering of downhole equipment S2 (623.0 to 634.5 m) Start of Chemmac measurements and borehole pump Lifting, due to no flow. Changing of non-return valve on borehole pump. Lowering Start of borehole pump	
	Water sampling: uranine	15027
070726	Water sampling: SKB class 5	11983
070727	Communication lost, due to thunderstorm	
070731	Communication problem, due to thunderstorm	
070801	Printed circuit card and opto swith changed. Water sampling: SKB class 5 (U, Th isotopes not analysed)	15028
070806	Water sampling: SKB class 5 including all options Water sampling: SKB class 5, control sample Stop of borehole pump at 15:57	15008 15009
070807	PVP-sampler: opening of valve at 04:44 and start of borehole pump Sampling for colloids (analysis with ICP, LIBD and SEM) PVP-sampler: closure of valve at 06:03 Stop of borehole pump Calibration of borehole Chemmac Colloid filtration Calibration of surface Chemmac End of Chemmac measurements Lifting	15008

5.3 Water sampling, sample treatment and analyses

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

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

5.4 Collection of *in situ* water samples

The *in situ* water sampling was conducted successfully in section 623.0 to 634.5 m. The *in situ* sampling was repeated in order to increase the number of samples and includes in addition to the colloid determination using laser-induced breakdown detection, LIBD (Appendix 7), a colloid filtering experiment intended for a study by SEM /7/. Occasionally, in previous samples analysed by the LIBD technique, unreasonably high colloid contents have been observed. In order to investigate possible effects on the colloid content in the PVB containers, the borehole pump was stopped prior to opening of the valves of the containers during the *in situ* sampling for ICP, LIBD and SEM.

Dissolved gases were analysed by two independent laboratories. The purpose of each sample portion is given in Table 5-3.

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

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

Sample portion no.	Section 623.0–634.5 m 2007-07-16	Section 623.0–634.5 m 2007-08-07
1	Dissolved gas (Laboratory 1) N ₂	Colloids (Filtration – ICP)
2	Dissolved gas (Laboratory 2) N ₂	Colloids (Filtration – SEM)
3	Microbes	Colloids (LIBD)
4	Microbes	Colloids (LIBD)

5.5 Colloid filtration

Colloid filtration was performed in section 623.0 to 634.5 m. The method for sampling of colloids in groundwater entails filtering the groundwater through a series of connected filters in a closed system under an argon atmosphere. The pressure in the system is maintained at the same level as the pressure in the sampled borehole section. The intention is that colloids should be collected on the different filters (descending pore sizes) according to their sizes. Two of the four sample portions collected *in situ* in the borehole section 2007-08-07 are used for colloid filtration, analysis with two different methods. Data on performance of the filtration runs are given in Table 5-4.

The general filtration method that normally is used to obtain colloid samples for ICP-MS determinations was somewhat modified prior to performance of the filtering intended for SEM studies. The most important stages are filtering of one instead of two PVB containers, flushing of the filters with de-ionised water and handling of the filters in argon atmosphere. The modifications are documented in the activity plan AP PF 400-07-029, SKB internal document.

Each filtration results in five filter samples (two 2.0 µm, one 0.4 µm, one 0.2 µm and one 0.05 µm filter pore sizes) and two water samples (water in and water out). All samples from the filtration run “Filtration – ICP” and the water samples from “Filtration – SEM” were sent for ICP-MS analyses (major constituents and common trace metals).

A leakage test of the system at 10 bar, using deionised water, was also done prior to the sampling in order to eliminate the risk of leakage. No leakage was detected and the system was dried and assembled. The filters used during the test were sent for analysis of metals as blank samples.

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

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

Section / date	Entering pressure [bar]	Max. differential pressure over filter package [bar]	Temp. [°C]	Filtering time [min]	Filtered volume [ml]	Comments
623.0–634.5 m /2007-08-07 Filtration – ICP	~47.5	2.8	~17	25	162.5	Leakage test prior to filtration. No leakage was noticed.
623.0–634.5 m /2007-08-07 Filtration – SEM	~47.5	3.6	~18	16	150	Leakage test prior to filtration. No leakage was noticed.

5.6 Enrichment of humic and fulvic acids

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

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

5.7 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 (Mätssystembeskrivning för fraktionering av humus- och fulvosyror, SKB internal controlling document). Fractionation of humic and fulvic acids were made on samples from section 623.0 to 634.5 m.

Sampled water from the investigated sections was first filtered through a 0.45 μm filter and then filtered through membrane filters with cut-off sizes of 1,000 D and 5,000 D, respectively. The initial water volume, prior to filtration, was approximately 5 litres. The final retentate and permeate volumes following the filtration runs were approximately 1 and 4 litres, respectively, which gave an enrichment factor of five in the retentate.

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

5.8 Nonconformities

The *Complete chemical characterisation* in KLX15A has been conducted according to the SKB internal controlling documents AP PS 400-07-053 and SKB MD 430.017 with the following deviations and remarks:

- The allowed upper limit for flushing water content, 1%, was exceeded (4.4%).
- Extended investigation due to high flushing water content and slow response of electrodes (unstable values).
- Some equipment malfunctions were encountered during the investigation:
 - defective spring in borehole pump,
 - defective length mark detector,
 - loss of connection with the borehole Chemmac,
 - defective PVB container for gas analysis.

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

Borehole section [m]	Duration of enrichment [days]	Volume through ion exchanger [L]
623.0–634.5 m	22	1,400

6 Data handling and interpretation

6.1 Chemmac measurement data

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

6.1.1 Data file types and calculation software

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

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

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

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

6.1.2 Calculations and evaluation of pH and redox potential

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

- Calculation and choice of calibration constants.
- Calculation of one pH and one redox potential sequence for each electrode (i.e. three or six redox electrodes and two or four pH electrodes).
- Determination of representative pH and redox potential values as well as estimated measurement uncertainties for the investigated borehole section.

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

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

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

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

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

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

6.2 Water analysis data

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

Some components are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure on each fifth or tenth collected sample. All analytical results are stored in the SICADA database. The applied

hierarchy path “Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database” contains two types of tables, raw data tables and primary data tables (final data tables).

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

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

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

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

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

An overview of the data management is given in Figure 6-1.

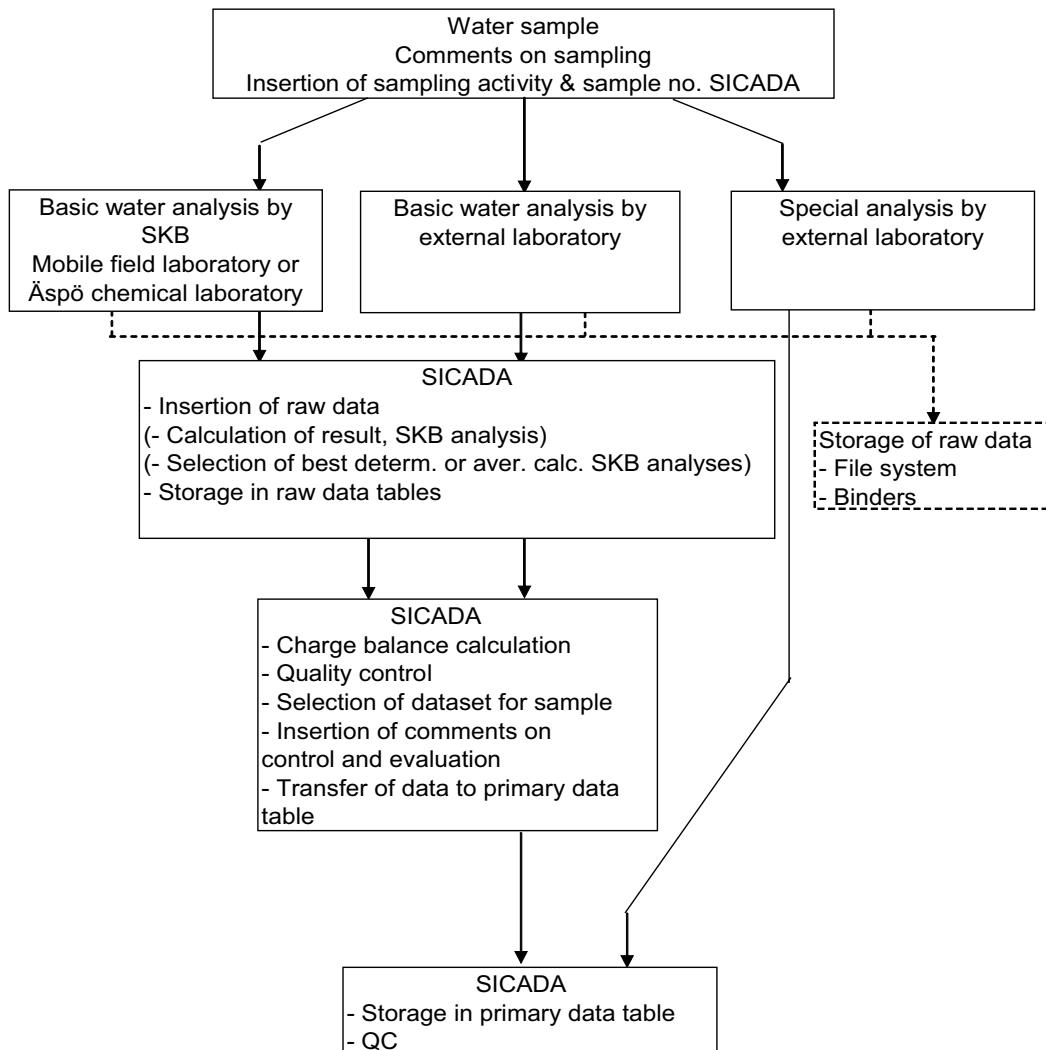


Figure 6-1. Overview of data management for hydrogeochemical data.

6.3 Data from special sampling methods

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

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

6.3.1 Colloid filtration

The concentration of the colloid portion caught on each filter (from the filtration followed by detection with ICP-MS) is calculated with the assumption that the water volume coming out in the collecting container is equal to the volume going into the system. This is not quite true as up to ten millilitres will be left in cavities in the filter holder package, in the tubing and in valves. A small volume of about 0.01 to 0.06 mL is left in each filter after the filtration and its content of the different elements is included in the analysis. The measurement uncertainty of each colloid concentration is calculated from the “sum” of the measurement uncertainties of the filter analyses and estimated volume error (volume passing through the filters) according to the equation below:

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

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

The 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.

6.3.2 Dissolved gases

The results of the gas analysis are stored in the primary data tables in SICADA. The gas results reported in SICADA correspond to values not corrected for air contamination. The results from laboratory number 2 are not presented in this report due to intrusion of air during analysis.

6.3.3 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.

6.3.4 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, (Mätsystembeskrivning för fraktionering av humus- och fulvosyror, SKB internal controlling system). Comparison of the four concentration values from the two filters results in values for three fractions i.e. less than 1,000 D, 1,000 to 5,000 D and more than 5,000 D.

7 Results

Original data from the reported activity are stored in the primary database Sicada. Data are traceable in Sicada by the Activity Plan number (AP PS 400-07-053). Only data in the database are accepted for further interpretation and modelling. The data presented in this report are regarded as copies of the original data. Data in the databases may be revised, if needed. However, such revision of the database will not necessarily result in a revision of this report, although the normal procedure is that major data revisions entail a revision of P-reports. Minor data revisions are normally presented as supplements, available at www.skb.se.

7.1 Chemmac measurements

The data sequences of pH, Eh, electrical conductivity, oxygen and temperature values from the Chemmac measurements in borehole section 623.0 to 634.5 m are plotted versus time in Appendix 6. The measured time series were evaluated in order to obtain a representative value of pH, Eh, electrical conductivity and dissolved oxygen for the borehole as described in Section 6.1. Data were selected from the last part of the measured time series sequences (where the electrodes show stable values), marked with an arrow in the diagrams. The evaluated results from the measurements in the investigated section are given in Table 7-1 together with the corresponding results from the LIBD measurement.

The redox potentials of the electrodes in borehole and surface Chemmac were not stable or consistent. The readings from the borehole electrodes were slightly negative at the end of the measurement period (range -18 mV to -52 mV). During the investigation there were several interruptions in the measurements due to equipment malfunctions and in addition the response of the electrodes was slow. When lifting the equipment and recalibrating, a thin white film was observed on the electrodes. A possible explanation for the film and slow response of the electrodes could be an abundance of drilling debris from drilling of the borehole. The redox potentials measured in the LIBD containers were positive; 11 and 24 mV, respectively. The results are consistent with the on line measurement; the measured redox potentials were positive at the end of the measurement period due to stop of the borehole pump (and water flow) some hours before sampling the PVB containers.

The pH electrodes at the ground surface and in the borehole were consistent and stable.

Table 7-1. Evaluated results from the Chemmac and LIBD measurements in KLX15A.

Borehole section [m]	Electrical conductivity* [mS/m]	pH (borehole chemmac)**	pH (surface chemmac)**	Eh [mV]	Dissolved oxygen*** [mg/L]
623.0–634.5	1,690 ± 50	7.7 ± 0.2	7.5 ± 0.3	–	0.01 ± 0.01
623.0–634.5 PVB (LIBD)(1)****	1,589	–	7.63	11	< 0.277
623.0–634.5 PVB (LIBD)****	1,576	–	7.62	24	< 0.036

*The electrical conductivity is measured between 0–10,000 mS/m with a total uncertainty of 3%.

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

*** Measurement interval 0–15 mg/L, resolution and measurement uncertainty ± 0.01 mg/L

**** See Appendix 7

– A representative Eh value was not chosen since the recorded redox potentials were unstable and inconsistent.

7.2 Water analyses

7.2.1 Basic water analyses

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

The charge balance errors give an indication of the quality and uncertainty of the analyses of major constituents. The errors exceed $\pm 5\%$ in one case (6.6%). The last sample in the section was analysed by a second laboratory. A comparison between results from different laboratories and methods shows that the agreement is acceptable in most cases; the difference is in general less than 10% for each analysed constituent.

The flushing water contents in the samples collected from the borehole sections are presented in Figure 7-1. The flushing water content should not exceed 1% in order for a sample to be considered representative for the groundwater of the sampled fracture zone. This condition was not met for any of the samples collected in section 623.0 to 634.5 m; the flushing water content was 4.4% at the end of the measurement period. The flushing water content is calculated using the average uranine concentration in the added flushing water during core drilling.

The concentration levels of sodium, calcium and chloride are presented in Figure 7-2.

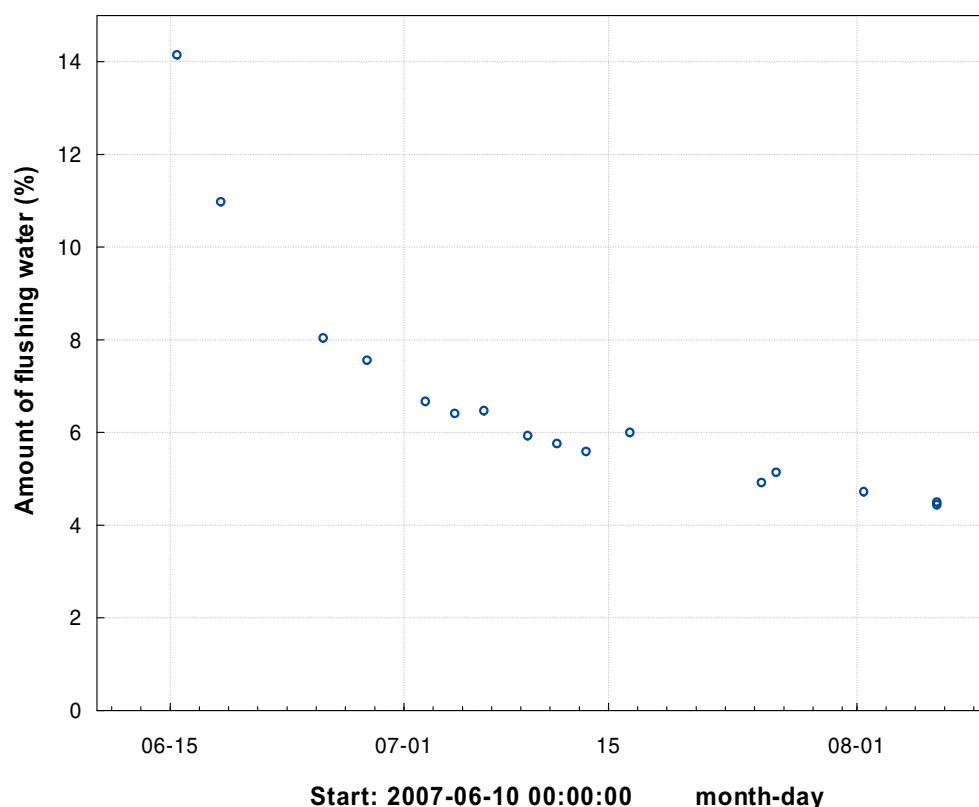


Figure 7-1. Flushing water content in the samples collected during pumping in borehole KLX15A section 623.0 to 634.5 m.

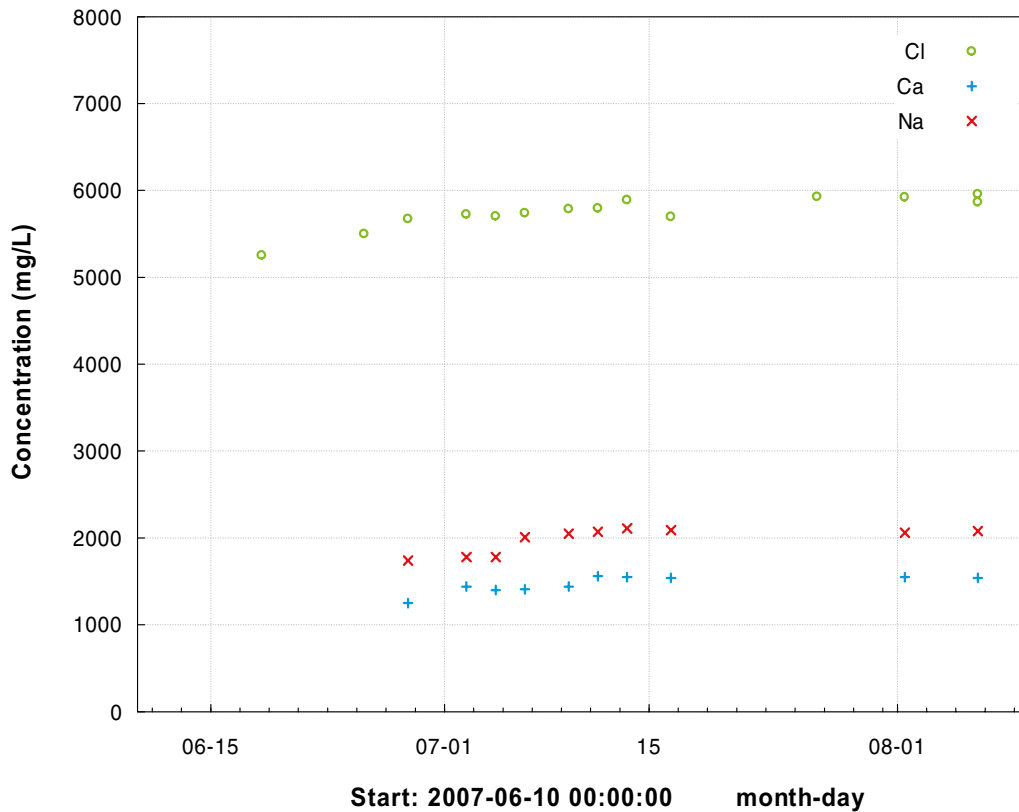


Figure 7-2. Sodium, calcium and chloride concentration trends from sample series at KLX15A 623.0 to 634.5 m.

The iron concentrations determined by ICP-AES (total Fe) and by spectrophotometry (Fe (+II) and Fe-tot) are compared in Figure 7-3. The total iron concentrations determined by ICP agree reasonably well with the results obtained by spectrophotometry.

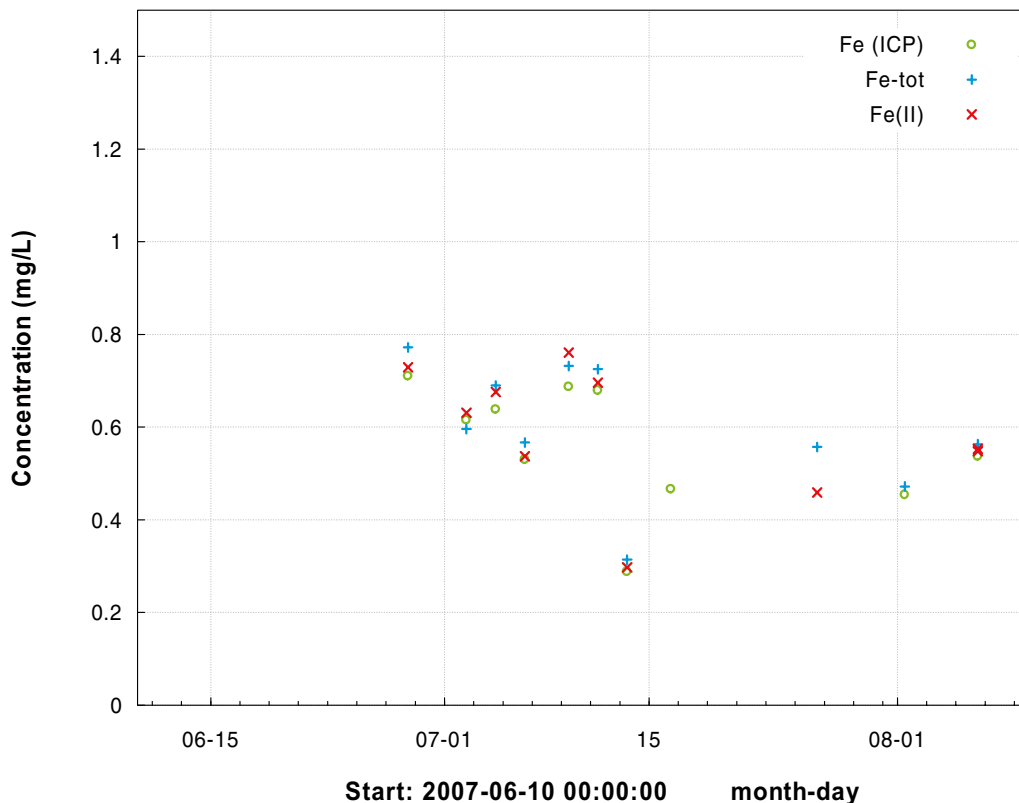


Figure 7-3. Comparison of iron concentrations obtained by ICP-AES and by spectrophotometry, borehole KLX15A section 623.0 to 634.5 m.

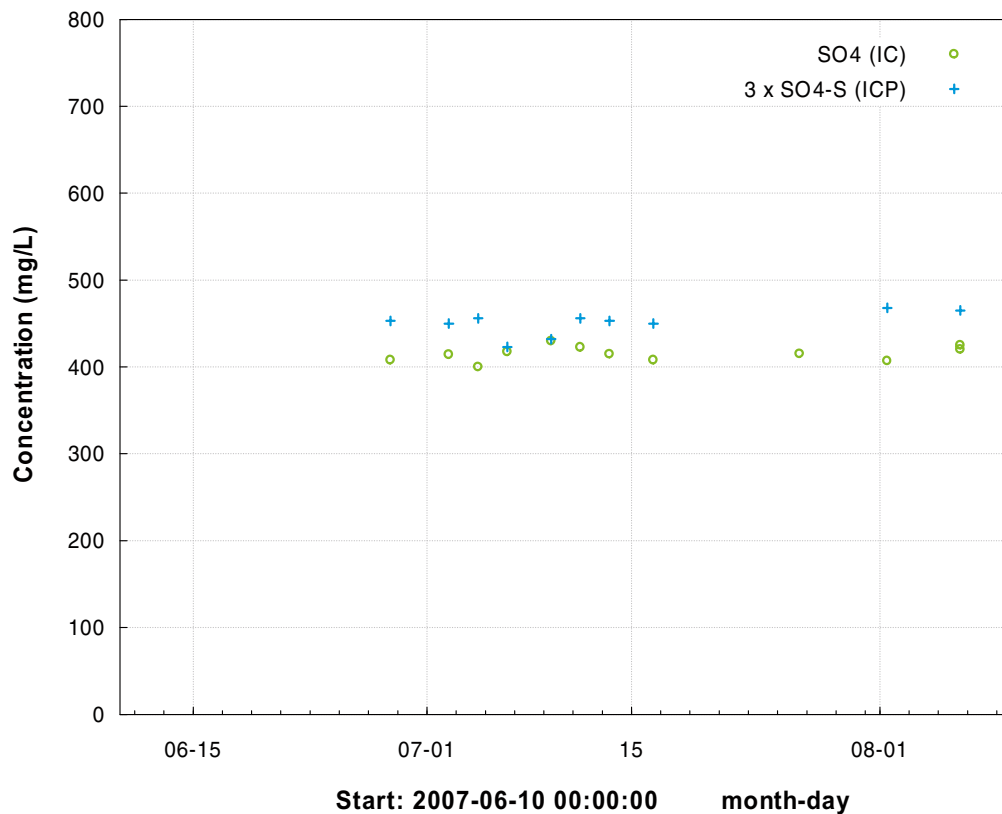


Figure 7-4. Sulphate (SO_4 by IC) and sulphate calculated from total sulphur ($3 \times SO_4-S$ by ICP) versus date, borehole KLX15A section 623.0 to 634.5 m.

Sulphate analysed by ion chromatography (IC) is compared with sulphate determined as total sulphur by ICP-AES in Figure 7-4. The sulphate concentrations remained more or less constant during the investigation sequence and the differences between the IC results and the ICP results are within the analytical error.

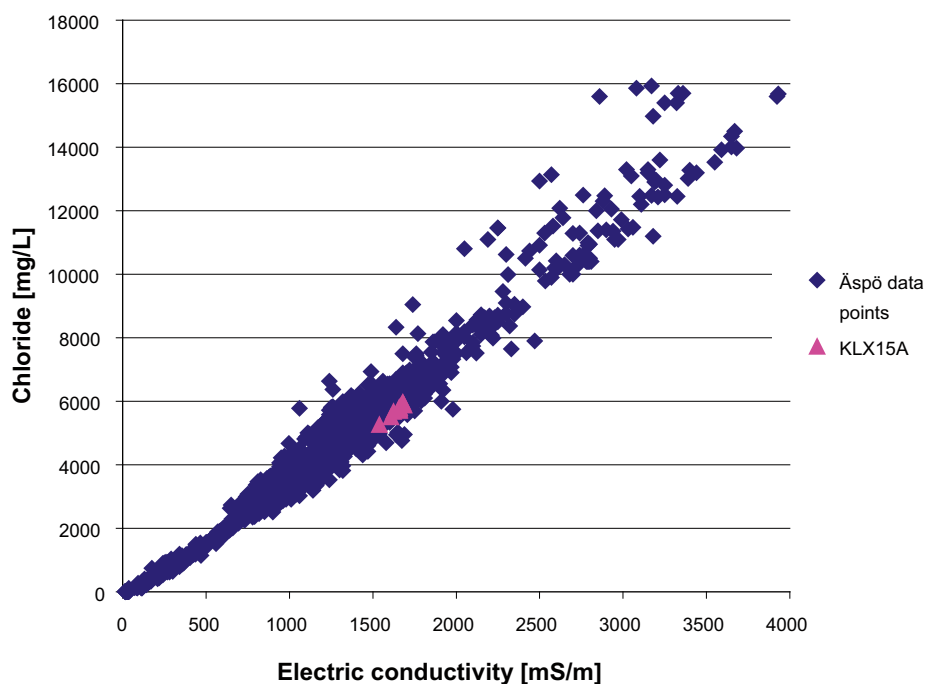


Figure 7-5. Chloride concentration versus electrical conductivity. Data from earlier investigations at the Äspö Hard Rock Laboratory are used to show the linear relationship. The data from KLX15A are consistent with previous investigations.

The chloride concentrations are plotted versus the corresponding electrical conductivity values in Figure 7-5. The plot gives a rough check of the data. As shown, the data from the borehole sections agree well with data obtained by earlier investigations from the Äspö Hard Rock Laboratory.

7.2.2 Trace elements (rare earth metals and others)

The analyses of trace and rare earth metals include U, Th, As, Sc, Cd, Hg, V, Rb, Y, Zr, In, Cs, Ba, 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 A9-2.

7.2.3 Stable and radioactive isotopes

The isotope determinations include the stable isotopes ^2H , $\delta^{18}\text{O}$, $^{10}\text{B}/^{11}\text{B}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ as well as the radioactive isotopes ^3H (tritium), ^{14}C (pmC), ^{238}U , ^{234}U , ^{230}Th , ^{226}Ra and ^{222}Rn . Isotope data are compiled in Appendix 9, Tables A9-3 and A9-4. The B-isotope ratio is given as $^{10}\text{B}/^{11}\text{B}$ (the result reported from the consulting laboratory). If one wants to use the notation according to international standard for environmental isotopes, $^{11}\text{B}/^{10}\text{B}$, it is necessary to invert the $^{10}\text{B}/^{11}\text{B}$ value ($1/^{10}\text{B}/^{11}\text{B}$).

The ^3H and $\delta^{18}\text{O}$ results are presented in Figure 7-6. The $\delta^{18}\text{O}$ ratios remained stable during the sampling periods.

$\delta^{13}\text{C}$ and pmC were determined both in inorganic carbon (hydrogen carbonate) and in organic constituents. The results are presented in Table 7-2. Enrichment of organic carbon was necessary in order to collect enough organic material.

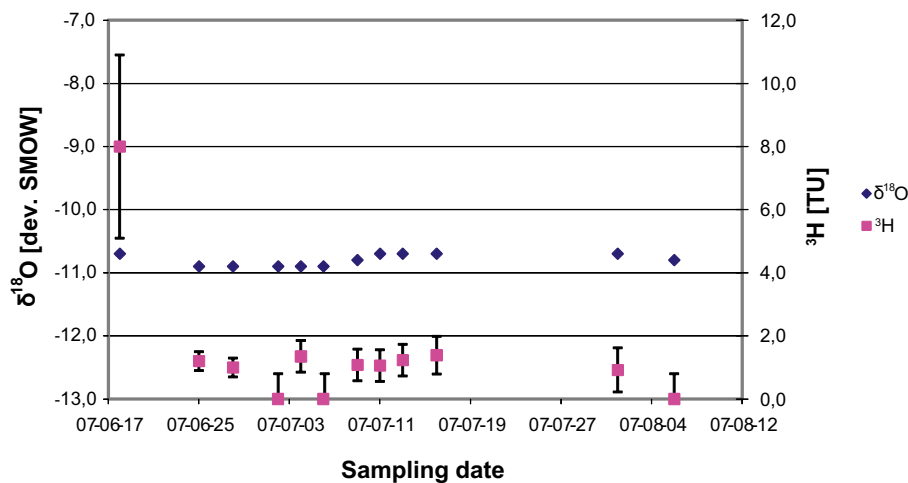


Figure 7-6. ^3H and $\delta^{18}\text{O}$ (‰ SMOW) data versus sampling data, KLX15A section 623.0 to 634.5 m.

Table 7-2. Inorganic and organic $\delta^{13}\text{C}$ and pmC in water samples from KLX15A.

Borehole section (m)	Inorg. $\delta^{13}\text{C}$ (dev. PDB)	Org. $\delta^{13}\text{C}$ (dev. PDB)	Inorg. pmC	Org. pmC
623.0–634.5	*	-26.4	*	3.6

* No result, analytical procedure could not be performed due to low alkalinity.

7.3 Dissolved gas

Sampling for gas was performed in section 623.0 to 634.5 m in two PVB, *in situ* water sample portions. The analyses were performed at two different laboratories, however, one of the analyses turned out unsuccessful because of air intrusion during analysis. Nitrogen gas was used for purging the samples. The analyses of dissolved gases include argon (Ar), helium (He), nitrogen (N₂), carbon dioxide (CO₂), carbon monoxide (CO) methane (CH₄), oxygen (O₂), hydrogen (H₂), ethane (C₂H₆), ethene (C₂H₄), ethyne (C₂H₂), propane (C₃H₈) and propene (C₃H₆). The gas data are presented in Appendix 9, Table A9-5.

Total gas content in the groundwater as well as the detected oxygen content is given in Table 7-3. The oxygen content indicates air leakage into the purging system at the consulted laboratory. The effects of air leakage may be corrected for, assuming that the oxygen content is zero, by removing the air effect (nitrogen, oxygen and argon).

The gas composition of the analysed sample from the section is presented in Figure 7-7 and 7-8.

Table 7-3. Total content of dissolved gas in KLX15A.

	Section 623.0–634.5 m (2007-07-16)
Total gas content [mL/L]	87
Oxygen content [mL/L]	0.089

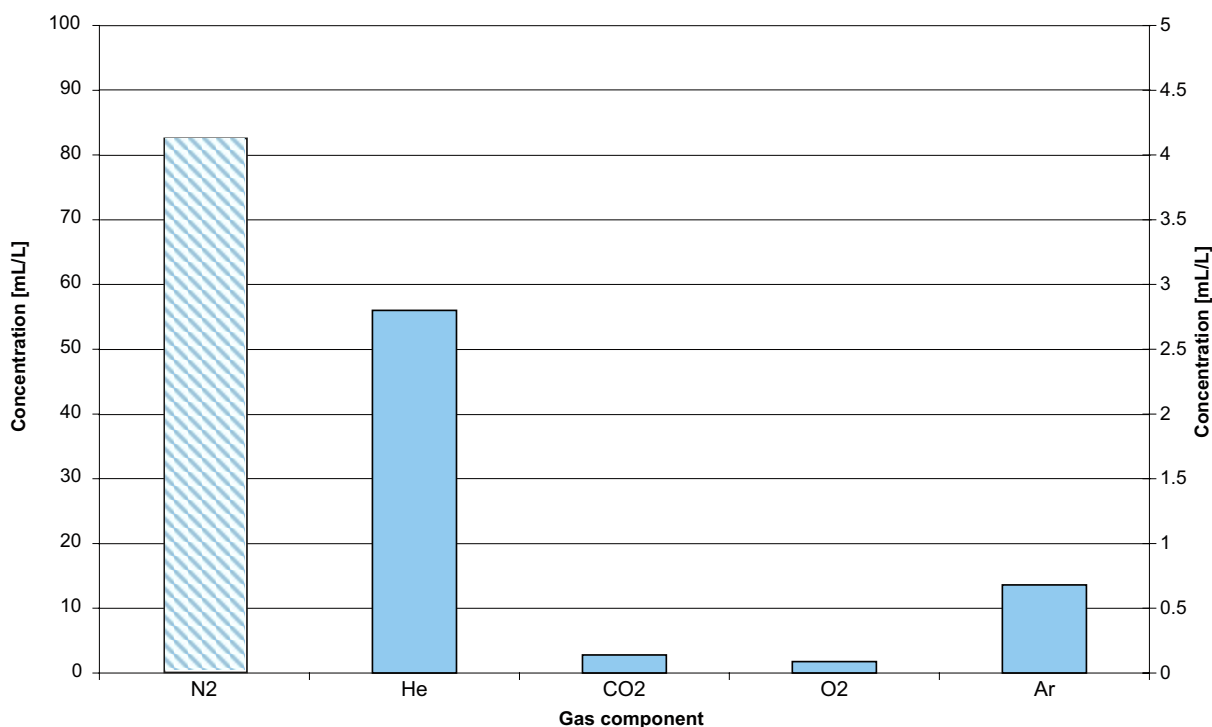


Figure 7-7. Gas components of high concentrations (N₂, He, CO₂, O₂, Ar and CH₄) in samples collected in KLX15A using the *in situ* sampling equipment. Striped and non-striped bars refer to the scales on left and right axis, respectively.

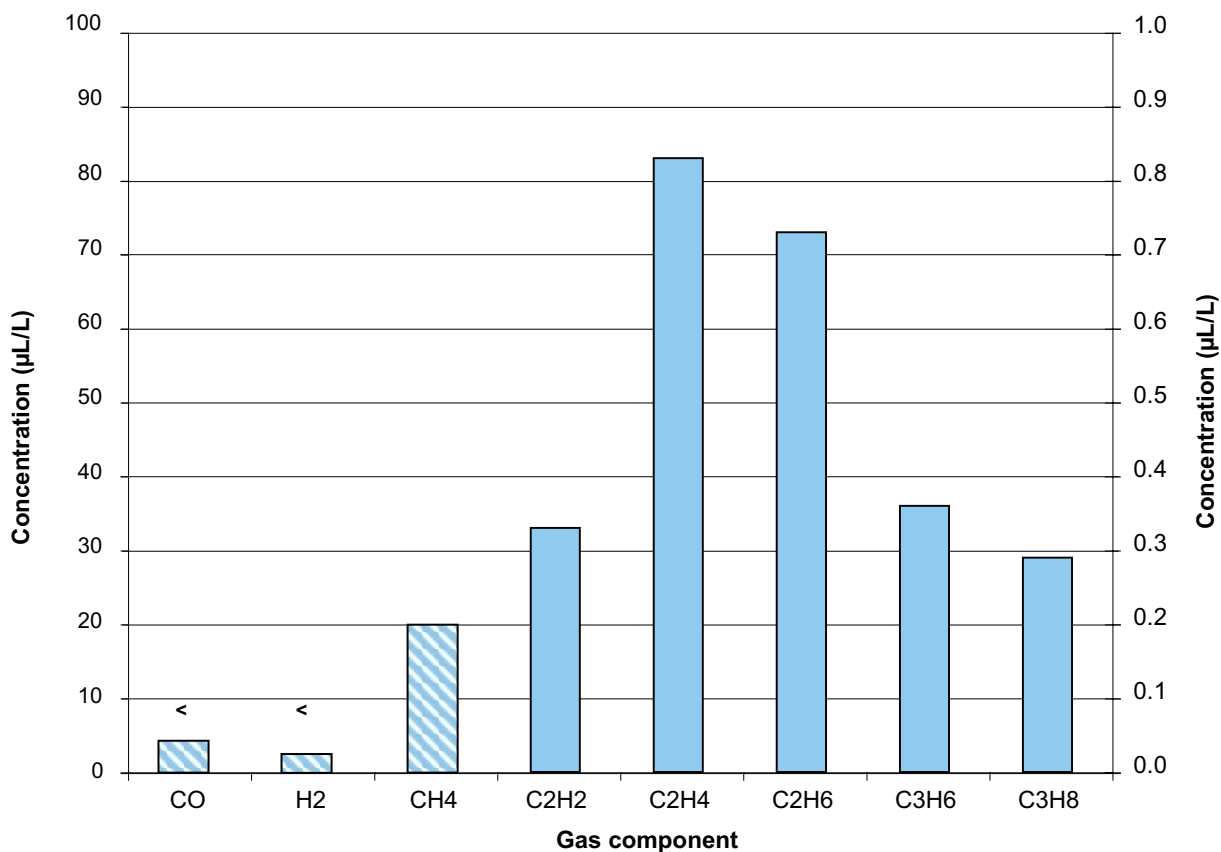


Figure 7-8. Gas components of low concentrations (CH_4 , CO , H_2 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 and C_3H_6) in samples collected in KLX15A using the in situ sampling equipment. Striped and non-striped bars refer to the scales on left and right axis, respectively.

7.4 Inorganic colloids

The presence of colloids in section 623.0 to 634.5 m was investigated using three methods; 1) filtration through a series of connected filters in an argon atmosphere (detection by ICP-MS, “Filtration – ICP” and by SEM, “Filtration – SEM” /7/, 2) fractionation/ultra filtration using cylindrical membrane filters with a cut-off of 1,000 D and 5,000 D 3) Laser-Induced Breakdown Detection, LIBD, Appendix 7.

The results from the two methods 1) and 2) are difficult to compare quantitatively but a qualitative agreement is identified. However, method 1) and 3) can be compared and the results from “Filtration – ICP”, “Filtration – SEM” and the LIBD determinations are presented in Table 7-4. The results from the filtration run are corrected by considering the remaining water volume in each filter (indicated by the sodium content) and excluding the amounts of the different dissolved elements. As the results of the blank filters were generally high, these values were also subtracted from the results. Furthermore, the analysed elements are re-calculated to amounts of their most probable mineral phases (iron hydroxide, manganese hydroxide and calcium carbonate). Sulphur is not re-calculated, as there are many possible mineral phases. The results from the four methods are difficult to compare quantitatively but a qualitative agreement is identified.

The table illustrates the difficulties associated with colloid determinations. Generally, it is expected that the measured colloid concentrations turn out higher than the natural amount of background colloids in the groundwater as additional colloids are easily generated by artefacts. The sources may be:

- Oxygen intrusion and formation of iron hydroxide.
- Decrease of pressure and precipitation of calcite.
- The sampling process or the equipment.

Table 7-4. Colloid concentrations measured in the groundwater sample from section 623.0 to 634.5 m. Comparison of results obtained by “Filtration – ICP”, “Filtration – SEM” and LIBD.

Filtration through series of connected filters							LIBD/SEM		
Idcode/ secup/ filter pore size (µm)	Filtrate volume (mL)	Element content on each filter per litre of water (µg/L)				Mineral phases (µg/L)		Idcode/ secup/ run no.	Content (µg/L)
		Fe	Mn	Ca	S	Total/ filter*	Sum**/ three filters		
KLX15A/ 623.0/0.4	162.5	0	0	0	0	0		KLX15A/ 623/1	< 1–5/20
KLX15A/ 623.0/0.2	162.5	0	0	0	0	0			
KLX15A/ 623.0/0.05	162.5	0.38	0.02	48	20	140	140	KLX15A/ 623/2	0.008–4/ –

* Total content on each filter. Iron is calculated as Fe(OH)₃ (106.8 g/mol), manganese is calculated as Mn(OH)₂ (88.9 g/mol), calcium as calcium carbonate (100.0 g/mol).

** Sum of content (mineral phases) on the three filters.

7.4.1 Inorganic colloids – colloid filtration

The results from the colloid filtration (Filtration – ICP) performed in section 623.0 to 634.5 m are presented in Figures 7-9 to 7-14.

Note that the filter leaching method at the consulted laboratory has been changed, compared with former colloid filtration studies. The nitric acid has been replaced by hydrofluoric acid, as the amounts of silicon seem to have been underestimated before.

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

The concentrations in blank samples (rinsing water), PVB-containers, collecting container and pumped groundwater are given in Table 7-5. The evaluation is complicated for iron and silicon since precipitation reactions and/or contamination has to be considered.

The amounts of aluminium detected on the blank filters from the leakage test were of the same magnitude as the amounts on the sample water filters. As the concentrations are very low and thereby have large analytical uncertainties, it is difficult to draw any conclusions.

The iron concentrations in the outgoing water are much lower than the amount detected in the pumped groundwater after passing the filters despite that low amounts are detected on the filters. This could be caused by precipitation of iron after passing the filtering system, possibly in the collecting container. Or, precipitation of iron might occur in the PVB container which would reduce the actual input concentration. Also for iron, the amounts on the blank filters were of the same magnitude as on the sample water filters.

The amounts of silicon detected on the blank filters from the leakage test were extremely high, and even slightly higher than the amounts on the sample water filters. As the concentrations of silicon in the incoming blank water were very low, contamination somewhere along the process of handling the filters must have occurred. The amount of silicon in the incoming sample water together with the amounts of silicon on the filters is not in balance with the outgoing water. Two blank filters where no water has passed have been analysed and low amounts of silicon (11.5 and 12.9 µg) were found on them.

The amounts of manganese and calcium were low, also on the blank filters. The sulphur content was higher and of the same magnitude in the sample filters as well as on the blank filters.

The following may be concluded from the colloid filtration results:

- The amounts present as colloidal aluminium and iron are somewhat difficult to evaluate since the output amount plus the amount collected on filters does not balance the input amount. The reasons for this are contamination and/or precipitation in the PVB containers or in the collecting container.
- Low amounts of the investigated metals are detected on the sample filters, except for silicon. The reason was most probably contamination.
- The amounts on the blank filters were high, and often of the same magnitude as in the samples.

Table 7-5. Concentrations in deionised water, remaining water in PVB container (deionised and borehole water), pumped water that has not passed the filter system and collected output water from the filter system, “Filtration – ICP”.

Section m	Sample origin	Al µg/L	Fe mg/L	Si mg/L	Mn µg/L	Ca mg/L	S mg/L
623.0–634.5	Blank, deionised water	< 0.7	0.0048	0.0651	0.904	< 0.1	< 0.2
	Blank, leakage test	2.25	0.0062	0.0381	2.62	< 0.1	< 0.2
	Pumped water (alt. input conc.)	1.31	0.556	5.46	545	1,580	154
	Rest volume PVB (input conc.)	1,800	3.41	6.27	646	1,490	152
	Collecting container	2.16	2.04	5.31	573	1,480	148

Blank, leakage test = remaining water in the PVB container after filtration of blank sample/de-ionised water.

Pumped water = sample collected at the surface and not *in situ* in the borehole section.

Rest volume PVB = remaining water, from the borehole section, in the PVB container after filtration of sample.

Collecting container = water from the borehole section that has passed the filter system.

Results of colloid filtering experiment, using water sample from borehole KLX15A section 623.0 to 634.5 m “Filtration – ICP”.

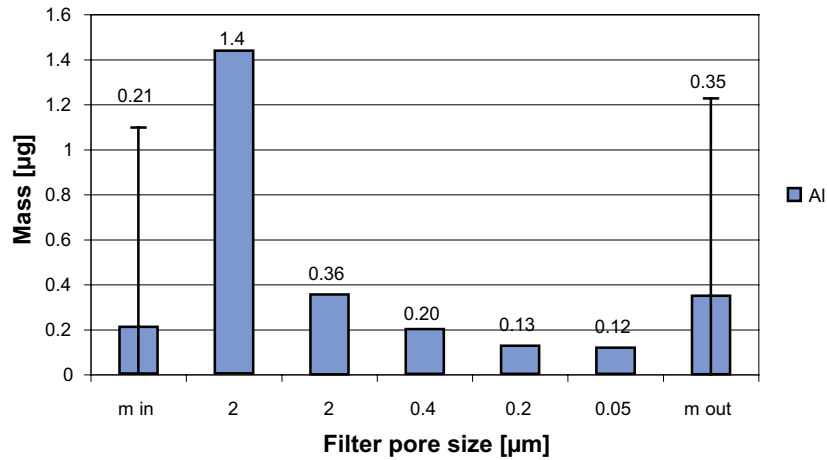


Figure 7-9. Amount of aluminium entering the filter system (m in), in the filters and in the collecting container (m out).

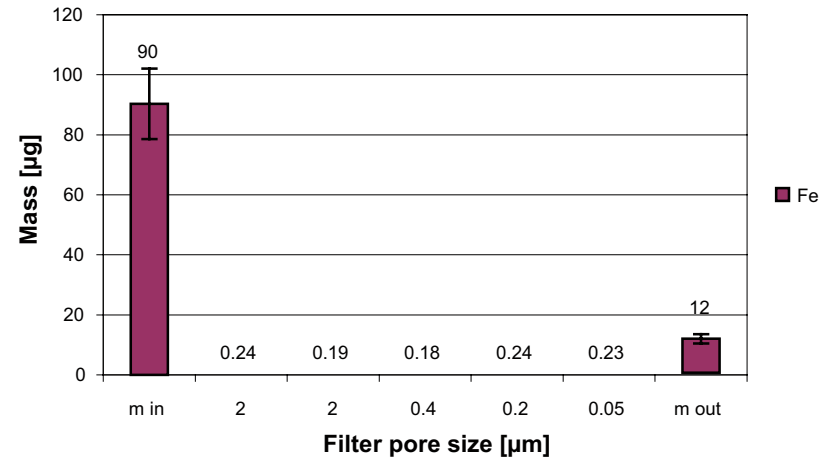


Figure 7-10. Amount of iron entering the filter system (m in), in the filters and in the collecting container (m out).

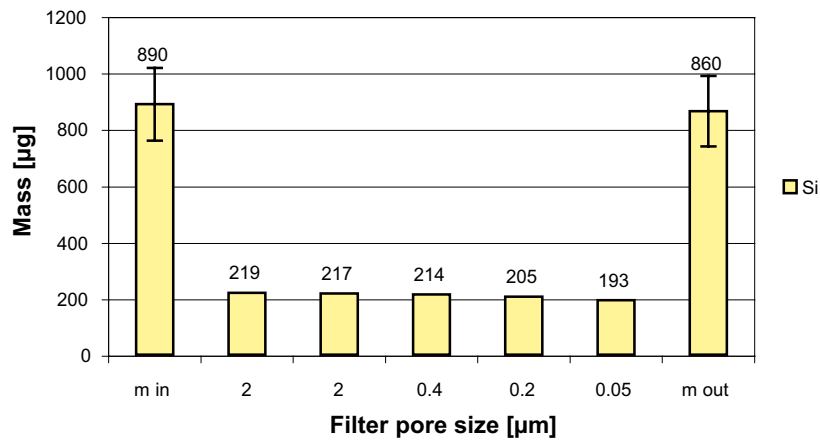


Figure 7-11. Amount of silicon entering the filter system (m in), in the filters and in the collecting container (m out).

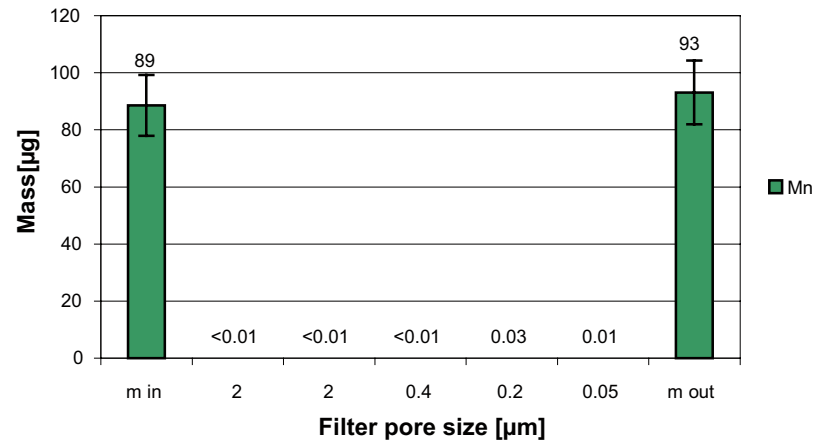


Figure 7-12. Amount of manganese entering the filter system (m in), in the filters and in the collecting container (m out).

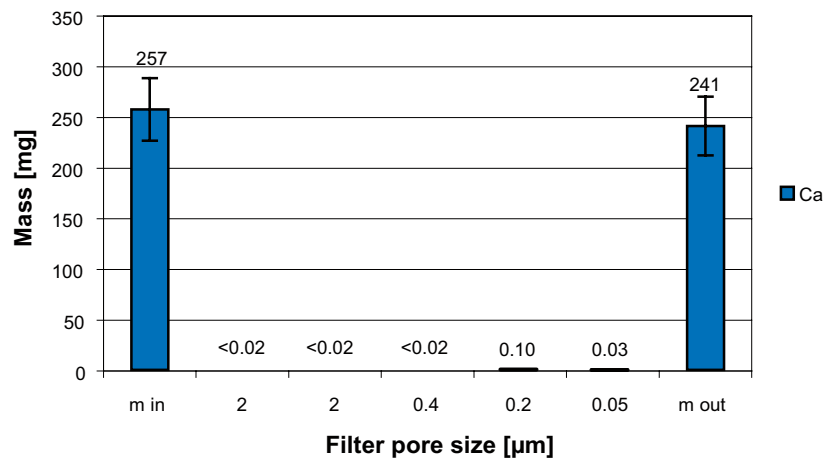


Figure 7-13. Amount of calcium entering the filter system (m in), in the filters and in the collecting container (m out).

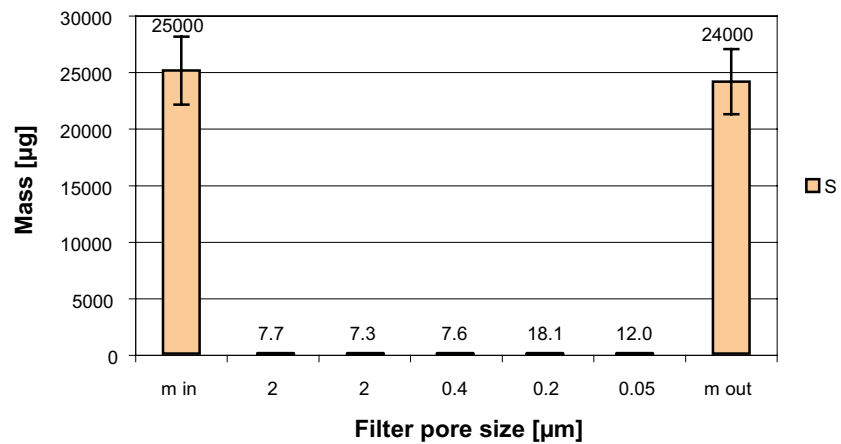


Figure 7-14. Amount of sulphur entering the filter system (m in), in the filters and in the collecting container (m out).

7.4.2 Inorganic colloids – fractionation

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

The results presented in 7-6 were calculated using mass balance equations. Silicon, aluminium, manganese, calcium and sulphur exist mainly as species (associated or non-associated with humic and fulvic acids) with a molecular weight less than 1,000 D (g/mol). Such species are too small to be referred to as colloids.

The results for iron are uncertain since precipitation might have occurred before or during filtering and also for aluminium because the concentrations are close to detection limit.

The blanks (de-ionised water collected after passing through the washed filters) showed insignificant concentrations of iron, silicon, calcium, aluminium, manganese, calcium and sulphur.

7.5 Humic and fulvic acids – fractionation

The results from fractionation of organic acids in section 623.0 to 634.5 m are presented in Table 7-7. The water in the section contains mainly of a fraction of organic acids with a molecular weight less than 1,000 D, which consist of fulvic acids and possibly other low molecular weight organic acids such as citric acid and oxalic acid. The results from the 5,000 D filter were excluded since there was an addition of organic carbon during the filtering process.

Table 7-6. Inorganic fractions (< 1,000 D, 1,000 D to 5,000 D and > 5,000 D) in section 623.0–634.5 m.

Fraction	Fe [mg/L]	Si [mg/L]	Mn [µg/L]	Ca [mg/L]	S [mg/L]
< 1,000 D	0.21 ± 0.03	4.9 ± 0.7	473 ± 57	1,410 ± 171	132 ± 16
< 5,000 D	0.07 ± 0.01	5.0 ± 0.7	489 ± 59	1,430 ± 172	142 ± 18
> 1,000 D but < 5,000 D	–	–	–	–	5.2 ± 4.9
> 5,000 D	0.017 ± 0.005	–	–	–	–
Adsorption 1,000 D	0.23 ± 0.07	–	–	–	–
Adsorption 5,000 D	0.13 ± 0.03	–	–	–	–

– = Below detection limit.

Table 7-7. Summary of humic and acids-fractionation results from KLX15A.

Fraction/Section	623.0–634.5 m DOC [mg/L]
< 1,000 D	1.5 ± 0.2
> 1,000 D	0.2 ± 0.1
Adsorption 1,000 D	–

– = Below detection limit.

8 Summary

The *Complete chemical characterisation* in KLX15A was, on the whole, performed successfully.

The main conclusions from the available experimental results are:

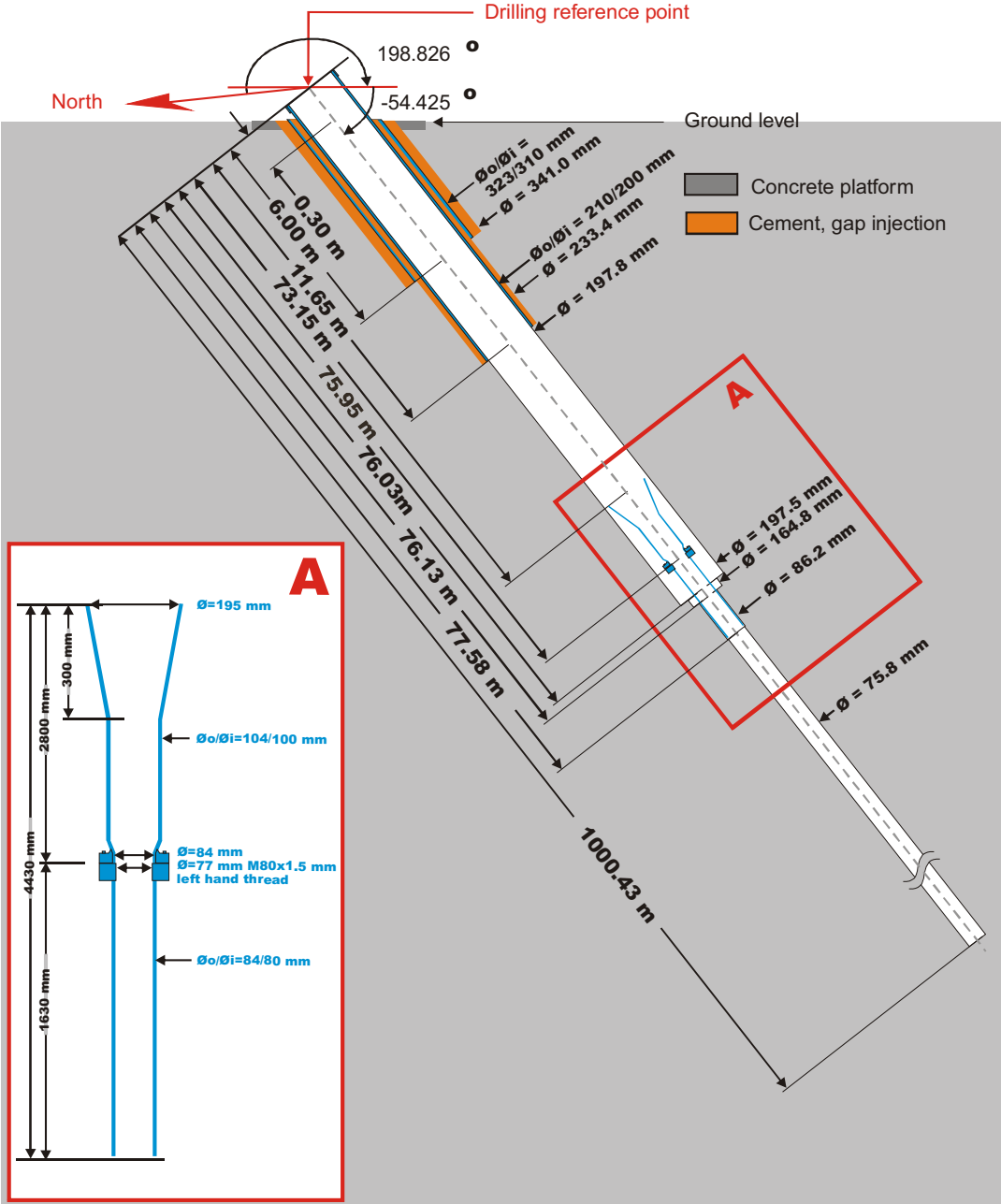
- The flushing water content at the beginning of the pumping/sampling period in section 623.0 to 634.5 m was above 14%, although there was a significant decrease after two weeks of pumping. By the end of the pumping period, the flushing water content was still somewhat high (4.4%).
- The major constituents showed stable concentrations during the pumping/sampling period, indicating that no mixing occurred with water from other fracture systems with a different water composition. Thus, the groundwater composition can be considered as fairly representative for the water-bearing fractures in the investigated section.
- The quality of the water analyses is generally high, based on comparisons between results from different laboratories and methods and that the charge balance errors were acceptable. The relative charge balance errors are in most cases within $\pm 5\%$.
- The redox potential measurements were not completed successfully. Slow responses of the electrodes and several interruptions during the measurement period gave inconsistent and unstable (slightly negative) redox values. Redox measurements in the LIBD experiments gave slightly positive values.
- The results from the colloid filtration indicate that the contents of manganese, sulphur and calcium colloids in the groundwater are low or non-existent. The evaluation is more complicated for aluminium, iron and silicon because of possible contamination and/or precipitation.
- The organic constituents are mainly present as fulvic acids and possibly other low molecular weight organic acids (citric and oxalic acids).
- The results from the colloid determination using LIBD as well as filtration followed by SEM show that the content of colloids are low; in the order of less than 1 to 20 $\mu\text{g/l}$. The results from filtration-ICP gave a higher concentration; 140 $\mu\text{g/l}$.

9 References

- /1/ **SKB, 2001.** Site investigations. Investigation methods and general execution programme. SKB TR-01-29, Svensk Kärnbränslehantering AB.
- /2/ **Pedersen K, 2008.** Oskarshamn site investigation. Microorganisms in groundwater from borehole KLX15A – numbers, viability and metabolic diversity. Results from one section: 623.00–634.51 m in KLX15A. SKB P-08-09, Svensk Kärnbränslehantering AB.
- /3/ **Ask H, Drilling of the cored borehole KLX15A.** Oskarshamn site investigation. SKB P-08-58, Svensk Kärnbränslehantering AB. In press.
- /4/ **Gustafsson J and Gustafsson C, 2007.** Oskarshamn site investigation. RAMAC, BIPS and deviation logging in boreholes KLX15A. SKB P-07-117, Svensk Kärnbränslehantering AB.
- /5/ **Pöllänen J, Sokolnicki M, Väisäsvaara J, 2007.** Oskarshamn site investigation. Difference flow logging of borehole KLX15A. Subarea Laxemar. SKB P-07-176, Svensk Kärnbränslehantering AB.
- /6/ **Nielsen U T and Ringgaard J, 2007.** Oskarshamn site investigation. Geophysical borehole logging in borehole KLX15A. SKB P-07-152, Svensk Kärnbränslehantering AB.
- /7/ **Hedqvist I and Degueldre C, 2008.** Granitic groundwater colloids sampling and characterisation. Colloids analysis from KLX17A (416.0 to 437.5 m) and KLX15A (623.0 to 634.5 m). SKB P-08-101, Svensk Kärnbränslehantering AB.

Design of cored borehole KLX15A

Technical data
Borehole KLX15A



Drilling reference point

Northing: 6365614.168 (m), RT90 2,5 gon V 0:-15
 Easting: 1547987.466 (m), RT90 2,5 gon V 0:-15
 Elevation: 14.590 (m), RHB 70

Drilling period

Drilling start date: 2006-12-21
 Drilling stop date: 2007-02-25

Selected results of differential flow logging in KLX15A

Laxemar, borehole KLX15A

Flow rate, caliper and single point resistance

- △ Without pumping (L=5 m, dL=5 m), (Flow direction = into the hole)
- ▽ Without pumping (L=5 m, dL=5 m), (Flow direction = into the bedrock)
- △ With pumping (Drawdown XX m, L=5 m, dL=5 m), (Flow direction = into the hole)
- Without pumping (L=5 m, dL=0.5 m), 2007-05-08 - 2007-05-08
- Without pumping (L=5 m, dL=0.5 m), 2007-05-08
- With pumping (Drawdown 7 m, L=5 m, dL=0.5 m), 2007-05-09 - 2007-05-10
- With pumping (Drawdown 7 m, L=1 m, dL=0.1 m), 2007-05-11 - 2007-05-14
- With pumping during fracture-EC (Drawdown 7 m, L=0.5 m, dL=0.1 m), 2007-05-XX - 2007-05-XX
- Lower limit of flow rate

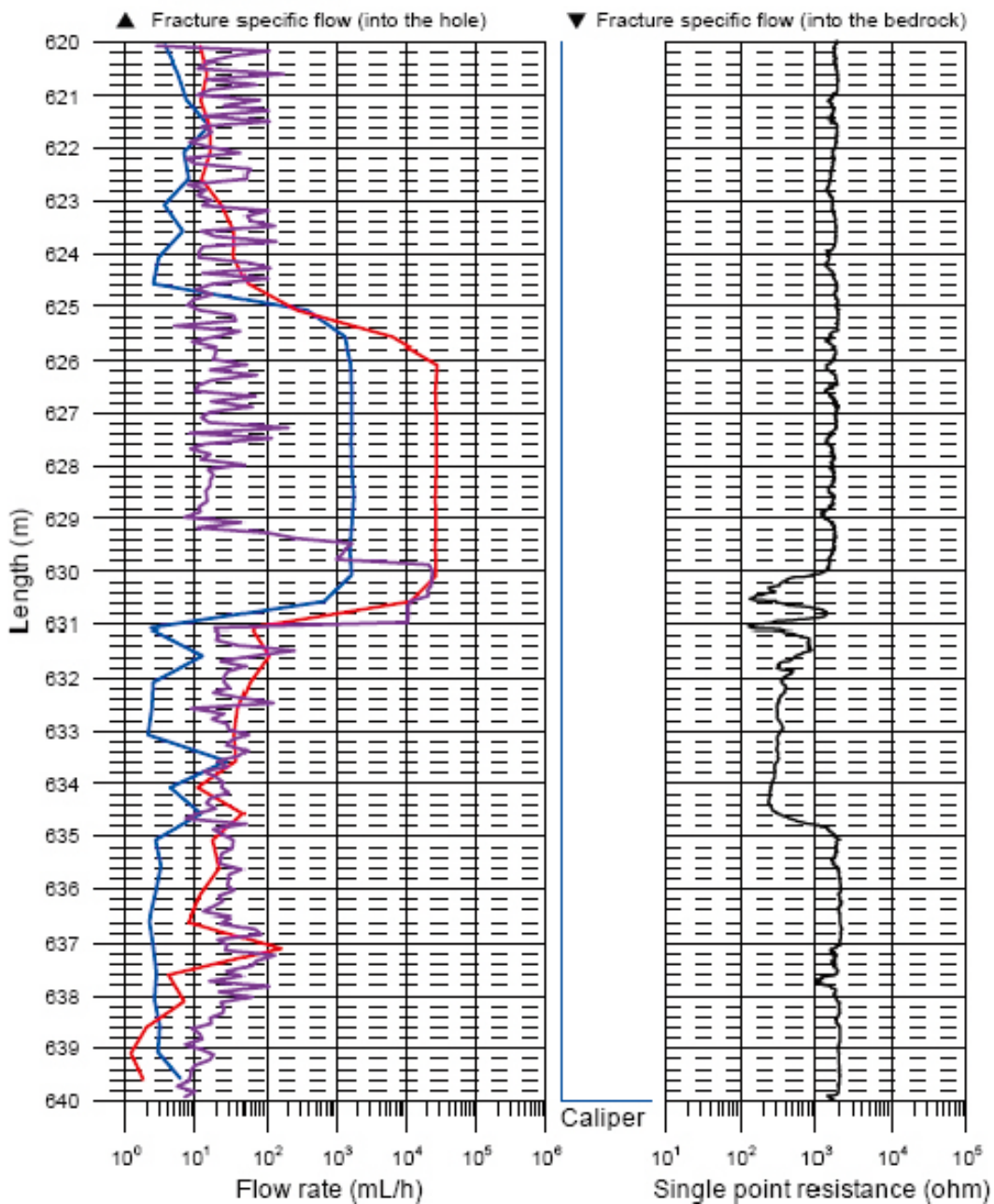


Figure A2-1. Borehole KLX15A: Differential flow measurements from 620–640 m including the water bearing fracture zone at 630 to 631 m /4/.

Selected images from BIPS logging in KLX15A

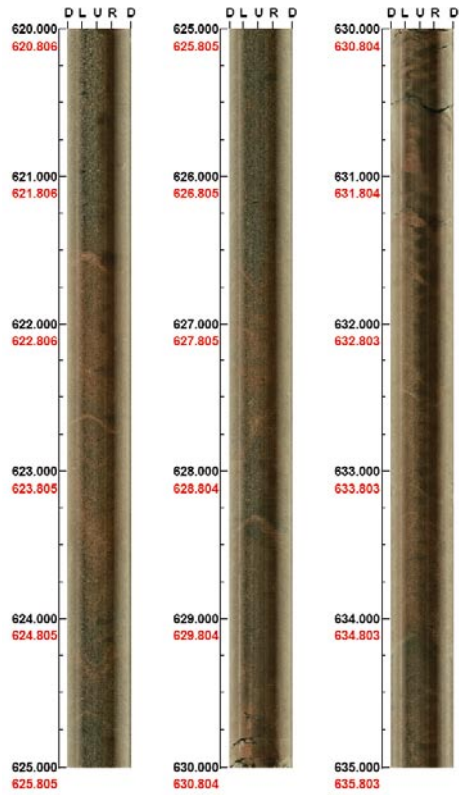


Figure A3-1. Borehole KLX15A: selected BIPS logging image from 620.0 to 635.0 m including the water bearing fractures at 630 to 631 m. The non-adjusted length is marked with black and the adjusted true length is marked with red /3/.

Measurement information, KLX15A

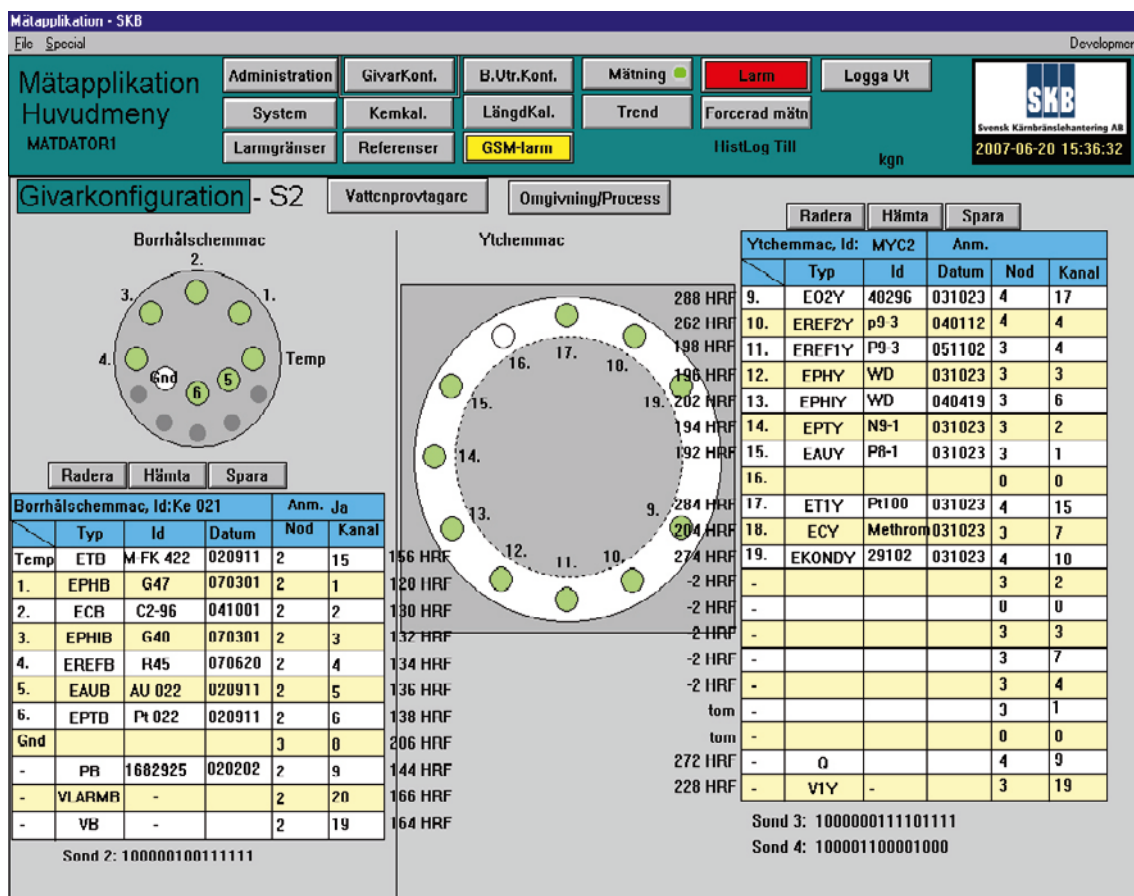


Figure A4-1. Electrode configuration, section 623.0 to 634.5 m, 2007-06-20.

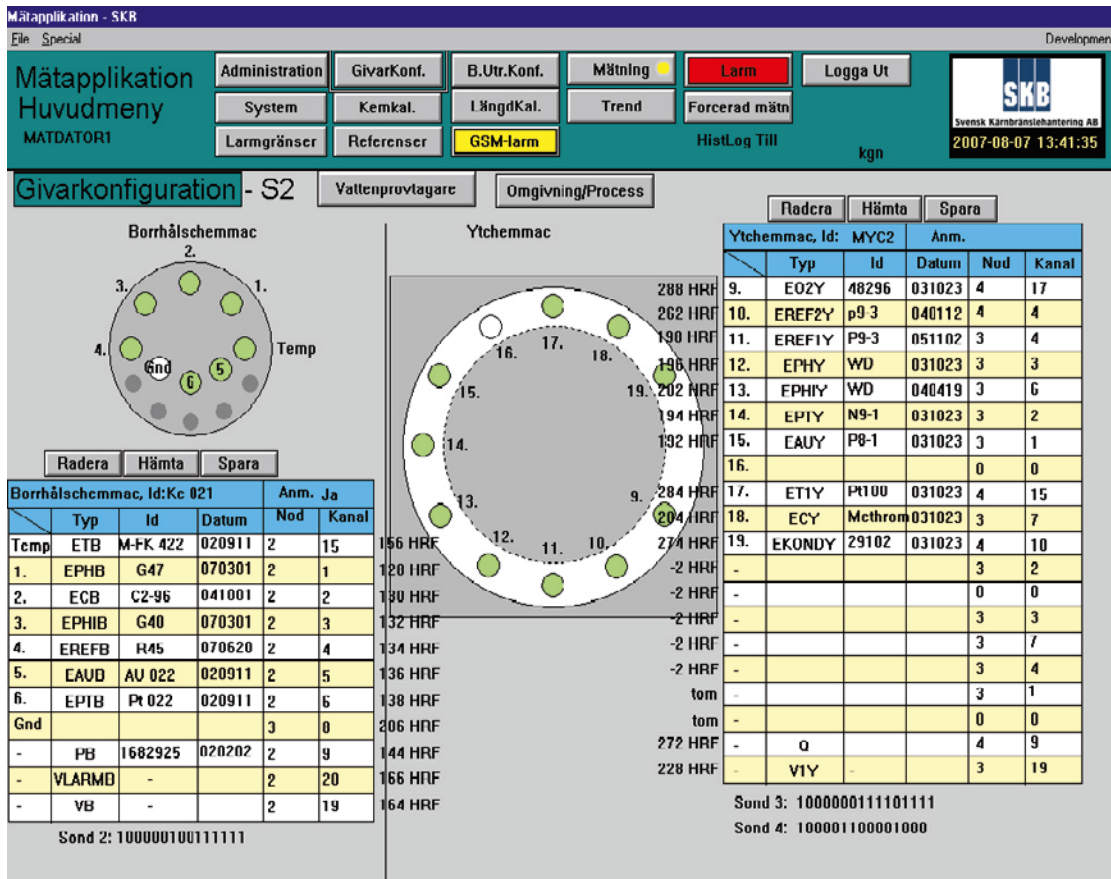


Figure A4-2. Electrode configuration, section 623.0 to 634.5 m, 2007-08-07.

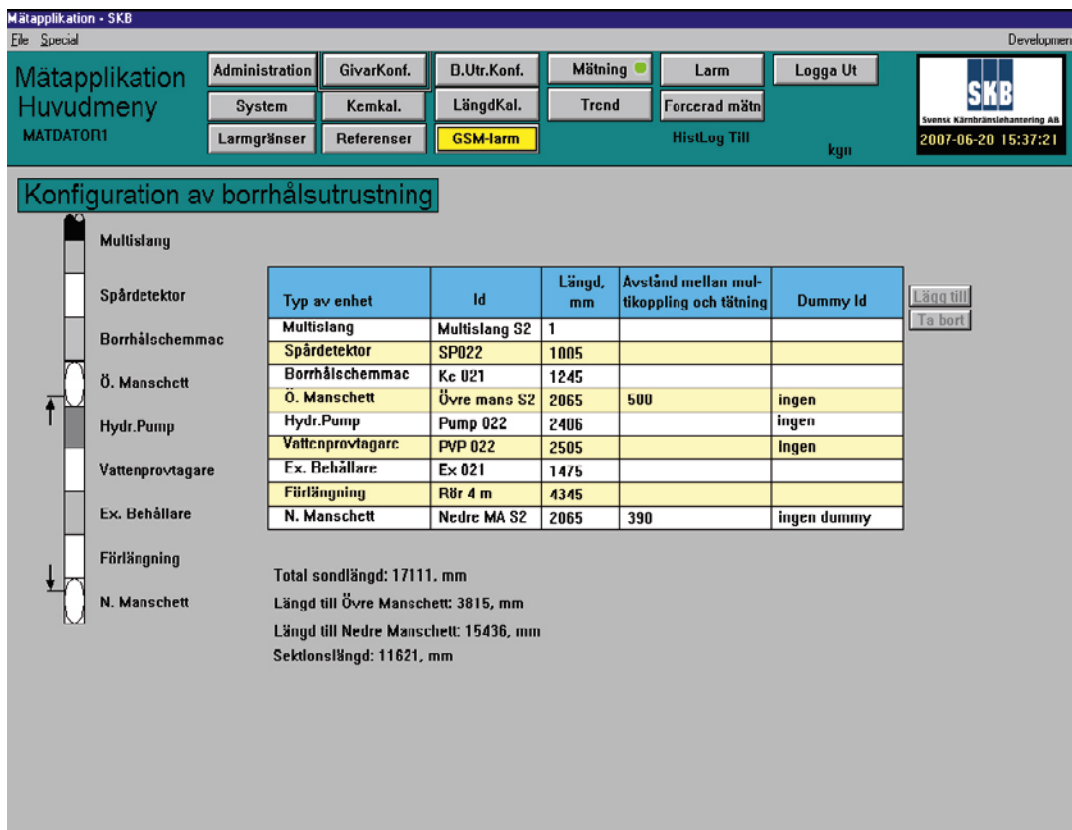


Figure A4-3. Configuration of downhole equipment, section 623.0 to 634.5 m, 2007-06-20.

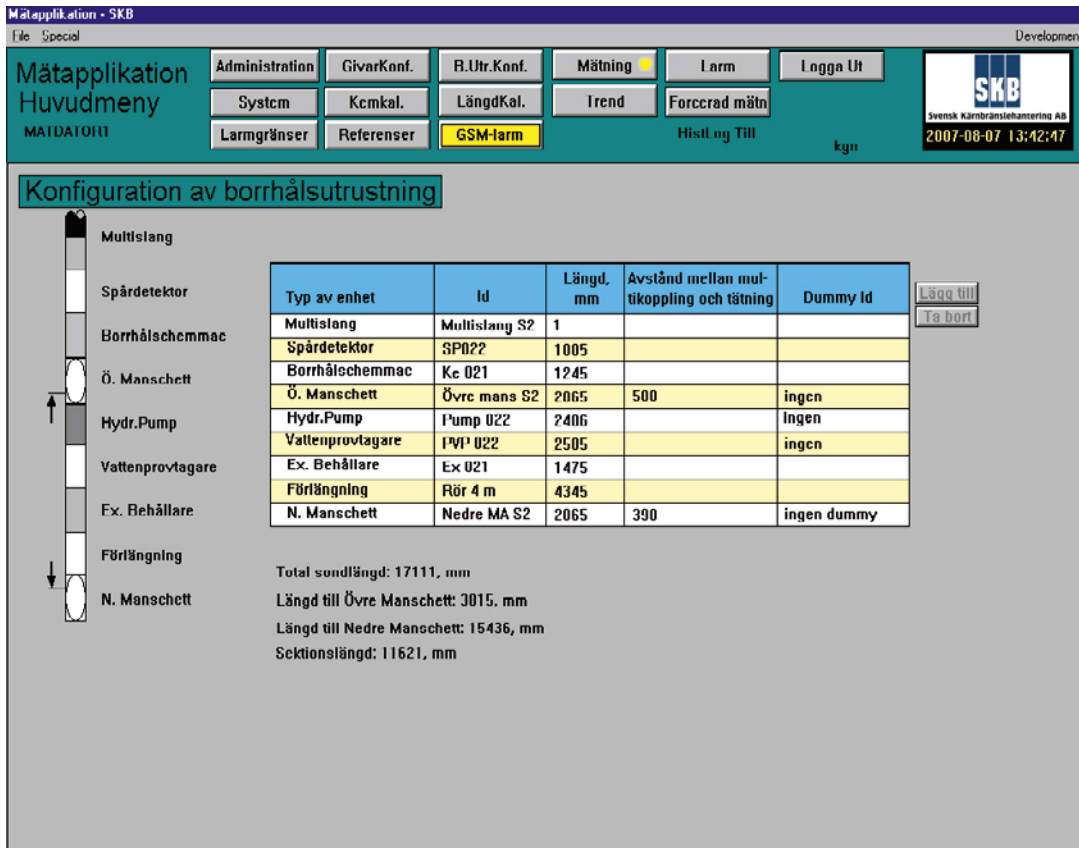


Figure A4-4. Configuration of downhole equipment, section 623.0 to 634.5 m, 2007-08-07.

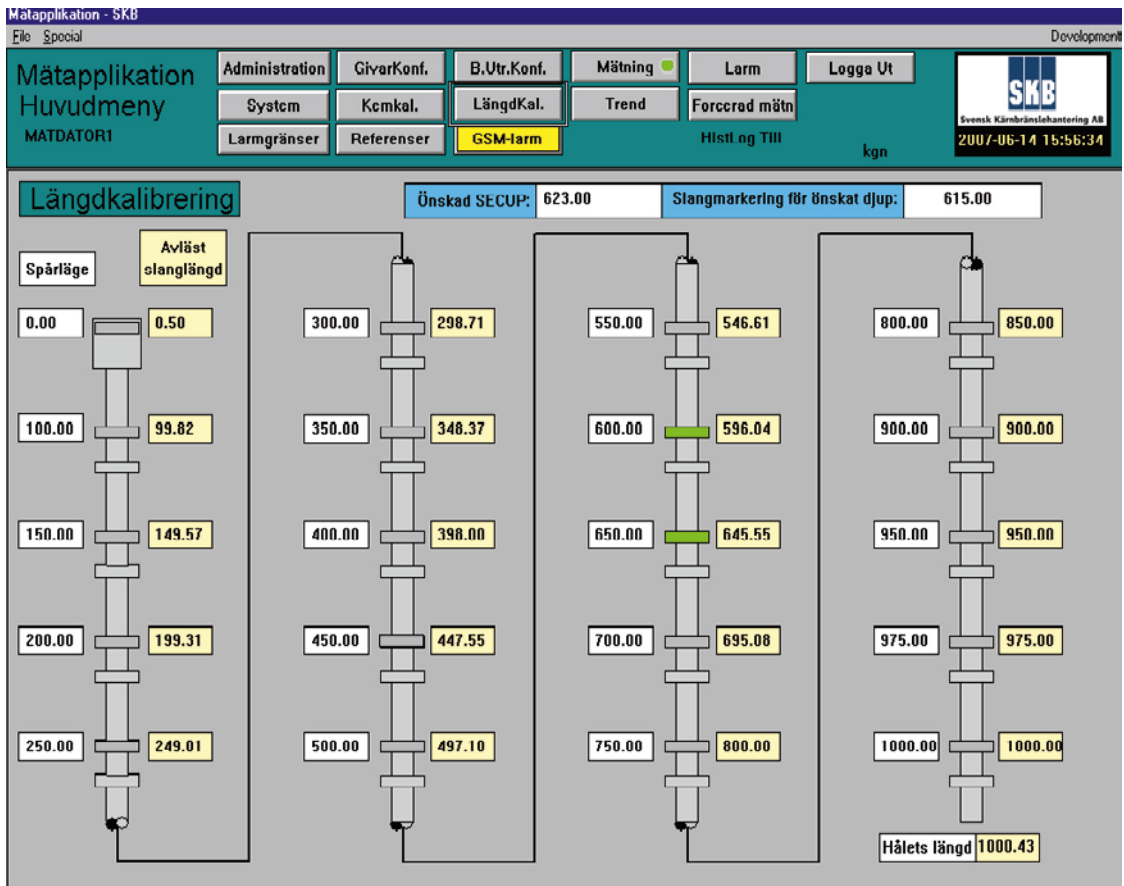


Figure A4-5. Length calibration, section 623.0 to 634.5 m, 2007-06-14.

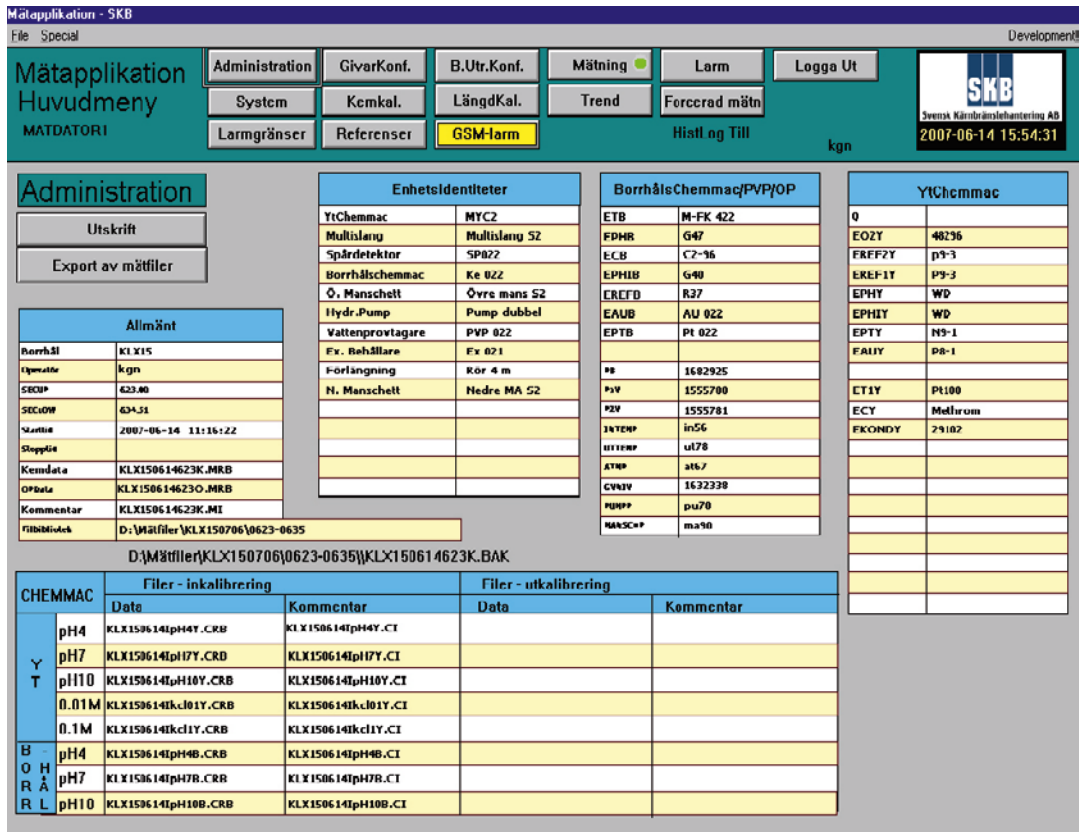


Figure A4-6. Administration, section 623.0 to 634.5 m, 2007-06-14.

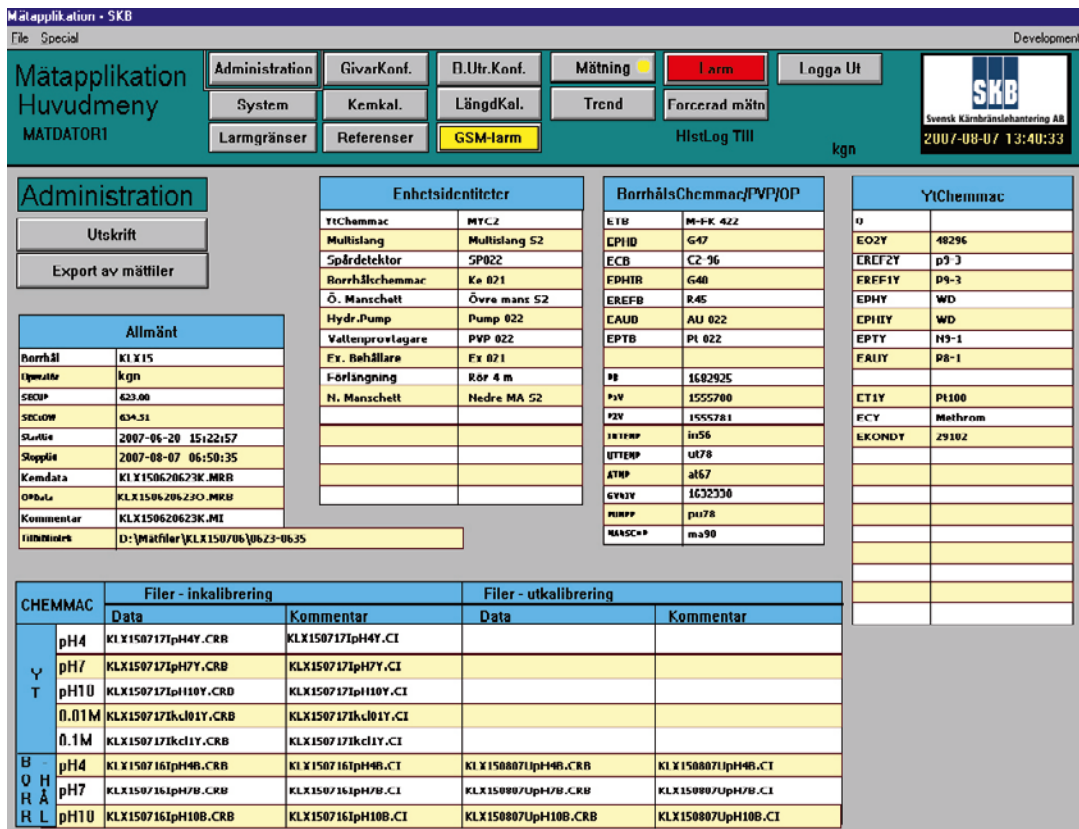


Figure A4-7. Administration, section 623.0 to 634.5 m, 2007-08-07.

Flow and pressure measurements, KLX15A

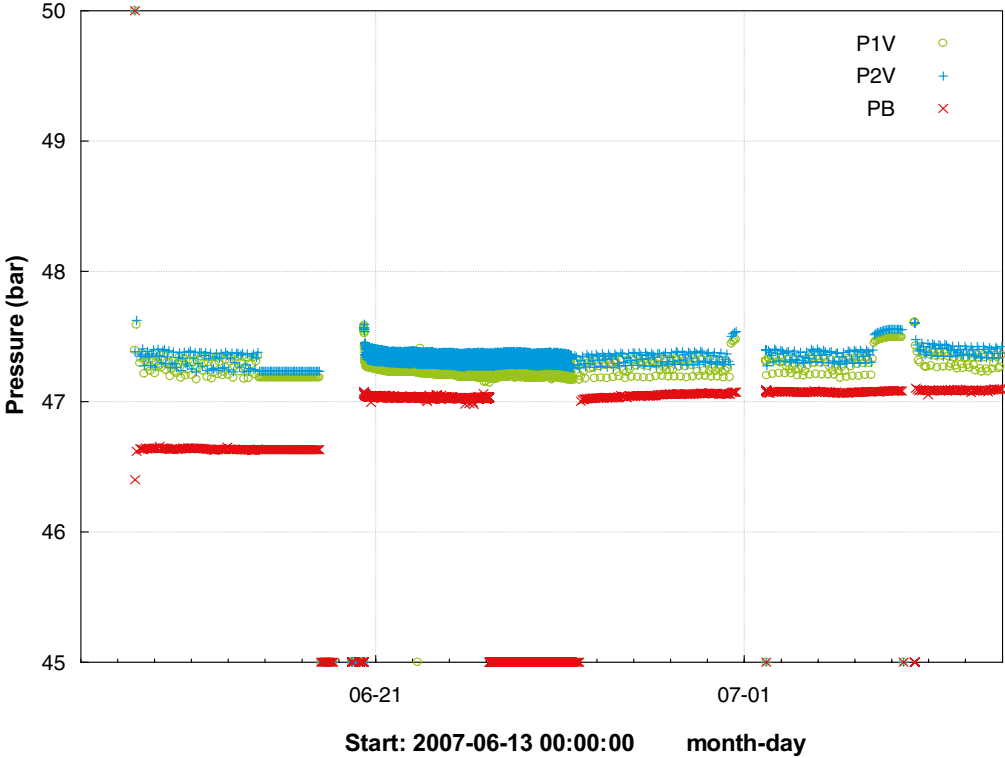


Figure A5-1. Pressure measurements (P1V, P2V and PB), section 623.0 to 634.5 m. The sensors P1V and P2V measure the pressure within the section and are both placed in the in situ sampling unit. The sensor PB, placed in the borehole Chemmac, measures the pressure above the section.

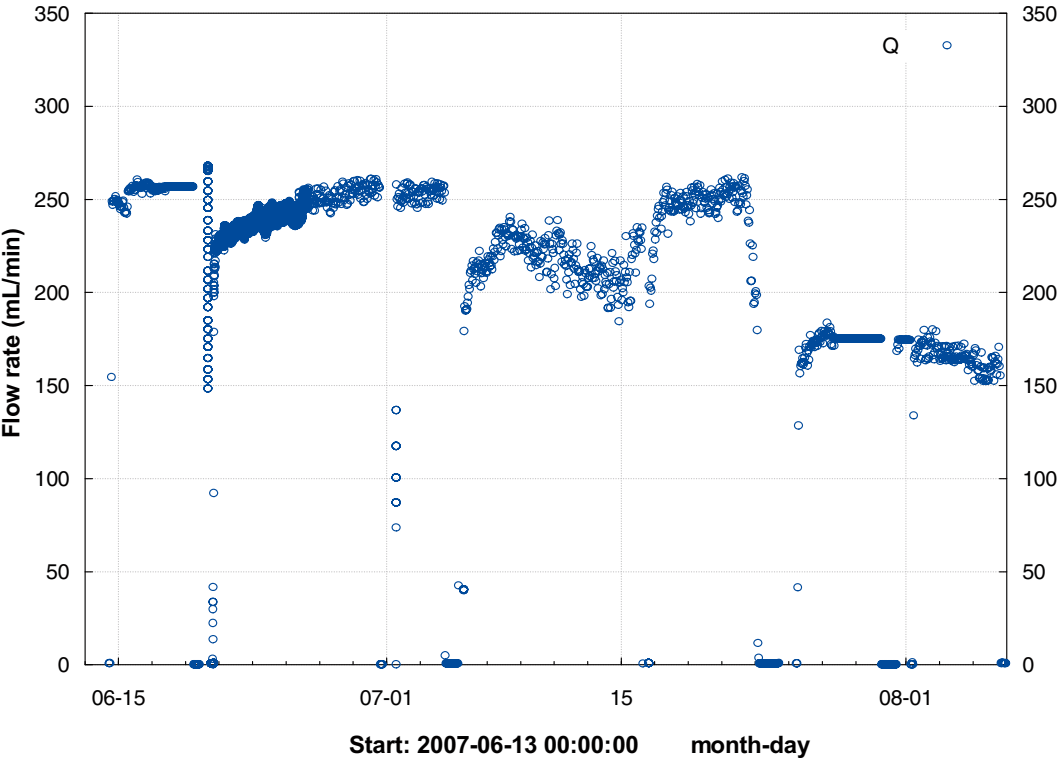


Figure A5-2. Pumping flow rate (Q), section 623.0 to 634.5 m

Chemmac measurements in KLX15A, section 623.0 to 634.5 m

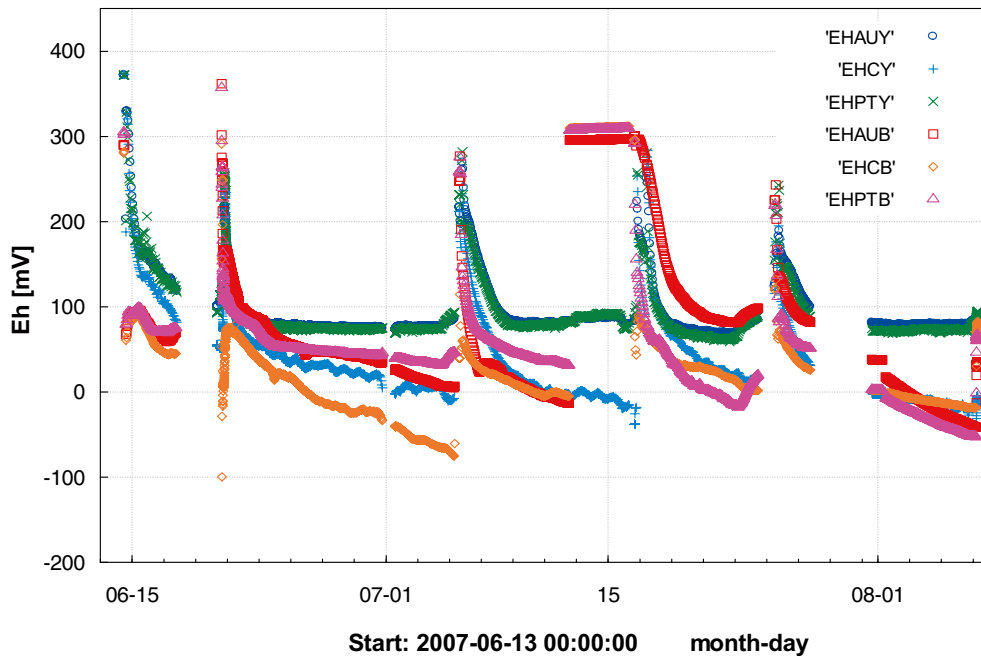


Figure A6-1. Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes in the borehole section (EHAUB, EHCB and EHPTB) and at the surface by gold, glassy carbon and platinum (EHAUY, EHCY and EHPTY). A representative Eh value for the borehole section was not chosen since the recorded redox potentials are unstable.

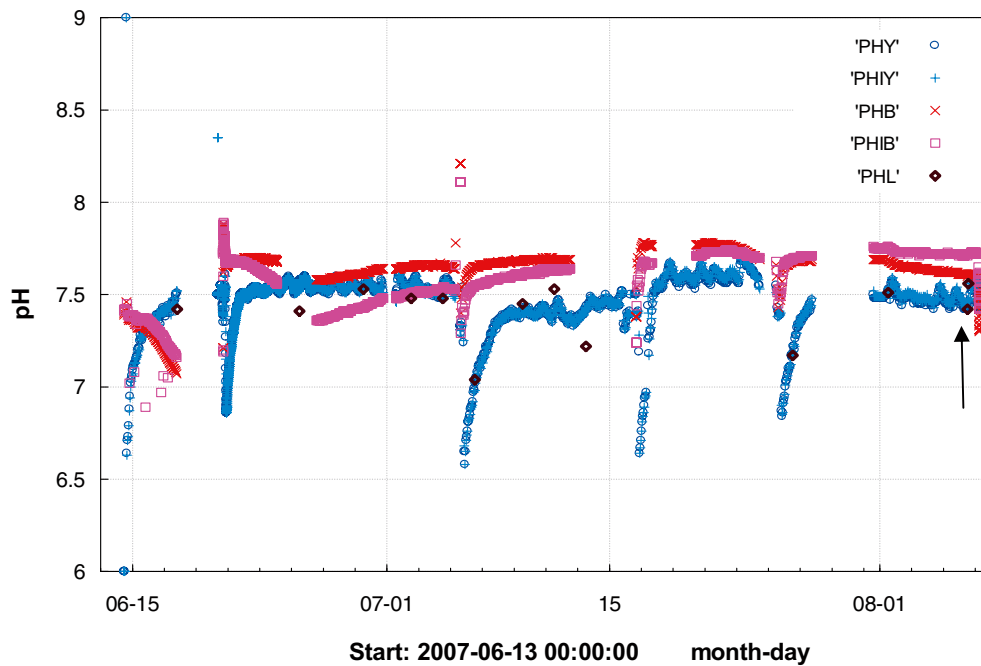


Figure A6-2. Measurements of pH by two glass electrodes in the borehole section (PHB and PHIB) and two glass electrodes at the surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.

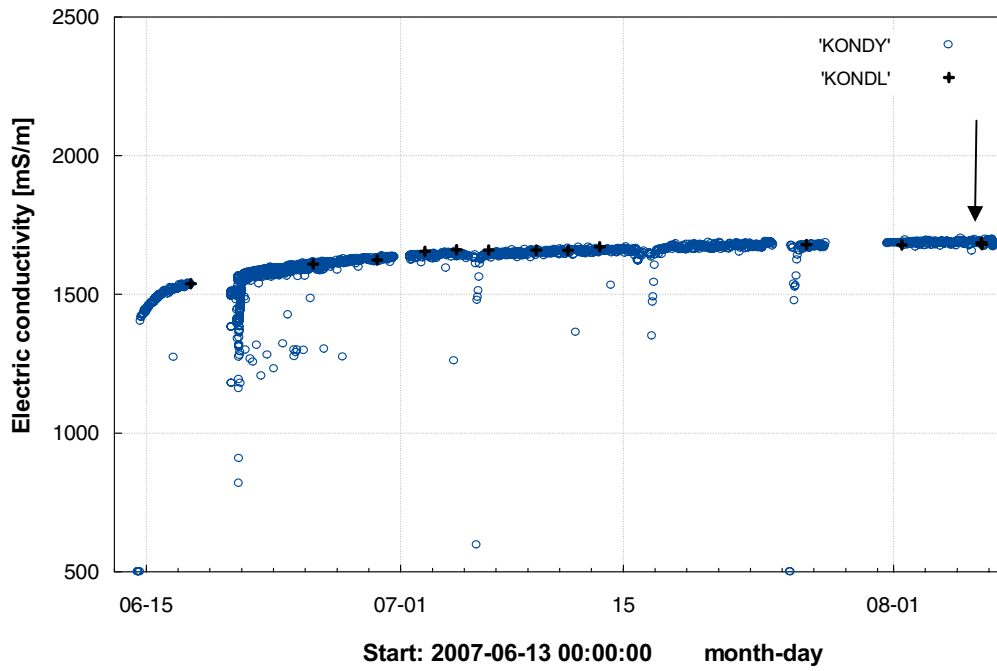


Figure A6-3. Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.

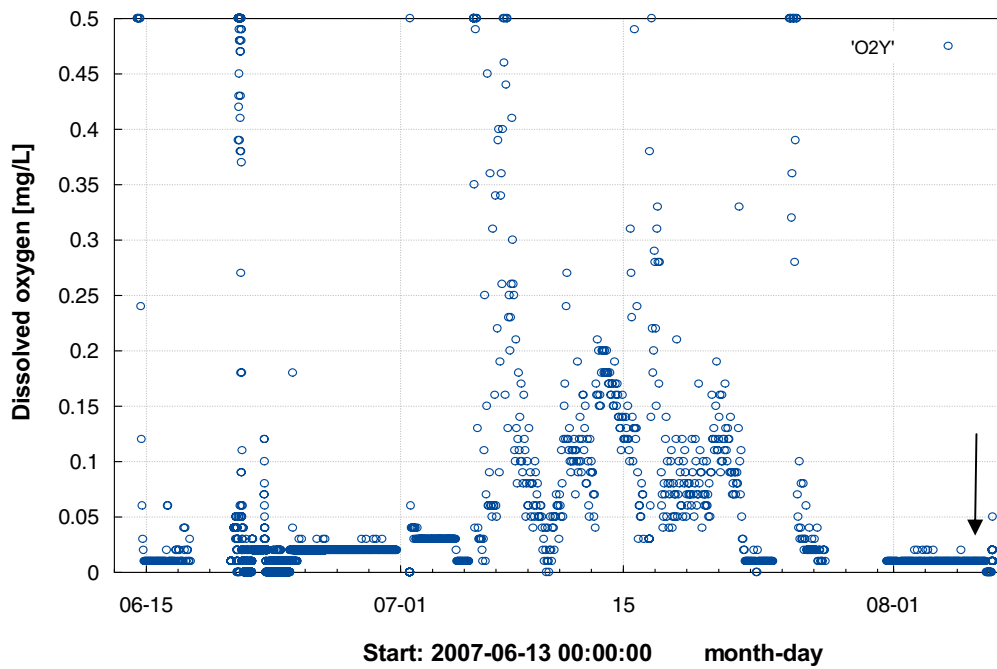


Figure A6-4. Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the chosen representative oxygen value for the borehole section.

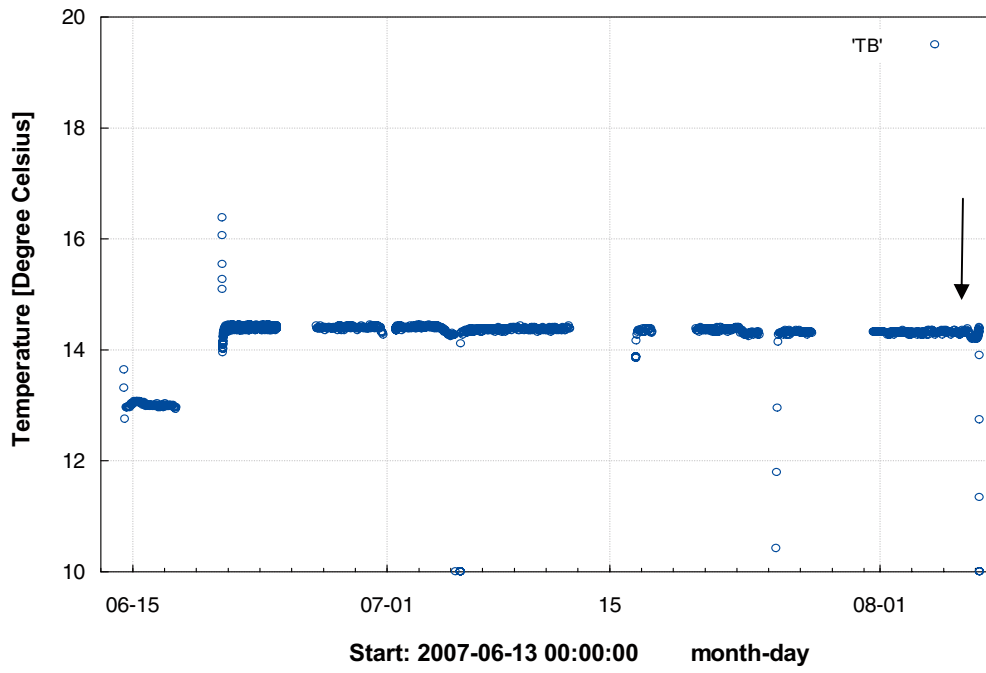


Figure A6-5. Temperature of the groundwater in the borehole section (TB).

Quantification of Colloids in Natural Groundwater from Laxemar Borehole KLX15A, Section (623–634.5) m

W. Hauser, R. Götz, T. Schäfer, H. Geckeis

Forschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgung (INE)
P.O. Box 3640, D-76021 Karlsruhe, Germany

Introduction

Colloid analysis has been performed in groundwater samples collected during the site investigation program at Laxemar (Oskarshamns kommun), close to the nuclear power station Oskarshamn, Sweden. Samples from one borehole have been collected in two stainless steel cylinders, preventing as much as possible the oxidation of the anoxic groundwater samples. They were sent to INE for laboratory analysis. Colloid analysis was subsequently performed by the laser-induced breakdown detection (LIBD) in the laboratory using a closed flow-through detection cell, again without atmosphere contact. Furthermore, a complete geochemical analysis of the water samples was performed.

The geological situation in Laxemar may be different from that found at various places in the Äspö tunnel. The aim of this study is to investigate the natural background colloid concentration in this specific borehole and to compare the data with those obtained from other sites.

Experimental

LIBD instrumentation

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

A schematic diagram of the mobile LIBD set-up used in the present work is shown Fig. 1. A pulsed laser beam with a frequency of 15 Hz at 532 nm wavelength from a small Nd:YAG-laser (Continuum Minilite I) is focused (15 mm focal length) into the center of a flow-through detection cell, after passing through a variable attenuator and a beam splitter. The plasma generated at a breakdown event is monitored by a microscope equipped with a CCD monochrome camera triggered by the incident laser pulse and recorded by a PC controlled image processing system. A breakdown shock wave propagated in the sample solution is detected simultaneously by an acoustic sensor (piezoelectric transducer) that is connected to the surface of the cell. Both, the energy and the acoustic signal are recorded by an analog-digital converter interface in a PC. Colloid concentrations are derived from the respective breakdown probability, represented by the number of breakdown events per number of laser shots, and the range of breakdown events within the laser beam axis determined by optical inspection of the laser focus area within the flow through cell. Colloid number concentrations (N/ml) are given relative to a calibration with polystyrene reference colloids. Mass concentrations are calculated by assuming an average colloid density of 2.7 g/cm³ and spherical particle shape. A more detailed description of data evaluation is given in ¹.

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

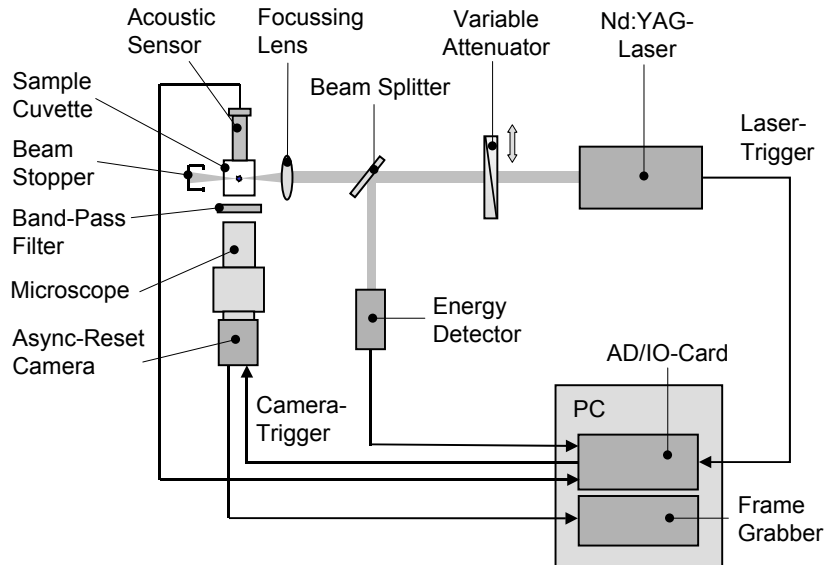


Fig. 1: Schematic diagram of the mobile laser-induced breakdown detection system

High-pressure flow-through detection cell

The LIBD has been operated in the CRR migration experiments (Grimsel Test-Site, Switzerland)¹ under low pressure conditions with commercially available quartz detection cells (fluorescence cells) for batch (laboratory experiments) or flow-through sampling. These cells have a sample volume of 3 ml at 10 mm absorption length. A new flow-through detection cell has been developed constraining water pressures of about 35 bar for in situ investigations in the Äspö Hard Rock Laboratory access tunnel (Sweden)², and in the Kraftwerke Oberhasli (KWO) access tunnel close to the Grimsel Test Site³. This detection cell has also been applied in connection with a borehole sampling system for the detection of groundwater colloids sampled at a natural analogue site (Ruprechtov, Czech Republic).

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

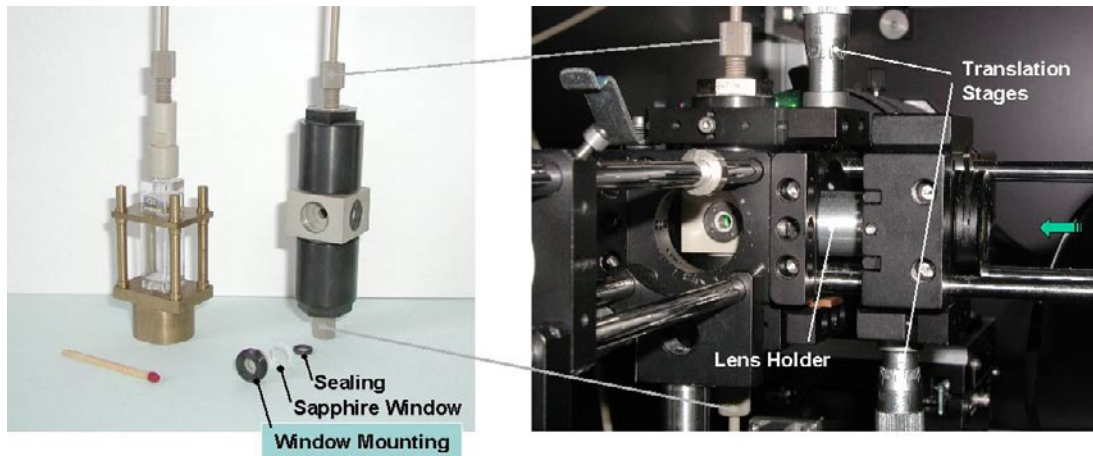


Fig. 2: LIBD high-pressure flow-through detection cell (left: conventional flow-through silica detection cell)

Borehole sampling

Samples were taken at August 7, 2007 from Laxemar borehole KLX15A, section between (623 – 634.5) m. The vertical depth was approximately 478 m with a measured pressure in the borehole section of 47 bar. The samples have been filled in the SKB steel cylinders PVB 220 and PVB 9506-6.

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



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

Configuration of laboratory experiments

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

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

At first the tubings around the sampling cylinder are intensively cleaned by evacuation and flushing with Argon. Then a HPLC-pump is used to fill all tubings on the water side of the sampling cylinder with ultra-pure water and to set the water pressure according to the hydrostatic pressure of the samples. This was the expected water pressure in the sampling cylinder. The gas side of the sampling cylinder is then filled with the corresponding Argon gas pressure.

Now one of the top valves of the sampling cylinder can be opened without contact of the sampled groundwater with atmospheric oxygen. With Argon gas the groundwater is pressed out from the sampling cylinder through the LIBD detection cell via a degasser to avoid occasionally occurring gas bubbles which interfere the colloid detection. Behind the LIBD system additional detection cells with pressure resistant electrodes for Eh, pH (back pressure regulator 1 set to 40 bar), Oxygen, a sensor for electrical conductivity and a sensor for the pressure detection are arranged downstream.

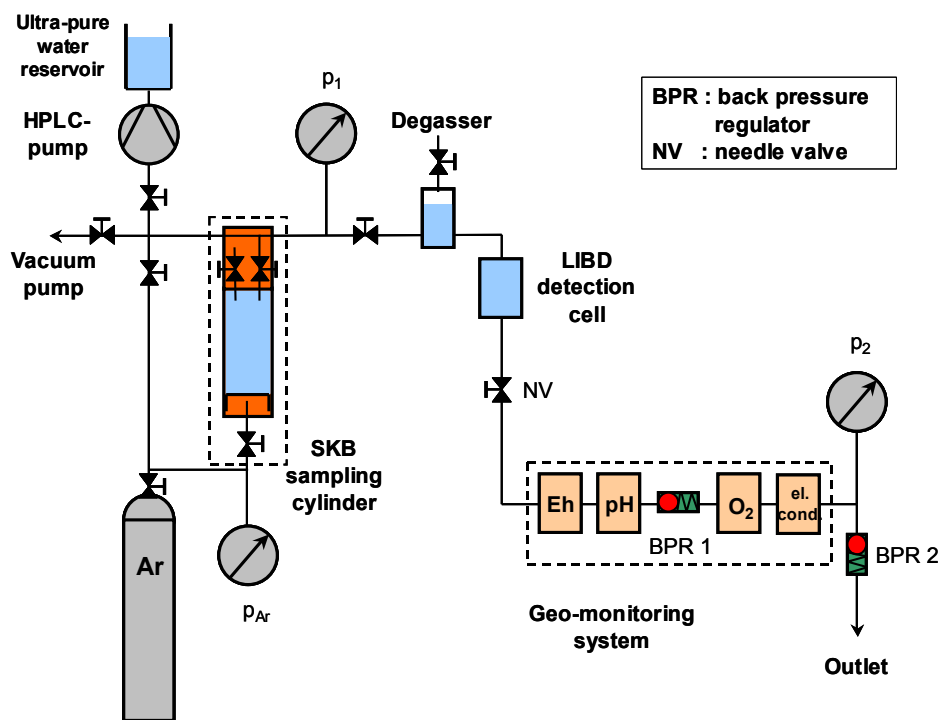


Fig. 4: Scheme of the laboratory setup for in-line LIBD colloid analysis and groundwater monitoring

Before the sampling outlet an additional back pressure regulator, set to 5 bar, is installed. This overpressure in the whole system avoids further contact to oxygen. Data of this geo-monitoring system are stored on a personal computer with a data logger as a function of time. This allows to separate temporary fluctuating data, especially during the starting period when the detection cell and the geo-monitoring system are contaminated and do not contain the sampled groundwater, respectively.

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

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



Fig. 5: Experimental configuration

Results

Chemical analysis

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

The groundwater pH 7.62 is lower than the pH of the other investigated Laxemar groundwater pH (8.0 – 8.5). But it is equivalent to the pH detected so far in other Forsmark (7.3 – 8.4) and Äspö groundwater samples (7.3 – 7.8). In this experiments for groundwater KLX15A (623 – 634.5) m we used a new Eh-electrode with a correct (plausible) detection of the Eh with time. The measured Eh values indicate that reducing conditions have been maintained in the sampling containers during transport, storage and colloid detection.

The oxygen sensor detects decreasing oxygen contents, but it seems to stabilize more than a factor of 10 above its detection limit (Logged raw data, Table 1). This does not correspond with the Eh detected reducing conditions. We estimate that gas bubbles blocked the streaming of the oxygen sensor.

This Laxemar groundwater is determined by a Cl⁻ -content of 5500 mg/l and a DOC of 10 – 11 mg/l.

Table 1: Monitored data of pH, Eh, el. conductivity, oxygen content and chemical analysis of the groundwater samples from Laxemar borehole KLX15A.

Borehole ID		KLX15A	
Secup - Seclow	m	623 - 634.5	
Sampling depth	m	478	
Hydr. pressure	bar	47	
Container ID		SKB PVB 220	SKB PVB 9506-6
Sample ID		LX8A	LX9A
pH		7.63	7.62
Redox (Ag/AgCl)	mV	-203	-190
Eh (SHE)	mV	11	24
el. cond.	mS/m	1589	1576
O ₂ content	mg/l	<0.277	<0.036
Na ⁺	mg/l	2011	1961
K ⁺	mg/l	19.1	18.9
Ca ²⁺	mg/l	1446	1449
Mg ²⁺	mg/l	52.7	54.2
Al ²⁺	mg/l	0.01	0.05
HCO ₃ ⁻ (a)	mg/l	11.59	11.32
Cl ⁻	mg/l	5652	5532
SO ₄ ²⁻	mg/l	358.6	355.2
Br ⁻	mg/l	38.2	33.9
F ⁻	mg/l	1.33	1.43
Si ⁴⁺	mg/l	2.17	2.09
Fe-ICP	mg/l	2.329	2.914
Mn ²⁺	mg/l	0.53	0.53
Li ⁺	mg/l	0.244	0.239
Sr ²⁺	mg/l	24.21	24.53
DOC	mg/l	11.47	10.06
IC	mg/l	2.28	2.23

(a) calculated from IC

Colloid analysis

Groundwater from KLX15A (623 – 634.5) m

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

After evaluation of image processed data colloid size distributions with two main average colloid fractions are derived. A 1st colloid fraction with diameters of 6 - 170 nm with corresponding mass concentrations of 0.008 - 5 µg/l are calculated.

1300 – 1900 nm particles with mass concentrations of 420 – 950 µg/l are the main part of the 2nd colloid fraction. This 2nd fraction contains more than 99 % of the total particle mass, whereas the total colloid number density is determined by the 1st (smaller) colloid fraction.

Table 2: LIBD data with average colloid diameter and colloid concentration of the analyzed groundwater from Laxemar borehole KLX15A, (623 –634.5) m

Borehole ID		KLX15A					KLX15A				
Secup - Seclow	m	623 - 634.5					623 - 634.5				
Sampling depth	m	478					478				
Hydr. pressure	bar	47					47				
Container ID		SKB PVB 220					SKB PVB 9506-6				
LIBD /det. ID		LX8A	LX8B	LX8C	LX8D	LX8F	LX9B	LX9C	LX9D	LX9E	LX9F
Trigger-pulses		3000	3000	3000	3000	3000	3000	3000	3000	2086	3500
1st coll. fraction (1):											
BD-events		463	338	314	222	262	352	132	153	144	305
BD-probability		0.154	0.113	0.105	0.074	0.087	0.117	0.044	0.051	0.069	0.087
coll. num. density	N/ml	3.1E+06	1.0E+07	3.2E+06		7.1E+05	3.7E+06	2.7E+07	3.0E+06	5.9E+05	5.4E+06
coll. diam.	nm	90	27	64	<20	174	62	6	37	168	36
coll. mass conc.	µg/l	3.146	0.282	1.147	<1	5.345	1.231	0.0083	0.218	3.927	0.363
2nd coll. fraction (2):											
BD-events		694	790	670	761	700	652	687	647	411	711
BD-probability		0.231	0.263	0.225	0.254	0.233	0.217	0.229	0.216	0.197	0.203
coll. num. density	N/ml	1.1E+05	1.5E+05	9.9E+04	1.5E+05	9.5E+04	1.2E+05	1.2E+05	1.1E+05	1.2E+05	1.1E+05
coll. diam.	nm	1715	1518	1797	1443	1920	1495	1558	1601	1336	1543
coll. mass conc.	µg/l	773	729	812	640	947	569	649	634	421	557
Sum (1)+(2):											
coll. num. density	N/ml	3.2E+06	1.1E+07	3.3E+06		8.1E+05	3.8E+06	2.7E+07	3.1E+06	7.1E+05	5.5E+06
coll. mass conc.	µg/l	776	729	813	640	953	571	649	635	425	557

Fig. 6 shows the corresponding SEM images of groundwater KLX15A (623 – 634.5) m colloids. The evaluation of the SEM images confirms that two major colloid fractions exist. A 1st small colloid fraction with a size ~ 100 nm. Additionally, this particles build agglomerates and they are the major component with the highest number density.

The 2nd, large particle fraction (size 1 – 2 µm) is the component with the lowest number density. But they are the major component which determines the colloid mass concentration. With EDX analyzed elements of this fraction are Al, Si, K, Ca, Fe (alumino-silicates, silicates, calcite ...).

For the 1st colloid fraction an EDX element analysis was not possible because of the small quantities of colloidal material.

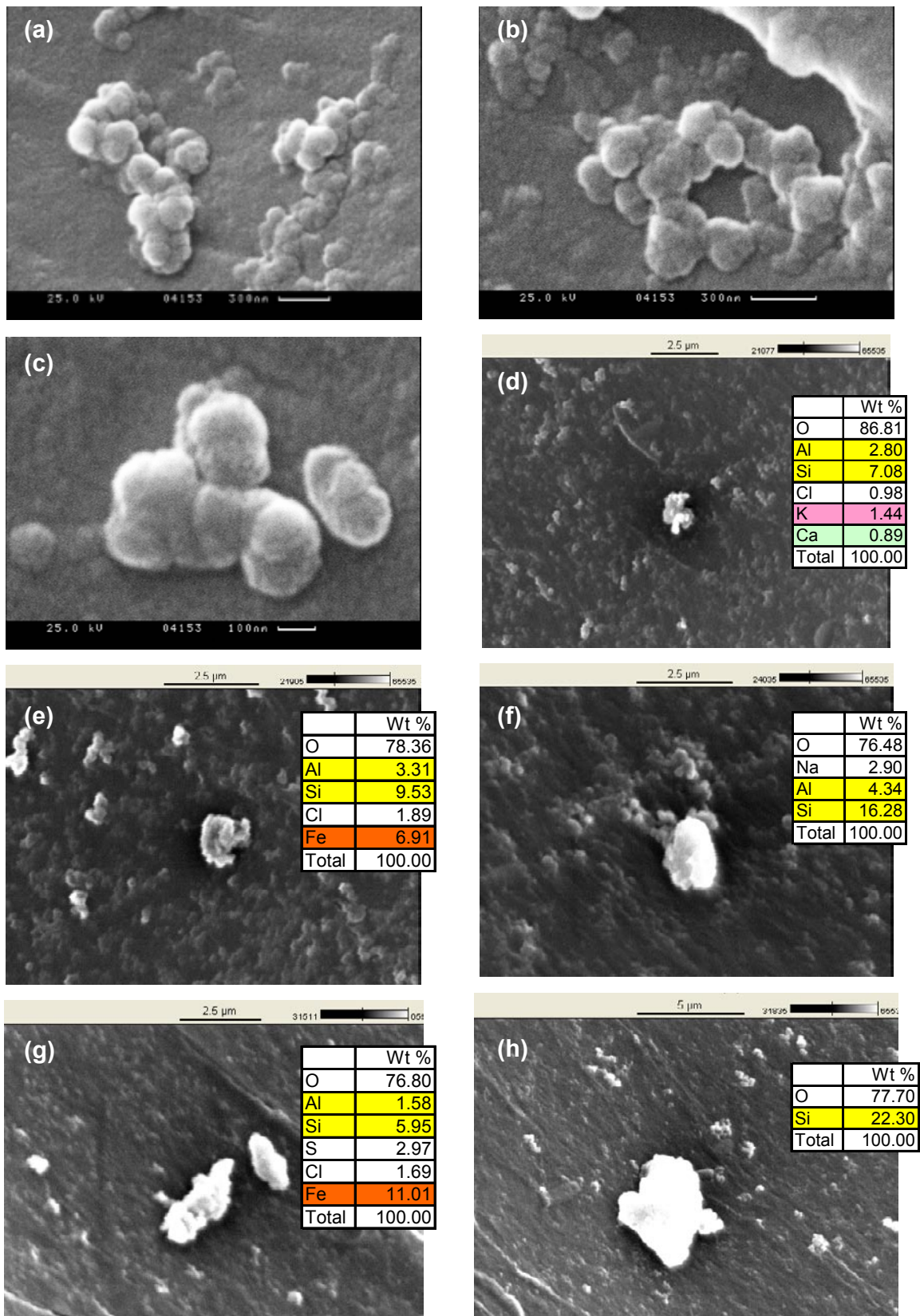


Fig. 6: SEM images of groundwater KLX15A (623 – 634.5) m colloids on a 50 nm track-etched Polycarbonate filter

Comparison with Äspö and Forsmark data

In the Äspö colloid project ⁶ a series of boreholes along the access tunnel have been sampled and their groundwater was directly analyzed with the mobile LIBD system. A correlation was drawn (Fig. 7) between the colloid concentration and the Cl⁻ concentration of the groundwater. At a Cl⁻ concentration of about 4000 mg/l a remarkable decrease of the colloid concentration over 4 orders of magnitude down to the LIBD detection limit of about 10 ng/l was observed.

The previously reported Laxemar KLX17A, KLX13A sample data fit quite well into this correlation. But according to the colloid concentration correlation with groundwater salinity we should expect a much lower colloid concentration for groundwater KLX15A from ~ 478 m sampling depth (Fig. 7).

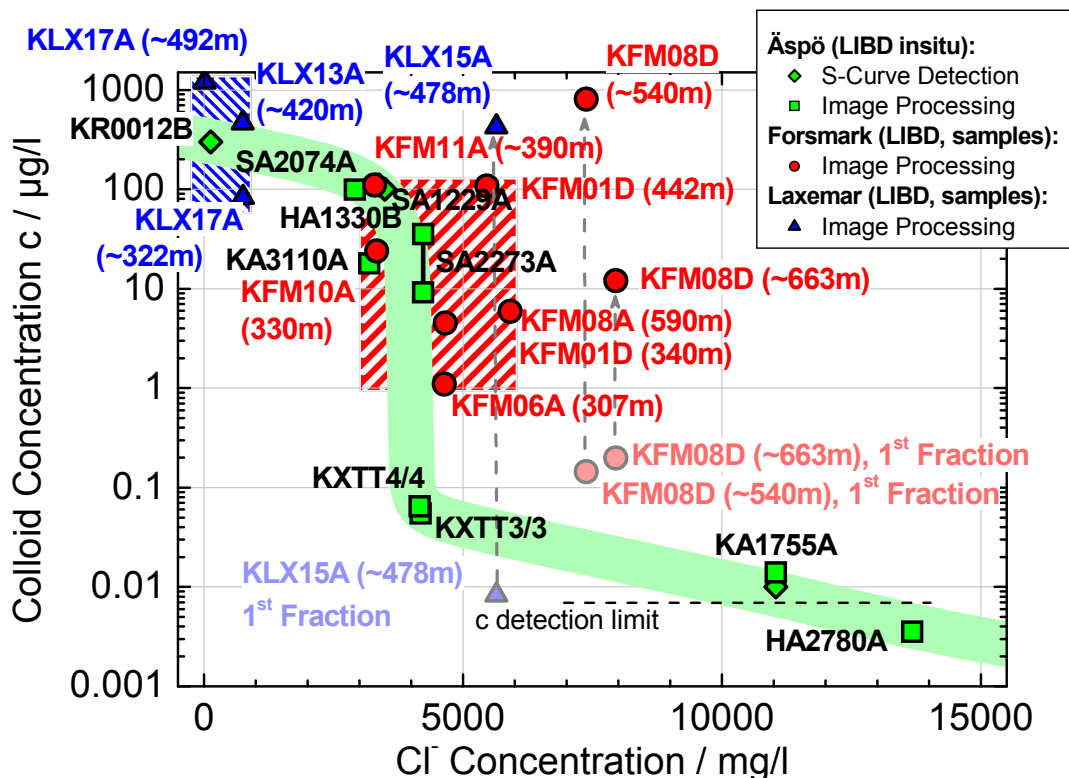


Fig. 7: Correlation between colloid concentration and chloride concentration in different groundwater from Äspö ^{2,6}, Laxemar and Forsmark samples.
(): sampling depths

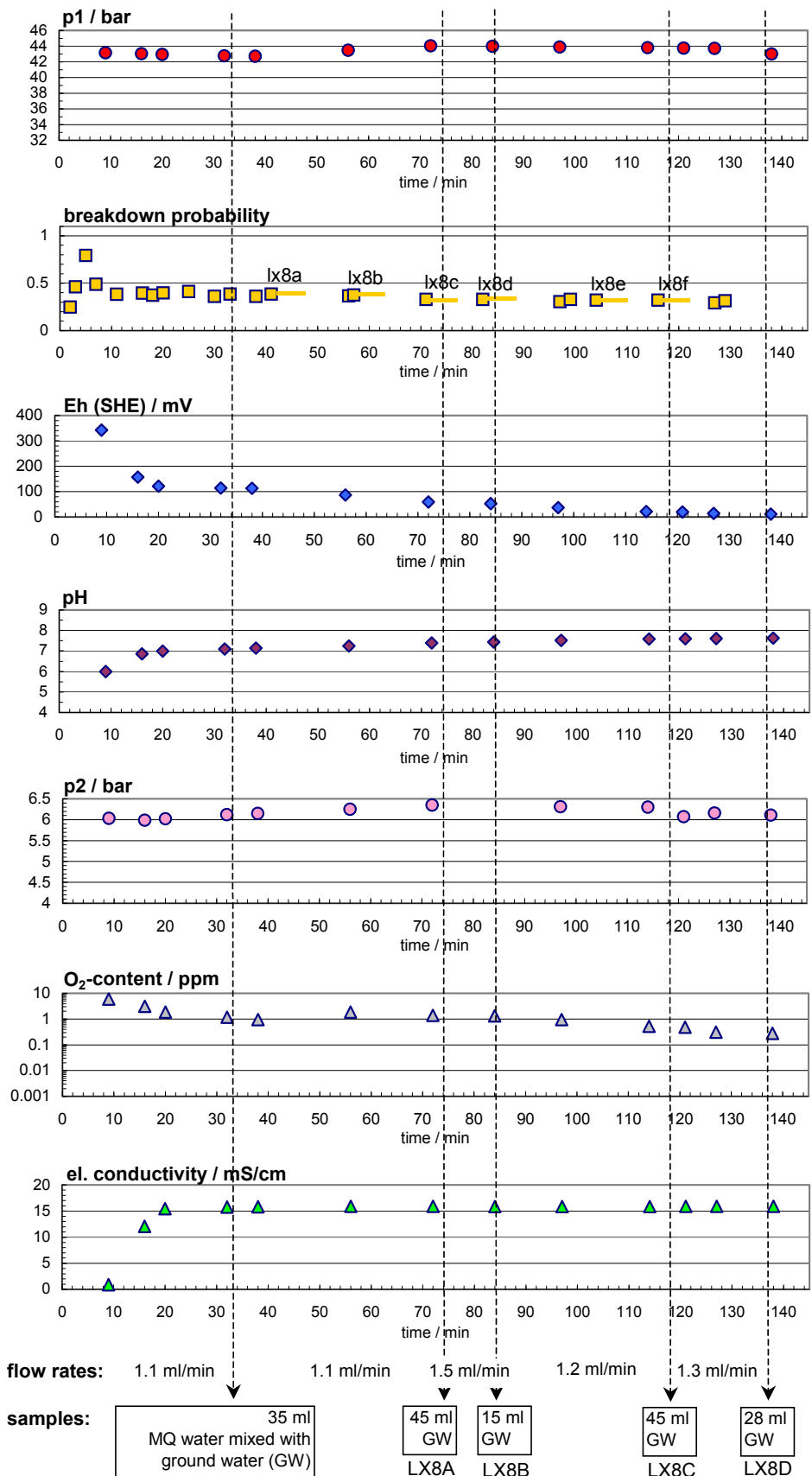
For the groundwater from KLX15A, vertical depth ~ 478 m it was possible to perform a 2 fraction evaluation of the LIBD data. This evaluation of a small 1st colloid fraction with particle sizes around the detection limit (20 nm) agrees well with the data derived from the SEM images (Fig. 6). If one postulates that the large 2nd colloid fraction (Calcite, Alumino-Silicates, Silicates, ..) are mainly mechanically eroded particles from borehole drilling, then the 1st colloid fraction may represent the undisturbed colloids of the natural groundwater in this borehole zone.

This new data come close to the Cl⁻ concentration dependency of the insitu-detected groundwater colloids in the Äspö-tunnel (Fig. 7), especially for groundwater with Cl⁻ concentrations > 5000 mg/l.

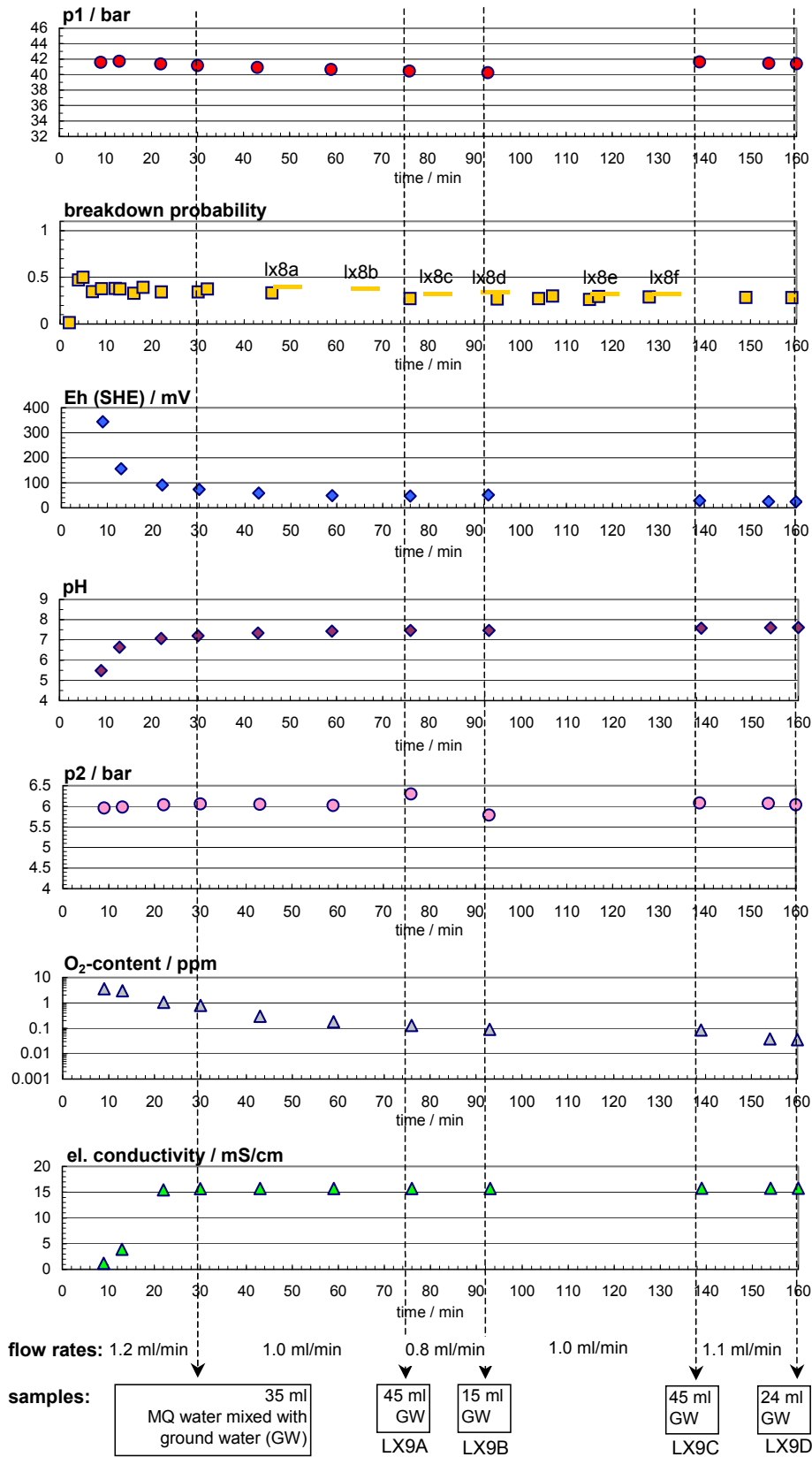
References

- ¹ W. Hauser, H. Geckeis, J.I. Kim, Th. Fierz, A mobile laser-induced breakdown detection system and its application for the in situ-monitoring of colloid migration, *Coll. Surf.* 203, 2002, 37-45
- ² W. Hauser, H. Geckeis, R. Götz, In situ determination of natural groundwater colloids in granite shear zones along the Äspö HRL Tunnel by LIBD, 27th Int. conf. on Scientific Basis for Nuclear Waste Management, Kalmar, S, June 15- 18, 2003
- ³ Geckeis, H., Schäfer, T., Rabung, T., Hauser, W., Möri, A., Missana, T., Eikenberg, J., Degueldre, C., Fierz, T., Alexander, W.R., Inorganic colloid borne actinide migration studied under in-situ conditions at the Grimsel test site, 9th Int. conf. on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Migration '03, Gyeongju, Korea, Sept. 21- 26, 2003
- ⁴ J. Källgarden, P. Andersson, M. Holmqvist, Äspö HRL, TRUE-1 continuation project, History and current status on flow, pressure, water chemistry and installations at the TRUE-1 site, SKB International Progress Report IPR-02-46, Stockholm, S, 2001
- ⁵ Cornell, R.M. and Schwertmann, U., 1996. The Iron Oxides -structure, properties, reactions, occurrence and uses-. VCH-Verlag, Weinheim, 573 pp.
- ⁶ Hauser, W., Götz, R., Geckeis, H., Kienzler, B., In-situ colloid detection in granite groundwater along the Äspö Hard Rock Laboratory access tunnel, In Laaksoharju, M., Äspö Hard Rock Laboratory, Status report of the Colloid investigation conducted at the Äspö HRL during the years 2000-2003, SKB International Progress Report IPR-03-38, Stockholm, S, 2003

Logged raw data from elution of sampling container SKB PVB 220 (KLX15A (623-634.5m))



Logged raw data from elution of sampling container SKB PVB 9506-6 (KLX15A (623-634.5m))



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	Analysis within – or delivery time to lab.
Drill water	Uranine	Glass (brown)	100	No	No	Spectrofluorometry	–
Anions	HCO ₃ ⁻	Plastic	250	No	No	Titration	The same day – maximum 24 hours
	pH (lab)					Pot. meas.	
	cond. (lab)					Cond. meas.	
	Cl ⁻ , SO ₄ ²⁻ , Br ⁻ , F ⁻	Plastic	250	Yes (in connection to the analysis)	No	Titration (Cl ⁻) IC (Cl ⁻ , SO ₄ ²⁻ , Br ⁻ , F ⁻) ISE (F ⁻)	Not critical (month)
	Br ⁻ (control sample to external laboratory)	Plastic	100	Yes	No	ICP MS	Not critical (month)
	I ⁻	Plastic	100	Yes	No	ICP MS	Not critical (month)
Cations etc.	Na, K, Ca, Mg, S(tot), Si(tot), Fe, Mn, Li, Sr	Plastic (acid washed)	100	Yes	Yes (1 mL HNO ₃)	ICP AES ICP MS	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic-PEH (acid washed)	500	Yes	Yes (5 mL HCl)	Spectrophotometry Ferrozine method	As soon as possible the same day
Hydrogen sulphide	HS ⁻	Glass (Winkler)	About 120×2	Yes	1 mL 1 M NaOH+ 1 mL 1M ZnAc	Spectrophotometry	Immediately or if conserved, a few days
Nutrient salts	NO ₂ -N, NO ₃ -N+NO ₂ -N, PO ₄ -P	Plastic	250	Yes	No	Spectrophotometry	Maximum 24 hours
	NH ₄ -N	Plastic cylinder	50	No	No	Spectrophotometry	Maximum 24 hours
Environmental metals etc.	Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn, In	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP AES ICP MS	Not critical (month)
Lanthanoids, U, Th, etc.	Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP AES ICP MS	Not critical (month)

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Analysis within – or delivery time to lab.
Dissolved organic Carbon	DOC	Plastic	250	Yes	Frozen, transported in isolated bag	UV oxidation, IR Carbon analyzer Shimadzu TOC5000	Short transportation time
Total organic Carbon	TOC	Plastic	250	No	Frozen, transported in isolated bag	UV oxidation, IR Carbon analyzer Shimadzu TOC5000	Short transportation time
Environmental isotopes	$\delta^2\text{H}$, $\delta^{18}\text{O}$	Plastic	100	No	–	MS	Not critical (month)
Tritium,	^3H (enhanced.)	Plastic (dry bottle)	500	No	–	LSC	Not critical (month)
Chlorine-37	$\delta^{37}\text{Cl}$	Plastic	500	No	–	ICP MS	Not critical (month)
Carbon isotopes	$\delta^{13}\text{C}$, pmC (^{14}C)	Glass (brown)	100×2	No	–	(A)MS	A few days
Sulphur isotopes	$\delta^{34}\text{S}$	Plastic	1,000	No	–	Combustion, ICP MS	No limit
Strontium-isotopes	$^{87}\text{Sr}/^{86}\text{Sr}$	Plastic	100	No	–	TIMS	Days or Week
Uranium and Thorium isotopes	^{234}U , ^{235}U , ^{238}U , ^{232}Th , ^{230}Th ,	Plastic	1,000	No	–	Chemical separat. Alfa/ gamma spectrometry	No limit
Boron isotopes	$^{10}\text{B}/^{11}\text{B}$	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP MS	No limit
Radon and Radium isotopes	^{222}Rn , ^{226}Ra	Plastic	1,000	No	No	EDA, RD-200	Immediate transport
Dissolved gas (content and composition)	Ar, He, N_2 , CO_2 , O_2 , CH_4 , H_2 , CO , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6	Cylinder of stainless steel	200	No	No	GC	Immediate transport

Component group	Component/element	Sample container (material)	Volume (mL)	Filtering	Preparation/Conservation*	Analysis method	Analysis within – or delivery time to lab.
Colloids	Filter series and fractionation (Analysis of cations and environmental metals)	Polycarbonate filters	2.0, 0.4, 0.2 and 0.05 µm	–	Ar atmosphere	ICP AES ICP MS	
Density	Density	Plastic	250	No	–	Pycnometer	
Archive samples with acid	–	Plastic (washed in acid)	100×2 **	Yes	Yes (1 mL HNO ₃)	–	
Archive samples without acid	–	Plastic	250×2 **	Yes	No	–	

* Suprapur acid is used for conservation of samples.

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

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
TIMS	Thermal Ionization 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
Uranine	Spectro-fluorometry	0.05	–	µg/L	15%	15%
HCO ₃ ⁻	Alkalinity titration	0.2	1	mg/L	4%	< 10%
pH	Pot. Meas.	–	–	–	5%	–
Cond.	Cond. Meas.	0.02	1	mS/m	4%	–
Cl ⁻	Mohr titration	5	70	mg/L	5%	< 10%
Cl ⁻	IC	0.2	0.5		6%	10%
SO ₄ ²⁻	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 ⁻	ISE	–	–		–	–
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	µg/L	8%	10%
Fe(II), Fe(tot)	Spectro-photometry	5	20	µg/L	15%	20%
					(> 30 µg/L)	
HS ⁻	Spectro-photometry	2	30–200	µg/L	18%	20%
			200–500		30 µg/L	
NO ₂ -N	Spectro-photometry	–	0.1–20	µg/L	µg/L	15%
			> 20		2%	
NO ₂ -N +NO ₃ -N	Spectro-photometry	–	0.2–20	µg/L	µg/L	15%
			> 20		2.5%	
NH ₄ -N	Spectro-photometry	–	0.5–20	µg/L	0.5 µg/L	15%
			> 20		2.4%	
PO ₄ -P	Spectro-photometry	–	0.5–20	µg/L	µg/L	15%
			> 20		2.2%	
Al, Zn	ICP	–	0.2–0.7	µg/L	12%	20%
Ba, Cr, Mo Pb	ICP	–	0.01–0.3	µg/L	7–10%	20%
Cd, Hg	ICP	–	0.002–0.5	µg/L	5–9%	20%
Co, V	ICP	–	0.005–0.05	µg/L	5–8%	20%
Cu	ICP	–	0.1–0.5	µg/L	8%	20%
Ni	ICP	–	0.05–0.5	µg/L	8%	20%
P	ICP	–	1–40	µg/L	6%	15%
As	ICP	–	0.01–0.5	µg/L	20%	Within the same size (low conc.)
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y, Hf	ICP	–	0.005–0.05	µg/L	10%	Within the same size (low conc.)
Sc, In, Th	ICP	–	0.05–0.5	µg/L	10%	Within the same size (low conc.)

Component	Method	Detection limit	Reporting limit or range	Unit	Measurement uncertainty ²	"Total" uncertainty ³
Rb, Zr, Sb, Cs, Tl	ICP	–	0.025–0.25	µg/L	10%	Within the same size (low conc.)
U	ICP	–	0.001–0.01	µg/L	12%	Within the same size (low conc.)
DOC	See Tab. A9-1	–	0.5	mg/L	8%	30%
TOC	See Tab. A9-1	–	0.5	mg/L	10%	30%
δ ² H	MS	–	2	‰ SMOW ⁴	1.0‰	–
δ ¹⁸ O	MS	–	0.1	‰ SMOW ⁴	0.2‰	–
³ H	LSC	–	0.8 or 0.1	TU ⁵	0.8 or 0.1 TU	–
δ ³⁷ Cl	ICP MS	–	0.2‰ (20 mg/L)	‰ SMOC ⁶	–	–
δ ¹³ C	A (MS)	–	> 20 mg carbon	‰ PDB ⁷	–	–
pmC (¹⁴ C)	A (MS)	–	> 20 mg carbon	PmC ⁸	–	–
δ ³⁴ S	ICP MS	–	0.2‰	‰ CDT ⁹	0.2‰	–
⁸⁷ Sr/ ⁸⁶ Sr	MS	–	–	No unit (ratio) ¹⁰	0.000020	–
¹⁰ B/ ¹¹ B	ICP MS	–	–	No unit (ratio) ¹⁰	0.0020	–
²³⁴ U, ²³⁵ U, ²³⁸ U,	Alfa spectr.	–	0.05	Bq/L ¹³	0.05 Bq/L	Right order of magnitude
²³² Th, ²³⁰ Th	LSC	–	0.1	Bq/L	0.05 Bq/L	
²²² Rn, ²²⁶ Ra						
Density	Pycnometer			g/mL	0.15%	Within the same size

1. Reporting limits at salinity ≤ 0.4‰ (520 mS/m) and ≤ 3.5‰ (3,810 mS/m) respectively.
2. Measurement uncertainty reported by consulted laboratory, generally 95% confidence interval.
3. Estimated total uncertainty by experience (includes effects of sampling and sample handling).
4. Per mill deviation¹¹ from SMOW (Standard Mean Oceanic Water).
5. TU=Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10⁻¹⁸ (1 Bq/L Tritium = 8.45 TU).
6. Per mill deviation¹¹ from SMOC (Standard Mean Oceanic Chloride).
7. Per mill deviation¹¹ from PDB (the standard PeeDee Belemnite).
8. The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: pmC = 100 × e^{((1.950-y-1.03t)/8.274)} where y = the year of the C-14 measurement and t = C-14 age
9. Per mill deviation¹² from CDT (the standard Canyon Diablo Troilite).
10. Isotope ratio without unit.
11. 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.
12. Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as: δ‰ = 1,000 × (K_{sample} - K_{standard}) / K_{standard}, where K = the isotope ratio and ‰ = ²H, ¹⁸O, ³⁷Cl, ¹³C or ³⁴S etc.

Compilation of water analysis data

Table A9-1. Water composition.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Charge Bal %	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	HCO ₃ ⁻ mg/L	Cl ⁻ mg/L	SO ₄ ²⁻ mg/L	SO ₄ -S mg/L	Br ⁻ mg/l	F ⁻ mg/L	Si mg/L	Fe mg/L	Fe-tot mg/L
KLX15A	623.00	634.51	11925	2007-06-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11926	2007-06-18	-	-	-	-	-	20.9	5,250	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11927	2007-06-25	-	-	-	-	-	17.8	5,500	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11928	2007-06-28	-0.78	2,090	13.5	1,430	52.8	17.0	5,670	408	154	29.9	1.7	3.86	0.721	0.77
KLX15A	623.00	634.51	11929	2007-07-02	-6.63	1,780	13.4	1,350	52.6	16.7	5,720	414	150	29.3	1.9	5.63	0.615	0.60
KLX15A	623.00	634.51	11930	2007-07-04	-0.33	2,110	13.4	1,460	53.2	16.6	5,700	400	155	29.3	1.8	4.00	0.650	0.69
KLX15A	623.00	634.51	11931	2007-07-06	-2.55	2,010	12.5	1,410	50.7	15.6	5,740	417	141	31.1	1.8	5.25	0.530	0.57
KLX15A	623.00	634.51	11932	2007-07-09	-1.98	2,050	12.7	1,440	52.0	16.0	5,790	430	144	28.8	1.8	5.43	0.687	0.73
KLX15A	623.00	634.51	11933	2007-07-11	0.01	2,070	13.2	1,560	56.4	15.7	5,790	423	152	29.1	1.8	5.50	0.679	0.73
KLX15A	623.00	634.51	11934	2007-07-13	-0.44	2,110	13.6	1,550	55.8	16.0	5,890	415	151	28.6	1.6	5.35	0.288	0.31
KLX15A	623.00	634.51	11935	2007-07-16	-	2,090	13.8	1,540	56.0	-	5,700	408	150	28.2	1.7	5.40	0.466	-
KLX15A	623.00	634.51	15027	2007-07-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11983	2007-07-26	-	-	-	-	-	14.2	5,930	415	-	27.8	1.6	-	-	0.56
KLX15A	623.00	634.51	15028	2007-08-01	-1.43	2,060	13.0	1,550	53.9	14.8	5,920	407	156	28.0	1.8	5.37	0.454	0.47
KLX15A	623.00	634.51	15008	2007-08-06	-1.05	2,080	13.8	1,540	54.0	14.1	5,870	425	155	29.0	1.7	5.34	0.537	0.56
KLX15A	623.00	634.51	15009	2007-08-06	-	-	-	-	-	14.4	5,960	420	-	30.4	1.6	-	-	0.56

- = Not analysed

< "value" = result less than detection limit

ChargeBal % = Rel. charge balance error %

SICADA: water_composition

Idcode	Secup m	Seclow m	Sample no.	Fe(II) mg/L	Mn mg/L	Li mg/L	Sr mg/L	I ⁻ mg/L	pH	DOC mg/L	TOC mg/L	HS ⁻ mg/L	Drill water %
KLX15A	623.00	634.51	11925	–	–	–	–	–	–	–	–	–	14.1
KLX15A	623.00	634.51	11926	–	–	–	–	–	7.43	–	–	–	11.0
KLX15A	623.00	634.51	11927	–	–	–	–	–	7.41	–	–	–	8.0
KLX15A	623.00	634.51	11928	0.73	0.553	0.299	26.0	0.253	7.53	1.5	1.5	< 0.006	7.6
KLX15A	623.00	634.51	11929	0.63	0.527	0.277	26.6	0.239	7.48	1.4	1.3	< 0.006	6.7
KLX15A	623.00	634.51	11930	0.68	0.544	0.303	27.5	0.256	7.48	1.4	1.4	0.015	6.4
KLX15A	623.00	634.51	11931	0.54	0.513	0.270	25.4	0.216	7.04	1.5	–	0.027	6.5
KLX15A	623.00	634.51	11932	0.76	0.509	0.273	26.0	0.280	7.45	1.5	1.5	0.023	5.9
KLX15A	623.00	634.51	11933	0.70	0.530	0.291	26.9	0.263	7.53	1.4	–	0.018	5.8
KLX15A	623.00	634.51	11934	0.30	0.513	0.290	26.8	0.240	7.22	1.5	–	< 0.006	5.6
KLX15A	623.00	634.51	11935	–	0.510	0.288	26.4	0.221	–	2.2	–	–	6.0
KLX15A	623.00	634.51	15027	–	–	–	–	–	–	–	–	–	4.9
KLX15A	623.00	634.51	11983	0.46	–	–	–	–	7.17	–	–	< 0.006	5.1
KLX15A	623.00	634.51	15028	0.43	0.533	0.288	27.3	0.257	7.51	1.4	1.2	< 0.006	4.7
KLX15A	623.00	634.51	15008	0.55	0.549	0.293	27.7	0.257	7.42	1.5	1.4	0.007	4.4
KLX15A	623.00	634.51	15009	0.55	–	–	–	–	7.56	–	–	0.008	4.5

– = Not analysed

< "value" = result less than detection limit

ChargeBal % = Rel. charge balance error %

SICADA: water_composition

Idcode	Secup m	Seclow m	Sample no.	EiCond mS/m	NH ₄ -N mg/L	NO ₂ -N mg/L	NO ₃ -N mg/L	NO ₂ -N+NO ₃ -N mg/L	PO ₄ -P mg/L	P mg/L	Density g/mL
KLX15A	623.00	634.51	11925	–	–	–	–	–	–	–	–
KLX15A	623.00	634.51	11926	1,540	–	–	–	–	–	–	–
KLX15A	623.00	634.51	11927	1,610	–	–	–	–	–	–	–
KLX15A	623.00	634.51	11928	1,620	0.0501	0.0002	< 0.0003	0.0003	< 0.0005	0.00227	1.0043
KLX15A	623.00	634.51	11929	1,660	0.0831	< 0.0002	0.0004	0.0005	< 0.0005	0.00378	–
KLX15A	623.00	634.51	11930	1,660	0.0898	0.0018	0.0003	0.0021	< 0.0005	0.00352	–
KLX15A	623.00	634.51	11931	1,660	0.0755	< 0.0002	0.0003	0.0004	< 0.0005	–	–
KLX15A	623.00	634.51	11932	1,660	0.0987	< 0.0002	0.0055	0.0055	< 0.0005	< 0.040	–
KLX15A	623.00	634.51	11933	1,660	0.0917	0.0002	< 0.0003	0.0003	< 0.0005	–	–
KLX15A	623.00	634.51	11934	1,670	0.0792	< 0.0002	< 0.0003	< 0.0003	< 0.0005	–	–
KLX15A	623.00	634.51	11935	–	0.0807	0.0002	< 0.0003	0.0004	< 0.0005	–	–
KLX15A	623.00	634.51	15027	–	–	–	–	–	–	–	–
KLX15A	623.00	634.51	11983	1,680	0.0811	–	–	–	–	–	–
KLX15A	623.00	634.51	15028	1,680	0.0821	0.0002	0.0009	0.0011	< 0.0005	< 0.040	–
KLX15A	623.00	634.51	15008	1,690	0.0813	0.0002	< 0.0003	0.0003	< 0.0005	< 0.040	1.0046
KLX15A	623.00	634.51	15009	1,680	0.0785	–	–	–	–	–	–

– = Not analysed

< "value" = result less than detection limit

ChargeBal % = Rel. charge balance error %

SICADA: water_composition

Table A9-2. Trace elements.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	U mg/L	Th mg/L	As mg/L	Sc mg/L	Cd mg/L	Hg mg/L	V mg/L	Rb mg/L	Y mg/L	Zr mg/L	In mg/L	Cs mg/L	Ba mg/L	La mg/L
KLX15A	623.00	634.51	11928	2007-06-28	0.202	< 0.2	< 1	< 0.5	< 0.002	< 0.002	0.089	36.2	0.172	< 0.3	< 0.5	1.85	102.0	< 0.05
KLX15A	623.00	634.51	11929	2007-07-02	0.195	< 0.2	< 1	< 0.5	< 0.002	< 0.002	0.104	36.5	0.157	< 0.3	< 0.5	1.83	99.2	< 0.05
KLX15A	623.00	634.51	11930	2007-07-04	0.190	< 0.2	< 1	< 0.5	< 0.002	< 0.002	0.120	35.7	0.107	< 0.3	< 0.5	1.77	97.2	< 0.05
KLX15A	623.00	634.51	11932	2007-07-09	0.142	< 0.2	1.4	< 0.5	< 0.05	< 0.002	0.103	35.3	0.296	< 0.3	< 0.5	1.79	98.8	< 0.05
KLX15A	623.00	634.51	15028	2007-08-01	0.168	< 0.2	< 1	< 0.5	< 0.05	< 0.002	0.186	33.5	0.407	< 0.3	< 0.5	1.69	95.0	< 0.05
KLX15A	623.00	634.51	15008	2007-08-06	0.144	< 0.2	< 1	< 0.5	< 0.05	< 0.002	0.082	34.5	0.397	< 0.3	< 0.5	1.82	91.8	< 0.05

< "value" = result less than detection limit

SICADA: trace_elements

Idcode	Secup m	Seclow m	Sample no.	Hf mg/L	Tl mg/L	Ce mg/L	Pr mg/L	Nd mg/L	Sm mg/L	Eu mg/L	Gd mg/L	Tb mg/L	Dy mg/L	Ho mg/L	Er mg/L	Tm mg/L	Yb mg/L	Lu mg/L	
KLX15A	623.00	634.51	11928	< 0.05	< 0.005	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KLX15A	623.00	634.51	11929	< 0.05	< 0.005	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KLX15A	623.00	634.51	11930	< 0.05	< 0.005	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KLX15A	623.00	634.51	11932	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KLX15A	623.00	634.51	15028	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
KLX15A	623.00	634.51	15008	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

< "value" = result less than detection limit

SICADA: trace_elements

Table A9-3. Isotopes I (^3H , $\delta^2\text{H}$, $\delta^{18}\text{O}$, $^{10}\text{B}/^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$ and ^{14}C).

Idcode	Secup m	Seclow m	Sample no	Sampling date	$\delta^2\text{H}$ 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
KLX15A	623.00	634.51	11926	2007-06-18	-81.7	8.00	-10.70	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11927	2007-06-25	-79.2	1.20	-10.90	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11928	2007-06-28	-79.9	1.00	-10.90	0.2363	16.7	x	0.715622	x	x	0.09
KLX15A	623.00	634.51	11929	2007-07-02	-80.0	< 0.8	-10.90	0.2355	17.0	x	0.715620	x	x	0.31
KLX15A	623.00	634.51	11930	2007-07-04	-79.5	1.35	-10.90	0.2354	16.7	x	0.715591	x	x	0.21
KLX15A	623.00	634.51	11931	2007-07-06	-79.0	< 0.8	-10.90	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11932	2007-07-09	-79.3	1.08	-10.80	0.2364	19.0	x	0.715592	x	x	0.20
KLX15A	623.00	634.51	11933	2007-07-11	-79.7	1.06	-10.70	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11934	2007-07-13	-79.5	1.23	-10.70	-	-	-	-	-	-	-
KLX15A	623.00	634.51	11935	2007-07-16	-79.3	1.39	-10.70	-	-	-	-	-	-	-
KLX15A	623.00	634.51	15028	2007-08-01	-79.8	0.92	-10.70	0.2371	18.0	x	0.715597	x	x	0.34
KLX15A	623.00	634.51	15008	2007-08-06	-80.8	< 0.8	-10.80	0.2374	17.3	x	0.715614	x	x	0.49

- = Not analysed

x = Not analysed due to analytical problems

< "value" = result less than detection limit

SICADA: isotopes_1

Table A9-4. Isotopes II (²³⁸U, ²³⁴U, ²³⁰Th, ²²⁶Ra and ²²²Rn).

Idcode	Secup m	Seclow m	Sample no.	Sampling date	²³⁸ U	²³⁵ U	²³⁴ U	²³² Th	²³⁰ Th	²²⁶ Ra	²²² Rn	²²² Rn
					mBq/L	mBq/L	mBq/L	mBq/L	mBq/L	Bq/L	Bq/L	Bq/L
											At time of analysis	At time of collection
KLX15A	623.00	634.51	11928	2007-06-28	2.4	0.07	5.4	0.31	0.89	< 0.015	49.0	115
KLX15A	623.00	634.51	11929	2007-07-02	2.2	< 0.02	5.0	0.31	0.68	0.091	78.0	124
KLX15A	623.00	634.51	11930	2007-07-04	2.3	0.28	4.9	0.15	0.41	< 0.015	55.7	92.8
KLX15A	623.00	634.51	11932	2007-07-09	2.4	< 0.02	4.1	0.40	0.66	< 0.015	49.4	79.7
KLX15A	623.00	634.51	11983	2007-07-26	3.5	0.11	8.4	0.13	0.12	< 0.015	3.3	68.2
KLX15A	623.00	634.51	15028	2007-08-01	–	–	–	–	–	0.269	14.8	98.3
KLX15A	623.00	634.51	15008	2007-08-06	2.0	0.07	4.3	0.31	0.62	0.336	38.4	90.0
KLX15A	623.00	634.51	15009	2007-08-06	–	–	–	–	–	0.085	33.9	81.1

– = Not analysed

< "value" = result less than detection limit

SICADA: isotopes_2

Table A9-5. Dissolved gases.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Ar mL/L	He mL/L	N2 mL/L	CO2 mL/L	CH4 mL/L	O2 mL/L	H2 μL/L	CO μL/L	C2H6 μL/L	C2H4 μL/L	C2H2 μL/L	C2H2+C2H4	C3H8 μL/L	C3H6 μL/L	DISS_GAS mL/L H2O
KLX15A	623.00	634.51	15008	2007-08-07	< 0.15	2.88	713.4	0.123	0.020	3.323	32.3	2.92	0.60	–	–	< 0.046	< 0.05	< 0.05	703
KLX15A	623.00	634.51	15008	2007-08-07	0.68	2.80	83.0	0.140	0.021	0.089	< 2.6	< 4.3	0.73	0.83	0.33	–	0.29	0.36	87

< "value" = result less than detection limit

SICADA: Gas_dissolved