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Chemical-, microbiological- and dissolved gas data from groundwater in four borehole sections

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Abstract

This report describes a study performed during 2009 which focused on the production of sulphide (microbial sulphate reduction) in deep groundwater that was implemented in the core drilled boreholes KLX06, –475 to 482 meter above sea level, m a s l, KAS03,–97 to 241 and –613 to 984 m a s l, and KAS09, –96 to –125 m a s l, at Laxemar and Äspö. The study aimed to increase knowledge of background groundwater levels of sulphide and its variations in time and space through the analysis of sulphide and parameters related to sulphide production. Sampling of groundwater was conducted in three core drilled boreholes of varying age as time series with continuous pumping and as single samples. The analysis program covered chemical parameters (pH, chloride, sulphate, iron, and organic carbon), dissolved gas composition, stable isotopes in groundwater (δ^2H, $\delta^{18}O$, $\delta^{34}S$, $\delta^{13}C$), stable isotopes of gaseous compounds (δ^2H, $\delta^{13}C$, $\delta^{18}O$), microbiological parameters (sulphate- and iron reducing bacteria, SRB and IRB), phthalates and low molecular mass organic acids (LMMOA).

The sampling in KLX06 was carried out as time series with a 9 week pause in pumping. When the water volume discharged was about 150 times that of the packer-isolated borehole section, sulphides decreased from 7 mg L^{-1} to 0.05 mg L^{-1} and the salinity increased from 740 to 1,480 mg L^{-1}. After a 9 weeks pause in pumping, the sulphide concentration and salinity again approached the original values, i.e. 7 mg L^{-1} of sulphide and 450 mg L^{-1} of chloride. The SRB and IRB showed high concentrations that were reduced during pumping in the borehole. The water in the standpipe which has a different water composition than the groundwater, also showed similar high concentrations of sulphide and SRB. The standpipe is a plastic pipe in the wider upper part of the borehole; connected with the tube from the packer of the borehole section and used to accommodate a filter and a groundwater pump when collecting samples. Analyses of $\delta^{34}S$ in dissolved sulphide and sulphate showed a fractionation corresponding to about +20 ‰, which is expected for open systems where microbial sulphate reduction occurs. Analyses of dissolved gases showed that those gases that are biochemically active (carbon dioxide, hydrogen and methane) decreased in concentration during pumping, while the concentrations of gaseous compounds such as nitrogen and argon were unchanged.

In KAS03 and KAS09, drilled and equipped at the end of the 1980s, the installed equipment was lifted up and inspected visually following completion of sampling. Water standpipes were partially filled with black sludge; connection pipes and tubing were covered with deposits that seemed to be of salt and rust.

Analyses of the water in the standpipes reflected the conditions in which water was not exposed to the impact of pumping for a couple of years back. The concentrations of SRB were high (> 10^4 cells mL^{-1}), especially in KAS09, where sulphides were sometimes also very high – between 92 and 102 mg L^{-1}. A comparison of the ionic product of iron (II) and sulphide with the saturation indices of amorphous and crystalline (mackinawite) monosulphides shows that the measured sulphide in KAS09 results in significant supersaturation. Given the fast kinetic processes for precipitation of monosulphides, supersaturation is unlikely. A possible reason for the supersaturation, which was mainly observed in samples with high content of organic matter and particulates, could be that the analysis of sulphide most likely included both dissolved and particulate sulphide.

Overall, this study has shown that elevated sulphide concentrations in core drilled boreholes may occur in the periods between pumping. Different chemical and physical conditions prevail in the isolated borehole section, in the tubes and in the standpipe as compared with the surrounding rock fractures. For example, new surfaces and materials are added (drilled borehole walls and installed equipment), chemical gradients may be generated during pumping and by differences in composition between standpipe and section water. Further studies are required in order to understand what parameters are important for the growth of sulphate reducing bacteria in the borehole sections, tubes and standpipe, and to demonstrate the relative importance of the possible reductants, hydrogen, methane, acetate, biogenic carbon, and organic carbon in equipment material, which are involved in the reduction of sulphate.

Sammanfattning

En undersökning fokuserad på produktionen av sulfid (mikrobiell sulfatreduktion) i djupa grundvatten har genomförts i kärnborrhålen KLX06, –475 till –482 meter över havsytan, m ö h, KAS03, –97 till 241 och –613 till –984 m ö h, och KAS09, –96 till 125 m ö h, på Laxemar och Äspö. Syftet med undersökningen var att öka kunskapen om bakgrundshalter sulfid och variationer i tid och rum i kärnborrhål genom att analysera sulfid och parametrar relaterade till sulfidproduktion. Provtagning av grundvatten genomfördes i tre kärnborrhål av varierande ålder, dels som tidsserier under kontinuerlig pumpning och dels som enstaka prov. Analysprogrammet omfattade kemiska parametrar (pH, klorid, sulfid, sulfat, järn och organiskt kol), gassammansättning, stabila isotoper i grundvatten ($\delta^{34}S$, $\delta^{13}C$), stabila isotoper i gaser ($\delta^{2}H$, $\delta^{13}C$, $\delta^{18}O$), mikrobiologiska parametrar (sulfat- och järnreducerande bakterier, SRB och IRB) samt ftalater och lågmolekylära organiska syror.

I KLX06 utfördes provtagningen som tidsserier med ett längre uppehåll i pumpningen. När sektionsvattnet omsatts ca 150 gånger hade sulfidhalten sjunkit från 7 mg L^{-1} till 0,5 mg L^{-1} och kloridhalten ökat från 740 mg L^{-1} till 1 480 mg L^{-1} Då ett 9 veckor långt uppehåll gjordes i pumpningen steg sulfidhalten återigen till det ursprungliga 7 mg L^{-1} och kloridhalten sjönk till 450 mg L^{-1}.Även halterna SRB och IRB var höga i sektionsvattnet och minskade vid pumpning i borrhålet. Vattnet i vattenståndsröret (plaströr i den bredare övre delen av borrhålet) hade en annan kemisk sammansättning än sektionsvattnet och motsvarande höga halter sulfid och SRB. Analyser av $\delta^{34}S$ i löst sulfid och sulfat visade att fraktioneringen motsvarade 20 ‰, vilket motsvarar det förväntade i öppna system. Analyserna av lösta gaser visade att gaser som är biokemiskt aktiva, koldioxid, väte, metan, minskade i koncentration under det att pumpning pågick medan koncentrationen av gaser som kväve och argon var oförändrade.

I KAS03 och KAS09, som borrades och instrumenterades i slutet av 1980-talet, lyftes den installerade utrustningen upp och inspekterades visuellt efter utförd provtagning. Vattenståndsrören var delvis fyllda av en svart slamliknande utfällning, rörstänger och slangar var till synes belagda med utfällningar av salt och rost. Analyserna av vattnet i vattenståndsrör och avgränsade sektionerna avspeglade förhållanden i vatten som inte utsatts för påverkan av pumpning sedan ett par år tillbaka i tiden. Halterna SRB var höga (> 10^4 celler mL^{-1}), speciellt i KAS09, där även sulfidhalten var mycket hög – mellan 92 och 102 mg L^{-1}. En jämförelse av jonprodukten för järn (II) och sulfid med mättnadsindex för amorfa och kristallina (mackinawite) monosulfider visar dock att de uppmätta sulfidhalterna i KAS09 resulterar i stor övermättnad. Med tanke på de snabba kinetiska förloppen för utfällning av monosulfider är övermättnad av dessa i grundvatten osannolikt. Jonprodukten översteg mättnadsindex i vattenprover med hög halt organiskt material och partiklar, vilket kan förklaras av att analysen av sulfid sannolikt omfattat både löst och partikulärt sulfid.

Sammantaget har undersökningarna visat att förhöjda sulfidhalter i kärnborrhål kan uppstå i perioder mellan pumpningar. Andra kemiska och fysiska förhållanden råder i borrhålet än i det omgivande bergets spricksystem. Dessa förhållanden kan uppstå av flera anledningar; nya ytor och material tillkommer (borrhålsväggar och installerad utrustning), kemiska gradienter kan uppstå vid pumpning och genom olikheter i sammansättning mellan vattenståndsrör och sektionsvatten. Ytterligare studier behövs dock för att förstå vilka parametrar som är viktiga för tillväxt av sulfidproducerande bakterier i borrhål och vilka reduktanter som medverkar vid reduktionen av sulfat (möjliga reduktanter är väte, metan, acetat, biogent kol, organiskt kol från material i utrustningen).

Contents

1 Introduction

1.1 General

Hydrogen sulphide produced by microbial sulphate reduction under anaerobic conditions may corrode the copper canisters used for final disposal of spent nuclear fuel. Important aspects for the safety assessment are therefore information on the conditions that promote microbial sulphate reduction, the reduction rate and the variability of the hydrogen sulphide concentration in space and time.

Varying hydrogen sulphide concentrations (0.001–0.1 mM) have been observed in groundwater within the same borehole and between boreholes during the pre-investigations (1986–1990) at Äspö as well as during the site investigations and monitoring programmes at Laxemar and Forsmark. In general, low concentrations of hydrogen sulphide were reported from the site investigations at Laxemar and Forsmark using in situ sampling equipment[1], despite that in many cases the number of sulphate reducing bacteria (SRB) was high /Gimeno et al. 2009/. The subsequent monitoring campaigns showed in comparison enhanced sulphide concentrations in several boreholes and in some boreholes the sulphide concentrations were time dependent, i.e. the concentration decreased with pumping, while in others pumping had little or no effect. A number of explanations to the observed variation in sulphide concentration have been discussed, such as pumping method and velocity, sampling method, aging of boreholes and changed physical and chemical conditions due to addition of in situ equipment. The reason could be a single causing factor or a combination of several factors. During the process of reducing sulphate to sulphide a reducing agent must be involved, this could be either dissolved organic carbon or molecular hydrogen. The sources of organic carbon can be leaching of plastic material installed in the drill holes or biological autotrophic activity. The sources for molecular hydrogen can be deep crustal processes or corrosion processes of metal equipment.

This project is focused on the concentration of sulphide and sulphide related parameters in core drilled boreholes KLX06, KAS03 and KAS09 at Laxemar and Äspö, see Figure 1-1. The project includes two activities; one concerning sampling and analyses and one regarding the removal and installation of equipment in borehole KAS03.

1.2 Objective and scope

This project focused on the sulphide production in core drilled boreholes at Laxemar and Äspö. The overall objective was to perform detailed chemical and microbiological characterisation of groundwater in three core drilled boreholes (four delimited sections) with a previous history of elevated sulphide concentrations. The aim was to provide useful information for describing the processes involved in microbiological sulphide production.

Single samples (KAS03, KAS09) and time series of samples (KLX06) were collected and analysed. The analytical programme included analyses of basic chemical parameters including sulphide and Fe^{2+}, dissolved gas composition, stable isotopes ($\delta^{13}C$ and $\delta^{2}H$) in gaseous compounds, $\delta^{34}S$ in sulphide and sulphate, analyses of iron- and sulphate reducing microbes and in situ measurements of pH and redox (KLX06).

[1] Sampling using the Complete chemical characterisation method, CCC. The method is further described in Section 1.5.2.

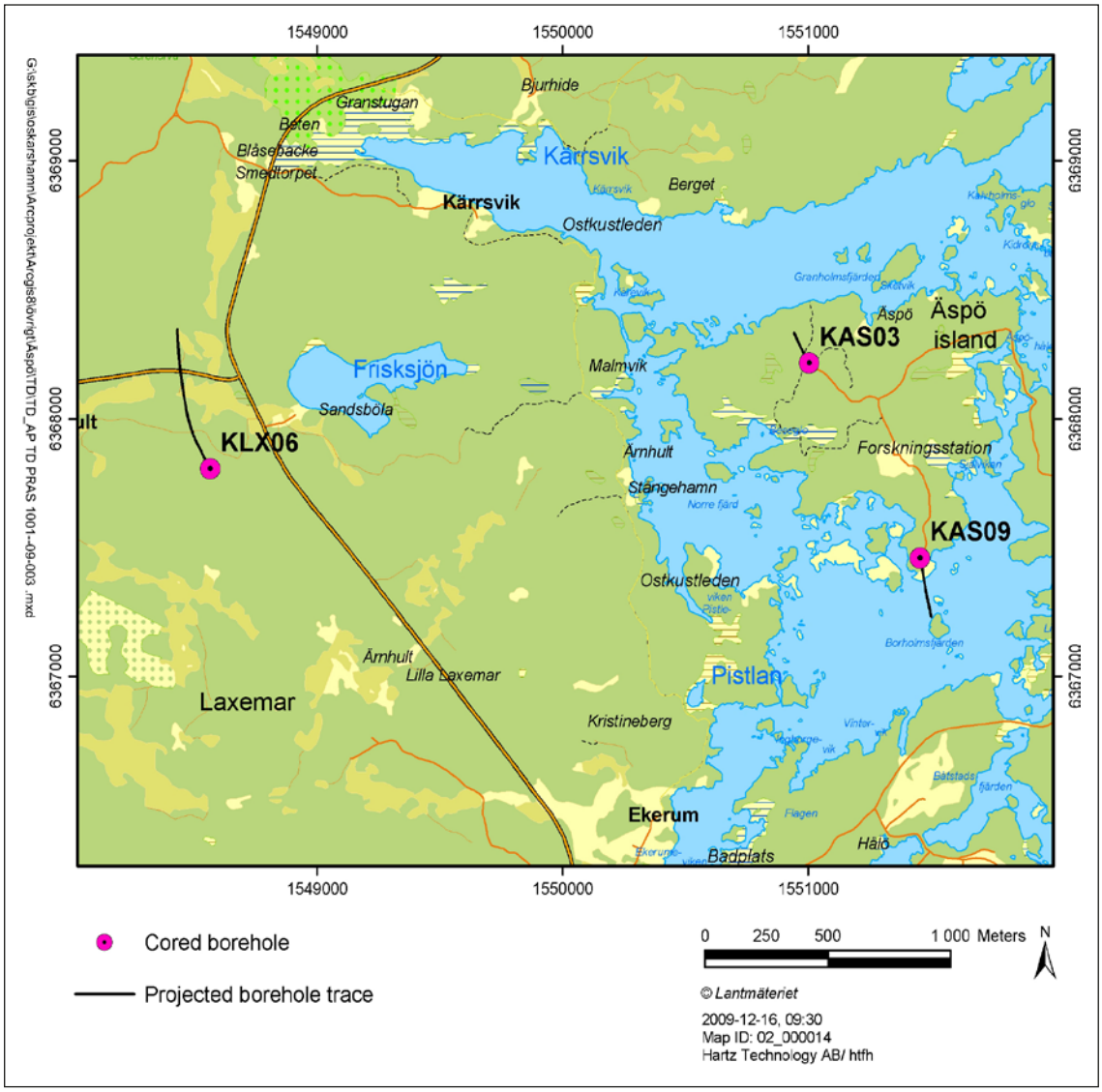

Figure 1-1. *Locations of the core drilled boreholes KLX06, KAS03 and KAS09 at Laxemar and Äspö island.*

1.3 Quality Assurance

This document reports performance and results from the activity *Undersökning av sulfidproduktion i grundvatten på Äspö och Laxemar* in cored boreholes KLX06, KAS03 and KAS09 at Laxemar and Äspö. The work was carried out in accordance with activity plan AP TD PRAS1001-09-002. In Table 1-1 controlling documents for performing this activity are listed. Both activity plan and measurement systems descriptions are SKB's internal controlling documents. This report presents hydrogeochemical and microbiological data from field work carried out during the period of February to May 2009. The obtained data from the activity are reported to the SICADA database and are traceable by the activity plan number.

The locations of KLX06, KAS03 and KAS09 are shown in Figure 1-1.

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

Project plan	**Number**	**Version**
Investigation of sulphide production processes in groundwaters at Äspö and Laxemar.	SKBdoc 1189707	1.0
Activity plan		
Undersökning av sulfidproduktion i grundvatten på Äspö och Laxemar.	APTDPRAS1001-09-002	1.0
Measurement system descriptions	**Number**	**Version**
Mätsystembeskrivning (MSB) – Handhavande del, System för hydrologisk och meteorologisk datainsamling. Vattenprovtagning och utspädningsmätning i observationshål.	SKB MD 368.010	2.0
Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation.	SKB MD 434.004 SKB MD 434.005 SKB MD 434.006 SKB MD 434.007 SKB MD 434.018	1.0
Instructions		
Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning.	SKB MD 600.004, SKB doc 1191443	1.0
Provtagning och analys-kemilaboratorium.	SKB MD 452.001-019	

1.4 Selection of boreholes

When selecting suitable boreholes and borehole sections for the investigation several criteria were considered;

- the physical condition of the borehole and the installed equipment,
- the presence of a circulation section, which enables water sampling,
- previously observed enhanced sulphide concentrations,
- elapsed time since drilling of the borehole.

The aim was to investigate boreholes with elevated sulphide concentrations, but at the same time with various characteristics regarding age, location and water composition. KLX06, situated at Laxemar, was drilled during the site investigations in 2004. The borehole was however excluded from the monitoring programme at an early stage when the area of interest for a possible repository shifted. KAS03, located at Äspö, was drilled during the pre-investigations in 1986–1990. The borehole had been part of regular monitoring for several years until recently when the installed equipment (packers etc), required repair and exchange. Section 554–570 m in KLX06 and sections 107–252 m and 627–1,002 m in KAS03 were circulation sections that enabled water sampling using the equipment for hydrochemical monitoring. KAS09 (section 116–150 m) was later added to the investigation, since Äspö Laboratory planned to remove and replace the packer system. Descriptions of the investigated boreholes, previous investigations and historic sulphide concentrations are given in Section 3.

1.5 Investigations in core drilled boreholes

The following text describes the drilling and subsequent investigations that were typically performed in core drilled boreholes during the site investigations. The aim is to give an idea of what kind of impact boreholes are subjected to from drilling to the stage of performing different investigations.

1.5.1 From drilling to monitoring

Drilling of a borehole creates new surfaces and the surface to volume ratio is different compared to fractures. Installation of equipment creates new surfaces and adds new materials (metal, plastic, rubber) to a borehole. Intermittent pumping activities can generate new chemical conditions and physical effects (turbulence, high water velocity etc) that are unnatural to bacteria living in the underground.

In connection to different activities, special precautions are taken for boreholes that are intended for chemical and microbiological characterisation. Equipment that is being used in situ in the borehole before and during the investigation is cleaned according to specific routines involving ethanol and other antibacterial substances (SKB MD 600.004).

The sequence below describes a common line of activities in core drilled boreholes, from drilling of the borehole to different kinds of tests and installation of equipment for continuous monitoring of pressure and water chemistry.

- **Drilling of the borehole** involves formation of drilling debris, addition of drilling water marked with a tracer (Uranine[2]) and extensive pumping. After drilling 0–100 m, equipment for air-lift pumping (using gaseous nitrogen) is installed in the borehole. The air-lift pumpingcreates a pressure drawdown and helps remove water and cuttings while drilling between 100 m and 1,000 m. For KLX06, the amount of flushing water consumed during drilling was 1,800 m^3, giving an average consumption of about 2 m^3 per metre drilled. The amount of effluent return water from drilling was 3,300 m^3, giving an average of about 3.7 m^3 per metre drilled /Ask et al. 2005/.
- **Logging activities** (geophysical logging, flow logging, BIPS logging). The logging activities involve mixing of the water column as the equipment is raised and lowered. In addition, pumping takes place during flow logging. Filming of the borehole walls (Borehole Image Processing System, BIPS), is performed in order to get information on the occurrence of rock types and of fracture distribution and orientation. It is common knowledge that older boreholes are difficult to film since the borehole walls have developed a coating/black colour layer on the surface.
- **Chemical and microbiological characterisation** of the groundwater with in situ sampling equipment and on line measurements of pH, redox, dissolved oxygen and conductivity in a delimited section (see Section 2.4.1). The water flow is typically about 200 mL min^{-1} and the total discharged volume can amount to about 5–8 m^3. This investigation was performed in KAS03, but not in KLX06 or KAS09.
- **Hydraulic injection tests** using Uranine as a tracer. These tests are only performed in some boreholes. The water flow during hydraulic tests can amount to up to 300 L/min, depending on transmissivity of the fractures.
- **Installation of equipment** for continuous monitoring of groundwater level, groundwater sampling and groundwater flow measurements. Section 4.1 describes the design of the equipment and a review of the different materials added to the borehole.
- **Groundwater sampling** (monitoring) once or twice a year. The pumping equipment is placed in the standpipe above the delimited section and the water flow is typically 300 mL min^{-1}. The discharged volume is in general about 100 to 200 litres for every sampling occasion.
- **Monitoring of groundwater flow** by using a tracer dilution technique. Uranine is added to a delimited borehole section while pumping and reducing the water pressure in surrounding boreholes. A hydraulic interference test was performed in KLX06 in 2007 /Walger et al. 2007/.

1.5.2 Methods for groundwater sampling

Two different methods are used for sampling and characterisation of groundwater in core drilled boreholes; complete chemical characterisation (CCC) and hydrochemical monitoring. A brief description of the two methods and equipment is given below. During this project sampling was performed using the hydrochemical monitoring equipment. One of the differences between the two methods is that the CCC method is performed early in the chain of investigation, while the hydrochemical monitoring activity is carried out after the injection tests and groundwater flow measurements. There is a possibility that during this time the chemical, physical and biological conditions in the borehole have changed due to aging and other investigation activities, although most likely the actual drilling with mammoth pumping and use of drilling water causes the most serious perturbation of all borehole activities.

[2] Uranine was added to the flushing water that supplies the drilling head during drilling of a borehole to give an estimation of the amount of flushing water that has been lost to the borehole and adjacent bedrock. Uranine is a fluorescein sodium derivative, formula: $C_{20}H_{10}Na_2O_5$, CAS no: 518-47-8.

Complete chemical characterisation (CCC)

The purpose of the CCC during the site investigations in Oskarshamn and Forsmark was to obtain as undisturbed groundwater samples as possible and therefore the CCC was generally performed 1–2 months after drilling of the borehole. To promote pristine conditions, only few other activities (BIPS logging, flow logging) were allowed before CCC and all equipment used in the borehole was cleaned and disinfected according to special cleaning instructions (SKB MD 600.04). During the pre-investigations at Äspö, the CCC was performed several months after completed drilling (up to 10–12 months).

The equipment for CCC consists of an umbilical hose (1,000 m) with down hole units; upper and lower packers for delimiting a borehole section, a down hole piston pump controlled by a pump unit at the ground surface, a measuring probe for in situ measurements of pH, Eh, pressure and water temperature and a sampling unit for collecting in situ samples at maintained pressure. The sample water is pumped through the downhole units and further through a Tecalan (polyamide) tube in the umbilical hose to the ground surface where samples for different analyses are collected. Figure 1-2 gives an overview of the equipment. The surfaces that are in contact with the borehole/groundwater are either polyamide or high quality stainless steel. Lubricants (Vaseline or Teflon spray, Locktite) are used sparsely on o-rings in valves and at different types of joints.

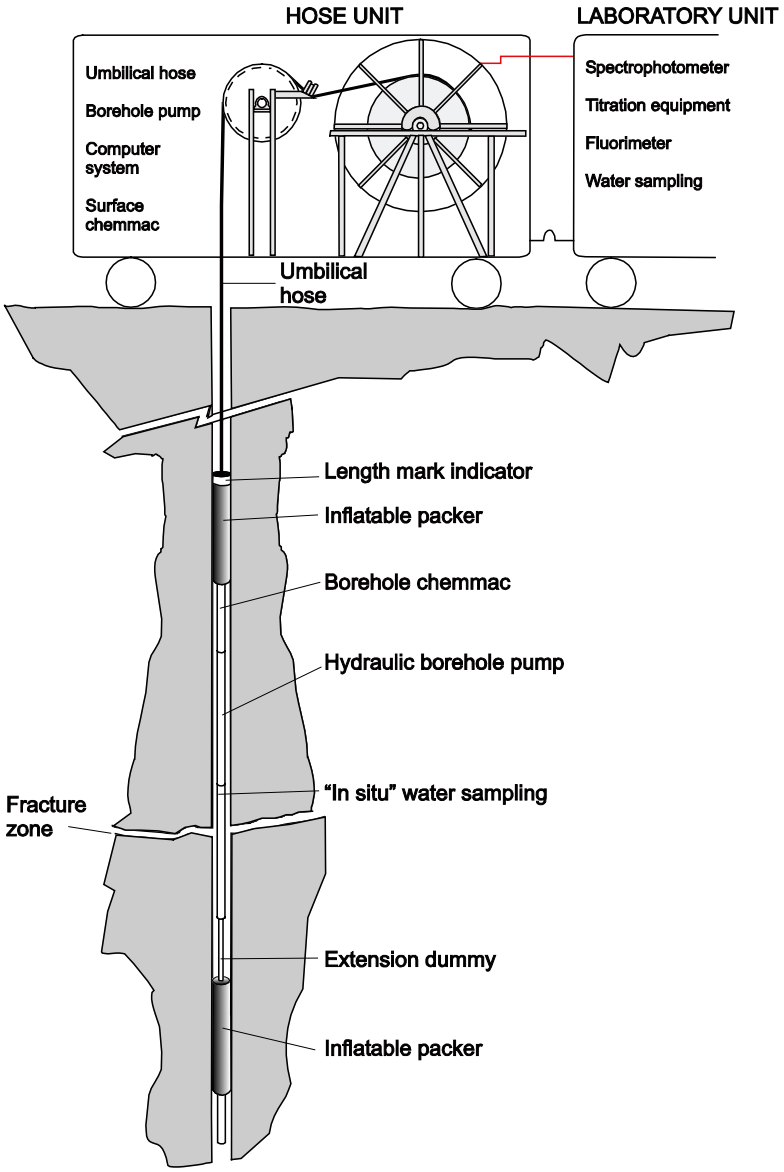

Figure 1-2. *The mobile laboratory including laboratory unit, hose unit and down hole equipment. The configuration of the down hole units in the borehole can be varied depending on desired section length. However, the in situ water sampler must always be positioned first in the sample water path.*

During the site investigations the length of the delimited borehole sections were in general a few metres and the water flow rate between 10 to 250 mL min^{-1} depending on the water yield. The pumping periods were minimum three weeks and generally two samples were collected per week. The advantage with this method compared to the hydrochemical monitoring is that there is a shorter contact time between the sampled water and the equipment material.

Hydrochemical monitoring

After completion of the principal investigations, the borehole was prepared for future monitoring of groundwater levels and chemical parameters. A packer system was installed, dividing the borehole into maximum of ten sections. The in situ equipment consists of different materials; plastic, rubber and metal. A detailed description of the equipment and sampling procedure is given in Section 2.

1.6 Microbiology and gaseous compounds

The biological mechanisms and responsible reactions behind the evolution of sulphide in the monitoring boreholes in Laxemar and Forsmark are at present not known in detail. The reactions introduced next in Equations 1-1 to 1-5 are possible; however, it remains to be demonstrated if only one or combinations of the reactions are causing the high sulphide concentrations.

1.6.1 Sulphate reducing bacteria

Sulphate reduction at temperatures and pressures prevailing in deep groundwater environment is a microbiological process. The chemical reduction to hydrogen sulphide at these conditions is extremely slow as revealed by the calculated half life for thermo-chemical sulphate reduction in the presence of acetate and elemental sulphur at 100°C that is 372,000 years /Cross et al. 2004/.

The SRB use the S atom in the sulphate molecule as an electron-acceptor and the reduced product is hydrogen sulphide. The energy and electron donor for SRB can be either organic compounds or hydrogen. With a general organic compound, written as CH_2O, the reaction with sulphate can be written (Equation 1-1):

$$2(CH_2O) + SO_4^{2-} + 2H^+ \rightarrow 2HCO_3^- + HS^- + 3H^+ \qquad \text{(Eq. 1-1)}$$

Organic compounds that can be used by different types of SRB are fermentation products like short chain organic acids, fatty acids and higher molecular weight hydrocarbons. Many SRB, especially of the genus *Desulfovibrio,* can grow on lactate. The lactate molecule is incompletely oxidized to acetate and carbon dioxide and the electrons are transported to electron transport enzymes in the cell membrane and then further to the sulphate reduction enzymes in the cytoplasm. The overall reaction is written (Equation 1-2):

$$2 \text{ lactate} + SO_4^{2-} + 2H^+ \rightarrow 2 \text{ acetate} + 2CO_2 + HS^- + H^+ + 2H_2O \qquad \text{(Eq. 1-2)}$$

In this metabolism lactate is used as an energy and electron source as well as a carbon source for biomass production.

There are also SRB that utilize hydrogen as electron donor and energy source. The reaction for the reduction of SO_4^{2-} with H_2 is written (Equation 1-3):

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O \qquad \text{(Eq. 1-3)}$$

Note that there is no carbon involved in this energy transforming reaction (Equation 2-4). The carbon sources for hydrogen utilizing SRB are either short chain organic compounds like acetate or carbon dioxide. The carbon is used for biomass production and the biosynthesis is energy consuming. Acetate and carbon dioxide are incorporated into the cell metabolism via the molecule acetyl coenzyme A (acetyl-CoA) to produce pyruvate in the following way (Equation 1-4):

$$CH_3COO^- – CoA + CO_2 + H_2 \rightarrow CH_3COCOO^- + CoA + H_2O \qquad \text{(Eq. 1-4)}$$

The pyruvate then enters the cell metabolism and will be incorporated into new bio molecules.

Finally, some microbial consortia can use methane as a source of energy and produce hydrogen sulphide.

$$CH_4 + SO_4^{2-} \text{ g } HCO_3^- + HS^- + H_2O \quad \text{(Eq. 1-5)}$$

For methane to act as an energy source the SRB require a symbiotic relationship with anaerobic methane oxidising microorganisms in the *Archaea* domain (ANME); a situation which until now has been demonstrated only in sea bed sediments /Lösekann et al. 2007/. Hydrogeochemical, isotopic and microbiological evidences indicate, however, that the process does indeed occur under deep bedrock conditions in Olkiluoto /Pedersen et al. 2008/.

1.6.2 Anaerobic biocorrosion of metals

Hydrogen sulphide is a compound that can mediate anaerobic corrosion of metals. There are steel materials in the investigated monitoring boreholes that may corrode and form hydrogen gas (H_2), which can be utilised by SRB to produce hydrogen sulphide. The oxidation of metallic iron with sulphate is regarded as the principal reaction in anaerobic corrosion of iron. The suggested reaction mechanism for the corrosion, see scheme in Figure 1-3, is that the negative redox potential (Fe^{2+}/Fe, E_0'[3] = −0.44 V) of iron can liberate hydrogen ($2H^+/H_2$, E_0' = −0.41 V) and may in this way indirectly act as an electron donor for SRB /Cord-Ruwisch 2000/. Another possible mechanism in anaerobic corrosion has been proposed: a direct utilization of the electrons liberated during the oxidation of metallic iron ($Fe \rightarrow Fe^{2+} + 2e^-$). This mechanism is kinetically more favourable than consumption of the electrochemically formed hydrogen.

In the anaerobic copper corrosion, electrons from the metal reduce protons to hydrogen in the presence of sulphide produced by SRB, see Equation 1-6.

$$2Cu + HS^- + H^+ \rightarrow Cu_2S + H_2 \quad \text{(Eq. 1-6)}$$

The produced hydrogen can be used by SRB that produce more hydrogen sulphide which may react with the copper and produce copper sulphides. It is therefore of great importance to characterize the potential for hydrogen sulphide production in groundwater in a repository for spent nuclear fuel. One set of the parameters that are crucial is the growth kinetics of SRB when grown on different energy sources.

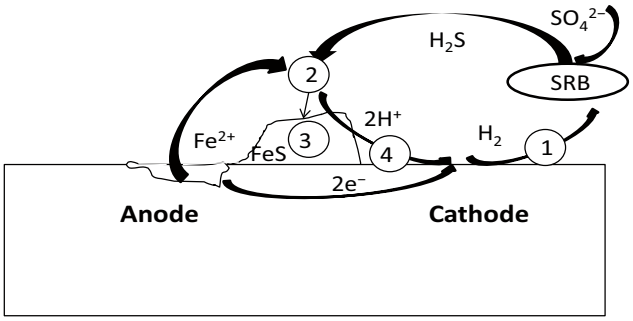

Figure 1-3. *The principle of anaerobic corrosion of metallic iron mediated by SRB. 1. The hydrogen produced by the reduction of protons by electrons from the oxidation of iron is consumed by SRB. 2. The H_2S produced precipitates with the Fe^{2+} and is deposited as 3. FeS on the steel surface. 4. During the precipitation protons are liberated.*

[3] E_0 means the standard redox potential of a redox reaction (for example the redox couple Fe^{2+}/Fe) when all substances are in their standards states of unit activity. E_0' denote the E_0 for the half-reaction at pH 7.

1.6.3 Dissolved gases

Gaseous species are taken to be substances that exist as gases under the range of temperatures and pressures in the sampled drill holes. In this investigation, 9 different gaseous compounds were found at various concentrations above trace amounts in the investigated groundwaters. The process of formation and the place of origin differ for different geosphere gas species. It can be biological processes in the atmosphere, radioactive decay at different places or thermogenic, chemical processes in deep crustal and mantle layers of Earth. Several gases have a primordial origin, meaning that they were formed before the Earth was formed; they were aggregated during the condensation of the Earth, and have been degassing to the atmosphere, through the geosphere since then.

Hydrogen

Hydrogen is the most abundant element in the universe and consists of three isotopes with mass number 1, 2 and 3. Hydrogen gas (H_2) is explosive in oxygenic environments and it can act as a strong reducing agent as is revealed by the negative redox potential of proton/hydrogen ($2H^+/H_2$, $E_0' = -0.41$ V). H_2 can be formed in microbiological fermentation processes and by a range of different processes not involving life. Fermentation occurs in anaerobic systems such as water logged soils and anoxic groundwater, i.e. in the geosphere. Fermentative processes cannot produce high concentrations of hydrogen /Madigan and Martinko 2006/; hydrogen produced during fermentation is commonly combined with carbon dioxide to methane by methanogens. The radiolysis of water has been proposed by /Lin et al. 2005/ as a possible H_2 generation process occurring in the Precambrian granitic system including the Fennoscandian Shield (yield rate calculated to 9.4×10^{-9} nM s^{-1}). Radiolysis of water to O_2 and H_2 can consequently produce small amounts of H_2 in the geosphere, but the main natural source of hydrogen to the geosphere is likely transport from deep layers by diffusion and advection. Anaerobic corrosion of metals, mainly iron and steel, in engineered borehole installations will also produce H_2.

There are at least six possible processes by which crustal H_2 is generated: (1) reaction between dissolved gases in the C-H-O-S system in magmas, especially in those with basaltic affinities; (2) decomposition of methane to carbon (graphite) and hydrogen at temperatures above 600°C; (3) reaction between CO_2, H_2O, and CH_4 at elevated temperatures in vapours; (4) radiolysis of water by radioactive isotopes of uranium and thorium and their decay daughters and by radioactive isotopes of potassium; (5) cataclasis of silicates under stress in the presence of water; and (6) hydrolysis by ferrous minerals in mafic and ultramafic rocks /Apps and van De Kamp 1993/.

H_2 is not expected to react chemically at significant rates under the conditions found in KLX06 and the KAS drill holes. However, H_2 is an important compound in several anaerobic microbial metabolisms in deep groundwater, such as methanogenesis by autotrophic methanogens and acetate production by acetogens /Kotelnikova and Pedersen 1997/. There are also autotrophic iron- and sulphate-reducing bacteria that can use H_2 as an energy and electron source, concomitant with iron or sulphate reduction /Badzoing et al. 1978/. The main products from biological anaerobic reactions are methane and acetate. H_2 can be used by sulphate reducing bacteria with sulphide as the final reaction product and by bacteria that reduce ferric iron to ferrous iron. If oxygen is available, H_2 is oxidised by some bacteria to water. H_2 can thereby contribute to the reduction of oxygen via microbial processes. Biological reactions consequently remove H_2 from groundwater.

Carbon dioxide

Most of the world's carbon is contained in the geosphere, primarily in the form of carbonate rocks. Carbon dioxide is mainly contained in the oceans and to some extent in the atmosphere. The processes of formation of carbon dioxide and places of origin are a complex system, as it includes gas-water-mineral reactions, combustion of fossil and modern fuels, biological respiration of organic material and processes in the mantle. Inherent in this is that the places of origin are diverse as well.

Dissolved carbon dioxide, is important to natural mineralogical processes that occur in the geosphere. It dissolves readily to form carbonate and bicarbonate, which can take part in a large number of chemical processes, for example the well-known dissolution-precipitation reaction of fracture filling carbonates (calcite),

$$CO_2 + H_2O + CaCO_3\,(s) \leftrightarrow Ca^{2+} + 2HCO_3^-(aq) \qquad \text{(Eq. 1-7)}$$

and the weathering of minerals in the rock matrix (here exemplified by the weathering reaction of Ca-feldspar, anorthite, into kaolinite):

$$CaAl_2Si_2O_8(s) + 2H_2CO_3(aq) + H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 2HCO_3^- + Ca^{2+} \qquad \text{(Eq. 1-8)}$$

Carbon dioxide is reduced to organic carbon by photosynthetic organisms and by chemolithotrophic bacteria. Photosynthesis is not a possible process in the geosphere. Chemolithotrophy includes methanogenesis and acetogenesis reducing carbon dioxide to methane and acetate, respectively.

Methane

Methane forming processes comprise thermogenic, hydrolysis and biogenic reaction routes. Thermogenic generation occurs in deep crustal layers, while hydrolysis processes such as serpentinisation of ferrous materials can occur in both the geosphere in shallow layers and in deep layers. The oxidation of ferrous material is coupled to the reduction of water to hydrogen, carbon dioxide to carbon or carbon to methane. Biological methane production takes place in anaerobic systems with hydrogen and carbon dioxide, within the temperature limits of life, i.e. < 113 ºC. Methane can also be formed by biological degradation of C-1 compounds such as methanol and formic acid and by degradation of acetate. Biological methane formation then is restricted to the geosphere and the shallow part of deep layers.

There are no chemical reactions that involve CH_4 in groundwater under the conditions in this investigation. However, microorganisms can readily oxidise CH_4 with O_2. Intruding O_2 to the geosphere will be reduced with CH_4 if present /Chi Fru 2008/. Anaerobic CH_4 oxidation with sulphate can occur /Boetius et al. 2000, Lösekann et al. 2007/.

1.7 Isotope geochemistry

The various isotopes of an element have slightly different chemical and physical properties because of their mass differences. Under the proper circumstances, such differences can manifest themselves as a mass-dependent isotope fractionation effect. As a result of fractionation processes, unique isotopic compositions develop (ratios of heavy to light isotopes) that may be indicative of their source or the processes that formed them.

Two main types of phenomena produce isotopic fractionations: isotope exchange reactions and kinetic processes. Isotope exchange reactions can be viewed as a subset of kinetic isotope reactions where the reactants and products remain in contact in a closed, well-mixed system such that back reactions can occur and chemical equilibrium can be established. Under such circumstances, isotopic equilibrium can be also established. By measurement of stable isotopes δ^2H, $\delta^{13}C$, $\delta^{34}S$ in organic and inorganic compounds, reactions such as those involved in the sulphate reduction processes can be determined.

1.7.1 Biological (microbial) fractionations

Biological processes are generally unidirectional and are excellent examples of kinetic isotope reactions. Microorganisms preferentially use the lighter isotopic species because of the lower energy “costs” associated with breaking the chemical bonds in these molecules, resulting in significant fractionations between the substrate (heavier) and the biologically mediated product (lighter). Kinetic isotopic fractionations of biologically-mediated processes vary in magnitude, depending on reaction rates, concentrations of products and reactants, environmental conditions, and – in the case of metabolic transformations – species of the organism.

The variability of the fractionations makes interpretation of isotopic data difficult, particularly for nitrogen and sulphur. The fractionations due to microbial activity are typically larger than the equivalent inorganic equilibrium reaction. The magnitude of the fractionation depends on the reaction pathway utilized (i.e. which is the rate-limiting step) and the relative energies of the chemical bonds severed and formed by the reaction. In general, slower reaction steps show greater isotopic fractionation than faster steps because the organism has time to be more selective (i.e., the organism saves internal energy by preferentially breaking light-isotope bonds).

If the substrate concentration is large enough and the isotopic composition of the reservoir undergo small changes by the reaction it will represent an "open system model"/O'Leary 1981/. In contrast, if there is a considerable change in isotopic composition of the residual reservoir substrate relative to the product then it can be defined by the so called Rayleigh equation as described in Section 1.7.2 below /Mariotti et al. 1981/.

1.7.2 The Rayleigh destillation equations

The Rayleigh distillation equations describe the isotope fractionation system very well in a closed system (the equations are so-named because the original equation was derived by Lord Rayleigh for the case of fractional distillation of mixed liquids). The principle relates to an exponential relation that describes the partitioning of isotopes between two reservoirs as one reservoir decreases in size.

The equation is commonly referred to;

$R = R_o\, f^{(\alpha-1)}$

where R = ratio of the isotopes (e.g. $^{34}S/^{32}S$) in the reactant, R_o = initial ratio, f = fraction of initial substrate remaining, α = fractionation factor.

The equation can be used to describe an isotope fractionation process for sulphate reduction processes if, a) material is continuously removed from a mixed system containing molecules of two or more isotopic species (e.g. $^{34}S/^{32}S$), b) the fractionation accompanying the removal process is described by the fractionation factor α, and c) α does not change during the process. The enrichment factor of $\delta^{34}S$ relative to $\delta^{32}S$ for sulphate when it is progressively reduced to sulphide can be calculated using the method as described by /Strebel et al. 1990/.

2 Investigated boreholes

2.1 Borehole KLX06

Borehole KLX06 is located in the Laxemar subarea, see Figure 1-1. Drilling of the borehole was performed between August and November 2004 as a part of Laxemar site investigation programme.

The borehole was core drilled to a depth of 994.94 m and with an inclination of 65.12º from the horizontal plane. The interval 0–100.3 m is percussion-drilled with a diameter of approximately 200 mm and the interval 100.3–994.94 m is core-drilled with a diameter of 76 mm /Ask et al. 2005/. The borehole design of KLX06 is presented in Appendix 1.

The results from differential flow logging /Sokolnicki and Rouhiainen 2005/ showed in total 186 flowing fractures in KLX06. High-transmissive fractures were found at 108.4 m, 196.0 m, 264.7 m and 562.5 m. Previous field activities in KLX06 are listed in Table 2-1 below. Water sampling and analysis of sulphide were performed on two occasions in 2006 in Section 554–570 m (–475.27 to –481.78 m a s l[4]) and the obtained concentrations after turnover of about 5 section volumes were 0.5 and 1.0 mg L^{-1}. In addition to the listed activities in Table 2-1 the groundwater levels in each of the sections in the borehole has been recorded manually on a monthly basis (see Section 4.2).

Table 2-1. Previous field activities in KLX06.

Activity	Date of completion	Length or section (m)	Reference/SKB no
Percussion drilling	2004-08-10	0.0–100.3	Ask et al. 2005
Core drilling	2004-11-25	100.3–994.94	Ask et al. 2005
Hydrochemical logging	2004-12-21	0–940	Berg 2005
BIPS-logging	2004-12-28	11–961	Gustafsson and Gustafsson 2005
Geophysical logging	2005-01-05	100–995	Nielsen et al. 2005
Difference flow logging	2005-02-28	96.5–987.5	Sokolnicki and Rouhiainen 2005
Packer and section installation	2005-07-05	554–570	
Dilution test natural gradient	2005-11-28	554–570	
Water sampling, class 5	2006-07-04	554–570	
Hydraulic interference test	2006-09-28	554–570	Walger et al. 2007
Water sampling, class 5	2006-10-24	554–570	
Dilution test natural gradient	2006-11-23	554–570	
Dilution test natural gradient	2007-11-20	554–570	

[4] Meter above sea level.

2.2 Borehole KAS03

Borehole KAS03 is located at Äspö, see Figure 1-1. Drilling of the borehole was performed between January and April 1988 as part of the Äspö pre-investigation programme.

The borehole was core drilled to a depth of 1,002.26 m, the interval 0–100.8 m is percussion-drilled with a diameter of approximately 200 mm and the interval 100.8–1,002.26 m is core-drilled with a diameter of 56 mm.

In this project, water samples were collected in sections 107–252 m (–97.45 to –241.40 m a s l) and 627–1,002 m (–613.34 to –984.13 m a s l). Figure 2-1 shows the obtained variation in sulphide concentrations in the collected water samples from Section 107–252 m during the hydrochemical monitoring from 1996 to 2007, the sulphide concentration ranged from 0.09 to 0.95 mg L^{-1}. Before sampling, a volume of water equivalent to about 5 times the borehole section was discharged in order to obtain mostly water from the fractures. In 1989 (about 10 months after drilling) an investigation was performed using CCCin a delimited Section 129–134 m. The obtained sulphide concentrations from this sampling campaign were in the same order of magnitude as during hydrochemical monitoring. In this investigation only 3 litres of water were discharged before sampling (1% of the section volume), which means that the water that was collected and analysed consisted mostly of isolated section water. The obtained sulphide concentration was 9.1 mg L^{-1}.

In Section 627–1,002 m, analysis of sulphide was performed twice in 2007 after discharging about 5 section volumes. The obtained sulphide concentrations obtained in 2007 were 2.1 and 0.6 mg L^{-1}. In this study, 35 litres of water (from tubing and section) was discharged before sampling and analysis of sulphide. This corresponds to a turnover of about 4% of the section volume. The obtained sulphide concentration was 0.5 mg L^{-1}.

2.3 Borehole KAS09

Borehole KAS09 is located at Äspö, see Figure 1-1. Drilling of the borehole was performed between January and April 1988 as part of the Äspö pre-investigation programme.

The borehole was core drilled to a depth of 450.62 m, the interval 0–100.65 m is percussion-drilled with a diameter of approximately 200 mm and the interval 100.65–450.62 m is core-drilled with a diameter of 56 mm.

Water sampling was performed in Section 116–150 m (–95.99 to –125.09 m a s l) from 1995 to 2008. The sulphide concentration ranged from 0.05 to 5.6 mg L^{-1} (0.002–0.2 mM) during the hydrochemical monitoring, where about 5 times the section volume was pumped out before sampling (Figure 2-2). In this project about 18 litres (discharge of water in tubing and section) of water was turned over before sampling (20% of the section volume), which means that the water that was collected and analysed consisted mostly of isolated section water. The obtained sulphide concentration was 92 mg L^{-1} (1mM).

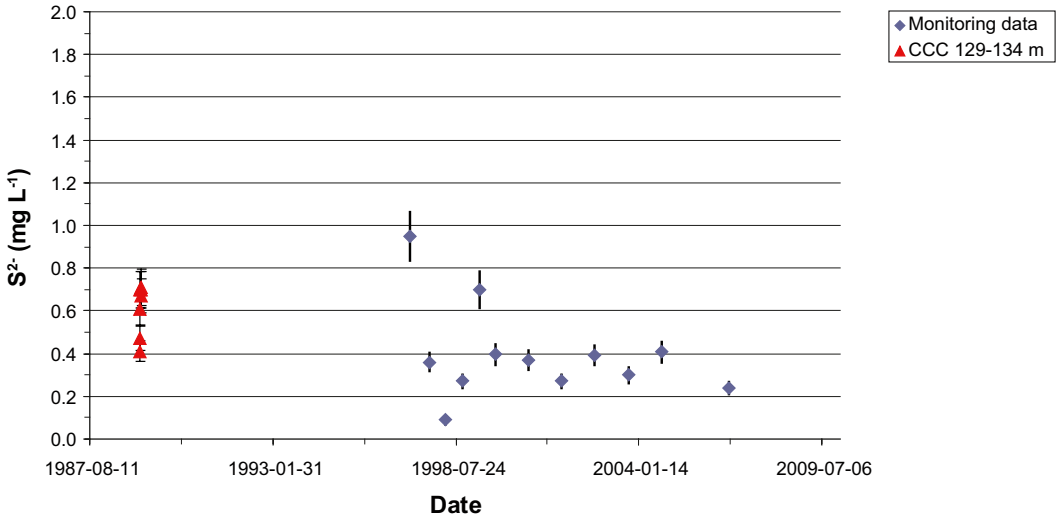

Figure 2-1. *Sulphide concentrations in water samples collected from KAS03. Data from hydrochemical monitoring (blue diamond) in Section 107–252 m and CCC (red triangle) in delimited Section 129–134 m. CCC (n = 2), Hydrochemical monitoring 1997–2005 (n = 2). Sulphide concentration 0.47 ± 0.02 (95% confidence interval).*

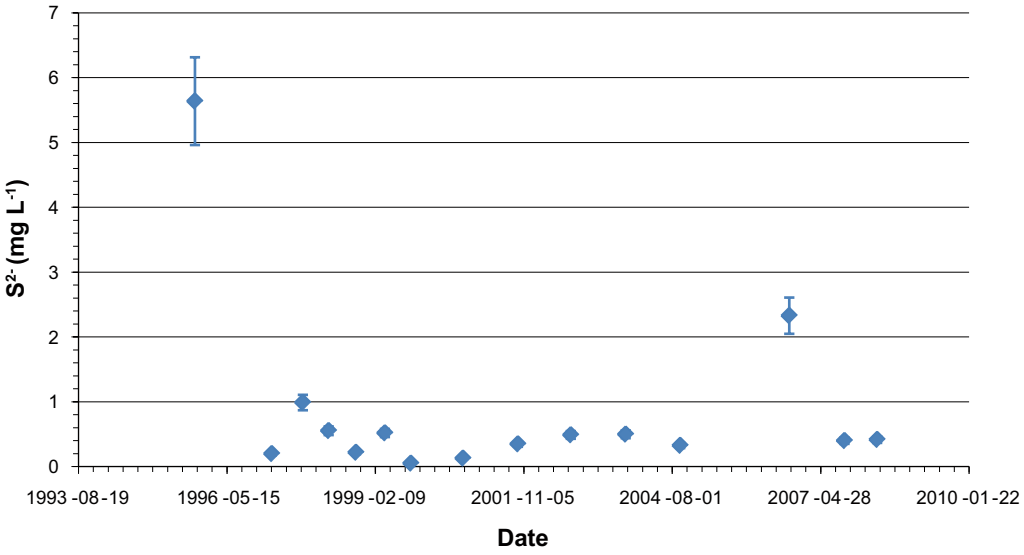

Figure 2-2. *Sulphide concentrations in water samples collected from KAS09, Section 116–150 m. Data from hydrochemical monitoring 1995–2008 (n = 2. Sulphide concentration 0.87 ± 0.22 (95% confidence interval).*

3 Equipment

3.1 Stationary equipment

In order to perform a regular pressure and hydrochemical monitoring in delimited borehole sections, the boreholes are installed with stationary equipment (Figure 3-1 and Figure 3-2). The equipment includes a packer system dividing the borehole into maximum of ten sections for groundwater level monitoring. Each borehole section is connected by tubing to a standpipe (Ø 34/23.5 mm; inner and outer diameters) in the wider upper part of the borehole. This standpipe is supplied with a pressure transducer for groundwater level monitoring. In order to calibrate the transducers the water level in the standpipe of each section is measured manually once every month. When performing such a measurement, the mini-packer in the standpipe is released one or two days before so that the water level will be representative.

Maximum two of the sections are in addition to the narrow standpipe connected to another second wider standpipe (Ø 66/53.5 mm; inner and outer diameters) for chemical water sampling and groundwater flow measurements. These sections are denoted pressure and circulation sections in contrast to the sections with a single standpipe that are denoted pressure sections. The two standpipes of a pressure and circulation section are each one connected to the section by tubing (Figure 3-1). The section and its standpipes constitute a connected system constructed for obtaining representative groundwater levels (pressure measurements). This implies that any change in water level and pressure in one of the standpipes, during for example lowering of sampling equipment and sampling of water in the standpipe, will influence the pressure and water level in the other standpipe as well as in the section. However, the changes of the system is not instantaneous, it needs some time to restore (up to several hours).

The packer-isolated sections also contain so called dummies of PEM or PEHD plastics (Figure 3-2, Figure 3-3, Figure 3-4 and Figure 3-5). Dummies were installed to reduce the section volumes and facilitate exchange of water during water sampling and groundwater flow measurements. Table 3-1 lists the different equipment details and materials that constitute the standard installed equipment in core drilled boreholes and that come more or less into contact with the sampled groundwater.

The standpipes reach a depth of about 40 to 45 m below ground level. The lower part of a standpipe (10 cm) is made of stainless steel and the upper part of polyethylene or polyvinylchloride.

A mini-packer connected to a stainless steel die is located in the lower part of the standpipe. The mini-packer minimises the fluctuations of the groundwater level in the standpipe. When sampling water from the borehole section this mini-packer is removed.

The groundwater level in the sections is determined by a pressure sensor in the standpipes. In order to determine the absolute pressure in the sections it is necessary to know the density of the water and the depth of the section. The general idea was therefore to perform clean-up pumping of the tubing every 6 or 12 months, to prevent clogging of the tubing and to obtain a known density of the water. However, this clean up procedure was never or seldom implemented during the site investigations.

The materials that constitute the equipment and that are in contact with sample water are listed in Table 3-1. Materials in some of the details differ between the KAS-boreholes and the more recently drilled KLX- boreholes. The standpipes are made of PVC (polyvinylchloride) in the KAS-boreholes, while in the KLX-boreholes they are made of PEHD (high density polyethylene). Only a small part of the packers and mini-packer (short end) is in contact with the sample water.

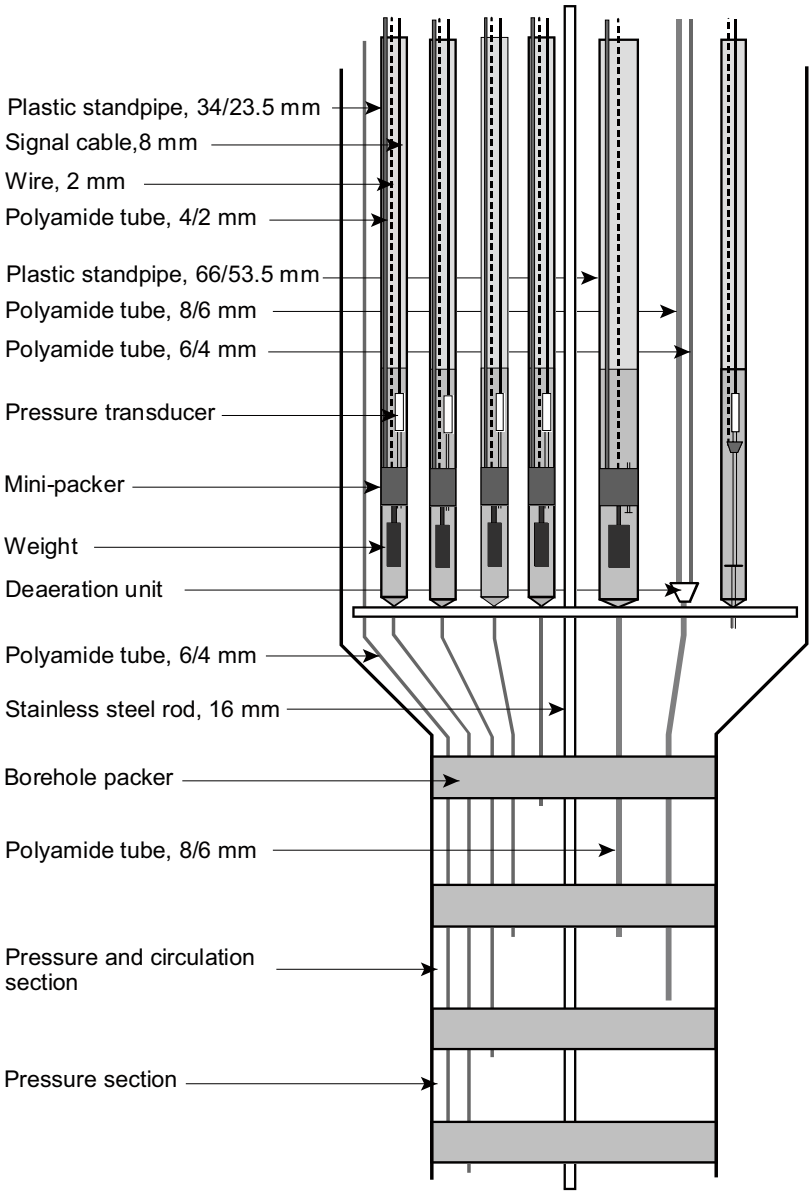

Figure 3-1. *Schematic picture of the instrumentation in a conventional core drilled borehole.*

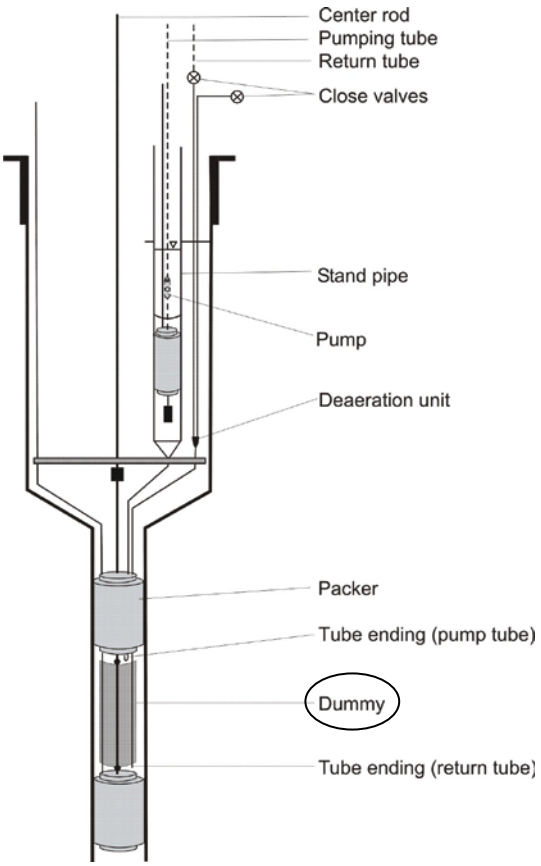

Figure 3-2. *Schematic picture of the instrumentation in the borehole that illustrates the location of the dummy in the isolated section between two packers. In the picture, only the standpipe for water sampling and groundwater flow measurements is shown. Pressure and circulation sections also have a connected standpipe for pressure measurements.*

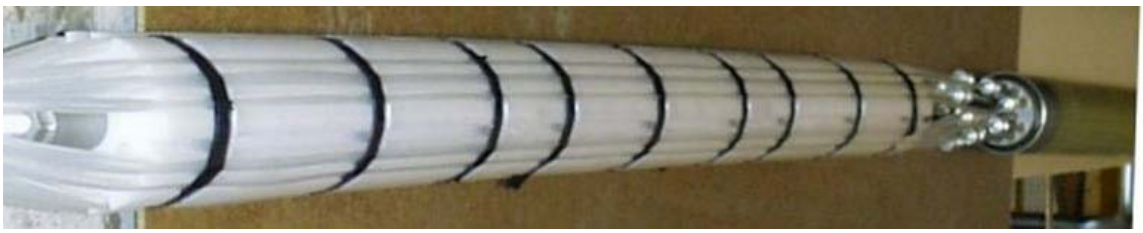

Figure 3-3. *Dummy with attached tubing. Black tape (PVC) is used to keep the tubing together.*

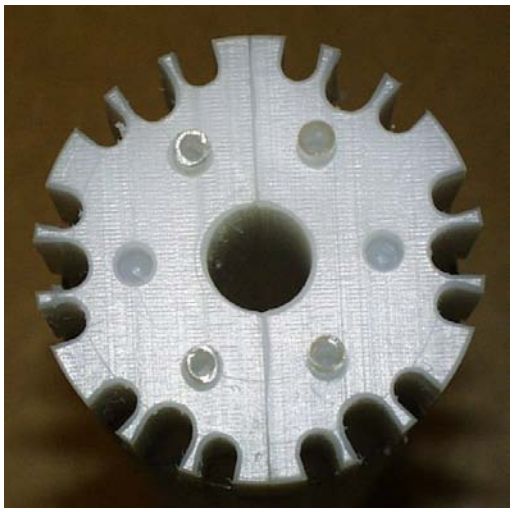

Figure 3-4. *Cross section of a dummy (Ø76 mm). The tubing is placed in the tracks.*

Figure 3-5. *Detail between packer and dummy. The black tape that surrounds the couplings and tubing is missing in the picture.*

Table 3-1. Equipment details and materials.

Detail	Material
Water standpipe	PEHD[1] and stainless steel in KLX06, PVC[2] in KAS03 and KAS09.
Tubing	Tecalane (polyamide).
Casing rubber	PUR[3] in KLX06, EPDM[4]-rubber in KAS03 and KAS09.
Connection pipes and supporting frame, stainless steel die	Stainless steel in KLX06, Aluminium in KAS03 and KAS09.
Dummy	PEHD in KLX06, PEM[5] in KAS03 and KAS09.
Other details	Tape (PVC).

[1] High density polyethylene.
[2] Polyvinylchloride.
[3] Polyurethane.
[4] Ethylene-Polypropylene Rubber.
[5] Medium density polyethylene.

3.2 Sampling equipment

When sampling from the borehole section or performing dilution tests, a circulation pump adapted to low water flow and large pressure differences is installed in the wider standpipe (Figure 3-6). The circulation pump is connected to a filter of polyamide (Figure 3-7) and empty tubing at the ground surface. When starting the circulation pump with the packer inflated, the pressure in the space below the packer is lowered and the groundwater from the connected borehole section is sucked to the standpipe and pumped to the ground surface.

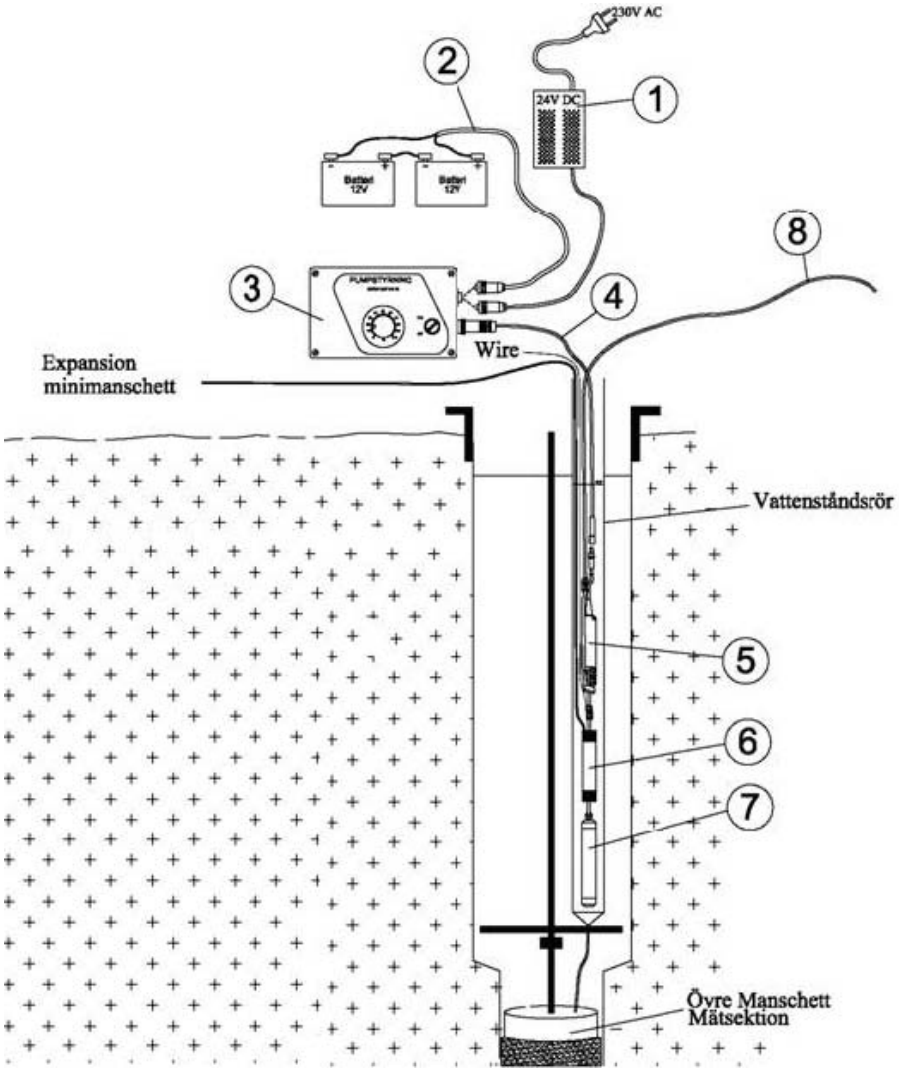

Figure 3-6. *Schematic picture of hydrochemical monitoring in core drilled boreholes. Note that only one of the two standpipes is shown in this drawing: the pressure measurements standpipe is not shown. 1. Power supply. 2. Cable for storage battery. 3. Control unit for circulation pump. 4. Cable for circulation pump. 5. Circulation pump. 6. Mini-packer. 7. Filter. 8. Tubing for water sampling (Ø8/6 mm polyamide).*

3.3 Uncertainties associated with the sampling procedure

The water in a standpipe does not necessarily derive from the same source (fractures) as the corresponding borehole section water. This is seen in the large differences in the concentrations of major components, e.g. chloride. Observations of water in standpipes show that the microbe content and dissolved sulphide concentration are both high. In some standpipes, the water is characterised as dirty (rich is particles) and smelling from hydrogen sulphide gas. The filter is inevitably in contact with the water from the standpipe and any solid particles during the sampling procedure. The volume of the filter and the space below and around the filter constitute about 2–3 litres of water from the standpipe. When sampling section groundwater, the extent of contribution from this volume of water has not been investigated. During hydrochemical monitoring, the water is exchanged about 5 section volumes before sampling, and the contribution of water from the standpipe is then reduced. In addition, a microbial coating (biofilm) grows with time on the walls of the standpipes, tubing and perhaps also the rock walls of the borehole sections, which may contaminate the groundwater samples.

Figure 3-7. *Lowering of sampling equipment in the standpipe in order to collect water from the connected borehole section. From bottom: filter, small inflatable packer and circulation pump. The standpipe with wider diameter is used for water sampling, while the standpipes with narrow diameter are used for pressure measurements.*

4 Field activities within the project

4.1 Overview of field work procedure

The boreholes with installations are situated inside containers. At KAS03 and KAS09, water was sampled and the samples prepared in the container. Figure 4-1 shows the setup at KLX06 with a mobile laboratory unit L2 for sampling of water and preparation of samples and a computer unit MYC 2 and a flow-through cell with electrodes and sensors (surface Chemmac). The tubing from the circulation pump in the standpipe was led to the flow-through cell in the computer unit and to the laboratory unit. When sampling of water was performed a valve was switched so that the water was led to the laboratory unit instead of the measurement cell. The tubing was Tecalan and its length kept as short as possible in order to reduce any intrusion of oxygen.

Sampling for chemical parameters including sulphide was performed in the laboratory unit while the microbiological parameters and acetate were sampled immediately after the circulation pump when the water had reached the ground surface. The same applied to the gas traps, except for the first pumping period in KLX06, where the gas traps were located after the flow-through cell of the surface Chemmac as well as inside the laboratory unit.

The sampling followed a pre-determined order, where the microbiological parameters and acetate were collected first, then sulphide, general chemical parameters, isotopes, phthalates and low molecular mass organic acids (LMMOA). Each sample consisted of between 2 and 11 litres of water depending on the number of included parameters.

Figure 4-1. *The mobile units used at KLX06; from left laboratory unit, unit for computer work and surface Chemmac with pH and redox electrodes. To the right the container with the installed borehole.*

Table 4-1 gives the water volumes of the standpipes, tubing and sections for KLX06, KAS03 and KAS09. The volumes were calculated using the recorded groundwater levels in year 2008.

Table 4-1. Investigated borehole sections and water volumes in tubing, standpipes and sections.

Idcode	Section (m)	Volume tubing* (L)	Volume standpipe (L)	Volume section (L)
KLX06:3	554–570	14.5	61	20.2**
KAS03:5	107–252	0.3	146	357
KAS03:1	627–1,002	6.6	181	923
KAS09	116–150	1.9	57	84

* Tubing between standpipe and section.
** The volume that can be occupied by water in the isolated borehole section; that is, the total volume of the section with the volume of the dummies subtracted.

4.2 Performance in KLX06, section 554–570 m

Pumping and sampling was performed from February to May 2009 during two time periods, with an interruption of 9 weeks in between. Totally 145 section volumes were turned over in the first pumping period and 14 samples were collected, while the corresponding for period 2 were 7 section volumes and 6 collected samples. The analytical programme in KLX06 included the following numbers of parameters:

- 20 HS^-, Fe_{total} and Fe^{2+}.
- 14 pH, conductivity.
- 14 HCO_3^-, Cl^-, SO_4^{2-}, Br^-, F^-.
- 14 major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}).
- 4 minor cations, trace elements and lanthanides.
- 10 microbiological analyses.
- 10 acetate.
- 5 gaseous compositions (3 released gas and 5 dissolved gas).
- 3 isotopes in gaseous compounds (δ^2H, $\delta^{13}C$ and $\delta^{18}O$).
- 7 $\delta^{34}S$ in dissolved sulphide and sulphate.
- 3 phthalates.
- 3 low molecular mass acids (fractionation and identification).

Samples were collected with short time intervals in the beginning of the pumping in order to closely follow the expected decrease in sulphide concentration. After 14 days, the investigation was interrupted for 9 weeks before the second period of pumping, to check if the sulphide concentration was restored to the initial level. Then followed 2 days of further pumping and sampling before the investigation was completed. The events and collected samples in KLX06 are listed in Table 4-2. Analysis results are compiled in Appendix 8.

The pumping flow rate varied between 50 and 200 mL min^{-1} and the drawdown was negligible during the entire investigation period, the flow rate versus time is shown in Appendix 2. Pressure registrations (HMS system) recorded during the first pumping period did not give any responses in the other delimited sections in KLX06 (Appendix 3), which suggests that there were no leakage of water over the packers.

The procedure followed allowed samples to be taken from the water in the standpipe and tubing before sampling the water in the borehole section. While sampling the water in the standpipe, the water level in the standpipe was monitored in order to check any effect on the water level in the tubing and section. The aim was to collect an initial sample from the section with as little contribu-

tion as possible of water from the fractures in the surrounding bedrock. After sampling of water from the standpipe the circulation pump and filter were lowered to the bottom of the standpipe and the water in the tubing (14.5 litres) and another 2 litres from the section (10% of the section water volume) was discharged before collecting samples from the section water (KLX06-2 and KLX06-2-3).

Released gas was collected with a gas trap in the first pumping period, however the results were only qualitative. Due to high counter pressure from the Chemmac unit, gas from the limited initial water volume in the section could not be collected properly, but represents an average of the first 12 sections. Another two samples of gas were collected after about 17 and 140 section volumes. The gas samples were analysed for composition and isotopes (δ^2H, $\delta^{13}C$, $\delta^{18}O$). During the second pumping period, the gas sampling was improved with quantitative sampling for determination of dissolved gas composition using PVB samplers (see Section 5.8.2). The amount of dissolved gas in these samples was not sufficient for analysis of isotopes.

Samples for analyses of phthalates and low molecular mass organic acids (size fractionation and identification) were collected from the standpipe and section water.

Table 4-2. Events during the sampling campaign in KLX06, section 554–570 m.

Date	Event	Sample no./SKB no.
090203	Hydrogeological measurement of groundwater level in the thin standpipe for pressure measurements, connected to the borehole section of interest.	
	Pumping period 1	
090209	Calibration of surface Chemmac	
	Defect diesel generator and subsequent loss of power supply. Replacement of diesel generator.	
	Release and removal of mini-packer in standpipe. Measurement of water level in standpipe with (12.32 m) and without (12.50 m) pumping equipment. The level is measured as the distance from top of the standpipe to the surface of the water.	
	Start of circulation pump in standpipe. The pump and filter were situated close to the groundwater surface level in the standpipe, that is, it was not lowered as deep as possible, as it is normally done. Also note that the packer was not inflated. **Sampling of water in standpipe**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major and minor cations, trace metals, lantanoids , SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate. Measurement of water level (15.25 m). The difference in water level in the standpipe before and efter sampling (12.32 and 15.25 m respectively) corresponds to the collected water volume. This suggests that the water column in the tubing and section was not effected (discharged). Start of measurements of pH and Eh in the flow-through cell. The water in the standpipe was cloudy and gas bubbles appeared on the surface. The filter contained black particles after sampling.	KLX06-1/14712
	Lowering the circulation pump to the bottom of the standpipe and inflating the packer. Discharging water from the tubing between the standpipe and section.	
	13:10–14:27: **Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, NO_2, NO_3, NO_2+NO_3, PO_4, HS^-, Fe_{total}/Fe^{2+}, major and minor cations, trace metals, lantanoids , SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, Br^-, I^-, $\delta^{37}Cl$, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of released gas with gas trap (in laboratory unit).	KLX06-2/14713
	15:07–15:54: **Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, NH_4.	KLX06-3/14714
090210	04:08–06:45: **Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate.	KLX06-4/14715
	09:40–10:45: **Sampling of section water**; H, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC.	KLX06-5/14716
090211	**Sampling of section water**, HS^- and Fe_{total}/Fe^{2+}. The water that was collected contained more gas than previous samples.	KLX06-6/14718

Date	Event	Sample no./SKB no.
090212	**Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, NO_2, NO_3, NO_2+NO_3, PO_4, HS^-, Fe_{total}/Fe^{2+}, major and minor cations, trace metals, lantanoids , SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, Br^-, I^-, $\delta^{37}Cl$, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of released gas with gas trap (after circulation pump).	KLX06-7/14719
090213	**Sampling of section water**, HS^- and Fe^{total}/Fe^{2+}.	KLX06-8/14720
090214	Pumping stopped due to power failure., The diesel generator was exchanged and the pumping restarted.	
090216	**Sampling of section water**, pH, conductivity, anions, DOC, HS^-, Fe^{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC.	KLX06-9/14721
090217	**Sampling of section water**, HS^- and Fe^{total}/Fe^{2+}.	KLX06-10/14722
090218	**Sampling of section water**, HS^- and Fe^{total}/Fe^{2+}.	KLX06-11/14723
090219	**Sampling of section water**, HS^- and Fe^{total}/Fe^{2+}.	KLX06-12/14724
090220	**Sampling of section water**, HS^- and Fe^{total}/Fe^{2+}.	KLX06-13/14725
090223	12:10–15:45 Gas trap assembled in laboratory unit. 14:20–15:10: **Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of released gas with gas trap (after circulation pump).	KLX06-14/14726
090224	Calibration of surface Chemmac.	
	Pumping stopped, pumping equipment lifted and disassembled. Mini-packer in standpipe lowered and inflated.	
090401	Hydrogeological measurement of groundwater level in the thin standpipe for pressure measurements, connected to the borehole section of interest.	
	Pumping period 2	
090505	Calibration of surface Chemmac. Removal of mini-packer from standpipe.	
090505	Lowering the pump to bottom of the standpipe and inflating the packer. Discharging of water from the tubing between the standpipe and section. **Sampling of water from tubing**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe^{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, phthalates, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of dissolved gas with PVB sampler (after circulation pump).	14727/KLX06-2-1
090505	Release of packer and lifting of circulation pump. **Sampling of water in standpipe**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe^{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, NH_4, phthalates, low molecular weight acids, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of dissolved gas with PVB sampler (after circulation pump).	14728/KLX06-2-2
090505	Lowering the pump to bottom of the standpipe and inflating the packer. Pumping of water from the section. **Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, phthalates and low molecular weight organic acids, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of dissolved gas with PVB sampler (after circulation pump).	14729/KLX06-2-3
090505	**Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, NH_4.	14730/KLX06-2-4
090506	**Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, NH_4, low molecular weight organic acids, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of dissolved gas with PVB sampler (after circulation pump).	14731/KLX06-2-5
090507	**Sampling of section water**, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, NH_4. Sampling of dissolved gas with PVB sampler (after circulation pump).	14732/KLX06-2-6
	Calibration of surface Chemmac. Pumping stopped, pumping equipment lifted and disassembled. Mini-packer in standpipe lowered and inflated.	

4.3 Performance in KAS03, sections 107–252 m and 627–1,002 m

Pumping and sampling was performed in February 2009. Samples were collected from the standpipes and attached borehole sections. The analytical programme in KAS03, sections 107–252 m and 627–1,002 m, included the following numbers of parameters:

- 4 HS^-, Fe_{total} and Fe^{2+}.
- 4 pH, conductivity.
- 4 HCO_3^-, Cl^-, SO_4^{2-}, Br^-, F^-.
- 4 major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}).
- 4 microbiological analyses.
- 4 acetate.
- 3 $\delta^{34}S$ in dissolved sulphide and sulphate.

The events and collected samples in KAS03 are listed in Table 4-3. Results from the analysed parameters are compiled in Appendix 8.

Table 4-3. Events during the sampling campaign in KAS03 sections 107–252 m and 627–1,002 m.

Date	Event	Sample no./SKB no.
	Section 107–252 m	
090217	Release and removal of mini-packer in standpipe.	
090217	Start of circulation pump in standpipe. **Sampling of water in standpipe**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate. Water flow 162 mL min^{-1}.	KAS03-SP1/14746
090217	Lowering the circulation pump to bottom of the standpipe and inflating the packer. **Sampling of section water**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate.	KAS03-SE1/14747
	Section 627–1,002 m	
090217	Release and removal of mini-packer in standpipe. Lowering of bladder pump in standpipe. The groundwater level is low (−41 m) and there is a demand for prolonged tubing in order to be able to collect a water sample.	
090218	Lowering the bladder pump attached to a prolonged tubing. **Sampling of water in standpipe**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe^{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate. Water flow 25 mL min^{-1}.	KAS03-SP2/14748
090218	Lowering the bladder pump further down the standpipe in order to discharge water from the tubing between the standpipe and section. A decreasing water flow indicates that the tubing is clogged.	
090219–090223	Discharging of water in tubing between standpipe and section (totally 35 litres).	
090223	**Sampling of section water**, microbiological parameters, acetate, pH, conductivity, HCO_3^-, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, TOC. Due to the low water flow (clogged tubing) the water for analysis of chemical parameters was collected in a 5 L plastic can. To prevent air contact the sampling is performed under an argon atmosphere. The sampling is completed after approximately 6 hours and the water is portioned into separate bottles using a low speed pump. Since the amount of water that could be collected was limited, the analytical programme had to be reduced.	KAS03-SE2/14749
090331–090401	Sampling and analysis of deposits on pipe strings during dismantling of equipment (equipment located between 100 and 300 m depth).	

The water in section 627–1,002 m was collected using a bladder pump due to the low water level (−41 m). The bladder pump "lifts" the water to the ground surface by applying a pressure using nitrogen. During the procedure it cannot be excluded that the quality of the samples was compromised due to contact with air (oxygen sensitive parameters such as S^{2-} and Fe^{2+} might have been oxidised to some extent). Discharge of water from the tubing and section before sampling correspond to a turnover of about 4% of the section volume (35 litres). Before sampling from the standpipes of each section about 3 litres of water was discharged. For section 107–252 m, 5 litres of section water were discharged before sampling.

4.4 Performance in KAS09, section 116–150 m

Pumping and sampling was performed in March 2009. Samples were collected from the standpipe and attached borehole section. The analytical programme in KAS09 included the following numbers of parameters:

- 2 HS^-, Fe_{total} and Fe^{2+}.
- 2 pH, conductivity.
- 2 HCO_3^-, Cl^-, SO_4^{2-}, Br^-, F^-.
- 2 major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}).
- 2 microbiological analyses.
- 2 acetate.
- 2 gaseous composition (released gas).
- 1 $\delta^{34}S$ in dissolved sulphide and sulphate.

The events and collected samples in KAS09 are listed in Table 4-4. Results from the analysed parameters are compiled in Appendix 8. Released gas was collected from the standpipe and section for analysis. A curved standpipe made it impossible to lower the pump and filter to the bottom, and additional water was therefore discharged from the tubing and section before sampling in order to minimise the contribution from water in the standpipe. In total 30 litres were discharged, of those about 18 litres from the tubing and borehole section (the discharge corresponds to about 35% of the section volume). About 3 litres were discharged before sampling from the standpipe.

Three solid samples consisting of precipitate (salt, rust, biofilm) were collected from the pipe strings during removal of the monitoring borehole equipment and an elemental analysis was performed (Appendix 8, Table 8-12).

Table 4-4. Events during the pumping and sampling campaign in KAS09 section 116–150 m.

Date	Event	Sample no./SKB no.
090318	Release and removal of mini-packer in standpipe.	
090319	Start of circulation pump in standpipe. **Sampling of water in standpipe**, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4. Sampling of released gas with gas trap. Water flow 160 mL min^{-1}.	KAS09-SP/14750
090319	Lowering the circulation pump in the standpipe and inflating the packer. Due to a curved form of the standpipe, the circulation pump can be lowered down to −38 m and not to the bottom of the standpipe. A water volume of about 12 L is enclosed between the filter and bottom of the standpipe. In order to minimise the influence of this water on the water collected from the section about 30 litres were discharged before sampling.	
	Sampling of section water, microbiological parameters, acetate, pH, conductivity, anions, DOC, HS^-, Fe_{total}/Fe^{2+}, major cations, SO_4-S, Si, Uranine, TOC, δ^2H, $\delta^{18}O$, ^3H, $\delta^{13}C$, pmC, NH_4, $\delta^{34}S$ in dissolved sulphide and sulphate. Sampling of released gas with gas trap. Water flow between 90 and 120 mL min^{-1}.	KAS09-SE/14751
090331–090401	**Sampling of solid precipitate on pipe strings,** elemental analysis of solid precipitates on pipe strings.	14866, 14867, 14869

4.5 Water sampling, sample treatment and analyses

The pumped water from the borehole sections was led from the hose unit into the laboratory unit where sampling and sample filtration was carried out. Filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. A water sample consists of several sample portions (bottles), labelled with the same sample number (SKB number).

An overview of sample treatment and analysis methods for chemical analyses is given in Appendix 6. The Appendix compiles sampling handling routines, analytical methods, reporting limits and measurement uncertainties. Sample treatment and analysis methods for microbiological analyses and gas samples are described in Appendix 7. Table 4-5 give the laboratories that were consulted for the analyses in this project.

Table 4-5. Laboratories consulted for the analyses.

Analysis	Laboratory
Microbiological parameters Acetate Gas content and composition	Microbial Analytics Sweden AB/Gothenburg Sweden
Uranine pH Conductivity Anions[1] HS^- Fe^{2+}, Fe^{tot}	Äspö Water chemistry laboratory/Äspö Sweden
Cations, Evironmental metals, Lanthanoids[2]	ALS Scandinavia/Luleå Sweden
Nutrients salts (NH_4-N, NO_2-N + NO_3-N, PO_4-P)	Systemekologen/Stockholm University Stockholm
TOC, DOC	Systemekologen/Stockholm University Stockholm
Carbon isotopes ($\delta^{13}C$, pmC)	Ångström Laboratory/Uppsala Sweden
Environmental isotopes (δ^2H, $\delta^{18}O$)	IFE, Institutt for energiteknikk/Kjeller Norway
Sulphur isotopes ($\delta^{34}S$ in sulphate and sulphide)	IFE, Institutt for energiteknikk/Kjeller Norway
Isotopes in gases	Hydroisotop gmbh/Schweitenkirchen Germany
Fractionation of LMMOA	Institutionen för geologiska vetenskaper/ Stockholm University Stockholm

[1] HCO_3^-, Cl^-, SO_4^{2-}, Br^-, F^-
[2] Na, K, Ca, Mg, S, Si, Fe, Mn, Li, Sr, Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn, In, 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.

4.6 Nonconformities

- The investigation in KAS09, section 116–150 m, was added to the investigation at a later stage. The equipment that was installed was malfunctioning and before the equipment was brought up and the water perturbed, water samples from the standpipe and section were collected and analysed. The borehole was well-known to smell of hydrogen sulphide gas from earlier sampling occasions.
- The initially planned investigation in KAS03, sections 129–134 m and 860–1,002 m using the complete chemical characterisation equipment were cancelled. A packer was stuck during lowering of the sampling equipment and after performing a risk analysis of the borehole it was decided that an investigation using in situ equipment was associated with an unacceptable risk.
- Water sampling in KAS03, section 627–1,002 m, was performed with a bladder pump due to low groundwater level. The water was "lifted" to the ground surface by applying a pressure using nitrogen gas. The volume of water that was obtained during sampling was not enough for performing the complete analysis programme and the sampling procedure might have affected the quality of the samples, especially parameters that are sensitive to oxygen, such as sulphide and Fe^{2+}.
- Sample no 14750, $\delta^{34}S$ in dissolved sulphide and sulphate from KAS09 (standpipe) was accidently spilled during transportation to IFE in Norway.

- The standpipe in KAS09 was curved and hence the circulation pump and filter could not be lowered to the bottom when sampling from the section. To reduce the influence of water from the standpipe (the volume between the filter and bottom of standpipe was approximately 12 litres), additional water (18 litres) was discharged from the tubing and section before collecting the sample.
- Analyses of phthalates and low molecular mass acids (fractionation and determination of species) were added to the analysis programme in KLX06 during the second period of pumping and sampling. The determination of species of low molecular mass acids was not completed due to high sulphate concentrations in the matrix that interfered with the method of separation (liquid chromatography).

5 Results

5.1 Observations during the investigation

5.1.1 KLX06

The water in the standpipe contained a lot of dissolved gas as could be observed from the gas bubbles at the surface and there was a strong smell of hydrogen sulphide gas. After completed sampling campaign, the filter connected to the circulation pump in the standpipe was covered with black particles, indicating that precipitates (perhaps solid sulphides) were present in the standpipe.

5.1.2 KAS03 and KAS09

Photos of the borehole equipments in KAS03 and KAS09 are compiled in Appendix 5. When lifting the equipment in KAS03, the connection pipes down to 300 m were covered by a thin film, with a light brown colour. Below 300 m the connection pipes were visibly free from precipitate.

There was a strong smell of hydrogen sulphide gas during pumping and sampling. The bottom of the standpipes contained a considerable amount of a black precipitate (sulphides, organic material etc), the water in contact with the precipitate was collected and analysed when sampling from the standpipe was done. When sampling from the section, the pump and filter is located in the bottom of the standpipe and thus contamination from the precipitate can occur.

5.2 On-line measurements

Time series of pH, Eh, electrical conductivity, dissolved oxygen and temperature from the on-line measurements in KLX06 during the first pumping and sampling period (2009-02-09 to 2009-02-24) are presented in Appendix 4. Electrical conductivity and pH were measured in the laboratory on samples collected during the measurement period and agreed well with the on-line measurements. Values for pH, Eh, electrical conductivity and dissolved oxygen after discharge of about 150 section volumes (3 m^3) are given in Table 5-1. The values were selected from the last part of the measured time series, where the electrodes show (the most) stable values.

The obtained redox values from the carbon-, gold- and platinum electrodes were fairly stable but inconsistent and did not reach an expected low value, although the readings suggested reducing conditions. Redox measurements are extremely sensitive to oxygen and the reason for the inconsistent readings could be the design of the equipment: measurement cell, tubing or other details of the in-situ borehole equipment. During the site investigations, the measurements of redox at the ground surface were sometimes successful, but not in all cases. In this investigation, an effort was made to minimise the diffusion of oxygen through the tecalan tubing that connects the measurement cell (surface chemmac) to the circulation pump in the borehole. This was done by applying nitrogen gas between double tubing, however, the nitrogen was not completely oxygen free and not continuously flowing, and so the protecting measures that were taken were not sufficient.

Table 5-1. Results from the on-line measurements in KLX06.

pH	Eh [mV]	Electrical conductivity [mS/m]	Dissolved oxygen [mg/L]
8.5 ± 0.3	Carbon: −33 Gold: −38 Platinum: −120	550 ± 50	0.01± 0.01

The readings from the oxygen electrode were not consistent with the redox measurements in that the dissolved oxygen did not decrease until after 4 or 5 days, while the redox electrodes gave negative values almost immediately. The response from the oxygen electrode is considered uncertain, since negative redox values imply that oxygen is not present. Slow response from oxygen electrodes was sometimes observed during the site investigations and was remediated by changing the membrane and condition of the electrode.

The conductivity stabilised after about 5 days and a discharge of about 30 section volumes (600 litres) and its behaviour is connected to the variation in chloride concentration which is described in the next section.

5.3 Water analyses – general

The analysis results are complied in Appendix 8. The charge balance errors exceeded ± 5% in two samples (14712, 14729). High charge balance errors may indicate large concentrations of particles and/or high uncertainty in the analyses. The two samples 14712 and 14729 represent water from the standpipe in sampling session 1 and section in sampling session 2. Analytical values from these samples are reported in the text and graphs of this report.

The percentage of drill water content (Uranine) is reported for samples from KAS03 and KAS09. For KLX06 the amount of Uranine is given in mg L^{-1}, since additional Uranine was added during previous dilution tests.

Some samples were analysed for sulphide by two laboratories (Appendix 8-1). The agreement was acceptable for low concentrations, while for higher concentrations (> 1 mg L^{-1}) the deviation was about 20%, which is above the limit for measurement uncertainty. For sulphide, the numbers of replicates (n) are 1 or 2 for each sample.

In one sample (14727, tubing), DOC exceeded TOC beyond the confidence intervals (8 and 10%).

5.4 Chloride and main cations

The variation of the chloride concentration over time in KLX06 is shown in Figure 5-1. Before conducting the first pumping period, the borehole section had not been sampled since late 2007. Pumping period 2 was preceded by an interruption in pumping of 9 weeks. The difference flow logging in KLX06 /Sokolnicki and Rouhiainen 2005/ shows anomalies with high hydraulic transmissivity at 561.2 and 562.2 m and when measuring conductivity during pumping of separate parts of the borehole, a raise in the conductivity was observed at about 550–560 m.

During both pumping period 1 and 2, the chloride concentrations are increasing as more water from the borehole section is discharged. The concentrations of chloride in the first collected samples of section water in the two pumping sessions were 742 and 453 mg L^{-1} respectively, while after discharging between 5 and 30 section volumes the chloride concentrationincreased to about 1,400 mg L^{-1}. Considerably lower chloride concentrations were obtained in the standpipe and tubing; 70 and 140 mg L^{-1}.

The KLX06 data in Appendix 8 show a good linear correlation between Cl^- and Na^+, Ca^{2+}, SO_4^{2-}, etc, and there is a good negative linear correlation between Cl^- and HCO_3^-. The data from both pumping periods follow the same correlation trends. This indicates a mixing process where water with low salinity and high alkalinity, initially present in the standpipe, tubing and borehole section, is gradually replaced during pumping by a groundwater with high salinity and low alkalinity. The difference in concentrations between the initial section water and the water after discharging several section volumes is too large to be explained by a natural and slow transport of water, with different composition, from the fractures intersecting the isolated section. A more probable explanation is leakage in the coupling that attaches the bottom of the standpipe and the upper end of the tubing connected to the section. Water from fractures located at lower depths (and with lower salinity) may penetrate through the coupling and reach the section if the pressure at this depth is sufficiently higher than the pressure in the section. This situation could be confirmed for KLX06 after checking pressure data from shallower borehole sections. The pressure difference for the current depths corresponded to a 6 metres water column, which would be enough to create a transport of water from lower to higher depths.

The chloride concentration in the standpipe can be explained by the procedure during installation of the equipment. For the function of pressure measurements in a section the density and hence the chemical conductivity need to be uniform in all tubing (and standpipes). Tubing and standpipe are continuously filled with water until a stable conductivity is reached, however, during this procedure the packers of the borehole section are not inflated and so the water does not necessarily originate from fractures in the section, but rather from fractures with high hydraulic transmissivity located anywhere along the borehole.

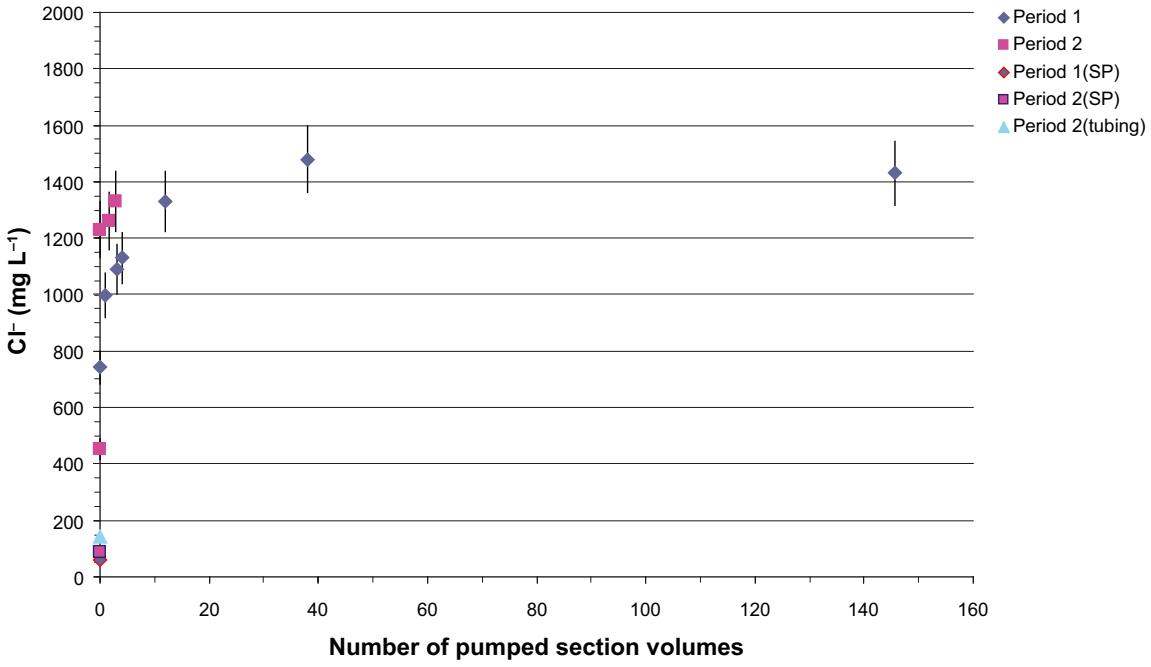

Figure 5-1. *The chloride concentration in KLX06 during pumping period 1 and 2 (n = 1). The denotation SP and tubing represent chloride concentrations in the standpipe and tubing.*

5.5 Sulphate and sulphide

5.5.1 Concentrations

Two different analyses of sulphate were performed; ion-chromatography (IC) and Inductively Coupled Plasma (ICP). For the ICP method, sulphur is analysed and then recalculated to the corresponding sulphate concentration. The agreement between the results was not good for all samples (Figure 5-2). The concentration of sulphate analysed with ICP tend to be overestimated in samples with high sulphide concentration, since hydrogen sulphide (gaseous) is released from the sample and heated in the plasma during analysis. Therefore the results from the analysis with IC are considered more reliable.

Figure 5-3 shows the concentrations of sulphate (analysed with IC) and sulphide in KAS03 and KAS09, section water and standpipes. There were very high concentrations of sulphide in the upper and lower sections of KAS03 and extremely high in KAS09 (102 mg L^{-1} in the standpipe and 92.3 mg L^{-1} in the section water). It is likely that water from the standpipe is mixed with section water during pumping and sampling from the section, since the pump and filter could not be lowered completely in the standpipe. Sulphate was not analysed with IC in KAS03, section 627–1,002 m, due to the small amount of collected water, sulphate analysed with ICP gave a value of 78 mg L^{-1}.

The sulphate concentrations were low at the beginning of each pumping period of KLX06 and they increased along the pumping period. As noted in previous section there is a good linear correlation between Cl^- and SO_4^{2-}. The data from both pumping periods follow the same correlation trends.

The concentration of sulphide was high in the beginning of pumping in KLX06 both times and decreased to about 0.1 mg L^{-1} as the pumping continued (Figure 5-4). In opposite, ferrous iron increased during pumping (Figure 5-5). There was a clear inverse relationship between sulphide and ferrous iron during the first pumping interval, less pronounced during the second, shorter interval (Figure 5-6). The change in manganese concentration was less pronounced, but showed a similar increase with pumping time as did ferrous iron (Figure 5-7).

In Figure 5-4 to Figure 5-7 samples from pumping series 1 and 2 are denoted KLX06-1 to KLX06-14 and KLX06-2-1 to KLX06-2-6, respectively. Note that KLX06-1 and KLX06-2-2 represent water from the standpipe and KLX06-2-1 corresponds to water from the tubing between the standpipe and the section.

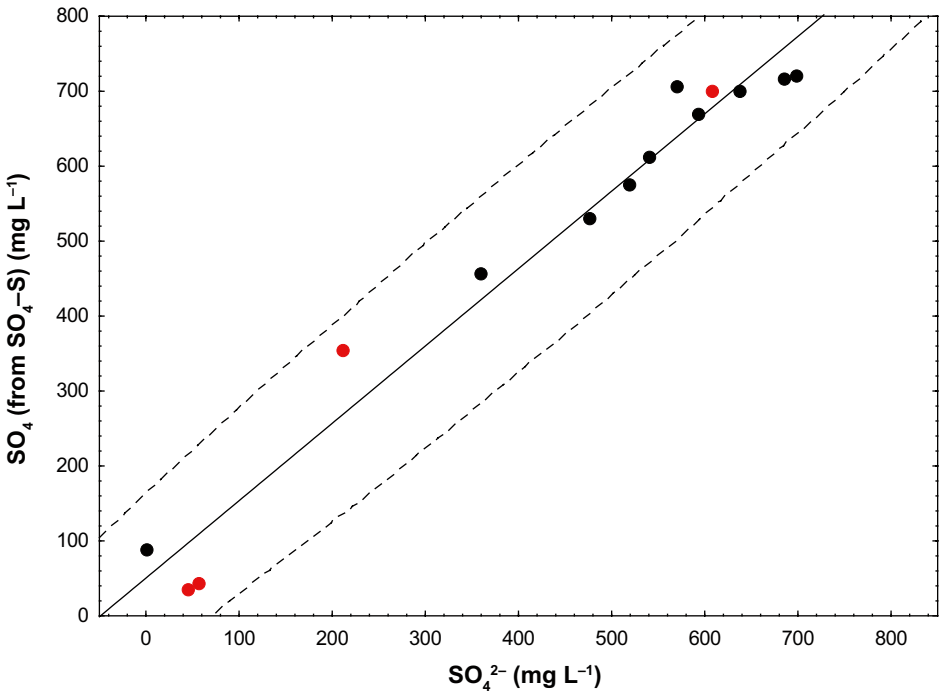

Figure 5-2. *The relation between sulphates analysed with two different methods. Sulphate analysed with ICP (e.g. analysed sulphur recalculated to sulphate) on the y-axis and with IC on the x-axis. The hatched lines denote a 95% confidence interval.*

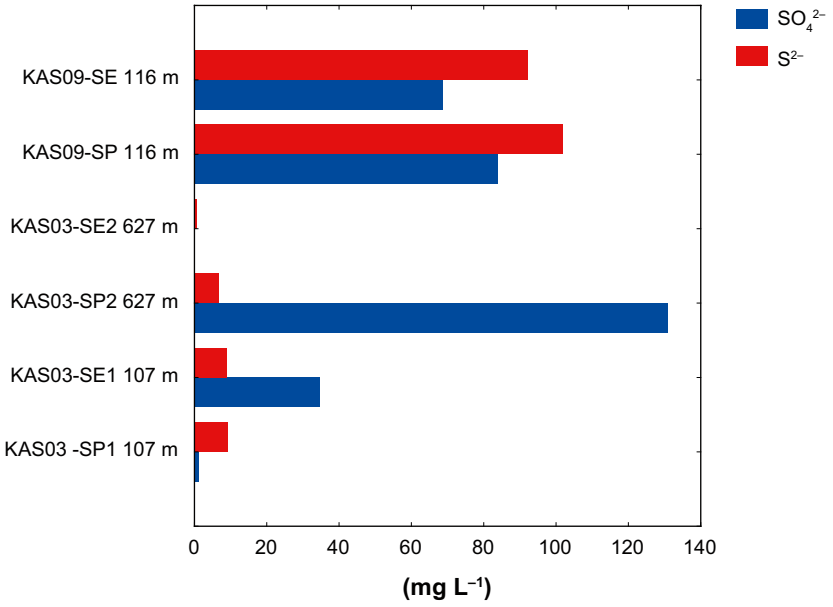

Figure 5-3. *Amounts of sulphate (analysed with IC) and sulphide in the water present in the isolated borehole sections from two levels in borehole KAS03 and one level in KAS09. SE: section; SP: standpipe. Sulphate was not analysed with IC for KAS03-SE2 627 m.*

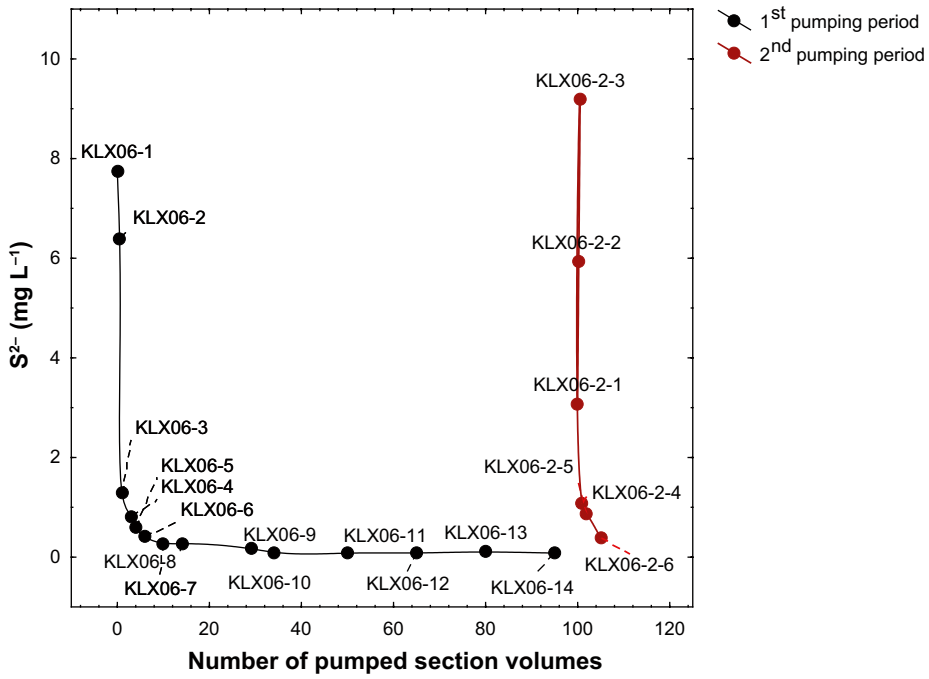

Figure 5-4. *Amount of sulphide versus the number of pumped section volumes from two sampling series in groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). The line shows a spline fitting function. KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

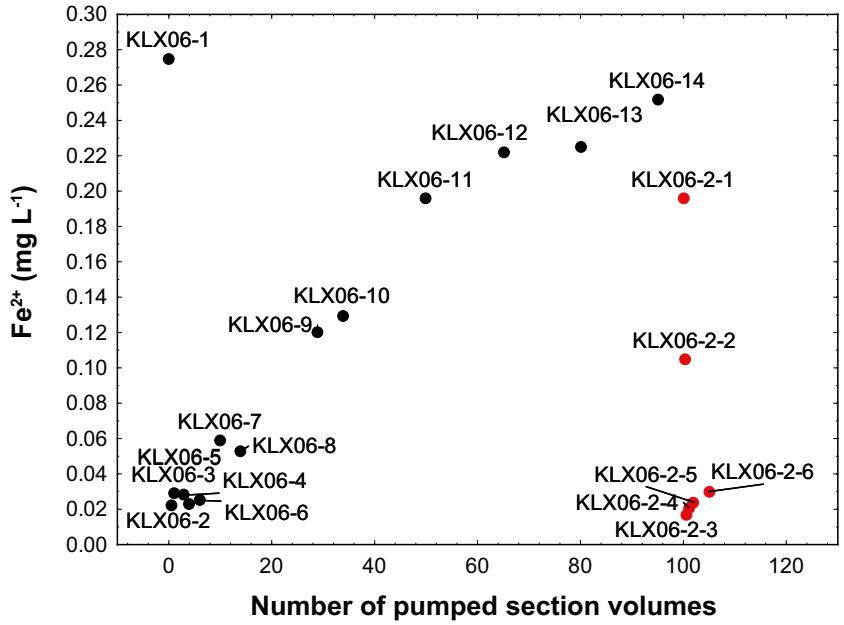

Figure 5-5. *Amount of ferrous iron versus the number of pumped section volumes from two sampling series in groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water from the tubing.*

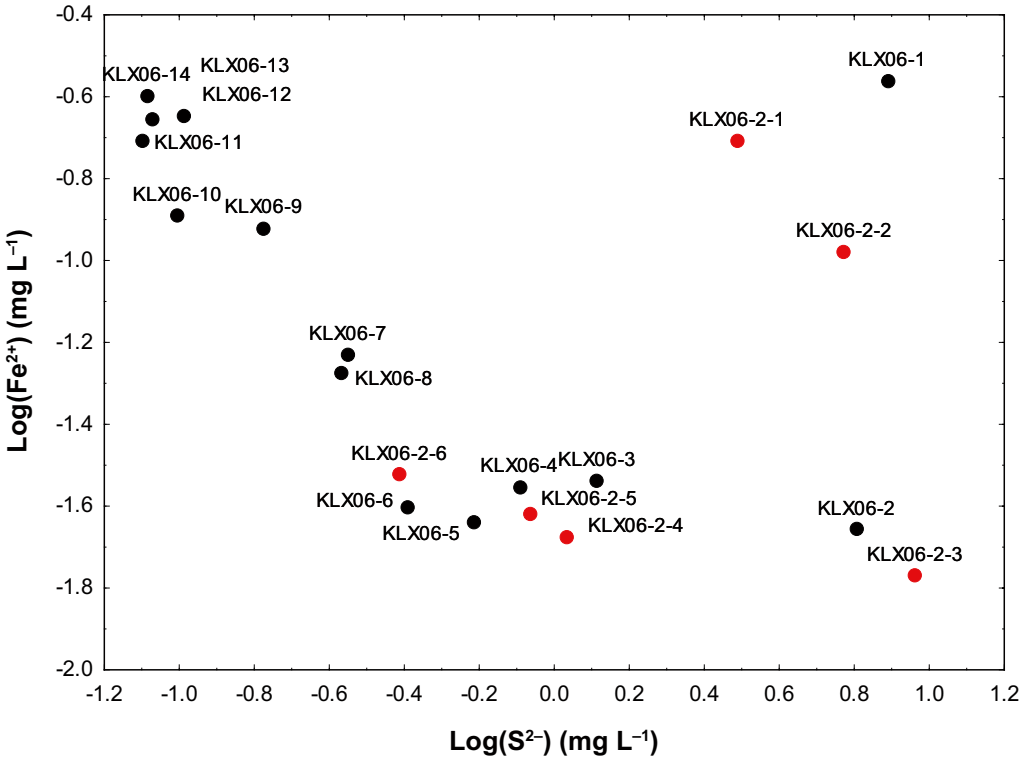

Figure 5-6. *Ferrous iron versus sulphide in groundwater from two sampling series in borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water from the tubing.*

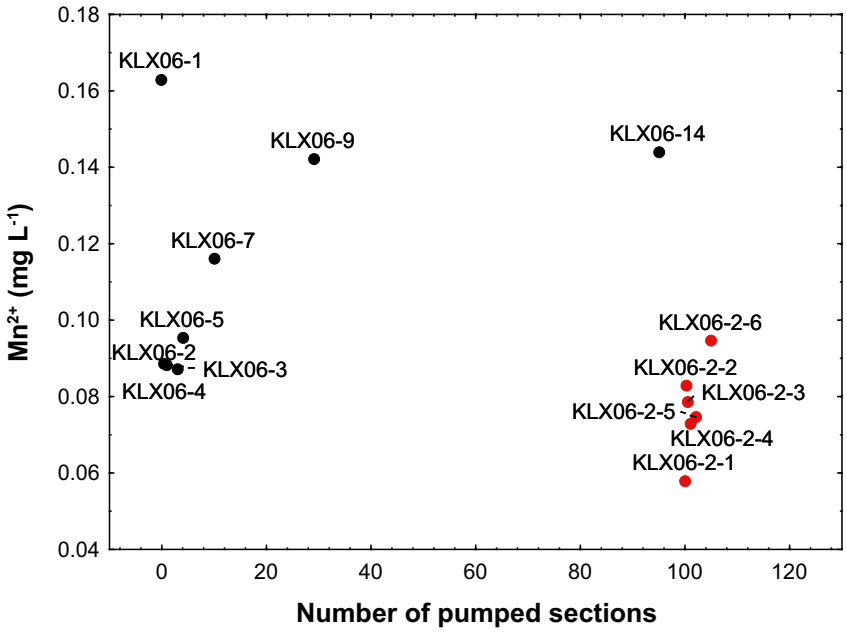

Figure 5-7. *Amount of dissolved manganese versus the number of pumped section volumes of groundwater from two sampling series in borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water from the tubing.*

5.5.2 Sulphide concentration as a function of discharged water during pumping in KLX06

The sulphide concentration in KLX06 decreased during pumping (Figure 5-8 and Figure 5-9). The hypothesis is that the sulphide originates from the volume of water occupying the standpipe, the tubing and the isolated borehole section before the start of pumping activities. The decrease in sulphide concentration would then coincide with an increasing amount of formation groundwater, i.e. water that originates directly from water-bearing fractures in the surrounding rock. To test this hypothesis the results from the analysis of sulphide concentrations during pumping are compared to the expected ratio between water from the section and groundwater from the fractures of the investigated section. The plug-flow model used was derived during the hydrochemical monitoring campaign in Forsmark in 2009 /Nilsson et al. 2010/. Sulphide data from totally eleven borehole sections were modelled.

Figure 5-10 illustrates the contribution (in %) of the total flow from the two fractures (flow anomalies) in the isolated borehole section. The height of the staples represents the accumulated part of the totally discharged flow from the present anomalies. Anomaly 2, located at 562.2 m dominates and contributes with ~99% of the total flow. The water from this anomaly has reached the outlet from the tubing at the top of the section after approximately 1 hour. This coincides well with the abrupt decrease in sulphide concentration after 2 hours of pumping (discharged 1 section volume) illustrated in Figure 5-9. The anomaly located at 561.2 m contributes to the total flow with only 1% after ~0.9 hours.

After pumping 2 hours with a mean flow of 150 mL min^{-1}, about 1 section volume of 14.2 litres has been turned over and at this point the sampled water almost entirely consists of water from anomaly 2. However, the sulphide concentration has not reached a low and stable concentration until after about 100 to 150 hours of pumping. There might be several more or less combined explanations to this: 1) the flow in the borehole is not entirely a plug flow. Depending on flow velocities, roughness of surfaces and geometric conditions in the borehole section the flow has a certain distribution across the borehole. In this case where the borehole is filled with dummies and tubes it is reasonable to assume that it will take at least 1.5 to 2 times the calculated figures before most of the water from a certain anomaly contributes to the flow at the outlet; 2) the equipment in the borehole and in the standpipe (around filter, pump and at the end of the packers) creates “dead volumes” of water that

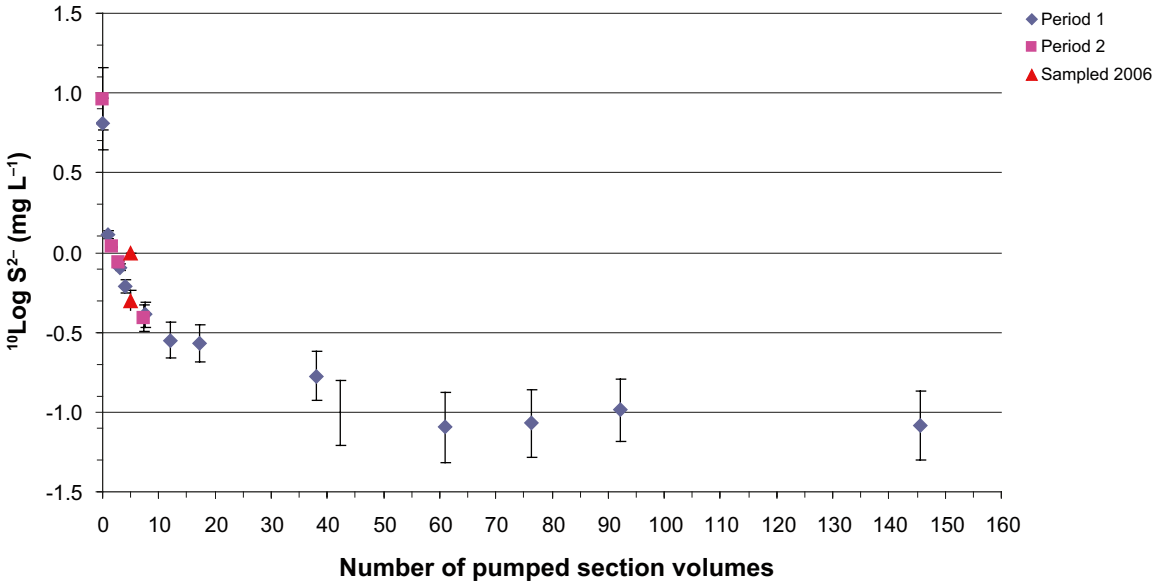

Figure 5-8. *Sulphide versus time in KLX06 (samples KLX06-1 to KLX06-14 and KLX06-2-3 to KLX06-2-6). The sulphide concentration at time 0.2 hours represent sampling from the initial water in the section, only 2 litres of water was discharged before the sample was collected. Red triangles represent the samples that were collected after discharge of 5 section volumes during hydrochemical monitoring in 2006.*

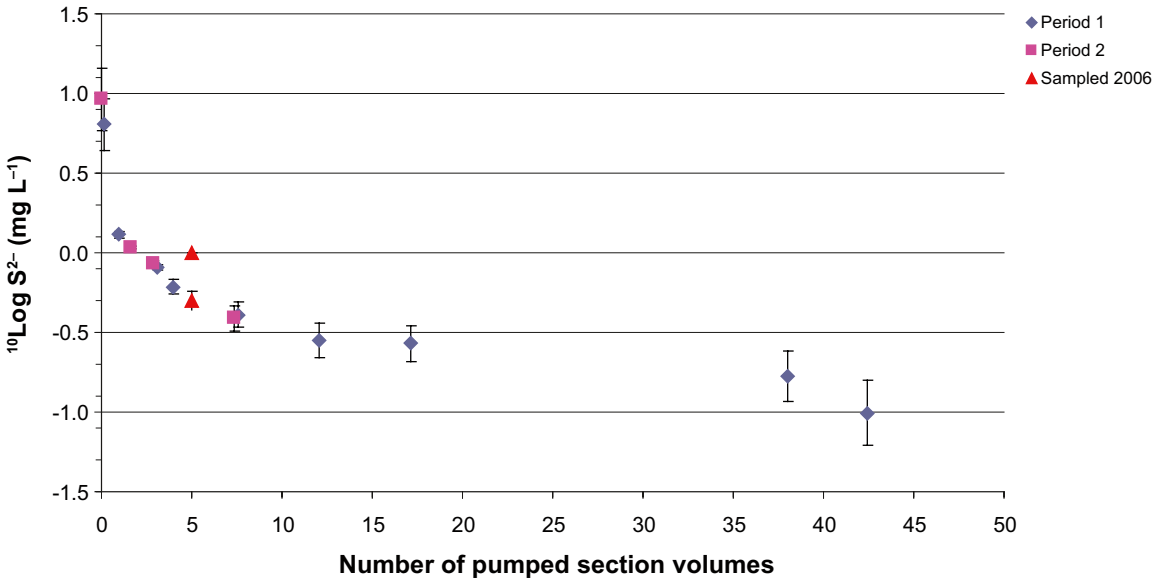

Figure 5-9. *Sulphide versus time in KLX06 (samples KLX06-1 to KLX06-5 and KLX06-2-3 to KLX06-2-6), close-up. Red triangles represent the samples that were collected after discharge of 5 section volumes during hydrochemical monitoring in 2006.*

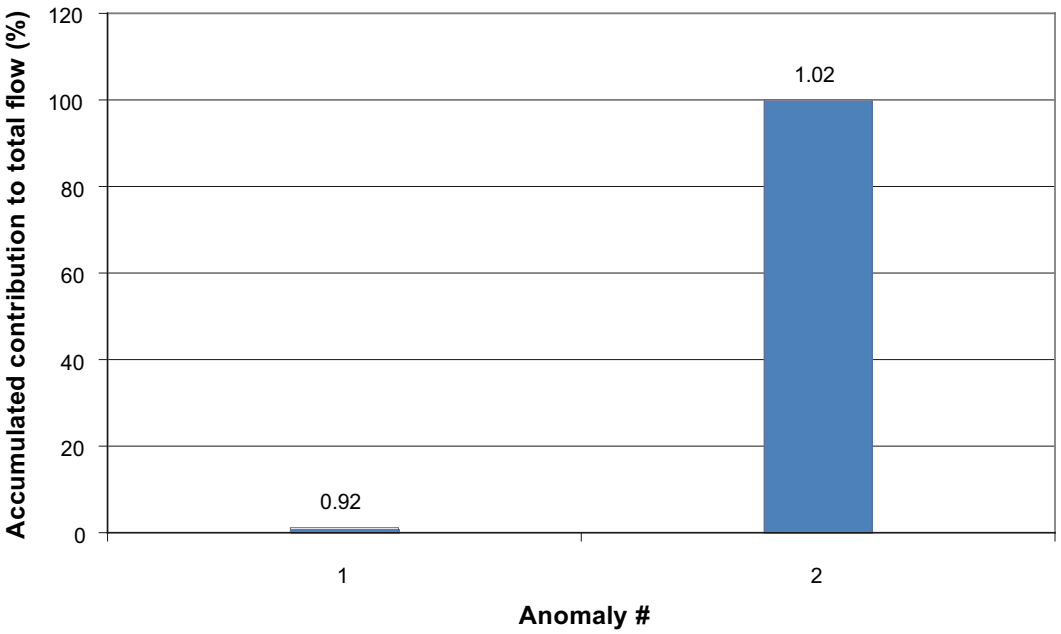

Figure 5-10. *Accumulated distribution (in % of total flow) from the two flow anomalies, numbered from top of section (1) and downwards (2) in borehole KLX06 section 554–570 m. The figures above the staples indicate calculated travel time (in hours) for water from anomalies to the top of section and tube ending.*

are not as actively mixed as water in other parts of the borehole; 3) a closer study of the PFL-logging (Posiva Flow Logging) and BIPS-logging in KLX06 reveal a possible anomaly at 564.5 m. The contribution from this anomaly is calculated to having reached the outlet at approximately 135 hours and considering the low flow during pumping, the turnover of water from this fracture should be an extended process. The presence and contribution of such a fracture coincides well with the lowering of the sulphide concentration after 100–150 hours of pumping. The contribution of this anomaly is uncertain, due to the small size and low flow from this anomaly.

An implication of the results above is that the time for replacing the water in borehole sections can differ a lot and this must be taken into consideration when monitoring boreholes and collecting representative samples. For example, a single fracture with high hydraulic transmissivity in the uppermost part of the borehole section, near the tube ending from which the water is pumped, means that a dominant part of the discharged groundwater will consist of formation water after a short time. If, on the other hand, there are a number of fractures distributed over the entire section it may take considerable time before the initial section water is totally replaced.

5.5.3 Continuous Stirred-Tank Reactor modelling

The concept of a CSTR–model (Continuous Stirred-Tank Reactor) was applied to the concentrations of chloride, sodium, calcium and sulphide analysed in KLX06 during pumping. The idea was to compare experimental data with the CSTR-model, evaluate the agreement and to attain an analytical solution.

The CSTR-model assume complete mixing and hence that the output water composition is identical to the composition of the water inside the reactor. In general, for engineering purposes, the approximation of ideal mixing is can be applied (approached) when the residence time is about 5–10 times the mixing time. Figure 5-11 illustrates the principle of a CSTR and the associated mass-balance equation for the assumption of complete mixing.

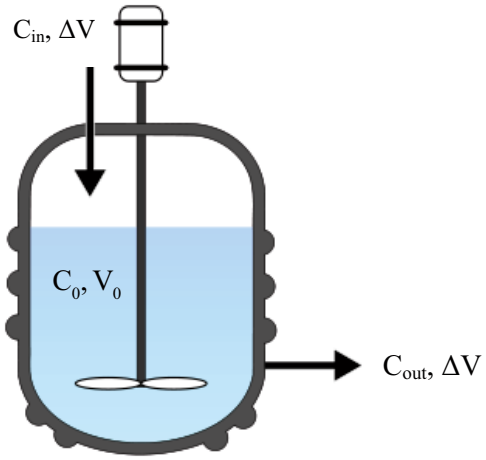

Figure 5-11. *Illustration of the principle of a CSTR. [Accumulation] = [in] – [out] ± [generation/ consumption], the integral mass balance on number of moles N_i of species i in a reactor of volume V can be described as: $\partial N_i/\partial t = C_{in}\Delta V + C_0V_0 \pm C\ (V_0+\Delta V)$.*

When CSTR is applied to a borehole section during pumping, the water from the fractures is entering the isolated section (reactor), mix with the water in the section, and leave the section through a tubing to reach the ground surface and place for sampling.

The mass balance equation for this scenario can be written as;

$$C_{out} = C = \frac{C_0 \times V_0 + C_{in} \times \Delta V - C_{out} \times \Delta V}{V_0}$$

The equation that gives the relation between the changes in concentration C (C_{out}) of a species with a change in the volume can be written as;

$$\frac{\partial C}{\partial V} = \frac{1}{V_0}(C_{in} - C)$$

Which has the following solution;

$$C = C_{in} + (C_0 - C_{in}) \times e^{-\frac{1}{V_0} \times V}$$

Where V is the accumulated pumped volume at time t and V_0 is the volume at time 0. This expression has an analytical solution. A value for the initial section volume, V_0, is obtained while fitting the model curve to the experimental data. The concentration (C_{out} = C) is plotted as a function of exp ($-V/V_0$).

The section volume was 14.5 L, the volume of water in the tubing connected to the section 14 L. The first sample was collected after discharging the volume of the tubing and additional 2.5 L of the section water. This means that when the first sample was collected, a little more than one section volume was discharged; sample number two was collected after discharging two section volumes and the final sample after more than 200 volumes.

The concentrations of chloride, sodium and calcium analysed during the first pumping session in KLX06 were fitted to the model. An initial volume, V_0, of 101 L gave the best fit (R^2) for the three components. Figure 5-12 shows the experimental data and the model curves. The true volume of the water between the packers was 14.5 L; about 7 times lower than the predicted volume. This indicates that the mixing of water from the fractures with the water in the section is not ideal and complete. Assuming a volume of 14.5 L, the experimental concentrations would be 7 times lower than the observed values during sampling. Chloride, sodium and calcium are likely to be conservative components; i. e. they are not involved in reactions or kinetics that may alter the concentrations during

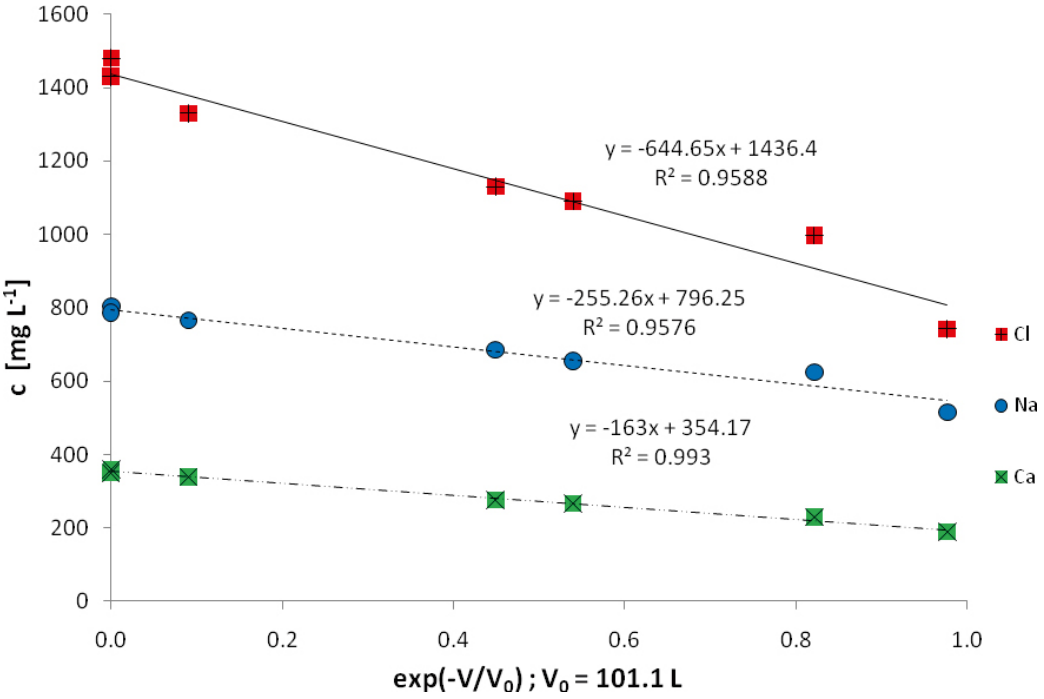

Figure 5-12. *Experimental concentrations of chloride, sodium and calcium from the first pumping session (2009-02-09 – 2009-02-23) and fitting of model curves.*

pumping. The curves show a clear trend of linear increase in concentration with pumping; indicating that water in the section is mixed with water from the fractures having a different chemical composition. When the initial water in the section is completely replaced with water from the fractures, the concentrations of chloride, sodium and calcium are stabilised (Figure 5-12).

Figure 5-13 and Figure 5-14 shows the sulphide concentration in KLX06 during pumping and the fitted model curve. Figure 1-3 includes all samples, while in Figure 1-4 the first sampling point was omitted. The fit is better when the first experimental sulphide value of 6.4 mg L^{-1} is excluded; i e more experimental data points agree with the model curve. The fit with all data points present gives an apparent section volume (V_0) of about 10 L. When the first sulphide value is omitted the section volume is predicted to be about 88 L, close to the predicted V_0 for chloride, sodium and calcium.

Given the location of the fractures in the section it is likely that the mixing of water is not complete. A fracture with high hydraulic transmissivity is located in the middle of the section (562.2 m), see previous Section 5.5.2, which means that section water below this fracture is not to an equal extent involved in the mixing with fracture water. Water from the dominating fracture has reached the outlet of the tubing at the ground surface after about 1 to 2 hours of pumping (discharged about 1 section volume). As described in Section 5.2.2 this coincide well with the abrupt decrease in sulphide concentration between the first and second sample (6.4 and 1.3 mg L^{-1} respectively). As discussed in Section 5.4 the concentrations of observed chloride, sodium and calcium in the section are likely an effect of mixing with water closer to the surface (due to defect equipment). The sulphide concentration is highest in the beginning of the pumping and then decreases. This may indicate production of sulphide in the section due to either addition of an organic carbon source from the surface water and/or a source of organic carbon, methane gas or hydrogen gas in the section. However, the reactions and phase transformations involving sulphide is complex and other explanations cannot be excluded. Since sulphide besides dissolved and solid form also exists in gaseous form, it is sensitive to oxygen and pressure. Reactions such as adsorption (to minerals in fractures and borehole) and precipitation (with iron) may also alter the concentration of sulphide.

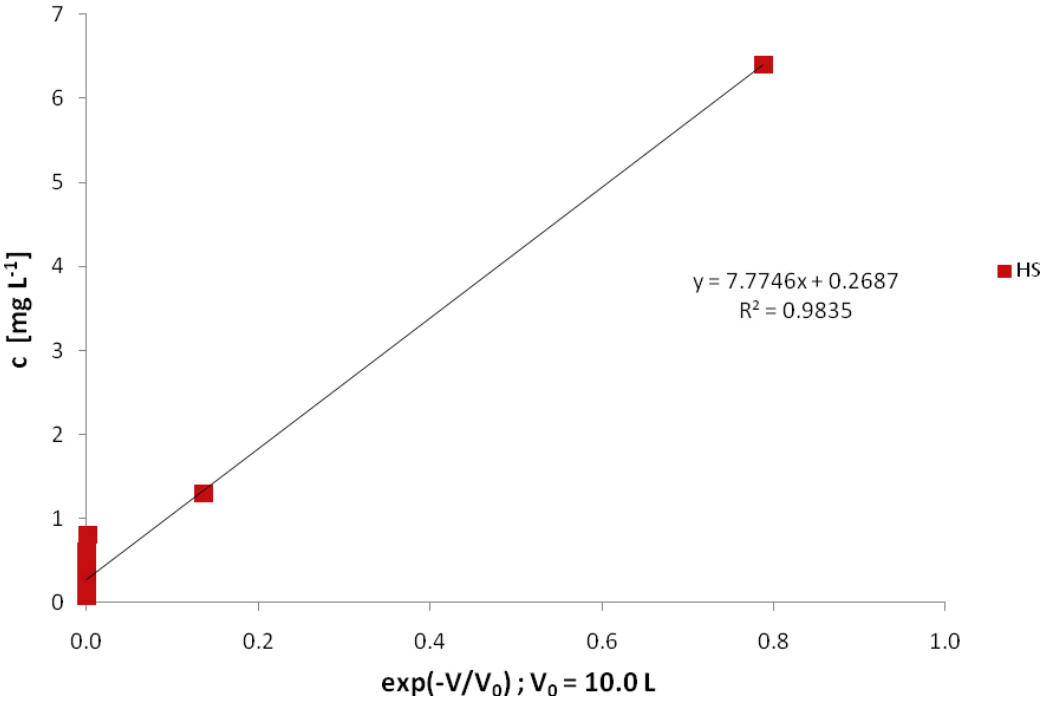

Figure 5-13. *Experimental concentration of sulphide from the first pumping session (2009-02-09 – 2009-02-23) in KLX06 and fitting of model curve.*

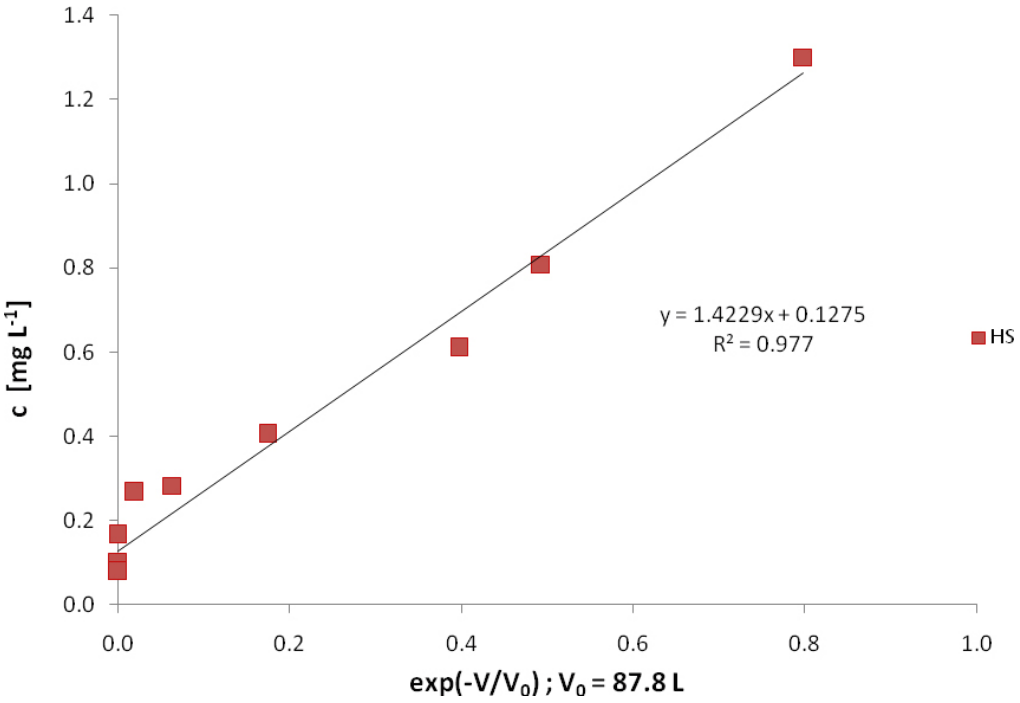

Figure 5-14. *Experimental concentration of sulphide from the first pumping session (2009-02-09 – 2009-02-23) in KLX06 and fitting of model curve. The first sample in the series (KLX06-2) was omitted.*

5.5.4 Ferrous iron monosulphides

Fe^{2+}-monosulphides have been shown to control the dissolved iron and sulphide concentrations in systems such as those that are studied here (/Gimeno et al. 2009/ and references therein). The amorphous monosulphide (so called disordered or nanoparticulate mackinawite) is the first solid phase that typically precipitates in most natural aqueous systems. Its precipitation kinetics are very fast (seconds) although it is the most soluble of the iron sulphides. Since the precipitation kinetics are fast, a significant oversaturation is not expected to occur in natural groundwater (/Gimeno et al. 2009/ and references therein) and analytical data that lead to oversaturation is then very doubtful. Mackinawite, the crystalline monosulphide, is slightly less soluble but its precipitation kinetics is also fast (days).

Saturation indices were calculated for ferrous iron monosulphides in samples collected from KLX06, KAS03 and KAS09, by comparing the ionic products of analysed concentrations of Fe^{2+} and S^{2-} to the solubility product for ferrous monosulphide. The solubility product (ionic activity product) for amorphous monosulphide was determined for sulphidic groundwater in the Laxemar area to log K = −2.98 by /Gimeno et al. 2006/ using PHREEQC and the WATEQ4F database.

In KLX06 the groundwater samples are clearly undersaturated except for the water in the standpipes that are closer to saturation or oversaturated (Figure 5-15). For KAS03 the waters in the two sections and in the standpipe of section 107–252 m are undersaturated with respect to ferrous monosulphide, while in the standpipe of section 627–1,002 m the water is close to saturation or oversaturated. In KAS09, the water from both section and standpipe is oversaturated with respect to ferrous mono-sulphides (Figure 5-16).

There are two standard methods for analysis of sulphide; non-contaminated natural waters (SIS 028115) and sewage water (SIS 021117), both are colorimetric methods. In the latter the water solution is acidified and hydrogen sulphide degassed in order to avoid any precipitated sulphide. In this inves-tigation, the method for non-contaminated water was used. The samples from KAS09, standpipe and section water, had high sulphide concentrations (102 and 92 mg L^{-1}), the waters contained high concentrations of DOC and were visibly turbid and coloured after sampling and filtrating with 0.45 µm filter. The spectrophotometric analysis was not corrected for the sample matrix, but the samples were diluted 50 times before analysis to fit into the calibration curve. A possible explanation to the exceeded saturation indices is presence of particulate sulphide (smaller than the filter) that reacts with the added ZnAc so that the analysis includes both dissolved and particulate sulphide.

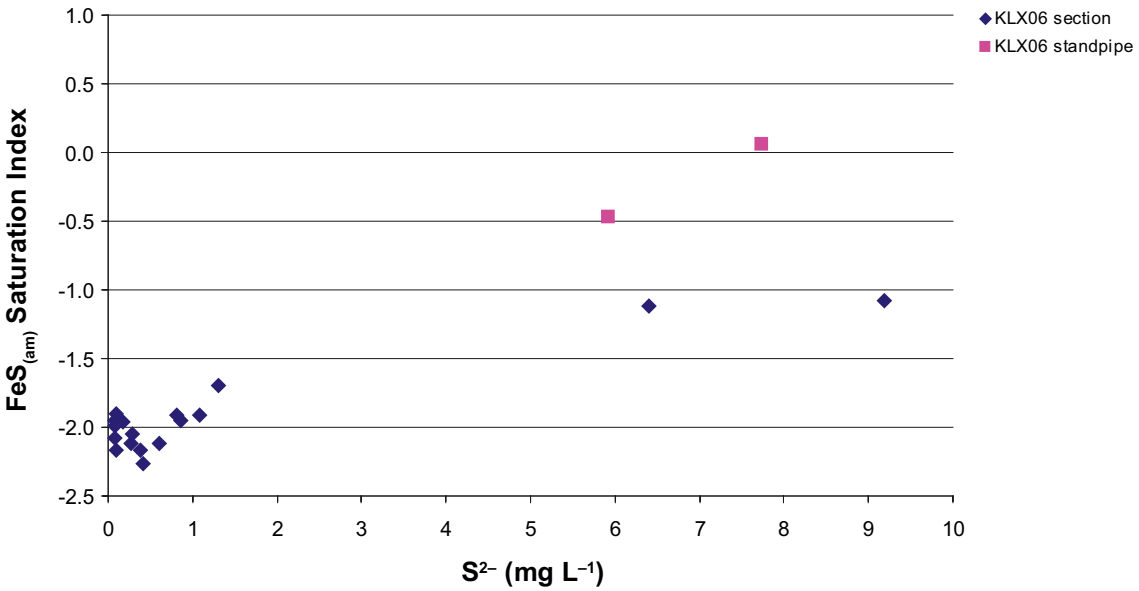

Figure 5-15. Experimental concentration of sulphide from the first pumping session (2009-02-09 – 2009-02-23) in KLX06 and fitting of model curve. The first sample in the series (KLX06-2) was omitted.

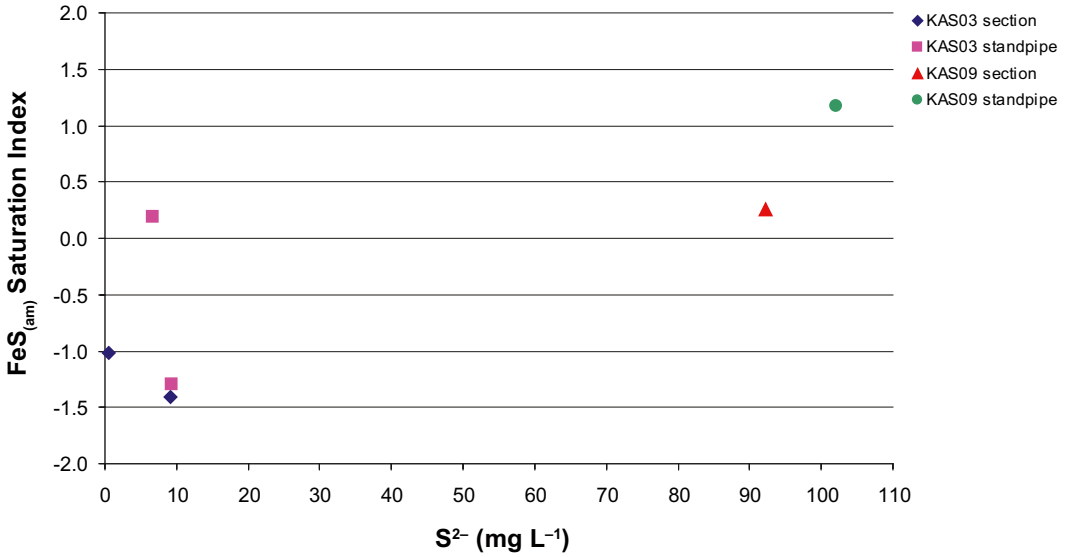

Figure 5-16. *Saturation indices for ferrous iron monosulphides (FeS) as a function of sulphide concentration in KAS03 and KAS09.*

5.5.5 Sulphur isotopes

The $\delta^{34}S$ values of the dissolved sulphate show a wide variation between +8.6 and +13.8 ‰ in the KLX06 sample series including the standpipe (KLX06-1). The $\delta^{34}S$ values of the sulphides vary between +24.9 and −19.3 ‰. The positive value (+24.9 ‰) which is observed in the standpipe is extremely high assuming that the sulphide is a product of sulphate reduction of the dissolved sulphate. The first sample from the section water in KLX06 (KLX06-2) has a sulphide concentration of 6.4 mg L^{-1} and a $\delta^{34}S$ value of −6.1 ‰. The corresponding $\delta^{34}S$ value of the dissolved sulphate of +14 ‰ typically reflects the expected fractionation of around 20 ‰ or more (Table 5-2). This fractionation pattern is repeated in the two following samples with a decrease in the $\delta^{34}S$ value of the sulphide and a corresponding lowering in $\delta^{34}S$ of the dissolved sulphate. After about 95 pumped section volumes (sample KLX06-14), however, the $\delta^{34}S$ value of the sulphide increases.

The sulphide concentrations for all samples in the first sample series in KLX06 are plotted versus Fe^{2+} in Figure 5-17 and Figure 5-18. As can be seen the S^{2-} concentration decreases as the concentration of Fe^{2+} increases. The continuous drop in the $\delta^{34}S$ isotope value of the dissolved sulphate with time followed by an increase in chloride and sulphate concentration (Figure 5-19 and Figure 5-20), suggests continuous in-mixed saline groundwater during pumping. It is also shown as a mixing line by plotting the reciprocal concentration of the dissolved sulphate ($1/SO_4^{2-}$) versus $\delta^{34}S$ in Figure 5-21.

Table 5-2. $\delta^{34}S$ isotope data from sulphide and dissolved sulphate in KLX06.

	Sample ID	$\delta^{34}S$ in Sulphate	$\delta^{34}S$ in Sulphide	Δ ‰
Standpipe	KLX06-1	+13.8	+24.9	11.1
Section	KLX06-2	+14.1	−6.1	20.2
Section	KLX06-4	+11.3	−11.3	22.6
Section	KLX06-7	+9.3	−19.3	28.6
Section	KLX06-14	+8. 6	−3.5	12.1

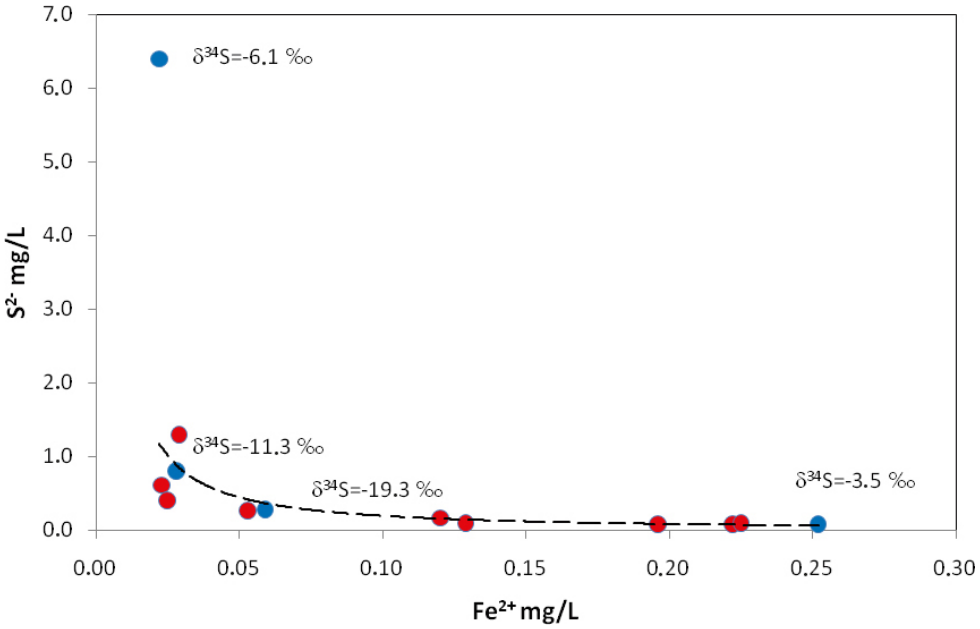

Figure 5-17. *Concentrations of S^{2-} versus Fe^{2+} in groundwater from the first sampling series in borehole KLX06, section water. Fe^{2+} (red dots), S^{2-} (blue dots). The dashed line has been drawn to help the eye.*

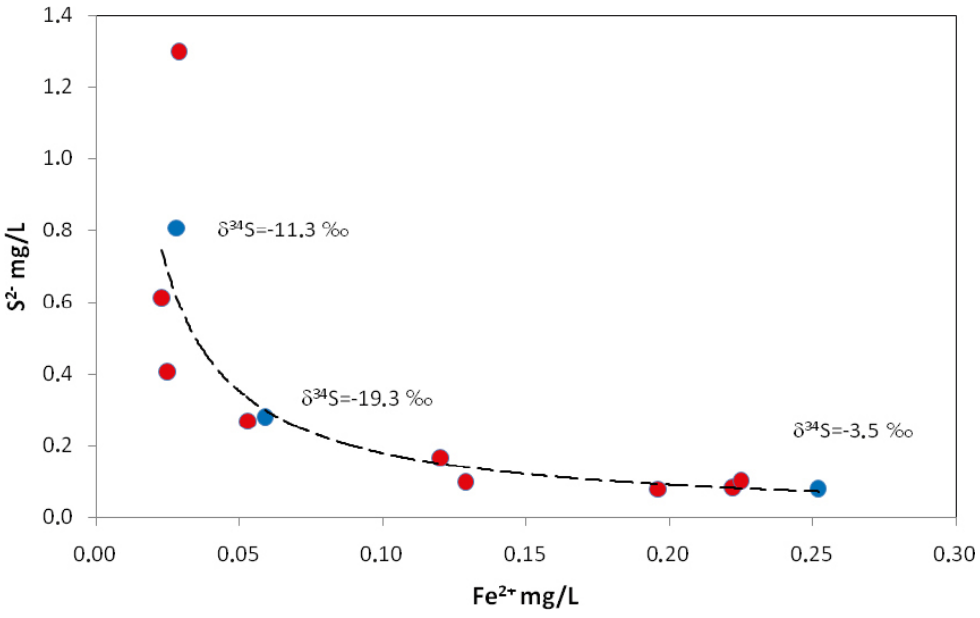

Figure 5-18. *Concentrations of Fe^{2+} versus S^{2-} in groundwater from the first sampling series in borehole KLX06, section water. Close-up of Figure 5-13. (KLX06-2 omitted). Fe^{2+} (red dots), S^{2-} (blue dots). The dashed line has been drawn to help the eye.*

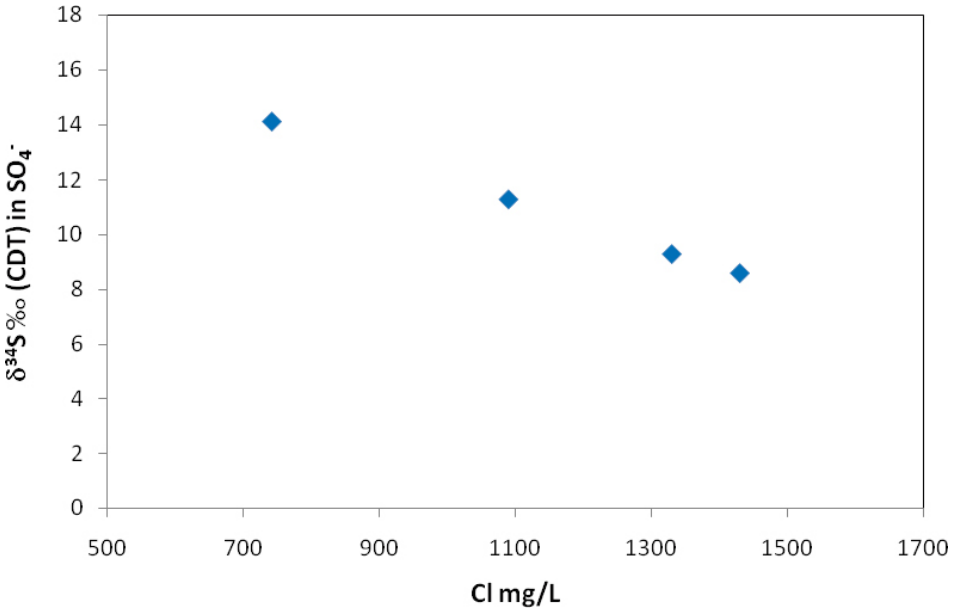

Figure 5-19. *$\delta^{34}S$ in dissolved sulphate versus chloride concentration in the groundwater of the first sample series in KLX06, section water.*

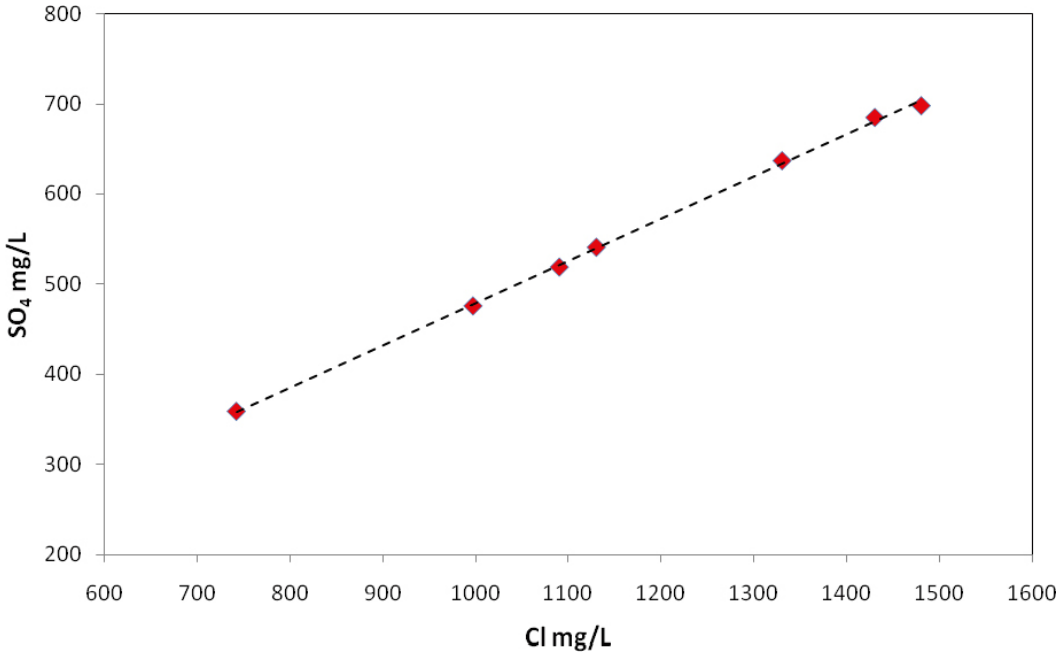

Figure 5-20. *Sulphate concentration versus chloride concentration in groundwater from the first sampling series in borehole KLX06, section water. The dashed line has been drawn to help the eye.*

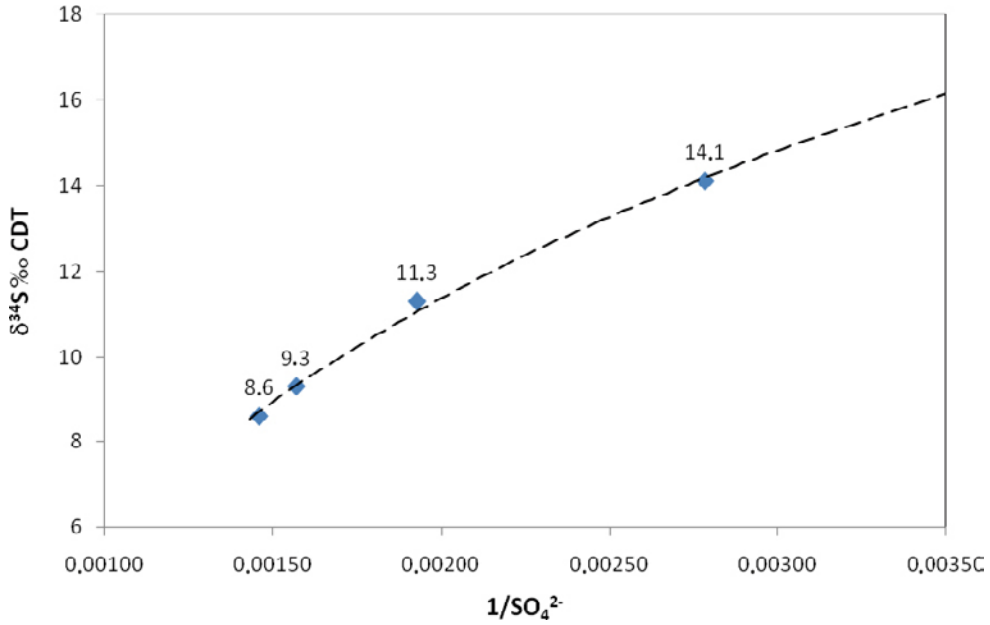

Figure 5-21. *$\delta^{34}S$ in dissolved sulphate versus the reciprocal value of dissolved sulphate in the first sample series in KLX06, section water. The dashed line has been drawn to help the eye.*

5.6 Carbon

5.6.1 Concentration and molecular weight

Acetate constituted between 0 and 10% of the dissolved organic carbon in KLX06, except in the standpipe (sample KLX06-1) where it constituted about 50%. There was a similar relation between acetate and DOC in the KAS boreholes, where the proportion acetate of DOC varied between 0 and 10%. The results for TOC and DOC (Total organic carbon and Dissolved organic carbon, respectively) gave good agreement in most cases; however, in one sample DOC exceeded TOC (14727) beyond the confidence intervals. The values for TOC and DOC were high in the standpipes of all borehole sections (6–50 mg L^{-1}) and also in the section water of KAS03, 627–1,002 m (146 mg L^{-1}). The DOC concentrations in water samples collected from the sections ranged from 2 to 16 mg L^{-1}. Considering the observed precipitate in the standpipes during dismantling of the equipment in KAS03 and KAS09, it is likely that the filter connected to the pump is contaminated during pumping and sampling (DOC in tubing 367 mg L^{-1}). This can explain the high concentrations of TOC and DOC in the standpipes and the varying concentrations within one sample. The DOC and TOC results are compiled in Appendix 8-1.

Dissolved organic carbon from three samples in KLX06 (standpipe and section) was fractionated using ultrafiltration technique and three membrane filters with cut-off 10kD (kilo Dalton), 3kD and 1kD, see Table 5-3. One kD corresponds to a molecular weight of about 1,000 g mol^{-1}. For the section water, most of the organic matter passed through the 1kD filter, while for the standpipe a small amount of organic carbon passed the 10kD and 3kD filters but not the 1kD filter.

Table 5-3. Fractionation of dissolved organic carbon in KLX06.

Sample ID	DOC (< 0.22µm) mg L^{-1}	DOC ≤ 10 kDa mg L^{-1}	DOC ≤ 3 kDa mg L^{-1}	DOC ≤ 1 kDa mg L^{-1}
KLX06-2-2 Standpipe	27	27	26	23
KLX06-2-3 section	11	11	11	11
KLX06-2-5 Section	7	7	7	7

5.6.2 Carbon isotopes

A summary of all measurements of $\delta^{13}C$ (%PDB) and ^{14}C (pmC) for the inorganic carbon (bicarbonate) performed in KAS03, KAS09 and KLX06 show a wide range in the isotope values, indicating a mixture of carbon sources. $\delta^{13}C$ values are plotted versus pmC in Figure 5-22 in order to show the wide range of the carbon source in the groundwater system. The $\delta^{13}C$ values in all samples collected vary between −9 and −21 ‰. The ^{14}C show a range in values between 97.6 and 30 pmC.

As can be seen in Figure 5-23 there is a constant decrease in pmC with the decrease in $\delta^{13}C$ in KLX06 in the first sample series. Figure 5-24 shows a decreasing trend in HCO_3^- while pumping.

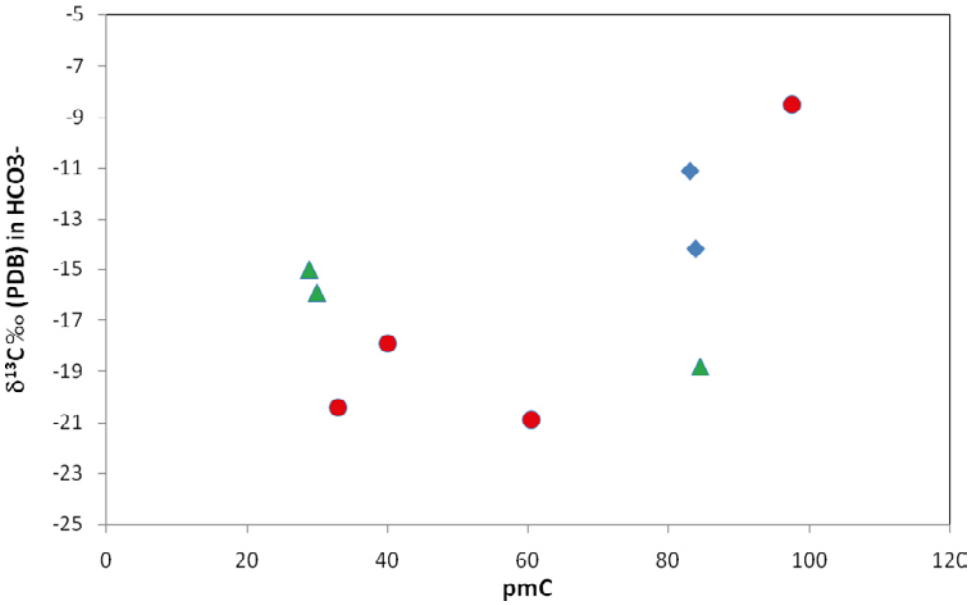

Figure 5-22. *$\delta^{13}C$ and pmC in bicarbonate for all data collected from KLX06 in sample series 1 and 2 (red dot), KAS03 (green triangle) and KAS09 (blue diamond).*

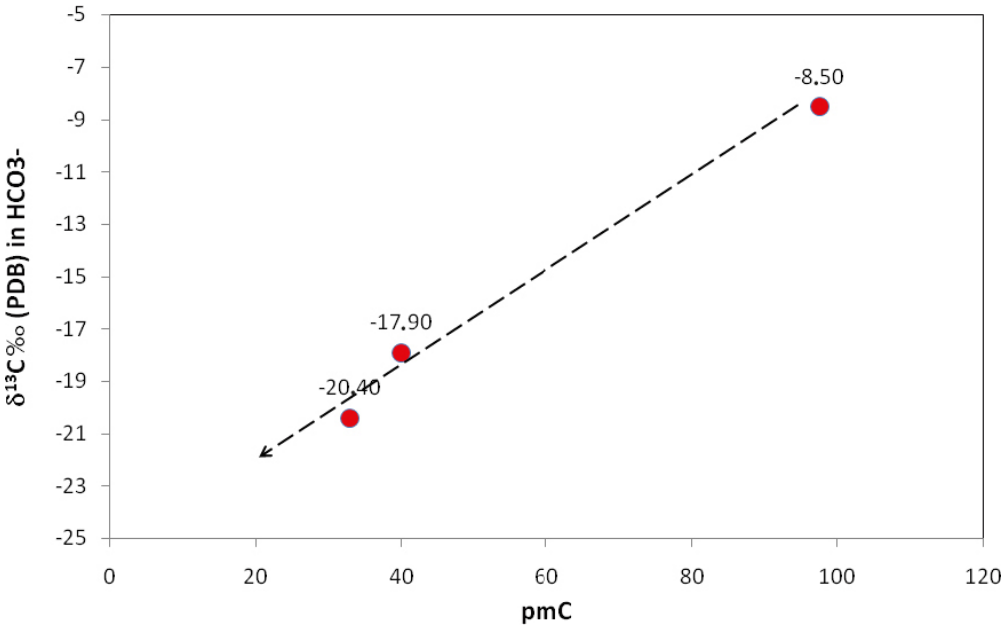

Figure 5-23. *$\delta^{13}C$ and pmC in bicarbonate for data collected only during the first sample series in KLX06, standpipe included (samples KLX06-1, KLX06-2 and KLX06-7). The $\delta^{13}C$ values are given next to the sample points in the diagram. The dashed line has been drawn to help the eye.*

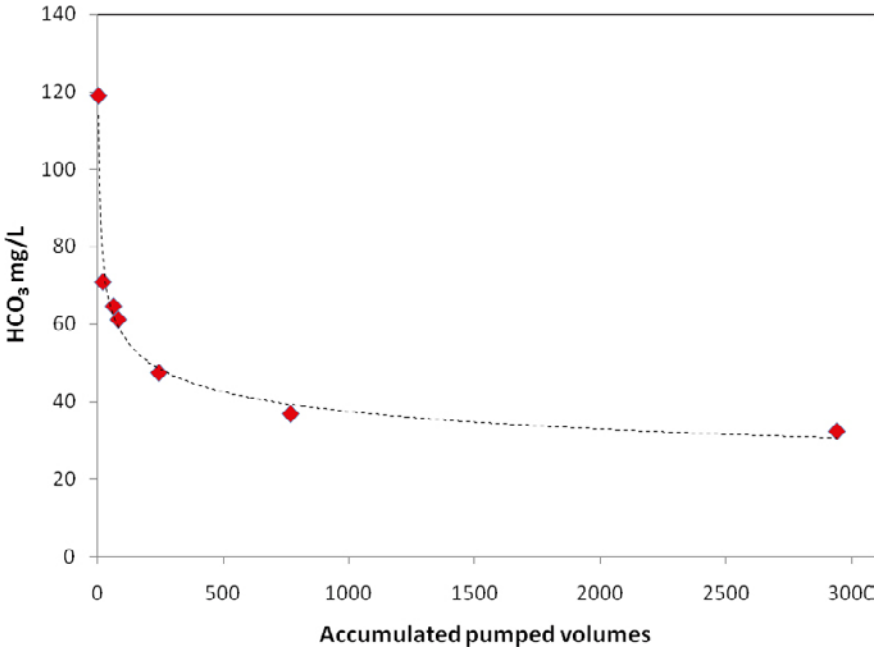

Figure 5-24. *Bicarbonate concentrations versus accumulated discharged section volumes in borehole KLX06. The dashed line has been drawn to help the eye.*

5.7 Microbiological analyses

5.7.1 Numbers

The amount of ATP (adenosine triphosphate) is a measure of biomass and one amole is approximately equivalent to one microbial cell /Eydal and Pedersen 2008/. The ATP value corresponds to all types of microorganisms in a sample. Beside this fact there was a reasonable agreement between ATP and MPN (most probable numbers) of SRB in most samples indicating that SRB constitute a large part of the microbial populations even though there were other microbial groups present (Figure 5-25, Figure 5-29 and Figure 5-30). The MPN values have upper and lower limits of approximately 30% and the standard deviation of ATP measurements is below 10%. No total numbers of cell analyses were performed in these sampling campaigns. The numbers of SRB were highest in KAS09 both in the standpipe and in the borehole section samples (10^5 cells mL^{-1}), these also showed the highest concentrations of sulphide, suggesting vivid bacterial sulphate reduction in KAS09. Also in KAS03 at 627 m depth, both in stand pipe and in the borehole section, the SRB numbers were high (10^3–10^4 cells mL^{-1}) compared to the numbers that are usually found in Fennoscandian Shield (1–10^3 cells mL^{-1}). The numbers of IRB were high and in several cases, they exceeded the range (> 1,600 cells mL^{-1}) of the MPN analysis. The ATP data from KLX06 showed that there was more ATP in the initial KLX06 groundwater samples at both pumping occasions, than after some time of pumping (Figure 5-28). In other words, the number of microorganisms in the samples was reduced during pumping.

The qPCR (quantitative real time polymerase chain reaction) of domain *Bacteria* agreed with the detected ATP values for sampling series 2 (Figure 5-27) This suggests that the majority of the living biomass in the groundwater was from the domain *Bacteria* and that organisms belonging to *Eukary*a and *Archaea* were absent, or present in low numbers (Appendix 8, Table 8-7). For sampling series 1, the qPCR values in most cases exceeded the ATP values, which might indicate an overestimate of the qPCR and/or an underestimate of the ATP values. The discrepancy in the qPCR values between the two sampling occasion with lower values for the second sampling campaign support that the qPCR overestimated the number of *Bacteria* in the first sampling campaign. The qPCR may needs more method development and adjustments to the specific conditions in groundwater samples.

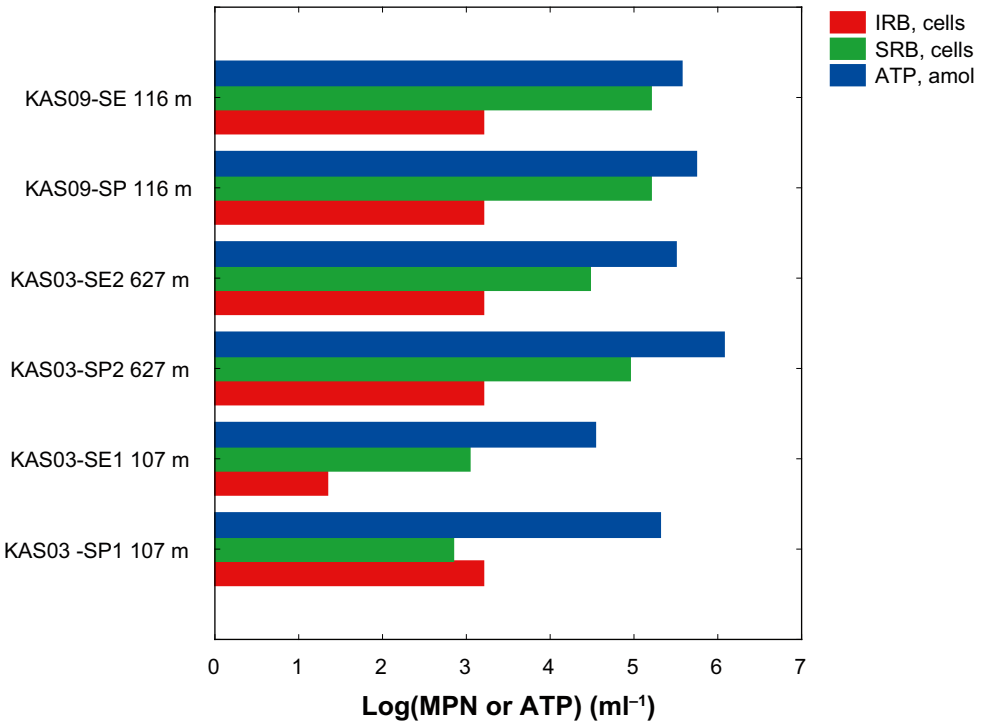

Figure 5-25. *MPN of IRB and SRB and amount of ATP in groundwater from two levels in borehole KAS03 and one level in KAS09. SE: section; SP: standpipe. The IRB was above the detection range of 1,600 cells mL^{-1} in KAS03-SP2 and both KAS09 samples.*

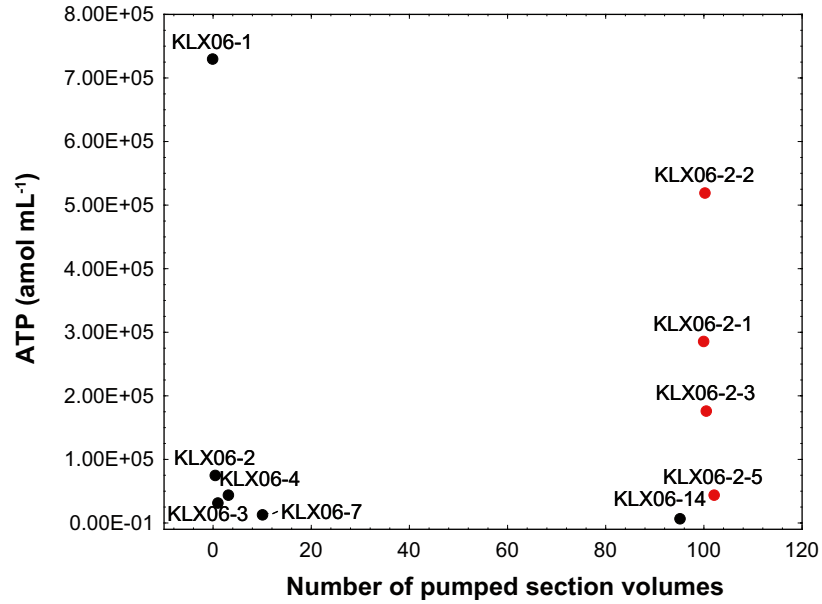

Figure 5-26. *ATP concentration versus the number of pumped section volumes from two sampling series in groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

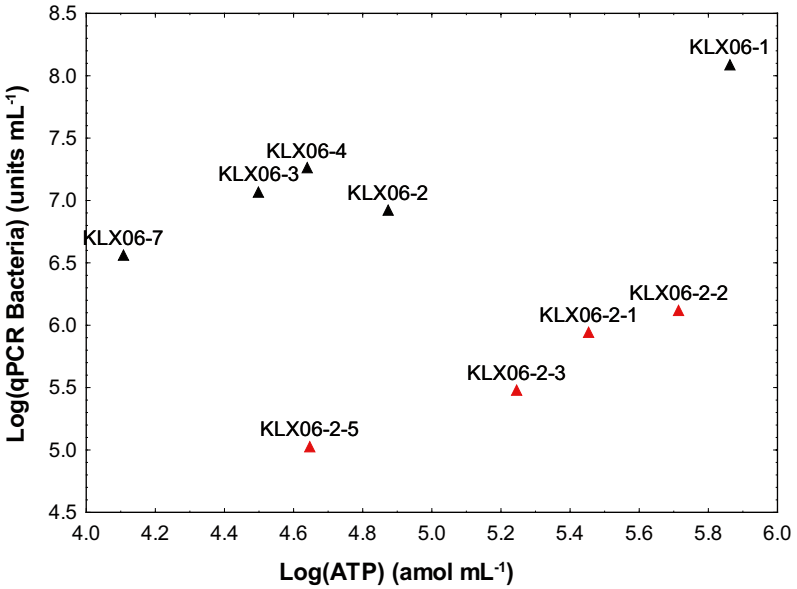

Figure 5-27. The amount of adenosine tri-phosphate (ATP) versus the amount of Bacteria analysed with qPCR as the number of 16S rRNA gene units (qPCR Bacteria) in groundwater from two sampling series in borehole KLX06 (black triangles first sampling series, red triangles second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.

5.7.2 Sulphate reducing bacteria (SRB)

The numbers of SRB were highest at start of pumping of KLX06 and decreased as pumping continued (Figure 5-28). There was a good agreement between MPN SRB and ATP in all samples (Figure 5-29, Figure 5-30). The qPCR and MPN of SRB generally agreed well in the KAS boreholes (Figure 5-31). However, the absolute numbers may differ because of differences between the used standard SRB (*Desulfovibrio aespoeensis*) and the SRB present in the samples. The qPCR for SRB did not work well in the KLX06 samples for unknown reasons. The qPCR for activity of SRB, qPCR *apsa*, showed good agreement between MPN numbers and activity in KAS09 (Figure 5-32). This result suggests that the SRB were active and produced sulphide in the sampled waters. There was no good correlation between SRB and sulphide (Figure 5-33), which was expected as a standing population of SRB will continue to produce sulphide as long as there is energy available for the reduction of sulphate.

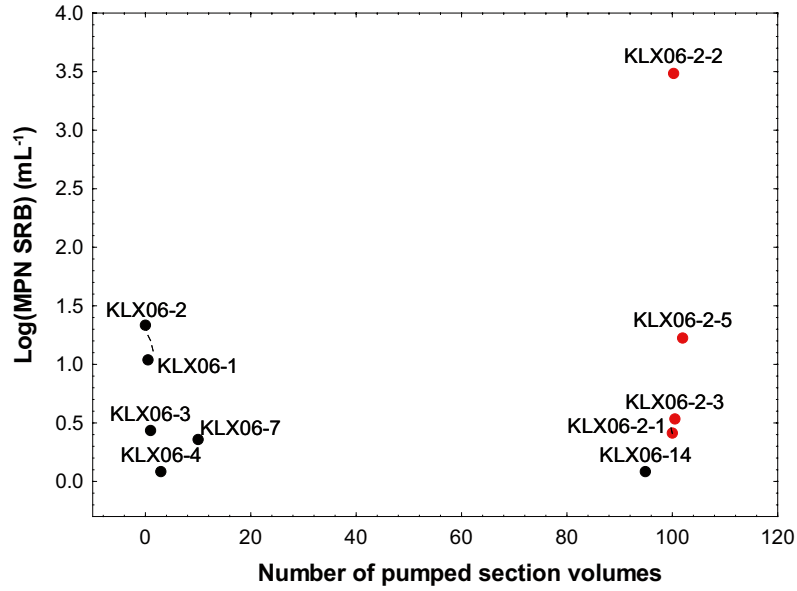

Figure 5-28. Log(MPN SRB) from two sampling series of groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.

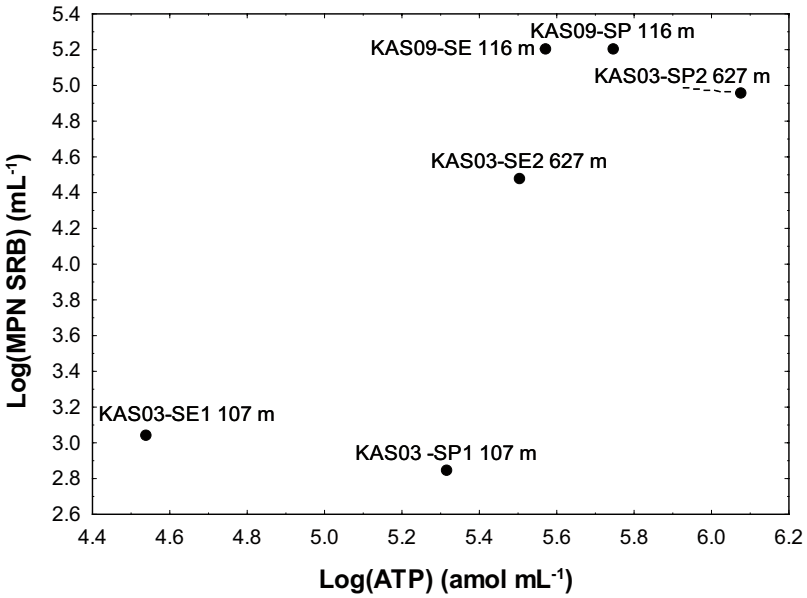

Figure 5-29. *Log(MPN SRB) versus Log(ATP) from two levels in borehole KAS03 and one level in KAS09.*

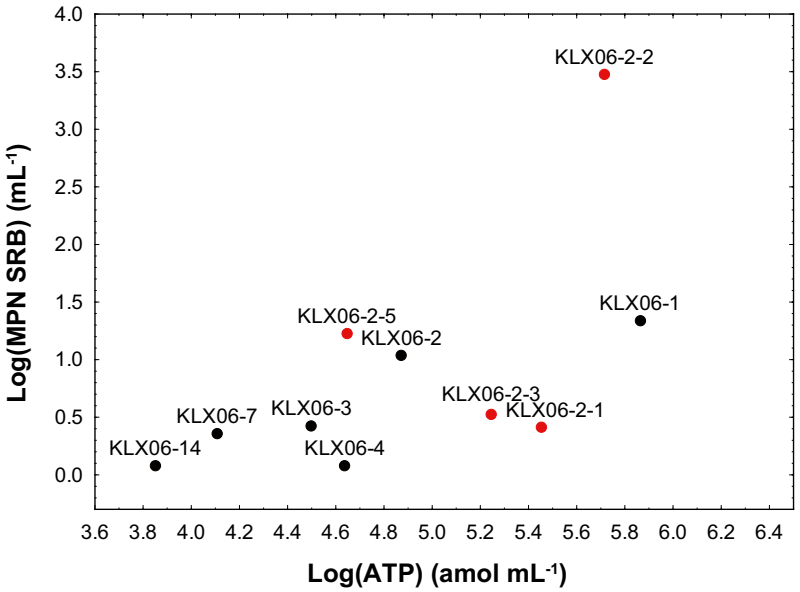

Figure 5-30. *Log(MPN SRB) versus Log(ATP) from two sampling series in groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

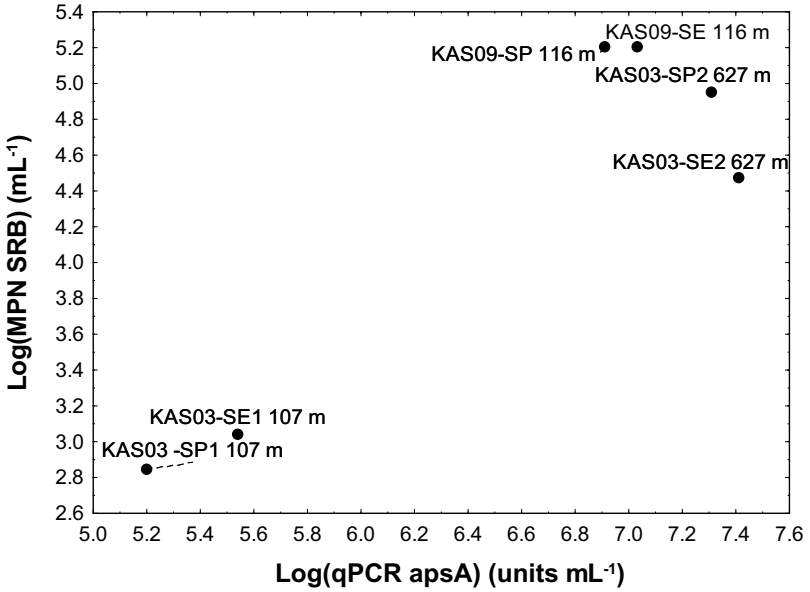

Figure 5-31. *The number of sulphate reducing bacteria determined with most probable number cultivation (MPN SRB) versus the amount of sulphate reducing bacteria analysed with qPCR as the number of apsA gene units (qPCR apsA) from two levels in borehole KAS03 and one level in KAS09. KAS09.*

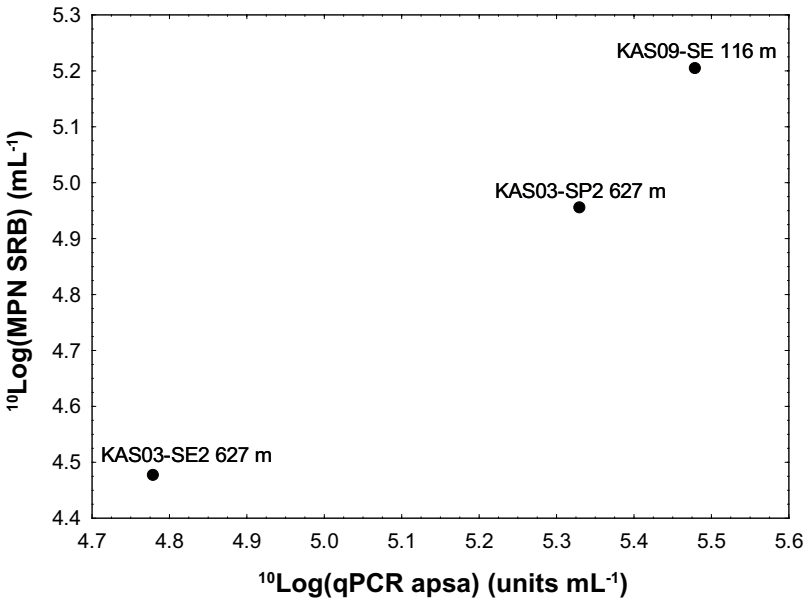

Figure 5-32. *The number of sulphate reducing bacteria determined with most probable number cultivation (MPN SRB) versus the expressed activity of sulphate reducing bacteria analysed with qPCR as the number of apsa mRNA units (qPCR apsa).*

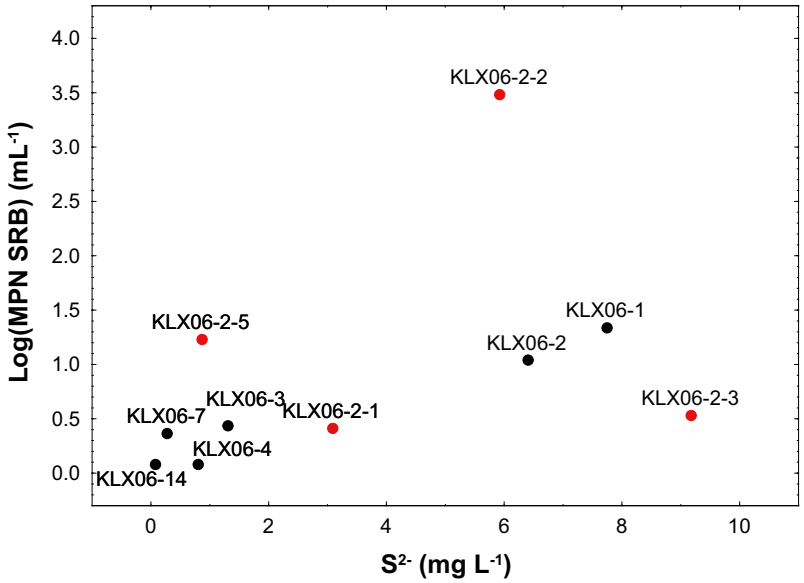

Figure 5-33. *Log (MPN SRB) versus the amount of S^{2-} in groundwater from two sampling series in borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

5.7.3 Iron reducing bacteria (IRB)

The numbers of IRB were high at the start of the pumping of KLX06, similar to what was observed for SRB. However, unlike SRB they did not decrease, except for after prolonged pumping time in KLX06-14 (Figure 5-34). There was a fairly good correlation between MPN IRB and ATP in most samples (Figure 5-35, Figure 5-36). The MPN of IRB and MPN of SRB generally disagreed in the KLX06 borehole (Figure 5-37). There was not a good correlation between IRB and ferrous iron (Figure 5-38), which was expected as a standing population of IRB will continue to produce ferrous iron as long as there is energy available for the reduction of ferric iron.

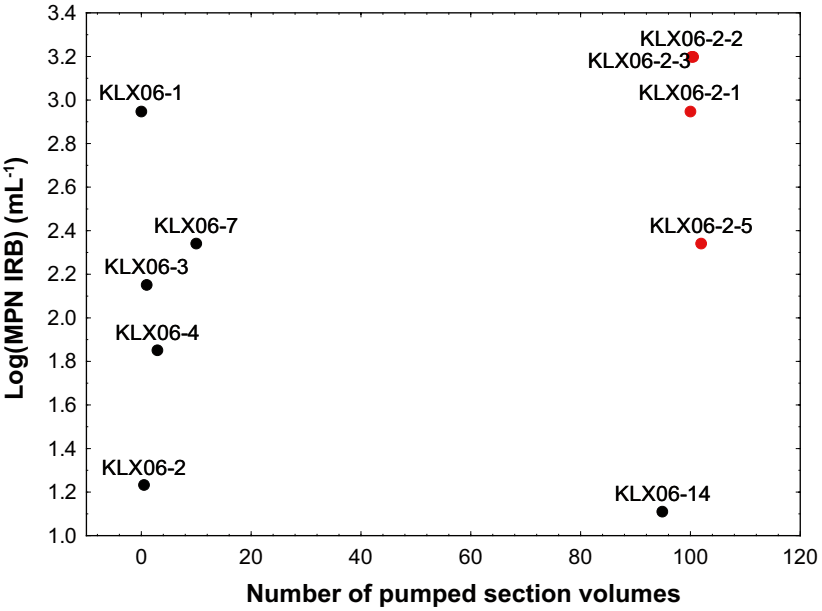

Figure 5-34. *Log(MPN IRB) from two sampling series of groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

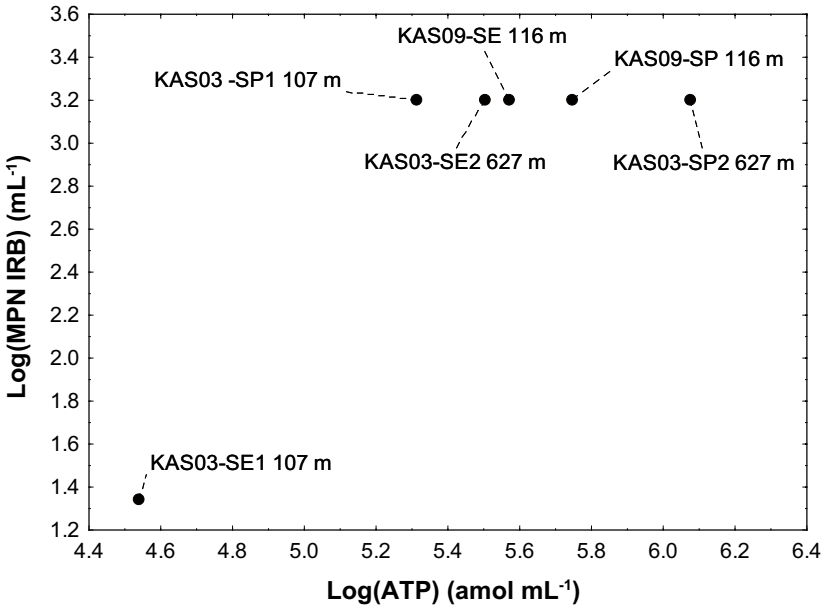

Figure 5-35. *Log(MPN IRB) versus Log(ATP) from two levels in borehole KAS03 and one level in KAS09.*

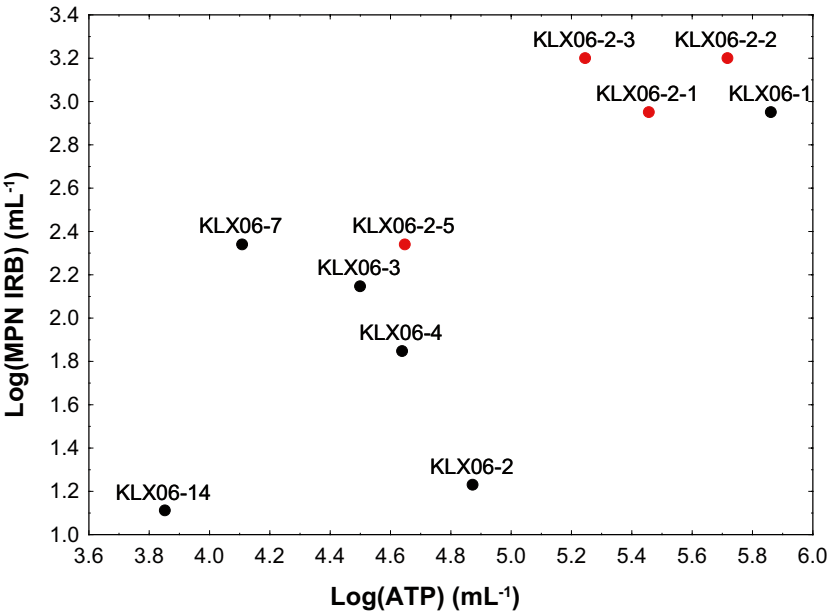

Figure 5-36. *Log(MPN IRB) versus Log(ATP) from two sampling series in groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

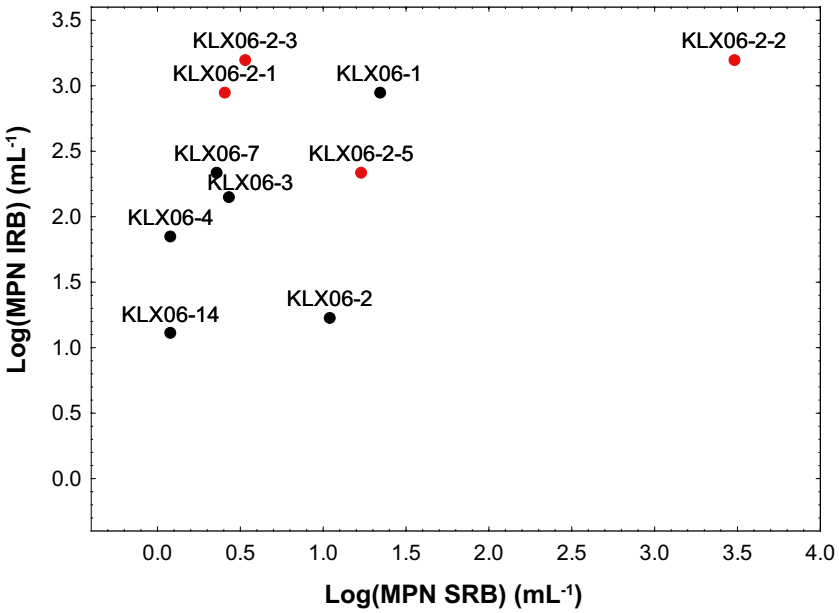

Figure 5-37. *Log(MPN IRB) versus Log(MPN SRB) from two sampling series in groundwater from borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

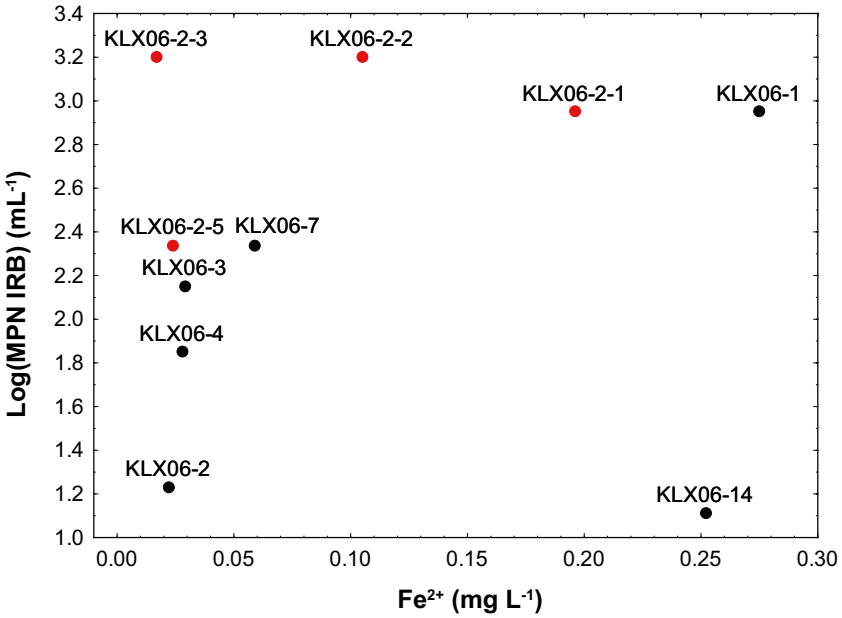

Figure 5-38. *Log (MPN IRB) versus amount of Fe^{2+} in groundwater from two sampling series in borehole KLX06 (black dots first sampling series, red dots second sampling series). KLX06-1 and KLX06-2-2 correspond to water from the standpipe and KLX06-2-1 to water in the tubing.*

5.8 Gaseous compounds

Released gaseous compounds were analysed in KAS09 (standpipe and section) and in KLX06 during the first pumping session (section). The samples collected in KLX06 were in addition to analysis of composition also sent for analysis of stable isotopes (see Section 5.8.3). The methods for sampling are described in detail in Appendix 7.

5.8.1 Released gaseous compounds in KAS09 and KLX06

There were large amounts of hydrogen in groundwater from the borehole section of KAS09, but not in the standpipe. Both the standpipe and the section water had significant amounts of methane and carbon dioxide. The KLX06 groundwater was different from the water sample collected in the isolated section in KAS09, and its gaseous contents was dominated by nitrogen with only traces of methane, carbon dioxide and hydrogen but with some significant amounts of helium instead. There was no clear trend in the composition of the gas samples over time in KLX06 (Figure 5-39). The gas samples collected consist primarily of released gaseous compounds from water from the fractures and less from the isolated section since they were sampled after discharge of between 4 and 145 section volumes.

5.8.2 Dissolved gaseous compounds in KLX06

Dissolved gases were analysed quantitatively in KLX06 during the second pumping period (Figure 5-40 to Figure 5-44). The gases methane, hydrogen and carbon dioxide decreased significantly in concentration during pumping, while nitrogen showed a tendency to increase, except for the first sample that showed a much higher concentration. This effect was also revealed by the composition of dissolved gases in KLX06 (Figure 5-45). While nitrogen and argon stayed approximately on the same proportion throughout the pumping, gases that influence microbial activity changed significantly. Hydrogen decreased 50 times from 1,080 ppm to 21.9 ppm. Methane decreased 10 times from 55,700 ppm to 5,580 ppm and carbon dioxide decreased 7.5 times from 5,640 ppm to 752 ppm. The result suggests that these gas species build up in concentration in the standpipe, in the tubing and in the isolated borehole section during periods when pumping is not performed.

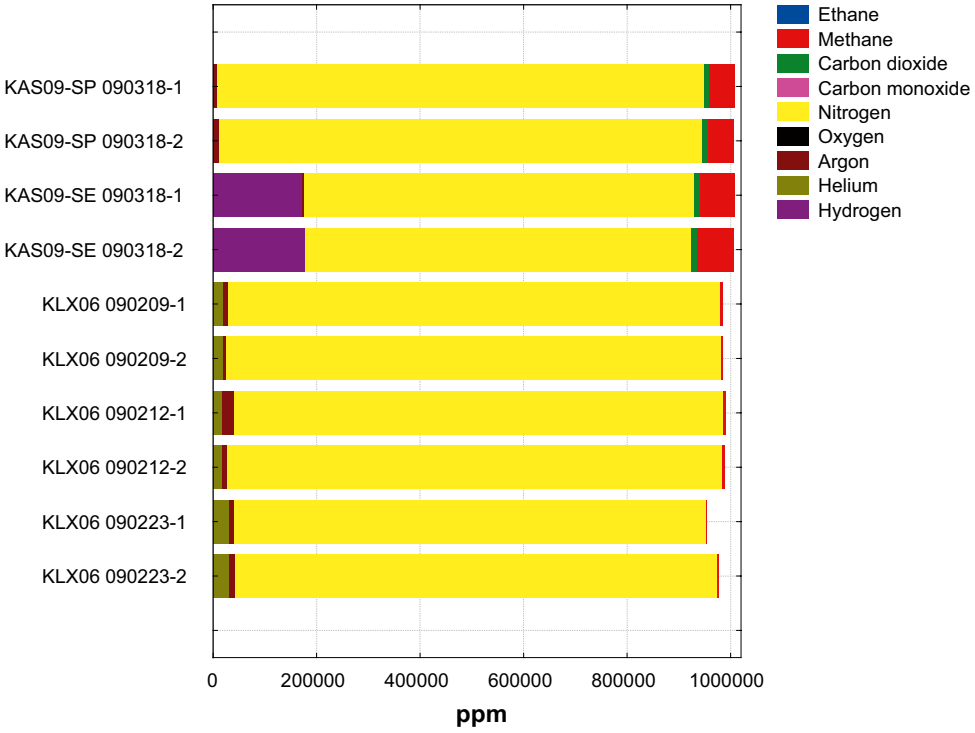

Figure 5-39. *The composition of extracted gas sent for isotopic analysis for KAS09 and KLX06. Two analyses were run on each isotope container. KAS09-SP represents sample from the standpipe and KAS098-SE from the section. For KLX06 samples were collected from section water as a time-series.*

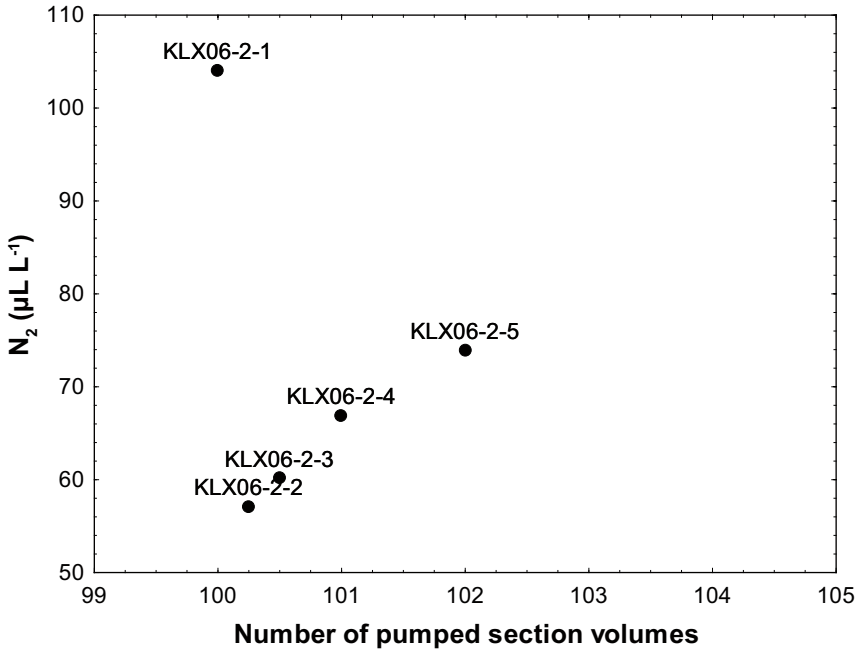

Figure 5-40. *Amount of N_2 in groundwater in borehole KLX06. KLX06-2-1 corresponds to water from the tubing.*

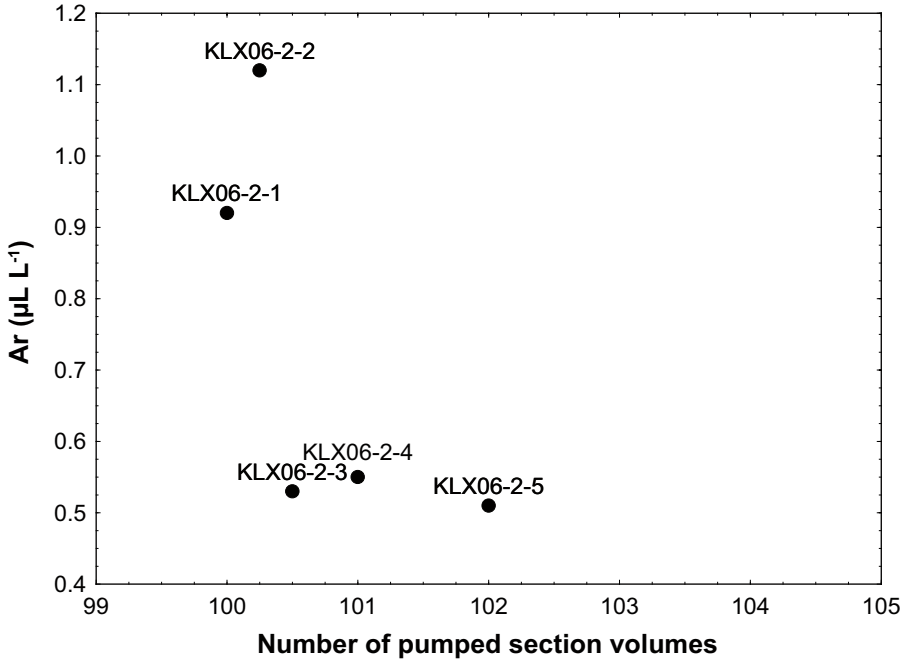

Figure 5-41. *Amount of Ar in groundwater in borehole KLX06. KLX06-2-1 corresponds to water from the tubing.*

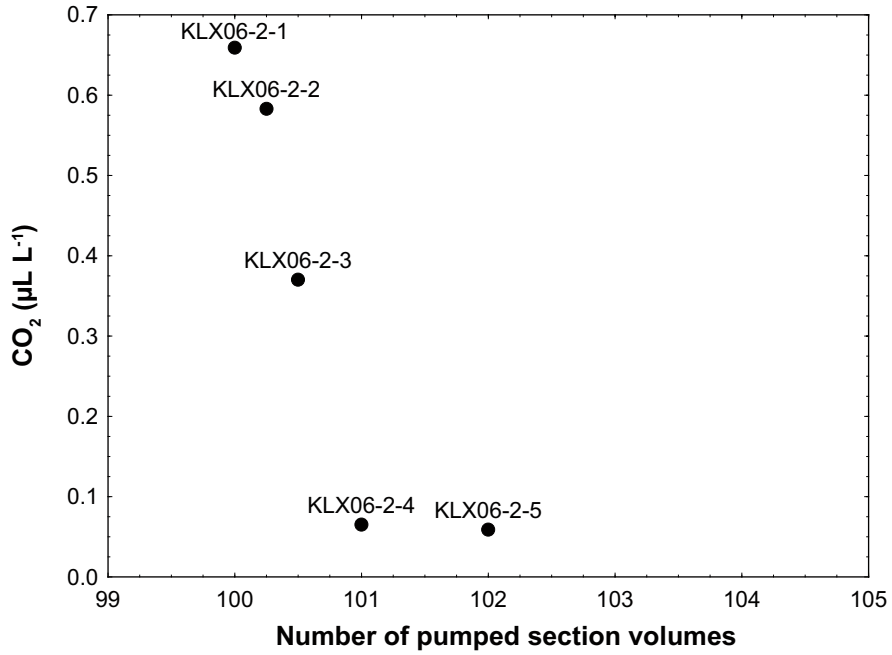

Figure 5-42. *Amount of CO_2 in groundwater from borehole KLX06. KLX06-2-1 corresponds to water from the tubing.*

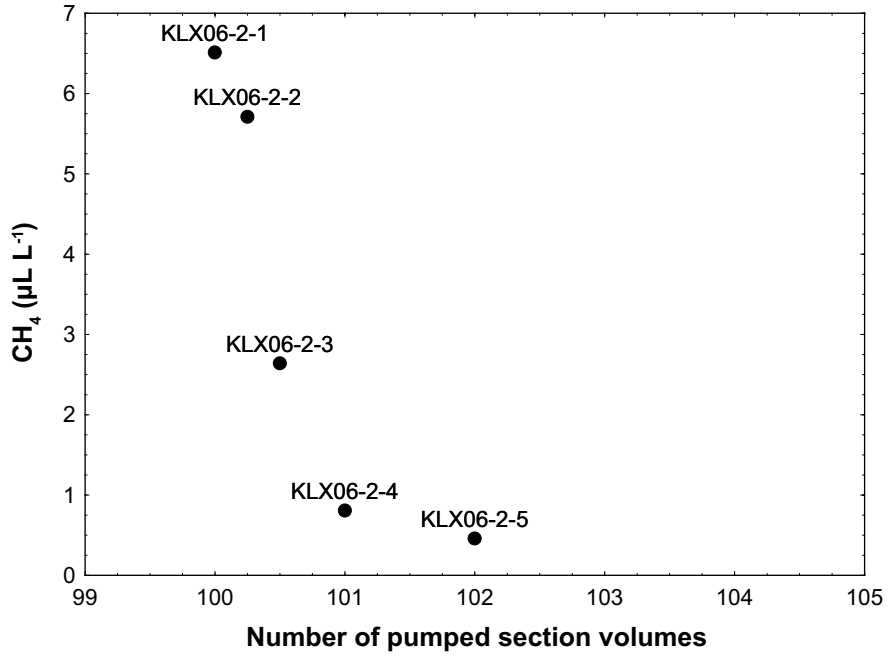

Figure 5-43. *Amount of CH_4 in groundwater from borehole KLX06. KLX06-2-1 corresponds to water from the tubing.*

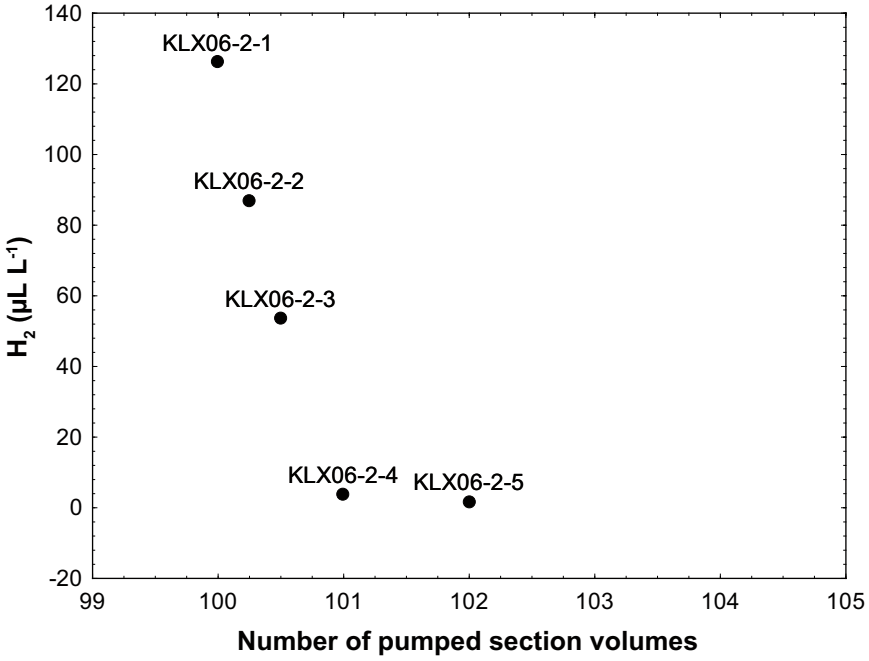

Figure 5-44. *Amount of H_2 in groundwater from borehole KLX06. KLX06-2-1 corresponds to water from the tubing.*

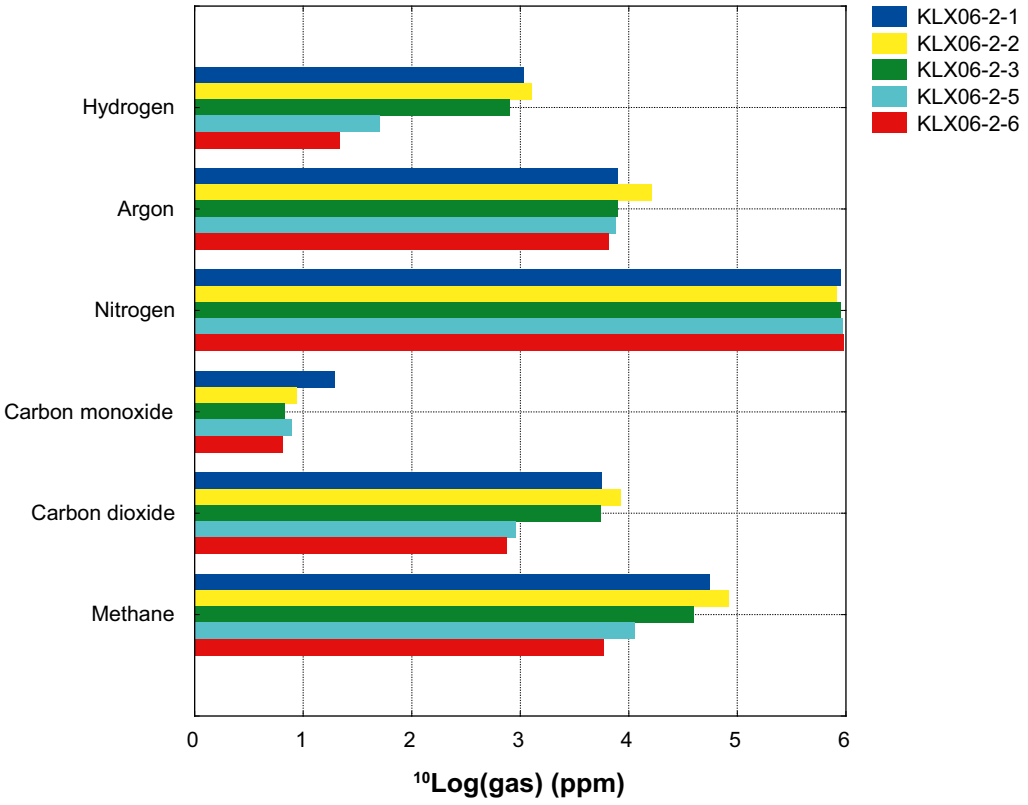

Figure 5-45. *The proportion of analysed gases in KLX06 during pumping. KLX06-2-1 corresponds to water from the tubing.*

5.8.3 Stable isotopes in CO_2 and CH_4

Three samples of released gas were collected in KLX06 at the depth of 554–570 m, and analysed for $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ in CO_2 and CH_4. The gas samples were collected after discharging of several section volumes, which means that the released gas mainly originated from the fractures and to a minor extent from the isolated borehole section water. $\delta^{13}C$ isotope data for CO_2 are listed in Table 5-4. The $\delta^{13}C$ isotopes in the CH_4 vary between −44.4 and −47.8 ‰ PDB. The $\delta^{13}C$ isotopes in the CO_2 of the gas samples show a narrow range between −14.5 and −14.9 ‰ PDB.

The fractionation of $\delta^{2}H$ is a useful tool and an indication of the methane source. The isotope signature observed in the $\delta^{2}H$ of the methane reflects the deviation from the initial substrate, if it has undergone methanogenesis. Moreover, the fractionation is a result of a kinetic effect and will therefore be indicative of its formation process. Figure 5-46 and Figure 5-47 show the results for $\delta^{2}H$ and $\delta^{13}C$ analysis of methane and carbon dioxide in KLX06.

Table 5-4. $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ isotope data obtained from analyses of dissolved CO_2 and CH_4 in KLX06.

$\delta^{13}C$ in CH_4 (‰ PDB)	$\delta^{13}C$ in CO_2 (‰ PDB)	$\delta^{2}H$ in CH_4 (‰ SMOW)	$\delta^{18}O$ in CO_2 (‰ SMOW)
−47.8	−14.9	−352	29.5
−47.6	−14.5	−351	32.1
−44.4	−14.8	−316	30.8

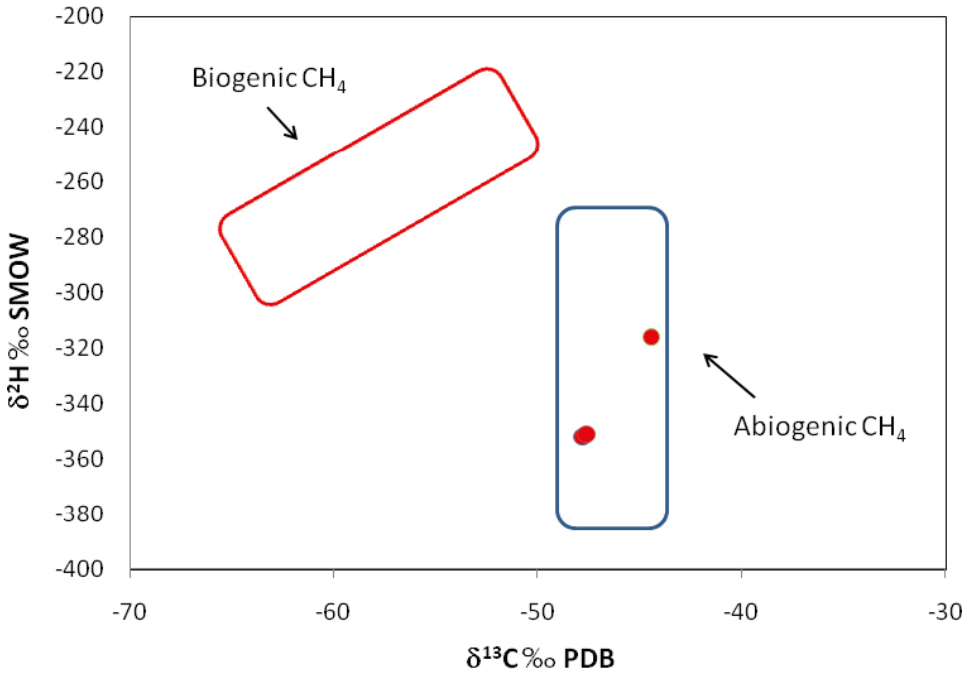

Figure 5-46. $\delta^{2}H$ versus $\delta^{13}C$ in methane collected in borehole KLX06. The red rectangle illustrates the field range of biogenic methane and the blue rectangle illustrates the field range of abiogenic methane.

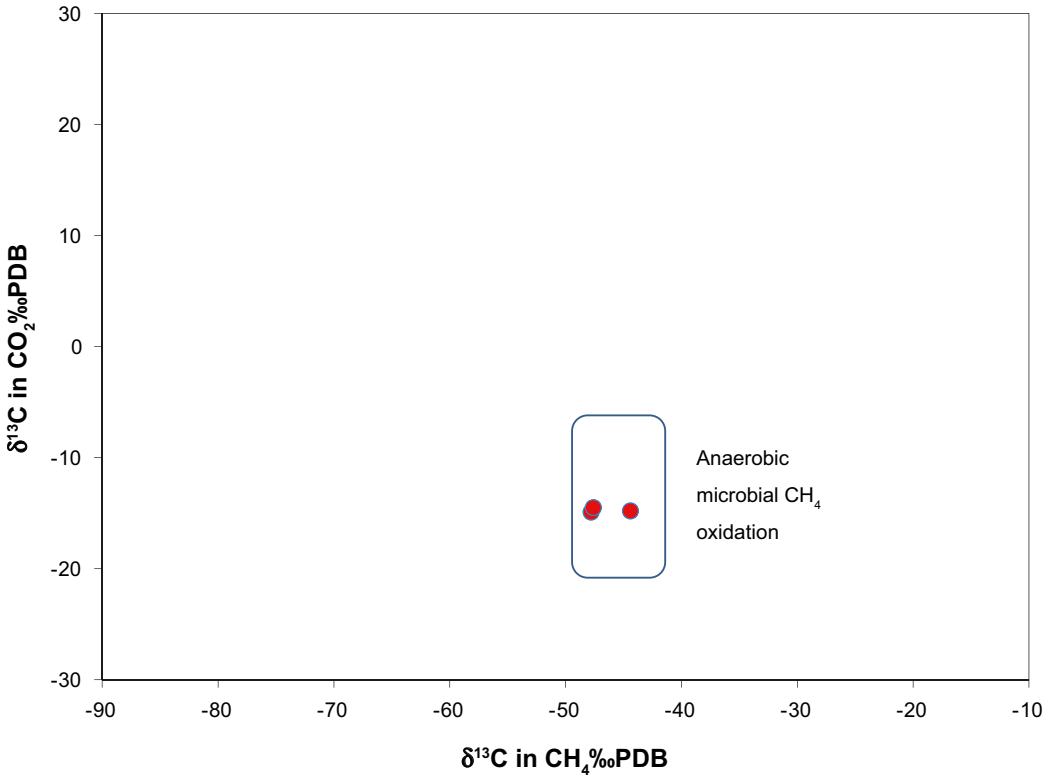

Figure 5-47. *$\delta^{13}C$ in carbon dioxide versus $\delta^{13}C$ in methane collected in borehole KLX06. The samples project in an area which signifies anaerobic microbial oxidation of CH_4.*

6 Discussion

6.1 Dissolved gaseous compounds

In this investigation the most important gas species are those that are biochemically active: oxygen, carbon dioxide, methane and hydrogen. Oxygen was not found in the investigated groundwater, and is, therefore not further discussed. The place of origin for each of these three gases is identified together with the main processes of formation in Section 2.5.3.

6.1.1 Composition of gases in KLX06, KAS03 and KAS09

The concentration of dissolved gases was analysed during pumping of the drill hole KLX06 (Figure 5-45). The proportion of the major gas compounds, argon and nitrogen, did not change during pumping contrary to the biochemically active gaseous compounds that all decreased in concentration. Hydrogen decreased 50 times after discharging about 150 section volumes while methane and carbon dioxide decreased 10 and 7.5 times, respectively. The reasons for this observation are, at present, unknown. The results suggest that the concentration of hydrogen, methane and carbon dioxide build up in the standpipe, tubing and in the isolated section water between pumping activities. Hydrogen can increase in concentration due to corrosion processes or as a result of transport from deep crustal (mantle) layers. Methane is produced via microbial reduction of carbon dioxide concomitant with oxidation of hydrogen. However, this is not a plausible cause to the found increase of methane in this study, because that scenario would imply that carbon dioxide and hydrogen should decrease in concentration concomitant with an increase in methane. This was not the case here, all three gaseous species increased during the period when no pumping was being performed. A possible hypothesis for this increase can be that gas compounds diffuse from the rock matrix into the pumped groundwater. However, this would imply very large concentrations of dissolved gases in the rock matrix, and in addition, this could not be confirmed by an observed increase in helium or radon. The concentrations of helium in the samples were below detection limit and radon was not included in the analysis. Hydrogen may increase more due to an additional source term, namely anaerobic corrosion of metals. The reason for a decrease of all these gas compounds during pumping has not been fully demonstrated. It can be speculated that the aquifer groundwater that replaces the pumped water in the standpipe, tubing and borehole section carries less of these gas species, reflecting the natural state of fracture groundwater and including ongoing processes such as precipitation and/or microbial consumption reactions. Further research is needed before the results depicted in Figure 5-45 can be fully explained.

Dissolved gases in KAS09 were only analysed qualitatively (Figure 5-39). There was a very large proportion of hydrogen in KAS09 standpipe and borehole section water constituting almost 20% of the dissolved gas. This is far more gas than can be explained by transport from crustal reactions, leaving anaerobic corrosion as the only possible explanation. Indeed, the equipment in this drill hole was severely corroded (see photograph in Appendix 5). The concentration of methane was rather high. The source is unknown, although it may be speculated that it is microbial methanogenesis. Methanogens were however not analysed in this project.

6.1.2 Stable isotopes in CO_2 and CH_4

Stable isotope data on the carbon in methane in KLX06 suggested an abiogenic origin (Figure 5-46). The relationship between $\delta^{13}C$ data observed in the CO_2 and methane suggests that an anaerobic methane oxidation may be taking place. This has been observed in Olkilouto, Finland /Pedersen et al. 2008/. The reaction pathway would then follow Equation 1-5 in Section 1.6.1 and represent an acetate fermentation or CO_2 reduction. The most diagnostic tool to identify the pathway is the estimate of the $\delta^{13}C$ fractionation between coexisting CH_4 and CO_2 as illustrated in Figure 5-47. A conclusion can therefore be made that the $\delta^{13}C$ isotope data in the CO_2 (around −14.5 ‰ PDB) suggest a methane oxidation as the most likely process.

Considering the indication of methane oxidation as mentioned above it is most likely that the methane collected in KLX06 reflects an abiogenic origin. Also, judging from the high $\delta^{13}C$ values in the methane in combination with the negative $\delta^{2}H$ values it is indicative of abiogenic methane. In the case it should have been biogenic, then during autotrophic methanogenesis the hydrogen concentration should change disproportional over time in comparison to methane. This is not the case in this study.

6.2 Carbon

The sources of DOC to the waters sampled in this study can be from leaching plastic material installed in the drill holes, or from biological autotrophic activity. Biological activity can be either photosynthetic or chemosynthetic. Photosynthetic carbon must entered groundwater environments from the surface, while chemosynthetic carbon can be produced from hydrogen and carbon dioxide.

The concentration of DOC ranged from a couple of mg L^{-1} up to 360 mg L^{-1} in KLX06. KAS03 had high DOC values as well (between 4 and 146 mg L^{-1}). About 10% of this carbon was acetate. The source of organic carbon appeared to be very scattered as judged from Figure 5-22. The progressive lowering in $\delta^{13}C$ of the HCO_3^- with time in addition to the dramatic decrease in the HCO_3^- concentration at the beginning of the pumping (Figure 5-24) clearly indicates that the bicarbonate, which is assumed to be produced in the sulphate reduction process, has at least two different carbon sources. It may also support a mixing of two different waters as discussed in Section 5.6.2.

Acetate may have been produced by homoacetogens from hydrogen and carbon dioxide but the evidence for this process is not clear because most of the Q-PCR analyses failed to detect homoacetogens. This may be due to their absence, or a problem with the selection of primers for this group of bacteria. In future studies, both Q-PCR and MPN analyses are recommended. Acetate may also be produced from degradation of organic material. Such organic material should then be either of photosynthetic or installation plastic origin. The fact that DOC rapidly decreased during pumping strongly suggests that the high DOC values were some kind of artifact generated by the drill hole, the installations in the drill hole, contamination during the sampling procedure, or all these effects combined. In any case, organic carbon is used by bacteria, including sulphate reducing bacteria, and may be one of the explaining reducing agents for some of the sulphate reduction that generated sulphide in the investigated systems.

6.3 Sulphide

6.3.1 Microbial sulphide production processes

The MPN analysis results showed the presence of SRB (Figure 5-25 and Figure 5-28) and IRB (Figure 5-25 and Figure 5-34) in all samples analysed for these metabolic groups. Q-PCR DNA data (Figure 5-31) confirmed the presence of SRB and Q-PCR RNA data (Figure 5-32) that they were active and produced sulphide. There are several processes that will lead to sulphide production to the groundwater as well as the removal of sulphate to solid phases. The microbial and inorganic processes involved in sulphur transformations can be summarized in the following conceptual model of the coupled reactions that lead to sulphide production and precipitation.

Microbial processes

AA: $H_2 + CO_2 \Rightarrow$ acetate (Eq. 6-1)

IRB: acetate + $Fe^{3+} \Rightarrow Fe^{2+} + CO_2$ (Eq. 6-2)

SRB: acetate + SO_4^{2-} (+ H_2) $\Rightarrow H_2S + CO_2$ (Eq. 6-3)

SRB: DOC + $SO_4^{2-} \Rightarrow H_2S + CO_2$ (Eq. 6-4)

AM + SRB: $CH_4 + SO_4^{2-} \Rightarrow H_2 + CO_2 + SO_4^{2-} \Rightarrow H_2S + CH_2O$ (Eq. 6-5)

(AA = Autotrophic acetogens, IRB = Iron reducing bacteria, SRB = Sulphate reducing bacteria, AM = Autotrophic methanogens)

Inorganic processes (pH > 6.5)

$H_2S + 2FeOOH \Rightarrow S^0 + 2Fe^{2+} + 4OH^-$ (Eq. 6-6)

$H_2S + Fe^{2+} \Rightarrow FeS + 2H^+$ (Eq. 6-7)

$3FeS + 3S^0 \Rightarrow Fe_3S_4 + 2S^0 \Rightarrow 3FeS_2$ (Eq. 6-8)

In the studied drill holes, the model suggests that autotrophic acetogens (AA) can produce acetate from hydrogen and carbon dioxide at a rate determined by the inflow of hydrogen and the production of hydrogen from corrosion processes (Equation 6-1). The acetate produced can be utilized by IRB as a source of carbon and energy; as a result, ferrous iron and carbon dioxide are formed from ferric iron minerals and acetate, respectively (Equation 6-2). Sulphate-reducing bacteria oxidize the acetate produced by AA to carbon dioxide, while sulphate is reduced to sulphide (Equation 6-3). Several genera of SRB can oxidize acetate, but *Desulfovibrio* species need hydrogen to be able to utilize acetate. If degradable organic carbon (i.e., DOC and TOC) is available, SRB will produce sulphide and carbon dioxide from this energy and carbon source (Equation 6-4). A special type of sulphate reduction is coupled to anaerobic methane oxidation (Equation 6-5). This reaction is common in many marine sedimentary environments /Boetius et al. 2000/, but has not yet been demonstrated in deep groundwater. If present, it may have an impact on any sulphide production model, if the amount of available methane is large. The above microbial reactions result in the production of sulphide, ferrous iron, acetate, and carbon dioxide, all of which were found in a large range of concentrations in the studied groundwater drill holes. Hydrogen sulphide produced via Equations 6-3 to 6-5 may reduce iron in minerals such as goethite, resulting in the formation of elemental sulphur and ferrous iron (Equation 6-6). Together with hydrogen sulphide, the ferrous iron produced via Equations 6-2 and 6-6 can form iron sulphide (Equation 6-7). This is a solid compound, and the dissolved sulphide that reacts with ferrous iron in Equation 6-7 will precipitate from the groundwater. Finally, pyrite may form (Equation 6-8) when oversaturation occurs. Equations 6-1 to 6-8 may explain the observations reported here. However, the situation in the KLX06, KAS03 and KAS09 was very complex and several combinations of energy sources, electron acceptors and electron donators may have been in play.

Merely knowing the concentrations of chemical markers provides insufficient information with which to judge whether or not a microbial process is taking place. The rationale behind, and regulation of rates of microbial processes are complicated. Above all, if the reactions listed above are occurring at similar rates, the result will be steady-state concentrations of dissolved ferrous iron and sulphide within a fairly narrow range of values. Inspecting the concentration profiles of ferrous iron versus sulphide in KLX06 (Figure 5-6) reveals a clear inverse relationship, with exception for data from the first samples in each pumping period. This relationship may be explained if it is assumed that reactions 6-1, 6-3 and 6-4 are dominating between pumping periods and those reactions 6-2, 6-6 and 6-7 come into play during pumping concomitant with a down regulation of the microbial sulphide producing processes. If these assumptions are correct, the proper way to investigate if sulphide production occurs in times with standing water is to follow the development of the analysed parameters in this report between periods of pumping. The advantage with such an approach would be that the electron donor for the sulphate reduction may be revealed. The main task will be to clarify which of the possible donors; hydrogen, methane, acetate, photosynthetic organic carbon or leaching carbon from installations supports the microbial sulphide producing process.

6.3.2 Sulphur isotopes

It is assumed that the sample series in KLX06 are not representing a fully closed system. This results in a typical difference in the $\delta^{34}S$ value of 20 ‰ between the dissolved sulphate and sulphide (Table 5-2). The progressive increase in the difference (Δ) of the $\delta^{34}S$ value observed between the sulphate and sulphide with time in the first series of KLX06 may be explained by preferential removal of the sulphide by Fe^{2+}. Such a process may explain the slight increase in $\delta^{34}S$ in the sulphide with time.

In the standpipe sample of KLX06, however, it is hard to explain the extremely positive $\delta^{34}S$ value of +24 ‰ by use of the corresponding $\delta^{34}S$ value for the dissolved sulphate of +13.8 ‰. Assuming an enrichment factor for the dissolved sulphate of about 20 ‰, the $\delta^{34}S$ value for the dissolved sulphate would be +44 ‰. It is therefore possible that the sulphur isotope analysis is not correct in the sulphide.

Sulphur isotope data ($\delta^{34}S$) from KAS03, Section 107–252 m, may reflect a result of a Rayleigh distillation considering the $\delta^{34}S$ data from the dissolved sulphate (+54 ‰) and sulphide (+17.5 ‰). The very low sulphate concentration of 6 mg L^{-1} is enough for developing an enrichment factor in $\delta^{34}S$ in the residual sulphate, and hence it supports such a possible scenario. Another example of a closed system may have been developed in the standpipe of KAS03, Section 627–1,002 m. The fractionation of $\delta^{34}S$ typically reflects a Rayleigh distillation with very high (positive) $\delta^{34}S$ values of the residual sulphate in the groundwater.

7 Summary

The results and conclusions from the investigations included in this activity can be summarised as follows;

- High concentrations of sulphide (5–90 mg L^{-1}) and sulphate reducing bacteria were found in the standpipes and section water in core drilled boreholes that had not been subjected to previous pumping.
- Discharging water from the borehole section in KLX06 resulted in decreasing concentrations of sulphide, bicarbonate, SRB and IRB, while chloride, sulphate, sodium and calcium, etc increased. After a 2 months interruption in pumping in KLX06, the sulphide concentration and microbial populations had increased to approximately the level as before pumping. The major anions such as chloride, sulphate, bicarbonate and the major cat ions had decreased.
- While pumping water from a delimited section, the water column in the section and water from the fracture(s) and to some extent water from the standpipe, are mixed. A plug-flow model was used to predict the time for the fracture water in KLX06 to completely substitute the section water during pumping. The predicted time coincide well with the observed decrease in the sulphide concentration. The plug-flow model takes into consideration the location, the hydraulic transmissivity of the water bearing fracture(s) and the pumping rate. In addition, the concentrations of sulphide, chloride, sodium and calcium were compared to a CSTR-model. The model assumes inflow of water with known composition from the fracture(s), complete mixing of section water and fracture water and an outflow of mixed water from the section. The observed concentrations are well described by the model. However, the model overestimates the volume of the delimited section, indicating non-complete mixing of section water and fracture water. This condition can be expected considering the low pumping rate (low degree of turbulence) and the location of the main water-bearing fracture to the middle of the section.
- A leakage in the coupling between the standpipe and tubing is a likely explanation for the observed decrease in chloride concentration (and other major anions and major cat ions) in KLX06 during periods when water is not discharged (pumped). Water from lower depths with lower salinity thus effects the chemical composition of the water column in the section. It cannot be ruled out that also the sulphide concentration is influenced, either directly or indirectly by addition of for instance an organic carbon source.
- Analyses of sulphide in water with high concentration of particles and organic matter resulted in high values for sulphide and oversaturation with respect to monosulphides (amorphous and crystalline). Most likely both dissolved and particulate sulphide were analysed in these samples. To avoid such an artefact the analysis of sulphide in such samples should be carried out by degassing of hydrogen sulphide after acidification.
- In KLX06 the water from the standpipe was found to be different in composition to the corresponding section water and to the fracture groundwater. The concentrations of chloride and other major anions and cat ions were lower in the standpipe and tubing. During the installation of packers and equipment, tubing and standpipe were filled with water of unknown composition that could.
- The standpipe is a possible source of contamination during water sampling using the hydrochemical monitoring equipment. A black “precipitate” (sulphides or oxihydroxides, organic material etc) was observed in the standpipes and this may influence the quality of the water samples during hydrochemical monitoring. In addition different water compositions in standpipe and section may create chemical gradients that can give rise to chemical and microbiological reactions (such as production of sulphide).
- The $\delta^{34}S$ values in dissolved sulphide and sulphate in KLX06 suggest that sulphate reduction takes place in a semi-open system with in-mixing of groundwater.
- The molecular data confirmed that the present SRB were active since one of the enzymes active in sulphate-reduction was extensively expressed.

- The concentration of dissolved organic carbon (DOC) in section water is low and constant during pumping. Acetate constitutes about 0 to 10% of the organic carbon.
- The isotope signatures of $\delta^{13}C$ and pmC in bicarbonate suggest that the hydrogen carbonate originate from more than one carbon source.
- The $\delta^{13}C$ signature in dissolved carbon dioxide from KLX06 suggests that it is produced from microbial anaerobic oxidation of methane.
- The isotope signatures of $\delta^{2}H$ and $\delta^{13}C$ in methane from KLX06 suggest that the methane is produced in abiogenic processes. This analysed methane originates primarily from the fractures and not from the isolated section.
- Dissolved gaseous compounds that influence microbial activity (methane, hydrogen and carbon dioxide) decreased in concentration during pumping in KLX06, i.e. these gas species build up in concentration in the standpipe and in the isolated borehole section during periods when pumping is not performed.
- The qualitative released gas analysis from KAS09 revealed a high relative proportion of hydrogen.

The main conclusion of this project is therefore that when a borehole section is not being pumped some yet unidentified processes drastically change the chemical composition in the standpipe, tubing and isolated borehole section. The main chemical components, such as chloride, sodium and calcium etc must be affected by some non-microbial process. Other components change due to microbial activity: sulphide, carbon dioxide, etc. Finally some other components are apparently affected both by microbial and non-microbial processes, for example organic carbon, methane, perhaps bicarbonate, etc. When the borehole section is pumped, groundwater from the surrounding fractures replaces the water in the borehole section. Plug-flow simulations show that this may be a slow process depending on the location of water-bearing fractures in the isolated borehole section.

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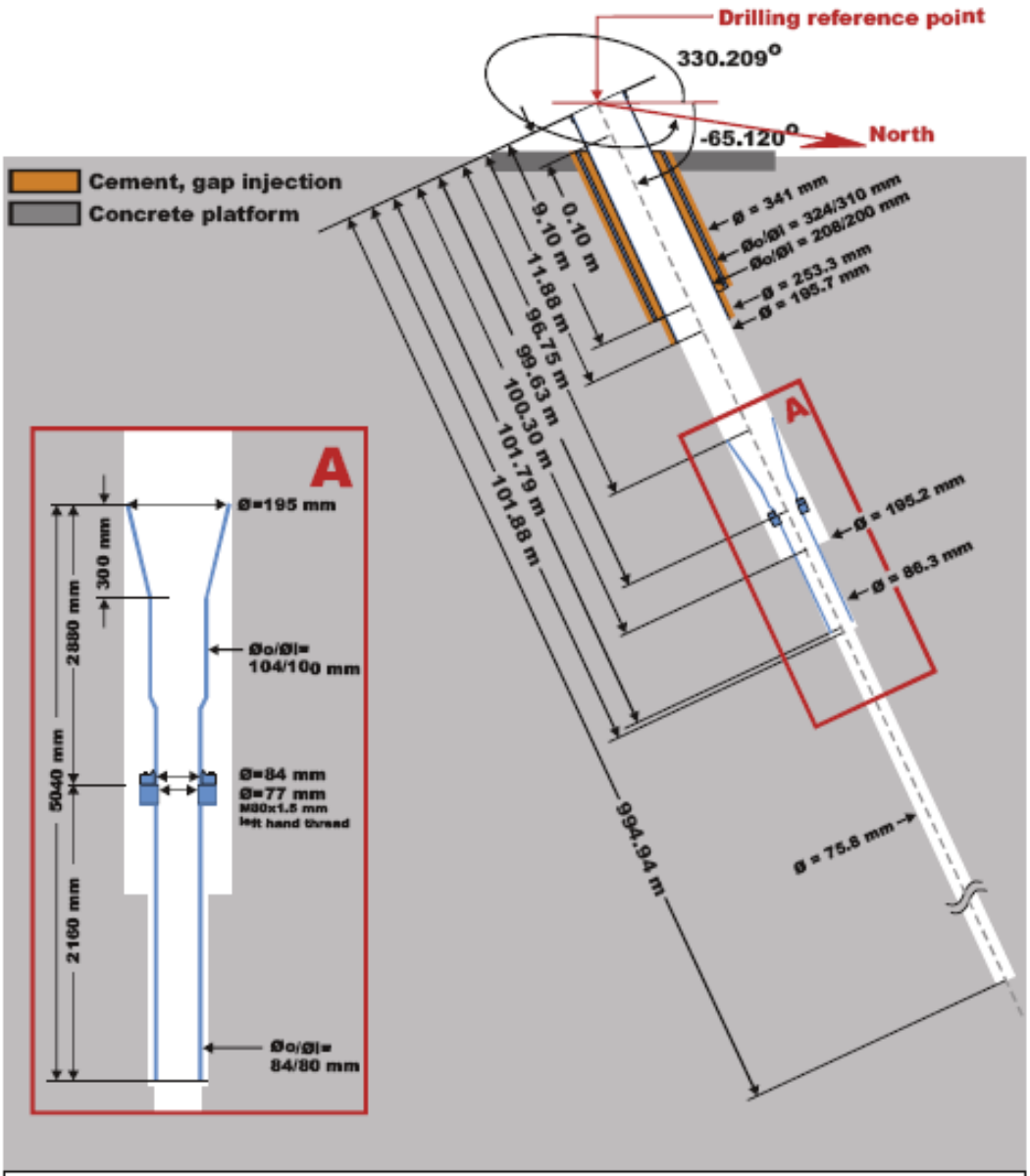
Design of cored borehole KLX06

Technical data

Borehole KLX06



Drilling reference point

Northing: 6367806.64 (m), RT90 2,5 gon V
Easting: 1548566.88 (m), RT90 2,5 gon V
Elevation: 17.68 (m), RHB 70

Drilling period

Drilling start date: 2004-08-03
Drilling stop date: 2004-11-25

Appendix 2

Flow measurements in KLX06

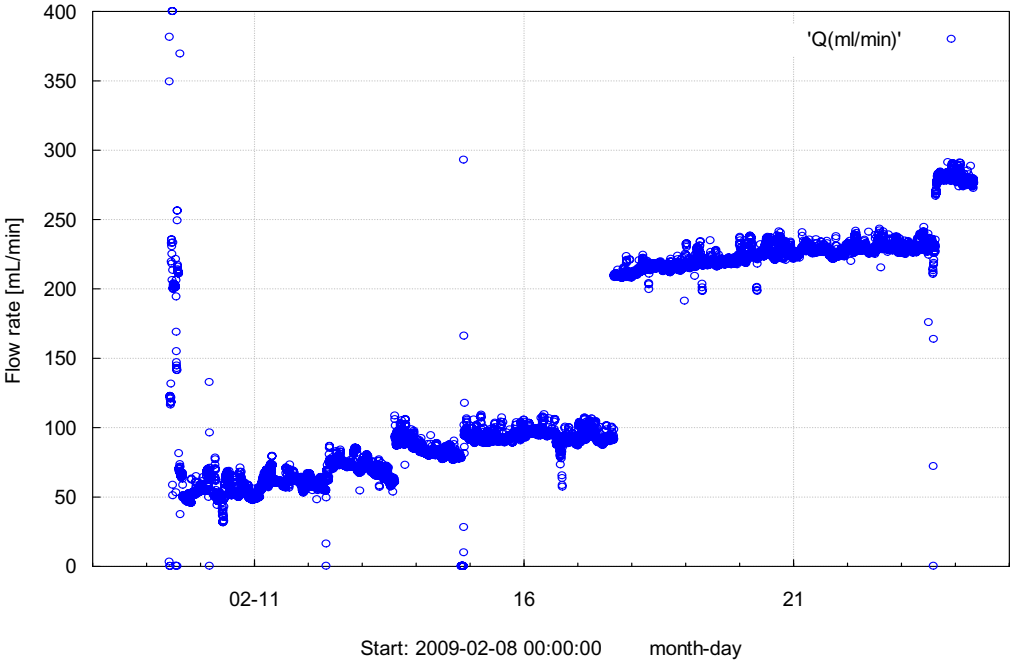


Figure A2-1. *Pumping flow rate (Q) in KLX06, 2009-02-09 – 2009-02-24.*

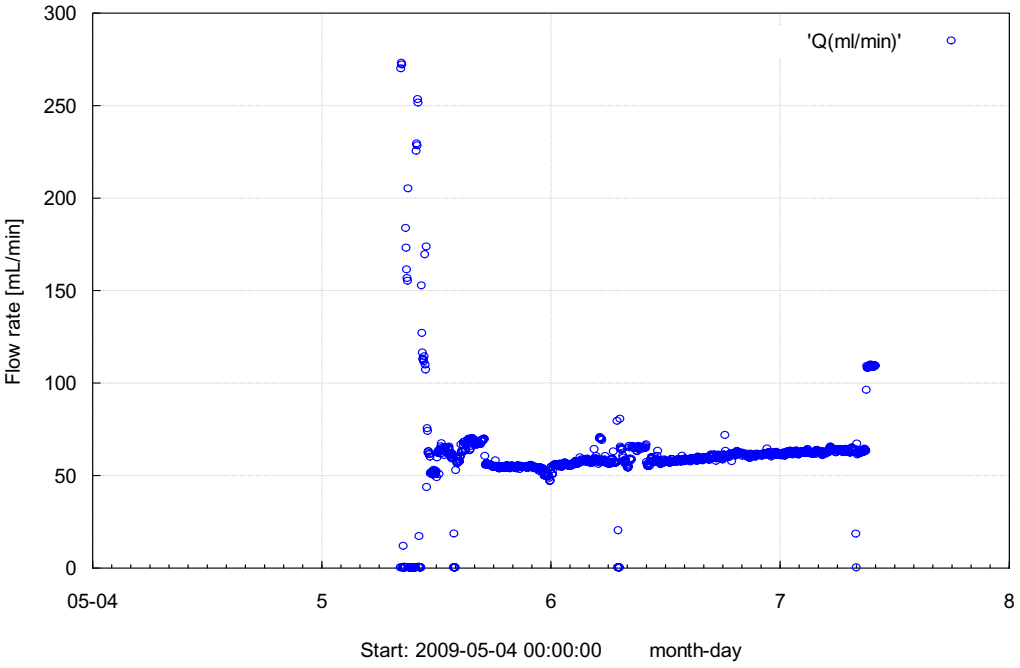


Figure A2-2. *Pumping flow rate (Q) in KLX06, 2009-05-05 – 2009-05-07.*

Appendix 3

Pressure registrations during measurements and sampling, HMS system

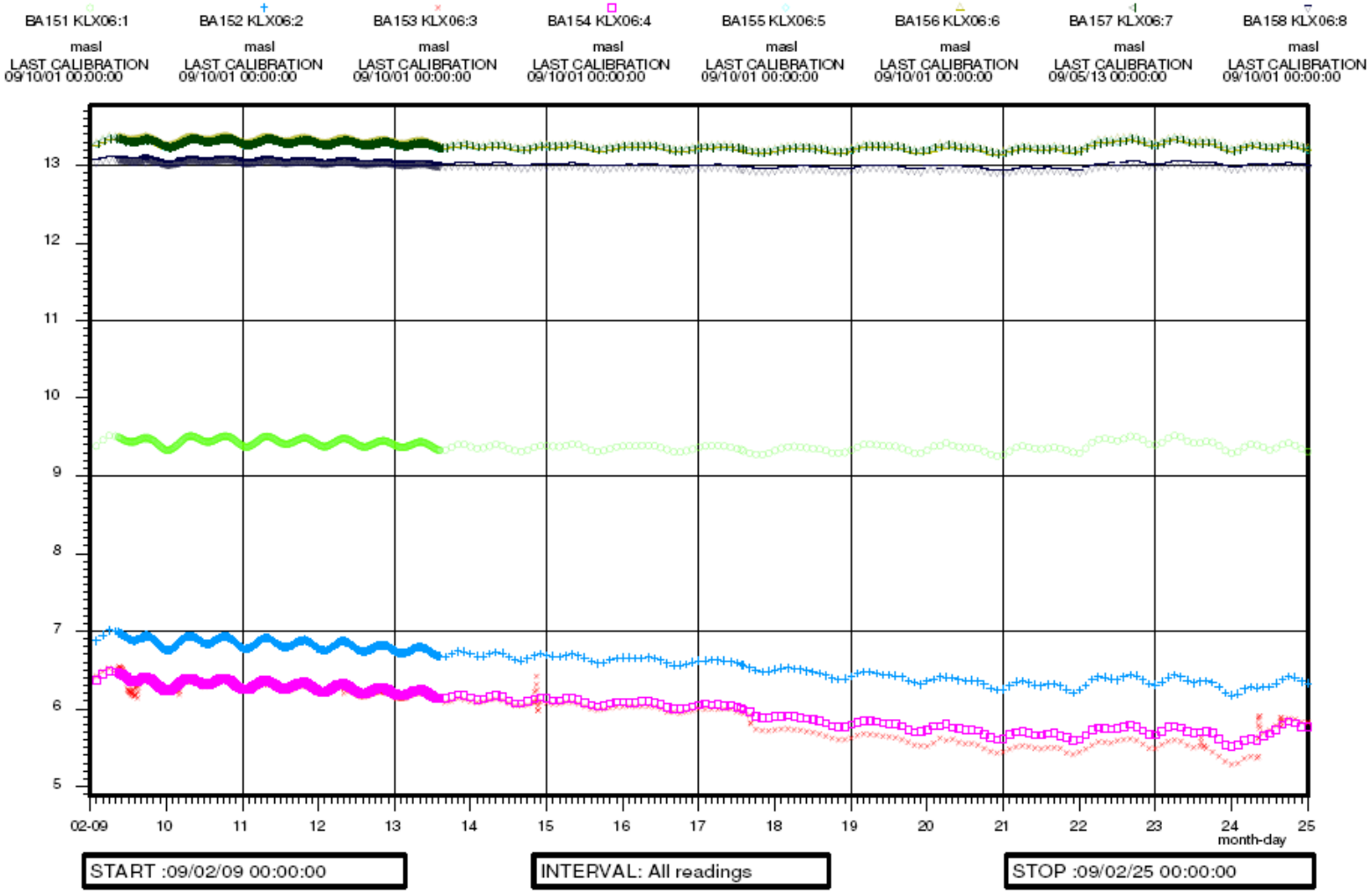


Figure A3-1. *Pressure registration (masl= meter above sea level) in KLX06 during pumping and sampling in February 2009. The figure shows the pressure registration in all eight sections in KLX06. Pumping was performed in section 3 (554.0–570.0 m, red cross) from February 9th to February 24th 2009. No responses were observed in any of the other sections.*

Appendix 4

Chemmac measurements in KLX06, section 554.0–570.0 m

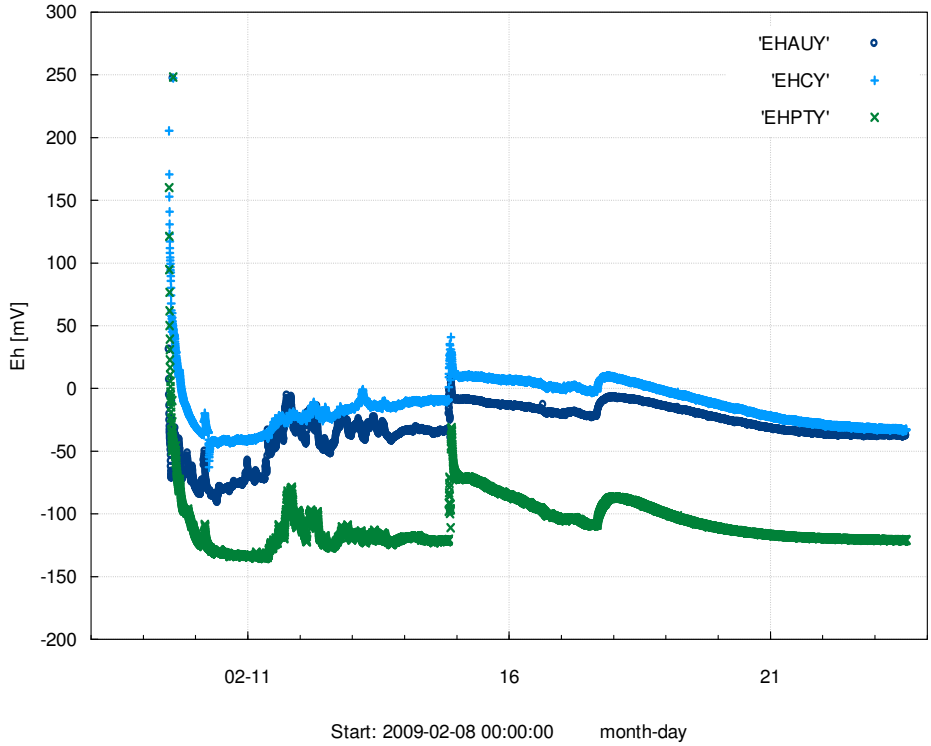


Figure A4-1. *Redox potential measurements (Eh) by gold, glassy carbon and platinum electrodes (EHAUY, EHCY and EHPTY). The recorded redox potentials are influenced by intrusion of oxygen through the tubing.*

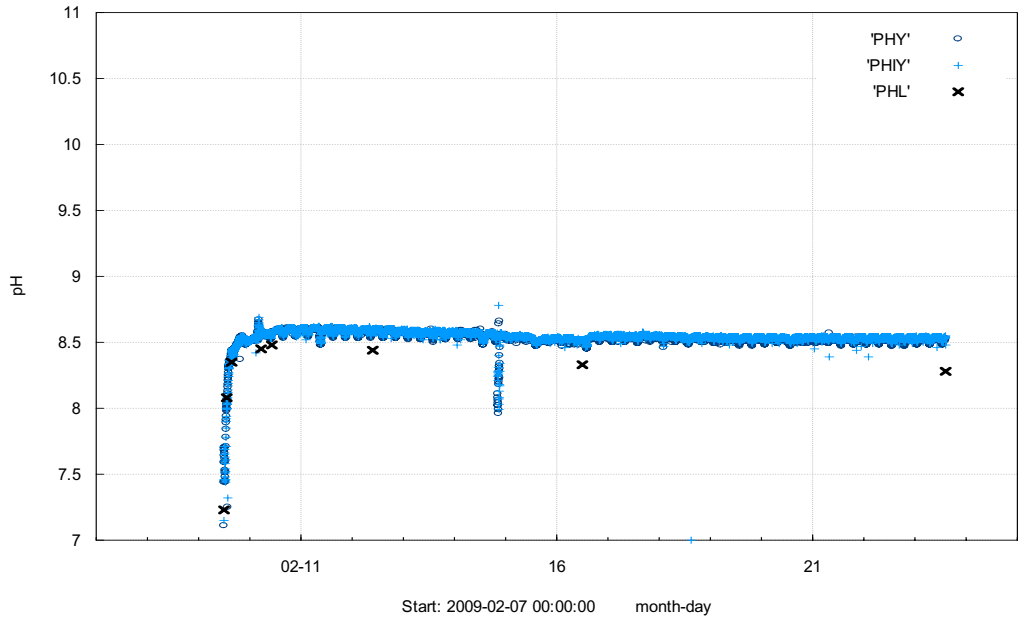


Figure A4-2. *Measurements of pH by two glass electrodes at the ground surface (PHY and PHIY). The laboratory pH in each collected sample (PHL) is given for comparison. The obtained pH values show good agreement with pH measured at the laboratory.*

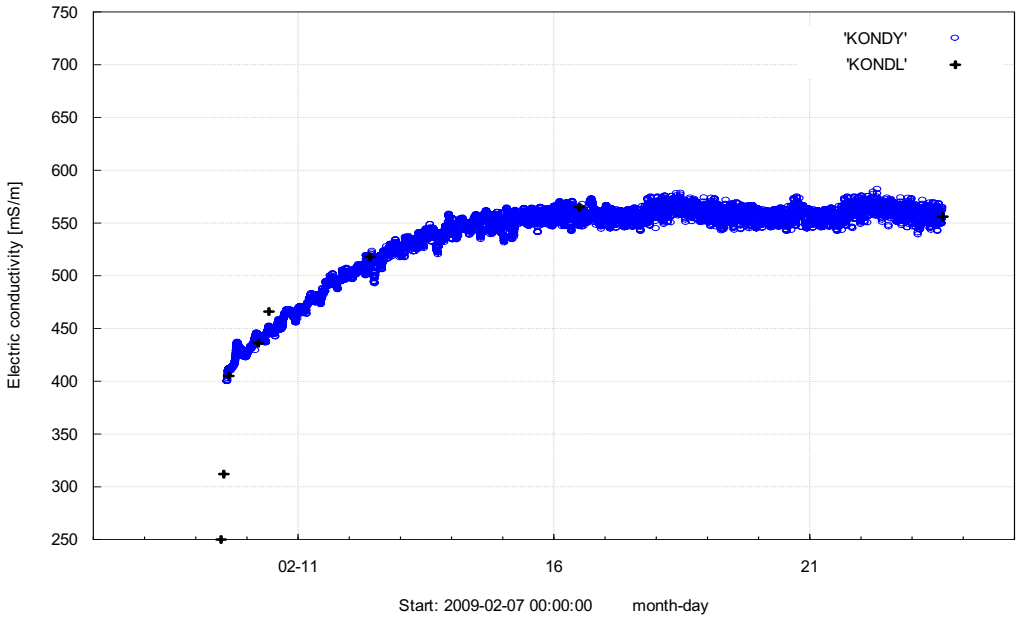


Figure A4-3. *Electric conductivity measurements in the surface Chemmac cell (KONDY). The laboratory conductivity in each collected sample (KONDL) is given for comparison.*

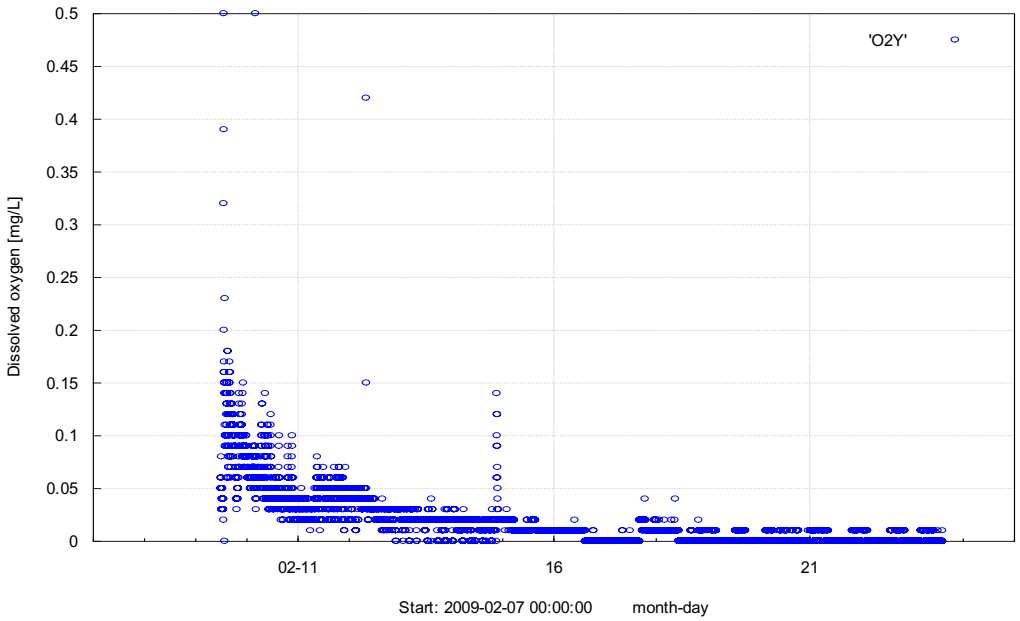


Figure A4-4. *Dissolved oxygen measurements (O2Y) in the surface measurement cell.*

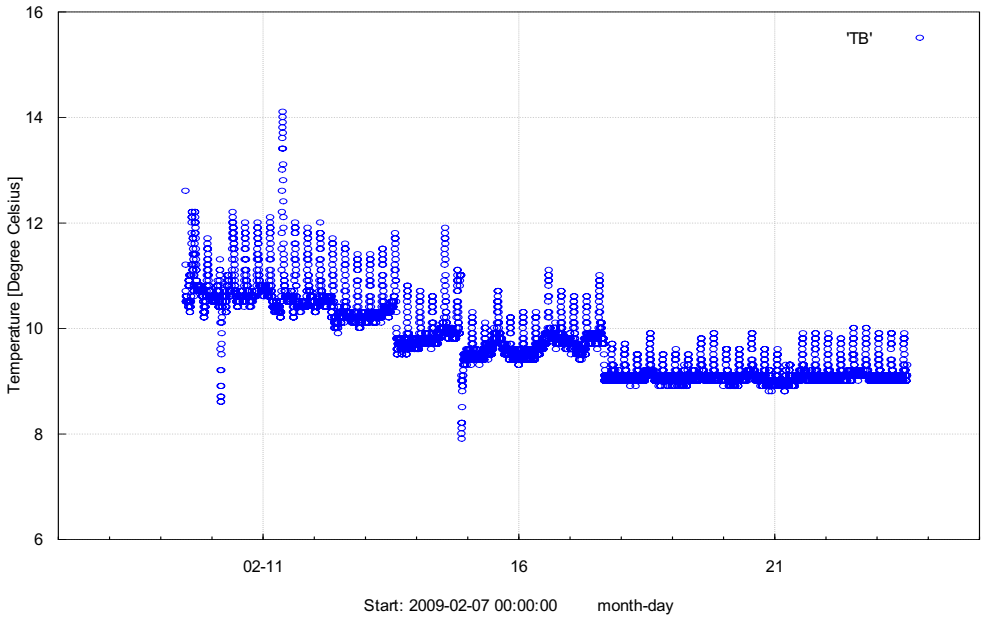


Figure A4-5. *Temperature of the groundwater in the borehole section (TB).*

Appendix 5

Photographs from the field investigations

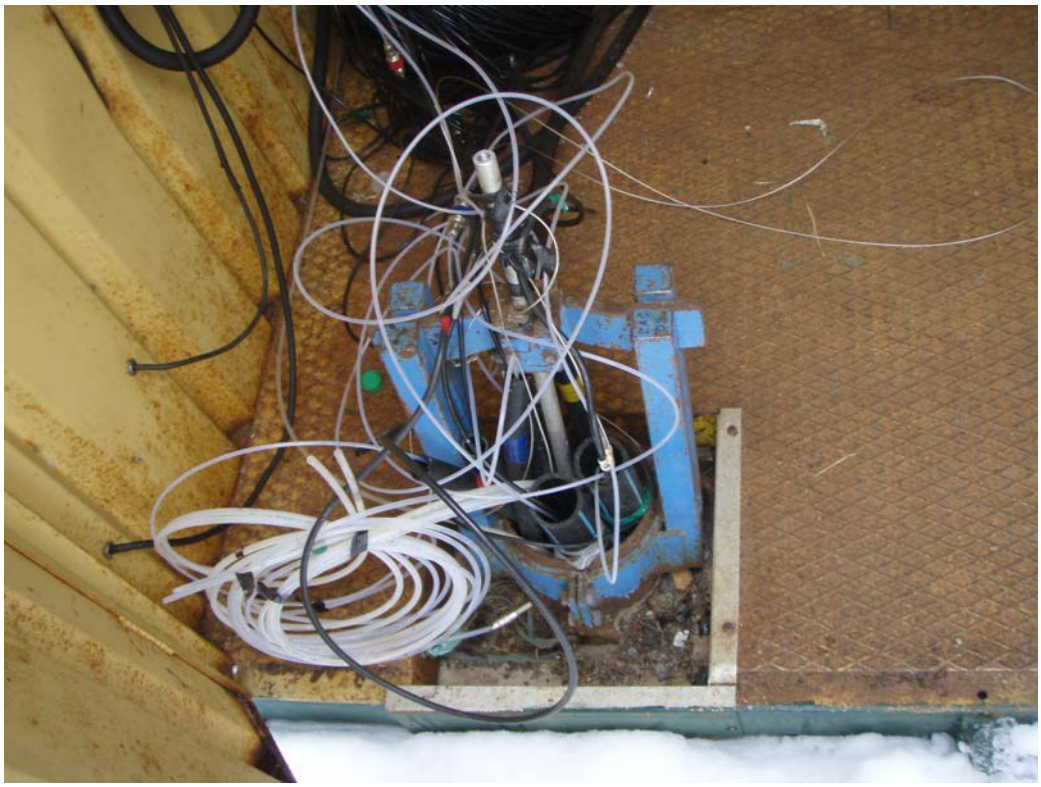


Figure A5-1. *Tubing for pressure measurements and top of standpipes in KAS03.*

Figure A5-2. *Standpipes in KAS03 with black precipitate. A strong smell of hydrogen sulphide gas.*

Figure A5-3. *Bottom of standpipe (stainless steel) in KAS03. Tubing for pressure measurements and water sampling hold together by black tape (PVC).*

Figure A5-4. *Connection pipe in KAS03, at 44 m b sl.*

Figure A5-5. *Corroded connection pipe in KAS09.*

Appendix 6

Sampling and analytical methods – water chemistry

Table A6-1. Sample handling routines and analytical methods.

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation	Analysis method	Analysis within - or delivery time to lab.
Anions 1.	HCO_3 pH (lab) cond (lab)	Plastic	250	Yes (not in the field)	No	Titration Pot. meas, Cond. meas	The same day – maximum 24 hours
Anions 2	Cl, SO_4, Br^-, F^-, I^-	Plastic	100	Yes (not in the field)	No	Titration (Cl^-) IC (Cl^-, SO4, Br^-, F^-) ISE (F^-)	Not critical (month)
	Br, I	Plastic	100	Yes (not in the field)	No	ICP MS	Not critical (month)
Cations, Si and S	Na, K, Ca, Mg, S(tot), Si(tot), Li, Sr	Plastic (acid washed bottles)	100	Yes (not in the field)	Yes (not in the field, 1 mL HNO_3)	ICP-AES ICP-MS	Not critical (month)
Cations, Si and S	Na, K, Ca, Mg, S(tot), Si(tot), Fe, Mn, Li, Sr	Plastic (Acid washed)	100	Yes (immediately in the field)	Yes (1mL HNO_3)	ICP-AES ICP-MS	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic (Acid washed)	500	Yes	Yes (5 mL HCl))	Spectrophotometry Ferrozine method	As soon as possible the same day
Hydrogen sulphide	HS-	Glass (Winkler)	About 120×2	Yes	1 mL 1 M NaOH+ 1 mL 1M ZnAc	Spectrophotometry	Immediately or if conserved, a few days
Environmental metals	Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn	Plastic (Acid washed)	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	Not critical (month)
Lantanoids, U, Th and so on.	Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th	Plastic (Acid washed)	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	Not critical (month)
Dissolved organic Carbon	DOC	Plastic	100	Yes	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Short transportation time

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation	Analysis method	Analysis within - or delivery time to lab.
Total organic Carbon	TOC	Plastic	100	No	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Short transportation time
Environmental isotopes	^{2}H, ^{18}O	Plastic	100	No	- -	MS	Not critical (month)
Tritium	^{3}H (enhanced.)	Plastic (dry bottle)	500	No	- -	LSC	Not critical (month)
Carbon isotopes	^{13}C, ^{14}C	Glass (brown)	100×2	No	-	(A)MS	A few days
Sulphur isotopes	^{34}S	Plastic	500 –1000	Yes	-	Combustion, MS	No limit
Phtalates	12 phtalates	Glass	1000 mL	No	-	GC-MS	Short transportation time
Low molecular organic acids (fractionation and identification)	LMW organic acids	Plastic	500 mL+ 500 mL distilled water (blank)	No	-	LC-MS	Short transportation time
Archive samples with acid	-	Plastic (washed in acid)	100×2	Yes	Yes (1 mL HNO_3)	-	Storage in freeze container
Archive samples without acid	-	Plastic	250×2	Yes	No	-	Storage in freeze container
Nutrient salt	NO_2, NO_3, NO_2+NO_3, NH_4, PO_4	Sample tubes, plastic	25×2	Yes (in the field)	No, frozen immediately	Spectrophotometry	Short transportation time

Abbreviations and definitions:

ISE	Ion selective electrode
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MS	Mass Spectrometry
TIMS	Thermal Ionization Mass Spectrometer
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
GC	Gas Chromatography

Table A6-2. Reporting limits and measurement uncertainties, updated 2008.

Component	Method[1]	Reporting limits (RL), detection limits (DL) or range[2]	Unit	Measurement uncertainty[3]
pH	Potentiometric	3-10	pH unit	±0.1
EC	Electrical Conductivity meas.	1-150 150-10,000	mS/m	5% 3%
HCO_3	Alkalinity titration	1	mg/L	4%
Cl^- Cl^-	Mohr- titration IC	≥ 70 0.5 – 70	mg/L	5% 8%
SO_4	IC	0.5	mg/L	12%
Br^-	IC	DL 0.2, RL 0.5	mg/L	15%
Br	ICP SFMS	0.001, 0.004, 0.010[4]	mg/L	25%[5]
F^- F^-	IC Potentiometric	DL 0.2, RL 0.5 DL 0.1, RL 0.2	mg/L	13% 12%
I^-	ICP SFMS	0.001, 0.004, 0.010[4]	mg/L	25%[5]
Na	ICP AES	0.1	mg/L	13%
K	ICP AES	0.4	mg/L	12%
Ca	ICP AES	0.1	mg/L	12%
Mg	ICP AES	0.09	mg/L	12%
S(tot)	ICP AES	0.16	mg/L	12%
Si(tot)	ICP AES	0.03	mg/L	14%
Sr	ICP AES	0.002	mg/L	12%
Li	ICP AES	0.004	mg/L	12.2%
Fe	ICP AES	0.02	mg/L	13.3%[6]
Fe	ICP SFMS	0.0004, 0.002, 0.004[4]	mg/L	20%[6]
Mn	ICP AES	0.003	mg/L	12.1%[5]
Mn	ICP SFMS	0.00003, 0.00004, 0.0001[4]	mg/L	53%[6]
Fe(II), Fe(tot)	Spectrophotometry	DL 0.006, RL 0.02	mg/L	0.005 (0.02-0.05 mg/L) 9% (0.05-1 mg/L) 7% (1-3 mg/L)
HS^-	Spectrophotometry, SKB	SKB DL 0.006, RL 0.02	mg/L	25% (0.019-0.03 mg/L) 20% (0.03-2 mg/L)
HS^-	Spectrophotometry, external laboratory	0.01	mg/L	0.02 (0.01-0.2 mg/L) 12% (>0.2 mg/L)
NO_2 as N	Spectrophotometry	0.1	µg/L	2%

Component	Method[1]	Reporting limits (RL), detection limits (DL) or range[2]	Unit	Measurement uncertainty[3]
NO_3 as N	Spectrophotometry	0.2	µg/L	5%
NO_2+NO_3 as N	Spectrophotometry	0.2	µg/L	0.2 (0.2-20 µg/L) 2% (> 20 µg/L)
NH_4 as N	Spectrophotometry, SKB	11	µg/L	30% (11-20 µg/L) 25% (20-50 µg/L) 12% (50-1200 µg/L)
NH_4 as N	Spectrophotometry external laboratory	0.8	µg/L	0.8 (0.8-20 µg/L) 5% (> 20 µg/L)
PO_4 as P	Spectrophotometry	0.5	µg/L	0.7 (0.7-20 µg/L) 3% (> 20 µg/L)
Tot-N[7]	/1/	10	µg/L	4%
Tot-P[7]	/1/	0.5	µg/L	6%
Al,	ICP SFMS	0.2, 0.3, 0.7[4]	µg/L	17.6%[6]
Zn	ICP SFMS	0.2, 0.8, 2[4]	µg/L	15.5, 17.7, 25.5%[6]
Ba, Cr, Mo	ICP SFMS	0.01, 0.04, 0.1[4]	µg/L	Ba 15%[4], Cr 22%[5] Mo 39%[6]
Pb	ICP SFMS	0.01, 0.1, 0.3[4]	µg/L	15%[6]
Cd	ICP SFMS	0.002, 0.02, 0.5[4]	µg/L	15.5%[6]
Hg	ICP AFS	0.002	µg/L	10.7%[6]
Co	ICP SFMS	0.005, 0.02, 0.05[4]	µg/L	25.9%[6]
V	ICP SFMS	0.005, 0.03, 0.05[4]	µg/L	18.1%[6]
Cu	ICP SFMS	0.1, 0.2, 0.5[4]	µg/L	14.4%[6]
Ni	ICP SFMS	0.05, 0.2, 0.5[4]	µg/L	15.8%[6]
P	ICP SFMS	1, 5, 40[4]	µg/L	16.3%[6]
As	ICP SFMS	0.01 (520 mS/m)	µg/L	59.2%[6]
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	ICP SFMS	0.005, 0.02, 0.05[4]	µg/L	20%, 20%, 25%[6]
Sc, In, Th	ICP SFMS	0.05, 0.2, 0.5[4]	µg/L	25%[6]
Rb, Zr, Sb, Cs	ICP SFMS	0.025, 0.1, 0.25[4]	µg/L	15%, 20%, 20%[5] 25%[6]

Component	Method[1]	Reporting limits (RL), detection limits (DL) or range[2]	Unit	Measurement uncertainty[3]
Y, Hf	ICP SFMS	0.005, 0.02, 0.05[4]	µg/L	15%, 20%, 20%[5] 25%[6]
U	ICP SFMS	0.001, 0.005, 0.01[4]	µg/L	13.5%, 14.3%, 15.9%[5] 19.1%, 17.9%, 20.9%[6]
DOC	UV oxidation, IR Carbon analysator	0.5	mg/L	8%
TOC	UV oxidation, IR Carbon analysator	0.5	mg/L	10%
$\delta^{2}H$	MS	2	‰ SMOW[7]	0.9 (one standard deviation)
$\delta^{18}O$	MS	0.1	‰ SMOW[7]	0.1 (one standard dev.)
^{3}H	LSC	0.8	TU[8]	0.8
$\delta^{13}C$	A (MS)	-	‰ PDB[9]	0.3[17]
^{14}C pmc	A (MS)	-	PMC[10]	0.4[17]
$\delta^{34}S$[12]	MS	0.2	‰ CDT[11]	0.4 (one standard dev.)

1. Many elements may be determined by more than one ICP technique depending on concentration range. The most relevant technique and measurement uncertainty for the concentrations normally encountered in groundwater are presented. In cases where two techniques were frequently used, both are displayed.
2. Reporting limits (RL), generally 10×standard deviation, if nothing else is stated. Measured values below RL or DL are stored as negative values in SICADA (i.e. –RL value and –DL value).
3. Measurement uncertainty reported by the laboratory, generally as ± percent of measured value in question at 95% confidence interval.
4. Reporting limits at electrical cond. 520 mS/m, 1440 mS/m and 3810 mS/m respectively.
5. Measurement uncertainty at concentrations 100×RL
6. Measurement uncertainty at concentrations 10×RL
7. Per mille deviation[16] from SMOW (Standard Mean Oceanic Water).
8. TU=Tritium Units, where one TU corresponds to a tritium/hydrogen ratio of 10^{-18} (1 Bq/L Tritium = 8.45 TU).
9. Per mille deviation[16] from PDB (the standard PeeDee Belemnite).
10. The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: pmC = $100 \times e^{((1950\text{-}y\text{-}1.03t)/8274)}$
where y = the year of the C-14 measurement and t = C-14 age.
11. Per mille deviation[16] from CDT (the standard Canyon Diablo Troilite).
12. Analyses of $\delta^{34}S$ in dissolved sulphide and sulphate: Unfiltrated groundwater was collected in a 5 litre plastic bottle with excess ZnAc (5 g) to precipitate sulphide as ZnS (s). The bottle was filled with the tubing at the bottom to prevent air contact and flushed with argon gas before and during sampling. The sample was sent to IFE (Institute for Energy Technology) in Norway for further treatment, which included filtration and precipitation of sulphate with $BaSO_4$ in the residual. The ZnS was converted to AgS by titration with $AgNO_3$. The AgS and $BaSO_4$ were filtrated, dried and combusted to SO_2 for analysis of $\delta^{34}S$ by mass spectrometry (IRMS).

Appendix 7

Sampling and analytical methods – microbiology and gases

Microbiological analyses

These analyses comprised analysis of acetate and the bio-molecule adeno-tri-phosphate (ATP) together with cultivation and nucleic acid analyses of specific groups of microorganisms.

Acetate

Samples of 10 mL groundwater were collected in a sealable, 27 mL sterilized anaerobic glass tube (no. 2048-00150; Bellco Glass, Vineland, NJ, USA), sealed with butyl rubber stoppers (no. 2048-117800; Bellco Glass) and aluminium crimp seals (no. 2048-11020, Bellco Glass) and deep frozen (-20 ºC) on site. Acetate was later analysed in the laboratory by means of an enzymatic UV method (Enzymatic Bioanalysis kit order number 10 139 084 035; Boehringer, Mannheim, Germany) with a UV visible spectrophotometer (Ultraspec 2000; Amersham Pharmacia Biotech, Uppsala, Sweden).

ATP analysis

Samples of 50 mL groundwater were collected in 50 mL sterile plastic tubes with screw caps and ATP was immediately analysed on site. The ATP Biomass Kit HS for determining total ATP in living cells was used (no. 266-311; BioThema, Handen, Sweden). This analysis kit was developed based on the results of Lundin et al. (1986) and Lundin (2000). The ATP biomass method used in this work has been described, tested in detail and evaluated for use with Fennoscandian groundwater, including Olkiluoto groundwater (Eydal and Pedersen 2007).

Analysis of most probable number of cultivable iron and sulphate reducing bacteria

Samples for most probable number (MPN) of IRB and SRB were taken at the pumping time intervals using sterile syringes directly into sampling vessels. Two sealable, 27 mL sterilized anaerobic glass tubes (no. 2048-00150; Bellco Glass, Vineland, NJ, USA), sealed with butyl rubber stoppers (no. 2048-117800; Bellco Glass) and aluminium crimp seals (no. 2048-11020, Bellco Glass), were each filled with approximately 10 mL of sampled groundwater for analysis of the most probable number of cultivable microorganisms as described next.

Anaerobic media for determining the most probable number of microorganisms in groundwater were prepared according to the procedures described by Widdel and Bak (1992). The specific media details were formulated based on previously measured chemical data from Laxemar. This allowed the formulation of artificial media that most closely mimicked *in situ* groundwater chemistry for optimal microbial cultivation (Hallbeck and Pedersen 2008). Media for the iron-reducing bacteria (IRB) and the SRB were autoclaved and anaerobically dispensed according to Hallbeck and Pedersen (2008). Inoculations for IRB and SRB were performed in the field laboratory directly after sampling of the groundwater. The MPN procedures resulted in protocols with tubes that scored positive or negative for growth. The results of the analyses were rated positive or negative compared with control levels. Three dilutions with five parallel tubes were used to calculate the MPN of each group, according to the calculations found in Greenberg et al. (1992). The lower and upper 95% confidence intervals for the MPN method applied to five parallel tubes equalled approximately 1/3 and 3 times the obtained values, respectively. The detection limit was 0.2 cells mL^{-1}. Further details about the procedures can be found in Hallbeck and Pedersen (2008).

Quantification of DNA and RNA specific for sulphate-reducing bacteria and acetogenic bacteria

Samples of 50 mL groundwater was collected in 50 mL sterile plastic tubes with screw caps and transferred to the laboratory in Göteborg for subsequent DNA extraction. The samples were centrifuged at 7500 g for 15 min, the supernatant was discarded, and the DNA was extracted from the pellet using the DNeasy Blood&Tissue kit (no. 69504; QIAGEN) according to the manufacturer's protocol for Gram positive bacteria. DNA concentrations were measured with a NanoDrop ND-1000 UV-Vis spectrophotometer (NanoDrop Technologies, Wilmington, DE, USA) and extracted DNA was stored at –80°C.

RNA extraction

RNA was directly extracted from 500-mL of groundwater that was filtered at the sampling site within a few minutes of sampling in a 500-mL sterile plastic Filtropur BT50 0.2 µm, 500-mL bottle top filter (no.

83.1823.101; Sarstedt, Landskrona, Sweden) applied to a 1-L glass bottle (Fisher Scientific, Göteborg, Sweden) and connected to a vacuum pump (no. N810FT.18; KF LAB, Neuberger, Germany). The filter was immediately cut out and placed in 15-mL RNA Later solution (no. AM7021; Ambion, Stockholm, Sweden). The filter was washed with the RNA Later solution and then discarded. In the laboratory, the RNA Later solution with the cells was centrifuged at 7500 g for 15 min, the supernatant discarded, and the total RNA was extracted from the pellet using the RNeasy Mini kit (no. 74104;QIAGEN, Solna Sweden) according to the manufacturer's protocol. RNA concentrations were measured with a NanoDrop ND-1000 UV-Vis spectrophotometer (NanoDrop Technologies, Wilmington, DE, USA) and the RNA quality was checked on a 1% formaldehyde agarose gel. Extracted RNA was stored at –80°C.

qPCR of different genes

qPCR was used to quantify three different genes in the groundwater populations. The total amount of microorganisms belonging to the domain *Bacteria* was determined by quantification of the 16S rRNA gene universal for all *Bacteria*. A standard curve for the quantification of this gene was produced by extracting total DNA from 1 mL of a pure culture of *Desulfovibrio aespoeensis* (Motamedi et al 1998). The DNA from the pure culture was extracted according to the manufacturer's protocol as was done for DNA in groundwater samples described above. The amount of SRB in the samples was determined by qPCR of the adenosine-5'-phosphosulphate reductase alpha subunit DNA (*apsA*). A standard curve for this gene was prepared in a similar way as for the 16S rRNA gene. Homoacetogenic bacteria were quantified with qPCR for the formyltetrahydrofolate synthetase (*fthfs*) gene. The standard curve for this gene was prepared with DNA from *Acetobacterium carbonolicum* as standard and the DNA extraction was made from 1 mL of a pure culture of the organisms.

qPCR was also used to determine the amount of active SRB, by extraction and quantification ot the expressed mRNA for the *apsA* gene from the SRB population in the groundwater. A standard curve for quantifying *apsa* mRNA was produced by extracting total mRNA from 1 mL of a pure culture of *Desulfovibrio aespoeensis*. The mRNA from the pure culture was extracted according to the manufacturer's protocol (QIAGEN).

16S rRNA, *apsA* and *fthfs* gene qPCR were run on samples to analyse the total biomass of *Bacteria*, SRB and acetogens in the different samples as described above. DNA and cDNA were used as the templates in the q-PCR depending on the gene of interest. The DNA was serially diluted six times in ¼ increments, 1 ng per reaction being the most concentrated standard sample for the 16S rRNA q-PCR for *Bacteria* 1 ng for apsA q-PCR. The q-PCR reactions were run in duplicate to evaluate the precision of measurements of the Ct values. Each PCR mixture contained 0.5-1.0 µL of the respective primer solution (10 pmol µl-1), 1-16 ng of DNA, 12.5 µL of Brilliant SYBR II Q-PCR Mastermix (no. 600548; Stratagene, AH Diagnostics AB) in a final reaction volume of 25 µL. Amplification was carried out on a q-PCR thermal cycler (Mx3005P; Stratagene, AH Diagnostics AB). The primers were temperature optimized and the products with the standard samples were checked on agarose gels to verify the size of the fragments. The dissociation curves (melting curves) were also checked to evaluate the specificity of the primers.

Dissolved gases

The SKB PVB sampler was used to collect groundwater for analysis of gas composition and total amount of gas during the second pumping period of KLX06. Water from the immersed borehole pump was led via poly-ether-ether-keton (PEEK) tubing to the PVB sample vessel that filled by the pressure from the pump. In the laboratory, the PVB samplers were attached to an extraction unit for the extraction of all dissolved gas. After extraction, the gas was compressed and transferred to a 10-mL syringe (SGE Analytical Science, Victoria, Australia) and the volumes of extracted gas and water were measured. The captured gas was subsequently transferred to a 6.6-mL glass vial with a butyl rubber stopper and aluminium crimp seal. The vial had previously been evacuated and flushed twice with nitrogen, in two cycles, and left at high vacuum (1 Pa). Copper sulphate (dehydrant) was added to adsorb any traces of water remaining in the gas (water causes troublesome baseline drifts in the gas chromatographs). Thereafter analysis was performed using gas chromatography.

Two different chromatographs were used with standard calibration gases and equipped as follows. Hydrogen and carbon monoxide were analysed on a KAPPA-5/E-002 analytical gas chromatograph (AMETEK/Trace Analytical, formerly Trace Analytical, Menlo Park, CA, USA) equipped with a 156 × 1/16-inch stainless steel HayeSep column in line with a 31 × 1/8-inch stainless steel molecular sieve 5A column, which was subsequently attached to a reductive gas detector (RGD). Helium, argon, and nitrogen were analysed on a Varian Star 3400CX gas chromatograph (Varian Analytical Instruments, Varian AB, Bromma, Sweden) using a thermal conductivity detector (TCD) with an oven temperature of 65°C, a detector temperature of

120°C, and a filament temperature of 250°C. The gases were separated using a Porapak-Q column (2 m × 1/8 inch diameter) followed by a molecular sieve 5A column (6 m × 1/8 inch) with argon (for helium and nitrogen) and nitrogen (for argon) as the respective carrier gases. Methane, ethane and ethylene were analysed on a Varian Star 3400CX gas chromatograph using a flame ionization detector (FID) with an oven temperature of 65°C and a detector temperature of 200°C. The gases were separated using a Porapak-Q column (2 m × 1/8 inch diameter) and analysed on the FID with nitrogen as the carrier gas. Carbon dioxide was transformed to methane using a 10% Ni_2NO_3 "methanizer" fed with hydrogen gas (9.375 × 1/8 inch diameter, temperature 370°C) and analysed as methane on the FID with nitrogen as the carrier gas.

Stable isotopes in released gases

Samples for analysis of isotopic compositionin released gas were collected from KLX06 during the first pumping period. Groundwater was pumped through a stainless 316L steel, Teflon coated, sample cylinder (Swagelok) equipped with valves and a side tube. During pumping groundwater gas will be released inside the cylinder due to the decrease in water pressure. A balance was used to control the replacement of groundwater with released gas. The cylinder was closed when at least 100 mL of released gas had been collected and shipped to the laboratory. The sampled gas was extracted as done for dissolved gas and transferred to 27 mL glass tubes with butyl rubber stopper and aluminium crimp seal. The tube had previously been evacuated and flushed twice with nitrogen, in two cycles, and left at high vacuum (1 Pa). The tubes were subsequently sent to an external laboratory (Hydroisotop GmbH, Woelkestr. 9, D-85301 Schweitenkirchen, Germany) for isotope analysis (δ^2H, $\delta^{13}C$, $\delta^{18}O$) according to their protocols. In addition, the composition of the collected gas was analysed as described above.

Appendix 8

Compilation of water analysis data (October 2010)

Table A8-1. Water Composition.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Charge balance %	Na mg L^{-1}	K mg L^{-1}	Ca mg L^{-1}	Mg mg L^{-1}	HCO_3^- mg L^{-1}	Cl^- mg L^{-1}	SO_4^{2-} mg L^{-1}	SO_4-S mg L^{-1}	Br^- mg L^{-1}	F^- mg L^{-1}	Si mg L^{-1}
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	–3.87	313	2.95	65.9	7.88	155	562	1.23	8.49	1.98	2.58	5.79
KAS03	107.00	252.00	14747	2009/02/17	Section	–0.55	303	2.63	58.9	7.49	112	515	34.7	7.93	1.87	2.65	5.54
KAS03	627.00	1,002.00	14748	2009/02/18	Standpipe	–1.75	2,010	8.23	1,860	36.3	119	6,570	131	50.3	43.2	1.54	4.98
KAS03	627.00	1,002.00	14749	2009/02/23	Section	–	1,640	7.99	1,060	61.2	48.2	–	–	78.0	–	–	5.49
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	–4.69	1,660	41.4	151	162	357	3,180	84.0	123	11.9	1.74	5.00
KAS09	116.00	150.00	14751	2009/03/18	Section	–5.26	1,660	40.8	167	163	346	3,220	68.6	144	11.5	–	4.90
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	–13.8	93.5	1.71	21.3	3.40	218	58.3	1.55	29.3	0.219	3.47	7.98
KLX06	554.00	570.00	14713	2009/02/09	Section	0.43	515	6.31	190	9.04	119	742	359	152	3.76	3.38	7.32
KLX06	554.00	570.00	14714	2009/02/09	Section	–0.97	625	8.52	229	10.2	71.0	997	476	177	5.13	2.98	7.07
KLX06	554.00	570.00	14715	2009/02/10	Section	–1.10	656	8.68	266	11.2	64.7	1,090	519	192	5.55	3.12	6.79
KLX06	554.00	570.00	14716	2009/02/10	Section	–1.04	685	9.45	276	11.5	61.3	1,130	541	204	5.70	2.73	7.19
KLX06	554.00	570.00	14718	2009/02/11	Section	–	–	–	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14719	2009/02/12	Section	–1.28	766	10.0	339	13.1	47.6	1,330	637	233	6.89	2.63	7.46
KLX06	554.00	570.00	14720	2009/02/13	Section	–	–	–	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14721	2009/02/16	Section	–2.82	805	9.14	360	12.4	37.0	1,480	698	240	7.77	2.60	7.72
KLX06	554.00	570.00	14722	2009/02/17	Section	–	–	–	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14723	2009/02/18	Section	–	–	–	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14724	2009/02/19	Section	–	–	–	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14725	2009/02/20	Section	–	–	–	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14726	2009/02/23	Section	–2.74	787	8.14	350	11.5	32.5	1,430	685	239	7.34	2.52	8.38
KLX06	554.00	570.00	14727	2009/05/05	Tubing	7.01	167	2.50	42.3	3.32	210	141	57.8	14.2	0.756	2.84	7.54
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	0.16	122	1.80	26.3	2.93	212	89.8	46.0	11.7	0.455	3.00	7.71
KLX06	554.00	570.00	14729	2009/05/05	Section	8.91	410	4.92	187	7.54	185	453	212	118	2.20	3.92	7.89
KLX06	554.00	570.00	14730	2009/05/05	Section	–1.18	722	8.38	319	11.2	55.4	1,230	593	223	6.73	2.79	7.82
KLX06	554.00	570.00	14731	2009/05/06	Section	–0.90	752	8.88	325	11.8	52.0	1,260	608	233	6.51	2.99	7.76
KLX06	554.00	570.00	14732	2009/05/07	Section	–0.72	776	9.06	345	12.2	42.0	1,330	570	235	6.56	2.87	7.81

SICADA: water_composition.

– = not analysed.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Charge balance %	Fe mg L^{-1}	Fe-tot mg L^{-1}	Fe(II) mg L^{-1}	Mn mg L^{-1}	Li mg L^{-1}	Sr mg L^{-1}	I^- mg L^{-1}	pH	TOC mg L^{-1}
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	–3.87	< 0.02	0.017	0.010	0.082	0.061	0.998	–	8.42	5.7
KAS03	107.00	252.00	14747	2009/02/17	Section	–0.55	< 0.02	0.014	0.008	0.056	0.062	1.00	–	7.88	4.0
KAS03	627.00	1,002.00	14748	2009/02/18	Standpipe	–1.75	0.375	0.436	0.422	0.395	1.38	35.6	–	7.35	49.4
KAS03	627.00	1,002.00	14749	2009/02/23	Section	–	0.309	0.319	0.307	0.398	0.815	20.9	–	8.06	146
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	–4.69	0.299	0.280	0.272	0.093	0.060	2.90	–	8.33	20.7
KAS09	116.00	150.00	14751	2009/03/18	Section	–5.26	0.023	0.050	0.036	0.131	0.064	3.08	–	8.32	13.8
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	–13.8	0.245	0.293	0.275	0.163	0.015	0.250	–	7.22	10.7
KLX06	554.00	570.00	14713	2009/02/09	Section	0.43	0.022	0.032	0.022	0.089	0.085	3.55	0.050	8.08	4.1
KLX06	554.00	570.00	14714	2009/02/09	Section	–0.97	0.026	0.036	0.029	0.088	0.100	4.35	–	8.35	4.2
KLX06	554.00	570.00	14715	2009/02/10	Section	–1.10	0.029	0.036	0.028	0.087	0.105	4.53	–	8.45	3.4
KLX06	554.00	570.00	14716	2009/02/10	Section	–1.04	0.028	0.026	0.023	0.095	0.114	5.19	–	8.48	3.7
KLX06	554.00	570.00	14718	2009/02/11	Section	–	–	0.034	0.025	–	–	–	–	–	–
KLX06	554.00	570.00	14719	2009/02/12	Section	–1.28	0.056	0.069	0.059	0.116	0.126	6.37	0.075	8.44	2.9
KLX06	554.00	570.00	14720	2009/02/13	Section	–	–	0.054	0.053	–	–	–	–	–	–
KLX06	554.00	570.00	14721	2009/02/16	Section	–2.82	0.116	0.126	0.120	0.142	0.134	7.07	–	8.33	2.3
KLX06	554.00	570.00	14722	2009/02/17	Section	–	–	0.137	0.129	–	–	–	–	–	–
KLX06	554.00	570.00	14723	2009/02/18	Section	–	–	0.202	0.196	–	–	–	–	–	–
KLX06	554.00	570.00	14724	2009/02/19	Section	–	–	0.230	0.222	–	–	–	–	–	–
KLX06	554.00	570.00	14725	2009/02/20	Section	–	–	0.232	0.225	–	–	–	–	–	–
KLX06	554.00	570.00	14726	2009/02/23	Section	–2.74	0.239	0.257	0.252	0.144	0.134	6.67	–	8.28	2.0
KLX06	554.00	570.00	14727	2009/05/05	Tubing	7.01	0.143	0.196	0.196	0.058	0.023	0.750	–	7.55	118
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	0.16	0.095	0.116	0.105	0.083	0.016	0.420	–	7.77	22.8
KLX06	554.00	570.00	14729	2009/05/05	Section	8.91	0.019	0.024	0.017	0.079	0.066	3.18	–	8.11	11.9
KLX06	554.00	570.00	14730	2009/05/05	Section	–1.18	< 0.02	0.031	0.021	0.073	0.114	5.59	–	8.34	7.7
KLX06	554.00	570.00	14731	2009/05/06	Section	–0.90	< 0.02	0.023	0.024	0.075	0.116	5.78	–	8.82	5.5
KLX06	554.00	570.00	14732	2009/05/07	Section	–0.72	0.033	0.033	0.033	0.095	0.121	5.95	–	8.30	3.9

SICADA: water_composition.

– = not analysed.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Charge balance %	DOC mg L^{-1}	HS^{-1} mg L^{-1}	HS^{-2} mg L^{-1}	Drill water %	Uranine µg L^{-1}	Cond mS m^{-1}	NH_4-N mg L^{-1}	NO_2-N mg L^{-1}
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	–3.87	6.0	9.40	–	0.07	–	208	0.540	–
KAS03	107.00	252.00	14747	2009/02/17	Section	–0.55	4.0	9.08	7.30	0.05	–	186	0.100	–
KAS03	627.00	1,002.00	14748	2009/02/18	Standpipe	–1.75	49.4	6.75	5.80	0.18	–	1810	0.185	–
KAS03	627.00	1,002.00	14749	2009/02/23	Section	–	146	0.587	–	–	–	1340	–	–
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	–4.69	22.3	102	–	0.49	–	998	0.019	–
KAS09	116.00	150.00	14751	2009/03/18	Section	–5.26	17.4	92.3	–	0.27	–	977	–	–
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	–13.8	10.9	7.74	5.30	–	3.11	55.2	0.021	–
KLX06	554.00	570.00	14713	2009/02/09	Section	0.43	3.9	6.40	4.00	–	15.00	312	0.083	0.000
KLX06	554.00	570.00	14714	2009/02/09	Section	–0.97	4.4	1.30	–	–	18.90	405	0.103	–
KLX06	554.00	570.00	14715	2009/02/10	Section	–1.10	3.3	0.808	–	–	19.30	436	0.106	–
KLX06	554.00	570.00	14716	2009/02/10	Section	–1.04	3.6	0.613	–	–	20.50	466	0.091	–
KLX06	554.00	570.00	14718	2009/02/11	Section	–	–	0.408	–	–	–	–	–	–
KLX06	554.00	570.00	14719	2009/02/12	Section	–1.28	2.9	0.282	0.210	–	22.60	518	0.092	0.000
KLX06	554.00	570.00	14720	2009/02/13	Section	–	–	0.270	–	–	–	–	–	–
KLX06	554.00	570.00	14721	2009/02/16	Section	–2.82	2.4	0.168	–	–	–	565	0.068	–
KLX06	554.00	570.00	14722	2009/02/17	Section	–	–	0.099	–	–	23.90	–	–	–
KLX06	554.00	570.00	14723	2009/02/18	Section	–	–	0.080	–	–	–	–	–	–
KLX06	554.00	570.00	14724	2009/02/19	Section	–	–	0.085	–	–	–	–	–	–
KLX06	554.00	570.00	14725	2009/02/20	Section	–	–	0.103	–	–	–	–	–	–
KLX06	554.00	570.00	14726	2009/02/23	Section	–2.74	2.0	0.082	–	–	20.70	556		–
KLX06	554.00	570.00	14727	2009/05/05	Tubing	7.01	367	3.08	–	–	2.74	91.4	0.109	–
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	0.16	22.9	5.93	–	–	2.74	72.6	0.027	–
KLX06	554.00	570.00	14729	2009/05/05	Section	8.91	15.7	9.18	–	–	13.00	188	0.031	–
KLX06	554.00	570.00	14730	2009/05/05	Section	–1.18	7.5	1.08	–	–	17.90	480	0.057	–
KLX06	554.00	570.00	14731	2009/05/06	Section	–0.90	5.5	0.860	–	–	18.50	492	0.066	–
KLX06	554.00	570.00	14732	2009/05/07	Section	–0.72	4.1	0.387	–	–	20.30	521	0.064	–

SICADA: water_composition.

– = not analysed.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Charge balance %	NO_3-N mg L^{-1}	NO_2NO_3-N mg L^{-1}	PO_4-P mg L^{-1}	PO_4-P^3 mg L^{-1}	P mg L^{-1}
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	–3.87	–	–	–	–	–
KAS03	107.00	252.00	14747	2009/02/17	Section	–0.55	–	–	–	–	–
KAS03	627.00	1,002.00	14748	2009/02/18	Standpipe	–1.75	–	–	–	–	–
KAS03	627.00	1,002.00	14749	2009/02/23	Section	–	–	–	–	–	–
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	–4.69	–	–	–	–	–
KAS09	116.00	150.00	14751	2009/03/18	Section	–5.26	–	–	–	–	–
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	–13.8	–	–	–	–	0.063
KLX06	554.00	570.00	14713	2009/02/09	Section	0.43	0.001	0.001	0.008	0.009	0.018
KLX06	554.00	570.00	14714	2009/02/09	Section	–0.97	–	–	–	–	–
KLX06	554.00	570.00	14715	2009/02/10	Section	–1.10	–	–	–	–	0.013
KLX06	554.00	570.00	14716	2009/02/10	Section	–1.04	–	–	–	–	–
KLX06	554.00	570.00	14718	2009/02/11	Section	–	–	–	–	–	–
KLX06	554.00	570.00	14719	2009/02/12	Section	–1.28	< 0.0003	0.000	0.004	0.005	0.011
KLX06	554.00	570.00	14720	2009/02/13	Section	–	–	–	–	–	–
KLX06	554.00	570.00	14721	2009/02/16	Section	–2.82	–	–	–	–	–
KLX06	554.00	570.00	14722	2009/02/17	Section	–	–	–	–	–	–
KLX06	554.00	570.00	14723	2009/02/18	Section	–	–	–	–	–	–
KLX06	554.00	570.00	14724	2009/02/19	Section	–	–	–	–	–	–
KLX06	554.00	570.00	14725	2009/02/20	Section	–	–	–	–	–	–
KLX06	554.00	570.00	14726	2009/02/23	Section	–2.74	–	–	–	–	–
KLX06	554.00	570.00	14727	2009/05/05	Tubing	7.01	–	–	–	–	–
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	0.16	–	–	–	–	–
KLX06	554.00	570.00	14729	2009/05/05	Section	8.91	–	–	–	–	0.035
KLX06	554.00	570.00	14730	2009/05/05	Section	–1.18	–	–	–	–	–
KLX06	554.00	570.00	14731	2009/05/06	Section	–0.90	–	–	–	–	–
KLX06	554.00	570.00	14732	2009/05/07	Section	–0.72	–	–	–	–	–

SICADA: water_composition.

– = not analysed.

Table A8-2. Trace elements.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	U µg L^{-1}	Th µg L^{-1}	Cd µg L^{-1}	Hg µg L^{-1}	V µg L^{-1}	Rb µg L^{-1}	Y µg L^{-1}	Zn µg L^{-1}	Sc µg L^{-1}	Ba µg L^{-1}
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	0.306	< 0.02	0.057	0.007	0.740	4.14	0.393	5.85	< 0.05	25.5
KLX06	554.00	570.00	14713	2009/02/09	Section	0.277	0.028	0.008	0.014	0.365	17.4	0.335	2.11	< 0.05	117
KLX06	554.00	570.00	14715	2009/02/10	Section	0.288	< 0.02	< 0.002	< 0.002	0.299	26.2	0.120	2.34	< 0.05	208
KLX06	554.00	570.00	14719	2009/02/12	Section	0.261	< 0.02	< 0.008	< 0.002	0.282	28.5	0.063	2.74	< 0.05	290
KLX06	554.00	570.00	14729	2009/05/05	Section	0.253	< 0.02	0.012	0.003	0.347	13.0	0.168	5.91	< 0.05	111

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Ba µg L^{-1}	La µg L^{-1}	Hf µg L^{-1}	Tl µg L^{-1}	Ce µg L^{-1}	Pr µg L^{-1}	Nd µg L^{-1}	Sm µg L^{-1}	Eu µg L^{-1}	Gd µg L^{-1}
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	25.5	0.199	< 0.005	< 0.01	0.382	0.056	0.275	0.055	0.006	0.058
KLX06	554.00	570.00	14713	2009/02/09	Section	117	0.148	< 0.005	< 0.01	0.172	0.022	0.097	0.018	< 0.005	0.028
KLX06	554.00	570.00	14715	2009/02/10	Section	208	0.067	< 0.005	< 0.01	0.077	0.010	0.044	0.009	< 0.005	0.010
KLX06	554.00	570.00	14719	2009/02/12	Section	290	0.048	< 0.005	< 0.01	0.059	0.007	0.030	0.006	< 0.005	< 0.005
KLX06	554.00	570.00	14729	2009/05/05	Section	111	0.122	< 0.005	< 0.01	0.142	0.018	0.072	0.011	< 0.005	0.015

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Tb µg L^{-1}	Dy µg L^{-1}	Ho µg L^{-1}	Er µg L^{-1}	Tm µg L^{-1}	Yb µg L^{-1}	Lu µg L^{-1}	Cr µg L^{-1}	Cu µg L^{-1}	Co µg L^{-1}
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	0.009	0.048	0.012	0.040	0.005	0.042	0.008	3.25	0.272	0.226
KLX06	554.00	570.00	14713	2009/02/09	Section	< 0.005	0.032	0.008	0.022	< 0.004	0.017	< 0.005	0.476	0.174	0.050
KLX06	554.00	570.00	14715	2009/02/10	Section	< 0.005	0.012	< 0.005	0.008	< 0.004	0.007	< 0.005	0.283	0.153	0.030
KLX06	554.00	570.00	14719	2009/02/12	Section	< 0.005	0.006	< 0.005	< 0.005	< 0.004	0.006	< 0.005	0.201	0.154	0.027
KLX06	554.00	570.00	14729	2009/05/05	Section	< 0.005	0.015	< 0.005	0.012	< 0.004	0.011	< 0.005	0.875	< 0.1	0.031

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Mo µg L^{-1}	Ni µg L^{-1}	Pb µg L^{-1}	Zr µg L^{-1}	In µg L^{-1}	Sb µg L^{-1}	Cs µg L^{-1}	Al µg L^{-1}	As µg L^{-1}
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	2.70	12.3	0.980	0.190	–	0.106	0.284	35.4	–
KLX06	554.00	570.00	14713	2009/02/09	Section	10.7	1.79	0.032	0.278	< 0.05	0.022	0.500	8.87	0.17
KLX06	554.00	570.00	14715	2009/02/10	Section	24.8	0.815	0.043	0.088	–	0.026	0.404	7.18	–
KLX06	554.00	570.00	14719	2009/02/12	Section	25.1	0.651	0.027	0.094	< 0.05	0.061	0.416	5.86	0.55
KLX06	554.00	570.00	14729	2009/05/05	Section	1.47	1.92	0.092	0.085	–	0.024	0.419	10.8	–

SICADA: trace_elements.

– = not analysed.

Table A8-3. Isotopes I (H-, O-, B-,S-, C- and Cl isotopes).

Idcode	Secup m	Seclow m	Sample no	Sampling date	Water type	$\delta^{2}H$ dev SMOW	^{3}H TU	$\delta^{18}O$ dev SMOW	$^{10}B/^{11}B$ no unit	$\delta^{34}S\_SO_4$ dev CDT	$\delta^{34}S\_HS$ dev CDT	$\delta^{13}C$ pmC	$\delta^{13}C$ dev PDB	$\delta^{37}Cl$ dev SMOC
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	–98.7	–	–13.50	–	–	–	30.0	–15.9	–
KAS03	107.00	252.00	14747	2009/02/17	Section	–97.6		–13.60	–	41.2	9.9	28.8	–15.0	–
KAS03	627.00	1,002.00	14748	2009/02/18	Standpipe	–97.7	1.20	–13.90	–	54.0	17.5	84.6	–18.8	–
KAS03	627.00	1,002.00	14749	2009/02/23	Section	–	–	–	–	–	–	–	–	–
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	–	–	–	–	–	–	83.1	–11.1	–
KAS09	116.00	150.00	14751	2009/03/18	Section	–	–	–	–	67.4	11.3	83.9	–14.2	–
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	–78.7	2.70	–11.30	–	13.8	24.9	97.6	–8.5	–
KLX06	554.00	570.00	14713	2009/02/09	Section	–91.9	< 0.8	–13.00	0.241	14.1	–6.1	40.0	–17.9	0.26
KLX06	554.00	570.00	14714	2009/02/09	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14715	2009/02/10	Section	–	–	–	–	11.3	–11.3	–	–	–
KLX06	554.00	570.00	14716	2009/02/10	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14718	2009/02/11	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14719	2009/02/12	Section	–100.0	< 0.8	–13.80	0.240	9.3	–19.3	32.9	–20.4	–0.10
KLX06	554.00	570.00	14720	2009/02/13	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14721	2009/02/16	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14722	2009/02/17	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14723	2009/02/18	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14724	2009/02/19	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14725	2009/02/20	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14726	2009/02/23	Section	–	–	–	–	8.6	–3.5	–	–	–
KLX06	554.00	570.00	14727	2009/05/05	Tubing	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14729	2009/05/05	Section	–105.8		–13.30	–	16.0	–31.5	60.6	–20.9	–
KLX06	554.00	570.00	14730	2009/05/05	Section	–	–	–	–	–	–	–	–	–
KLX06	554.00	570.00	14731	2009/05/06	Section	–	–	–	–	6.5	–32.2	–	–	–
KLX06	554.00	570.00	14732	2009/05/07	Section	–	–	–	–	5.5	–30.5	–	–	–

SICADA: isotopes.

– = not analysed.

Table A8-4. Phtalates.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Dimetyphthalate µg L^{-1}	Dietylphthalate µg L^{-1}	Di_N_Propylphthalate µg L^{-1}	Di_N_Butylphthalate µg L^{-1}	Di_Isobutylphthalate µg L^{-1}
KLX06	554.00	570.00	14727	2009/05/05	Tubing	< 1	< 1	< 1	< 1	< 1
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	< 1	< 1	< 1	< 1	< 1
KLX06	554.00	570.00	14729	2009/05/05	Section	< 1	< 1	< 1	< 1	< 1

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Di_Pentylphthalate µg L^{-1}	Di_N_Octylphthalate µg L^{-1}	Di_2_Etylhexyl_Phthalate µg L^{-1}	Butylbenzylphthalate µg L^{-1}
KLX06	554.00	570.00	14727	2009/05/05	Tubing	< 1	< 1	< 1	< 1
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	< 1	< 1	< 1	< 1
KLX06	554.00	570.00	14729	2009/05/05	Section	< 1	< 1	< 1	< 1

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Di_Cyklohexyphthalate µg L^{-1}	Di_Isodecylphthalate µg L^{-1}	De_Isononylphthalate µg L^{-1}
KLX06	554.00	570.00	14727	2009/05/05	Tubing	< 1	< 10	< 10
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	< 1	< 10	< 10
KLX06	554.00	570.00	14729	2009/05/05	Section	< 1	< 10	< 10

SICADA: phtalates.

Table A8-5. Released gases.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	He ppm	H_2 ppm	Ar ppm	N_2 ppm	CO_2 ppm	CO ppm	O_2 ppm	CH_4 ppm	C_2H_2 ppm	C_2H_4 ppm	C_2H_6 ppm	C_3H_8 ppm	C_3H_6 ppm
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	0.00	48.00	5,890	942,000	10,400	16.80	0.00	48,900	0.00	0.00	3.96	0.00	0.00
KAS09	116.00	150.00	14751	2009/03/18	Section	0.00	172,000	1,970	755,000	10,500	15.60	0.00	69,100	0.00	0.00	4.50	0.00	0.00
KLX06	554.00	570.00	14713	2009/02/09	Section	18800	5.79	9,200	951,000	161	0.88	0.00	4,890	0.00	0.32	3.21	0.00	0.00
KLX06	554.00	570.00	14719	2009/02/12	Section	16900	8.46	23,500	944,000	189	3.46	0.00	5,730	0.00	0.36	4.52	0.00	0.00
KLX06	554.00	570.00	14726	2009/02/23	Section	29900	5.93	11,000	933,000	78.10	0.47	0.00	1,900	0.00	0.00	2.06	0.00	0.00

SICADA: Released_gases.

Table A8-6. Dissolved gases.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Ar ml L^{-1}	He ml L^{-1}	N_2 ml L^{-1}	CO_2 ml L^{-1}	CH_4 ml/l	H_2 µl L^{-1}	CO µl L^{-1}	C_2H_6 µl L^{-1}	C_2H_4 µl L^{-1}	C_2H_2 µl L^{-1}	C_3H_8 µl L^{-1}	C_3H_6 µl L^{-1}	Gas vol ml L^{-1}
KLX06	554.00	570.00	14727	2009/05/05	Tubing	0.92	< 0.078	104.0	0.659	6.510	126.0	2.310	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	113.00
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	1.12	< 0.021	57.1	0.583	5.710	86.9	0.600	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	64.60
KLX06	554.00	570.00	14729	2009/05/05	Section	0.53	0.106	60.1	0.370	2.640	53.4	0.450	0.12	< 0.07	< 0.07	< 0.07	< 0.07	63.80
KLX06	554.00	570.00	14731	2009/05/06	Section	0.55	< 0.012	66.9	0.065	0.806	3.7	0.560	0.25	0.05	< 0.06	< 0.06	< 0.06	68.30
KLX06	554.00	570.00	14732	2009/05/07	Section	0.51	< 0.011	73.9	0.059	0.458	1.7	0.500	0.20	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

SICADA: dissolved_gases.

Table A8-7. Microbial presence.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Q PCR Gene	Nucleic acid	Standard sample	CT value number	Ra cells ml^{-1}
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	fthfs	RNA	A. carb. T		
KAS03	107.00	252.00	14746	2009/02/17		apsA	RNA	D. aespo T		
KAS03	107.00	252.00	14746	2009/02/17		fthfs	DNA	A. carb. T		
KAS03	107.00	252.00	14746	2009/02/17		apsA	DNA	D. aespo T	33.5	159,000
KAS03	107.00	252.00	14746	2009/02/17		16S rRNA B	DNA	D. aespo T	22.5	44,700,000
KAS03	107.00	252.00	14747	2009/02/17	Section	fthfs	RNA	A. carb. T		
KAS03	107.00	252.00	14747	2009/02/17		apsA	RNA	D. aespo T		
KAS03	107.00	252.00	14747	2009/02/17		16S rRNA B	DNA	D. aespo T	25.2	6,600,000
KAS03	107.00	252.00	14747	2009/02/17		fthfs	DNA	A. carb. T		
KAS03	107.00	252.00	14747	2009/02/17		apsA	DNA	D. aespo T	32.4	349,000
KAS03	627.00	1,002.00	14748	2009/02/17	Standpipe	fthfs	RNA	A. carb. T	38.8	745
KAS03	627.00	1,002.00	14748	2009/02/17		fthfs	DNA	A. carb. T	32.0	1,180
KAS03	627.00	1,002.00	14748	2009/02/17		apsA	DNA	D. aespo T	26.9	20,300,000
KAS03	627.00	1,002.00	14748	2009/02/17		16S rRNA B	DNA	D. aespo T	21.4	97,600,000
KAS03	627.00	1,002.00	14748	2009/02/17		apsA	RNA	D. aespo T	26.7	214,000
KAS03	627.00	1,002.00	14749	2009/02/23	Section	fthfs	RNA	A. carb. T		
KAS03	627.00	1,002.00	14749	2009/02/23		16S rRNA B	DNA	D. aespo T	25.3	6,250,000
KAS03	627.00	1,002.00	14749	2009/02/23		apsA	RNA	D. aespo T	33.5	59,800
KAS03	627.00	1,002.00	14749	2009/02/23		apsA	DNA	D. aespo T	26.6	25,500,000
KAS03	627.00	1,002.00	14749	2009/02/23		fthfs	DNA	A. carb. T	33.2	494
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	16S rRNA B	DNA	D. aespo T	23.0	31,100,000
KAS09	116.00	150.00	14750	2009/03/18		fthfs	RNA	A. carb. T		
KAS09	116.00	150.00	14750	2009/03/18		apsA	RNA	D. aespo T		
KAS09	116.00	150.00	14750	2009/03/18		fthfs	DNA	A. carb. T		
KAS09	116.00	150.00	14750	2009/03/18		apsA	DNA	D. aespo T	28.1	8,090,000
KAS09	116.00	150.00	14751	2009/03/18	Section	apsA	RNA	D. aespo T	26.2	303,100
KAS09	116.00	150.00	14751	2009/03/18		16S rRNA B	DNA	D. aespo T	24.4	11,800,000
KAS09	116.00	150.00	14751	2009/03/18		fthfs	DNA	A. carb. T		
KAS09	116.00	150.00	14751	2009/03/18		apsA	DNA	D. aespo T	27.8	10,800,000
KAS09	116.00	150.00	14751	2009/03/18		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14712	2009/02/09		16S rRNA B	DNA	D. aespo T	21.1	124,000,000

SICADA: microbial_presence.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Q PCR Gene	Nucleic acid	Standard sample	CT value number	Ra cells ml^{-1}
KLX06	554.00	570.00	14712	2009/02/09		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14712	2009/02/09		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14712	2009/02/09		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14713	2009/02/09	Section	fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14713	2009/02/09		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14713	2009/02/09		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14713	2009/02/09		16S rRNA B	DNA	D. aespo T	24.9	8,240,000
KLX06	554.00	570.00	14713	2009/02/09		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14714	2009/02/09	Section	16S rRNA B	DNA	D. aespo T	24.4	11,700,000
KLX06	554.00	570.00	14714	2009/02/09		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14714	2009/02/09		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14714	2009/02/09		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14714	2009/02/09		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14715	2009/02/10	Section	16S rRNA B	DNA	D. aespo T	23.8	18,100,000
KLX06	554.00	570.00	14715	2009/02/10		apsA	DNA	D. aespo T	36.0	24,800
KLX06	554.00	570.00	14715	2009/02/10		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14715	2009/02/10		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14715	2009/02/10		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14719	2009/02/12	Section	16S rRNA B	DNA	D. aespo T	26.2	3,590,000
KLX06	554.00	570.00	14719	2009/02/12		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14719	2009/02/12		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14719	2009/02/12		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14719	2009/02/12		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14726	2009/02/23	Section	16S rRNA B	DNA	D. aespo T	0.0	
KLX06	554.00	570.00	14726	2009/02/23		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14726	2009/02/23		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14726	2009/02/23		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14726	2009/02/23		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14727	2009/05/05	Tubing	apsA	DNA	D. aespo T	43.8	100
KLX06	554.00	570.00	14727	2009/05/05		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14727	2009/05/05		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14727	2009/05/05		fthfs	RNA	A. carb. T		

SICADA: microbial_presence.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Q PCR Gene	Nucleic acid	Standard sample	CT value number	Ra cells ml^{-1}
KLX06	554.00	570.00	14727	2009/05/05		16S rRNA B	DNA	D. aespo T	23.5	879,000
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	16S rRNA B	DNA	D. aespo T	22.9	1,310,000
KLX06	554.00	570.00	14728	2009/05/05		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14728	2009/05/05		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14728	2009/05/05		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14728	2009/05/05		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14729	2009/05/05	Section	16S rRNA B	DNA	D. aespo T	25.1	300,000
KLX06	554.00	570.00	14729	2009/05/05		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14729	2009/05/05		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14729	2009/05/05		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14729	2009/05/05		fthfs	RNA	A. carb. T		
KLX06	554.00	570.00	14731	2009/05/06	Section	16S rRNA B	DNA	D. aespo T	26.7	108,000
KLX06	554.00	570.00	14731	2009/05/06		apsA	DNA	D. aespo T		
KLX06	554.00	570.00	14731	2009/05/06		fthfs	DNA	A. carb. T		
KLX06	554.00	570.00	14731	2009/05/06		apsA	RNA	D. aespo T		
KLX06	554.00	570.00	14731	2009/05/06		fthfs	RNA	A. carb. T		

SICADA: microbial_presence.

Table A8-8. Microbial concentrations in groundwater.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Sampling place	IRB cells ml^{-1}	IRB_LLIM cells ml^{-1}	IRB_ULIM cells ml^{-1}	SRB cells ml^{-1}	SRB_LLIM cells ml^{-1}	SRB_ULIM cells ml^{-1}	ATP amol ml^{-1}	ATP_SD amol ml^{-1}	ATP_N number
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	900	300	2,900	22	10	58	729,000	30,300	9
KLX06	554.00	570.00	14713	2009/02/09	Section	17	7	48	11	4	29	74,700	6,280	9
KLX06	554.00	570.00	14714	2009/02/09	Section	140	60	360	3	1	7	31,600	1,690	9
KLX06	554.00	570.00	14715	2009/02/10	Section	70	30	210	1	0	2	43,500	2,980	9
KLX06	554.00	570.00	14719	2009/02/12	Section	220	100	580	2	1	9	12,800	1,150	9
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	1,600	600	5,300	700	300	2,100	206,000	29,800	9
KAS03	627.00	1,002.00	14748	2009/02/17	Standpipe	1,600			90,000	30,000	290,000	1,190,000	70,400	9
KAS03	107.00	252.00	14747	2009/02/17	Section	22	10	58	1,100	400	3,000	34,600	1,430	9
KAS03	627.00	1,002.00	14749	2009/02/23	Section	1,600	600	5,300	30,000	10,000	130,000	318,000	22,200	9
KLX06	554.00	570.00	14726	2009/02/23	Section	13	5	39	0	0	2	7,100	785	9
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	1,600			160,000			555,000	60,400	9
KAS09	116.00	150.00	14751	2009/03/18	Section	1,600			160,000	60,000	530,000	372,000	27,100	9
KLX06	554.00	570.00	14727	2009/05/05	Tubing	900	300	2,900	3	1	7	285,000	4,990	9
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	1,600	600	5,300	3,000	1,000	12,000	519,000	15,800	9
KLX06	554.00	570.00	14729	2009/05/05	Section	1,600			3	2	8	176,000	26,600	9
KLX06	554.00	570.00	14731	2009/05/06	Section	220	90	560	17	8	41	44,300	3,640	9

SICADA: microbial_concentration_in_groundwater.

Table A8-9. Isotopes in gases

Idcode	Secup m	Seclow m	Sample no	Sampling date	Water type	$d^{13}C\_CH_4$ dev PDB	$d^{13}C\_CO_2$ dev PDB	$d^{2}H\_CH_4$ dev SMOW	$d^{18}O\_CO_2$ dev SMOW
KLX06	554.00	570.00	14713	2/9/2009	Section	–47.8	–14.9	–352	29.5
KLX06	554.00	570.00	14719	2/12/2009	Section	–47.6	–14.5	–351	32.1
KLX06	554.00	570.00	14726	2/23/2009	Section	–44.4	–14.8	–316	30.8

SICADA: isotopes_in_gases.

Table A8-10. Acetate

Idcode	Secup m	Seclow m	Sample no	Sampling date	Water type	Acetate mg L^{-1}
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	0.59
KAS03	107.00	252.00	14747	2009/02/17	Section	0.00
KAS03	627.00	1,002.00	14748	2009/02/17	Standpipe	2.36
KAS03	627.00	1,002.00	14749	2009/02/23	Section	5.27
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	1.19
KAS09	116.00	150.00	14751	2009/03/18	Section	3.53
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	13.7
KLX06	554.00	570.00	14713	2009/02/09	Section	0.00
KLX06	554.00	570.00	14714	2009/02/09	Section	0.59
KLX06	554.00	570.00	14715	2009/02/10	Section	0.00
KLX06	554.00	570.00	14719	2009/02/12	Section	0.00
KLX06	554.00	570.00	14726	2009/02/23	Section	0.6
KLX06	554.00	570.00	14727	2009/05/05	Tubing	40.6
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	0.58
KLX06	554.00	570.00	14729	2009/05/05	Section	1.16
KLX06	554.00	570.00	14731	2009/05/06	Section	1.16

Table A8-11. Discharged volumes.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Water type	Discharged volume before sampling L
KAS03	107.00	252.00	14746	2009/02/17	Standpipe	3
KAS03	107.00	252.00	14747	2009/02/17	Section	5
KAS03	627.00	1,002.00	14748	2009/02/18	Standpipe	3
KAS03	627.00	1,002.00	14749	2009/02/23	Section	35
KAS09	116.00	150.00	14750	2009/03/18	Standpipe	3
KAS09	116.00	150.00	14751	2009/03/18	Section	30
KLX06	554.00	570.00	14712	2009/02/09	Standpipe	3.7
KLX06	554.00	570.00	14713	2009/02/09	Section	16.7
KLX06	554.00	570.00	14714	2009/02/09	Section	34.2
KLX06	554.00	570.00	14715	2009/02/10	Section	76.6
KLX06	554.00	570.00	14716	2009/02/10	Section	95.2
KLX06	554.00	570.00	14718	2009/02/11	Section	167.4
KLX06	554.00	570.00	14719	2009/02/12	Section	257.2
KLX06	554.00	570.00	14720	2009/02/13	Section	360.9
KLX06	554.00	570.00	14721	2009/02/16	Section	781.5
KLX06	554.00	570.00	14722	2009/02/17	Section	870.8
KLX06	554.00	570.00	14723	2009/02/18	Section	1,244
KLX06	554.00	570.00	14724	2009/02/19	Section	1,555.7
KLX06	554.00	570.00	14725	2009/02/20	Section	1,875.5
KLX06	554.00	570.00	14726	2009/02/23	Section	2,956.3
KLX06	554.00	570.00	14727	2009/05/05	Tubing	1.6
KLX06	554.00	570.00	14728	2009/05/05	Standpipe	3.6
KLX06	554.00	570.00	14729	2009/05/05	Section	15.5
KLX06	554.00	570.00	14730	2009/05/05	Section	48.9
KLX06	554.00	570.00	14731	2009/05/06	Section	73.8
KLX06	554.00	570.00	14732	2009/05/07	Section	164.6

Table A8-12. Elemental analysis of solid samples.

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Sample type	Al mg kg^{-1}	Sb mg kg^{-1}	As mg kg^{-1}	Ba mg kg^{-1}	Be mg kg^{-1}	Pb mg kg^{-1}	B mg kg^{-1}	Br mg kg^{-1}	Ce mg kg^{-1}	Cs mg kg^{-1}
KAS09	116.00	150.00	14866	2009/04/01	Solid sample	62,000	0.8	< 5	79	0.8	2	39	< 10	1.6	33
KAS09	116.00	150.00	14867	2009/03/31	Solid sample	1,400	0.4	< 7	107	0.9	< 0.5	< 2	< 10	3.2	21
KAS09	116.00	150.00	14869	2009/03/31	Solid sample	240,000	1.7	< 4	6	0.2	3	98	< 10	< 0.05	< 0.5

Idcode	Secup m	Seclow m	Sample no.	Dy mg kg^{-1}	Er mg kg^{-1}	Eu mg kg^{-1}	P mg kg^{-1}	Gd mg kg^{-1}	Ga mg kg^{-1}	Ge mg kg^{-1}	Au mg kg^{-1}	Hf mg kg^{-1}	Ho mg kg^{-1}	Ir mg kg^{-1}	I mg kg^{-1}	Fe mg kg^{-1}
KAS09	116.00	150.00	14866	0.6	0.6	0.04	120	0.3	1	< 0.5	< 0.05	0.03	0.16	< 0.02	< 3	60,000
KAS09	116.00	150.00	14867	1.2	1.1	0.08	160	0.7	< 0.5	< 0.5	< 0.05	0.03	0.32	< 0.02	< 3	41,000
KAS09	116.00	150.00	14869	< 0.01	< 0.01	< 0.01	35	< 0.01	3	< 0.5	< 0.05	0.13	< 0.01	< 0.02	< 3	92,000

Idcode	Secup m	Seclow m	Sample no.	Cd mg kg^{-1}	Ca mg kg^{-1}	K mg kg^{-1}	Si mg kg^{-1}	Co mg kg^{-1}	Cu mg kg^{-1}	Cr mg kg^{-1}	Hg mg kg^{-1}	La mg kg^{-1}	Li mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	Mo mg kg^{-1}
KAS09	116.00	150.00	14866	< 0.1	220,000	190	5,800	1.9	15	13	< 0.1	1	< 5	4,000	5,600	8.0
KAS09	116.00	150.00	14867	< 0.1	280,000	92	1,800	0.6	5	8	< 0.1	2	< 5	5,600	7,000	5.2
KAS09	116.00	150.00	14869	< 0.1	18,000	200	9,400	5.9	40	47	< 0.1	< 0.05	< 5	1,200	1,100	16

Idcode	Secup m	Seclow m	Sample no.	Na mg kg^{-1}	Nd mg kg^{-1}	Nb mg/kg TS	Ni mg/kg TS	Os mg/kg TS	Pd mg/kg TS	Pt mg/kg TS	Pr mg/kg TS	Re mg/kg TS	Rh mg/kg TS	Rb mg/kg TS	Ru mg/kg TS	Sm mg/kg TS
KAS09	116.00	150.00	14866	1,000	0.9	0.2	12	< 0.02	< 0.5	< 0.01	0.2	< 0.01	< 0.02	3.4	< 0.02	0.25
KAS09	116.00	150.00	14867	1,000	1.8	0.2	4.4	< 0.02	< 0.5	< 0.01	0.4	< 0.01	< 0.02	2.6	< 0.02	0.48
KAS09	116.00	150.00	14869	1,100	< 0.05	0.2	28	< 0.02	< 0.5	< 0.01	< 0.01	< 0.01	< 0.02	< 0.2	< 0.02	< 0.01

mg/kg TS = mg/kg dry substance.

Idcode	Secup m	Seclow m	Sample no.	Se mg/kg TS	Ag mg/kg TS	Sc mg/kg TS	Sr mg/kg TS	S mg/kg TS	Ta mg/kg TS	Te mg/kg TS	Tl mg/kg TS	Sn mg/kg TS	Tb mg/kg TS	Ti mg/kg TS	Th mg/kg TS	Tm mg/kg TS
KAS09	116.00	150.00	14866	< 1	< 0.1	0.2	860	13,000	< 0.1	< 0.5	< 0.1	< 0.6	0.075	31	0.05	0.08
KAS09	116.00	150.00	14867	1.9	< 0.1	0.2	1,100	5,100	< 0.1	< 0.5	< 0.1	< 0.6	0.15	11	0.07	0.18
KAS09	116.00	150.00	14869	1.5	< 0.1	< 0.1	230	10,000	< 0.1	< 0.5	< 0.1	2	< 0.01	47	< 0.01	< 0.01

Idcode	Secup m	Seclow m	Sample no.	U mg/kg TS	V mg/kg TS	Bi mg/kg TS	W mg/kg TS	Yb mg/kg TS	Y mg/kg TS	Zn mg/kg TS	Zr mg/kg TS
KAS09	116.00	150.00	14866	110	6.2	0.04	1.3	0.5	8	38	1.8
KAS09	116.00	150.00	14867	33	2.0	< 0.01	0.6	1.0	17	9.3	2.1
KAS09	116.00	150.00	14869	16	18	0.04	2.8	< 0.01	< 0.05	110	4.3