P-06-127

Oskarshamn site investigation

Hydro chemical monitoring programme for core drilled boreholes 2005

Summary of analyses from water sampling

Pia Wacker, Geosigma AB

September 2006

Svensk Kärnbränslehantering AB

Swedish Nuclear Fuel and Waste Management Co Box 5864 SE-102 40 Stockholm Sweden Tel 08-459 84 00 +46 8 459 84 00 Fax 08-661 57 19 +46 8 661 57 19



ISSN 1651-4416 SKB P-06-127

Oskarshamn site investigation

Hydro chemical monitoring programme for core drilled boreholes 2005

Summary of analyses from water sampling

Pia Wacker, Geosigma AB

September 2006

Keywords: Groundwater, Borehole, Chemical analyses, Isotope determinations, AP PS 400-05-091.

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

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

Abstract

This report summarises water sampling from five sections in permanent installed core-drilled boreholes, KAV01:3, KSH01A:4, KSH01A:7 KSH02:1 and KSH02:4, within the site investigation programme at Oskarshamn. This is the first water sampling performed in the monitoring programme and is planned to be repeated twice every year. The objective is to determine the groundwater composition in the sections instrumented for this purpose.

The results from this activity include groundwater chemistry data in accordance with SKB class 3 chemistry from one section in KAV01 (section 3; 391–434 m), two sections in KSH01A (section 4 and 7; 535–572 and 238–277 m) and two sections in KSH02 (section 1 and 4; 955–963 and 411–439 m). The data were obtained during November 2005.

All analytical data from the activity are stored in the SICADA database.

Sammanfattning

Denna rapport sammanfattar vattenprovtagning från fem sektioner i de permanent installerade kärnborrhålen KAV01:3, KSH01A:4, KSH01A:7 KSH02:1 och KSH02:4 inom platsundersökningen i Oskarshamn. Denna mätning är den första som genomförts i moniteringsprogrammet, framöver är provtagningen planerad att utföras två gånger per år. Syftet är att bestämma grundvattensammansättningen i samtliga för ändamålet instrumenterade borrhålssektioner.

Resultaten från denna aktivitet inkluderar vattenkemidata enligt SKB kemiklass 3 från en sektion i KAV01 (sektion 3; 391–434 m), två sektioner i KSH01A (sektion 4 och 7; 535–572 och 238–277 m) och två sektioner i KSH02 (sektion 1 och 4; 955–963 och 411–439 m). Proverna är tagna under november 2005.

Alla resultat från vattenanalyserna finns i databasen SICADA.

Contents

1	Introduction	7
2	Objective and scope	9
3	Equipment	11
3.1	Description of equipment	11
4	Execution	13
4.1	General	13
4.2	Preparations	13
4.3	Execution of field work	13
4.4	Handling of water analytical data	16
4.5	Water sampling, sample treatment and analyses	17
4.6	Nonconformities	18
5	Results	19
5.1	Basic water analyses	19
5.2	Stable and radioactive isotopes	21
6	Summary	23
App	endix 1 Sampling and analytical methods	25
App	endix 2 Groundwater chemistry data	27

1 Introduction

This document reports data collected within the Hydro chemical monitoring programme for core drilled boreholes 2005, which is one of the activities performed within the site investigation at Oskarshamn. The work was carried out in accordance with activity plan AP PS 400-05-091. Controlling documents for performing this activity are listed in Table 1-1. The activity plan and method description are SKB internal controlling documents. The field work was performed during November 2005 and is reported in the database SICADA, traceable using the activity plan number.

The activity includes water sampling from one section in KAV01 (section 3; 391–434 m), two sections in KSH01A (section 4 and 7; 535–572 and 238–277 m) and two sections in KSH02 (section 1 and 4; 955–963 and 411–439 m) according to SKB chemistry class 3 including options of the isotopes deuterium, tritium and O–18. Determination of density and field measurements of pH and temperature were also performed. Archive samples were stored in a freezer. A map showing the investigation site at Oskarshamn including the boreholes KAV01, KSH01A and KSH02 is presented in Figure 1-1.

Activity plan	Number	Version
Hydrokemiskt moniteringsprogram för kärnborrhål 2005	AP PS 400-05-091	1.0
Method description	Number	Version
System för hydrologisk och meterologisk datainsamling	SKB MD 368.010	1.0 (2004-05-26)

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

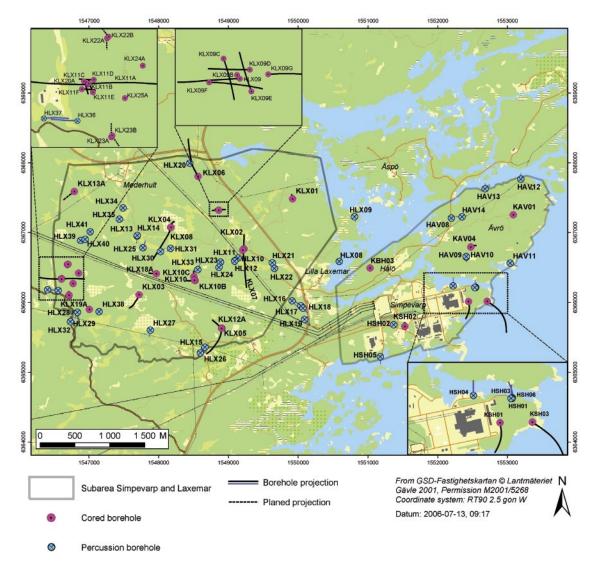


Figure 1-1. Overview of the Oskarshamn site investigation are, including the boreholes KAV01, KSH01A and KSH02.

2 Objective and scope

This report summarises the results from the SKB chemistry class 3 water samples collected within the Hydro chemical monitoring programme for core drilled boreholes 2005, one section in KAV01 and two sections in KSH01A and KSH02 respectively.

According to the general programme for the site investigation area, the core drilled boreholes are monitored. The water sampling is performed in circulation sections that are sealed off using permanently installed packers. The monitoring programme will last at least until the decision about a future repository is made. This activity will present the only water sampling according to Hydro chemical monitoring programme for core drilled boreholes 2005, the first year.

3 Equipment

3.1 Description of equipment

The water sampling is performed in borehole sections with permanently installed packers. The pump equipment used for the water sampling is schematically presented in Figure 3-1.

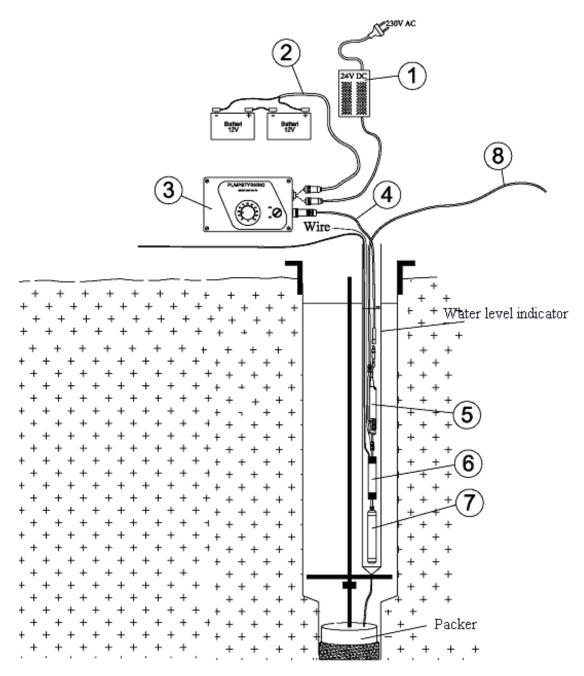


Figure 3-1. Schematic drawing of the equipment used for water sampling; 1. Battery eliminator 2. Battery cable 3. Pump control GEOPUMP UV 45 4. Pump Cable 5. GEOPUMP UV 45 6. Mini packer 7. Filter holder with filter 8. Pump tube, polyamide 8/6 mm.

4 Execution

4.1 General

The water sampling was performed using five identical equipment set-ups, one in each borehole section, a schematic drawing is shown in Figure 3-1. The water volume in the pipe plus the volume in the section should preferably be converted five times, but at least three times before the water sample is taken. The pumping volume is controlled by the down-hole pump. The drawdown is not allowed to exceed 20 m.

All of the pumped water is collected in a tank and emptied onto the rinse plate at Simpevarp.

The activity was performed in accordance with the activity plan AP PS 400-05-091 and following the method description SKB MD 368.010 (System för hydrologisk och metrologisk datainsamling. Vattenprovtagning och utspädningsmätning i observationshål, SKB internal controlling document).

4.2 Preparations

The function of each pump was checked using a bucket. The pipes were cleaned, particles were wiped off, before installation in the borehole.

4.3 Execution of field work

The water sampling was performed in five sections listed in Table 4-1. The samples were taken after conversion of water in each section, at least three times. For a detailed description see method description SKB MD 368.010 (System för hydrologisk och metrologisk datainsamling. Vattenprovtagning och utspädningsmätning i observationshål, SKB internal controlling document).

The logging interval for water level measurements in the borehole sections was changed to log each 5 minute (2005-11-11) in order to determine the maximal drawdown during the sampling period.

	KAV01:3	KSH02:4	KSH02:1	KSH01A:7	KSH01A:4
Volume, pipe+section (L)	35.8	39.3	61.6	37.7	47.9
Volume x 3 (L)	107.5	117.8	184.9	113.1	143.8

The following parameters for each borehole section during the field work are listed in Table 4-2:

- Converted water volume.
- Volume of water sample.
- Drawdown, maximum, during pumping.
- Temperature of water sample measured in the field.
- pH of water sample measured in the field.
- Pump effect, maximum, during pumping.
- Flow during maximum pump effect.
- Date of water sampling.

Pumping was performed twice in KSH02:4, KSH02:1 and KSH01A:4.

The events during the field work are listed in Table 4-3 to 4-7.

After the water sampling, the pumps were left in the borehole sections for Groundwater flow measurements.

Table 4-2. Sampling conditions.

	KAV01:3	KSH02:4	KSH02:1	KSH01A:7	KSH01A:4
Pumped,converted water volume (L)	227.3	265.5 + 470.4	259.3 + 243.2	232.7	102.6 + 165.5
Water sample, volume (L)	4.6	4.6 + 4.6	4.6 + 4.6	5.0	4.6 + 4.6
Maximum drawdown (m.a.s.l.)*	0.2	2.2 and 3.0	6.9 and ~5.5	0.7	6.6 and 12.4
Temperature _{field}	9.8	8.8	7.1	8.1	10.9
pH _{field}	7.5	7.3	8.1	7.6	7.3
Maximum pump effect (%)	80	40 and 50	40 and 40	40	40 and 65
Maximum flow (mL/min)	570	250 and 294	260 and ~166	280	230 and 430
Water sampling date	2005-11-15	2005-11-15 2005-11-18	2005-11-15 2005-11-18	2005-11-15	2005-11-15 2005-11-18

* (m.a.s.l.) metre above see level.

Table 4-3. Events in KAV01, 391–434 m, section 3.

Date	Events Improvement/deviation	SKB sample no.
2005-11-11	Deflation of packer.	
2005-11-14	Installation of pump.	
2005-11-15	Start of pump.	
	Water sampling: SKB class 3. T _{field} = 9.8°C, pH _{field} = 7.48 Stop of pump.	10611

Date	Events Improvement/deviation	SKB sample no.
2005-11-10	Deflation of packer.	
2005-11-11	Installation of pump.	
2005-11-14	Start of pump.	
2005-11-15	Water sampling: SKB class 3. T_{field} = 8.1°C, pH _{field} = 7.55	10615
	Stop of pump.	

Table 4-4. Events in KSH01A, 238–277 m, section 7.

Table 4-5. Events in KSH01A, 532–572 m, section 4.

Date	Events Improvement/deviation	SKB sample no.
2005-11-10	Deflation of packer.	
2005-11-11	Installation of pump.	
2005-11-15	Start of pump.	
	Water sampling: SKB class 3 (pH, electric conductivity, HCO_3^- , CI^- , SO_4^{2-} , Br^- , F^- and density) T_{field} = 7.5°C, pH _{field} = 6.99	10614
	Converted volume, not enough.	
2005-11-18	Start of pump.	
	Water sampling: SKB class 3. T _{field} = 10.9°C, pH _{field} = 7.25	10635
	Stop of pump.	

Table 4-6. Events in KSH02, 411–439 m, section 4.

Date Events Improvement/deviation		SKB sample no.
2005-11-10	Deflation of packer.	
2005-11-11	Installation of pump.	
2005-11-14	Start of pump.	
2005-11-15	Water sampling: SKB class 3. The sample was discarded due to the presence of a smell and an oily film on top of the sample portions.	10613
	Stop of pump.	
2005-11-17	Deflation of packer, filter and tube were exchanged.	
2005-11-17	Start of pump.	
	Reduced smell.	
2005-11-18	Water sampling: SKB class 3. $T_{field} = 8.8^{\circ}C, pH_{field} = 7.31$	10634
	Stop of pump.	

Date	Events Improvement/deviation	SKB sample no.
2005-11-10	Deflation of packer.	
2005-11-11	Installation of pump.	
2005-11-14	Start of pump.	
2005-11-15	Water sampling: SKB class 3. The sample was discarded due to the presence of a smell and an oily film on top of the sample portions.	10612
	Stop of pump.	
2005-11-17	Deflation of packer, filter and tube were ex- changed.	
2005-11-17	Start of pump.	
	Reduced smell.	
2005-11-18	Water sampling: SKB class 3. Tfield= 7.1°C, pHfield=8.08	10633
	Stop of pump.	

Table 4-7. Events in KSH02, 955–963 m, section 1.

4.4 Handling of water analytical data

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

Some of the constituents are determined by more than one method and/or laboratory. All analytical results are stored in the SICADA database. The applied hierarchy path "Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database" contains two types of tables, raw data tables and primary data tables (final data tables).

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

- Comparison of the results from different laboratories and/or methods.
- Calculation of charge balance errors, equation (1). Relative errors within ± 5% are considered acceptable.

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

• General judgement of plausibility based on earlier results and experience.

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

An overview of the data management is given in Figure 4-1.

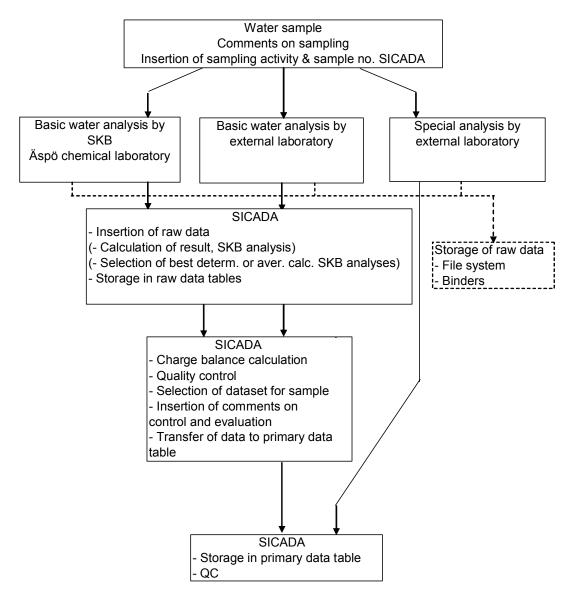


Figure 4-1. Overview of data management for hydrogeochemical data.

4.5 Water sampling, sample treatment and analyses

The pumped water from the borehole section is conveyed from the pipe into the sample bottles. The sampling bottles consist of one 5 litre plastic can, one acid washed plastic bottle for main components and a bottle for tritium. Filtration was performed at the Äspö laboratory before portioning into sample bottles. A water sample is defined as groundwater collected during one day and consists of several sample portions, labelled with the same sample number.

An overview of sample treatment and analysis methods is given in Appendix 1. The routines are applicable independently of sampling method or type of sampling object. One sample (10634) was sent for control analysis of main components to a control laboratory.

4.6 Nonconformities

Nonconformities during the activity:

- No extra sample for analysis of Br, from the deepest section in each borehole, was sent for analysis.
- Missing data of Uranine, converted to drill water content, from KAV01:3 and KSH01A:7.
- In KSH01A:4, not enough water was converted before the first sample was taken therefore, a second sample was taken.
- In each of the borehole sections KSH02:4 and KSH02:1 the first samples were discarded due to an oily film on the top of the sample portions, therefore, a second sample was taken in each section.

5 Results

The results obtained within this activity are water chemistry data from borehole sections KAV01:3, KSH01A:7, KSH01A:4, KSH02:4 and KSH02:1. The second sampling occasion in KSH01A:4 are denoted KSH01A:4:2. The results from the chemical analysis are presented below. The results are stored in the SICADA data base and are traceable by the activity plan number and sample number. It is the data in the data base that will be used for further interpretation (modelling).

5.1 Basic water analyses

The basic water analyses include Na, K, Ca, Mg, Si, Li, S, Sr, SO_4^{2-} , Cl⁻, HCO_3^{-} , Br⁻ and F⁻. Furthermore, measurements are made of pH, electrical conductivity, drill water content and density. The basic water analysis data and relative charge balance errors are compiled in Appendix 2, Table A2-1.

The charge balance error gives an indication of the quality and uncertainty of the analyses of major constituents. The charge balance error exceeds the acceptable level of \pm 5% in one case, for KSH01A:7.

The drill water content in the samples collected during the pumping/measurement periods in the borehole sections are compiled in Appendix 2, Table A2-1.

Values of pH from laboratory and field analyses are compared in Figure 5-1.

Sulphate (SO₄^{2–}) analysed using ion chromatography (IC) is compared with sulphate determined as total sulphur using inductively coupled plasma atomic emission spectrometry (ICP-AES) in Figure 5-2.

The chloride concentrations are plotted versus the corresponding electric conductivity values in Figure 5-3. The plot gives an approximate indication that the values are reasonable. The data from the borehole sections agree well with earlier data from the Äspö Hard Rock Laboratory.

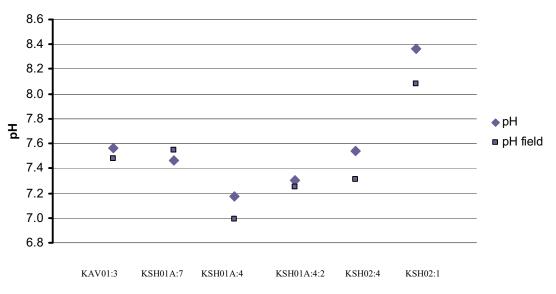


Figure 5-1. pH from laboratory and field analyses.

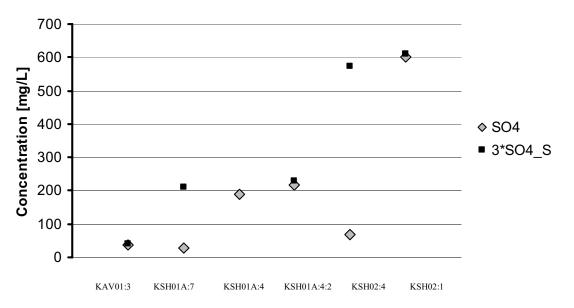


Figure 5-2. Sulphate (SO₄ by IC) data compared to sulphate calculated from total sulphur ($3 \times SO_4$ -S by ICP) data from samples collected in the investigated sections.

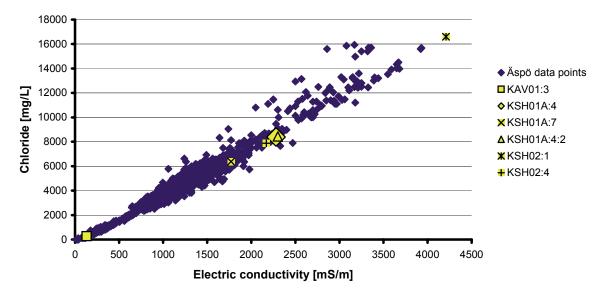


Figure 5-3. Chloride concentration versus electrical conductivity. Data from earlier investigations at the Äspö Hard Rock Laboratory are used to show the overall trend.

5.2 Stable and radioactive isotopes

The isotope determinations include the stable isotopes $\delta^2 H$, and $\delta^{18}O$ as well as the radioactive isotope ³H (TU). The isotope data are compiled in Appendix 2, Table A2-2.

The ³H and δ^{18} O results from the investigated sections are presented in Figure 5-4. The ³H content was below the detection (BD) limit (0.8 Tritium Units (TU)) in KSH02A, section KSH02:4 and KSH02:1.

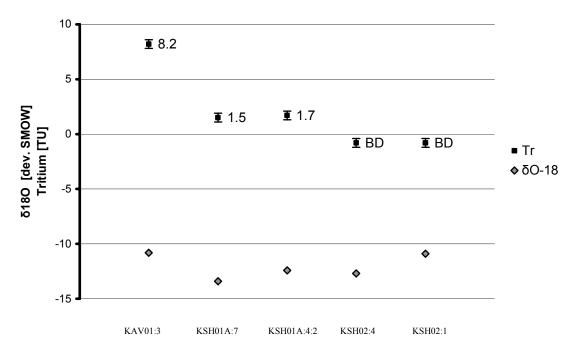


Figure 5-4. ³*H* and $\delta^{18}O$ data from samples collected in the investigated sections.

6 Summary

- Comparison of the results from different laboratories and/or methods showed agreement in most cases.
- The charge balance error exceeds the acceptable level of \pm 5% in one case, for KSH01A:7.
- General judgement of plausibility based on earlier results and experience indicated reasonable values, in most cases.

Appendix 1

Sampling and analytical methods

Table A1-1. Sample handling routines and analytical methods. SKB class 3 chemistry.

Analysis	Sample container (material)	Preparation	SKB label	Analysis method	Comment
pH, conductivity, alkalinity	250 ml plastic	-	Green	Titration Pot. meas, Cond. meas	Analysed within 24 hours.
Anions (F⁻, Br⁻, Cl⁻, SO₄²⁻)	250 ml plastic	Filtering in connection with analysis	Green	Titration (Cl⁻) IC (Cl⁻, SO₄²⁻, Br⁻, F⁻) ISE (F⁻)	
Uranine	100 ml brown glass	-	Green		
Density	250 ml	-	Green	Pycnometer	
Cations: Na, K, Ca, Mg, Si, Li, Sr and S	Analytica's 100 ml acid washed	1 ml HNO ₃ suprapur, filtering membrane filter	Red	ICP-AES ICP-MS	
Archive samples	2 × 250 ml plastic	Filtering Pallfilter	Green		Stored in a freezer.
Deuterium, O-18	100 ml square plastic	-	Green	MS	
Tritium	500 ml dried plastic	-	Green	LSC	Flooded at least once.

Component	Method	Detection limit	Reporting limit or range	Unit	Measurement uncertainty ²	"Total" uncertainty ³
HCO₃	Alkalinity titration	0.2	1	mg/L	4%	<10%
Cŀ Cŀ	Mohr titration IC	5 0.2	70 0.5	mg/L	5% 6%	<10% 10%
SO ₄	IC	0.2	0.5	mg/L	6%	15%
Br- Br-	IC ICP	0.2	0.7 0.001–0.010 ¹	mg/L	9% 15%	20%
F- F-	IC Potentiometry	0.2	0.6	mg/L	10% _	20% _
Na	ICP	-	0.1	mg/L	4%	10%
К	ICP	-	0.4	mg/L	6%	15%
Са	ICP	_	0.1	mg/L	4%	10%
Mg	ICP	-	0.09	mg/L	4%	10%
S(tot)	ICP	_	0.160	mg/L	10%	15%
Si(tot)	ICP	-	0.03	mg/L	4%	15%
Sr	ICP	-	0.002	mg/L	4%	15%
Li	ICP	-	0.2–2 ¹	μg/L	10%	20%
δ²H	MS	-	2	‰ SMOW ⁴	1.0‰	-
δ18Ο	MS	-	0.1	‰ SMOW ⁴	0.2‰	-
³Н	LSC	-	0.8 or 0.1	TU⁵	0.8 or 0.1 TU	-
Density	Pycnometer	_	-	g/mL	0.15%	-

Table A1-2. Reporting limits and measurement uncertainties.

1. Reporting limits at salinity \leq 0.4% (520 mS/m) and \leq 3.5% (3,810 mS/m) respectively.

2. Measurement uncertainty reported by consulted laboratory, generally 95% confidence interval.

3. Estimated total uncertainty by experience (includes effects of sampling and sample handling).

4. Per mill deviation⁶ from SMOW (Standard Mean Oceanic Water).

5. TU=Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10⁻¹⁸ (1 Bq/L Tritium = 8.45 TU).

6. Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:

 $\delta^{y}I = 1,000 \times (K_{sample} - K_{standard})/K_{standard}$, where K= the isotope ratio and $yI = {}^{2}H$ or ${}^{18}O$.

Appendix 2

Groundwater chemistry data

Table A2-1. Water composition.

KAV01	391.00		uo.	date and time	time	рн теіа	lemperature tield degree Celcius		Charge Bal %	Na mg/L	K mg/L	ca mg/L	Mg mg/L	HCO ₃ - mg/L	CI ⁻ mg/L	SO4 ²⁻ mg/L
		434.00	10611	2005/11/1	2005/11/15 15:24:00	7.48	9.8	1	-1.35	163	3.94	80.3	8.7	228	269	38
KSH01A	200.002	277.00	10615	2005/11/1	2005/11/15 16:26:00	7.55	8.1		10.01	2,790	12.00	2,010	42.9	21	6,380	27
KSH01A	532.00	572.00	10614	2005/11/1	2005/11/15 16:26:00	6.99	7.5		I	I	I	I	I	39	8,390	188
KSH01A	532.00	572.00	10635	2005/11/1	2005/11/18 14:35:00	7.25	10.9	1	-2.64	2,840	11.50	2,070	42.2	22	8,440	216
KSH02	411.00	439.00	10634	2005/11/1	2005/11/18 14:05:00	7.31	8.8	1	-3.69	2,960	11.50	1,780	12.9	96	7,880	68
KSH02	955.00	963.00	10633	2005/11/1	2005/11/18 14:05:00	8.08	7.1		-0.66	4,910	14.80	5,200	5.7	7	16,600	602
ldcode	Secup m	Seclow m	Sample no.	SO₄-S mg/L	Br mg/l	F- mg/L	Si Fe mg/L mg	Fe mg/L	Mn mg/L	Li mg/L	Sr mg/L	Hq	Drill _%	Drill_water %	ElCond mS/m	Density g/mL
KAV01	391.00	434.00	10611	13.3	1.3	2.26	6.83 0	0.390	0.5350	0.057	0.94	7.56	I		131	0.9971
KSH01A	238.00	277.00	10615	70.6	32.2	1.14	6.34 0	0.762	0.5640	0.567	34.60	7.46	I		1,770	1.0040
KSH01A	532.00	572.00	10614	I	57.8	1.48	I	I	I	I	I	7.17	I		2,280	1.0067
KSH01A	532.00	572.00	10635	76.9	58.3	1.46	5.73 0	0.452	0.4610	0.576	35.90	7.30	12.50	0	2,300	1.0066
KSH02	411.00	439.00	10634	191.0	52.7	1.41	9.85 <0	<0.04	0.1390	0.363	30.10	7.54	16.20	0	2,170	1.0055
		00000														

ldcode	Secup m	Seclow m	Sample no	Sampling date and time	δ²H dev SMOW	³H TU	δ ¹⁸ O dev SMOW
KAV01	391.00	434.00	10611	2005/11/15 15:24:00	-78.3	8.2	-10.8
KSH01A	238.00	277.00	10615	2005/11/15 16:26:00	-99.8	1.5	-13.4
KSH01A	535.00	572.00	10635	2005/11/18 14:35:00	-89.7	1.7	-12.4
KSH02	411.00	439.00	10634	2005/11/18 14:05:00	-92.8	<0.8	-12.7
KSH02	955.00	963.00	10633	2005/11/18 14:05:00	-78.0	<0.8	-10.9

Table A2-2. Isotopes I (H-, O-, B-, S-, CI- and C-isotopes).