An Evaluation of Methanol Impact on Groundwater and Subterranean Seawater Quality

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Introduction

At the Carbon Recycling International methanol plant in Svartsengi, effluent containing methanol is being discharged into well SV-1. The main focus of this project was to respond to comments of authorities regarding the possible contamination of methanol into the fresh groundwater above as well as the issue of the methanol accumulating in the subterranean seawater around the injection part of the well. This short report presents results of numerical modelling and discusses the fate of methanol in the aquifers. This project is conducted at the request of Carbon Recycling International.

Methods and data

Methanol impact on the groundwater and underlying subterranean seawater is assessed using numerical modelling. For this purpose, the Visual MODFLOW software was employed. Visual MODFLOW simulates three-dimensional groundwater flow through porous media. For this project, two numerical codes were implemented to determine the fate of methanol. First of all, *MODFLOW-2000* was applied to define the groundwater flow in the area (Harbaugh et al., 2000). Secondly, *MT3DMS* was implemented to determine the distribution and behaviour of methanol in the aquifers (Zheng and Wang, 1999).

Effluent from CRI´s plant will bedischarged into well SV-1 in the vicinity of the plant. The well is 262 m deep, cased down to 238 m depth and has a perforated liner between 238 and 262 m depth, where the effluent can exit the well.

The underlying geology determines groundwater and effluent flow in the area. It is known that hyaloclastite and tuff formations lie between 165 and 220 m depth (Arnórsson et al., 1975) (Annex 1). Naturally, these formations have a low hydraulic conductivity and groundwater movement though such media is limited (Franzson et al., 2011). Underlying basaltic breccia (220–262 m depth) has relatively high hydrolic conductivity; hence both groundwater and effluent can be transmitted easily (Arnórsson et al., 1975; Annex 1). Groundwater flow direction was determined using available groundwater level measurements around study area, sea level, surface elevation and the Vatnaskil regional groundwater model (Vatnaskil, 2015). Groundwater in the study area flows from north to south, in agreement with the general rule of thumb that groundwater flows from higher to lower elevations.

Groundwater conductivity below 30 m depth is 40000 µS/cm, which indicates that fresh groundwater overlies subterranean seawater (Hafstað, 2015; Annex 2). Hence, the effluent is discharged into subterranean seawater below impermeable hyaloclastite and tuff formations. The chemical composition of the effluent is quite variable, as it is a mixture of several components; mineral-rich water (1500 L/h), steam condensate (2000 L/h), water from distillation and vent scrubbing (600 L/h) and variable amounts of rainwater (Sigurðsson, 2016). The average injection rate is 0.7 L/s, with discharge temperature ~50°C and average methanol concentration of 536 mg/L (Þórðarson, 2017).

Simulation

The fate and transport of methanol released into the subterranean seawater was evaluated by performing several numerical simulations. In each numerical simulation, hydrogeological parameters and dispersivity were adjusted, whereas methanol injection rate (0.7 L/s), concentration (536 mg/L) and discharge depth (238–262 m) remained unchanged. No degradation of the methanol was taken into account.

The initial simulation was based on the geological setting of well SV-1 (Arnórsson et al., 1975) and typical conductivity values for each geological unit were assigned. It is assumed that conductivity of the aquifer (basaltic breccia) where methanol is injected is 0.0001 m/s and the conductivity of the overlying aquitard (hyaloclastite and tuff) is 0.000001 m/s (Figure 2). As the overlying aquitard has relatively low conductivity it is assumed that vertical groundwater movement is negligible.

Groundwater flow, the fate and transport of methanol was evaluated in the context of three periods: 1) 1 week; 2) 1 month; 3) 70 days. The obtained results indicate that after one week of constant injection, maximum methanol concentration in the aquifer is 8 mg/L and the radius of methanol distribution around the well is approximately 38 m (Figure 1). After one month of injection, methanol concentration in the aquifer has increased up to 200 mg/L and the methanol plume expanded to 75 m (Figure 1). Both simulations indicate that the methanol impact is local and affects groundwater just in the proximity of the well. On the other hand, both methanol and groundwater movement southwards are observed when numerical simulations are run for a longer period of time. After 70 days of constant effluent injection, the maximum methanol concentration around the well equals to 300 mg/L and the plume radius has increased to 90 m (Figures 1 and 2). From the performed simulations, it is clear that the effluent is slowly moving southwards and does not accumulate around the well.

For further simulations, the hydraulic bedrock conductivity was adjusted as well as its dispersivity. It was observed that with greater hydraulic conductivity the effluent is distributed to greater distances, whereas lower hydraulic conductivity results in a narrower distribution of the effluent. Increased dispersion values reduced the methanol concentration in aquifer. Nevertheless, all performed simulations confirmed minimal effluent dispersion around the well.

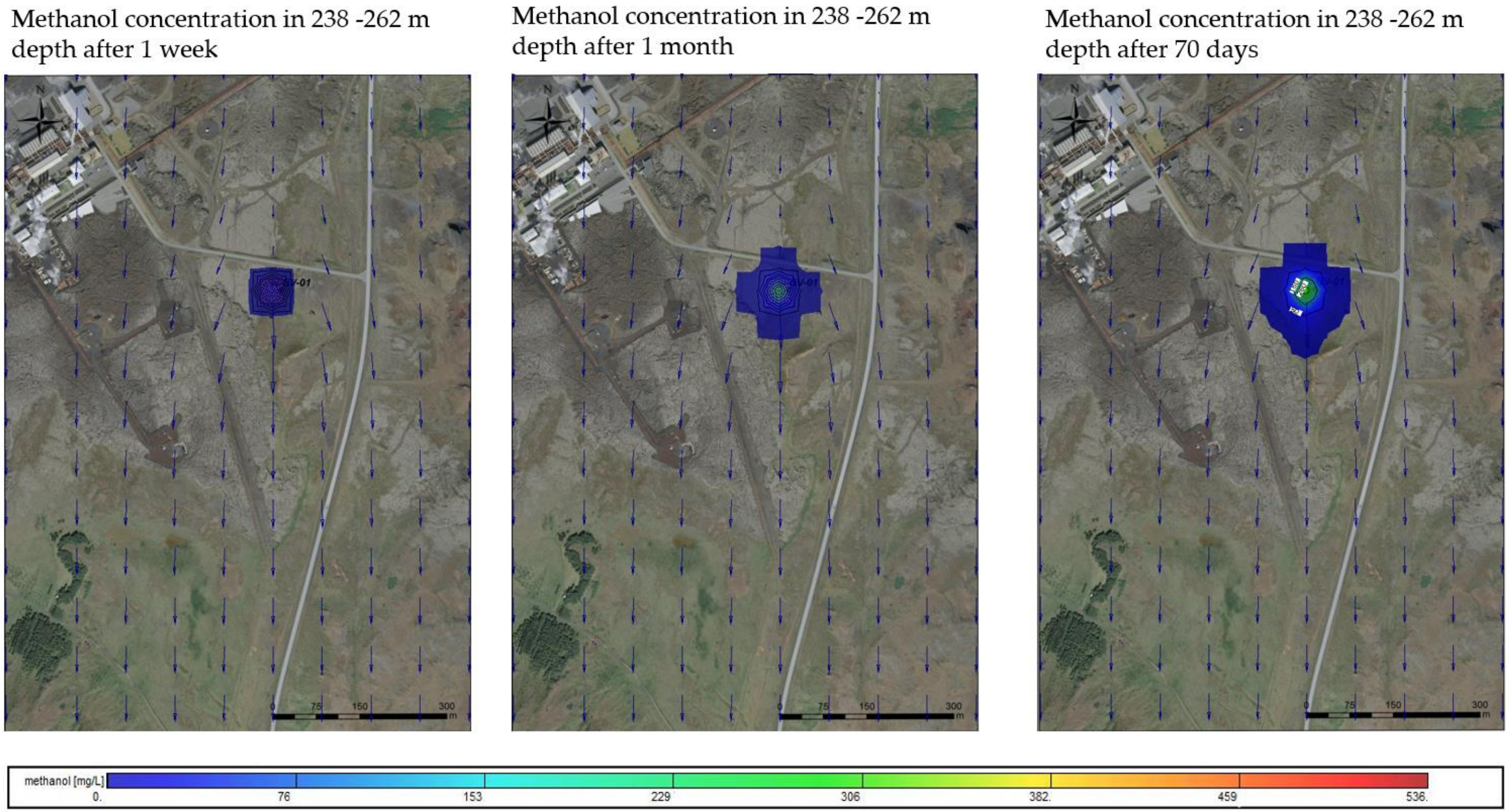

Figure 1. *Methanol concentration between 238 and 262 m depth after 1 week, 1 month and 70 days of injection. Colour gradient on the map indicate methanol concentration (0 to 536 µg/L) and blue arrows indicate groundwater flow direction.*

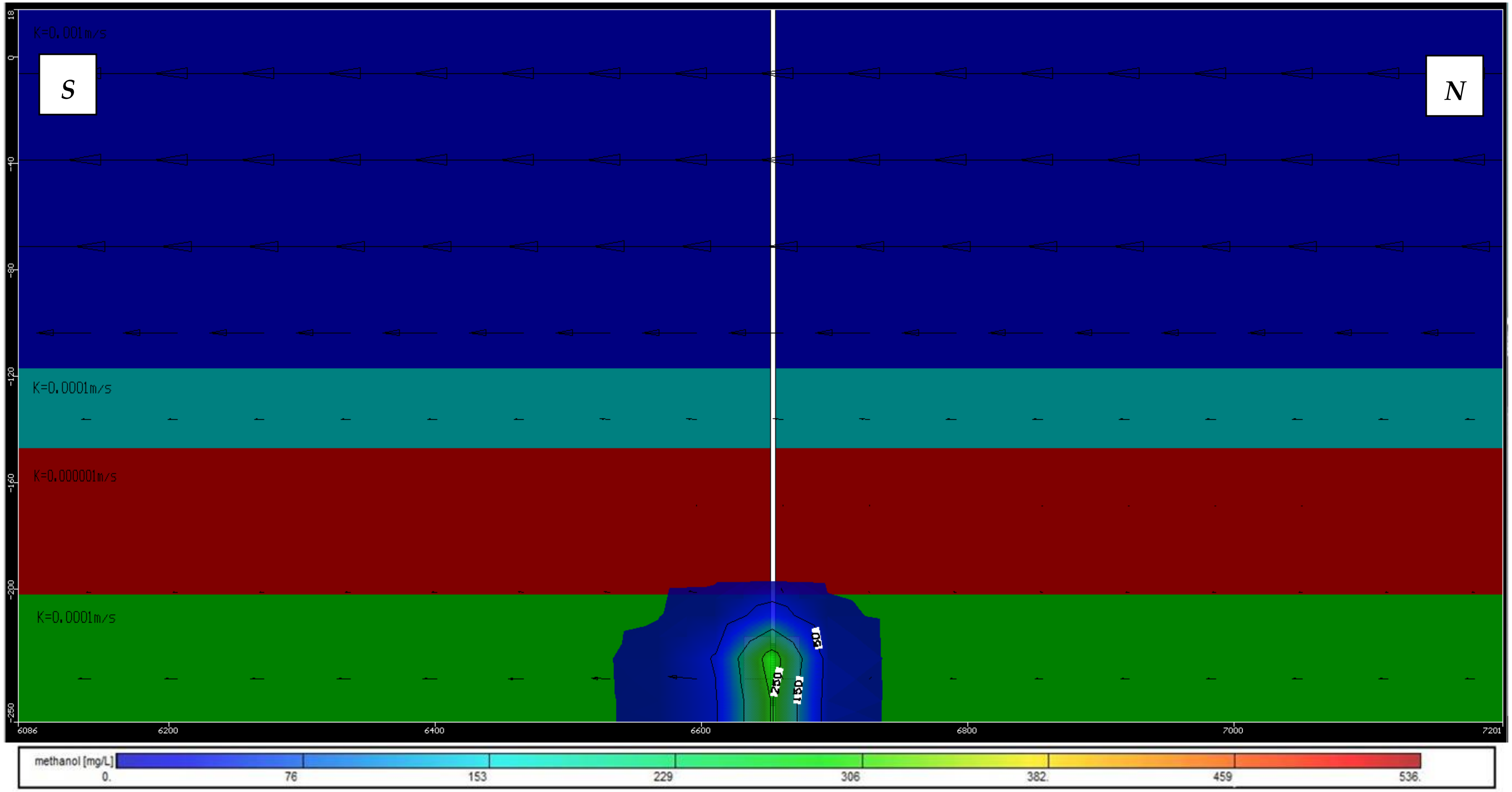

Figure 2. *Methanol concentration in S-W cross section after 70 days of injection. Colour gradient on the image indicates methanol concentration (0 to 536 µg/L), arrows indicate groundwater flow direction and relative flow rates and different colours in the cross section indicate conductivity (K) values of each geological unit (dark blue, K=0.001 m/s, light blue, K=0.0001 m/s, red, K=0.000001 m/s, green, K=0.0001 m/s).*

Methanol degradation

The performed numerical simulations only take into account the physical properties of methanol. Therefore the results do not reflect how methanol concentration may change due to degradation in the aquifer. Methanol is miscible with water and readily degrades in both aerobic and anaerobic groundwater conditions (Novak et al., 1985). Aronson and Howard (1997) summarised data from both field and laboratory experiments on methanol biodegradation in different environments, and found first order rate constants ranging from 0.0022 d^{-1} ($t_{1/2}$ = 315 d) to 0.88 d^{-1} ($t_{1/2}$ = 0.8 d) with an average half-life of about 8 days. Assuming the average half-life, after 70 days the initial concentration of methanol in the effluent would have been reduced 430-fold, i.e. to about 1.2 mg/L due to biodegradation. The actual methanol concentrations are therefore expected to be lower than those predicted by the simulations.

Other chemical aspects

This study has focused on methanol, and the results show that it is very unlikely that methanol in the suggested concentrations will have substantial effects on the aquifer chemistry or water-rock interaction. This is because of the low effluent flow-rate and methanol degradation. The distribution of other chemical components from the effluent in the aquifer as well as the impact of fluid mixing will be comparable, even though a more complete chemical analysis of the effluent is needed.

The chemistry of the subterranean seawater may be fairly well approximated using chemical data from nearby wells, such as HSK-11 (Hafstað and Kristinsson, 2011), which has the composition of slightly altered seawater (higher SiO_2, lower Mg) at a depth of 100 m. In particular, the sulphate concentration of the water is about 2300 mg/L, suggesting that electron acceptors for the degradation of methanol should be abundant and the degradation rates high (Novak et al., 1985).

An attempt was made to estimate the dilution of the subterranean seawater by the effluent from the CRI plant, as the subterranean seawater is regarded as a potential resource e.g. for fish farming. Chemical analysis of the subterranean seawater around well SV-1 is not available. The seawater resource is located within the area of the Svartsengi geothermal field, above the cap rock of the high temperature geothermal system. Rising steam derived from the boiling of the geothermal fluid (in a steam cap) has affected the chemical composition and the electric conductivity observed in well SV-1 (fig. 2 in Annex 2) where the salinity of fluid at 30 m depth is approx. 85% that of seawater.

To give an estimate of the possible magnitude of the effect involved, the results of a simple volumetric, average calculation is presented. The calculation is based on the following assumptions made regarding the flow and composition of the effluent, size and porosity of the aquifer and the size of the subterranean seawater resource: 1) The effluent water consists of 1 L/s fresh water, which is slightly more than the 0,7 L/s presented in a memo from CRI (Sigurðsson, 2016). 2) The aquifer available is 100 m thick, based on the vertical distance from the exit point of the effluent water in the well to the estimated top of the cap rock of the geothermal system (Franzson, 2017). 3) The porosity of the bedrock in that depth-range is 15% (Franzson, 2017). 4) The size of the resource is 1 km in width (Vatnaskil, 2015) and 3 km long, hence having a total volume 0.3 km^3. 5) No groundwater flow is assumed. It should be noted that most of these assumptions make the calculation results conservative regarding the dilution. The purpose of the calculation and assumptions is to indicate the maximum possible average dilution to be expected at the conditions around well SV-1, using the limited data available.

Based on the assumptions presented, the calculated average dilution of the subterranean seawater resource around well SV-1 is about 0.07% pr. year, which can be considered insignificant. The regional flow of the subterranean seawater, which is neglected in the calculations, will reduce the dilution.

Conclusions

According to the numerical simulations, taking into account the geological settings and chemical properties of methanol, methanol in the effluent from CRI´s plant has a local and limited impact on the subterranean seawater aquifer at 238–262 m depth. Furthermore, due to the low hydraulic conductivity of the overlying geological units it is very unlikely that injected methanol will have an impact on the overlying fresh groundwater. Simulations of the methanol plume performed with the Visual MODFLOW software, suggest that the effluent impact on the aquifer reaches less than 90 m around the injection point after 70 days of injection. The plume is distorted towards the south, as it follows the flow of the subterranean seawater.

Based on the data presented in this report; the current amount and composition of the effluent fluid, hydrological model for the Reykjanes Peninsula and stratigraphy from well SV-1, the results of the simulations in this report indicate no long term affect from the disposed effluent from CRI on the subterranean seawater in the Svartsengi area. It should be noted that the discharge well of the CRI plant is located within the high temperature geothermal field of Svartsengi. The geothermal field is estimated to be about 30 km^2 in size (Ketilsson J. et al. 2009) and results presented here indicate that the maximum area of seawater affected, around well SV-1, to be about 0,04 km^2. The Svartsengi geothermal field has been in production since 1976 and recent modelling of reinjection into the geothermal reservoir of Svartsengi indicates that injection of 115 kg/s of a 95°C brine from the power plant into the 240°C reservoir will result in cooling of less than a tenth of a degree (Óskarsson and Galeczka, 2017; Sverrisdóttir, 2016).

Methanol is a simple organic compound which biodegrades readily in aerobic and anaerobic environments. Taking into account the kinetics of methanol degradation, the methanol concentration in the initially 536 mg/L effluent should have decreased to about 1.2 mg/L after 70 days in the aquifer. Groundwater flow, dispersion and degradation ensures that methanol from the effluent does not accumulate around the injection point and the area of impact will not exceed 90 m from well SV-1.

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Annex 1

Geological column of well SV-1 determine groundwater flow in the study area (Arnórsson et al., 1975). Hyaloclastite and tuff formations lie between 165 m and 220 m depth and basaltic breccia lie between 220 m and 262 m depth (Figure 1).

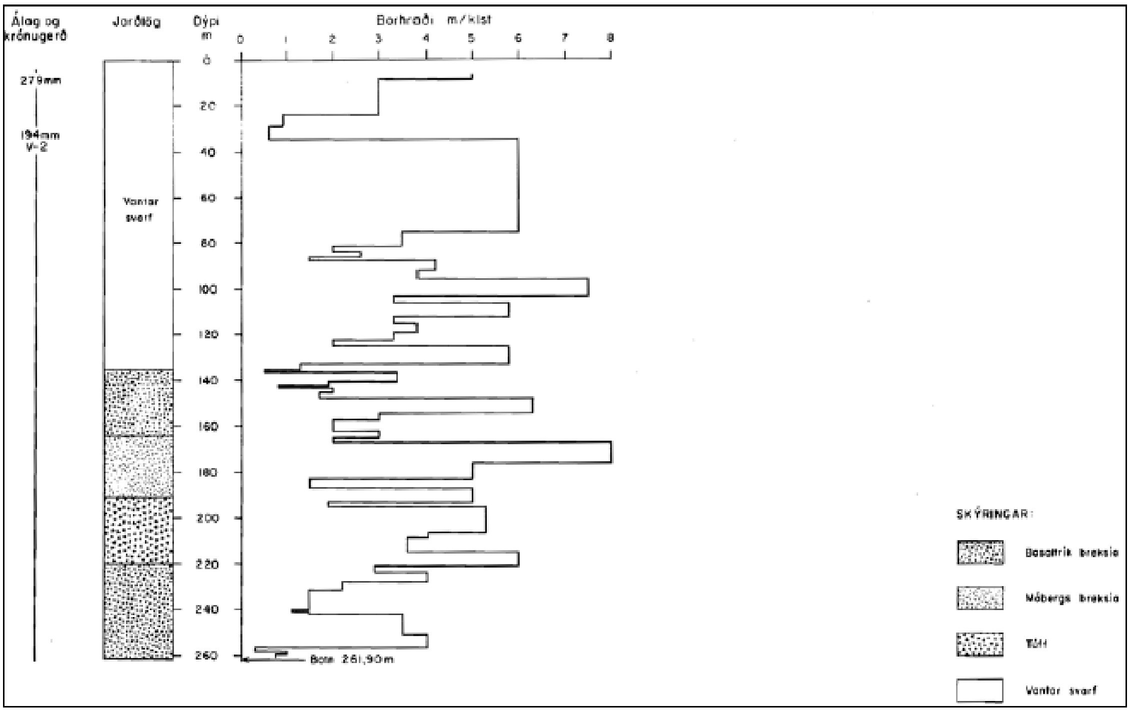
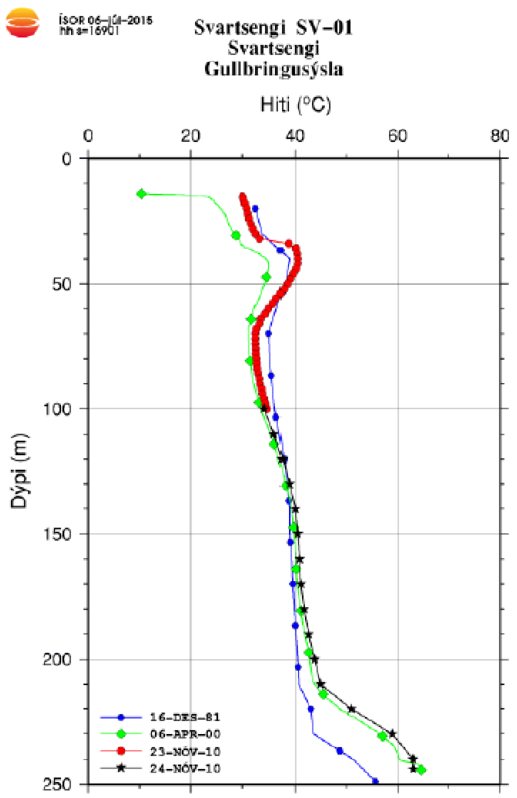


Figure 1. *Geological column of well SV-1. Tuff, hyaloclastite and basaltic breccia are identified in well SV-1.*

Annex 2

In 2010 groundwater conductivity and temperature were measured in well SV-1 (Hafstað, 2015) (Figure 1 and 2). Groundwater temperature steadily increases with depth, i.e. 34.2°C at 100 m depth and 45°C at 210 m. Sharp groundwater temperature increase is observed between 210 m and 240 m depth, where temperature increases from 45°C to 63°C (Figure 2). Conductivity measurements indicate that at 30 m depth conductivity increases sharply from 174 to 40000 µS/cm (Figure 2). High groundwater conductivity indicates a transition from fresh groundwater to subterranean seawater.



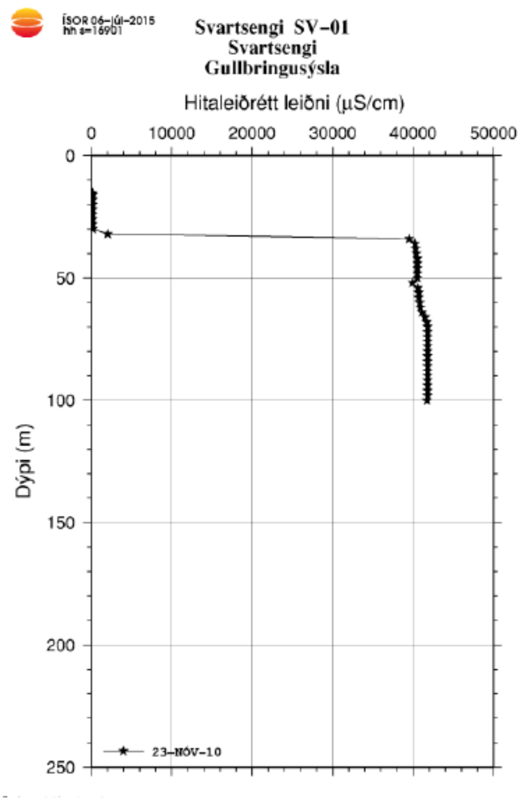


Figure 1. *Temperature measurements in SV-1.* **Figure 2.** *Conductivity measurement in SV-1.*