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**Title page**

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4 Title: Analysis of <sup>3</sup>H, <sup>36</sup>Cl, <sup>133</sup>Ba, <sup>134</sup>Cs and <sup>22</sup>Na from synthetic granitic groundwater: an  
5 in-situ through diffusion experiment at ONKALO

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11 **Analysis of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{133}\text{Ba}$ ,  $^{134}\text{Cs}$  and  $^{22}\text{Na}$  from synthetic**  
12 **granitic groundwater: an in-situ through diffusion**  
13 **experiment at ONKALO**

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19 **Abstract**

20 A method for analyzing  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  from simulated groundwater  
21 (SGW) samples was introduced. Gamma emitting radionuclides  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$   
22 were measured by using an HPGe-detector. Beta emitting  $^3\text{H}$  and  $^{36}\text{Cl}$  were separated  
23 from gamma emitting  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$ . AgCl precipitation was used for the  
24 separation of  $^{36}\text{Cl}$  from SGW samples with yields of  $98 \pm 2\%$ .  $^3\text{H}$  was separated by  
25 distillation with recoveries of  $97 \pm 3\%$ . This method was used for the determination of  
26 activity concentrations of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  in SGW samples collected from  
27 an in-situ through diffusion experiment (TDE).

28 **Keywords**

29  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{133}\text{Ba}$ ,  $^{134}\text{Cs}$ ,  $^{22}\text{Na}$ , distillation, AgCl precipitation, gamma spectroscopy, liquid  
30 scintillation counting

## 31 **Introduction**

32 The final disposal of spent nuclear fuel (SNF) from present nuclear power plants in  
33 Finland (Olkiluoto and Loviisa) is planned to take place in a crystalline granitic rock at  
34 Olkiluoto island (Eurajoki, Finland) [1]. The SNF will be protected by multiple barrier  
35 system. The fuel elements are placed into iron canisters with an outer layer of copper.  
36 The canisters are sealed and placed in vertical holes drilled in tunnels around 420 meters  
37 below ground, in Olkiluoto island. In the vertical holes, the canisters are embedded in  
38 compacted bentonite clay. The tunnels will be backfilled and the last barrier will be the  
39 bedrock itself. Behavior of radionuclides in fractured crystalline rock has been studied for  
40 the safety assessment calculations [2, 3]. The evaluation of the safety is done for  
41 hundreds of thousands of years in the final disposal site [4]. If released into the bedrock,  
42 radionuclides will be transported by advection along water conducting fractures and their  
43 retardation may occur by molecular diffusion from the fractures into the stagnant pore  
44 water and/or by sorption onto mineral surfaces in the adjacent rock matrix [5].

45 In-situ diffusion experiments in crystalline rock have been performed in several countries  
46 e.g. Sweden [6, 7, 8], Switzerland [9, 10] and Canada [11, 12] to demonstrate the  
47 behavior of radionuclides which might be released from the canisters into the bedrock in  
48 the disposal site of spent nuclear fuel. In 1996, in Canada series of in-situ experiments  
49 with iodide were conducted to study diffusion in sparsely fractured rock (SFR) [11, 12].  
50 In Switzerland, the retention of several radionuclides was studied in-situ in Grimsel  
51 granodiorite via a long-term diffusion (LTD) experiment [9, 10]. In Sweden at the Äspö  
52 Hard Rock Laboratory, a Long Term Diffusion Experiment (LTDE) studied retention of  
53 22 radionuclides in granodiorite [7, 8]. The focus in the Swedish experiment was more  
54 directed towards sorption rather than diffusion due to the relatively short experimental  
55 time of about six months.

56 The laboratory data of rock porosity and diffusion might be overestimated because of  
57 drilling artefacts caused by stress release and/or prehandling the rock core samples by  
58 sawing. The data that is used in safety case calculations is conservative and performed  
59 mostly in laboratory conditions. The in-situ experiments are performed to increase  
60 understanding and realism of diffusion data. This is the first time that diffusion of  
61 radionuclides is studied in-situ in Olkiluoto. In addition, this is one of the first through  
62 diffusion experiments in-situ in the world.

63 A project “rock matrix REtention PROPERTIES” (REPRO) at ONKALO, which is the  
64 underground rock characterization facility in Olkiluoto, Finland, consists of extensive  
65 series of in-situ sorption and diffusion experiments that are supplemented by laboratory  
66 work [13, 14]. One of these in-situ experiments is a Through Diffusion Experiment  
67 (TDE) launched in autumn 2015 for studying the diffusion and sorption of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  
68  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  in the Olkiluoto bedrock. The bedrock in the experimental site is mainly  
69 veined gneiss with veins of coarse-grained pegmatitic granite. The veined gneiss shows a  
70 weak to moderate banded foliation but locally also irregular foliation [15].

71 The radionuclides were chosen to cover different types of elements existing in the spent  
72 nuclear fuel. We decided to avoid radionuclides having several oxidation states because  
73 we wanted to “keep it simple”.  $^3\text{H}$  is a conservative tracer,  $^{36}\text{Cl}$  might show anion  
74 exclusion properties of rocks.  $^3\text{H}$  (HTO) and  $^{36}\text{Cl}$  are not assumed to have chemical  
75 reaction on the mineral surfaces in granitic rock. The scoping calculations done before  
76 the experiment showed that  $^3\text{H}$  and  $^{36}\text{Cl}$  could have a breakthrough from the injection  
77 borehole into the observation boreholes in a few years’ time during the in-situ experiment  
78 and possible anion exclusion could be seen as well [16]. For the sorbing tracers, it is  
79 likely that only slightly sorbing  $^{22}\text{Na}$  could be seen from the observation boreholes in  
80 reasonable timescales. Distribution coefficient of  $^{22}\text{Na}$  varied between  $1 \times 10^{-4}$  and  $1 \times 10^{-2}$   
81  $\text{m}^3/\text{kg}$  in the granitic rock and its main minerals [14, 17].  $^{22}\text{Na}$  is often used in in-situ  
82 experiments because it can be measured with online gamma measurements contrary to  
83 the beta emitters  $^3\text{H}$  and  $^{36}\text{Cl}$ . Besides these above mentioned three radionuclides,  
84 strongly sorbing elements  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  were added. Both cesium and barium are  
85 known to sorb by ion exchange mechanism having distribution coefficients between

86  $1 \times 10^{-1} \text{ m}^3/\text{kg}$  and  $1 \times 10^{-3} \text{ m}^3/\text{kg}$  [3, 18-21].  $^{134}\text{Cs}$  was chosen as an analogue for another  
87 cesium isotope,  $^{135}\text{Cs}$ , which is one of the most important radionuclides after 100 000  
88 years of deposition and might find its way into the biosphere [22].  $^{133}\text{Ba}$  is a chemical  
89 analogue of  $^{226}\text{Ra}$  which is safety relevant radionuclide in the spent fuel deposition  
90 because of the ingrowth of  $^{226}\text{Ra}$  from uranium [23].

91 In TDE, concentrated mixture of non-sorbing and sorbing radionuclides  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  
92  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  was injected to a meter long packed-off section of a drill hole filled with  
93 simulated groundwater (SGW) at a depth of 11–12 m from the niche wall. Some of the  
94 tracers used in the TDE experiment occur naturally in trace amounts in the groundwater.  
95 For example, 1.2 Bq/L  $^3\text{H}$  has been measured [24] in the Olkiluoto groundwater.  
96  $^{36}\text{Cl}/\text{total Cl}$  ratio has been examined from 34 samples from the Olkiluoto groundwater  
97 taken from different depths (from ground level down to -819 m) and different locations in  
98 the Olkiluoto island, and the values of  $(3-123) \times 10^{-15}$  were found [25]. Thus it is not  
99 possible that the background level of  $^{36}\text{Cl}$  disturbs the measurement of it in the in-situ  
100 experiment. Concentrations of  $6.8 \times 10^{-9}$  to  $8.3 \times 10^{-6} \text{ mol/L}$  of stable natural cesium and  
101  $5.9 \times 10^{-7}$  to  $1.9 \times 10^{-5} \text{ mol/L}$  of stable natural barium has been measured from Olkiluoto  
102 groundwater in previous studies [26]. Breakthrough of the radionuclides is followed from  
103 the circulation SGW into two observation drill holes which are at a depth of about 10  
104 centimeters from the injection borehole. In addition, the activity variation of the  
105 radioactive tracers is followed from the injection drill hole. In this work the activity of  
106 radionuclides in the injection hole was followed for 440 days.

107 The radionuclides  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  cannot be measured straight from the  
108 TDE tracer cocktail because some of them are disturbing each other in the radioanalytical  
109 determination.  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  are gamma emitting radionuclides, but they have  
110 also beta/electron emissions that will interfere the measurements of purely beta emitting  
111  $^3\text{H}$  and  $^{36}\text{Cl}$ . Therefore, to measure beta emitting  $^3\text{H}$  and  $^{36}\text{Cl}$  from the SGW,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$   
112 and  $^{134}\text{Cs}$  need to be separated from the sample.  $^{36}\text{Cl}$  can be separated by  $\text{AgCl}$   
113 precipitation which is a well-known method to separate chloride from solutions [27, 28].  
114  $^{133}\text{Ba}$  could be moved out from the SGW by precipitation as well and precipitation of  
115 barium as sulfates or carbonates [29, 30] is widely used procedure.  $^{134}\text{Cs}$  could be

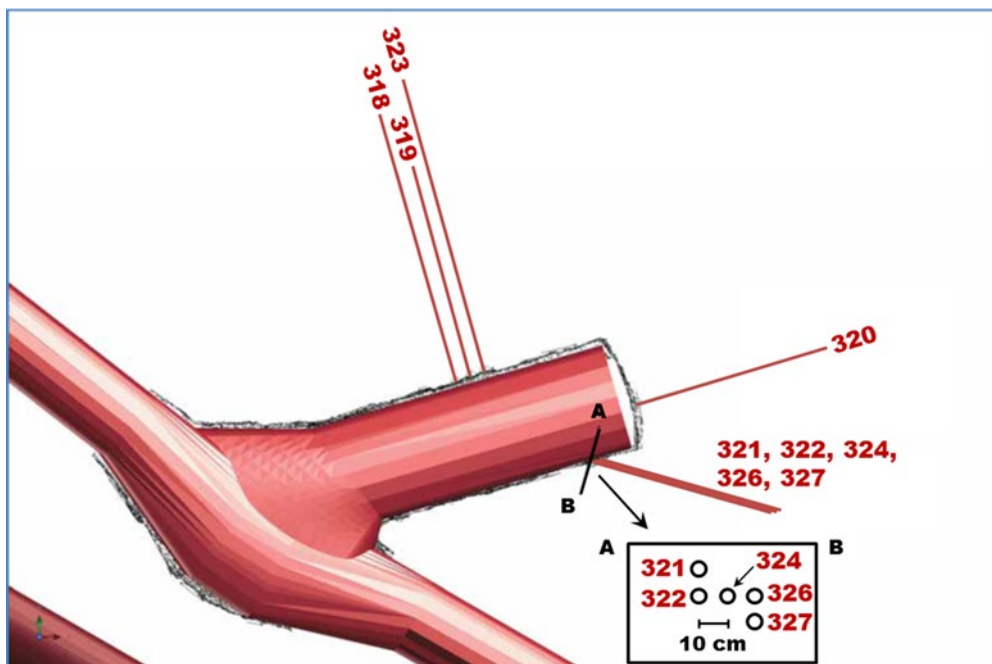
116 separated from the SGW by ion exchange method, e.g. with cation exchange resin  
117 CsTreat® (Fortum, Espoo, Finland) [31, 32]. After the above-mentioned separation  
118 procedures,  $^3\text{H}$  could be measured together with  $^{22}\text{Na}$  by liquid scintillation counting  
119 (LSC) because  $^{22}\text{Na}$  interference is known to be low; only about 3-4 % of  $^{22}\text{Na}$  betas are  
120 shown in the energy window of  $^3\text{H}$  [28]. The  $^{22}\text{Na}$  activity (after gamma measurement)  
121 was subtracted from the LSC measurement results in the previous WPDE1&2 work [14,  
122 28]. In this work, we decided to use another approach to separate  $^3\text{H}$  from the three  
123 gamma emitting radionuclides as well as from  $^{36}\text{Cl}$ . A distillation procedure, which is  
124 widely used for measuring  $^3\text{H}$  in natural waters, was introduced for analyzing the TDE  
125 tracers from the SGW solutions.

126 The aim of this work was to optimize the analysis procedure of the five radionuclides in  
127 the TDE tracer mixture, and to quantify the possible losses and interferences in the  
128 chemical separations. This procedure provides then analytically accurate data for the in-  
129 situ TDE experiment.

## 130 **Materials and methods**

### 131 *The REPRO site*

132 Fig. 1 presents the drill holes in the Rebro niche where the in-situ experiments for  
133 studying radionuclides migration in Olkiluoto bedrock are done [14, 33]. Injection drill  
134 holes ONK-PP324, ONK-PP326 and ONK-PP327 were used in the TDE. ONK-PP326 is  
135 the injection drill hole and the observation drill holes are ONK-PP324 and ONK-PP327.  
136 The experiments are conducted at a depth of about 420 m in the REPRO-niche [33]. The  
137 bedrock of Olkiluoto is crystalline rock that is mainly composed of veined gneiss,  
138 diatexite and granitic pegmatoids [15]. In the REPRO niche at the depth where long term  
139 experiments are being performed, the main rock types are veined gneiss, pegmatitic  
140 granite, quartz gneiss and diatexitic gneiss [33].



141

142 **Fig. 1** The experimental drill holes in REPRO niche Onkalo, Olkiluoto, Finland where  
143 the various in-situ experiments for studying radionuclides retention in Olkiluoto bedrock  
144 were performed. The locations of REPRO drill holes in the investigation niche ONK-  
145 TKU-4219 [14, 33]

146 *Ground water*

147 Before the TDE in-situ experiment, the groundwater sample was taken from the drill hole  
148 ONK-PP319 at Repro niche and it was analysed for chemical composition in the  
149 laboratory of TVO nuclear power company at Olkiluoto island. The SGW for the TDE  
150 was made to resemble this water. 260 mL of SGW was circulated in the injection drill  
151 hole and in the two observation drill holes each for 6 months before the experiment  
152 started and the radioactive tracers were injected into the SGW circulation. Circulation  
153 pumps with PEEK material in contact with the water were used for water circulation in  
154 all the three drill holes. The pumps ran continuously with a flow rate of 2 mL/min - 4  
155 mL/min. During the 6 months equilibration period, four water samples from the  
156 circulated SGW were taken and the analysis of chemical composition were performed in  
157 Labtium Oy (Espoo, Finland). pH of the SGW was  $7.9 \pm 0.1$  and the average chemical  
158 composition of the initial SGW and the one after the equilibration period are presented in

159 Table 1. It can be seen from the Table 1 that the concentrations of all components of the  
 160 SGW decreased slightly during equilibration period. This is due to minor chemical  
 161 processes between the elements of rock minerals and the synthetic ground water.

162 **Table 1** The chemical composition of ONK-PP319 water and that of the SGW after six  
 163 months equilibration period in the TDE in-situ injection drill hole

Element	Concentration in ONK-PP319 water <sup>1</sup>  (mg/L)	Concentration in SGW after equilibration period of 6 months <sup>2</sup>  (mg/L)
Br	34 ± 0.4%	33.8 ± 1.3
Ca	690 ± 0.3%	472 ± 6
K	14 ± 0.7%	10.7 ± 1.1
Sr	5.7 ± 0.6%	4.20 ± 0.04
Mg	34 ± 0.5%	28.2 ± 0.4
SiO <sub>2</sub>	5.4 ± 0.5%	4.9 ± 0.3
Na	2 840 ± 0.9%	2 560 ± 20
Cl	5 890 ± 0.3%	5 310 ± 70

164 <sup>1</sup>TVO laboratory

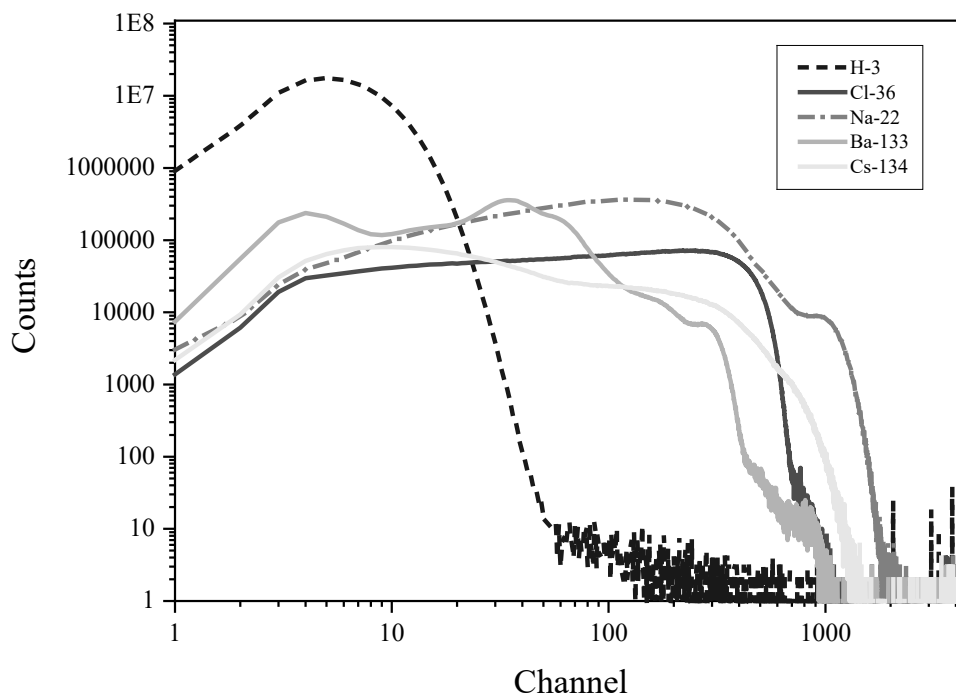
165 <sup>2</sup>Labtium Oy, Espoo, Finland

166 *Radionuclides*

167 The rough activities of radionuclides that were injected into the TDE injection drill hole  
 168 circulation in a 10 mL volume, were 200 MBq of <sup>3</sup>H as tritiated water (HTO), 7 MBq of  
 169 <sup>36</sup>Cl as NaCl, 10 MBq of <sup>22</sup>Na as NaCl, 1 MBq of <sup>133</sup>Ba as BaCl<sub>2</sub> and 1 MBq of <sup>134</sup>Cs as  
 170 CsCl [34]. Initially 11 mL of tracer solution was prepared, and 1 mL sample was saved  
 171 for the accurate radioactivity analysis as well as this surplus solution was used to test the  
 172 analysis methods.



173 Fig. 2 shows the beta/electron spectra of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  measured with  
174 LSC. As can be seen from the Fig. 2, the beta/electron emissions of  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$   
175 are interfering with the  $^{36}\text{Cl}$  spectrum. They all are also interfering somewhat the  $^3\text{H}$   
176 measurement and therefore it was decided that tritium will be separated from the sample  
177 solution by distillation [35] and measured with LSC alone. LSC measurements of  $^3\text{H}$  are  
178 sensitive to quenching effects as well as to other radionuclide's interference. Distillation  
179 is a good method to separate  $^3\text{H}$  from other radionuclides since most of the impurities  
180 vaporize poorly at the boiling point of water [36]. Possible radionuclides that would  
181 vaporize are iodine isotopes as iodine gas and  $^{14}\text{C}$  as carbon dioxide but these were not  
182 used in this experiment  $^{36}\text{Cl}$  has been separated from a weakly acidic water solution by  
183  $\text{AgCl}$  precipitation in previous experiments [27, 35]. The same method was used also in  
184 this work. After precipitation, the  $\text{AgCl}$  precipitate was separated from the liquid phase  
185 and dissolved to ammonia and the solution was measured by LSC.



186  
187

188 **Fig. 2** Beta/electron spectra of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  measured with Tri-Carb  
189 2910 TR liquid scintillation counter (Perkin Elmer)

190 The radionuclides  $^3\text{H}$  (37 MBq/g 29.7.2015) and  $^{22}\text{Na}$  (7.609 MBq/g 15.11.2012) were  
 191 purchased from Perkin Elmer (Boston, USA). The producer gives 10% uncertainty for the  
 192 product; these are not precision calibrated solutions.  $^{36}\text{Cl}$  ( $9.612 \pm 0.106$  MBq/g  
 193 20.12.2013),  $^{133}\text{Ba}$  ( $5.00 \pm 0.12$  MBq/g 1.3.2008) and  $^{134}\text{Cs}$  ( $35.22 \pm 0.35$  MBq/g  
 194 25.9.2014) were purchased from EuroStandard CZ (Prague, Czech Republic). Table 2  
 195 shows the decay-modes, energy information and half-lives of the radionuclides used in  
 196 this work. Activities of gamma emitting radionuclides  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  were  
 197 measured directly from the subsamples taken from the ONK-PP326 circulation water by  
 198 using a HPGe-detector (Canberra XtRa; Extended Range Coaxial HPGe Detector with  
 199 spectral analysis program Gamma Acquisition & Analysis Genie/Canberra).  $^3\text{H}$  and  $^{36}\text{Cl}$   
 200 were measured with LSC (Perkin Elmer Tri-Carb 2910 TR, spectrum analyzer  
 201 SpectraWorks). Liquid scintillation cocktail used in this work was OptiPhase HiSafe 3  
 202 (Perkin Elmer) that is capable of handling a broad range of solutes, particularly high ionic  
 203 strength ones.

204 **Table 2** Radionuclides used in the TDE and their main decay-modes, energies and half-  
 205 lives [37]

Nuclide	Main decay-mode/intensity (%)	Energies of $\gamma$ and $\beta$ emissions used in analyses (keV)	Half-life (years)
$^3\text{H}$	$\beta^-/100$	$\beta$ $18.591 \pm 0.003$	$12.32 \pm 0.02$
$^{22}\text{Na}$	$\beta^+/90.38 \pm 0.03$	$\gamma$ $1\ 274.537 \pm 0.007$	$2.602 \pm 0.002$
$^{36}\text{Cl}$	$\beta^-/98.10 \pm 0.14$	$\beta$ $709.55 \pm 0.05$	$301\ 000 \pm 2\ 000$
$^{133}\text{Ba}$	$\epsilon/100\%$	$\gamma$ $356.0129 \pm 0.0007$	$10.551 \pm 0.011$
$^{134}\text{Cs}$	$\beta^-/99.9997 \pm 0.0001$	$\gamma$ $604.721 \pm 0.002$	$2.0652 \pm 0.0004$

206

207 AgCl precipitation for  $^{36}\text{Cl}$  measurement and  $^3\text{H}$  distillation were tested with two sets of  
 208 samples. One set (four samples) included only radioactive  $^{36}\text{Cl}$  (1 400-2 400 Bq) in 5 mL  
 209 of SGW for testing AgCl precipitation. Another set (ten samples) included only  $^3\text{H}$  (240 –  
 210 36 000 Bq) in 10 mL SGW for testing of the distillation. The three gamma emitting

211 radionuclides were not included into the test samples because by this way the recoveries  
212 of beta emitting radionuclides could be determined accurately without interferences.

213 *AgCl precipitation tests*

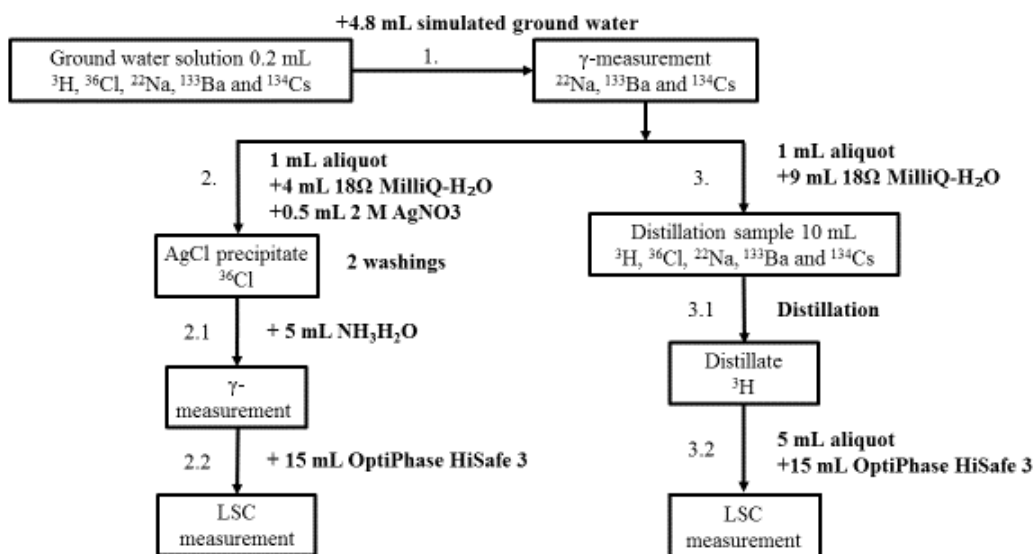
214 The testing of the separation of  $^{36}\text{Cl}$  by AgCl precipitation was performed adding 0.5 mL  
215 of 2 mol/L  $\text{AgNO}_3$  to 5 mL SGW which chloride concentration was about 5 g/L. SGW  
216 contains 5310 mg/L of chloride (see Table 1) and no additional carrier for  $^{36}\text{Cl}$  was  
217 needed because in 5 mL of SGW there is 26.55 mg of chloride which is equivalent for  
218 0.15 mol/L and thus the  $\text{AgNO}_3$  concentration ( $0.0005 \text{ L} \times 2 \text{ mol/L} / 0.005 \text{ L} = 0.2 \text{ mol/L}$ )  
219 was sufficient to precipitate all chloride from the solution. After mixing the solutions  
220 together, the mixture was stirred vigorously to ensure precipitation of all  $^{36}\text{Cl}$ . AgCl  
221 precipitate was separated from supernatant by centrifugation (4500 rpm for 15 minutes,  
222 Sigma centrifuge 3-16KL, Rotor 1180). Then the precipitate was washed twice with 5  
223 mL of 18 $\Omega$  MilliQ- $\text{H}_2\text{O}$  and dissolved into 5 mL of 17%  $\text{NH}_3$  solution. The dissolved  
224 precipitate was first measured with HPGe detector to check if there is any leak of  
225 gamma-emitting nuclides into the precipitate. After that, the dissolved chloride solution  
226 was mixed with 15 mL of liquid scintillation cocktail and beta activity of  $^{36}\text{Cl}$  was  
227 measured by LSC. The quenching curve for  $^{36}\text{Cl}$  was determined with 800 Bq  $^{36}\text{Cl}$  in 5  
228 mL of SGW, 15 mL OptiPhase HiSafe 3 liquid scintillation cocktail and  $\text{CCl}_4$  as a  
229 quenching substance.

230 *Distillation tests for separating  $^3\text{H}$*

231 In the distillation procedure for determining  $^3\text{H}$ , the 10 mL SGW samples with known  
232 amount of  $^3\text{H}$  was heated with thermophore and the vapor was condensed in the water  
233 circulation condenser. The distillate that contained  $^3\text{H}$  as tritiated water was collected into  
234 a round-bottomed glass flask. These samples were distilled to near dryness to ensure  
235 good recovery for  $^3\text{H}$ . After that 5 mL aliquots were taken from the distillates (Fig. 3 step  
236 3.2) and the  $^3\text{H}$  activity was measured with LSC. The quenching curve for  $^3\text{H}$  was  
237 determined with  $^3\text{H}$  internal standard capsules (Perkin Elmer, Boston, USA) with activity  
238 of  $3\ 100 \pm 40$  Bq dissolved in 5 mL of SGW, 15 mL OptiPhase HiSafe 3 and  $\text{CCl}_4$  as a  
239 quenching substance.

240 *Final procedure for water sample analysis*

241 The activities of radionuclides in the TDE injection solution were analysed with the  
 242 developed procedure. In addition, the TDE water samples from the injection drill hole  
 243 for following the variation of tracer activities were measured. Fig. 3 shows the  
 244 schematics used for the accurate activity analysis of the TDE injection tracer solution (1  
 245 mL) and the TDE water samples (0.2 mL).



246 **Fig. 3** Analysis scheme for activity measurements of water samples taken from the  
 247 injection drill hole of the TDE. Separation of  $^{36}\text{Cl}$  is done by  $\text{AgNO}_3$  precipitation and  $^3\text{H}$   
 248 by distillation  
 249

250 *The tracer activities of the TDE injection solution*

251 The activities of the tracers in the TDE injection solution were analysed from a 1 mL  
 252 surplus tracer solution (called now-on S1) that was made at the same time as the initial  
 253 tracer solution. The S1 solution had to be diluted before analysis and first it was diluted  
 254 to 10 mL with SGW (called now-on S2 dilution). Secondly 0.5 mL of the S2 dilution was  
 255 diluted to 100 mL with MilliQ-H<sub>2</sub>O (called now-on S3 dilution). From this S3 dilution  
 256 two about 0.2 mL samples were taken for the activity analysis of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  
 257  $^{134}\text{Cs}$ . One of these 0.2 mL samples was further diluted with SGW to 5 mL for  $\text{AgCl}$   
 258 precipitation (called now-on S4a dilution) (marked to Fig. 3 as step 2) and the other

259 sample was diluted to 10 mL for distillation (called now-on S4b dilution) (marked to Fig.  
260 3 as step 3). The S4a dilution has a chloride content of 25.48 mg and concentration of  
261 0.14 mol/L so the 0.2 mol/L AgNO<sub>3</sub> concentration in the solution is sufficient for  
262 precipitate all chloride in the sample. Every dilution was weighed for the accurate  
263 calculation of injected tracer activities. Gamma activities of <sup>22</sup>Na, <sup>133</sup>Ba and <sup>134</sup>Cs were  
264 first measured from the S4a dilution (Fig. 3 step 1) by using HPGe-detector with  
265 measurement time of 4.4 hours. In long measurements with Ge-detector the background  
266 activities consist mainly of daughters of <sup>238,235</sup>U and <sup>232</sup>Th and of <sup>40</sup>K, from the  
267 surrounding building materials and of daughters of <sup>222</sup>Rn. No background gamma peaks  
268 were overlapping with the energies of gamma-emitting radionuclides analysed in this  
269 work.

270 After gamma measurement, 0.5 mL of 2 M AgNO<sub>3</sub> was added (Fig. 3 step 2) to the 5 mL  
271 S4a dilution sample to precipitate AgCl. The AgCl precipitate was diluted to 5 mL of  
272 17% NH<sub>3</sub> solution and the dilution was measured with Ge-detector (5 mL measurement  
273 geometry) for any gamma-active residue that could have been left to the sample despite  
274 the washing of the precipitate. After the gamma measurement, 15 mL of liquid  
275 scintillation cocktail was added (Fig. 3 step 2.2) and the sample was measured for <sup>36</sup>Cl  
276 activity with LSC.

277 The 10 mL S4b dilution sample was distilled to near dryness and the distillate was  
278 measured with HPGe-detector for any gamma active residue. 15 mL of liquid scintillation  
279 cocktail was added and the <sup>3</sup>H activity of injection tracer solution was measured from 7  
280 mL distillate sample with LSC.

#### 281 *Analysis of the water samples from TDE injection drill hole ONK-PP326*

282 The decrease of the activities of tracers were followed by taking about 0.2 mL water  
283 samples from the injection drill hole ONK-PP326. Water samples were weighed for  
284 accurate mass. The first groundwater samples from the TDE injection drill hole was taken  
285 6 hours after the experiment started in November 2015. Groundwater samples from the  
286 drill hole ONK-PP326 were taken frequently in the first week of the experiment. In total,  
287 7 samples were collected in the first week. After that samples were taken every two  
288 weeks and after three months of the experiment samples were taken once a month. From

289 nine months on samples were taken once per every two months. Total amount of 23  
 290 samples (until spring 2017) have been collected in 440 days.

291 Before measurements, the 0.2 mL TDE groundwater samples were diluted to 5 mL with  
 292 SGW (Fig. 3 step 1) and activities of  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  were measured by HPGe-  
 293 detector. The separations of  $^{36}\text{Cl}$  and  $^3\text{H}$  were performed as described in Fig. 3. All  
 294 samples were weighed before and after dilutions and distillations and all the results were  
 295 corrected to the initial 0.2 mL sample.

## 296 **Results and discussion**

### 297 *AgCl precipitation tests*

298 Table 3 shows the results of AgCl precipitation tests.  $^{36}\text{Cl}$  from the supernatant,  
 299 precipitate dissolved in  $\text{NH}_3$  and two washing solutions was measured by LSC with a  
 300 measurement efficiency of  $89 \pm 1\%$ . The average yield of AgCl precipitation was  $98 \pm$   
 301  $2\%$  in the four measured test samples.

302 When  $^{36}\text{Cl}$  was analyzed from the water samples with all five tracer radionuclides, no  
 303 gamma emitting radionuclides were present in the AgCl precipitate. A disturbance from  
 304  $^3\text{H}$  possibly staying in sample is ruled out by setting the lower level of the  $^{36}\text{Cl}$  counting  
 305 window to exceed the maximum energy of  $^3\text{H}$  betas. A detection limit of 0.15 Bq/g with a  
 306 measurement time of 2 h was obtained for  $^{36}\text{Cl}$ . The yield results are in good agreement  
 307 with results of Hou et al. [26] and Qian et al. [27].

308 **Table 3** The separation of  $^{36}\text{Cl}$  by AgCl precipitation. Activity of  $^{36}\text{Cl}$  in different  
 309 solutions and the yield of AgCl precipitation are given

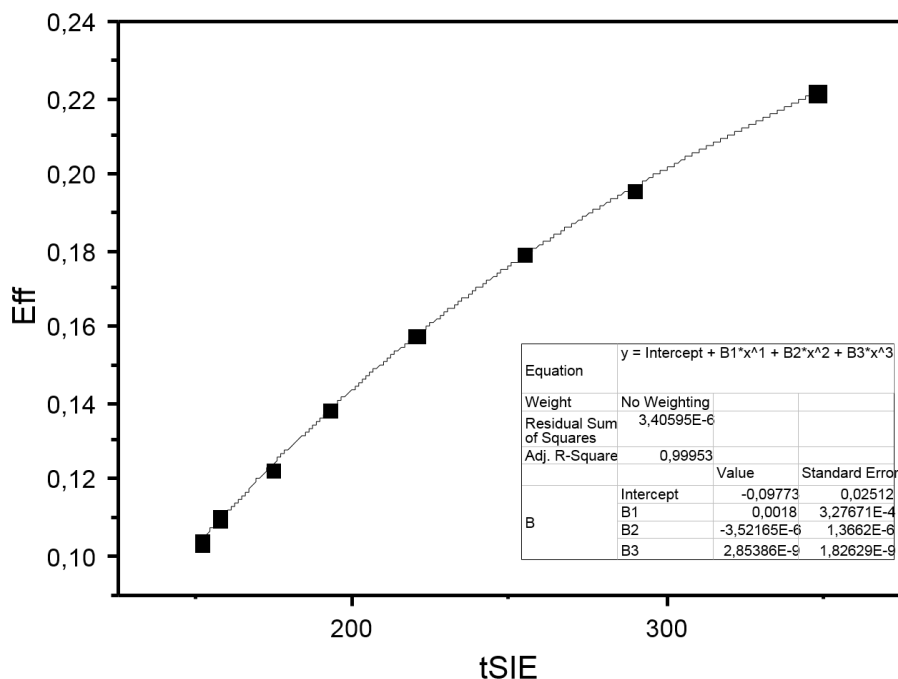
Sam ple	Initial $^{36}\text{Cl}$ activity (Bq)	$^{36}\text{Cl}$ activity in supernatant (Bq)	$^{36}\text{Cl}$ activity in wash 1 (Bq)	$^{36}\text{Cl}$ activity in wash 2 (Bq)	$^{36}\text{Cl}$ activity in AgCl precipitate (Bq)	$^{36}\text{Cl}$ yield (%)
1	$1\ 380 \pm 15$	$64 \pm 1$	$0.289 \pm$	$0.30 \pm 0.01$	$1\ 340 \pm 15$	$97 \pm 1$

			0.014			
2	1 380 ± 15	63 ± 1	0.283 ± 0.014	0.55 ± 0.02	1 320 ± 14	96 ± 1
3	2 380 ± 30	0.32 ± 0.01	0.309 ± 0.014	0.44 ± 0.02	2 390 ± 90	100 ± 4
4	2 380 ± 30	0.47 ± 0.02	0.317 ± 0.014	0.37 ± 0.02	2 370 ± 90	100 ± 4

310

311 *Distillation tests for separating <sup>3</sup>H*

312 Fig. 4 shows the quench correction curve for <sup>3</sup>H. The recovery of <sup>3</sup>H was calculated by  
 313 comparing the known activity concentration of the 10 mL distillation sample to the  
 314 measured activity concentration in the distillate. An average recovery of 97 ± 3 % was  
 315 obtained, that is in good agreement with Atkinson et al. [38], who have reported  
 316 distillation recoveries of >98% for <sup>3</sup>H from environmental water samples. No gamma  
 317 emitting radionuclides nor <sup>36</sup>Cl were observed to leak to the distillate. Therefore <sup>3</sup>H could  
 318 be measured clean from disturbing spectral components with low detection limit of 0.4  
 319 Bq/g (measurement time 2 h).



321  
 322 **Fig. 4** Quench correction curve for  $^3\text{H}$ . 5 mL SGW sample mixed with 15 mL of  
 323 OptiPhase HiSafe 3 liquid scintillation cocktail. Samples measured with TriCarb 2910  
 324 TR (Perkin Elmer)

325 *Activity of the TDE injection tracer solution*

326 Activity of the injection tracer solution was analysed from the S4a and S4b dilutions.  
 327 Gamma emitting radionuclides  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  were measured from the S4a  
 328 dilution by Ge-detector with detection limits of 0.45 Bq/g for  $^{22}\text{Na}$  (1275 keV), 0.65 Bq/g  
 329 for  $^{133}\text{Ba}$  (365 keV) and 0.50 Bq/g for  $^{134}\text{Cs}$  (604 keV) with a measurement time of 4.4 h.  
 330 Beta emitting radionuclide  $^{36}\text{Cl}$  was separated from S4a dilution and  $^3\text{H}$  was distilled  
 331 from S4b dilution. Results of the TDE tracer solution analysis are shown in Table 4. The  
 332 total amount of injected tracer activities of gamma emitting nuclides  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  
 333  $^{134}\text{Cs}$  as well as beta emitting radionuclides  $^3\text{H}$  and  $^{36}\text{Cl}$  were corrected to the injected  
 334 tracer volume which was 9.7 g.

335 **Table 4** Injected tracer solution activities in TDE

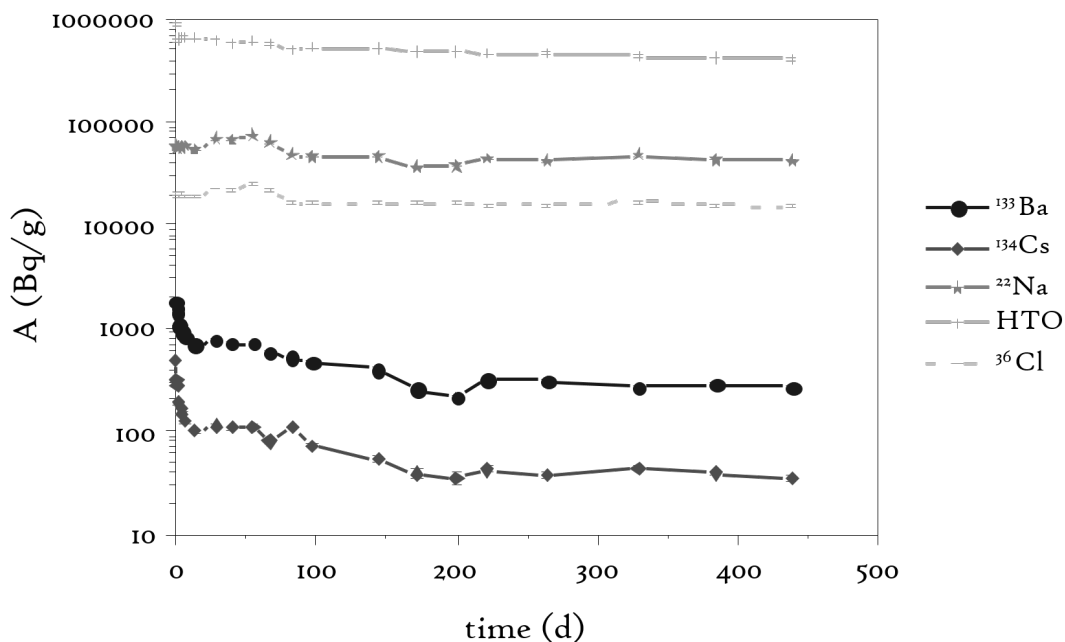


Radionuclide	Injected activity (MBq)
$^3\text{H}$	$198 \pm 3$
$^{36}\text{Cl}$	$5.5 \pm 0.2$
$^{22}\text{Na}$	$22.4 \pm 0.2$
$^{133}\text{Ba}$	$2.09 \pm 0.04$
$^{134}\text{Cs}$	$1.92 \pm 0.06$

336

337 *Analysis of the water samples from the TDE injection drill hole ONK-PP326*

338 The variation of radionuclide activities (Bq/g of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$ ) in the  
339 TDE injection drill hole as a function of time are shown in Fig. 5. All activities are half-  
340 life corrected to the start of the experiment (19.11.2015). The general trend in all  
341 activities is falling;  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  the most and  $^{36}\text{Cl}$  the least. After 440 days from the  
342 start of the experiment, about 69% of the initial  $^{36}\text{Cl}$  concentration and about 52% of the  
343 initial  $^3\text{H}$  concentration is still present, whereas only 3% of initial  $^{133}\text{Ba}$  and 0.4% of the  
344 initial  $^{134}\text{Cs}$  is left in the injection drill hole circulation SGW. This is explained by the  
345 non-sorbing nature of  $^3\text{H}$  and  $^{36}\text{Cl}$  which decrease in the system only by diffusion into the  
346 pores of surrounding rock whereas the sorbing  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  activity decrease fast in  
347 the SGW due to the chemical reactions with the mineral surfaces of the rock.  $^{133}\text{Ba}$  and  
348  $^{134}\text{Cs}$  distribution coefficients ( $K_d = 1 \times 10^{-1} - 1 \times 10^{-3} \text{ m}^3/\text{kg}$ ) [3, 26] are found to be large on  
349 veined gneiss which is the dominant rock type in the TDE area. Approximately 47% of  
350  $^{22}\text{Na}$  is present in the injection drill hole circulation SGW after 440 days of the  
351 experiment. No radionuclides migration into the two observation drill holes ONK-PP324  
352 and ONK-PP327 were observed during the 440 days of the experiment. Not even the  
353 non-sorbing radionuclides  $^3\text{H}$  and  $^{36}\text{Cl}$  had diffused through the 10 cm distance in the  
354 rock.



355  
 356 **Fig. 5** Activities (Bq/g) of  $^3\text{H}$  (plus),  $^{36}\text{Cl}$  (minus),  $^{22}\text{Na}$  (star),  $^{133}\text{Ba}$  (dot) and  $^{134}\text{Cs}$   
 357 (squares) in the TDE injection drill hole as a function of time (in days)

### 358 Conclusions

359 Analysis method for  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{133}\text{Ba}$ ,  $^{134}\text{Cs}$  and  $^{22}\text{Na}$  from synthetic groundwater solution  
 360 was introduced. It includes separation of  $^{36}\text{Cl}$  by  $\text{AgCl}$  precipitation and  $^3\text{H}$  separation by  
 361 distillation. Gamma emitting nuclides are measured precisely from the groundwater  
 362 samples without any sample treatment. The developed separation procedure for analysis  
 363 of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{133}\text{Ba}$ ,  $^{134}\text{Cs}$  and  $^{22}\text{Na}$  for the TDE in-situ experiment at ONKALO was found  
 364 to be effective and simple, with detection limits for all the nuclides close to 0.5 Bq/g.

365 The radionuclide analyses show that the activities of  $^3\text{H}$ ,  $^{36}\text{Cl}$ ,  $^{22}\text{Na}$ ,  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  in  
 366 TDE injection hole are decreasing during the observation period of 440 days. Anyhow  
 367 there were anomalies in the decreasing trend. These are most probably originated from  
 368 strong pressure changes in the packed off drill hole sections in the early part of the  
 369 experiment.

370  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  have adsorbed strongly onto the rock matrix which is shown in fast  
371 decrease of their activity concentrations in the beginning of the experiment. 96% of the  
372 initial  $^{133}\text{Ba}$  and >99% of  $^{134}\text{Cs}$  has been retained to the surroundings after 440 days  
373 experiment. From the weakly sorbing  $^{22}\text{Na}$  and non-sorbing  $^3\text{H}$  and  $^{36}\text{Cl}$  app. 31-53% of  
374 the activity is retained in the rock matrix of the injection drill hole surface and its  
375 surroundings, but no activity has migrated to the observation holes at the time of this  
376 analysis. All activities in the injection drill hole are still well above the detection limits.

### 377 **Acknowledgements**

378 The work described here was funded by Posiva Oy, Finland.

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