Longtime behavior of cesium (Cs) in natural spring drinking water

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ABSTRACT

Large amounts of radioactive cesium (Cs^A) have been introduced into the underground environments, through a natural process, as a result of nuclear power plant accidents. It is known that the active Cs sorption onto colloidal-size clay minerals in groundwater is observed and the active Cs can be transported with the colloidal fraction of groundwater by water flows. However, the longtime behavior of radioactive Cs, contained in the flowing groundwater in the aquifers of groundwater source areas, is unknown in terms of the natural water cycle. Herein, we investigate the Cs concentration in natural spring drinking water with the residence time in a groundwater source area of a mountainside composed of volcanic rock, compared with those of other trace elements. This investigation demonstrates that the observed Cs concentration in natural spring drinking water exponentially decreases slowly with the groundwater residence time (~ 45 yr), while several trace elements, namely, P, V, Ga, and Ge, increase in concentration with the

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23 groundwater residence time through chemical weathering. The findings suggest that Cs^{A} ,
24 contained in flowing groundwater in mountain water source areas, may decrease exponentially
25 at the rate of one-tenth in twenty-two years, by sorption onto the aquifer through rock-water
26 interaction excluding radioactive decay. For the sustainable management of water sources and
27 ecosystems, the long-term (~50 yrs.) monitoring of the active Cs in groundwater is needed in
28 mountain water source areas where radioactive cesium has been dispersed at times of nuclear
29 power plant accidents.

30

31 Keywords:

32 Groundwater / Cesium / Sorption / Residence time / Sulfur hexafluoride / Nuclear power plant
33 accidents

34

35 **1. Introduction**

36 The longtime (~100 yr) effect of radioactive cesium (Cs^{A}), dispersed at the time of nuclear
37 power plant accidents (e.g., [von Gunten et al., 1988](#); [Mizuno and Kubo, 2013](#); [Tsuji et al., 2014](#)),
38 is a major environmental issue. As Cs^{A} is sorptive onto colloidal-size clay in groundwater
39 ([Francis and Brinkley, 1976](#); [Comans et al., 1991](#); [Kersting et al., 1999](#)) and the distribution
40 coefficient to the subsurface soil of Cs^{A} decreases with depth in the soil ([Comans et al., 1989](#)),
41 the active Cs can be transported by water flows with the colloidal fraction, with suspended
42 particles of sub micrometer size ([von Gunten et al., 1988](#); [Buddemeier and Hunt, 1988](#); [Kersting](#)
43 [et al., 1999](#); [Tsuji et al., 2014](#)), and can reach the groundwater surface ([Kersting et al., 1999](#)).
44 Although Cs^{A} sorption onto soil has been reported ([Francis and Brinkley, 1976](#); [Comans et al.,](#)

1991; Buddemeier and Hunt, 1988), the temporal variation in field groundwater Cs^A by sorption onto rock aquifers is still unknown in terms of the natural water cycle, and the longtime behavior (10–50 yr) of the Cs^A concentration in groundwater has rarely been observed.

In order to evaluate the longtime behavior of Cs^A in the flowing groundwater of an important source area, this study focuses on the Cs in the spring water of the Yatsugatake Mountains, which form an important source area for drinking water in Central Japan. In the Saku district, a high land area, 650 m ~ 2,500 m in altitude, in the northeastern section of the Yatsugatake Mountains in Nagano, Japan, 280 km southwest of the site of the Fukushima Daiichi Nuclear Power Plant accident (Fig. 1), the groundwater, spring water, and well water in the volcanic rock aquifer have been used for 99%, 47%, and 52%, respectively, of the drinking water and tap water in that district for a long time. According to all the local Government HPs in the Saku district, no Cs^A was detected (detection limit < 0.1~ 10 Bq/kg) from the groundwater for the water works, but Cs^A was detected from the drainage sludge in certain areas. Spring water is still the major source of drinking and tap waters in high land areas of Japan. As the sorption and desorption behavior of the Cs in groundwater should be equal to that of Cs^A (e.g., Cornell, 1993; Yoshida et al., 2004), the longtime behavior (10–50 yr) of the Cs^A concentration in the groundwater flowing through aquifers is expected to be obtainable by field monitoring the relationship between the Cs concentration in groundwater and the residence time of the groundwater in a rock aquifer that includes Cs-bearing minerals. In this study, the Cs concentration in natural spring drinking water was measured with the groundwater residence time, in order to evaluate the longtime behavior of Cs^A in the flowing groundwater of an important source area for drinking water in terms of the natural water cycle.

67

68 **2. Material and methods**

69 2.1 Sampling locations and geological setting of the study area

70 Sampling points are located in the northeastern part of the Yatsugatake volcanic area, which is
71 part of the Yatsugatake-Chūshin Kōgen Quasi-National Park. The Yatsugatake volcanic body,
72 formed by Quaternary volcanic activity from 0.8 to 1.2 Ma, is comprised mainly of several thin
73 flows of pyroclastics, including volcanoclastic, basaltic lava, and basaltic andesitic lava ([Nishiki](#)
74 [and Takahashi, 2012](#)). The slopes are about 0.13 for higher than 1,600 m a.s.l., and about 0.08
75 for lower than 1,600 m a.s.l. and for higher than 1,000 m a.s.l. Most parts of the study area
76 belong to the Yachiho Group of early Pleistocene, consisting of five formations. These
77 formations are comprised mostly of volcanic sand and gravel with scoria and tuff breccia;
78 namely, pyroclastics, including the volcanoclastic of [Nishiki and Takahashi \(2012\)](#), compose the
79 aquifers of 30 m to 50 m in thickness ([Kumai, 1980](#)). After the Yachiho Group was
80 uncomfortably covered and leveled by a gravel formation, the mountain ridges separated from
81 one another due to the erosion of valleys in the geologic body ([Kumai, 1980](#)). [Kumai \(1980\)](#)
82 also reported that each hydraulic parameter of the aquifers in the Yachiho Group ranged from
83 10^{-6} to 10^{-4} m/sec in hydraulic conductivity and from 0.06 to 0.4 in effective porosity,
84 respectively.

85

86 2.2 Sampling and analysis of spring water

87 We collected groundwater samples from July to August 2011 from the 17 (cold) springs, 780 m
88 to 1,940 m a. s. l. in altitude ([Table 1](#)), that are being used for drinking and tap waters as supplied

89 from the local government in the Saku district (Fig. 1). In addition, the water from 25 rivers, as
90 well as the 17 springs, was sampled for measuring the hydrogen and oxygen stable isotopic
91 ratios (δD and $\delta^{18}\text{O}$) to trace the origin and the recharge area of the water. The pH, the electrical
92 conductivity (EC), the oxidation reduction potential (ORP), and the dissolved oxygen (DO) of
93 the groundwater samples were measured in the field using portable instruments (SC82,
94 Yokogawa Electric Co., Japan; D-25, Horiba, Ltd., Japan). The groundwater samples were
95 collected using a nylon tube, with each spring purged until the monitoring values for EC, pH,
96 DO, ORP, and temperature (T) became stable. Samples for the chemical composition were
97 collected in 50-mL and 250-mL polyethylene bottles filtered through a 0.2- μm membrane filter.
98 The groundwater samples for the sulfur hexafluoride (SF_6) and chlorofluorocarbons (CFCs:
99 CFC-12 and CFC-113) dating were collected unfiltered and without exposure to the air in 1-L
100 glass bottles for SF_6 and in 100-mL glass bottles for CFCs, as described by [Busenberg et al.](#)
101 [\(2006\)](#) in the IAEA (International Atomic Energy Agency) guidebook. SF_6 and CFCs were
102 measured separately by purge-and-trap gas chromatography systems, namely, Shimadzu GC-8A
103 and Shimadzu GC-14B, respectively, with an electron capture detector after pre-concentration
104 by cryogenic methods for SF_6 ([Busenberg and Plummer, 1992](#)) and CFCs ([Busenberg and](#)
105 [Plummer, 2000](#)). The detection limit of the CFC concentrations in water depended on the
106 standard CFCs gas or SF_6 gas concentrations used for the calibration curve. The limit was ~0.1
107 pg/L (0.01 pmol/L) for the CFCs and ~0.1 fg/L (0.01 fmol/L) for the SF_6 . The major and trace
108 elements were analyzed with inductively coupled plasma-mass spectrometry (ICP-MS: Agilent
109 7500 cx) with a detection limit of minimum 0.1 parts per trillion (ppt). The values for δD and
110 $\delta^{18}\text{O}$ were determined by the $\delta\text{D}/\delta^{18}\text{O}$ Isotopic Water Analyzer (Picarro L2130-i) with an

111 accuracy of 0.1‰ and 0.02‰, respectively. The alkalinity was measured by titration against
112 0.02 N HCl using a mixture of bromocresol green and methyl red (BCG-MR) as the indicator
113 (pH 4.8). Major anions, Cl^- , NO_3^- , and SO_4^{2-} , were determined in the laboratory by ion
114 chromatography (PIA-1000, Shimadzu) with a detection limit of less than 0.1 mg/L.

115

116 **3. Results**

117 3.1 Recharge area, recharge temperature, and residence time of spring water

118 Figure 2a shows the delta-diagram, the relationship between the observed hydrogen and the
119 oxygen stable isotopic ratios (δD and $\delta^{18}\text{O}$) of the 17 spring waters (Table 2) and the 25 river
120 waters with two terrestrial meteoric lines, which are $\delta\text{D} = 8\delta^{18}\text{O} + 10$ on the Pacific Ocean side
121 (Craig, 1961) and $\delta\text{D} = 8\delta^{18}\text{O} + 17$ on the Sea of Japan side (Matsubaya et al., 1973). δD and
122 $\delta^{18}\text{O}$ are plotted around a line, expressed by $\delta\text{D} = 5.85\delta^{18}\text{O} - 12.6$, between the two meteoric
123 lines, indicating that the origin of the spring water and the river water is local meteoric water
124 affected by rain and vapor from the Pacific Ocean and the Sea of Japan. Figure 2b shows the
125 relationship between $\delta^{18}\text{O}$ and the two altitudes at the sampling point and at the starting point of
126 the river water with those of the $\delta^{18}\text{O}$ in Central Japan (Waseda and Nakai, 1983). This river
127 water follows the general, isotopic altitude effect of $\delta^{18}\text{O}$ in Central Japan (Waseda and Nakai,
128 1983).

129 As shown in Table 2, the spring water is presumed to be originally recharged at 1,340 m to
130 2,150 m a. s. l. (H^*) in average altitude and to be 8.3°C to 5.4°C in average recharge temperature
131 (T^*) from the observed hydrogen and oxygen stable isotopic ratios (δD and $\delta^{18}\text{O}$) using the
132 isotopic altitude effect of $\delta^{18}\text{O}$ in Central Japan (Waseda and Nakai, 1983; Komiya et al., 2003;

133 Nakaya et al., 2007) and the spring water temperature (Fig. 2). Therefore, the location of each
134 recharge zone of spring water can be estimated by tracing back from the location of the spring to
135 the recharge altitude H^* along the topography. Referring to the mountain's slope, groundwater is
136 estimated to migrate a minimum distance of about 2.8 km and a maximum distance of about 10
137 km through the aquifer between the recharge zone and the spring. Figure 3 shows the
138 relationship among CFC-12, CFC-113, and SF_6 , converted to atmospheric concentration by
139 Henry's law under the recharge temperature and the recharge altitude (Wanninkhof et al., 1991;
140 Busenberg and Plummer, 1992; Busenberg and Plummer, 2000), with a line for the piston flow
141 model for which the hydraulic head of the new recharge groundwater can induce the movement
142 of the old groundwater without mixing. As each relationship among CFC-12, CFC-113, and SF_6
143 is fitted to each line of the piston flow model (Fig. 3), the groundwater flow is presumed to be a
144 piston flow. When defining the residence time as the arrival time of the groundwater from the
145 recharge zone to the spring through the aquifer, the groundwater residence time is calculated by
146 simply obtaining the difference between the sampling time and the recharge time measured by
147 the dating tracer for the groundwater in the case of a piston flow. The residence times for the
148 spring water samples range from 17 years to 45 years according to three dating tracers (Table 2).
149 From the migration distance of the spring water and the groundwater residence time, described
150 above, the groundwater migration velocity lies in the range of approximately 120 m/yr to 550
151 m/yr. In this study area, the concentrations of more than 40 trace elements, including Cs, were
152 also detected for each filtered (0.2 μm) spring water sample (Fig. 1). As a result, a water source
153 area within the Yatsugatake Mountains provides a unique field for studying the longtime
154 behavior of field sorption-desorption reactions onto mineral surfaces of some trace elements in

155 flowing groundwater through chemical weathering with groundwater residence times in the
156 natural water cycle in a confined aquifer composed originally of the same Quaternary volcanic
157 rock, pyroclastics, and lava layers (Kumai, 1981; Nishiki et al., 2007; Nishiki et al., 2012) with
158 little anthropogenic pollution.

159

160 3.2 Longtime behavior of several trace elements including Cesium

161 The pH of the spring water samples shows a tendency to increase with the residence time
162 (Tables 1 and 2). In general, the temporal decrease in groundwater H^+ , produced by the reaction
163 between H_2O and CO_2 , suggests the temporal increase in the major cation in the groundwater by
164 the cation-exchange reaction between the groundwater and the silicate minerals composing the
165 volcanic rocks through chemical weathering. While the SiO_2 in the groundwater is apparently
166 close to saturation with the dissolution of the silicate minerals, both major and trace elements,
167 such as total cation, Ca, Mg, As, Ge, and P, but excluding Cs in the spring water, increase in
168 concentration due to the dissolution of the silicate minerals in the range of 5°C to 15°C in water
169 temperature (Fig. 4 and Tables 1 and 2). It is an important feature that the concentration of Cs
170 does not correlate with SiO_2 , even though Cs was once released from the SiO_2 mineral that
171 included Cs. Concentration of Cs in the flowing groundwater cannot be explained by the
172 dissolution of the silicate.

173 Groundwater cesium (Cs^+), belonging to the alkaline metal group, indicates a negative
174 correlation coefficient γ with the apparent groundwater residence time, measured by SF_6 dating
175 of the spring water, despite the fact that Li, Na, and K (alkaline metal group) indicate a weak
176 positive correlation with the groundwater residence time (Fig. 5a). The γ order is $Na^+ > Li^+ > K^+$

177 $> \text{Rb}^+ > \text{Cs}^+$ for the aquifer in this study region. Ions of the alkaline metal group, excluding Fr,
178 apparently show a reverse trend in terms of the relationship between correlation coefficient and
179 the ionic radius. This γ order may be related to the replacement series $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
180 based on the ion exchange capacity in the water-rock interaction (e.g., [Ames, 1960](#)). Moreover, a
181 noteworthy point is that Cs indicates a stronger negative correlation with the groundwater
182 residence time, while trace elements P, V, Ga, and Ge indicate a stronger positive correlation ([Fig.](#)
183 [5a](#)). To understand the longtime behavior of Cs in spring water, a comparison of Cs with P, V, Ga,
184 and Ge will be an effective means, considering the conflicting longtime behavior between
185 groundwater Cs and, P, V, Ga, and Ge. The P, V, Ga, and Ge, dissolving as an anion or a hydrate
186 (nonionic soluble species) in the groundwater, according to the redox (Eh-pH) diagram
187 ([Schweitzer and Pesterfield, 2010](#)) ([Table 1](#)), are more than 0.7 in correlation coefficient (γ)
188 between the concentration and the groundwater residence time. Therefore, [Figure 5](#) shows the
189 notable feature that as the groundwater residence time increases from 15 to 45 years, the
190 groundwater Cs decreases exponentially in concentration, while P, V, Ga, and Ge increase in the
191 spring water. The temporal increase in concentrations of groundwater trace elements, such as P,
192 V, Ga, and Ge, indicates the release associated with the dissolution of silicate minerals through
193 chemical weathering.

194 Although groundwater Cs would increase in concentration in the initial mineral dissolution
195 phase through chemical weathering, the Cs gradually decreases in concentration for 45 years in
196 groundwater residence time through the rock-water interaction, despite the reaction that the
197 several trace elements in the groundwater increase with the groundwater residence time. As the
198 redox diagram indicates that Cs^+ is highly stable in resisting both oxidation and reduction

199 (Schweitzer and Pesterfield, 2010), one of the reasons why only the groundwater Cs decreases
200 in concentration with residence time in the alkaline metal group may be the Cs sorption onto
201 aquifer minerals based on its having a larger cation-exchange capacity (Comans et al., 1989)
202 than other lighter metals in the alkaline metal group. However, Cs sorption onto an aquifer in the
203 Quaternary volcanic area requires a long residence time in the natural water cycle.

204

205 4. Discussion

206 4.1 Relationship between concentration of trace elements, and temperature and pH

207 The concentrations of several major and trace elements, such as total cation, Ca, Mg, As, and Ge,
208 as well as SiO₂ (Fig. 4a), in the spring water also apparently correlate weakly with the water
209 temperature, while the concentration of Cs does not correlate with the water temperature (Fig. 6).
210 The dissolution of silicate minerals, in general, proceeds with the equilibrium influenced by the
211 water temperature. In this study area, the water temperature depends on the altitude (Fig. 2c),
212 and the residence time of the spring water sampled at a lower altitude is likely to be longer than
213 that sampled at a higher altitude (Tables 1 and 2). As the spring water has a longer residence
214 time, and therefore, a higher temperature, it is not easy to figure out whether the concentration of
215 some trace elements is determined by the water temperature or by the residence time. In the
216 hydrogeological setting of this study area, both the temperature and the residence time cause
217 some trace elements to increase in concentration. However, the concentration of cesium is not
218 associated with temperature in the range of water temperature of 5 °C to 15 °C in the
219 groundwater, since the concentration of Cs does not apparently correlate with the water
220 temperature (Fig. 6e), as is the case for SiO₂ as well (Fig. 4a), and it correlates negatively with

221 the residence time (Fig. 5).

222 Many trace element concentrations may be controlled by adsorption-desorption reactions at
223 the mineral surface, with the equilibrium strongly influenced by pH (Elprince, 1978; Fuller and
224 Davis, 1989). Figure 7 shows the relationship between the concentration of several trace
225 elements and pH. Since Ge, Ga, P, and V weakly correlate with pH, they may be influenced by
226 pH. However, since the Ge, Ga, P, and V in groundwater dissolve into H_2GeO_3 , $\text{Ga}(\text{OH})_3$,
227 H_2PO_4^- or HPO_4^{2-} , and H_2VO_4^- or HVO_4^{2-} , respectively, from the Eh-pH diagram (Schweitzer
228 and Pesterfield, 2010) (Table 1), desorption of P and V is likely to occur as pH increases with the
229 residence time. Although As weakly correlates with pH, it is unclear whether As is controlled by
230 pH. Since Cs does not correlate with pH (Fig. 7a), the Cs is not controlled by pH in the range of
231 pH of 6.7 to 8.5 in the groundwater. As the groundwater Cs is apparently independent of the pH,
232 Cs^+ adsorption onto the mineral surface should be small in comparison to the sorption of Cs.
233 Caron and Mankarios (2004) indicated that ^{137}Cs was predominantly in the anionic fraction, in
234 the larger-sized colloidal fraction, and in the strong-hydrophobic fraction of groundwater,
235 suggesting an association with natural organic matter (NOM). Some researchers also reported
236 that ^{137}Cs displayed a behavior consistent with a NOM association (e.g., Champ et al., 1984).
237 NOM may influence the long-term behavior of Cs. Considering the results described above, the
238 trace elements, excluding Cs, are likely to increase with water temperature and pH through the
239 water-rock interaction, while it is natural view that Cs is not controlled by water temperature and
240 pH in flowing groundwater in the mountain water source area.

241

242 4.2 Sorption of Cs on aquifer material in being coexistent with other ions

243 Curti (1999) reported that partition coefficients on calcite increase logarithmically with the ionic
244 radius of the co-precipitated ions, based on a review of laboratory investigations and
245 geochemical data. According to Curti (1999), because the ionic radius of Cs is the largest in the
246 alkaline metal group, excluding Fr, not detected in this field, the sorption of Cs on the mineral
247 surface is expected to be larger than that of other alkaline metals. As water-rock interaction, in
248 general, promotes mineral dissolution and the release of trace elements with residence time
249 between the flowing groundwater and the aquifer, Cs^+ becomes coexistent with the other ions in
250 the groundwater. Fukui and Katsurayama (1976) reported that the competitive sorption between
251 Cs^+ and other ions occurs through a saturated sandy layer, and that the univalent ion having a
252 larger ionic radius is more sorptive than the other ions in competitive sorption. When Cs^+ is
253 coexistent with other ions in the groundwater, the Cs sorption onto the aquifer is, therefore,
254 expected to be relatively stronger than that of other ions, even though the aquifer is not a sandy
255 layer. Consequently, the strong sorption of Cs onto the aquifer should cause Cs removal from the
256 flowing groundwater with residence time, even though some trace elements increase in
257 concentration through the water-rock interaction in the competitive sorption. As shown in Fig.
258 5a, for correlation coefficient γ between the concentration of ions of the alkaline metal group and
259 the groundwater residence time of the groundwater, the only Cs^+ , in point of fact, demonstrates a
260 negative correlation of less than -0.7 (Fig. 5b).

261

262 4.3 Estimation of longtime behavior on radioactive Cesium

263 von Gunten et al. (1988) reported that when measuring the radioactive fall-out from the
264 damaged nuclear power station at Chernobyl (USSR) in a shallow groundwater stream in May

1986, Ru-103, I-131, and Te-132 were found in the water (filtrate < 0.05 μm) infiltrating into the groundwater, while no Cs-134 or 137 was detected from wells at distances of 2.5 m and 5 m from the river in which Cs-134 and 137 were detected. They also reported that very small radioactivity was found on colloids > 0.05 μm . The data for Cs-134 and -137 indicate complete sorption on the aquifer material during infiltration (von Gunten et al., 1988). On the other hand, Kersting et al. (1999) reported that radionuclides, including Cs, observed in groundwater samples from aquifers at the Nevada Test Site, 1.3 km north of the sample site, were associated with the colloidal fraction (> 1 μm , 50 nm – 1 μm , 7 nm – 50 nm, < 7nm) of the groundwater. The data demonstrate that Cs is not immobile in the subsurface, but can be transported over significant distances (Kersting et al., 1999).

As described above, from the CFCs and SF₆, which are derived from the atmosphere, and the δD and $\delta^{18}\text{O}$ in the spring water, the spring water migrates a minimum distance of about 2.8 km and a maximum distance of about 10 km through the aquifer between the recharge zone and the spring for several decades. Therefore, the data presented here for Cs through a filter (0.2 μm) in the spring water of the Yatsugatake Mountains provide field evidence that Cs is mobilized over a long distance (~10 km) for several decades through volcanic rock aquifers. Assuming that the longtime behavior of Cs^A in groundwater is the same as that of Cs (e.g., Cornell, 1993; Yoshida et al., 2004), based on the relationship between the groundwater residence time and the concentration of Cs in the spring water, radioactive Cs in the groundwater in mountain water source areas may move along groundwater flow paths (Nakaya et al., 2011) and may decrease exponentially, at the rate of one-tenth in twenty-two years (Fig. 5b), by sorption onto the aquifer through the rock-water interaction, excluding radioactive decay. Laboratory results of Cs⁺

sorption to siliceous mudstone and to compacted sodium montmorillonite by through-diffusion and batch sorption experiments under constant pH (7.0 or 8.5), constant temperature (25°C), and aerobic conditions for over 100 days extrapolate that water Cs^+ decreased exponentially, at the rate of one-tenth in more than two years, in a competitive ion exchange (Tachi et al., 2011; Tachi and Yotsduji, 2014). The major difference in the sorption rate of Cs, between their results and our observation, is caused by the large differences between the permeable rocks (sorbent) and/or between the water conditions. However, their experimental results and transient diffusion model with Freundlich sorption qualitatively agree with our observed longtime behavior of Cs^+ sorption onto a rock aquifer. Although the exponential water Cs^+ decreases due to the Cs^+ sorption onto a permeable layer, this decrease in Cs^+ does not advance for a short term in the field, compared with the laboratory results for the Cs^+ sorption. Therefore, the long-term (~50 yrs.) monitoring of groundwater active Cs is needed in mountain water source areas where radioactive cesium has been dispersed at the times of nuclear power plant accidents. When considering the geological disposal of water that includes active Cs, the artificial injection of active Cs into deep rock aquifers (Smith et al., 2001; Rumynina et al., 2005) may follow the longtime behavior of the Cs sorption observed in the volcanic rock aquifers.

303

304 **5. Conclusions**

305 As the sorption and desorption behavior of the Cs in groundwater should be equal to that of Cs^{A} ,
306 the longtime behavior (10–50 yr) of the Cs^{A} concentration in flowing groundwater through
307 aquifers is expected to be obtainable by field monitoring the relationship between the Cs
308 concentration in groundwater and the residence time of the groundwater in a rock aquifer that

309 includes Cs-bearing minerals. In this study, the Cs concentration in natural spring drinking water
310 was measured with the groundwater residence time, in order to evaluate the longtime behavior
311 of Cs^A in the flowing groundwater of an important source area for drinking water in terms of the
312 natural water cycle.

313

314 1) Groundwater Cs is mobile over a long distance (~10 km) from the recharge area to the spring
315 for several decades through volcanic rock aquifers.

316 2) The Cs concentration in flowing groundwater exponentially decreases slowly with the
317 groundwater residence time (~ 45 yr), while several trace elements, namely, P, V, Ga, and Ge,
318 increase in concentration with the groundwater residence time through chemical weathering.

319 3) The Cs, contained in flowing groundwater in mountain water source areas, decreases
320 exponentially, at the rate of one-tenth in twenty-two years, by sorption onto the aquifer
321 through rock-water interaction.

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323

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325

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429 **Table 1 - Chemical parameters for spring water samples**430 **in Yatsugatake Mountains, Nagano, Japan**

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No	H (mASL)	T (°C)	pH	EC (μS/cm)	DO (mg/L)	ORP (mV)	Geological facies
1	1,013	9.6	7.32	28.3	2.12	53.0	pyroclastics
2	833	13.2	8.26	44.1	2.85	-22.0	pyroclastics
3	1,109	10.4	7.28	46.8	5.91	96.0	pyroclastics
4	947	12.6	6.79	74.5	3.25	-72.0	pyroclastics
5	778	13.0	7.80	65.2	4.20	242	pyroclastics
6	1,051	10.0	6.68	21.6	4.45	313	pyroclastics
7	1,943	5.5	6.71	14.67	4.29	359	Lava
8	971	11.2	8.42	42.7	3.58	359	pyroclastics
9	879	-	-	-	-	-	pyroclastics
10	1,187	9.9	7.03	38.7	4.82	313	pyroclastics
11	1,224	10.3	8.01	35.2	3.95	282	pyroclastics
12	1,246	9.3	7.35	30.5	4.79	276	Lava
13	1,022	10.7	7.29	33.0	5.58	286	Lava
14	835	12.5	7.04	53.8	3.75	289	pyroclastics
15	820	14.9	8.49	54.0	2.99	2.60	pyroclastics
16	799	14.3	7.75	75.7	4.25	282	pyroclastics
17	1,215	8.8	6.89	26.8	4.85	258	Lava

432

433 H: Altitude of sample point; T: Water temperature ; EC: Electrical conductivity;

434 DO: Dissolved oxygen; ORP: Oxidation reduction potential; Eh of the redox

435 diagram can be calculated using ORP and water temperature (T) by

436 $Eh(mV) = ORP(mV) + 206 - 0.7(T - 25)$; - : not measured.

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Table 2 - Dating tracers and stable isotopes of oxygen and hydrogen for spring water samples in Yatsugatake Mountains, Nagano, Japan

No	SF ₆ (fg/L)	CFC -12 (pg/L)	CFC -113 (pg/L)	t ₆ (yr)	t ₁₂ (yr)	t ₁₁₃ (yr)	¹⁸ O (‰ versus VSMOW)	D (‰ versus VSMOW)	H* (m ASL)	T** (°C)
1	181	304	53.1	17.2	22.0	25.6	-12.72	-87.24	1,770	6.2
2	9.14	76.1	1.78	43.0	41.1	44.4	-11.97	-83.14	1,446	7.7
3	45.0	144	28.4	31.2	35.4	30.2	-12.29	-84.55	1,583	7.0
4	87.8	639	17.8	25.2	OR	33.1	-11.72	-81.45	1,341	8.3
5	14.3	44.6	0.	39.8	45.3	>45	-12.19	-84.97	1,540	7.2
6	85.6	298	86.9	25.4	20.9	20.0	-11.74	-81.07	1,349	8.2
7	98.9	298	92.8	24.6	22.9	20.9	-13.13	-88.86	2,150	<5.4
8	13.1	140	19.6	40.5	35.7	32.7	-12.17	-84.66	1,533	7.2
9	11.8	82.4	10.5	41.2	40.3	36.4	-11.84	-82.93	1,390	8.0
10	104	391	79.5	23.5	OR	21.6	-11.88	-81.49	1,410	7.9
11	58.6	-	46.0	29.4	-	26.8	-12.92	-89.27	1,854	5.8
12	97.9	387	72.6	24.5	OR	23.1	-12.52	-85.75	1,682	6.5
13	87.1	272	129	25.5	23.9	OR	-12.12	-83.17	1,513	7.3
14	66.1	553	68.5	28.0	OR	23.0	-11.77	-81.80	1,362	8.1
15	50.3	352	34.2	30.3	OR	28.5	-11.91	-81.97	1,422	7.8
16	26.2	60.9	-	35.1	43.0	-	-12.28	-85.09	1,583	7.0
17	131	305	74.4	21.1	22.0	22.0	-12.71	-87.47	1,764	6.2

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H* is the estimated mean recharge altitude and T** is the water temperature estimated at H* from $\delta^{18}\text{O}$ and δD and its altitude effect⁹⁻¹¹ (Supplementary Fig. 1). t₆, t₁₂ and t₁₁₃ represent the residence times determined from dating tracers SF₆, CFC-12, and CFC-113, respectively. Henry's law is applied to the dating under (T**, H*) condition^{22,23}. OR (: over record) indicates that the residence time cannot be determined, because the CFC gas concentration in the groundwater sample exceeds the modern value. - : not measured.

450

451 **Table 3 - Major components for spring water samples in Yatsugatake Mountains, Nagano,**
 452 **Japan**

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No	Alk (meq/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Total Cation (meq/L)	Total Anion (meq/L)	SiO ₂ (mg/L)
*	<0.004	<0.1	<0.1	<0.1	<0.04	<0.04	<0.01	<0.003			<0.02
1	0.284	1.2	1.5	0.9	2.53	1.34	3.84	0.986	0.387	0.382	26.52
2	0.516	0.3	0.3	0.4	3.75	1.31	5.99	1.786	0.580	0.541	29.80
3	0.532	0.3	0.5	0.9	3.27	1.42	5.98	1.695	0.534	0.566	31.59
4	0.478	4.1	0.5	17.9	3.66	1.68	8.91	3.272	0.950	0.893	28.41
5	0.698	1.5	0.9	0.8	6.00	2.14	8.01	2.931	0.880	0.771	34.86
6	0.282	0.1	0.1	0.9	2.03	0.77	3.12	0.678	0.299	0.302	21.38
7	0.210	0.1	0.5	0.2	1.38	0.71	2.30	0.643	0.255	0.227	15.00
8	0.542	0.2	0.7	2.2	3.54	1.32	6.06	1.729	0.628	0.597	28.32
9	0.546	0.1	0.8	0.7	3.09	1.16	6.05	1.742	0.615	0.578	28.53
10	0.436	0.7	0.1	1.8	2.43	0.76	6.11	1.753	0.570	0.489	18.85
11	0.462	0.1	0.9	0.5	2.91	1.49	4.80	1.503	0.516	0.492	29.90
12	0.404	0.1	1.0	0.7	2.21	1.07	4.78	1.372	0.475	0.438	22.06
13	0.418	0.2	0.8	1.1	2.76	1.35	4.10	1.502	0.480	0.457	27.97
14	0.540	0.5	1.3	5.2	3.71	1.45	7.41	2.260	0.753	0.665	28.73
15	0.654	0.2	0.8	2.9	3.78	1.52	7.24	1.969	0.716	0.721	29.59
16	0.874	0.6	1.4	2.7	7.69	2.64	8.67	3.441	1.03	0.965	33.23
17	0.310	0.2	0.9	0.0	2.42	1.43	3.80	0.880	0.392	0.335	26.35

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455 Alk : alkalinity, *) lower quantification limit,

456 SiO₂ : First, Si was measured by ICP-MS(< 0.020 mg/L), and SiO₂ was determined by Si x (SiO₂/Si) using atomic weight.

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458 **Table 4 - Concentrations of several trace elements**
459 **for spring water samples in Yatsugatake**
460 **Mountains, Nagano, Japan**
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No	Cs (µg/L)	P (µg/L)	V (µg/L)	Ge (µg/L)	Ga (µg/L)	As (µg/L)
*	<0.004	<5	<0.004	<0.001	<0.0005	<0.004
1	0.129	14	3.168	0.012	0.0090	0.204
2	0.019	77	17.43	0.048	0.0580	0.403
3	0.029	72	13.01	0.031	0.0110	0.283
4	0.068	4.0	1.448	0.013	0.0	0.194
5	0.038	65	13.29	0.043	0.0190	0.449
6	0.079	37	1.047	0.007	0.0145	0.147
7	0.079	5.0	0.211	0.006	0.0015	0.160
8	0.020	80	13.02	0.030	0.0375	0.306
9	0.015	90	16.50	0.038	0.0249	0.191
10	0.043	19	2.838	0.010	0.0131	0.0710
11	0.063	67	12.31	0.023	0.0125	0.404
12	0.040	43	6.578	0.018	0.0155	0.165
13	0.090	62	6.106	0.020	0.00820	0.302
14	0.088	32	4.772	0.021	0.0050	0.341
15	0.077	58	8.750	0.032	0.0131	0.343
16	0.035	89	15.95	0.049	0.0141	0.539
17	0.173	28	4.874	0.008	0.0035	0.278

462 *) lower quantification limit

Figure 1

Fig. 1 - Study area. Circles indicate sample locations of spring waters. Bars denote cesium concentration of the spring water samples.

Figure2

Fig. 2 - Sources of the spring water samples and the surface water samples. Relationship between hydrogen and oxygen stable isotopic ratios (δD , $\delta^{18}O$) (a), altitude versus $\delta^{18}O$ for surface water (b), and altitude versus spring water temperature T (c).

Figure3

Fig. 3 - Dating tracers SF6, CFC-12, and CFC-113 concentrations in spring water samples. The concentrations are given in equivalent atmospheric concentrations (pptv). a, CFC-12 versus SF6; b, CFC-113 versus SF6; c, CFC-12 versus CFC-113. Solid curves indicate theoretical curves for the piston flow model. Numbers show the recharge ages of groundwater, in years (yr).

Figure4

Fig. 4 - Relationship between concentrations of major and trace elements, and SiO_2 in spring water samples, with the dissolution of the silicate minerals. a, pH (black solid circle) and water temperature (red solid square) versus SiO_2 ; b, Total cation (black solid circle) and Cs (red solid circle) versus SiO_2 , regression curve (R.C.) : $\text{SiO}_2 = 32.9 + 22.5 \log(\text{Total Cation})$; c, Ca (open triangle) and Mg (solid triangle) versus SiO_2 , R.C. : $\text{SiO}_2 = -27.7 + 17.1 \log(\text{Mg})$; d, As versus SiO_2 , R.C. : $\text{SiO}_2 = 38.6 + 19.2 \log(\text{As})$; e, Ga (open square) and Ge (solid square) versus SiO_2 , R.C. : $\text{SiO}_2 = 51.3 + 14.1 \log(\text{Ge})$; f, P (open triangle) and V (solid triangle) versus SiO_2 , R.C. : $\text{SiO}_2 = 21.3 + 7.92 \log(\text{V})$.

Figure 5

Fig. 5 - Relationship between the concentration of element and the groundwater residence time. Correlation coefficients (γ) between the concentration of element and the groundwater residence time, measured by SF_6 dating, for atomic number in the spring water samples (a). Relationship between the groundwater residence time and the groundwater Cs concentration (b), P concentration (c), V concentration (d), Ge concentration (e), and Ga concentration (f) of the spring water samples. Regression curves are (b) Residence time by SF_6 $t_6 = 2.00 - 21.6 \log(\text{Cs})$; (c) $t_6 = 20.1 \exp(0.00727P)$; (d) $t_6 = 21.2 \exp(0.0372V)$; (e) $t_6 = 19.9 \exp(15.4\text{Ge})$; (f) $t_6 = 57.9 + 14.5 \log(\text{Ga})$. The lines connected to the symbols indicate the residence time results for the same water.

Figure6

Fig. 6 - Relationship between concentration of dissolved elements and water temperature in spring water samples. a, Total cation; b, Ca; c, Mg; d, As; e, Cs; f, Ge. γ indicates correlation coefficient.

Figure7

Fig. 7 - Relationship between concentration of dissolved trace elements and pH in spring water samples. a, Cs; b, Ge; c, Ga; d, P; e, V; f, As. γ indicates correlation coefficient.