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Author(s)	Fujiyoshi, Ryoko; Takekoshi, Naoki; Okamoto, Kazumasa
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Corresponding Author	Family Name	<b>Fujiyoshi</b>
	Particle	
	Given Name	<b>Ryoko</b>
	Suffix	
	Division	Faculty of Engineering
	Organization	Hokkaido University
	Address	060-8628, Sapporo, Japan
	Email	fuji@eng.hokudai.ac.jp
Author	Family Name	<b>Takekoshi</b>
	Particle	
	Given Name	<b>Naoki</b>
	Suffix	
	Division	Faculty of Engineering
	Organization	Hokkaido University
	Address	060-8628, Sapporo, Japan
	Email	
Author	Family Name	<b>Okamoto</b>
	Particle	
	Given Name	<b>Kazumasa</b>
	Suffix	
	Division	Faculty of Engineering
	Organization	Hokkaido University
	Address	060-8628, Sapporo, Japan
	Email	
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Abstract	Radiopotassium isotopic composition ( $^{40}\text{K}/\text{K}$ , %) of several forest soils did not show a constant value of generally known $1.17 \times 10^{-2}\%$ , but they were varied significantly from $0.4 \times 10^{-2}\%$ to $1.3 \times 10^{-2}\%$ at different locations under different environmental conditions. Surface portion of a soil (2–4 cm in depth) gave always lower $^{40}\text{K}/\text{K}$ values compared with those of deeper soil layer (35–40 cm in depth). Ion exchange of $\text{K}^+$ with $\text{NH}_4^+$ did not affect the $^{40}\text{K}/\text{K}$ value in any soils, which revealed with chemical leaching experiments in the laboratory. Some plant species showed much lower $^{40}\text{K}/\text{K}$ values than those in the surface soil. Possible reasons for varying $^{40}\text{K}/\text{K}$ values obtained in this study may result from a dynamic behavior of potassium in soil, probably due to biological activity including root uptake and decomposing soil organic matter by microorganisms in the forest floor.	

Keywords (separated by '-') <sup>40</sup>K isotopic composition - Depth distribution - Carbonaceous soil - Volcanic soil - Soil organic matter

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Footnote Information

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## Variability of $^{40}\text{K}$ isotopic composition in forest soils under different environmental conditions

Ryoko Fujiyoshi · Naoki Takekoshi ·  
Kazumasa Okamoto

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**Abstract** Radiopotassium isotopic composition ( $^{40}\text{K}/\text{K}$ , %) of several forest soils did not show a constant value of generally known  $1.17 \times 10^{-2}$  %, but they were varied significantly from  $0.4 \times 10^{-2}$  to  $1.3 \times 10^{-2}$  % at different locations under different environmental conditions. Surface portion of a soil (2–4 cm in depth) gave always lower  $^{40}\text{K}/\text{K}$  values compared with those of deeper soil layer (35–40 cm in depth). Ion exchange of  $\text{K}^+$  with  $\text{NH}_4^+$  did not affect the  $^{40}\text{K}/\text{K}$  value in any soils, which revealed with chemical leaching experiments in the laboratory. Some plant species showed much lower  $^{40}\text{K}/\text{K}$  values than those in the surface soil. Possible reasons for varying  $^{40}\text{K}/\text{K}$  values obtained in this study may result from a dynamic behavior of potassium in soil, probably due to biological activity including root uptake and decomposing soil organic matter by microorganisms in the forest floor.

**Keywords**  $^{40}\text{K}$  isotopic composition · Depth distribution · Carbonaceous soil · Volcanic soil · Soil organic matter

### Introduction

Potassium (K) is an essential nutrient for plant growth and development. An extreme nutrition state was observed in a hilly region of tropical montane forest in northern Peru, where plants utilize a very small amount of K present only in the uppermost portion of the soil underlying acidic sand rock [1]. Potassium was supposed to circulate between

plants and topsoil with high (micro) biological activity. Likens et al. [2] summarized their long-term investigation of potassium and the environment as the biogeochemistry of potassium at Hubbard Brook in New Hampshire, USA. According to them, turnover rate for K (exchangeable K) in forest floor and mineral soil are relatively fast, 0.40 and 3.4 year, respectively. In spite of large quantities of K in abiotic and biotic pools and short residence time, K is the slowest to recover to pre-disturbance conditions such as clear-cutting and removal of harvest products compared with other major elements.

Potassium is believed to distribute rather homogeneously in soil within a horizon of interest [3]. Chemical speciation of K in soil revealed labile potassium ( $\text{K}^+$ ) to be predominant at a depth of 10 cm under temperate coniferous stands with different tree ages in Tharndt, Germany [4]. The result is reasonably explained for the plant roots to uptake nutrients easily from the surface portion abundant in bio-available K ( $\text{K}^+$  and ion exchangeable K). With respect to the behavior of K in plants, Szczerba et al. [5] reviewed  $\text{K}^+$  transport in plants in view of plant molecular biology and physiology. They showed a wide variety of  $\text{K}^+$  transport systems and catalyzing  $\text{K}^+$  uptake across a wide spectrum of external concentrations, mediating  $\text{K}^+$  movement within the plants as well as its efflux into the environment. There are many factors affecting  $\text{K}^+$  transport in plants, such as external  $\text{K}^+$  supply, the presence of other ions in the root environment and plant stresses. It is therefore important to elucidate dynamic properties of potassium in soil, which is closely related to the transportation in plants.

Naturally occurring potassium consists of stable isotopes of  $^{39}\text{K}$  and  $^{41}\text{K}$ , and a radioactive isotope  $^{40}\text{K}$  with their isotopic composition (atom %) of 93.2581, 6.7302 and 0.0117 %, respectively. With a half-life of  $1.25 \times 10^9$  year,

R. Fujiyoshi (✉) · N. Takekoshi · K. Okamoto  
Faculty of Engineering, Hokkaido University,  
Sapporo 060-8628, Japan  
e-mail: fuji@eng.hokudai.ac.jp

<sup>40</sup>K is changing by beta emission to <sup>40</sup>Ca (89 %) and by orbital electron capture to <sup>40</sup>Ar (11 %). In our previous investigation using <sup>40</sup>K as a natural radiotracer in soil, its distribution showed no smooth profile with depth within the same soil horizon. Radiopotassium isotopic composition (<sup>40</sup>K/K) calculated from sets of data on <sup>40</sup>K activity concentration and total K content in soil were not constant (0.0117 %), but varied to a great extent depending on environmental factors including geology of the sites [1]. Considering dynamic behavior of potassium in soil-plant systems, <sup>40</sup>K/K values in soil may change during uptake and transport processes of the nutrients. Isotope fractionation of light elements like H, C, N and O occurs under various environmental conditions. Several reports have recently been published on isotope fractionation of heavy metals in soils, in which stable isotope fractionation of chromium, copper, zinc, cadmium and mercury in contaminated soils are useful tracers for evaluating hydrological and biogeochemical processes and sources of the contaminants [6–9]. However, there is little data on <sup>40</sup>K/K values in forest soils in the literature in spite that only <sup>40</sup>K activity has been measured extensively for monitoring and assessing external natural radiation dose, and for determining potassium content in soil so far [3, 10, 11].

This study aims at evaluating <sup>40</sup>K isotopic composition (<sup>40</sup>K/K) in forest soils under different environmental conditions in Tomakomai (Hokkaido, Japan) and in Slovenia with non-destructive techniques of gamma spectrometry and of energy-dispersive X-ray fluorescence spectrometry (EDXRF), and at elucidating possible reasons for its inhomogeneous distribution in soil, and hopefully proposing <sup>40</sup>K/K values as a potential tracer to elucidate biogeochemical cycling of potassium in soil-plant systems.

## 104 Materials and methods

### 105 Description of the sites and soil sampling

106 Location map of the Tomakomai Experimental Forest of  
107 Hokkaido University in Tomakomai, Japan (42°40'N,  
108 141°36'N, 27 km<sup>2</sup> in total area) was shown in our previous  
109 paper [12]. Annual mean temperature and precipitation in  
110 the site are 6.4 °C and 1,450 mm, respectively. The ground  
111 surface of hilly site with altitude of 5–90 m a.s.l. was  
112 covered with volcanic ash derived from an active Mt.  
113 Tarumae which erupted 330 years ago. As shown in Fig. 1,  
114 a thin organic layer exists only on the uppermost part of the  
115 soil down to a depth of 6 cm from the ground surface,  
116 which then appears several laminar structures of volcanic  
117 ash down to a depth of 1 m. Each layer corresponds to past  
118 eruption of the volcano. About 100 tree species and 300  
119 herbaceous species were recorded in the Tomakomai



**Fig. 1** Cross sectional view of the volcanic soil in Tomakomai Experimental Forest, Tomakomai, Japan. Thin organic layer appeared only on the top 5 cm in depth. Several laminar layers of coarse volcanic ash were inter-located in the profile. The soil showed high permeability and low clay content (8 % in top soil and 0.5 % at a depth of 30 cm). The depth of the pit is 100 cm in depth

Experimental Forest in 1916 [13]. Predominant vegetation 120  
of the study site is deciduous broad-leaved stands like 121  
Mongolian oak (*Quercus crispula*), Painted maple (*Acer 122*  
*mono Maxim*) and Linden (*Tilia japonica*). The site was 123  
categorized to be high tree density (>70 % canopy occu- 124  
pancy) and high tree height (>16 m in mean height). The 125  
forest floor was covered with various plant species, with a 126  
lot of fallen leaves (twigs) and with snow depending on the 127  
season of the year. 128

Soil sampling was carried out in June 2009 and in 129  
November 2010. Each sample (~500 g in weight) was 130  
collected carefully at 2–5 cm intervals from the uppermost 131  
(organic layer) to a depth of about 40 cm (volcanic ash 132  
layer of different grain sizes). The samples dried at 110 °C 133  
for 24 h were sieved with a stainless filter of 2 mm in pore 134  
size, and stored in plastic bottles for further analyses. 135

Other sites investigated in this study were located in 136  
Slovenia, where three major landscape regions and four 137  
provinces are lying; Alpine-High Nordic (Alpine prov- 138  
ince), Euro-Siberian–North American (Central European 139  
and Illyrian provinces) and Mediterranean (Adriatic prov- 140  
ince) regions [14]. The predominant forest vegetation cover 141  
at each site was oak (*Quercus pubescens*, *Quercus petraea*) 142  
and beech (*Fagus sylvatica*) trees and some pine trees 143  
(*Pinus sylvestris*) in Žirovski vrh (P1), beech trees (*Fagus 144*  
*sylvatica*) in Idrija (P2), beech (*Fagus sylvatica*) and pine 145  
(*Pinus sylvestris*) trees in Kočevski rog (P3), pine trees 146  
(*Pinus sylvestris*) in Pohorje (P4), beech (*Fagus sylvatica*) 147

148 and oak (*Quercus pubescens*, *Quercus petraea*) trees in  
149 Gorišnica (P5) and beech (*Fagus sylvatica*) and pine (*Pinus*  
150 *sylvestris*) trees in Rakitna (P6). All the sites were cate-  
151 gorized to be high tree density (>70 % canopy occupancy)  
152 and high tree height (>16 m in mean height). Undergrowth  
153 was not dense in any sites except for that in Žirovski vrh  
154 where several types of shrubs grew. All the soils in  
155 Slovenia investigated in this study were collected in Sep-  
156 tember 2009.

#### 157 Soil properties

158 Table 1 shows the results of some soil properties (density,  
159 humidity, pH and soil organic matter) in Tomakomai and  
160 in Slovenian forest sites [15, 16]. Details of the experi-  
161 mental procedures were described previously [12].

#### 162 Activity measurements of $^{40}\text{K}$ with a HPGe detection 163 system

164 Gamma spectrometry with two types of HPGe detectors  
165 (GEM-25185P, GMX10P, AMETEC, USA) were applied  
166 to evaluate activity concentration of  $^{40}\text{K}$  in soil. Standard  
167 reference materials (IAEA 327 and IAEA 444) were used  
168 for the detector efficiency calibration with the same  
169 geometry under identical operating conditions. Energy and  
170 efficiency calibrations were periodically carried out as well  
171 as background check. In order to evaluate reliability of the  
172  $^{40}\text{K}$  activity measurement, a standard addition procedure  
173 was applied, in which aliquots of 2 M KCl aqueous solu-  
174 tion was added to a definite amount of reference soils to  
175 evaluate increase in counting.

#### 176 Determination of potassium in soil

177 Energy dispersive X-ray fluorescence spectrometry (JSX-  
178 3220, JEOL, Japan) was used for determining total K  
179 content of the soil. After energy calibration of the instru-  
180 ment with a Rh checking source, calibration curve of K  
181 was prepared with several standard soil samples of known  
182 K content. X-ray energy spectra of soil samples show some  
183 overlapping interference from the Ca ( $\text{K}\alpha$ ) peak on that of  
184 K ( $\text{K}\alpha$ ) from 3.4 to 3.5 keV. The energy range for counting  
185 was set from 3.14 to 3.32 keV in this study. Potassium in  
186 soil was determined with a calibration technique using  
187 standard soils of known K content (JSO-1, National Insti-  
188 tute of Advanced Industrial Science and Technology,  
189 Japan).

#### 190 Chemical leaching of potassium in selected samples

191 Change in  $^{40}\text{K}/\text{K}$  value was investigated in selected sam-  
192 ples including reagent grade clay minerals using a chemical

leaching technique with 1 M ammonium acetate aqueous 193  
solution or 1 M HCl. An aliquot of each chemical reagent 194  
was added to a soil suspension ( $5\text{ cm}^3$  per 1 g soil sample 195  
in dry weight), which was stirred for 24 h at room tem- 196  
perature. The suspension was filtered to collect the residual 197  
portion, which was then used for  $^{40}\text{K}$  and total K deter- 198  
mination. The samples used for this treatment were both 199  
surface and deeper portions from Slovenia (P1, P2, P4, P5 200  
and P6), and those from Tomakomai (P1). The leaching 201  
experiment was also conducted on several reagent grade 202  
clay minerals (bentonite, kaolinite and vermiculite) pur- 203  
chased from the Wako Pure Chemical Industries Ltd., 204  
Japan as references. 205

## 206 Results and discussion

Figure 2 shows depth distribution profiles of  $^{40}\text{K}/\text{K}$  ratio in 207  
forest soils collected from Slovenia (Fig. 2a) and from 208  
Tomakomai (Fig. 2b). Vertical lines in the figures denote 209  
the  $^{40}\text{K}/\text{K}$  value of  $1.17 \times 10^{-2} \%$  with its uncertainty 210  
including systematic error determined in our laboratory 211  
[17]. As shown in Fig. 2a,  $^{40}\text{K}/\text{K}$  values were not constant 212  
among soils in different locations and at different depths 213  
within the same horizon of interest in Slovenia. Lower  $^{40}\text{K}/$  214  
K values ( $0.75 \times 10^{-2}$  to  $0.78 \times 10^{-2} \%$ ) appeared in the 215  
surface portion (down to a depth of about 5 cm) compared 216  
with those ( $0.86 \times 10^{-2}$  to  $1.07 \times 10^{-2} \%$ ) in deeper part 217  
(lower than 30 cm in depth) of the soil independent of the 218  
location. Similar  $^{40}\text{K}/\text{K}$  depth distribution profiles were 219  
obtained in other locations of different geology [17]. 220  
Results in the carbonaceous soil in Rakitna (P6) showed 221  
high and variable  $^{40}\text{K}/\text{K}$  values with two peaks appearing 222  
about at 4–6 and 20–22 cm in depth, which may reflect 223  
different soil properties such as density and pH [15]. 224

In Tomakomai two types of soil horizon with different 225  
 $^{40}\text{K}/\text{K}$  ratio appeared on the profile, as shown in Fig. 2b. 226  
They are about  $0.50 \times 10^{-2}$  to  $0.66 \times 10^{-2}$  and  $0.7 \times$  227  
 $10^{-2}$  to  $1.0 \times 10^{-2} \%$  in the upper (<10 cm) and lower 228  
(>20 cm) portions of the soil, respectively, which reflects a 229  
boundary of distinct structures existing at a depth of about 230  
15 cm as shown in Fig. 1. Depth distribution profiles of 231  
soil organic matter (SOM) support the presence of this 232  
boundary layer below which SOM becomes quite low 233  
proportion (SOM <5 %) as shown in Table 1. The soil in 234  
Tomakomai is categorized to immature volcanic ash 235  
resulting in a specific  $^{40}\text{K}/\text{K}$  value shown in Fig. 2b. 236

In order to find possible factors (and processes) affecting 237  
 $^{40}\text{K}/\text{K}$  values in soil, they were compared with some soil 238  
properties. As summarized in Table 1, humidity and SOM 239  
correlate to each other depending on the soil depth 240  
regardless of the sites, since highest values on both prop- 241  
erties generally appear at the surface portion, and they 242

**Table 1** Properties of soils (dry density, humidity, pH and the amount of soil organic matter) investigated in Tomakomai (Japan) and Slovenian forest sites

Soil depth (cm)	Tomakomai experimental forest site (coarse-textured volcanic soil)							
	Point 1				Point 3			
	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )
0–2	4.88	56.8	20.0	1.27	–	55.0	18.9	1.39
2–4	4.81	49.0	15.4	1.38	–	46.8	13.7	1.12
4–6	4.93	33.1	6.2	1.51	–	39.9	10.5	1.53
6–8	5.12	25.1	3.1	1.76	–	33.4	8.8	–
8–10	5.27	19.0	1.8	1.67	–	27.5	5.5	–
10–12	5.52	18.7	1.3	1.76	–	18.0	2.5	–
12–15	5.42	21.5	1.6	1.98	–	16.7	1.4	–
15–20	5.36	22.3	0.7	1.66	–	21.0	1.6	–
20–25	5.58	19.9	0.5	1.86	–	22.4	–	–
25–30	–	19.7	0.6	1.76	–	23.6	–	–
30–35	–	21.6	0.6	1.67	–	21.8	–	–
35–40	5.4	23.1	1.1	1.68	5.04	20.6	0.8	1.67
Depth (cm)	Point 2				Point 4			
	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )
	0–2	5.2	57.3	18.2	1.36	5.3	43.8	10.5
2–4	5.33	45.4	10.0	1.40	5.23	–	4.4	1.39
4–6	5.32	35.4	7.0	1.67	5.16	18.0	2.2	1.40
6–8	5.47	25.7	3.8	1.76	4.95	15.1	1.1	1.44
8–10	5.64	18.9	2.3	1.67	5.04	17.1	1.2	1.51
10–12	–	17.4	1.3	1.86	5.04	22.7	1.2	1.51
12–15	5.61	21.1	1.5	–	4.94	22.2	1.8	1.58
15–20	–	24.4	1.5	1.75	5.14	22.6	0.9	1.58
20–25	–	25.5	1.0	1.62	–	–	1.0	1.30
25–30	–	21.2	0.7	1.74	–	–	0.7	1.67
30–35	–	20.1	0.6	1.76	–	–	–	–
35–40	5.78	21.4	0.6	1.86	–	–	0.6	1.64
Soil Depth (cm)	Slovenian forest sites <sup>a</sup>							
	Point 1 (Žirovski vrh) siliceous soil				Point 2 (Idria) carbonaceous soil			
	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )
0–2	3.96	23.1	15.0	0.98	6.62	34.9	26.6	0.91
2–4	3.81	23.9	12.5	0.97	6.85	34.7	30.0	0.95
4–6	3.67	27.1	12.5	0.87	6.67	32.2	29.2	0.95
6–8	3.71	27.3	12.7	0.91	6.86	33.3	29.1	0.98
8–10	3.77	27.2	12.9	0.86	6.88	31.5	29.0	1.05
10–12	3.51	26.8	11.5	0.93	6.87	30.3	27.3	1.06
12–15	3.56	26.0	11.6	0.94	6.26	27.3	21.8	1.17
15–20	3.68	26.0	11.0	0.95	6.47	24.8	17.7	1.24
20–25	3.68	24.8	9.5	1.03	7.00	20.6	13.4	1.24
25–30	3.71	23.5	10.2	1.01	6.92	18.8	13.8	1.25
30–35	3.63	23.4	8.5	1.03	6.67	17.0	10.4	1.26
35–40	3.65	13.1	7.8	1.07	6.85	13.1	8.5	1.29

**Table 1** continued

Depth (cm)	Point 3 (Kočevski rog) carbonaceous soil				Point 4 (Pohorje) siliceous soil			
	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )
0–2	5.86	22.9	22.5	1.02	3.48	21.3	19.2	0.96
2–4	–	–	–	–	3.62	21.4	13.6	1.06
4–6	6.09	21.5	17.7	1.17	3.69	21.1	12.4	0.94
6–8	–	–	–	–	3.70	21.4	11.9	1.03
8–10	–	–	–	–	3.75	21.2	11.7	1.01
10–12	6.02	21.8	16.2	1.24	3.69	20.7	10.3	0.92
12–15	–	–	–	–	3.76	19.8	9.5	1.07
15–20	6.13	21.5	15.9	1.13	3.85	19.8	9.2	1.06
20–25	6.41	20.1	14.2	1.19	3.91	19.6	8.5	1.11
25–30	6.70	20.0	14.8	1.21	3.92	20.6	8.9	1.09
30–35	–	–	–	–	3.96	28.4	8.3	1.11
35–40	–	–	–	–	4.02	17.9	8.3	1.07

Depth (cm)	Point 5 (Gorišnica) fluvial sediments				Point 6 (Rakitna) carbonaceous soil			
	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )	pH	Humidity (%)	SOM (%)	Density (g/cm <sup>3</sup> )
0–2	3.13	14.6	8.6	1.04	6.44	39.3	37.7	1.07
2–4	3.33	14.6	8.1	1.02	6.46	39.0	34.1	1.07
4–6	3.40	10.1	7.1	1.14	6.77	38.5	29.6	1.11
6–8	3.44	10.1	7.1	1.16	6.81	36.9	26.8	1.04
8–10	3.52	10.2	6.6	1.14	6.94	36.0	26.2	1.11
10–12	3.55	6.1	7.2	1.07	6.96	33.1	24.5	1.07
12–15	3.82	11.2	6.7	1.18	6.56	29.4	22.6	1.11
15–20	3.92	15.2	7.2	1.07	6.85	30.8	21.2	1.04
20–25	4.07	17.2	7.5	1.20	6.94	29.6	25.4	1.07
25–30	4.09	16.7	7.9	1.18	6.99	29.4	25.3	1.07
30–35	4.23	10.4	9.09	1.18	–	–	–	–
35–40	4.31	8.4	10.9	1.25	–	–	–	–

– No data

<sup>a</sup> Cited from the reference [16]

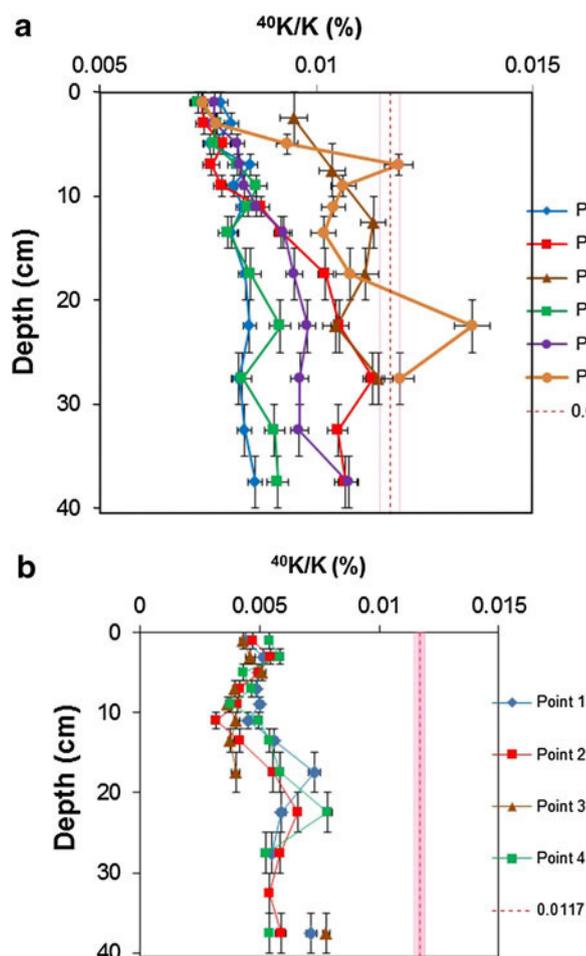
243 decrease with increasing soil depth. Also in the table,  
 244 carbonaceous surface soils in Slovenia (Points 2, 3 and 6)  
 245 contain higher SOM (30–40 %) than those (<20 %) in  
 246 siliceous soils (Points 1, 4 and 5). Depth distribution of  
 247 <sup>40</sup>K/K values (Fig. 2a) showed similar profiles to those of  
 248 SOM, which gives positive correlations between them in  
 249 all the Slovenian soils investigated in this study.

250 With respect to immature volcanic soil in Tomakomai,  
 251 good correlations also exist between humidity and SOM.  
 252 However, different patterns of <sup>40</sup>K/K–SOM relations to  
 253 those of Slovenian soils were obtained, in which lower <sup>40</sup>K/  
 254 K values appeared only at the uppermost portions with low  
 255 SOM. These findings suggest that the presence of SOM in  
 256 early diagenetic stage (or possible biological activity) may  
 257 affect <sup>40</sup>K/K values to a great extent. The presence of soil  
 258 organic matter and biological activity were suggested to  
 259 play an important role on <sup>40</sup>K/K distribution profiles in

Peruvian surface soil [17]. Further investigation is necessary  
 260 to elucidate biological effects on soil <sup>40</sup>K/K dynamics  
 261 by monitoring various soil components in the forest floor  
 262 for a long time.  
 263

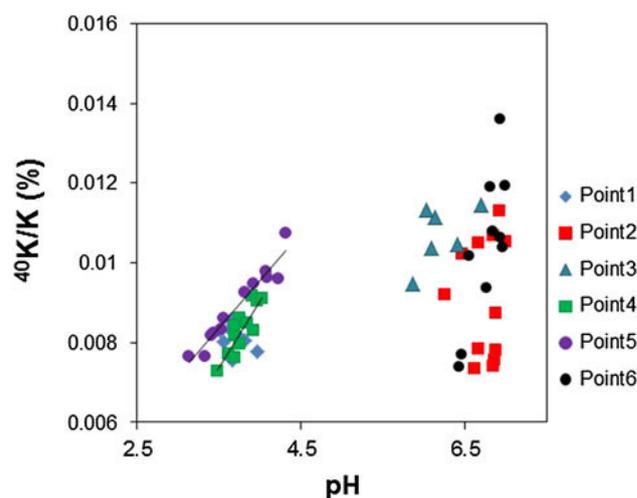
Figure 3 shows the relations between <sup>40</sup>K/K values and  
 264 soil pH in Slovenian soils. Positive correlations (correlation  
 265 coefficient  $r > 0.9$ ) exist in the case of siliceous soil types  
 266 (P4 and P5) in which a difference in 1 pH unit corresponds  
 267 to an increase of 0.002 to 0.003 % in <sup>40</sup>K/K value within a  
 268 small pH ranged from 3 to 4.5. In carbonaceous soils at  
 269 Points 2, 3 and 6, <sup>40</sup>K/K values vary to a great extent within  
 270 a narrow pH range ( $6 < \text{pH} < 7$ ) attributing to pH buffer  
 271 effect of carbonate minerals in soil–water systems. These  
 272 results indicate that K (and <sup>40</sup>K) in soil may be labile in  
 273 hydrogen exchange reactions in soil–water systems.  
 274

Ion exchange properties of potassium (<sup>40</sup>K and two other  
 275 stable isotopes of K) with hydrogen ions (H<sup>+</sup>) were  
 276

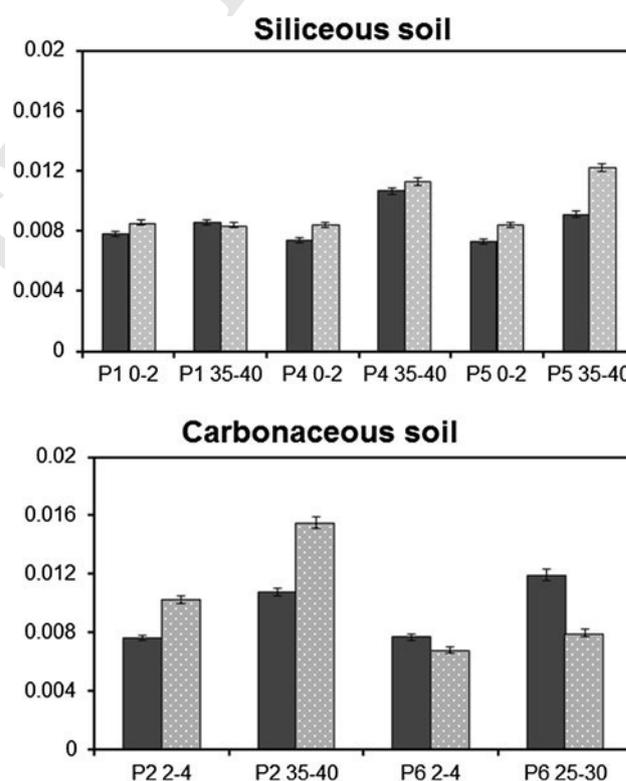


**Fig. 2** a Depth distribution profiles of  $^{40}\text{K}/\text{K}$  value in several forest soils from Slovenia. Žirovski VRH (Point 1), Idria (Point 2), Kočevski ROG (Point 3), Pohorje (Point 4), Gorišnica (Point 5), Rakitna (Point 6). A vertical line in the figure indicates the  $^{40}\text{K}/\text{K}$  value of  $1.17 \times 10^{-2} \%$  with uncertainty evaluated in this study. b Depth distribution profiles of  $^{40}\text{K}/\text{K}$  value in forest soils from Tomakomai Experimental Forest in Tomakomai, Japan. Four points (Points 1, 2, 3 and 4) in north eastern part of the flat zone in the forest ( $27.15 \text{ m}^2$  in area) were selected in this study. A vertical line in the figure indicates the  $^{40}\text{K}/\text{K}$  value of  $1.17 \times 10^{-2} \%$  with uncertainty evaluated in this study

277 investigated for several Slovenian soils with an acid dis-  
 278 solution experiment using 1 M HCl as a leaching agent. A  
 279 residue after the acid treatment was applied further to the K  
 280 and  $^{40}\text{K}$  determination. The results in Fig. 4 showed that  
 281  $^{40}\text{K}/\text{K}$  values in any samples have changed after the  
 282 treatment. The  $^{40}\text{K}/\text{K}$  values both in the surface (0–4 cm)  
 283 and deeper (30–40 cm) portions of clayey soils increased  
 284 about 10–15 % from those before leaching. Radioactivity  
 285 measurement of the residual samples after the acid treat-  
 286 ment gave the result that  $^{40}\text{K}$  preferably retains in residual  
 287 soil components. Pattern of the  $^{40}\text{K}$  dissolution was dif-  
 288 ferent with different carbonaceous soils at Points 2 and 6,  
 289 in which  $^{40}\text{K}/\text{K}$  values increased at Point 2 by acid



**Fig. 3** Plots of  $^{40}\text{K}/\text{K}$  values against soil pH in Slovenian forest soils investigated in this study. Siliceous soils at Points 1, 4 and 5 showed high positive correlation with pH, whereas scattered  $^{40}\text{K}/\text{K}$  values appeared in carbonaceous soils at Points 2, 3 and 6



**Fig. 4** Results of chemical leaching experiments with 1 M HCl on the surface and deeper portions of several Slovenian soils at Points 1, 2, 4, 5 and 6. Notation after each point in the figure indicates a range of depth. For example, a notation (P1 0–2) denotes to a depth range from 0 to 2 cm at Point 1. A bar on each plot shows an estimated uncertainty obtained by triplicate experimental results. All the soils except for that at deeper portion of the Point 1 showed increasing  $^{40}\text{K}/\text{K}$  values with acid treatments. No consistent trends appeared for carbonaceous soils at Points 2 and 6

290 leaching. In contrast, small amount of  $^{40}\text{K}$  in the soil at  
 291 Point 6 disappeared resulting in lower values of the  $^{40}\text{K}/\text{K}$   
 292 isotope ratio. Dissolution of carbonate minerals (calcite  
 293 and/or dolomite) in the carbonaceous soils at both points  
 294 appeared after the acid treatment by power X-ray diffraction  
 295 analyses [16]. The results suggest that potassium is  
 296 dissolved partly into the acid solution by dissolving carbon-  
 297 ate minerals (also some other soil components) rather  
 298 randomly without keeping its isotope ratio to be constant.  
 299 Dissolution of carbonate minerals (calcite) and subsequent  
 300 potassium leaching by the acid treatment result in  $^{40}\text{K}$   
 301 deficiency to a greater extent in carbonaceous soils at Point  
 302 6. It should be noted that dolomite contained in carbona-  
 303 ceous soils in deeper portion at Points 2 and 6 was little  
 304 dissolved with the acid treatment. Results of powder X-ray  
 305 diffraction analyses support the findings [16].

306 Jalali and Kolahchi [18] investigated short-term potas-  
 307 sium release and fixation in some calcareous soils in  
 308 Hamadan province, Iran. They used a modified quantity-to-  
 309 intensity experiment to evaluate exchangeable  $\text{K}^+$  and  
 310 nonexchangeable  $\text{K}^+$  in the laboratory. They proposed a set  
 311 of parameters characterizing the exchange equilibrium and  
 312 the release or fixation of potassium in agricultural soils.  
 313 Although their study is only concerned with agricultural  
 314 soils, it is likely to compare the findings on  $^{40}\text{K}/\text{K}$  values in  
 315 this study to theirs.

316 Another factor probably affecting  $^{40}\text{K}/\text{K}$  value is included  
 317 in various organic matter (SOM) present in forest soils (or  
 318 possibly biological activity). As shown in Fig. 2a, the  $^{40}\text{K}/\text{K}$   
 319 values were higher at organic-rich surface portion (30–40 %  
 320 in SOM) in carbonaceous soils at P2 and P6 in Slovenia. The  
 321 result indicates that  $^{40}\text{K}$  is enriched in the soils abundant in  
 322 SOM. Our previous investigation in Sapporo gave a similar  
 323 result [17]. As a possible evidence of changing  $^{40}\text{K}/\text{K}$  ratios,  
 324 a plant species (*Equisetum hyemale* L.) and a litter sample  
 325 gave quite different  $^{40}\text{K}/\text{K}$  values to those in the soil  
 326 ( $0.9 \times 10^{-2}$  to  $1.3 \times 10^{-2}$  %) collected in November 2010  
 327 from semi-natural woods on the campus of Hokkaido Uni-  
 328 versity in Sapporo, Japan. They were  $0.42 (\pm 0.01) \times 10^{-2}$   
 329 and  $0.59 (\pm 0.02) \times 10^{-2}$  % for the plant and litter,  
 330 respectively indicating reluctant uptake of radiopotassium  
 331 ( $^{40}\text{K}$ ) by the plant in late autumn.

332 The root-fungal association in forest ecosystems is known  
 333 to have a unique soil microenvironment different from the  
 334 bulk soil. Arocena et al. [19] studied the spatial variations in  
 335 the composition of soil solution and mineralogy of the rhi-  
 336 zosphere as influenced by the root-fungal association of  
 337 Norway spruce (*Piloderma croceum*) in the cultivated  
 338 experiment. They found significantly lower amounts of  $\text{K}^+$   
 339 and other nutrients in the *Piloderma*-colonized treatment  
 340 culture (closer to 1 cm from the roots) compared to the  
 341 control. They referred the result to an evidence of *Piloderma*

342 modified soil solution and mineralogy through acquisition of  
 343 essential elements for its own survival and/or for the uptake  
 344 by plant roots. Monitoring  $^{40}\text{K}/\text{K}$  value in soil environment  
 345 may be another indicator to evaluate bioavailability of  
 346 potassium in root-fungal association in forest ecosystems.

347 Dynamic behavior of potassium in undisturbed forest  
 348 soil environment influences its isotopic composition ( $^{40}\text{K}/\text{K}$ )  
 349 to a great extent. Biological activity and subsequent  
 350 properties of soil organic matter may play an important role  
 351 on changing  $^{40}\text{K}/\text{K}$  values in soil components. Further  
 352 investigation should be necessary to establish  $^{40}\text{K}/\text{K}$  as a  
 353 potential parameter to elucidate isotope fractionation of  
 354 potassium in forest soil environment.

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