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Abstract

Radiopotassium isotopic composition ($^{40}K/K$, %) of several forest soils did not show a constant value of generally known 1.17×10^{-2} %, but they were varied significantly from 0.4×10^{-2} to 1.3×10^{-2} % at different locations under different environmental conditions. Surface portion of a soil (2–4 cm in depth) gave always lower $^{40}K/K$ values compared with those of deeper soil layer (35–40 cm in depth). Ion exchange of K^+ with $NH_4{}^+$ did not affects the $^{40}K/K$ value in any soils, which revealed with chemical leaching experiments in the laboratory. Some plant species showed much lower $^{40}K/K$ values than those in the surface soil. Possible reasons for varying $^{40}K/K$ 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 '-')	^{40}K isotopic composition - Depth distribution - Carbonaceous soil - Volcanic soil - Soil organic matter
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Variability of ^{40}K isotopic composition in forest soils under different environmental conditions

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Abstract Radiopotassium isotopic composition (^{40}K/K, %) of several forest soils did not show a constant value of generally known 1.17×10^{-2} %, but they were varied significantly from 0.4×10^{-2} to 1.3×10^{-2} % at different locations under different environmental conditions. Surface portion of a soil (2–4 cm in depth) gave always lower ^{40}K/K values compared with those of deeper soil layer (35–40 cm in depth). Ion exchange of K^+ with $NH_4{}^+$ did not affects the ^{40}K/K value in any soils, which revealed with chemical leaching experiments in the laboratory. Some plant species showed much lower ^{40}K/K values than those in the surface soil. Possible reasons for varying ^{40}K/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}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 (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 (K^+ and ion exchangeable K). With respect to the behavior of K in plants, Szczerba et al. [5] reviewed K^+ transport in plants in view of plant molecular biology and physiology. They showed a wide variety of K^+ transport systems and catalyzing K^+ uptake across a wide spectrum of external concentrations, mediating K^+ movement within the plants as well as its efflux into the environment. There are many factors affecting K^+ transport in plants, such as external 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}K and ^{41}K, and a radioactive isotope ^{40}K with their isotopic composition (atom %) of 93.2581, 6.7302 and 0.0117 %, respectively. With a half-life of 1.25×10^9 year,

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^{40}K is changing by beta emission to ^{40}Ca (89 %) and by orbital electron capture to ^{40}Ar (11 %). In our previous investigation using ^{40}K as a natural radiotracer in soil, its distribution showed no smooth profile with depth within the same soil horizon. Radiopotassium isotopic composition ($^{40}K/K$) calculated from sets of data on ^{40}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, $^{40}K/K$ 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 $^{40}K/K$ values in forest soils in the literature in spite that only ^{40}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 ^{40}K isotopic composition ($^{40}K/K$) 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 $^{40}K/K$ values as a potential tracer to elucidate biogeochemical cycling of potassium in soil–plant systems.

Materials and methods

Description of the sites and soil sampling

Location map of the Tomakomai Experimental Forest of Hokkaido University in Tomakomai, Japan (42°40′N, 141°36′N, 27 km^2 in total area) was shown in our previous paper [12]. Annual mean temperature and precipitation in the site are 6.4 °C and 1,450 mm, respectively. The ground surface of hilly site with altitude of 5–90 m a.s.l. was covered with volcanic ash derived from an active Mr. Tarumae which erupted 330 years ago. As shown in Fig. 1, a thin organic layer exists only on the uppermost part of the soil down to a depth of 6 cm from the ground surface, which then appears several laminar structures of volcanic ash down to a depth of 1 m. Each layer corresponds to past eruption of the volcano. About 100 tree species and 300 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 of the study site is deciduous broad-leaved stands like Mongolian oak (*Quercus crispula*), Painted maple (*Acer mono Maxim*) and Linden (*Tilia japonica*). The site was categorized to be high tree density (>70 % canopy occupancy) and high tree height (>16 m in mean height). The forest floor was covered with various plant species, with a lot of fallen leaves (twigs) and with snow depending on the season of the year.

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

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

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and oak (*Quercus pubescens, Quercus petraea*) trees in Gorišnica (P5) and beech (*Fagus sylvatica*) and pine (*Pinus sylvestris*) trees in Rakitna (P6). All the sites were categorized to be high tree density (>70 % canopy occupancy) and high tree height (>16 m in mean height). Undergrowth was not dense in any sites except for that in Žirovski vrh where several types of shrubs grew. All the soils in Slovenia investigated in this study were collected in September 2009.

Soil properties

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

Activity measurements of ^{40}K with a HPGe detection system

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

Determination of potassium in soil

Energy dispersive X-ray fluorescence spectrometry (JSX-3220, JEOL, Japan) was used for determining total K content of the soil. After energy calibration of the instrument with a Rh checking source, calibration curve of K was prepared with several standard soil samples of known K content. X-ray energy spectra of soil samples show some overlapping interference from the Ca (Kα) peak on that of K (Kα) from 3.4 to 3.5 keV. The energy range for counting was set from 3.14 to 3.32 keV in this study. Potassium in soil was determined with a calibration technique using standard soils of known K content (JSO-1, National Institute of Advanced Industrial Science and Technology, Japan).

Chemical leaching of potassium in selected samples

Change in $^{40}K/K$ value was investigated in selected samples including reagent grade clay minerals using a chemical leaching technique with 1 M ammonium acetate aqueous solution or 1 M HCl. An aliquot of each chemical reagent was added to a soil suspension (5 cm^3 per 1 g soil sample in dry weight), which was stirred for 24 h at room temperature. The suspension was filtered to collect the residual portion, which was then used for ^{40}K and total K determination. The samples used for this treatment were both surface and deeper portions from Slovenia (P1, P2, P4, P5 and P6), and those from Tomakomai (P1). The leaching experiment was also conducted on several reagent grade clay minerals (bentonite, kaolinite and vermiculite) purchased from the Wako Pure Chemical Industries Ltd., Japan as references.

Results and discussion

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

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

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

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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^3)	pH	Humidity (%)	SOM (%)	Density (g/cm^3)
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^3)	pH	Humidity (%)	SOM (%)	Density (g/cm^3)
0–2	5.2	57.3	18.2	1.36	5.3	43.8	10.5	1.38
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[a]							
	Point 1 (Žirovski vrh) siliceous soil				Point 2 (Idria) carbonaceous soil			
	pH	Humidity (%)	SOM (%)	Density (g/cm^3)	pH	Humidity (%)	SOM (%)	Density (g/cm^3)
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

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Table 1 continued

Depth (cm)	Point 3 (Kočevski rog) carbonaceous soil				Point 4 (Pohorje) siliceous soil			
	pH	Humidity (%)	SOM (%)	Density (g/cm^3)	pH	Humidity (%)	SOM (%)	Density (g/cm^3)
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^3)	pH	Humidity (%)	SOM (%)	Density (g/cm^3)
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

[a] Cited from the reference [16]

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

With respect to immature volcanic soil in Tomakomai, good correlations also exist between humidity and SOM. However, different patterns of ^{40}K/K–SOM relations to those of Slovenian soils were obtained, in which lower ^{40}K/K values appeared only at the uppermost portions with low SOM. These findings suggest that the presence of SOM in early diagenetic stage (or possible biological activity) may affect ^{40}K/K values to a great extent. The presence of soil organic matter and biological activity were suggested to play an important role on ^{40}K/K distribution profiles in Peruvian surface soil [17]. Further investigation is necessary to elucidate biological effects on soil ^{40}K/K dynamics by monitoring various soil components in the forest floor for a long time.

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

Ion exchange properties of potassium (^{40}K and two other stable isotopes of K) with hydrogen ions (H^+) were

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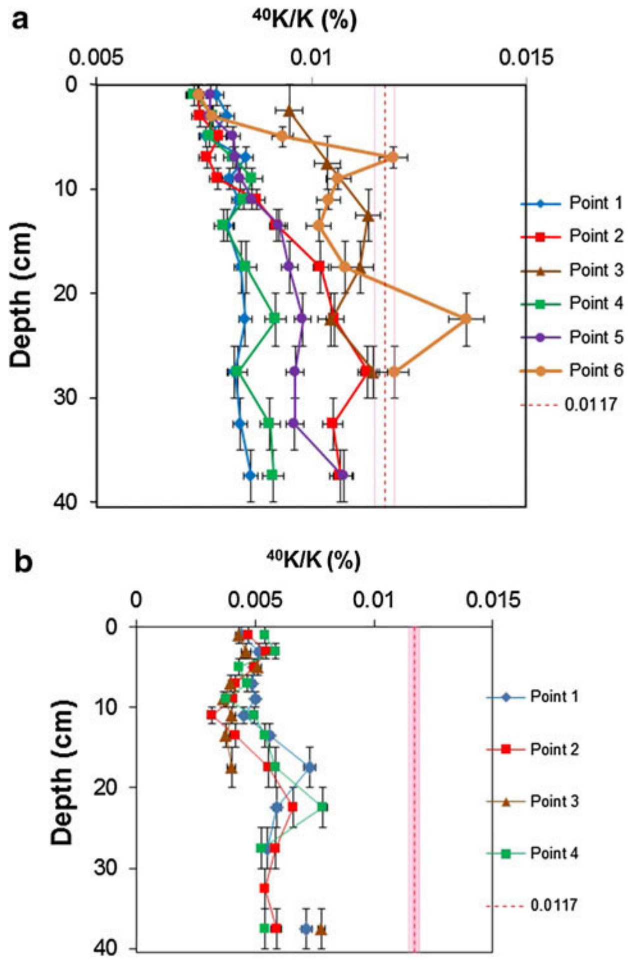

Fig. 2 **a** Depth distribution profiles of ^{40}K/K value in several forest soils from Slovenia. Žirovski VRH (*Point 1*), Idria (*Point 2*), Kočevski ROG (*Point 3*), Pohorje (*Point 4*), Gorišnica (*Point 5*), Rakitna (*Point 6*). A *vertical line* in the figure indicates the ^{40}K/K value of 1.17×10^{-2} % with uncertainty evaluated in this study, **b** Depth distribution profiles of ^{40}K/K values 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 m^2 in area) were selected in this study. A *vertical line* in the figure indicates the ^{40}K/K value of 1.17×10^{-2} % with uncertainty evaluated in this study

investigated for several Slovenian soils with an acid dissolution experiment using 1 M HCl as a leaching agent. A residue after the acid treatment was applied further to the K and ^{40}K determination. The results in Fig. 4 showed that ^{40}K/K values in any samples have changed after the treatment. The ^{40}K/K values both in the surface (0–4 cm) and deeper (30–40 cm) portions of clayey soils increased about 10–15 % from those before leaching. Radioactivity measurement of the residual samples after the acid treatment gave the result that ^{40}K preferably retains in residual soil components. Pattern of the ^{40}K dissolution was different with different carbonaceous soils at Points 2 and 6, in which ^{40}K/K values increased at Point 2 by acid

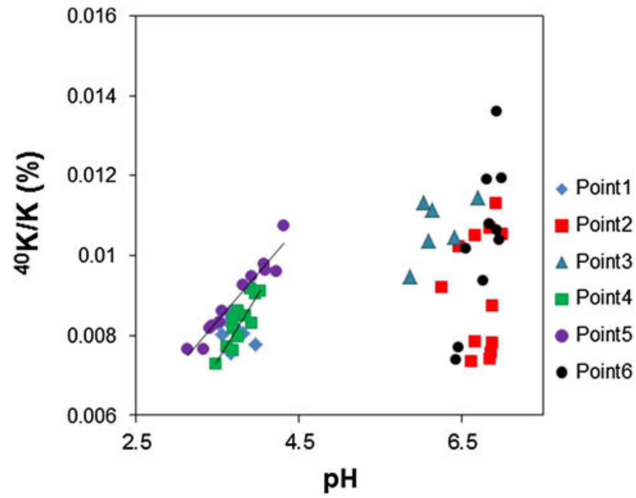

Fig. 3 Plots of ^{40}K/K values against soil pH in Slovenian forest soils investigated in this study. Siliceous soils at *Points 1, 4* and *5* showed high positive correlation with pH, whereas scattered ^{40}K/K values appeared in carbonaceous soils at *Points 2, 3* and *6*

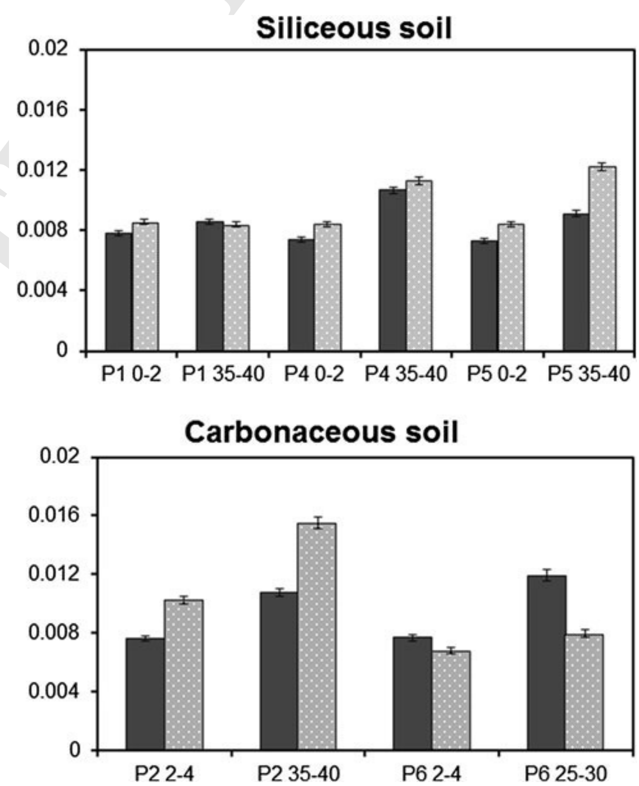

Fig. 4 Results of chemical leaching experiments with 1 M HCl on the surface and deeper portions of several Slovenian soils at *Points 1*, *2*, *4*, *5* and *6*. Notation after *each point* in the figure indicates a range of depth. For example, a notation (*P1 0–2*) denotes to a depth range from 0 to 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}K/K values with acid treatments. No consistent trends appeared for carbonaceous soils at Points 2 and 6

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

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

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

The root-fungal association in forest ecosystems is known to have a unique soil microenvironment different from the bulk soil. Arocena et al. [19] studied the spatial variations in the composition of soil solution and mineralogy of the rhizosphere as influenced by the root-fungal association of Norway spruce (*Piloderma croceum*) in the cultivated experiment. They found significantly lower amounts of K^+ and other nutrients in the *Piloderma*-colonized treatment culture (closer to 1 cm from the roots) compared to the control. They referred the result to an evidence of *Piloderma* modified soil solution and mineralogy through acquisition of essential elements for its own survival and/or for the uptake by plant roots. Monitoring $^{40}K/K$ value in soil environment may be another indicator to evaluate bioavailability of potassium in root-fungal association in forest ecosystems.

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

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References

1. Fujiyoshi R, Satake Y, Sumiyoshi S, Dietz J, Zimmermann R (2009) J Radioanal Nucl Chem 279(2):509
2. Likens GE, Driscoll CT, Buso DC, Siccama TG, Johnson CE, Lovett GM, Ryan DF, Fahey T, Reiners WW (1994) Biogeochem 25:61
3. Albers BP, Rackwitz R, Kleinschroth S, Bunzl K (2000) In: Markert B, Friese K (eds) Trace elements-their distribution and effect in the environment. Elsevier, New York
4. Fujiyoshi R, Sawamura S (2004) Sci Total Environ 320:177
5. Szczerba MW, Britto DT, Kronzucker HJ (2009) J Plant Physiol 166:447
6. Bergquist BA, Blum JD (2007) Sci 318(5849):417
7. Chen J, Gaillardet J, Louvat P (2008) Environ Sci Tech 42(17):6494
8. Foucher D, Ogrinc N, Bullen T (2009) Environ Sci Tech 43(1):33
9. Caldelas C, Dong S, Araus JL, Weiss DJ (2011) J Exp Bot 62(6):2169
10. Zikovsky L, Blagoeva R (1994) J Radioanal Nucl Chem 187(6):423
11. Petersen H, Wunderlich T, al Hagrey SA, Rabbel W (2012) J. Plant Nutr Soil Sci 175:651
12. Fujiyoshi R, Okabayashi M, Sakuta Y, Okamoto K, Sumiyoshi T, Kobal I, Vaupotič J (2013) Environ Earth Sci. doi:10.1007/s12665-012-2203-0
13. Hiura T (2005) Ecol Res 20:271
14. Repe B (2004) Slovenia Str. 57
15. Fujiyoshi R, Yamaguchi T, Okamoto K, Sumiyoshi T (2011) Cent Eur J Geosci 3(3):291
16. Fujiyoshi R, Amano H, Sakuta Y, Okamoto K, Sumiyoshi T, Kobal I, Vaupotič J (2012) Environ Earth Sci 67(1):133
17. Fujiyoshi R, Satake Y, Sumiyoshi T (2009) J Radioanal Nucl Chem 281(3):553
18. Jalali M, Lolahchi Z (2007) J Plant Nutr Soil Sci 170:530
19. Arocena JM, Göttlein A, Raidl S (2004) J Plant Nutr Soil Sci 167:479

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