

Variation in Uranium Isotopic Ratios $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/\text{total-U}$ in Japanese Soil and Water Samples —Application to Environmental Monitoring

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1. INTRODUCTION

1.1 OBJECTIVE OF THE WORK

The purpose of the present study is to clarify natural variation of $^{238}\text{U}/^{234}\text{U}$ and $^{235}\text{U}/\text{total uranium}$ ratios in soil and groundwater samples from Japan, and to examine the possibility of applying uranium isotopic ratios to detect discharge of artificially altered uranium from nuclear industries to the environment. We therefore measured isotopic ratios ($^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/\text{total uranium}$) of uranium in Japanese soil from Kumatori (Osaka), Naka (Ibaragi) and Nishi-Ku (Hiroshima), and Japanese groundwater from Shiogama (Tottori), Hokusui (Kumamoto) and Kujyu (Oita) using ICP-MS (inductively coupled plasma – mass spectrometry).

1.2 VARIATION IN URANIUM ISOTOPE RATIOS

Uranium has three naturally occurring isotopes, ^{234}U (progeny of ^{238}U , half-life 2.45×10^5 yrs), ^{235}U (half-life 7.04×10^8 yrs) and ^{238}U (half-life 4.47×10^9 yrs). IUPAC (22) has reported isotopic abundance of U-234, 235 and 238 in natural uranium to be 0.00548, 0.7200 and 99.2745 atom percent as “Best measurement from a single terrestrial source”, while Richter et al. (18) have proposed slightly different values (0.005420, 0.72041 and 99.27417 atom percent for U-234, 235 and 238). The “original” $^{235}\text{U}/^{238}\text{U}$ abundance ratio should have been established by nucleosynthesis in a presolar environment and have been decreased due to radioactive decay since then. ^{234}U and ^{238}U are in radiological equilibrium, namely activity ratio of ^{234}U to ^{238}U being 1.0, if the uranium was placed in closed system.

Isotopic fractionation of heavy elements such as uranium usually is less significant compared with that of light elements such as hydrogen and oxygen. $^{235}\text{U}/^{238}\text{U}$ ratio has not been found to deviate from $^{238}\text{U}/^{235}\text{U} = 137.5 \pm 0.5$ (20) in most environmental samples, except for Oklo uranite deposit where natural nuclear reactor existed 1.8×10^9 years ago and therefore ^{235}U was significantly depleted relative to ^{238}U (9). Fried et al. (2) found a subtle increase in $^{235}\text{U}/^{238}\text{U}$ ratio (0.007267) by 0.18 % to normally observed value of 0.007254 in some pre-historic volcanic materials by thermal ionisation mass spectrometry (TIMS), which is the most reliable and precise method for uranium isotope ratio analyses to date.

$^{234}\text{U}/^{238}\text{U}$ ratio, on the other hand, has been found to vary considerably due to natural cause in many water (17, 19, also reviewed in 1,15,16), soil (8, 10,11, 21, 26), sediment (reviewed in 16) and uranium ores of different geographical origin (18). The mechanism of such variation is preferential leaching of ^{234}U compared with ^{238}U from solid phase, caused by radiation damage of crystal lattice upon alpha decay of ^{238}U , oxidation of insoluble tetravalent ^{234}U to soluble hexavalent ^{234}U during decay, and alpha recoil of ^{234}Th (and its daughter ^{234}U) into solution phase (reviewed by 5, pp. 55-58). $^{234}\text{U}/^{238}\text{U}$ activity ratios in water reportedly vary from 0.5 to 40 (6, 14), while that in soil typically range from 0.5 to 1.2 (7, 14).

Emission from anthropogenic nuclear sources can also cause deviation in $^{235}\text{U}/^{238}\text{U}$ ratios in environmental samples (reviewed in 29). Because soils and sediments can dilute out uranium with unnatural isotopic abundance because of their high natural uranium contents, low-uranium materials such as biological and water samples are usually favorable for sensitive detection of anthropogenically altered uranium. In fact, depleted uranium (i. e. low $^{235}\text{U}/^{238}\text{U}$ ratio) of anthropogenic origin was detected in groundwater with low uranium content (23). Uranium from atmospheric nuclear explosion was found in rainwater using isotopic ratio as the fingerprint (12, 24, 25). If the amount of the uranium discharged from anthropogenic source was relatively large and isotopic composition of the discharged uranium was significantly different from that of natural uranium, however, “fingerprint” of the anthropogenic uranium could be detected even in environmental samples of high uranium content. For example, Taylor et al. (27) used TIMS to measure soil collected near the former United States Air Base in UK where enriched uranium was discharged into the environment in 1958, and found $^{238}\text{U}/^{235}\text{U}$ atom ratio in the range 111-174 for some soil samples while natural $^{238}\text{U}/^{235}\text{U}$ atom ratio is 137.9.

$^{234}\text{U}/^{238}\text{U}$ ratios also vary due to anthropogenic discharge. Fertilizer-derived uranium, for example, could be distinguished from indigenous uranium using $^{234}\text{U}/^{238}\text{U}$ as an indicator and could be used to trace the migration of fertilizer in the environment (30). Goldstein et al. (7) found depleted $^{234}\text{U}/^{238}\text{U}$ ratios in soil samples of elevated uranium concentrations and considered it to be a contribution from anthropogenic uranium.

2. MATERIALS AND METHODS

2.1 SOIL AND WATER SAMPLES

Three types of soil were collected from natural horizon in Japan to investigate the depth profile of $^{234}\text{U}/^{238}\text{U}$ activity ratios and $^{238}\text{U}/^{235}\text{U}$ atom ratios (3, 4, 13). The soils used were: (1) a brown forest soil (hereafter soil-b), Dystric Cambisols of FAO/UNESCO soil classification (28), sampled at Naka-machi, Ibaragi, Japan; (2) an Ando soil (soil-d hereafter), meaning a dark-colored soil in Japanese classification, Humic Andosols of FAO/UNESCO soil classification (1988), sampled at Naka-machi, Ibaragi, Japan; and (3) a red and yellow soil (hereafter soil-KUR), Orthic Acrisols or Dystric Cambisols of FAO/UNESCO soil classification (1988), sampled at the site of the Kyoto University Reactor in Kumatori-cho, Osaka, Japan. All the soils were sampled at 3-10 cm intervals to a depth of 70-90 cm.

Soil samples were collected at the depths of 0-4 cm and 4-15 cm in 8 stations (designated as A, B, C, D, E, F, G and H) from Nishi-Ku, Hiroshima where "black rain" containing high radioactivity had fallen after 1945 A-bomb explosion. The soil samples were sandy and were in incipient stage of pedogenesis. Groundwater samples were collected from Shiogama (Tottori), Hikusui (Kumamoto) and Kujyu (Oita).

Sampling locations are shown in Fig. 1.

2.2 REAGENT AND ANALYTICAL INSTRUMENT

The nitric acid (68 %) used was for a class-100 environment, AA-100 grade, supplied by Tama Chemical Co (Tokyo, Japan). Hydrofluoric (40 %) acid was suprapur grade supplied by Merck (New Jersey, USA), and perchloric (30 %) acid was ultrapure grade from Kanto Chemical Co (Tokyo, Japan).

Uranium isotope analyses was conducted by inductively coupled plasma - mass spectrometer HP-4500 manufactured by Yokogawa Analytical Systems (Tokyo, Japan).

2.3 ANALYRICAL METODS

Soil samples were ground to 150 mesh, ashed at 510°C for 3 days, decomposed by mixture of nitric, perchloric and hydrofluoric acid, and were evaporated to dryness. Groundwater samples were filtrated, evaporated to dryness, decomposed by mixture of nitric, perchloric and hydrofluoric acid, and were evaporated to dryness again. The evaporated samples were then treated with sulfric acid to remove insoluble fluorides and were redissolved in 2N nitric acid from which uranium was separated using U-TEVA resin (Eichrom) and its irotopes measured by ICP-MS.

3. RESULTS AND DISCUSSION

3-1. DEPTH PROFILES OF U-234/U-238 ACTIVITY RATIO IN SOIL

Depth profiles of $^{234}\text{U}/^{238}\text{U}$ activity ratios in soil-b, soil-d and soil-KUR are shown in Figs. 2, 3 and 4. $^{234}\text{U}/^{238}\text{U}$ profiles obtained in our investigation did not show much disequilibrium (such as activity ratio less than 0.8) as observed in other study (16). The distributions of $^{234}\text{U}/^{238}\text{U}$ with depths are relatively uniform in soil-b and soil-d, with activity ratio not much different from 1.0 (indicating radiological equilibrium between ^{234}U and ^{238}U). This probably is because parent materials of these soils are relatively new volcanic ejecta, which initially had $^{234}\text{U}/^{238}\text{U}$ activity ratio near 1.0 and has not been subjected to much leaching of ^{234}U since its deposition. Soil-KUR, on the other hand, had lower activity ratio near surface and the ratios varied with depths. This probably is due to intense weathering of its parent material, an old sediment belonging to the Plio-Pleistocene Osaka Group deposited 1 million years ago.

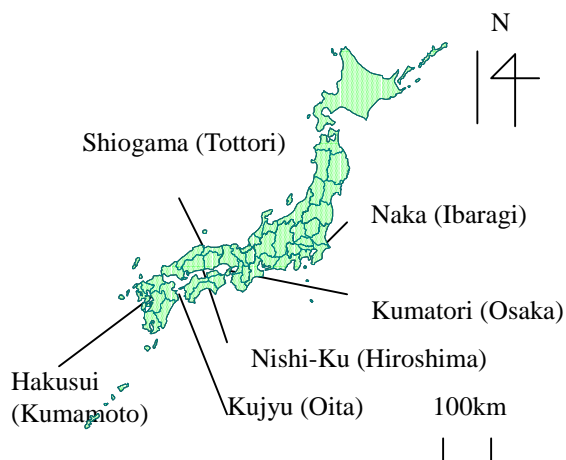


Fig.1 Sampling locations

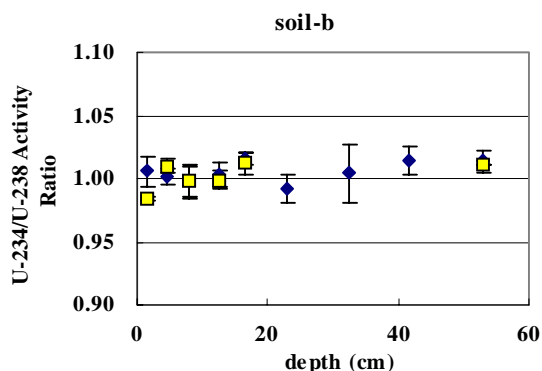


Fig. 2 U-234/U-238 profile in soil-b.

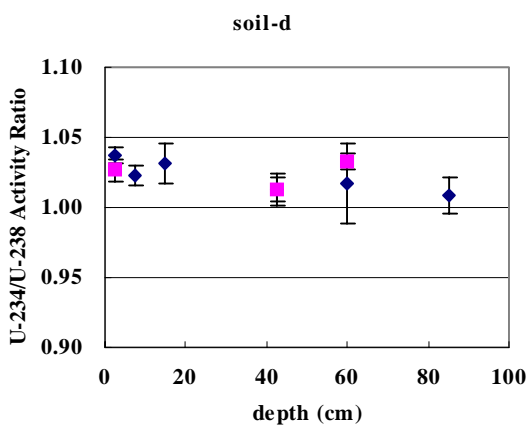


Fig. 3 U-234/U-238 profile in soil-d.

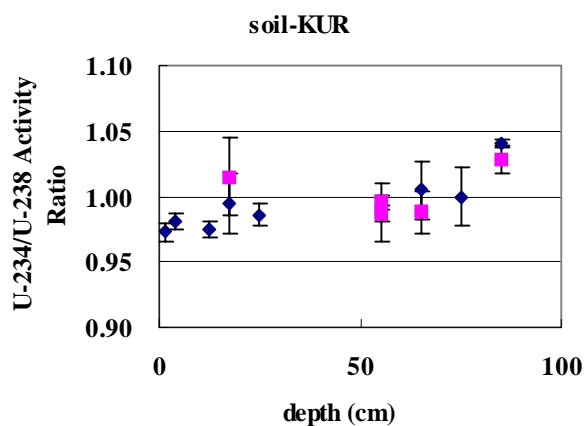


Fig. 4 U-234/U-238 profile in soil-KUR.

3-2 U-234/238 ACTIVITY RATIO AND U-235/TOTAL-U ATOM RATIO IN SOIL AND GROUNDWATER

In Table 1, $^{234}\text{U}/^{238}\text{U}$ activity ratios and U-235/total-U atom ratios in soil and groundwater are shown. $^{234}\text{U}/^{238}\text{U}$ activity ratios of most soil samples were around 1.0 (radiological equilibrium). The sample from station E in Hiroshima exhibited high $^{234}\text{U}/^{238}\text{U}$ activity ratio, the reason for which was unknown. Groundwater samples generally showed high $^{234}\text{U}/^{238}\text{U}$ ratios.

Table 1. U-234/238 activity ratio and U-235/total-U atom ratio in soil and groundwater samples

Sample name (Sampling location)	U-234/238 Activity Ratio	Relative standard deviation (%) for U-234/238	U-235/total U atom percent	Relative standard deviation (%) for U-235/U-total
soil-b (Naka, Ibaragi) ^{*1}	1.00	1.1	0.0071	0.4
soil-d (Naka, Ibaragi) ^{*1}	1.01	1.0	0.0071	0.5
soil-KUR (Kumatori, Osaka) ^{*1}	0.98	2.1	0.0071	0.6
St. A soil (Nishiku, Hiroshima 0-4 cm)	1.00	1.6	0.0071	0.6
St. A soil (Nishiku, Hiroshima 4-15 cm)	1.00	1.1	0.0071	0.2
St. B soil (Nishiku, Hiroshima 0-4 cm)	0.96	1.9	0.0070	0.3
St. B soil (Nishiku, Hiroshima 4-15 cm)	0.92	0.8	0.0070	0.1
St. C soil (Nishiku, Hiroshima 0-4 cm)	0.99	0.9	0.0070	0.2
St. C soil (Nishiku, Hiroshima 4-15 cm)	0.96	0.7	0.0070	0.1
St. D soil (Nishiku, Hiroshima 0-4 cm)	0.96	0.7	0.0071	0.7
St. D soil (Nishiku, Hiroshima 4-15 cm)	0.99	0.5	0.0071	0.3
St. E soil (Nishiku, Hiroshima 0-4 cm)	1.46	0.1	0.0071	0.3
St. E soil (Nishiku, Hiroshima 4-15 cm)	1.40	0.3	0.0070	0.5
St. F soil (Nishiku, Hiroshima 0-4 cm)	1.01	-	0.0071	-
St. F soil (Nishiku, Hiroshima 4-15 cm)	1.03	0.8	0.0072	0.1
St. G soil (Nishiku, Hiroshima 0-4 cm)	1.00	0.0	0.0071	0.1
St. G soil (Nishiku, Hiroshima 4-15 cm)	1.00	4.0	0.0071	0.7
St. H soil (Nishiku, Hiroshima 0-4 cm)	0.97	0.6	0.0070	0.1
St. H soil (Nishiku, Hiroshima 4-15 cm)	0.96	1.6	0.0070	0.7
Groundwater (Shiogama, Tottori)	1.48	0.3	0.0071	0.2
Groundwater (Hakusui, Kumamoto)	1.02	0.8	0.0071	0.6
Groundwater (Kuju, Oita)	1.10	0.9	0.0071	0.5

^{*1} averaged over depth (0-60 cm for soil-b and 0-100 cm for soil-d and soil-KUR).

U-235/total uranium atom ratios were 0.0071 for most of the samples. Soil samples from Hiroshima showed some variation from 0.0070 to 0.0072. In order to judge whether this is the effect of uranium bomb exploded in Hiroshima, more investigation is necessary. The reliability and precision of ICP-MS in isotope ratio measurement also limit the quality of data in this investigation.

4. CONCLUSION

We measured isotopic ratios ($^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/\text{total uranium}$) of uranium in Japanese soil collected at Kumatori (Osaka), Naka (Ibaragi) and Nishi-Ku (Hiroshima), and Japanese groundwater from Shiogama (Tottori), Hakusui (Kumamoto) and Kuju (Oita) using ICP-MS (inductively coupled plasma – mass spectrometry).

Most of soil samples, especially volcanic ash soil typically found all over Japan, exhibited secular equilibrium between ^{234}U and ^{238}U , and their deviation from the radiological equilibrium may indicate the contribution from anthropogenically altered uranium. Water samples, on the other hand, showed considerable natural variation in $^{234}\text{U}/^{238}\text{U}$ ratios, suggesting the necessity of thorough site-specific investigation to clarify the extent of their background variation in order to use $^{234}\text{U}/^{238}\text{U}$ ratio in water in environmental monitoring.

$^{235}\text{U}/\text{total-U}$ atom ratios in soil and groundwater samples were 0.0071 in most cases. Some soil samples collected from Nishi-ku, Hiroshima showed small deviation in the ratios from 0.0070 to 0.0072. Whether this deviation is related to Hiroshima A-bomb or not is to be investigated in the forthcoming study.

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