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Soil-to-crop Transfer Factors of Radium in Japanese Agricultural Fields

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The concentrations of ^{226}Ra in upland field crops (e.g., cabbage, leek, onion, potato, and so on) and associated soils collected from 45 locations throughout Japan were determined in order to obtain soil-to-crop transfer factors (TFs). Concentrations of ^{226}Ra in the soils collected in southwestern Japan were higher than those in northeastern Japan; however, no correlations between ^{226}Ra concentrations in crops and soils were observed. The TFs ranged from $<1.1 \times 10^{-3}$ to 5.8×10^{-2} with a geometric mean of 6.4×10^{-3}. These data were within the 95% confidential range of TF-Ra for several crops as reported in the IAEA Technical Reports Series No. 364. Among the alkaline earth metals, TF-Ba was similar to TF-Ra.

1. Introduction

Radium-226 (^{226}Ra), an α emitter with a half-life of about 1600 y, is a natural decay product of ^{238}U. Radium-226 is of special interest because it is an important radionuclide for the assessment of radioactive waste disposal. This radionuclide can reach humans through several transfer paths in the environment. Once Ra is taken into the human body by ingestion of food and water or inhalation, it can distribute into bone where it has a long biological half-life; exposure to Ra can cause cancers and other body disorders. Therefore, its long-term management is required and understanding of Ra behavior in the environment is important.

In mathematical models that are used for long-term radiological assessment, environmental transfer parameters are needed. Among them, the soil-to-crop transfer factor (TF) is a key parameter that directly affects the internal radiation dose assessment for the ingestion pathway. TF is defined as the ratio of radioactivity concentration in plant to radioactivity concentration in soil. Although ^{226}Ra is present in the environment, due to its low concentration in crops, TFs that have been obtained from agricultural fields are limited.[1–5] In many cases, therefore, TFs used in such models were from the Technical Report Series 364 (TRS-364) compiled by IAEA.[3] These data were obtained in temperate zones mainly from Europe and North America, and thus, the numbers of TFs for rice and crops native to Japan were limited. Yunoki et al.[2] measured TF-Ra for spinach and Chinese cabbage, but they collected their samples from only two fields. Recently, Sasaki et al.[4] tried to measure crop TF-Ra, however, most sample concentrations were under the detection limit, and only two hulled rice sample data were available from their study. Thus, it is necessary to collect TFs of Ra nationwide.

In this study, we determined the concentrations of ^{226}Ra in upland field crops (leafy vegetables, onion, potato, and so on) and associated soils collected from 45 locations throughout Japan in order to obtain TFs. We also measured alkaline earth metal concentrations to compare their behavior with Ra, which is the last member of this group and whose lighter members, Mg and Ca, are plant nutrients.

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2. Experimental

2.1. Samples. Upland field soils (plowed soil layer: up to ca. 20 cm depth) were collected nationwide from 45 fields in 2002–2004 (Figure 1). From each sampled field, 5 sub-samples, approximately 1 kg on fresh weight basis each, were collected in the harvesting season and these sub-samples were mixed well. About 15 kg amounts (on a fresh weight basis) of the edible part of crops were also collected for 13 green vegetable samples (cabbage, Chinese cabbage, etc.), 9 tuber samples (potato, sweet potato, and taro), 7 allium species samples (leeks and onion), 2 legume samples (bean and peanut), 7 fruit vegetable samples (cucumber, tomato, sweet pepper, and egg plant), 4 root vegetable samples (carrot and Japanese radish), and 5 cereal samples (wheat and barley).

Three kg of the soil sub-samples were air-dried and passed through a 2-mm mesh sieve. For crop samples, edible parts were washed with deionized water at least 3 times until the removal of dust and soil particles was completed. The washed

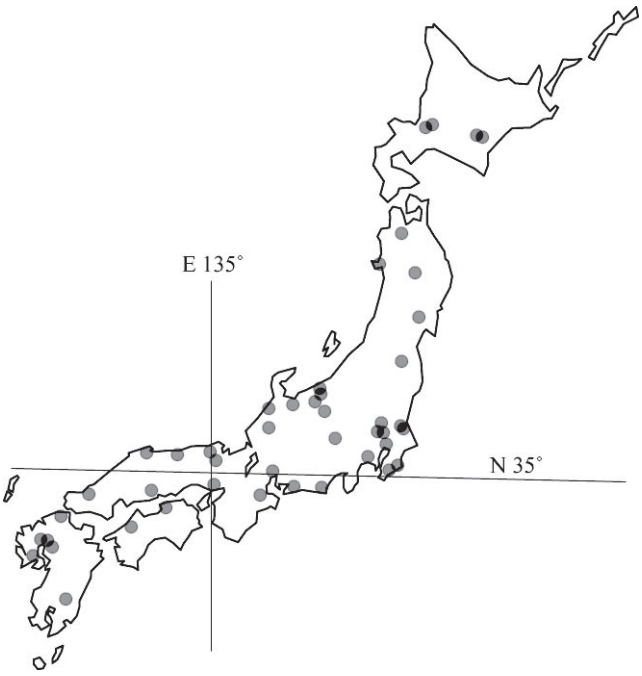

Figure 1. Sampling sites in Japan.

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parts were paper-towel dried, chopped and freeze-dried except for taro which was also peeled before chopping. For leek samples, green and white parts were separated. Leaves of Japanese radish are also edible parts so that roots and leaves were separated and elemental compositions of both of them were measured. Finally, 45 soil samples and 51 crop part samples were obtained.

2.2. Measurements. For the soil samples, about 60 g of each pretreated soil sample were charged and sealed into a plastic vessel. These samples were kept at room temperature for more than 30 days to reach an equilibrium condition with progeny nuclides of ^{226}Ra, that is, ^{222}Rn, ^{218}Po, ^{214}Pb, and ^{214}Bi. Then, the concentration of ^{214}Pb was measured with a Ge detector system (Seiko EG&G Ortec) from which ^{226}Ra could be calculated. To check the accuracy of the method, we used two reference materials, IAEA-315 (marine sediment) and IAEA-368 (Pacific Ocean sediment).

In order to measure ^{226}Ra, a chemical separation was carried out using about 15 g of each incinerated crop sample (450 °C, 24 h). Use of 5 g of incinerated crop has been recommended for the standard method used in Japan.[6] However, to obtain a lower level for the detection limit (DL), we tripled the sample amount in the present study. The radiochemical separation steps were the same as used in the standard method.[6] Since there is no stable Ra isotope, the chemical yield of Ra was obtained using barium (Ba), which is just above Ra in the periodic table. This selection was based on their similar chemical behaviors. In brief, the separation method was as follows: 30 mL of HNO_3 (1 + 1) were added to the incinerated sample and this was evaporated to dryness. The dried material was dissolved in HCl (1 + 1), and the residue was removed by filtration. After addition of Ba, Ra was coprecipitated with $BaSO_4$ and Ba recovery was measured by a gravimetric method. The sample was then dissolved in EDTA-4Na solution and 10 mL of organic solvent (Scintisol AL-1) were added. The mixture was kept for two weeks to reach radioactivity equilibrium with ^{222}Rn. Then, the organic layer that includes only ^{222}Rn was collected and the radioactivity of ^{222}Rn was measured with a liquid scintillation counter (Aloka, LB-2 or LB-5). From the counts, ^{226}Ra was calculated. No reference materials were used for plant samples, but, in order to obtain counting efficiency, we used a standard ^{226}Ra solution and ^{222}Rn was extracted.

For comparison, we measured concentrations of four alkaline earth metals, Mg, Ca, Sr, and Ba, and also U and Th by inductively coupled plasma mass spectrometry (ICP-MS) using a part of each soil and crop sample. The ICP-MS samples were thoroughly ground into fine powder and stored at room temperature. Before measurements, the samples were oven dried at 80 °C. We have reported method details elsewhere.[7]

3. Results and Discussion

3.1. ^{226}Ra concentrations in soils and crops. The concentrations of ^{226}Ra in the soil and the crop samples are listed in Table 1. The concentrations of ^{226}Ra in upland soil samples ranged from 13.9 to 60.3 Bq kg^{-1}-dry. Since the main island of Japan is geologically classified into two parts at the Itoigawa-Shizuoka Tectonic Line, the ^{226}Ra concentrations in samples collected in the northeastern and southwestern parts of Japan were compared and their probability distributions are plotted in Figure 2. T-test ($p < 0.01$) showed that the concentrations were higher in the southwestern part (geometric mean: 36.5 Bq kg^{-1}) than in the northeastern part (geometric mean: 25.7 Bq kg^{-1}), possibly due to geological differences between these areas.

Since potato, sweet potato, carrot, and Japanese radish samples were not peeled, ^{226}Ra contamination from soil particles that remained on the crop surface was suspected. In order to check for remaining soil particle amounts in these crop samples, Ti concentrations were checked.[7] The results showed that Ti concentrations in tuber and root vegetable samples were lower than in green vegetable samples which were not in contact with soil. Thus we assumed that ^{226}Ra contamination due to soil particles was negligible.

Radium-226 is a progeny nuclide of ^{238}U and the half-life of ^{226}Ra is shorter than that of ^{238}U, thus, after a long time, their radioactivities reach an equilibrium in soil. Thus, radioactivities between ^{226}Ra and U are compared as shown in Figure 3. We also compared Th radioactivities with ^{226}Ra ones because U and Th behave similarly geologically. In northeastern Japanese soil samples, correlations between ^{226}Ra and both U and Th were high (t-test, $p < 0.001$); in particular, U and ^{226}Ra had a 1:1 radioactivity ratio which means that they reached equilibrium. Southwestern soil samples had lower correlations for U and Th compared to northeastern soil samples, though U and ^{226}Ra in the southwestern soil samples had a 1:1 radioactivity ratio as well. The results implied that ^{226}Ra and U reached an equilibrium in these soil samples; however, we must consider the effect of excess U which could come from phosphatic fertilizers. Previously, we estimated that about 50% of total ^{238}U in upland field soils came from these fertilizers.[8] It is known that ^{226}Ra is included in the fertilizers[9,10] and their use in agricultural fields must have a small contribution as external radiation to the population. Thus, using the previously reported approach,[8] we estimated ^{226}Ra from the fertilizers (Ra_{ess}) as follows:

$$Ra_{ess} = Ra_{total} - [Th_{obs}] \times U/Th_N \times A \ ,$$

where Ra_{total} is the total ^{226}Ra radioactivity concentration in a soil sample, $[Th_{obs}]$ is Th concentration in the soil, U/Th_N is the average value of naturally observed [U]/[Th] concentration ratio (0.23), and A is a conversion factor from U concentration to ^{226}Ra radioactivity since 1 mg kg^{-1} U is equal to 12.3 Bq kg^{-1} of ^{226}Ra when U and ^{226}Ra reach equilibrium.

The Ra_{ess} values were 2.9–31.6 Bq kg^{-1} in the southwestern part (geometric mean: 15.5 Bq kg^{-1}) and 1.7–26.4 Bq kg^{-1} in the northeastern part (geometric mean: 14.3 Bq kg^{-1}). No regional difference was observed by t-test. Concerning the contributing percentages of Ra_{ess} to total ^{226}Ra in soil samples,

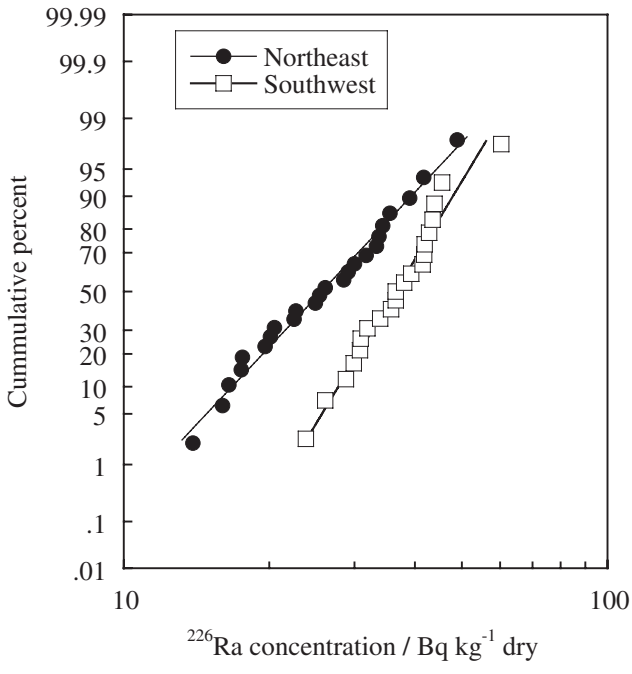

Figure 2. Probability distributions of ^{226}Ra concentrations in agricultural soils collected from northeastern and southwestern parts of Japan.

TABLE 1: Concentrations of ^{226}Ra in soil and crop samples on dry weight basis and transfer factors

Crop name	*Latin name*	^{226}Ra concentration / Bq kg^{-1}		TF ($\times 10^{-3}$)
		Soil	Crop	
Cabbage	*Brassica oleracea var. capitata*	20.5 ± 0.9	0.105 ± 0.015	5.1 ± 0.8
Cabbage	*Brassica oleracea var. capitata*	26.1 ± 1.0	0.594 ± 0.019	22.8 ± 1.1
Cabbage	*Brassica oleracea var. capitata*	39.0 ± 1.0	0.409 ± 0.014	10.5 ± 0.5
Cabbage	*Brassica oleracea var. capitata*	22.5 ± 0.9	0.242 ± 0.022	10.8 ± 1.1
Cabbage	*Brassica oleracea var. capitata*	23.8 ± 0.8	0.118 ± 0.015	5.0 ± 0.7
Chinese cabbage	*Brassica rapa L.*	13.9 ± 1.1	0.594 ± 0.029	42.7 ± 3.9
Chinese cabbage	*Brassica rapa L.*	36.5 ± 0.9	0.466 ± 0.025	12.8 ± 0.7
Spinach	*Spinacia oleracea L.*	28.8 ± 0.9	0.226 ± 0.038	7.8 ± 1.3
Lettuce	*Lactuca sativa L.*	41.7 ± 1.1	0.323 ± 0.031	7.7 ± 0.8
Lettuce	*Lactuca sativa L.*	30.9 ± 0.9	< 0.128	
Carrot (leaves)	*Daucus carota L.*	42.8 ± 0.9	1.147 ± 0.046	26.8 ± 1.2
Japanese radish (leaves)	*Raphanus sativus L.*	60.3 ± 1.2	0.463 ± 0.023	7.7 ± 0.4
Nozawana	*Brassica rapa var. hakabura*	17.6 ± 0.8	0.522 ± 0.046	29.7 ± 2.9
Leek (green)	*Allium fistulosum*	20.1 ± 1.0	0.125 ± 0.021	6.2 ± 1.1
Leek (green)	*Allium fistulosum*	16.5 ± 0.8	0.313 ± 0.015	19.0 ± 1.3
Leek (green)	*Allium fistulosum*	25.4 ± 0.9	0.416 ± 0.018	16.4 ± 0.9
Leek (green)	*Allium fistulosum*	29.9 ± 0.9	1.723 ± 0.047	57.6 ± 2.4
Leek (white)	*Allium fistulosum*	20.1 ± 1.0	0.116 ± 0.014	5.8 ± 0.8
Leek (white)	*Allium fistulosum*	16.5 ± 0.8	< 0.331	
Leek (white)	*Allium fistulosum*	29.9 ± 0.9	0.835 ± 0.035	27.9 ± 1.5
Leek (white)	*Allium fistulosum*	25.4 ± 0.9	0.414 ± 0.105	16.3 ± 4.2
Onion	*Allium cepa L.*	36.5 ± 0.9	0.074 ± 0.007	2.0 ± 0.2
Onion	*Allium cepa L.*	26.1 ± 0.9	< 0.029	
Onion	*Allium cepa L.*	43.9 ± 1.0	0.152 ± 0.010	3.5 ± 0.2
Carrot	*Daucus carota L.*	42.8 ± 0.9	1.431 ± 0.048	33.4 ± 1.3
Japanese radish	*Raphanus sativus L.*	60.3 ± 1.2	0.219 ± 0.030	3.6 ± 0.5
Japanese radish	*Raphanus sativus L.*	33.7 ± 1.1	0.519 ± 0.031	15.4 ± 1.0
Japanese radish	*Raphanus sativus L.*	38.0 ± 1.1	0.406 ± 0.026	10.7 ± 0.8
Potato	*Solanum tuberosum L.*	22.7 ± 1.0	0.039 ± 0.007	1.7 ± 0.3
Potato	*Solanum tuberosum L.*	35.7 ± 0.9	0.040 ± 0.004	1.1 ± 0.1
Potato	*Solanum tuberosum L.*	48.9 ± 1.0	0.122 ± 0.009	2.5 ± 0.2
Potato	*Solanum tuberosum L.*	31.7 ± 0.9	0.083 ± 0.008	2.6 ± 0.3
Potato	*Solanum tuberosum L.*	33.9 ± 1.0	0.066 ± 0.010	1.9 ± 0.3
Sweet potato	*Ipomoea batatas L.*	28.5 ± 0.9	0.047 ± 0.006	1.7 ± 0.2
Sweet potato	*Ipomoea batatas L.*	16.0 ± 0.6	0.040 ± 0.005	2.5 ± 0.3
Taro	*Colocasia esculenta*	45.5 ± 1.0	0.113 ± 0.013	2.5 ± 0.3
Taro	*Colocasia esculenta*	39.3 ± 1.0	< 0.051	
Cucumber	*Cucumis sativus L.*	29.1 ± 0.9	0.212 ± 0.033	7.3 ± 1.1
Sweet pepper	*Capsicum annuum L.*	33.3 ± 1.0	0.111 ± 0.015	3.3 ± 0.5
Sweet pepper	*Capsicum annuum L.*	30.8 ± 1.0	< 0.073	
Tomato	*Solanum lycopersicum L.*	43.5 ± 0.9	< 0.047	
Tomato	*Solanum lycopersicum L.*	41.9 ± 1.0	< 0.063	
Egg plant	*Solanum melongena L.*	19.6 ± 1.0	< 0.070	
Egg plant	*Solanum melongena L.*	41.8 ± 1.0	0.085 ± 0.018	2.0 ± 0.4
Soybean	*Glycine max*	30.0 ± 0.9	0.101 ± 0.010	3.4 ± 0.3
Peanut	*Arachis hypogaea L.*	17.5 ± 0.8	0.120 ± 0.006	6.9 ± 0.4
Wheat	*Triticum aestivum L.*	35.5 ± 1.1	0.171 ± 0.005	4.8 ± 0.2
Wheat	*Triticum aestivum L.*	24.9 ± 1.0	0.123 ± 0.006	4.9 ± 0.3
Wheat	*Triticum aestivum L.*	41.5 ± 0.9	0.059 ± 0.004	1.4 ± 0.1
Barley	*Hordeum vulgare L.*	34.3 ± 0.9	< 0.015	
Barley	*Hordeum vulgare L.*	31.9 ± 0.9	0.049 ± 0.005	1.5 ± 0.2

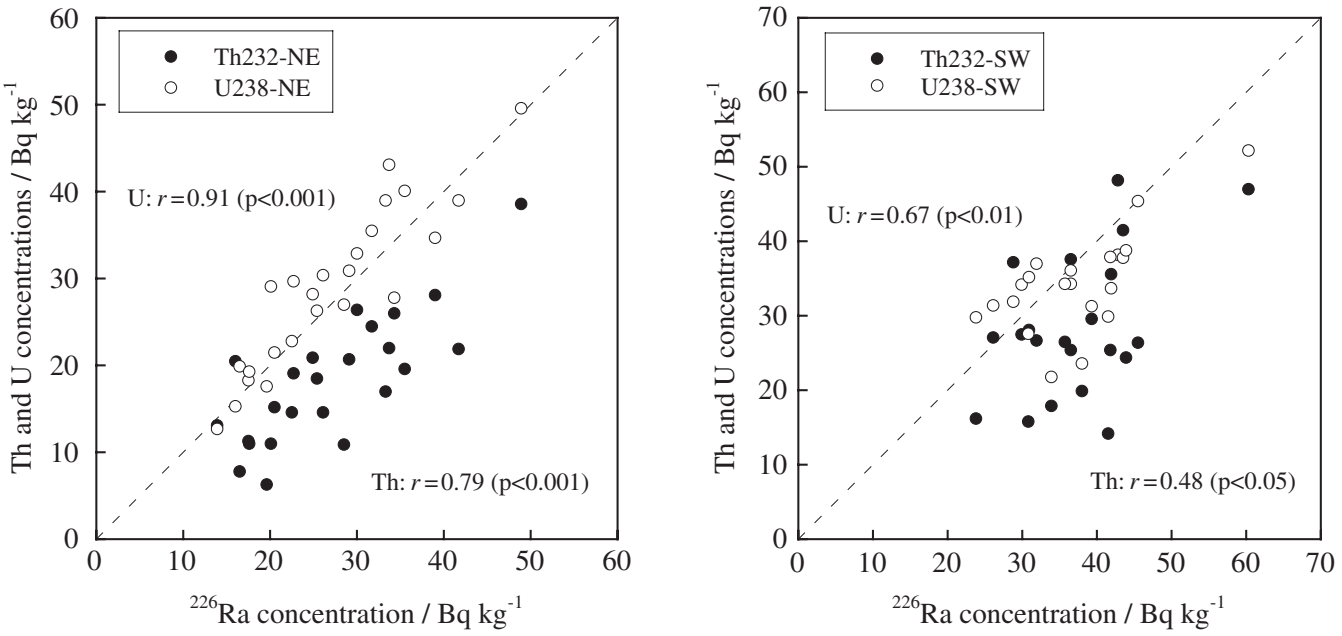

Figure 3. Correlations between concentration of ^{226}Ra and those of ^{232}Th and ^{238}U in soil samples collected in northeastern (left) and southwestern (right) parts of Japan.

TABLE 2: TF-Ra data in green vegetables

Crop	Number of data	AM[a]	GM[b]	95% confidence range	Reference
Cabbage	4	$(4.0 \pm 2.7) \times 10^{-1}$ [c]			1
	8	$(3.8 \pm 1.1) \times 10^{-1}$ [c]			1
Spinach	7	9.6×10^{-3} [c]			2
	6	1.3×10^{-2} [c]			2
Chinese cabbage	9	1.4×10^{-2}			2
	8	2.0×10^{-2}			2
Mixed green vegetables	9		4.9×10^{-2}	2.5×10^{-3}–9.8×10^{-1}	3
Spinach	4		$< 2.1 \times 10^{-2}$		4
Cabbage	8		$< 2.2 \times 10^{-2}$		4
Vegetables	96		2×10^{-2}		5
Leafy vegetables	13	1.6×10^{-2}	1.2×10^{-2}	3.0×10^{-3}–5.2×10^{-2}	This study
Cabbage	5	1.1×10^{-2}	9.2×10^{-3}	2.6×10^{-3}–3.2×10^{-2}	This study
Chinese cabbage	2	2.8×10^{-2}			This study

[a]Arithmetic mean. [b]Geometric mean. [c]Recalculated value from fresh weight basis TF to dry weight basis.

we obtained 10–76% in the southwestern part (geometric mean: 42%) and 11–77% in the northeastern part (geometric mean: 52%). The results implied that half of the total ^{226}Ra in agricultural soils was from phosphatic fertilizers.

In the radiochemistry procedures for ^{226}Ra measurements in the crops, Ba was used as a yield tracer of ^{226}Ra, and the recovery throughout the separation procedure was more than 97% for all the samples. The DL was lowered since a 15-g ash sample was used; that is, the DL obtained was about 0.7 Bq kg^{-1}-ash. If 5-g ash samples were used as recommended in the standard method,[6] the DL would be 2 Bq kg^{-1}-ash. Unfortunately, even though we lowered the DL, ^{226}Ra concentrations for 9 crop samples could not be measured in the present study. For measurable crop samples, the values ranged from 0.039 to 1.72 Bq kg^{-1}-dry (geometric mean: 0.19 Bq kg^{-1}-dry) as listed in Table 1; the values were much lower than those in the soils. Although Bettencourt et al.[1] reported that ^{226}Ra uptake depends on its concentration in the soil, we observed no correlation between ^{226}Ra concentrations in soil and crops in this study, possibly due to inclusion of many crop types. Concerning leek samples, we compared ^{226}Ra concentrations in green and white parts but t-test results showed no difference between them.

3.2. Soil-to-crop transfer factor of ^{226}Ra. Using the obtained data for ^{226}Ra in the 42 crops and the data for associated soil samples, we calculated the TFs. The TF can be quantified as

$$\mathrm{TF} = \frac{\text{Element concentration in the edible parts at harvest (Bq kg}^{-1}\text{-dry or mg kg}^{-1}\text{-dry)}}{\text{Element concentration in the soil (Bq kg}^{-1}\text{-dry or mg kg}^{-1}\text{-dry)}}.$$

The results ranged from 1.1×10^{-3} to 5.8×10^{-2} with a geometric mean of 6.4×10^{-3} (Table 1). These data were within the 95% confidential range of TF-Ra for several crops as reported in the TRS-364.[3] The TFs of leafy vegetables (cabbage, lettuce, etc.) had the highest values (geometric mean: 1.2×10^{-2}) compared to other crop types, i.e., root vegetables, fruit vegetables, legumes, cereals, and allium species. Then the values for leafy vegetables were compared with reported values; these are summarized in Table 2. Except for the results reported by Bettencourt et al.,[1] the reported values[2–5] were

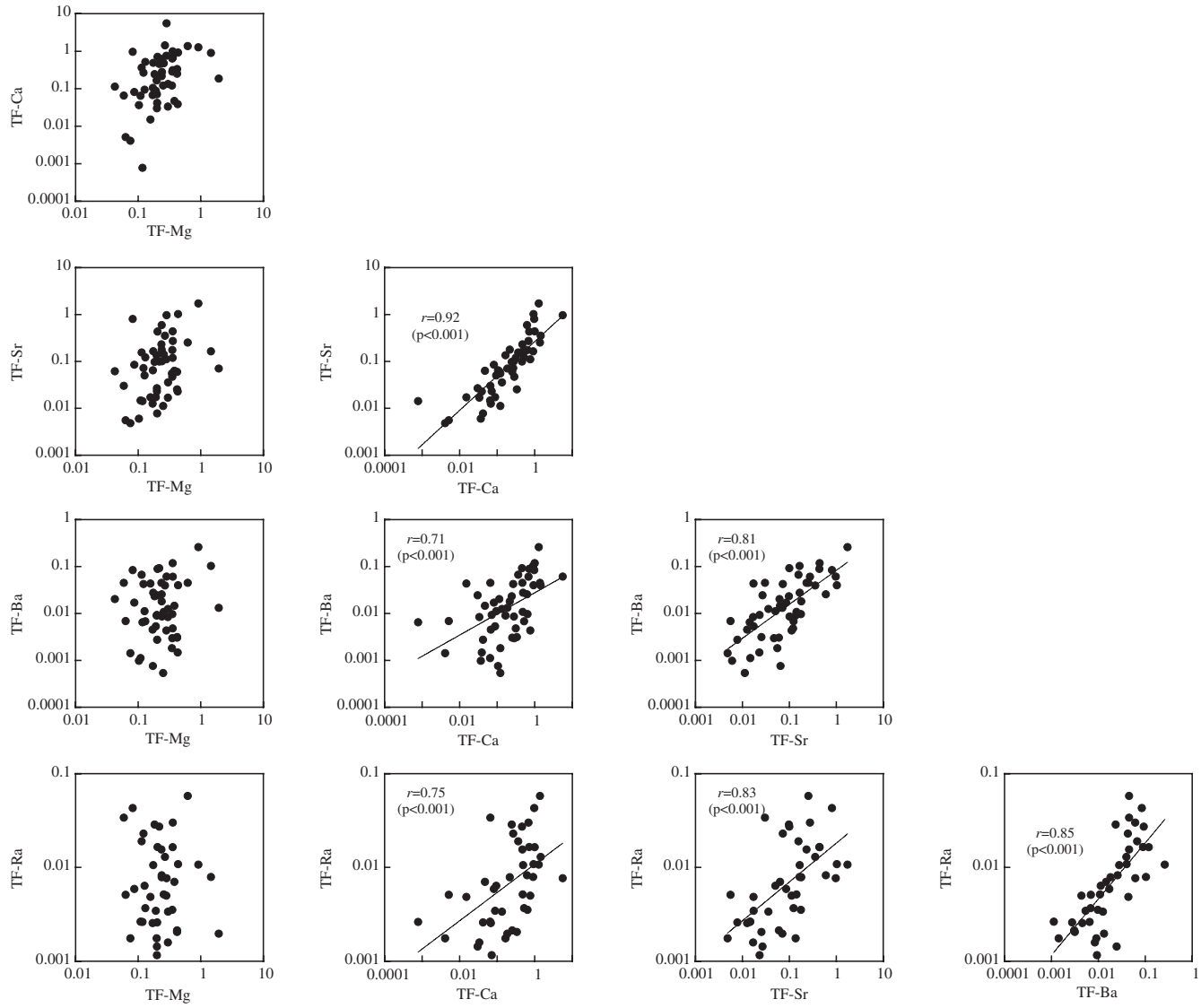

Figure 4. Correlations between TFs of alkaline earth metals for upland field crops.

almost the same as those in this study, i.e., on the order of 10^{-2}.

Since reported TFs of Ra are limited, we also measured TFs of Mg, Ca, Sr, and Ba which are in the same alkaline earth metal group. Comparison allowed us to clarify similarities in distribution of the TF values for Ra and these elements. Correlations between TFs of each element are plotted in Figure 4. Among the TFs of alkaline earth metals, t-test results showed no correlation for TF-Mg with other alkaline earth elements, while TF-Ca and TF-Sr showed the highest correlation (r = 0.92, $p < 0.001$). It is well known that Mg and Ca are essential elements for plants but their roles are different, so some difference in TF correlation was reasonable.

Relatively high correlations with TF-Ra ($p < 0.001$) were found in the following order: TF-Ba (r = 0.85) > TF-Sr (r = 0.83) > TF-Ca (r = 0.75). Except for Mg, TFs of elements next to each other in the periodic table, i.e., Ca-Sr, Sr-Ba, and Ba-Ra, showed higher correlations, possibly because their chemical properties are closer with respect to ionic radius, crystalline structure, and solubility. For instance, the ionic radius of Ra is 1.43 Å while that of Ba is 1.35 Å, so they are very close to each other; Since Ca is an essential element, Sr, Ba, and Ra might alternatively be absorbed by plants. Vandenhove et al.[11] reported that Ba is considered a better tracer for Ra than Sr, given the significant linear correlation found between the TF-Ba and TF-Ra in tracer studies although the regression curve does not have 1:1 slope as we observed in this study. Under agricultural environment conditions, TF-Ba would also be a good analogue of TF-Ra. However it should be noted that the range of TF-Ba was wider than that of TF-Ra.

In the present study, we measured TFs of Ra in various crop samples; however, it is difficult to compare area differences in Japan because each crop type did not have a large enough sample size. Further studies are needed for upland crops.

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