Iodine transfer from agricultural soils to edible part of crops

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Summary. Information about the distribution and cycling of stable iodine (I) in the environment is useful for dose estimation from its long-lived radioiodisotope, ^{129}I , which is one of the most critical radionuclides to be managed for the safe disposal of nuclear fuel waste. The soil-to-plant transfer factor (TF) is an important parameter to predict internal radiation exposure pathways through the food chains using mathematical models. Therefore, we have measured stable I and bromine (Br) for comparison, in 142 crop samples and associated agricultural field soil samples collected throughout Japan. The crops were classified into eight groups, *i.e.* leafy vegetables, white part of leeks, fruit vegetables, tubers, root crops, legumes, wheat and barley (WB), and rice. The results showed that Br and I concentrations were higher in upland field soil samples than in paddy field soil samples. However, when we compared TF values of WB and brown rice, no statistical difference was observed. The highest geometric mean of TF for I, 1.4×10^{-2} , was obtained for leafy vegetables and fruit vegetables and that for Br, 1.5, was for fruit vegetables. TF for I was much lower than Br, as reported previously, maybe due to their different chemical forms in soil and uptake behaviors by plant roots.

1. Introduction

Iodine (I) behavior is of interest because its very long-lived isotope ^{129}I (half life: 1.57×10^7 y) is often the most limiting and critical radionuclide in both transuranic and high level radioactive waste management due to its high mobility in the terrestrial environment. Since stable I can be used as a natural analogue of ^{129}I , information about the distribution and cycling of stable I in the environment is highly useful for estimating the dose from ^{129}I .

To predict internal radiation exposure pathways through food, mathematical models have been used and environmental transfer parameters have been applied in these models. The soil-to-plant transfer factor (TF) is an important parameter because a significant exposure pathway to humans is ingestion of contaminated food. Recently, the IAEA compiled TFs of I in several crops collected in temperate areas [1]. However, number of available data sets were still limited; for example, only one value for tubers

and fruit vegetable was given since data were only collected from radiotracer experiments. Sheppard *et al.* [2] recently provided concentration ratio data which are analogous to TF data; however, only one value for human foods, 0.005 was given. This is problematic, since it has been reported previously that TF values of I change for different crops [3, 4].

In Japan, several TF data have been reported for stable I [5–8], but the data were not collected from all over the country so that it is not clear whether such data could be generic for Japan or not. In this study, therefore, we measured I concentrations in 142 crop samples and associated agricultural field soil samples collected throughout Japan to supply more TF data.

2. Experimental

2.1 Samples

Surface layer (0–20 cm) soil samples from 79 upland fields and 63 paddy fields were collected nationwide in Japan from 2002 to 2006 during the harvesting season. Soils were classified as Fluvisols (77 sites), Andosols (35 sites), Cambisols (27 sites), and other soil types (5 sites) according to FAO/UNESCO soil taxonomy [9].

Edible parts from crops grown in these agricultural fields were also collected in the harvesting season. For 4 leek plants, green and white parts were separated as individual samples. For Japanese radish and carrot samples, leaves are also edible parts so that the roots and leaves were separated and elemental compositions were measured for both parts in one sample of each crop. Numbers of samples were; leafy vegetables, 22 (7 cabbage, 4 Chinese cabbage, 4 leek (green part), 2 lettuce, 2 spinach, 1 Nozawana, 1 Japanese radish, and 1 carrot); root crops, 14 (7 Japanese radish, 4 onion, and 3 carrot); tubers, 11 (6 potato, 3 sweet potato, and 2 taro); fruit vegetables, 18 (6 tomato, 5 egg plant, 4 cucumber, 2 green pepper, and 1 bitter cucumber); legumes, 7 (6 soybean and 1 peanut); cereals except rice, 9 (7 wheat and 2 barley); and rice, 63 (brown rice, white rice, and bran). Since the white part of leeks is grown underground, whether to classify it as a leafy vegetable or a root vegetable is unclear. Then, we classed the white part of leeks separately as its own group with 4 samples. In total, 148 crop part samples together with the associated soil samples were used in this analysis.

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2.2 Measurements

A simple extraction method was applied to measure stable I and Br in plant samples by inductively coupled plasma mass spectrometry (ICP-MS) [10]. About 100 mg of dried-sample were weighed into a 6 mL PFA vessel (026R, Savillex Co.). Then, 1 mL of super-pure grade 25% tetramethyl ammonium hydroxide, TMAH (TAMAPURE-AA-100, Tama Chemicals Co. Ltd.), was added and the vessel was closed tightly. The vessel was heated over night (about 12 h) at 60 °C. The sample was diluted to 50 mL with deionised water and centrifuged to obtain supernatant which contained about 0.5% TMAH for iodine measurement by ICP-MS. The method can successively recover *ca.* 100% of I from plant samples [10]. The same method is also applicable to Br concentration measurements.

For soil samples, energy dispersive X-ray fluorescence (Epsilon 5, PANalytical B. V.) was used as described before [11]. In brief, about 10 g amount of each soil sample were powdered and pressed into a 32-mm diameter pellet using a hydraulic press operated at 20 tons pressure. The Compton-scattered line was used as an internal standard to compensate for variations in sample matrix, particle size, packing density, and instrumental operating characteristics.

3. Results and discussion

Total Br and I concentrations in different agricultural uses, *i.e.*, upland fields and paddy fields, were compared and the results are shown in Fig. 1. Concentrations of Br and I were statistically higher (*t*-test, $p < 0.001$) in upland fields than in paddy fields. The results agreed well with previously reported ones [6, 12], while, the variations in Br and I concentrations observed in upland fields and paddy fields were due to different redox conditions.

In order to know which soil group contained the highest Br and/or I concentration, we compared the soil samples as shown in Fig. 2, and the geometric means (GMs) and ranges for four soil groups are listed in Table 1. Concentrations of Br in Andosol samples (GM: 31.8 mg kg⁻¹) collected in upland fields were significantly higher than in samples of other soil groups except for the Andosol samples collected in paddy fields. However, among soil groups excluding An-

Table 1. Geometric means (GMs) and ranges of Br and I concentrations in four soil groups for samples collected in upland and paddy fields on a dry weight basis.

Soil group	<i>N</i>	Bromine (mg kg ⁻¹)		Iodine (mg kg ⁻¹)	
		GM	Range (min–max)	GM	Range (min–max)
Upland fields					
Andosol	29	31.8	5.5–158	11.8	1.8–65.5
Fluvisol	31	6.3	1.6–80.7	3.0	1.3–37.4
Cambisol	19	7.3	2.0–34.1	4.2	0.8–19.9
Other	2	11.6*	0.3–22.9	11.5*	0.2–22.8
Paddy fields					
Andosol	6	12.8	4.0–42.7	3.8	1.1–10.1
Fluvisol	46	3.8	1.1–15.3	1.8	0.8–9.3
Cambisol	8	3.2	1.6–5.9	1.7	1.2–2.8
Other	3	8.7	6.3–12.0	3.4	2.8–3.7

Fig. 2. Box-and-whisker plot of Br (a) and I (b) concentrations in Andosol, Fluvisol, and Cambisol samples collected in upland and paddy fields. Number of samples *n* is given for each soil groups. The data followed by the same letter are not significantly different ($p < 0.05$).

Fig. 1. Box-and-whisker plot of Br (left) and I (right) concentrations in upland and paddy fields. Asterisks (**) show the statistical difference ($p < 0.001$) by *t*-test.

dosol collected in upland fields there were no differences. For I, Andosol samples collected in upland fields (GM: 11.8 mg kg⁻¹) had results that were different from other soil groups. GMs of Br and I excluding Andosol samples collected from upland fields were 5.0 mg kg⁻¹ and 2.4 mg kg⁻¹, respectively. The higher Br and I concentrations in upland fields were due to the characteristics of Andosol. Muramatsu and Yoshida [12] also reported that I concentrations were high in Andosol.

It was difficult to check the effect of concentration differences in upland fields and paddy fields for Br and I con-

Fig. 3. Box-and-whisker plot of Br (a) and I (b) concentrations in wheat and barley for upland fields, and brown rice in paddy fields for each soil group. Number of cereal samples n is given for each soil groups. The data in the right graph followed by the same letter are not significantly different ($p < 0.05$).

centrations in crops if we used all the crop samples. Thus we used Br and I concentration data for wheat and barley (WB) collected in upland fields for comparison with data for brown rice collected in paddy fields. The WB samples were only hulled, thus the data would be comparable to those for brown rice; besides, these crops are in the same plant family, Poaceae. As shown in Fig. 3, for Br, no concentration differences were observed for all soil groups, however, for I, the concentrations were higher in soil groups collected in upland fields than in paddy fields. GMs of Br in WB and brown rice were 1.3 and 0.86 mg kg^{-1} dry, respectively ($p > 0.05$), and those of I were 0.020 and $0.0077 \text{ mg kg}^{-1}$ dry, respectively ($p < 0.05$). From this result, we concluded that I concentrations in crops were not related to soil groups but rather to agricultural uses and/or crop species.

Since the main source of Br and I is seawater, their correlations were also compared in soil and crop samples (Fig. 4) to elucidate how these elements went from the sea through the terrestrial environment. In upland fields and paddy fields, Br and I concentrations were close to a log-normal distribution, thus, logarithms of the data were chosen for statistical analysis. In both agricultural uses, Br and I were well correlated, *i.e.*, the correlation coefficients were 0.89 ($p < 0.001$) for upland fields and 0.76 ($p < 0.001$) for paddy fields by t -test. However, when we compared Br and I concentrations in WB and brown rice, no correlation was observed. Thus, we concluded that chemical forms of Br and I in soil and Br and I uptake mechanisms by plant roots would be different.

Fig. 4. Correlations between Br and I concentrations in soil samples (a) and cereals (wheat and barley for upland fields and brown rice for paddy fields) (b).

Using the 148 data sets, we calculated TF values. The TF is defined as the plant/soil concentration ratio (on dry weight basis), and the results are listed in Table 2. The GM of TFs of I for fruit vegetables and leafy vegetables, 1.4×10^{-2} , was the highest among the crops, while the lowest value of 3.9×10^{-3} was obtained for brown rice samples. The TFs for brown rice were within the previously reported values, 1.5×10^{-4} to 3.9×10^{-2} [1, 5, 6]. The TFs of I for the white part of leeks were within the range of leafy vegetables, however, the GM value was much closer to that of root crops. The GM for each crop group in the present study were almost the same as previously reported values of radio-tracer experiments collected worldwide and in Japan [1, 3–7]. The GMs of tubers and fruit vegetables compiled by the IAEA [1] were, however, 1–2 orders of magnitude higher. The GM of TFs of I for WB were about 8 times higher than that for cereals compiled by the IAEA, which may be due to greater I mobility in the Japanese agricultural soil samples.

For Br, the highest GM of TFs was obtained for fruit vegetables, 1.5, and the lowest value was 0.16 for WB samples. For all crop groups, GMs of TFs of Br were 2 orders of magnitude higher than those of I. Yuita *et al.* [6] reported about a 40 times higher TF value for Br than that for I in wild plants. Thus, we observed the same tendency for crops. For the case of I, direct deposition onto plant surfaces would be negligible [8]; however, for Br, this phenomenon has not

Table 2. Soil to crop (edible part) transfer factors.

Crop parts	Bromine Geometric mean, number of data (min–max)	Iodine Geometric mean, number of data (min–max)	Ref.
Leafy vegetables	1.0, $n = 22$ (9.5×10^{-2} – 1.4×10^1)	1.4×10^{-2} , $n = 22$ (9.8×10^{-4} – 4.9×10^{-1})	This study
Leafy vegetables		6.5×10^{-3} , $n = 12$ (1.1×10^{-3} – 1.0×10^{-1})	[1]
Leek (white part)	1.9×10^{-1} , $n = 4$ (7.6×10^{-2} – 3.1×10^{-1})	4.0×10^{-3} , $n = 4$ (1.3×10^{-3} – 8.4×10^{-3})	This study
Root crops	6.7×10^{-1} , $n = 14$ (1.1×10^{-1} – 2.6×10^0)	6.1×10^{-3} , $n = 14$ (8.7×10^{-4} – 6.7×10^{-2})	This study
Root crops		7.7×10^{-3} , $n = 28$ (1.4×10^{-3} – 4.7×10^{-2})	[1]
Tubers	7.7×10^{-1} , $n = 11$ (1.1×10^{-1} – 1.2×10^1)	6.9×10^{-3} , $n = 11$ (9.4×10^{-4} – 9.4×10^{-2})	This study
Tubers		1.0×10^{-1} , $n = 1$	[1]
Fruit vegetables	1.5×10^0 , $n = 18$ (7.8×10^{-2} – $3.0 \times 10^{+1}$)	1.4×10^{-2} , $n = 18$ (1.6×10^{-3} – 1.4×10^{-1})	This study
Fruit vegetables		1.0×10^{-1} , $n = 1$	[1]
Legumes	2.9×10^{-1} , $n = 7$ (2.0×10^{-2} – 1.6×10^0)	4.7×10^{-3} , $n = 7$ (6.3×10^{-4} – 4.2×10^{-2})	This study
Legumes		8.5×10^{-3} , $n = 23$ (2.0×10^{-4} – 1.4×10^{-1})	[1]
Wheat and barley	1.6×10^{-1} , $n = 9$ (3.1×10^{-2} – 5.7×10^{-1})	4.9×10^{-3} , $n = 9$ (5.1×10^{-4} – 3.0×10^{-2})	This study
Cereals		6.3×10^{-4} , $n = 13$ (1.0×10^{-4} – 1.1×10^{-2})	[1]
Brown rice	2.0×10^{-1} , $n = 63$ (1.4×10^{-2} – 1.3×10^0)	3.9×10^{-3} , $n = 59$ (4.5×10^{-4} – 1.8×10^{-2})	This study
Brown rice		3.8×10^{-3} , $n = 8$ (1.1×10^{-3} – 7.6×10^{-3})	[1]
Bran	9.9×10^{-1} , $n = 63$ (8.9×10^{-2} – 6.4×10^0)	3.1×10^{-2} , $n = 63$ (3.3×10^{-3} – 1.6×10^{-1})	This study
White rice	1.5×10^{-1} , $n = 63$ (1.5×10^{-2} – 1.0×10^0)	2.1×10^{-3} , $n = 45$ (3.5×10^{-4} – 4.9×10^{-3})	This study

been clarified yet so that the effect of direct deposition is necessary to be considered for these TF differences between Br and I. Moreover, we previously found that Br was more mobile than I in agricultural soils [11], which would also cause big TF differences between Br and I.

Rice grains (brown rice) can be separated into white rice and bran parts, and consumption of the former is much higher. Thus, we measured TFs of these parts separately. The results are also listed in Table 2. The GM of TFs of Br in bran was 7 times higher than that in white rice, while GM of TFs of I in bran was 14 times higher than that in white rice. Tsukada *et al.* [8] reported that TF for rice bran was 18 times higher than that of white rice, which was similar to the value

of the present study. The observed variations could be due to chemical behavior differences between Br and I in rice plants. However, a further study is needed to learn the chemical behaviors of halogens in agricultural plants, especially in their edible parts.

4. Conclusions

Transfer factors of I for several crop groups were reported. We checked the soil group dependency of I and Br concentrations in crops using cereals (wheat, barley and brown rice) and observed no statistical differences, but rather to

agricultural uses and/or crop species. The GMs of TFs of I for eight crop groups ranged from 3.9×10^{-3} to 1.4×10^{-2} , which are relatively narrow ranges compared to TFs of other radionuclides/elements [1]. Thus, as Sheppard *et al.* [3] reported, these data could be combined to get a generic TF value for foods. However, each group has specifically different TF ranges and GMs, so if possible, different values should be used for more precise dose estimations for ^{129}I .

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