**Soil-To-Plant Transfer Factor of Uranium by Measuring Naturally Occurring Uranium at Trace Levels in Plants and Soils by ICP-MS -9105**

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## ABSTRACT

Uranium (U) concentrations in crop samples are usually low, making it difficult to obtain soil-to-plant transfer factors (TFs) under agricultural field conditions. In this study, U concentrations in rice and associated soil samples have been determined by inductively coupled plasma mass spectrometry (ICP-MS) after chemical separation with TRU resin (Eichrom). After U extraction on the resin by sample solution loading, tetramethyl ammonium hydroxide was studied for U elution behavior from the resin cartridges. Chemical recovery with this method was about 85%. Then U concentrations in three kinds of rice grain samples, brown rice (hulled rice), white rice (polished rice) and bran (63 samples each), were measured by ICP-MS after the TRU resin extraction method. U concentrations in all samples were measured and the geometric means in white rice, brown rice and bran samples were $7.3 \times 10^{-5}$, $9.7 \times 10^{-5}$ and $3.7 \times 10^{-4}$ mg/kg-dry, respectively. TFs for white rice ranged from $6.2 \times 10^{-6}$ to $7.9 \times 10^{-5}$ with a geometric means of $2.7 \times 10^{-5}$, whereas those for brown rice ranged from $5.5 \times 10^{-6}$ to $4.6 \times 10^{-4}$ with a geometric means of $3.6 \times 10^{-5}$. These values were 2 orders of magnitude lower than the TF for cereals of $1.3 \times 10^{-3}$ proposed by IAEA.

## INTRODUCTION

The safety of radioactive waste disposal in underground sites must be assessed into the far future. Mathematical models have been used for assessment of potential exposures to humans from these radioactive wastes. Among the environmental transfer parameters that have been used in the mathematical models, soil-to-crop transfer factor (TF) is a key parameter that directly affects the internal dose assessment for the ingestion pathway. For uranium (U), we can use naturally existing U to predict the behavior from radioactive waste disposal sites to the biosphere. However, due to its low concentration in plant samples, the number of reported TF-U values are limited [1].

In order to measure trace levels of U in various environmental samples, inductively coupled plasma mass spectrometry (ICP-MS) has been widely used. We also have used the method and obtained TFs of U in various soils and crops [2, 3]. A typical pretreatment method before ICP-MS analysis for plant samples is as follows: dissolution of a dried crop sample (100-500 mg) in a mixture of mineral acids using a microwave digestion system followed by dilution of the solution to a suitable total matrix concentration for ICP-MS, usually less than 1000 mg/L. This simple dilution-ICP-MS method makes U measurement difficult especially in grain crops because of extremely low U concentrations, e.g. µg/kg-dry or less. Indeed, we only could obtain measurement results for ca. 60% of any group of white rice (polished rice) samples using this simple dilution method.

To separate and concentrate U from sample matrix, we previously used TEVA resin (Eichrom

Technologies, Inc.) [4]. The U(+VI) adsorbability by TEVA resin is higher than that of U/TEVA or TRU resin in HCl solution. In our previous method, the water sample was evaporated to dryness first, and then, the residue was dissolved in 6M HCl. However, the evaporation process takes a long time, and even if the co-precipitation technique [5] were introduced instead of evaporation, the step can still be time consuming. Moreover, Fe in sample water interferes with U adsorption on the resin. Thus, it would be better to use nitric acid for U separation. U/TEVA resin has been used for U separation, but a high concentration of $HNO_3$, e.g. 3M $HNO_3$, is necessary to retain U on the resin, whereas TRU resin has the same ability to retain U at less than 0.5M $HNO_3$. Thus, TRU resin is attractive for U separation and it is more environment friendly than other resins.

In a typical U separation method [5], the U fraction (0.1M ammonium oxalate solution) is heated to decompose oxalate and this is followed by the U/TEVA resin separation steps; all these steps take time. In this study, we applied the previously developed method for U in water [6] to separate U from plant samples. By this TRU extraction method, we could measure trace levels of U in crop samples to provide TF data for precise dose assessment models.

## MATERIALS AND METHODS

Sixty-three rice grain samples were collected from paddy fields throughout Japan. At harvest, associated soil samples were also collected. Uranium concentrations in the soil samples were measured using the same method as previously [2, 3]. Three sub-samples were made for each rice grain sample, i.e., white rice (polished rice), brown rice (hulled rice) and bran. The 189 sub-samples were freeze-dried and thoroughly ground into fine powders.

From the pretreated sub-samples, 500 mg for each, were dissolved in a mixture of mineral acids using a microwave digestion system (CEM, Mars 5) and then heated to dryness. The residue was dissolved in 20 mL of 2% $HNO_3$ (40 times dilution). This sample preparation method is known as the dilution method. After diluting the acid solutions to a suitable concentration, U in the samples was directly measured using ICP-MS (Yokogawa, Agilent 7500a). A multi-element standard solution including U was purchased from SPEX Certiprep Inc. (XSTC-13).

A part of the 20-mL solution, about 5 mL, was weighed and acidified further with conc. $HNO_3$ (super pure grade) to obtain 1M $HNO_3$. Then the sample was loaded on a TRU resin cartridge; most elements did not adsorb on the resin during this sample loading step while U was extracted on the resin. After the cartridge was washed with 10 mL of 0.5 M HCl followed by 5 mL of deionzied water, U was eluted from the resin with 20 mL of 0.014M tetramethyl ammonium hydroxide and collected in a PTFE bottle. The solution was evaporated to near dryness on a hot plate and then redissolved in 2% $HNO_3$ to get a final volume of 5 mL. Concentration of U was determined by ICP-MS. Chemical recovery with the TRU resin extraction method was about 85% as confirmed by comparing a standard solution result to the initially added U amount.

## RESULTS AND DISCUSSION

A standard reference material, GBW-07603 (bush twigs and leaves, Institute of Geophysical and Geochemical Exploration, China) was used to check the applicability of the TRU extraction method. We found that the measured U concentration agreed well with the certified value when the recovery of 85%

was applied. Then U concentrations in rice grain samples were measured by ICP-MS after using the TRU extraction method. The measured concentrations by the TRU extraction method were compared with those obtained by the dilution method. We saw that when the TRU extraction method was applied, U

concentrations of all the samples could be measured, but by the dilution method 24 samples of white rice, 19 samples of brown rice and 2 samples of bran could not be measured because their U concentrations were close to the detection limit. The results are shown in Fig. 1. The results agreed well in bran samples
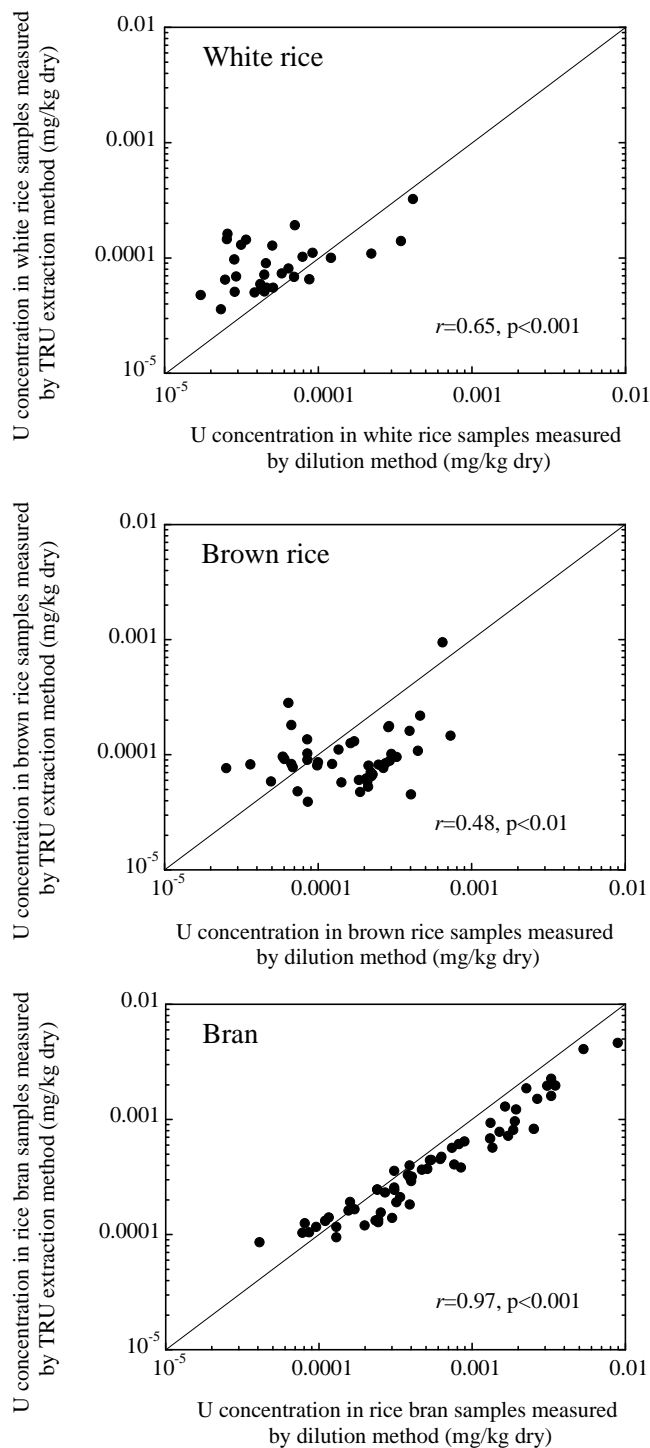


**Fig.1. Comparison of analytical results for U in white rice, brown rice and bran as determined by the TRU resin extraction method and dilution method.**

with a high correlation factor of 0.97 (p<0.001) by t-test. Lower correlations were found in white rice (r=0.65) and brown rice samples (r=0.48) due to low concentrations with large uncertainties by the dilution method (data not shown). These results indicated that the TRU extraction method for sample preparation followed by ICP-MS was applicable to trace level measurements of U in crop samples.

The cumulative probability distributions of U in the white rice, brown rice and bran samples by the TRU extraction method were closer to the log-normal lines (data not shown) so that geometric means (GMs) of U were calculated. The results were $7.3 \times 10^{-5}$ mg/kg-dry (range: $3.6 \times 10^{-5}$ to $3.3 \times 10^{-4}$ mg/kg-dry) for the white rice samples, $9.7 \times 10^{-5}$ mg/kg-dry (range: $3.9 \times 10^{-5}$ to $9.5 \times 10^{-4}$ mg/kg-dry) for the brown rice samples, and $3.7 \times 10^{-4}$ µg/g-dry (range: $8.6 \times 10^{-5}$ to $4.6 \times 10^{-3}$ mg/kg-dry) for bran samples. The bran weight was about 10% of the brown rice weight, and the remaining 90% of the brown rice weight was white rice; thus, about 1/3 of the total U in brown rice was distributed in the bran.

The U concentration data in brown rice, white rice and in associated soil samples were used to calculate TF. The TF value was calculated using the following equation:

$$TF = C_p / C_s$$

where $C_p$ (mg/kg-dry) is the elemental concentration in plant and $C_s$ (mg /kg-dry) is its concentration in soil. GMs of TFs for white rice and brown rice were $2.7 \times 10^{-5}$ (range: $6.2 \times 10^{-6}$ to $7.9 \times 10^{-5}$) and $3.6 \times 10^{-5}$ (range: $5.5 \times 10^{-6}$ to $4.6 \times 10^{-4}$), respectively.

The TFs were also compared between soil groups, that is, 46 Fluvisol, 8 Cambisol, 6 Andosol and 3 other soil type samples, based on the FAO/UNESCO classification [7]. The results for brown rice and white rice are shown in Fig.2. The GMs were $3.5 \times 10^{-5}$ for Fluvisol, $3.1 \times 10^{-5}$ for Cambisol, and $4.4 \times 10^{-5}$ for Andosols in brown rice samples, whereas those in white rice samples were $2.8 \times 10^{-5}$ for Fluvisol, $2.3 \times 10^{-5}$ for Cambisol, and $2.5 \times 10^{-5}$ for Andosol. The TF values did not differ significantly among the soil groups (t-test, p>0.05).
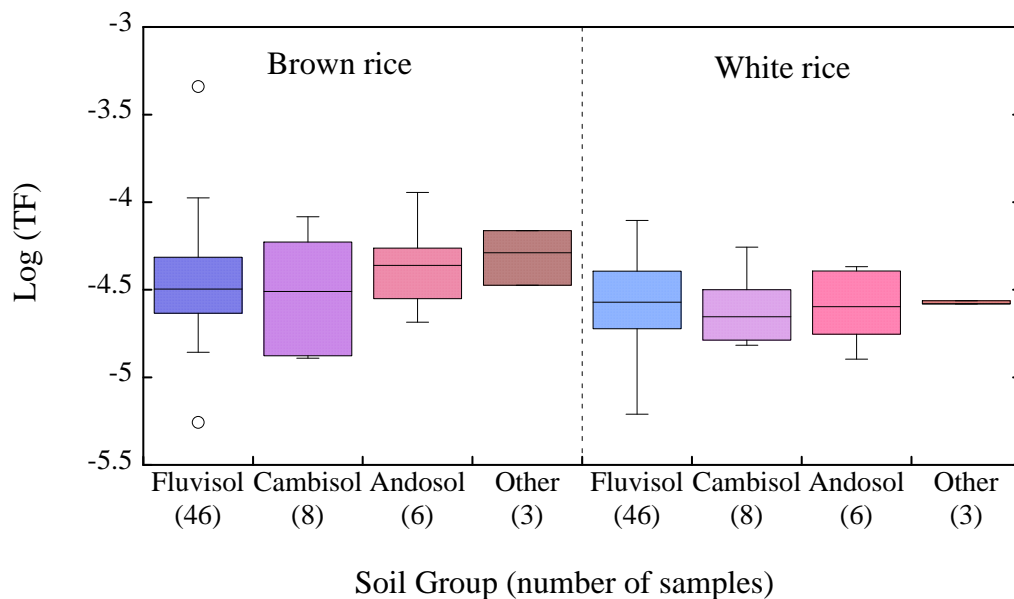


**Fig. 2. Box-and-whisker plot of TF values of the soil groups.**

The TF values obtained in this study and previously reported values [8-13] were compared and the values are listed in Table I. Our data were slightly lower than other Japanese data but 2-3 orders of magnitude lower than data for India. Compared to other cereals, rice TF values observed in Japan were 1-2 orders of magnitude lower than for temperate zone countries although Japan is also classified as the same zone country. Recently, it was reported that soil solution U concentration was not a good bioavailability index and U speciation would be necessary [14]. Since U is a redox sensitive element, the chemical forms might be different in paddy fields and upland fields conditions. Water management in rice paddy fields as well as soil characteristics might affect the results. Thus further field studies are necessary to understand U behavior.

Table I.   Transfer Factors for Cereals and Rice on Dry Weight Basis

| Crops | Place | Reported TF value | N | Reference |
|---|---|---|---|---|
| Cereal grains | World | $1.3 \times 10^{-3}$ | 2 | [1] |
| Cereal grains | World | $0.3 \times 10^{-2}$ | 55 | [8] |
| White rice | Japan | $1.4 \times 10^{-4}$ | 12 | [9]* |
| White rice | Japan | $7.1 \times 10^{-5}$ | 12 | [9]* |
| White rice | Japan | $1.9 \times 10^{-4}$ | 11 | [10] |
| White rice | Japan | $4.5 \times 10^{-5}$ | 10 | [11] |
| White rice | Japan | $2.7 \times 10^{-5}$ | 63 | This study |
| Brown rice | Japan | $1.4 \times 10^{-4}$ | 9 | [12]* |
| Brown rice | Japan | $1.5 \times 10^{-4}$ | 8 | [12]* |
| Brown rice | India | $1.9 \times 10^{-3}$ | - | [13] |
| Brown rice | India | $1.26 \times 10^{-2}$ | - | [13] |
| Brown rice | Japan | $1.5 \times 10^{-4}$ | 2 | [11] |
| Brown rice | Japan | $3.6 \times 10^{-5}$ | 63 | This study |

*Values were converted from fresh/ash weight basis TF to dry weight basis TF by applying dry/wet ratio of 0.85 and ash/dry ratio of 0.014.

**ACKNOWLEDGEMENT**

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