Estimation of Anthropogenic Uranium Concentration in Japanese Agricultural Soils from Phosphatic Fertilizers

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ABSTRACT

In this study, estimation of excess amount of uranium in Japanese agricultural soils due to phosphatic fertilizer application were carried out, by measuring concentrations of total U and Th in 82 soils collected throughout Japan by inductively coupled plasma mass spectrometry (ICP-MS). Since Japanese non-agricultural fields have an average U/Th ratio of 0.23, thus, using U/Th ratios in non-agricultural areas, we thought that it is possible to calculate amounts of excess U due to the application of fertilizers. It was estimated that about 50% of total U in paddy field soils (range: 4-78%) and about 48% of total U in upland field soils (range: 4-74%) were originated from the phosphatic fertilizers.

INTRODUCTION

Uranium (U) and thorium (Th) behavior in geological environment was relatively close compared to other elements, thus high relations between their concentrations were usually observed. Consequently, the concentration ratio of U/Th in rocks, non-agricultural field soils and river sediments, respectively, were almost the same [1-4]. However, applications of phosphatic fertilizers, which are known to contain high U (10-300 times higher than uncontaminated soils) but low in Th [5-7], might increase U concentrations in agricultural field. It is difficult to estimate the excess amount of U in agricultural field due to this technically enhanced naturally occurring radioactive material, thus, the excess amount was not clear.
In this study, estimation of excess amount of U in Japanese agricultural soils due to phosphatic fertilizer application were carried out, by measuring concentrations of total U and Th in 82 soils collected throughout Japan by inductively coupled plasma mass spectrometry (ICP-MS).

EXPERIMENTAL

Sample Collection

Paddy field soils and upland field soil (plowed soil layer: 0-20 cm) were collected nationwide from 37 and 45 sampling sites, respectively, in 2002 – 2004. These samples were air-dried and passed through a 2-mm mesh sieve. Then the samples were thoroughly ground into fine powder.

Total U and Th Measurement

After that, 100 mg each were digested with a mixed acid using a microwave digester (CEM, Mars

5). Following their digestion, soil samples were evaporated to near dryness at 140 Celsius degrees. The residue was dissolved with 1 mL of conc. nitric acid and 0.5 mL of hydrogen peroxide and evaporated again. Finally, the residue was dissolved with 1 mL of 40% nitric acid and diluted with deionized water (Milli-Q). After diluting the acid solutions to a suitable concentration, U-238 and Th-232 in the soil samples were measured using ICP-MS (Yokogawa, Agilent 7500). Standard solutions were obtained by diluting a multi-element standard solution for ICP (SPEX, XSTC-13 or 355)

RESULTS AND DISCUSSION

Concentrations of U and Th in Agricultural Fields in Japan

The results of U and Th concentrations and U/Th ratio are listed in Table I. There was no difference between land use and soil types, respectively. The geometric means of total U and Th in the paddy field soils were 2.7 mg kg^{-1} and 5.6 mg/kg, respectively, while those in the upland field soils were 2.4 mg/kg^{-1} and 5.2 mg kg^{-1}, respectively. Although the geometric means of total U and Th in the soils were within the range of reported values, concentration ratios of U/Th in paddy field and upland field soils were 0.49 and 0.47 on geometric mean, respectively. These values were much higher than those in Japanese crust (0.28) [3], non-agricultural fields (0.23) [1,4],and river sediments (0.20) [3].

Table I. Concentrations of U and Th, and the U/Th Ratios in Agricultural Soils Collected in Japan (2002-2004)

Land use	Soil Type	N	U (mg/kg)	Th (mg/kg)	U/Th
Paddy fields	All	37	2.7 (1.6 - 4.7)	5.6 (2.3 - 11.3)	0. 49 (0.24-1.09)
	Gray lowland soils	13	2.6 (1.8 - 3.8)	6.9 (3.6 - 11.3)	0.38 (0.24-0.59)
	Gley lowland soils	11	1. 7 (1.6 - 4.2)	5.5 (2.3 - 9.1)	0. 49 (0.37-0.72)
	Other soil types	13	2.9 (1.8 - 4.7)	4.5 (3.1 - 7.7)	0.65 (0.37 - 1.09)
Upland fields	All	45	2.4 (1.0 - 4.2)	5.2 (1.6-11.9)	0.47 (0.24 – 0.91)
	Andosols	8	2.5 (1.0-4.2)	5.1 (2.7-11.6)	0.49 (0.32-0.81)
	Gray lowland soils	7	2.6 (1.7-3.7)	6.2 (3.7-9.2)	0.42 (0.28-0.56)
	Other soil types	30	2.4 (1.2-3.5)	5.0 (1.6-11.9)	0.48 (0.24-0.91)

It is known that U and Th concentrations in rocks are well correlated. Consequently, non-agricultural field soils and river sediments also showed high U and Th correlations (about 0.9, $p<0.1\%$ level) as shown in Fig.1. Uranium and Th extractability from these materials are almost the same, however, U is more soluble than Th so that U/Th in river sediments are slightly smaller

than non-agricultural field soils, and also these two materials showed lower U/Th than Japanese crust. In agricultural field, U and Th did not show high correlations as shown in Fig.1. These results imply that phosphatic fertilizers, which have high U concentrations, increased the total U concentrations of Japanese agricultural fields; indeed, phosphatic fertilizers have been used in Japan almost 50-60 years.

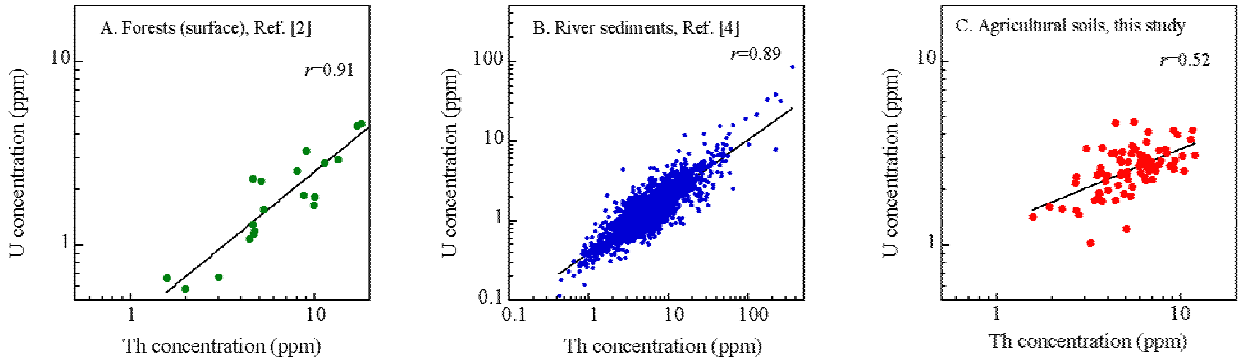

Fig.1. Relationships between U and Th concentrations in (A) forests, (B) river sediments and (C) agricultural fields in Japan.

Estimation of Excess Amount of U in Agricultural Fields

In order to estimate excess amount of U (U_{ess}), natural U/Th ratios could be used because U/Th ratios in phosphatic fertilizers are usually high. Thus, the following equation was used.

$$[U_{ess}]=[U_{obs}]-[Th_{obs}]* U/Th_N$$

Where U_{obs} is measured total U in soil, Th_{obs} is total Th in the soil and U/Th_N is U/Th in initial soil condition (natural ratio).

For a more realistic estimation, it should be better to the U/Th ratios in non-agricultural fields near the sampling sites, however, it is sometimes difficult to find such a place. However, as mentioned above, U and Th concentrations were highly correlated with each other in rock, forests and river sediments, thus, we thought that it is possible to calculate the amounts of excess U. Therefore, we used U/Th ratios in non-agricultural areas, 0.23, as an average U/Th ratio in agricultural fields before application of phosphatic fertilizers.

The $[U_{ess}]$ ranged from 0.05-1.45 mg/kg soil, with a geometric mean of 1.13 mg/kg. The results for paddy fields and upland fields are listed in Table II; there were no $[U_{ess}]$ differences between land uses. The each result is plotted in Fig.2. The highest sample numbers were found between 1-1.5 mg-$[U_{ess}]$/kg soil.

From the results, it was estimated that about 50% of total U in paddy field soils (range: 4-78%) and about 48% of total U in upland field soils (range: 4-74%) were originated from the phosphatic fertilizers. Although U in the fertilizers are more mobile than U originated from the soil [5], however, the uptake take ratio of U from soil (Bq/kg-dry or mg/kg-dry) to plant (Bq/kg-dry or

mg/kg-dry) through roots are very small [8], i.e. in the order of 0.001-0.01, the dose effect due to the excess U would be negligible.

Table II. Estimation of Excess U Concentration in Paddy fields and Upland fields

1Land use	N	Excess U ([U_{ess}]) (mg/kg)	Initial U (mg/kg)
Paddy fields	37	1.25 (0.1 – 3.6)	1.30 (0.5 – 2.6)
Upland fields	45	1.04 (0.05 – 2.2)	1.21 (0.4 – 2.8)

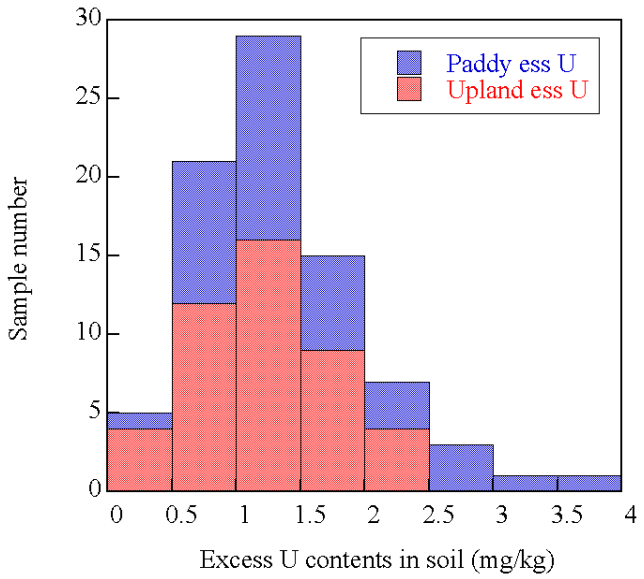

Fig. 2. Frequency distribution of excess U concentration in Japanese agricultural fields.

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