# **Global Fallout Technetium-99 Levels in Japanese Paddy Soils**

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Determination of global fallout <sup>99</sup>Tc in Japanese paddy field soil sample was carried out using a simple and rapid separation method by using a TEVA resin and determination by ICP-MS. The ranges of <sup>99</sup>Tc concentrations are 6 - 110 mBq kg<sup>-1</sup> dry. The <sup>99</sup>Tc values obtained were usually higher than the expected value of 6 mBq kg<sup>-1</sup> dry which was estimated from uniform <sup>99</sup>Tc distribution on the surface of the northern hemisphere. To explain the fate of <sup>99</sup>Tc in the paddy field environment, <sup>137</sup>Cs was used as an indicator. The activity ratios of <sup>99</sup>Tc/<sup>137</sup>Cs are (2.0 - 5.2) x 10<sup>-3</sup>. Since the activity ratio can be calculated theoretically from fission as 1.4 x 10<sup>-4</sup> at nuclear weapons' detonations, the ratio is now estimated to be about 3.0 x 10<sup>-4</sup> with correction of decay out. The measured ratios were one order of magnitude higher than the theoretical one from fission. The results of this study, at least, suggest that more Tc might be fixed on the soil than we expected before.

## **INTRODUCTION**

Technetium-99 is an important fission product which has been widely distributed in the environment as a result of global fallout from nuclear weapons testing (1-5) and discharges from nuclear facilities (6, 7). <sup>99</sup>Tc in the environment has been accumulating because of its long half-life of 2.1 x  $10^5$  y. The most stable chemical form of Tc in the surface environment is TcO<sub>4</sub>, which is known to have high mobility in soil and availability to plants. Thus, a knowledge of Tc behavior in the environment is of special interest because of potential long-term radiological consequences.

In previous reports, most of the data on Tc behavior in the soil environment were obtained by radiotracer experiments under upland field conditions, or aerobic conditions (8, 9). Because of its chemical form,  $TcO_4^-$ , Tc would be leached from the surface soil to a deeper layer or absorbed by plants through roots. However, the nuclide's transformation to lower oxidation states or insoluble forms under anaerobic conditions, such as in a rice paddy field, has been predicted by the Eh-pH-diagram of Tc (10, 11). With typical water management, the rice paddy fields are waterlogged during the seedling planting period. The surface water prevents the entry of oxygen from the atmosphere and soil microorganisms consume oxygen in the soil so that anaerobic conditions are generated. Consequently, Tc is supposed to be accumulated in the paddy field. The fact prompted us to obtain data for understanding of the nuclide behavior in the paddy field ecosystem because the paddy fields cover large areas of Japan and other Asian countries.

To obtain information for predicting the nuclide behavior, determination of global fallout <sup>99</sup>Tc in environmental samples is one of the useful methods. At present, generally, there is rare number of data on <sup>99</sup>Tc levels in the environment from which past and present assessments can be made due to its low concentration in environment. For the determination of global fallout <sup>99</sup>Tc in soil sample, we have been developed a simple and rapid separation method by using a TEVA resin column and determination by inductively coupled plasma mass spectrometry (ICP-MS) (5, 12, 13). Using the developed method, <sup>99</sup>Tc contents in several soil samples collected in paddy fields in Japan were determined in this study. The radionuclide behavior in Japanese paddy field is also discussed.

#### **EXPERIMENTAL**

Eight soil samples were collected from the surface layer (< 20 cm) of paddy fields throughout Japan (Figure 1). The samples were air-dried and passed through a 2-mm mesh sieve. For the determination, 300 to 500 g of each soil sample were used. They were heated for 8 hours at 450  $^{\circ}$ C to decompose organic matter because its presence in samples interfered with Tc separation. No loss of Tc was found during the heating (12).

The incinerated soil sample was added <sup>95m</sup>Tc as a yield tracer. Then, Tc was volatilized from the incinerated soil sample by volatilization in a combustion apparatus for 3 h at 1000 °C and trapped in deionized water (13). The volume of the trap solution was reduced to approximately 200 mL by evaporation on a hot plate at 100 °C.



Figure 1. Soil collection sites in Japan.

The solution was adjusted to 0.1 M HNO<sub>3</sub> and passed through a TEVA resin column (Eichrom Industries Inc.) to purify and concentrate Tc isotopes (14). Because ICP-MS cannot differentiate between 99Ru and 99Tc, it is necessary to separate all Ru from the final sample solution prior to ICP-MS measurement. Ruthenium present in the sample solution is not effectively retained on the TEVA resin. More than 95% of Ru passes directly through the column with the solution. The column was then washed with 2 M HNO<sub>3</sub> to remove any remaining trace Ru. Tc was eluted with 5 mL of 8 M HNO<sub>3</sub>. By the separation steps, Ru was completely removed. The strip solution containing Tc was evaporated to dryness, and the residue dissolved in 5 mL of 2% HNO<sub>3</sub>. The separation procedure was shown in Figure 2.

The nitric acid used was ultra pure grade (Tama Chemicals, AA-100). Throughout the



Figure 2. Separation procedure for <sup>99</sup>Tc in soil sample.

experiments,  ${}^{95m}$ Tc produced by the  ${}^{93}$ Nb ( $\alpha$ , 2n)  ${}^{95m}$ Tc reaction was used as a yield monitor (15). The tracer solution does not contain  ${}^{99}$ Tc, Ru, or Mo. After the separation procedure, the chemical recovery was obtained by counting  ${}^{95m}$ Tc in the sample on a NaI (Tl) scintillation counter (Aloka, ARC-380) and comparing the results with standard solutions.

The <sup>99</sup>Tc content of the sample solution were determined by ICP-MS (Yokogawa, PMS-2000) with 180 s counting time at mass 99. To check levels of potential interference elements (e.g., Ru, Mo), m/z = 98, 101 and 102 were also scanned at the same time. The detection limit of ICP-MS was 0.03 mBq mL<sup>-1</sup> of the solution that corresponds to 0.014 mBq g<sup>-1</sup>dw of soil sample under the operational conditions.

Fallout <sup>137</sup>Cs was used as an indicator for <sup>99</sup>Tc behavior because of large number of data and the fission yields of both radionuclides from <sup>235</sup>U and <sup>239</sup>Pu are close (e.g., 2, 3, 5 and 7). The <sup>137</sup>Cs activities in the soil samples were measured by a Ge detector (Seiko EG&G Ortec) coupled with a multi channel analyzer (Seiko EG&G, Model 7800). 100 mL of each soil sample were transferred into a plastic vessel and measured for 80000 seconds.

# **RESULTS AND DISCUSSION**

In recent years, ICP-MS is an attractive method for <sup>99</sup>Tc determination because the detection limit is lower than that of any radiation counting method. Although ICP-MS offers several advantages for <sup>99</sup>Tc analysis, the radioisotope is requited to be concentrated in solution, and Ru, which has an abundance of 12.7% at mass 99, is to be separated. Also, total elements' concentration in solution is requited to be less than 300 ppm due to instrumental limitation. To satisfy these conditions, a combination of a combustion apparatus and a TEVA resin had been developed previously (13). The combustion apparatus was used to separate <sup>99</sup>Tc from soil matrices by volatilization and then collected in a water trap. The total element concentrations can be effectively decreased in this step. Then Tc was separated and concentrated by TEVA resin. We developed a new separation method for <sup>99</sup>Tc in environmental samples using TEVA resin (Eichrom Industries Inc.) which was used instead of liquid-liquid extractions to avoid inclusion of organic solvents in the final solution. The developed method was applied for low-level <sup>99</sup>Tc measurement in soil samples.

Table 1 shows the results of <sup>99</sup>Tc and <sup>137</sup>Cs measurements. The ranges of <sup>99</sup>Tc and <sup>137</sup>Cs concentrations are 6 - 110 mBq kg<sup>-1</sup> dry and 1.7 - 28.2 Bq kg<sup>-1</sup> dry, respectively. It was estimated that if weapons fallout <sup>99</sup>Tc is uniformly present on the surface of the northern hemisphere, it should contribute a <sup>99</sup>Tc concentration of 6 mBq kg<sup>-1</sup> to the soil at a 25-cm depth. The obtained <sup>99</sup>Tc values were usually higher than the expected value of up to 17 times. However, it is well known from <sup>137</sup>Cs global fallout levels that fission products originating from nuclear bomb tests are not present uniformly on the earth's surface. Similar phenomena was observed for <sup>137</sup>Cs in this study, which may be a possible explanation <sup>99</sup>Tc.

In a certain area, the <sup>137</sup>Cs activity increase may have been caused by the Chernobyl accident, by comparison similar extension for <sup>99</sup>Tc could be inferred. However, in our previous report (16), it was recommended that comparing to <sup>137</sup>Cs activity, negligible amount of <sup>99</sup>Tc was spread in the environment. Aakrog (17) and García-León *et al* (18) reported a similar observation. This might be due to the differences in their volatilization behaviors during the accident or of their physico-chemical behaviors after they reach the environment. From these results, the <sup>99</sup>Tc originated from the Chernobyl accident did not notably affect the amount of global fallout <sup>99</sup>Tc in Japan.

To explain the fate of <sup>99</sup>Tc in the paddy field environment, <sup>137</sup>Cs was used as an indicator, because the fission yields from <sup>235</sup>U and <sup>239</sup>Pu are the same as those of <sup>99</sup>Tc. The activity ratios of <sup>99</sup>Tc/<sup>137</sup>Cs are (2.0 - 5.2) x 10<sup>-3</sup>. Since the activity ratio can be calculated theoretically from fission as  $1.4 \times 10^{-4}$  at nuclear weapons' detonations, the ratio is now estimated to be about 3.0 x  $10^{-4}$  with correction of decay out. The measured ratios were one order of magnitude higher than the theoretical one from fission. The higher <sup>99</sup>Tc/<sup>137</sup>Cs activity ratio in soil is presumably influenced by that of depositions containing rain and dry fallout. Ehrhardt and Attrep (19) reported that the range of the activity ratio of <sup>99</sup>Tc/<sup>137</sup>Cs in rain samples which were collected in the U. S. A. was (0.11 - 2.5) x  $10^{-2}$  during 1961-1974. In Spain, García-León *et al.* (18) measured similar values of (0.3 - 12.3) x  $10^{-2}$  in rain samples collected during 1984 - 1987. These ratios in rain samples were almost the same as those of soils. Previously, we reported that the mechanisms of Tc accumulated in paddy fields could be explained by the changes of Tc's chemical form in soil under waterlogged condition. Generally, during the planting period, the paddy field soils are waterlogged and subsequently, the redox potentials decrease, so that relatively low redox conditions are generated in the soils. Although the nuclide is expected to be in a soluble form as TcO<sub>4</sub><sup>-</sup> under an

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	Collection place	<sup>137</sup> Cs (Bq/kg)		<sup>99</sup> Tc (mBq/kg)		Activity ratio ( <sup>99</sup> Tc/ <sup>137</sup> Cs)	
А	Ogata Village, Akita Pref.	28.2	+/- 0.8	110	+/- 30	3.9E-3	+/- 1.1E-3
В	Omagari City, Akita Pref.	16.9	+/- 0.6	34	+/- 5	2.0E-3	+/- 3.0E-4
С	Morioka City, Iwate Pref.	10.1	+/- 0.6	52	+/- 10	5.1E-3	+/- 1.0E-3
D	Koriyama City, Fukushima Pref.	5.0	+/- 0.5	29	+/- 3.6	5.8E-3	+/- 9.5E-4
Е	Mito City, Ibaraki Pref.	3.2	+/- 0.4	8.4	+/- 1	2.6E-3	+/- 5.2E-4
F	Fukuyama City, Hiroshima Pref.	1.7	+/- 0.9	6.1	+/- 0.5	3.6E-3	+/- 1.9E-3
G	Kawazoe Town, Saga Pref.	4.9	+/- 0.5	22	+/- 3	4.5E-3	+/- 7.6E-4
Н	Imari City, Saga Pref.	16.8	+/- 0.7	88	+/- 15	5.2E-3	+/- 9.2E-4

Table 1. Concentration of <sup>99</sup>Tc and <sup>137</sup>Cs in paddy field soil samples in Japan on a dry weight basis and activity ratios of <sup>99</sup>Tc to <sup>137</sup>Cs.

(Note) +/-: Statistical erros in calculation (1 sigma).

aerobic condition in surface soils, this changes through a combination of factors such as redox conditions and microbial activity (20, 21). Probably, Tc is transformed from its soluble  $TcO_4^-$  form to a lower oxidation form such as  $TcO_2$ ,  $TcO(OH)_2$  or  $TcS_2$  under a relatively low redox condition. The sulfide might occur because  $H_2S$  gas can be produced in waterlogged soil when rice plants are growing. Thus, in a paddy field ecosystem, Tc would adsorb on to soil materials under a waterlogged condition and the transferred-Tc would hardly be mobile. Moreover, Tc in soil became less available with time due to a shift to less readily oxidizable forms. This suggests that Tc would be accumulating in soil. The results in this study indicate that a considerable amount of Tc might be fixed on the paddy field soil than we had expected before. Further studies are needed to clarify the phenomena of <sup>99</sup>Tc accumulation in the surface soil layer including upland field.

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