

MOBILITY AND BIOAVAILABILITY OF TECHNETIUM IN RICE PADDY FIELDS

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ABSTRACT

Field observations and radiotracer experiments were carried out to investigate the behavior of ^{99}Tc in paddy fields. The concentrations of global fallout ^{99}Tc in soil collected from paddy fields in Japan were 6 - 88 milli-bequerels per kilogram (mBq/kg)-dry and activity ratios of ^{99}Tc to ^{137}Cs ranged from 1.1×10^{-3} to 7.0×10^{-3} with an average of $(4.8 \pm 2.1) \times 10^{-3}$. (The theoretical activity ratio from nuclear fission yield is presently calculated as 3.3×10^{-4} with correction for radioactive decay.) This result implies that there was a tendency for ^{99}Tc to accumulate in rice paddy fields. To understand the mechanisms of the accumulation, a sequential extraction method was applied over a 6-month period to waterlogged soils contaminated with TcO_4^- . From the results, it was clear that the TcO_4^- in soil under waterlogged conditions was readily changed to other insoluble physicochemical forms, such as TcO_2 , TcS_2 and organically bound forms.

INTRODUCTION

Nuclear energy generates many radioactive wastes containing fission products and management of these wastes is inseparable from the peaceful use of nuclear energy. Technetium-99 is one of the most important long-lived fission products because the nuclide has a long half-life (2.1×10^5 years (y)) and it is fairly abundant since it is produced by fission of ^{235}U and ^{239}Pu at about a 6% yield. Additionally, its high mobility in geological barriers means that ^{99}Tc dose assessment for humans is especially important.

Oxidation-reduction reactions play an important role in controlling the mobilization and biological accumulation of some toxic trace elements in soils. Technetium is known to exist in all valence states from +7 to -1 and the dominant species in natural aqueous solutions in equilibrium with the atmosphere is pertechnetate, TcO_4^- (1). In this form, Tc has high geochemical mobility and availability for plants (2-5). Therefore, generally, a soil-to-plant system is one of the important pathways between released ^{99}Tc and humans. On the other hand, Tc sorption on soil or minerals has been reported under relatively low redox conditions (6, 7). Even in surface soil, microbial activity and/or chemical reactions may provide reducing conditions. In a rice paddy soil ecosystem, the low redox condition results from waterlogging of the soil during the cultivation period. Consequently, it is important to understand the behavior of Tc in paddy fields, because the area devoted to them in Japan and Southeast Asian countries is very large and rice is an important food in these countries. This study therefore focuses on the behavior of ^{99}Tc in paddy fields.

EXPERIMENTAL

Analysis of Low-levels of ^{99}Tc in Soils

Nine soil samples were collected from the surface layer (a depth of less than (<) 20 centimeters (cm)) from paddy fields in Japan. Nitric acid used was ultrapure-analytical grade (Tama Chemicals, AA-100). Deionized water (>17.5 megohm) was obtained from a Milli-Q water system (Millipore Co.). Pre-packed columns of Tc-selective chromatographic resin, TEVA (Eichrom Industries, Inc.) were used for the separation of Tc. A standard ^{99}Tc solution available from Amersham (TCZ.44) was used for calibrating an inductively coupled plasma mass spectrometer (ICP-MS). A spike solution of technetium-95m (half-life: 61 days (d)) was used as a yield monitor. It was prepared by irradiation of Nb in a cyclotron to avoid any ^{99}Tc contamination (8).

The separation procedure used for ^{99}Tc determination in soil samples was reported previously (9), hence, only a brief description of the experimental procedure is given here. The samples were air-dried and passed through a 2 millimeter (mm) mesh sieve. The samples were incinerated for 8 hours (h) at 450°C to decompose organic matter. After the addition of $^{95\text{m}}\text{Tc}$, the incinerated soil was heated in a combustion apparatus for 3 h at 1000°C and volatilized Tc was collected in two vertical traps. The volume of trap solution was reduced to approximately 200 milliliter (mL)

by evaporation on a hot plate at 100°C. The solution was adjusted to 0.1 molar (M) HNO₃ and passed through a TEVA resin column to separate and concentrate Tc isotopes. Finally, Tc isotopes were eluted from the column with 5 mL of 8 M HNO₃. The eluate was evaporated to dryness at temperatures below 70°C, and the residue was dissolved in 5 mL of 2% HNO₃. The radiochemical recovery of Tc was determined by comparing the count of ^{95m}Tc in the sample with that in the standard solution using a NaI (Tl) scintillation counter (Aloka, ARC-380). The ⁹⁹Tc content of the sample solution was then determined by ICP-MS (Yokogawa, PMS-2000).

For comparison, ¹³⁷Cs determination was carried out using a 100 mL portion of each air-dried sample. The activity was measured with a Ge detector (Seiko EG&G Ortec) coupled to a multi-channel analyzer (Seiko EG&G, Model 7800). Decay was corrected to January 1, 2001.

Tc Mobility in Soil under Waterlogged Conditions

One typical agricultural soil in Japan, classified as Gray lowland soil, was used. After air-drying, the soil was passed through a 2 mm mesh sieve. Two radiotracer experiments were carried out as follows.

1) Effect of Microbial Activity on Tc Mobility in Soil

Four subsamples of the air-dried soil were prepared. Two subsamples of the air-dried soil were sterilized by autoclaving at 121°C for 30 minutes. Glucose was then added to one of the unsterilized subsamples, and to one of the sterilized subsamples, at a concentration of 0.5% on a dry weight basis. The purpose of the glucose addition was to enhance microbial activity in the unsterilized subsample. Subsamples without glucose are referred to as the “0” samples, and with glucose as the “0.5” samples. Sterilization and glucose mixing of the soil samples were performed a day before the experiment started. The soil sub-samples, 40 g each, were placed in polystyrene vessels (120 mL). They were carefully waterlogged with 60 mL of deionized water contaminated with ^{95m}TcO₄⁻. The surface water depth (from the soil surface) was 1–2 cm. The vessels were sealed with polyethylene film to prevent microorganisms in the ambient air from entering. Activities of ^{95m}Tc in the surface solutions were measured with a well-type NaI(Tl) scintillation counter (Aloka, ARC-300).

2) Chemical Transformation of Tc in Soil under Waterlogged Conditions

To measure the physico-chemical forms of radionuclides, typical extraction methods were applied. We used a portion of the method of McLaren and Crawford (10) to extract several fractions of the soil (Table I).

The radiotracer experiment was carried out for 52 days using additional 150 g amounts of air-dried soil to observe Tc transformation as a function of time. A small quantity of deionized water containing ^{95m}Tc (Dupont, TcO₄⁻) was uniformly mixed with the soil samples. Then a sufficient amount of deionized water was added to the soils to obtain waterlogged or anaerobic conditions. The sample was stored in the dark while being kept at room temperature for 52 days.

At 1, 5, 14, 30, 52 days, selective extractions (CA, AA, PY and AO as shown in last column in Table I) of the soil samples were carried out. All of the extractions were performed in polyethylene containers. The solids and solutions were mixed at 20°C for 18 h in an end-over-end shaker at 150 rpm and were separated by centrifugation at 2000 rpm for 10 min. All extractions were carried out in duplicate. Radioactivity of ^{95m}Tc in each supernatant was measured with

Table I. Reagents Used in the Extraction

Reagent	Fraction	Soil weight (g)	Solution amount (mL)	Code
0.05 M calcium chloride	Exchangeable and water soluble	2	40	CA
0.5 M acetic acid	Specifically adsorbed	2	40	AA
0.1M sodium pyrophosphate	Organically bound	2	200	PY
0.175 M ammonium oxalate / 0.1 M oxalic acid	Sesquioxide bound	1	75	AO

Note: All soils were extracted at their experimental moisture contents for which the mass of the leached soil was chosen to be equivalent (±5%) to the air-dry weight listed above.

a Ge detecting system (Seiko EG&G).

RESULTS AND DISCUSSION

Global Fallout ⁹⁹Tc in Paddy Soils

The data for concentrations of ⁹⁹Tc and ¹³⁷Cs in paddy field soils measured by ICP-MS are listed in Fig.1. The ranges of ⁹⁹Tc and ¹³⁷Cs concentrations are 6 - 88 mBq/kg-dry (average: 29 mBq/kg-dry) and 1.4 - 14 Bq/kg-dry (average: 6.3 Bq/kg-dry), respectively. The activity ratios of ⁹⁹Tc to ¹³⁷Cs range from 1.1×10^{-3} to 7.0×10^{-3} with an average of $(4.8 \pm 2.1) \times 10^{-3}$. The theoretical activity ratio from nuclear fission yield is presently calculated as 3.3×10^{-4} with correction for radioactive decay, assuming that the major source of ⁹⁹Tc in Japan until now arises from fallout. Compared to the theoretical ratio, the activity ratios in the paddy field soils are approximately one order of magnitude higher.

The activity ratio was compared with that of other soils (Table II). Among the soils, the average activity ratio for paddy field soils is the highest. The ratios in paddy field soils are approximately twice as high as those in upland field soils and approximately one order of magnitude higher than those in other soils. These differences may result from

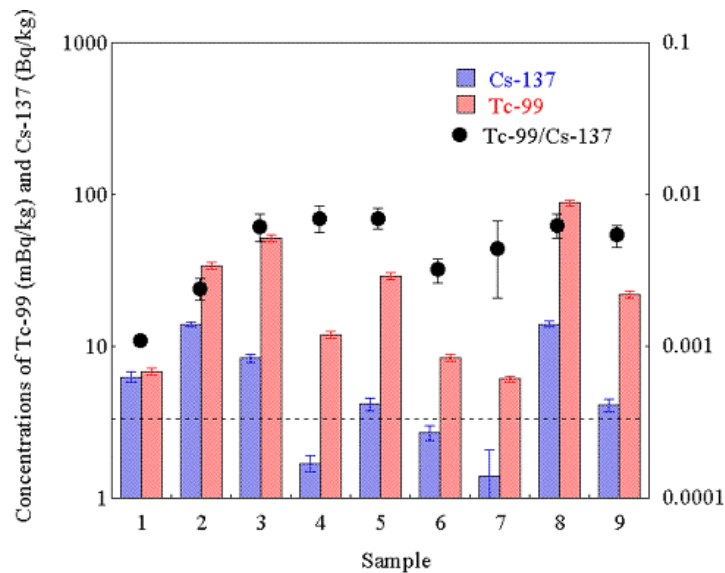


Fig. 1. Concentrations of Cs-137 and Tc-99 in paddy field soils in Japan on a dry weight basis and activity ratio of Tc-99 to Cs-137. Error bar shows 1 sigma analytical error. The dashed line shows the theoretical activity ratio from nuclear fission yield.

Table II. Concentrations of ¹³⁷Cs and ⁹⁹Tc in soils collected in Japan on a dry weight basis and activity ratio of ⁹⁹Tc to ¹³⁷Cs

Soil type	n	¹³⁷ Cs (Bq/kg) Decay corrected to 2001.1.1	⁹⁹ Tc (mBq/kg)	Activity ratio ⁹⁹ Tc/ ¹³⁷ Cs ($\times 10^{-3}$)
Paddy fields	9	1.7 - 14.0	6.1 - 88	1.1 - 7.0
Upland fields	6	<1.1 - 7.7	4.3 - 7.7	0.7 - 3.8
Other soils	6	<1.1 - 144	7.0 - 29	0.2 - 1.0
				0.33 (Theoretical ratio)

varying degrees of reducing conditions in the soils. The higher activity ratios found in this study compared to the theoretical suggest ^{99}Tc accumulation mechanisms in the paddy soils.

One of the Tc accumulation mechanisms in paddy fields can be explained by the change of Tc chemical form in soil under waterlogged conditions. The nuclide is expected to be in a soluble form as pertechnetate under aerobic conditions, such as in surface soils and surface water. However, paddy fields are generally waterlogged during the planting period and subsequently, the redox potentials of Eh decrease because microorganisms use up the oxygen present in the water or trapped in the soil. The relatively low redox condition is common in paddy fields during the planting period. Probably, Tc is transformed from TcO_4^- to a lower oxidation form such as TcO_2 , $\text{TcO}(\text{OH})_2$ or TcS_2 under a relatively low redox condition.

Effect of Microbial Activity on Tc Mobility in Soil

Relative concentration (RC) is defined as "the activity of $^{99\text{m}}\text{Tc}$ in surface solution (count per minute per mL, cpm/mL) at the sampling time" divided by "the initial activity of $^{99\text{m}}\text{Tc}$ in the solution (cpm/mL)". The RCs of Tc in the surface solutions are shown in Fig. 2 as a function of time. The pH values of all soil samples, which are not shown in the figure, were almost constant during the period. The RCs for both air-dried soil sub-samples dropped over time.

For each soil sample, the RCs of AD-0.5, which included 0.5% glucose, showed the fastest decrease, followed by that of AD-0, which did not contain glucose. The RCs of sterile soil sub-samples (S-0 and S-0.5) showed hardly any drop and those for the other soil samples showed only a slight decrease, compared to their initial values. The reduced RCs of the sterile soil sub-samples might be due to slow chemical reactions such as forming complexes with organic matter and/or metallic elements. When we compared the RC reduction of S-0.5 with that of S-0, it was clear that addition of glucose alone did not result in Tc decrease in the surface solution. The degree of the RC reduction was, however, influenced by glucose addition in the air-dried soil sub-samples. The data strongly suggested that microorganisms play an important role in determining Tc behavior in soil.

Chemical Transformation of Tc in Soil under Waterlogged Conditions

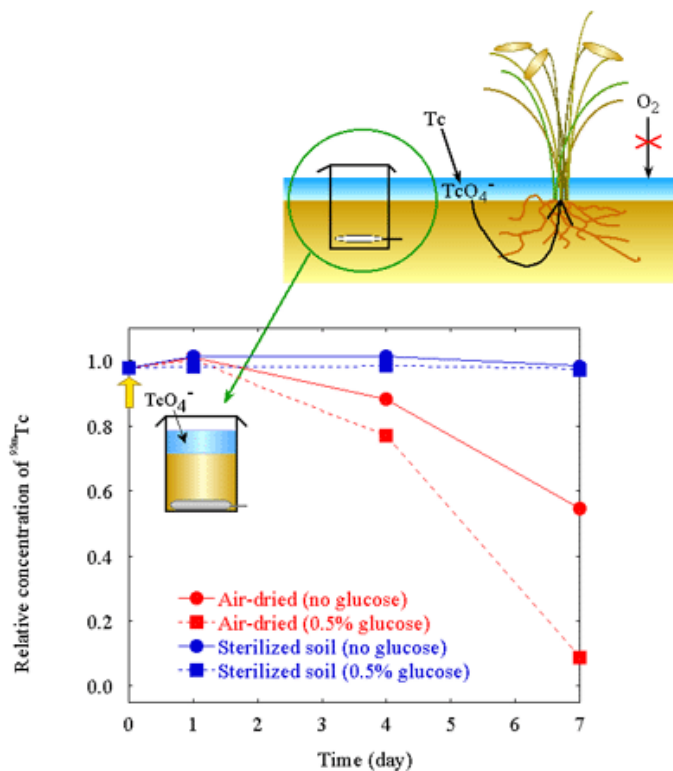


Fig. 2. Relative concentration of Tc in the surface solutions as a function of time.

As mentioned before, the method used (10) in this study contained one modification. In the original method, the extractions were carried out in a sequential fashion; the extractions in this study were carried out in parallel for two reasons. One reason is that it is unclear whether re-adsorption Tc might occur during sequential leaching. The other reason is that the prediction of pH and Eh changes, and hence the chemical form of Tc, is difficult during leaching. We previously found that a single extraction was less damaging to soil components than a sequential extractions and that Tc in the form of TcO_4^- does not re-adsorb onto the soil (11).

In Fig. 3, the relative activities of ^{95m}Tc in soil samples under waterlogged conditions extracted by the four reagents are shown as a function of time. The relative activity (*Qra*) was defined as "the total activity in the extracted solution from a unit soil sample at each sampling time" divided by "the total activity from a unit soil sample". The results of *Qras* for CA- and AA-extractable ^{95m}Tc (CA-Tc, AA-Tc, respectively) showed that under the paddy field conditions, *Qras* for CA-Tc and AA-Tc decreased steadily after the Tc had been added to the soil. That is, *Qra* of TcO_4^- decreased during the test period. For *Qras* for PY-Tc (organically-bound) and AO-Tc (associated with sesquioxides), it was observed that their sum was about 0.15 just one day after the Tc was initially added to the soil sample under

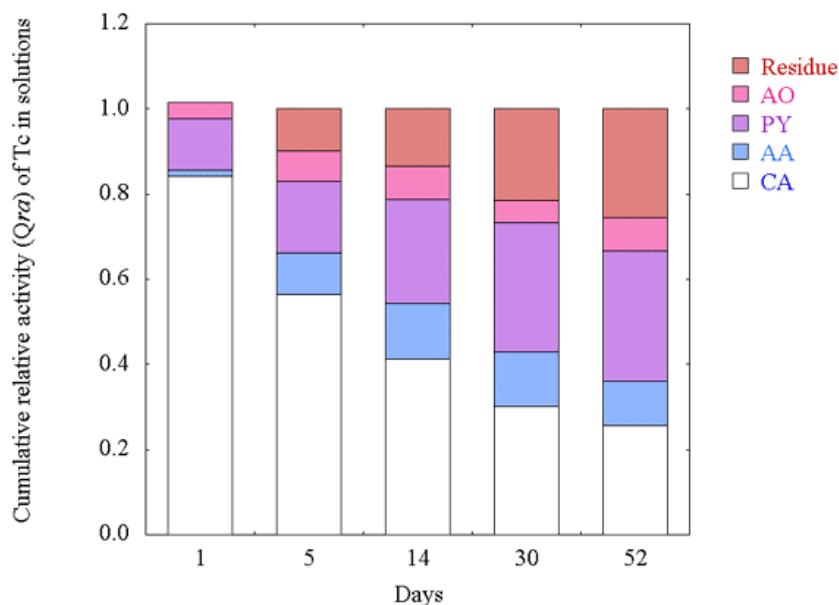


Fig. 3. Time dependence on *Qra* of Tc in CA, AA, PY, AO and residue fractions in a paddy soil under a waterlogged condition.

waterlogged conditions, but their *Qras* gradually increased for 52 days. The residual part of Tc was zero at the beginning of the test, but the *Qra* increased throughout the test. It was clear that the decreases of *Qras* for CA-Tc and AA-Tc waterlogged conditions were approximately matched by the total *Qra* for organically-bound (PY-Tc) and the residual part of Tc, possibly including TcO_2 , $TcO(OH)_2$ or TcS_2 .

In conclusion, from the radiotracer experiments, we predict that Tc transformation to lower oxidation states would be encouraged by waterlogging in a real rice paddy field. Furthermore the reaction of the adsorbed Tc form to TcO_4^- should be slow based on our previous work (12). In the absence of a process for Tc removal from soil (leaching and harvesting), Tc accumulated in the soil surface layer. These results are consistent with Tc accumulating in the surface layer of paddy fields.

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