Journal of Nuclear and Radiochemical Sciences, Vol. 4, No. 1, pp. A1-A8, 2003

Accounts

Technetium-99 Behavior in the Terrestrial Environment –Field Observations and Radiotracer Experiments–

Keiko Tagami*

Environmental and Toxicological Sciences Research Group, National Institute of Radiological Sciences
Anagawa 4-9-1, Inage-ku, Chiba 263-8555, Japan

Received: March 22, 2003; In Final Form: June 4, 2003

Obtaining data on ^{99}Tc in the rice paddy field environment is important because Tc is a redox sensitive element. The behavior of Tc is expected to be different under upland field and rice paddy field conditions since the redox conditions in the soil environment differ. However, most of the data on the nuclide behavior in soil were obtained under upland field conditions. To understand the global fallout ^{99}Tc distributions in soil samples collected in Japan, a simple and rapid separation method was developed in order to determine low-levels of ^{99}Tc in soil samples by an inductively coupled plasma mass spectrometry. Also, radiotracer experiments using soils under aerobic and anaerobic conditions were carried out to clarify the Tc behavior under paddy field conditions. The results of determination of global fallout ^{99}Tc in Japanese soils indicated that the radionuclide had been accumulating in rice paddy fields. The mechanisms can be explained by the immobilization of Tc in soil under anaerobic conditions. From the radiotracer experiments, it was clear that under waterlogged conditions, the highly mobile TcO_4^- in soil was readily changed to other immobilized forms, such as TcO_2, TcS_2 and organically bound forms. To this immobilization, the microbial activity seemed to have an important role in Tc sorption reactions. When the soil, which was once kept in anaerobic conditions, was air-dried again and kept in aerobic conditions, the chemical forms of immobilized Tc did not change remarkably. Interestingly, the similar Tc behavior was observed in a real wet forest near the Chernobyl Reactor.

1. Introduction

Technetium-99 (^{99}Tc) is of great practical importance because it is one of the fission products with a relatively high yield in the thermal neutron fission of ^{235}U and ^{239}Pu (ca. 6%) and it has a long half-life of 211,000 y. The major source of ^{99}Tc in the environment stems from fission in nuclear weapons and in reactors. The quantity of ^{99}Tc produced by nuclear weapon tests in the atmosphere can be estimated to be 140 TBq using an equal fission yield to that of ^{137}Cs and actual ^{137}Cs deposition.[1, 2] The estimated release of ^{99}Tc by nuclear industries through 1986 was of the order of 1000 TBq. This was mainly result of nuclear fuel reprocessing and most of the ^{99}Tc was discharged into the sea. The most significant discharge of ^{99}Tc nowadays is from Sellafield to the Irish Sea, total amount of 550 TBq of ^{99}Tc was released in 1995-1999 and the annual liquid discharge limit of 90 TBq for ^{99}Tc has been applied from 2000.[3] Compared to this, the amount introduced via nuclear medical use of ^{99m}Tc (half-life: 6.01 h) is negligible. In Japan, it is assumed that the major source of Tc in soils up to now arises from nuclear weapon tests in the atmosphere.

Technetium is known to exist in all valence states from +7 to –1 and the dominant species in natural aqueous solution in equilibrium with the atmosphere is the pertechnetate, TcO_4^-.[4, 5] In the terrestrial environment, TcO_4^- has a high geochemical mobility[6] and availability for plants.[7, 8] Several assessments have suggested that the Tc uptake by plants is one of the key parameters in governing the Tc radiation dose to humans. From experimental studies on Tc in plant-soil systems in upland fields, it was observed that the element has high transfer factors from soils to plants. Data for the soil-to-plant transfer of Tc in temperate area were reviewed in IAEA technical report series 364.[9] The transfer factor (TF) is defined as the following equation:

$$\mathrm{TF} = \frac{\text{Activity in vegetation on dry or wet weight basis (Bq/g)}}{\text{Average activity in soil during planting period (Bq/g)}}.$$

Transfer factors vary within and between species, with the mode of contamination and with the level of administration. In the edible parts of common plants, a TF of 5 (on wet weight basis) was recommended as allowable by the IAEA for Tc.[10]

The influence of the chemical form of Tc on its uptake by spinach[11] and tomato plants[12] was studied by using a mathematical analysis of the uptake. When Tc was added to spinach as a Tc-cysteine complex, the Tc was absorbed by the plant, but the TF was lowered by two orders of magnitude as compared with TcO_4^-. From this result, it is apparent that TcO_4^- was the most important form of Tc taken up by the plants. Although Tc was thought to be highly mobile in plants just as water is, Gast et al.[13] reported that the first and older leaves of wheat (grown to maturity in soil experiments) accumulated much greater concentrations of Tc than the new leaves. Probably due to the fixation of Tc by a certain part of plant, such as organic compounds, very little re-translocation of Tc took place from old tissues to new tissues. Similar results were obtained using tomato plant by Krijger et al.[12] and they explained the Tc fate in the tomato plant.

The uptake rate might be limited to the availability and concentration of Tc in soil; the recorded values from soil to plant TFs were accordingly high when these factors were high. The element mobility in soil has been studied, and the extent of the Tc-sorption is characterized by the following distribution coefficient K_d, which is defined as:

$$K_\mathrm{d}\,(\mathrm{mL/g}) = \frac{\text{Activity of Tc sorbed per gram of dry soil (Bq/g)}}{\text{Activity of Tc per mL of solution (Bq/mL)}}.$$

Available data on the K_d for Tc are tabulated in Table 1.[14–17] Coughtrey et al.[18] concluded that, “in all aerobic soils, contam-

---

*Corresponding author. E-mail: k_tagami@nirs.go.jp. FAX: +81-43-206-3267.

inated with Tc in the TcO_4^- form, 90% of added Tc can be assumed to remain in the solution either as a free ion or as weakly absorbed to ion-exchange sites". Routson et al.[15] reported that from low K_d values Tc could be assumed to adsorb poorly in soil as TcO_4^-. However, results of Wolfrum and Bunzl[19] indicated that the oxygen content in the leachate affected the K_d value. It was suggested that the availability of Tc in soils decreases with soil residence time, which is known as 'aging effect'.[20–23]

TABLE 1: Distribution Coefficients K_d for Sorption of Tc by Soils

Sample (N)	Solution	K_d (mL/g)	Reference
Soil (22)	0.01M $CaCl_2$	0.007 ± 2.8	Wildung et al.[14]
Soil (2)	0.02M $NaHCO_3$	−0.033 ± 0.01	Routson et al.[15]
	0.2M $NaHCO_3$	+0.010 ± 0.04	
Soil (7)	Not shown	0 – 0.9	Takebe and Deying[16]
Soil (129)	Deionized water	0.6 ± 0.6	Uchida and Tagami[17]
Soil (2)	Deionized water (pH=3–8)	0 – 0.7	Tagami and Payne (unpublished data)

In order to improve our understanding of the behavior of ^{99}Tc in the environment and to develop appropriate waste storage/disposal options, it is essential that we obtain more reliable information on the levels, distributions and fate of ^{99}Tc in the environment. The fate of Tc in the environment is influenced by combinations of chemical, physical and biological factors. Most studies to obtain environmental parameters have been carried out for upland fields in European countries, Canada and U.S.A., because these are in the majority in these countries. However, Tc is a redox sensitive element and it could be insoluble forms under reducing conditions.[4, 5, 23] The behavior of Tc is expected to be different under upland field and rice paddy field conditions.[24] In rice paddy fields, the reducing conditions are established by waterlogging in the soil during the cultivation period. The soil-rice plant system is an important path for transfer of ^{99}Tc to humans in Japan and other Asian countries because rice is the main crop in these areas.

A series of studies including field observations and radiotracer experiments were carried out in order to clarify the fate of ^{99}Tc in the paddy field environment. To measure low-levels of ^{99}Tc in environmental samples by an inductively coupled plasma mass spectrometry, ICP-MS, we developed a simple separation method.[25–30] Using the method, global fallout ^{99}Tc retained in rice paddy field soils collected in Japan were measured.[25, 26, 31] Also Tc behavior in soils under aerobic conditions and anaerobic conditions were observed because Tc is known as a redox sensitive element.[24] Further studies on Tc behavior under anaerobic conditions by controlling microbial activities in soil samples to find out the effect on the Tc immobilization.[23, 32] It was expected that Tc was immobilized in rice paddy fields from the above mentioned studies, therefore, plant and soil samples collected in three forests (one of them was so-called "wet forest"; the groundwater-level was higher than other two sites) within 30-km zone from the Chernobyl Reactor were used for ^{99}Tc measurement to obtain transfer parameters.[33–36]

2. Development of a Simple Separation Method for ^{99}Tc in Environmental Samples

Instruments. In recent years, ICP-MS is an attractive method for ^{99}Tc determination because the detection limit is lower than that of any radiation counting method as listed in Table 2.[31, 37–42] Although ICP-MS offers several advantages for ^{99}Tc analysis, the radioisotope is required 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 required to be less than 300 ppm due to instrumental limitation.

Tracers. In our experiments, the chemical recovery was monitored with ^{95m}Tc. The nuclide has a half-life of 61 days; it is useful as a yield monitor in the chemical separation of Tc compared to the other short half-life Tc isotopes such as ^{99m}Tc ($T_{1/2}$ = 6.01 h). It has been reported that ^{95m}Tc is preferable as a yield monitor when ICP-MS is used because of the difference of mass between ^{95m}Tc and ^{99}Tc.[43] However, some commercially available ^{95m}Tc solutions might contain ^{99}Tc when the ^{95m}Tc was produced by ^{96}Mo (p, 2n) ^{95m}Tc. If other Mo isotopes were included in the target, it could be ^{99}Tc which was produced at the same time. Therefore, ^{95m}Tc was obtained by irradiation of Nb foil (99.999%) using the reaction ^{93}Nb (α, 2n) ^{95m}Tc in a cyclotron at Tohoku University, Japan.[29] This reaction could not produce other long-lived Tc isotopes. Then ^{95m}Tc was separated in a quartz tube by heating the foil at 1000°C for 2h under oxygen stream. Tc was evaporated and transferred to a room temperature area of the quartz tube. The ^{95m}Tc was stripped from the tube with deionized water.

Sample Pretreatment. Soil samples were air-dried and passed through a 2 mm mesh sieve. They were incinerated for 8 h at 450°C to decompose organic matter. Soil incineration is usually performed to decompose soil organic matter that interferes with Tc chemical analysis. To clarify the Tc loss during incineration, we measured the loss ratios from aged and freshly contaminated soil samples during incineration. Long-contaminated soil samples (Andosol and Gray lowland soil) were contaminated with ^{95m}Tc for 1 or 6 months. Freshly contaminated soil samples were prepared 1-2 days before the test. Figure 1 shows loss of ^{95m}Tc by incineration as percentage of initial activity. The weight reductions of the Andosol sample and the Gray lowland soil sample were 19 - 25% and 9%, respectively. Despite a difference in organic matter content, there was no

TABLE 2: Analytical Methods for ^{99}Tc Determination

Detection limit	Type of apparatus	Reference
1 – 5 mBq	Anti coincidence shielded gas flow counting	
3 – 5 mBq	Neutron activation (n, γ)	Holm[37]
1 – 25 mBq	Liquid scintillation counting	
0.002 – 4 mBq	Inductively coupled plasma mass spectrometry	
3.8 mBq/mL	Q-ICP-MS	Crain and Gallimore[38]
1.1 mBq/mL	Q-ICP-MS	Morita et al.[39]
0.03 mBq/mL	Q-ICP-MS	Tagami and Uchida[31]
0.0021 mBq/mL	Q-ICP-MS with ultrasonic nebulizer	Morita et al.[40]
0.005 mBq/mL	HR-ICP-MS with ultrasonic nebulizer	Kim et al.[41]
0.003 mBq/mL	HR-ICP-MS	Tagami (unpublished data)
<0.5 pg (0.3 mBq)	Accelerator mass spectrometry	McAninch et al.[42]

Note) Q-ICP-MS: quadrupole ICP-MS, HR-ICP-MS: high resolution (or double focusing) ICP-MS.

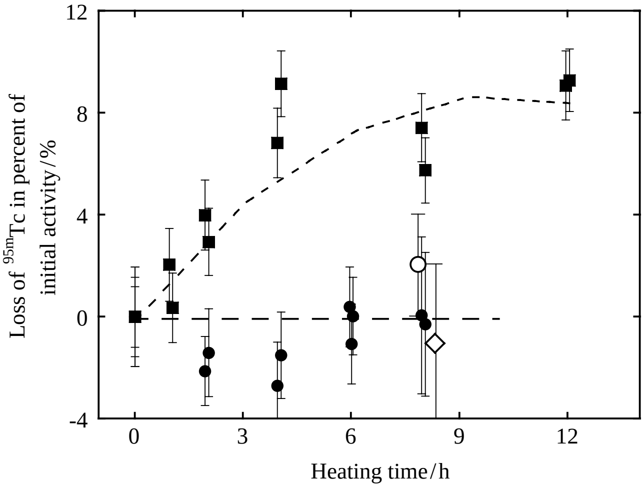

Figure 1. Loss of ^{95m}Tc from soil samples as a function of heating time when incinerated at 450˚C.
Freshly contaminated soil (■); 1-month contaminated Andosol (○); 1-month contaminated Gray lowland soil (◇); 6-month contaminated soil (●). Bars indicated counting errors.

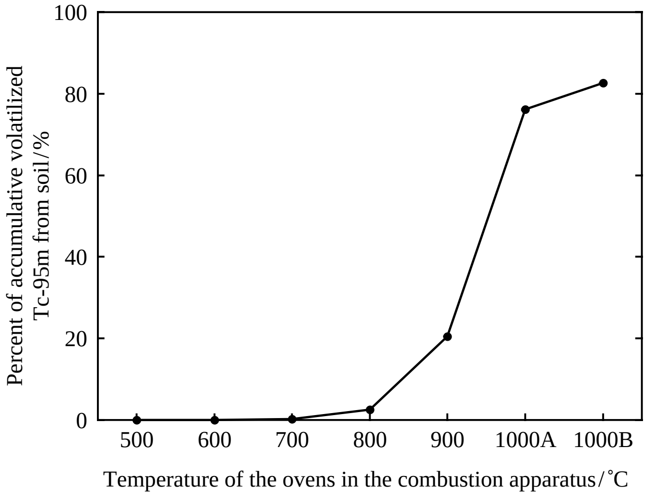

Figure 2. Temperature effect on Tc volatilization from a soil sample. The soil sample was volatilized for 1 h at each temperature. 1000A and 1000B: First and second volatilizations at 1000˚C.

loss of Tc in either 1-month contaminated soil during incineration. The results were the same as for 6-month contaminated soil. Loss of ^{95m}Tc gradually increased in freshly contaminated soil by incineration whereas the soil samples contaminated more than 1 month by ^{95m}Tc showed no increase.[26] This result suggested that most soil samples could be incinerated without any loss of fallout Tc. Thus the soil samples were incinerated at 450˚C for 8 hours. However, the loss must be considered when adding Tc freshly to soil samples as a yield monitor.

Combustion Apparatus. The volatility of ^{95m}Tc from the Andosol soil sample is shown in Figure 2. The volatility increased with temperature. However, second heating at 1000˚C showed no remarkable increase of Tc volatilization. It was suggested that Tc in the soil sample was not completely volatilized even if the temperature of 1000˚C was maintained for a long time. Probably, the Tc volatility was affected by the soil volume, soil components, etc. Although Tc volatility did not reach to 100%, the method could separate Tc from soil matrices. Consequently, the following separation steps can be simplified.

The percentages of ^{99}Tc and ^{95m}Tc volatilized from the soil were almost the same (data not shown); these Tc isotopes showed the same volatility behavior although their contamination periods differed.[28] Therefore, the freshly added ^{95m}Tc could be used as a yield monitor of originally included ^{99}Tc.

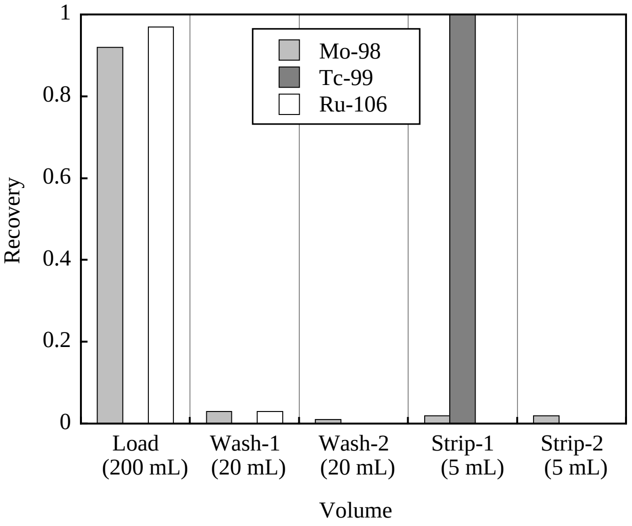

Figure 3. Recoveries of ^{99}Tc, Ru and Mo in load (0.1M HNO_3), wash (2M HNO_3) and strip (8M HNO_3) solutions. The sample solutions were pure water.

TEVA extraction. Each solution obtained by the above mentioned extraction procedure was adjusted to 0.1 M HNO_3 and passed through a TEVA resin column (Eichrom Industries Inc.) to separate and concentrate Tc isotopes.[27] Because ICP-MS cannot differentiate between ^{99}Ru and ^{99}Tc, it is necessary to remove all Ru from the final sample solution prior to ICP-MS measurement. Also, if the final solution for ICP-MS measurements contains large amounts of stable Mo, the isotopes ^{98}Mo and ^{100}Mo might interfere with ^{99}Tc count although there is no natural abundance at 99 for Mo. Figure 3 shows the elution behaviors of Tc, Ru and Mo in a 200-mL of deionized water sample adjusted to 0.1 M HNO_3. From the results, Ru and Mo present in the sample solution are not effectively retained on the TEVA resin, while Tc was extracted on the resin.[30]

Then, the column was washed with 2 M HNO_3 to remove any remaining traces of Ru. Technetium isotopes were eluted with 5 mL of 8 M HNO_3. The separation steps completely removed Ru; only $< 0.1\%$ was found in the 8 M HNO_3 eluate. The eluate containing Tc was evaporated to dryness at lower than 70˚C, and the residue was dissolved in 5 mL of 2% HNO_3 for ICP-MS.

Measurements. 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). The ^{99}Tc content of the sample solution was 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 instrumental detection limit for ^{99}Tc by ICP-MS was 0.03 mBq/mL of a sample solution, which corresponds to 0.014 mBq/g dry weight of soil sample under the operational conditions.

Fallout ^{137}Cs was used as an indicator for ^{99}Tc behavior because of large number of data and the fission yields of both radionuclides from ^{235}U and ^{239}Pu are close. The ^{137}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). A 100-mL of each soil sample was transferred into a plastic vessel and measured for 80000 s.

3. Distributions of ^{99}Tc in Japanese Agricultural Soils

The ^{99}Tc distribution in Japanese soils is shown in Figure 4. The ranges of ^{99}Tc and ^{137}Cs concentrations are <3.6 – 110 mBq/kg-dry and <1.1 –143 Bq/kg-dry, respectively. The average concentrations of ^{99}Tc and ^{137}Cs in paddy fields are 34

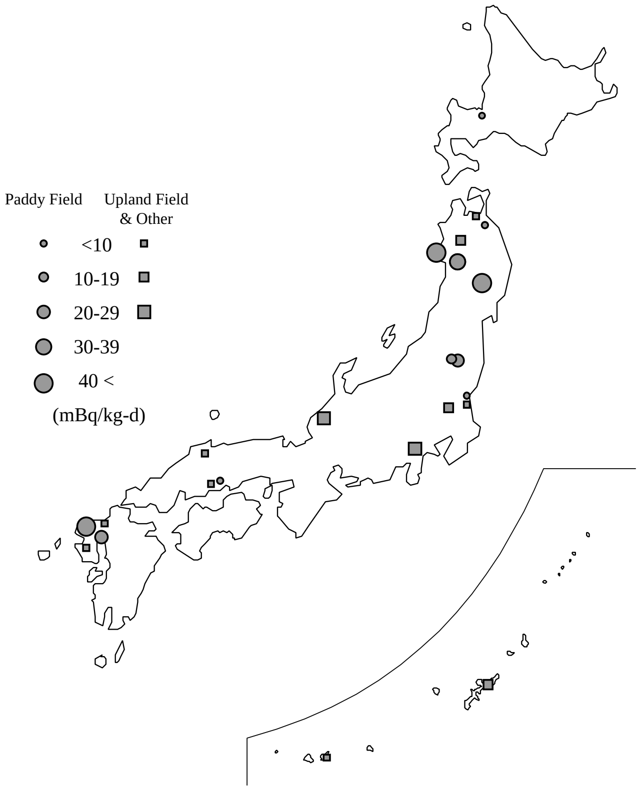

Figure 4. Global fallout ^{99}Tc concentrations (mBq/kg-dry) in Japanese agricultural soils.

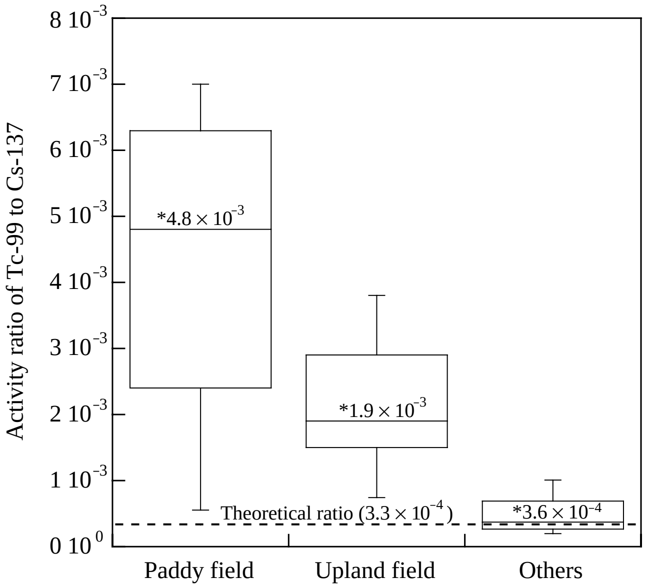

Figure 5. Activity ratios of ^{99}Tc to ^{137}Cs in soil samples collected in Japan. *: geometric mean

mBq/kg-dry and 7.8 Bq/kg-dry, respectively, those in upland fields are 5.9 mBq/kg-dry and 3.2 Bq/kg-dry, respectively, and those in other soils are 16.3 mBq/kg-dry and 44.8 Bq/kg-dry, respectively.[25, 26, 31] When the ^{99}Tc concentration was compared on the basis of several characteristics of the soils, the results showed that there is no correlation between ^{99}Tc concentrations and soil characteristics for paddy field soils, but slightly high correlations (r>0.5) between ^{99}Tc concentrations and some soil properties, such as cation exchange capacity, act-Fe, total-C, organic-C, and total-N, for upland field soils and other soils are found.

The activity ratios of ^{99}Tc to ^{137}Cs are given in Figure 5 and the geometric means are 4.8×10^{-3} for paddy field soils, 1.9×10^{-3} for upland filed soils and 3.6×10^{-4} for other soils. Theoretically, the activity ratio from nuclear fission yield is presently calculated as 3.3×10^{-4} with correction for radioactive decay, because it is assumed that the major source of ^{99}Tc in Japan arises from fallout. Compared to the theoretical ratio, the activity ratios in the paddy field soils are one order of magnitude higher. The average activity ratios for upland field soils are also higher than the theoretical ratio but those for other soils are close to the theoretical one. The ratios in paddy field soils are twice as much as those in upland field soils and one order of magnitude higher than those in other soils maybe because of different degrees of the soil reduction.

The higher or similar activity ratios found in this study as compared to the theoretical one suggest ^{99}Tc accumulation in the soils, even under aerobic conditions. Generally, the most preferable chemical form of Tc is TcO_4^- which shows a small possibility for changing to a lower oxidation state or less soluble form under aerobic conditions. Also, the reported distribution coefficient (K_d) of ^{99}Tc in Japanese soil samples generally showed low values as shown in Table 1, that is, no significant Tc fixation to surface soils is expected when Tc is added as TcO_4^-. Subsequently, TcO_4^- is thought to migrate much faster than cations, e.g. $^{137}Cs^+$, because of its highly soluble chemical form. However, the studied soils seemed to retain ^{99}Tc. It is necessary to identify chemical forms of Tc in natural soil conditions.

4. Radiotracer Experiments on Tc Immobilization in Soil

Oxidation-reduction reactions play an important role in controlling the mobilization and biological accumulation of some toxic trace elements from soils. The migration of Tc in soil and its absorption by plant roots are related to the sorption behavior in the soil-water system. Technetium is expected to be in a soluble form as pertechnetate under an aerobic condition, such as in surface soils and water. However, Tc sorption on soil or mineral has been reported under relatively low redox conditions.[23, 44–46] Even in surface soil, the reducing condition is generated by microbial activity and/or chemical reactions. For example, paddy fields are generally waterlogged during the planting period and subsequently, the redox potentials (E_h) decrease because microorganisms use up the oxygen present in the water or trapped in the soil.[47] The relatively low redox condition is common in paddy fields during the planting period. Thus, we carried out radiotracer experiments to obtain the influence of microbial activity on Tc behavior in surface soil under anaerobic conditions and to measure the change of Tc amounts in several soil fractions as a function of time.

4.1. Microbial Role in Immobilization of Tc Under Anaerobic Conditions. To clarify the influence of microbial activity on Tc behavior in surface soil under anaerobic conditions, glucose was added to the air-dried soil sub-samples from 0 to 0.5% on an air-dried soil basis to enhance microbial activities in soil, and a sterile soil sub-sample was prepared from the air-dried soil (without glucose) by autoclaving. Seven soil samples were used in this experiment. These pretreated air-dried and sterile soil samples were placed in polystyrene vessels along with a porous cup at the bottom. They were carefully waterlogged with 60 mL of deionized water contaminated with $^{95m}TcO_4^-$. The surface water depth (from the soil surface) was 1-2 cm. The vessels were sealed with polyethylene film to prevent microorganisms in the air from entering. At each sampling time, aliquots of the surface solution and the bottom solution (from the porous cup) were collected. The E_h and pH values of the surface soil (depth: ca. 5 mm) were also measured at each sampling time with a platinum complex electrode (Horiba pH meter, F-13). Activities of ^{95m}Tc in the collected solutions were measured with the well type NaI (Tl) scintillation counter.

The E_h values and relative concentrations (RCs) of surface and bottom solutions of one of the soil samples are shown in

Figure 6 as a function of time. The RCs of the surface solutions and also the E_h values decreased with increasing glucose contents, while the RCs of S-0 (Sterile soil with glucose 0%) were almost constant and had hardly any decrease. The RC for the surface solution of AD-0.5 (Air-Dried soil with addition of 0.5% glucose on an air-dried soil weight basis) was almost zero at the end of the experiment and the RCs for the bottom solutions of AD-0 (AD with 0% glucose), AD-0.05 (AD with 0.05% glucose) and AD-0.5 decreased to almost 0 within 3 days. The data suggested that not only reducing conditions, but also microbial activity seemed to have an important role in Tc sorption reactions. It was also found that the microbial activity could be controlled by adjusting the nutrient concentration in soil. The Tc decrease in the surface and bottom solutions could be explained by the lowered E_h values and consequently, changing the chemical form of Tc in the surface soil. The E_h of AD-0.5 was lower than that of AD-0; microbial activity in the surface solution of AD-0.5 was higher than that of AD-0 and Tc(+7) as TcO_4^- of AD-0.5 might reduce faster to Tc(+4) and be sorbed on the soil surface.[23]

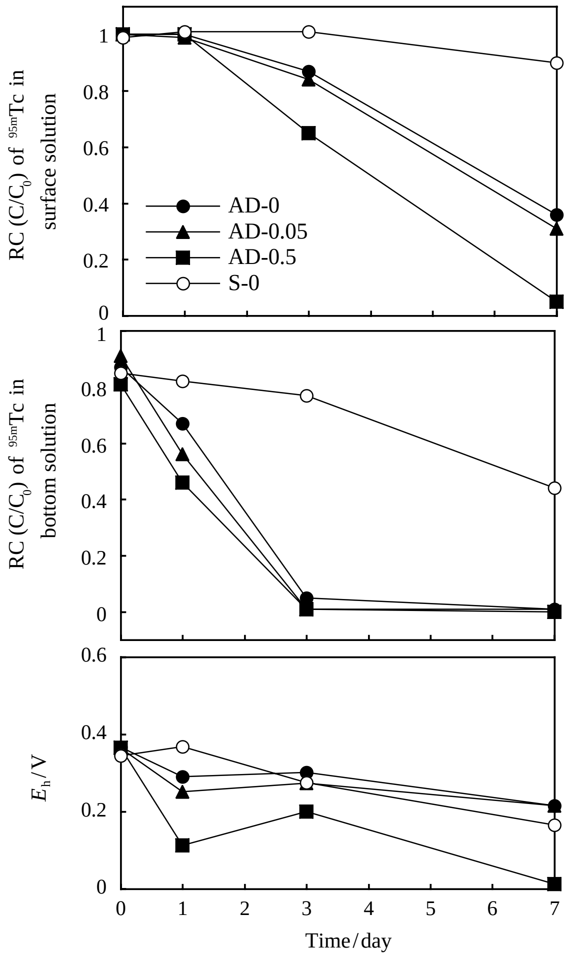

Figure 6. Time dependence for relative counts of ^{95m}Tc in surface and bottom solutions and E_h (V) of air-dried soil with addition of 0, 0.05 and 0.5% glucose on an air-dried soil weight basis (AD-0, AD-0.05 and AD-0.5) and sterile soil without glucose (S-0).

4.2. Identification of the Adsorption Behavior of Tc in Soils. For some nuclides, the amount of the available fraction may change substantially over time through a process sometimes called "aging". Although a strict delineation of specific chemical species or binding forms is difficult, speciation of toxic heavy metals in the environment has been carried out to assess the potential effects of soil contamination instead of total concentration.[48–52] These studies designed single or sequential extraction schemes to remove "exchangeable" or "bioavailable" fraction in soil and sediment, but the extraction methods have not been used to follow the change of extractable fraction as a function of time.

Two typical upland field and paddy field soils in Japan, classified as Andosol and Gray lowland soil (GLS), were used. The air-dried soils (ø<2-mm) were placed into plastic vessels and $^{95m}TcO_4^-$ was uniformly mixed with each sample. Then deionized water was added to adjust the soil water content to a desired level as follows: 1) waterlogged upland field soil (FW); 2) upland field soil with a typical upland moisture content (FO); 3) waterlogged paddy field soil (PW); and 4) paddy field soil with an upland field moisture content (PO). The water contents for numbers 1 and 3 were similar to those in paddy fields, that is, the waterlogged condition. All samples were stored in the dark while being kept at room temperature for 6 months. At 1, 3, 7, 14, 30, 60, and 180 days, 20 to 25g amounts from each soil sample were used for the extractions. The reagents used are listed in Table 3, which are modified from the method of McLaren and Crawford[48] to extract the fractions.[24]

TABLE 3: Reagents Used in the Extraction

Reagent	Fraction	Soil weight /g	Solution amount /mL	Code
0.05 M calcium chloride	Exchangeable & water soluble	2	40	CA
0.5 M acetic acid	Specifically adsorbed	2	40	AA
0.1 M sodium pyrophosphate	Organically bound	2	200	PY
	Sorbed onto the residue			Res

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.

Figure 7 shows the Tc fixation pattern in the soil samples

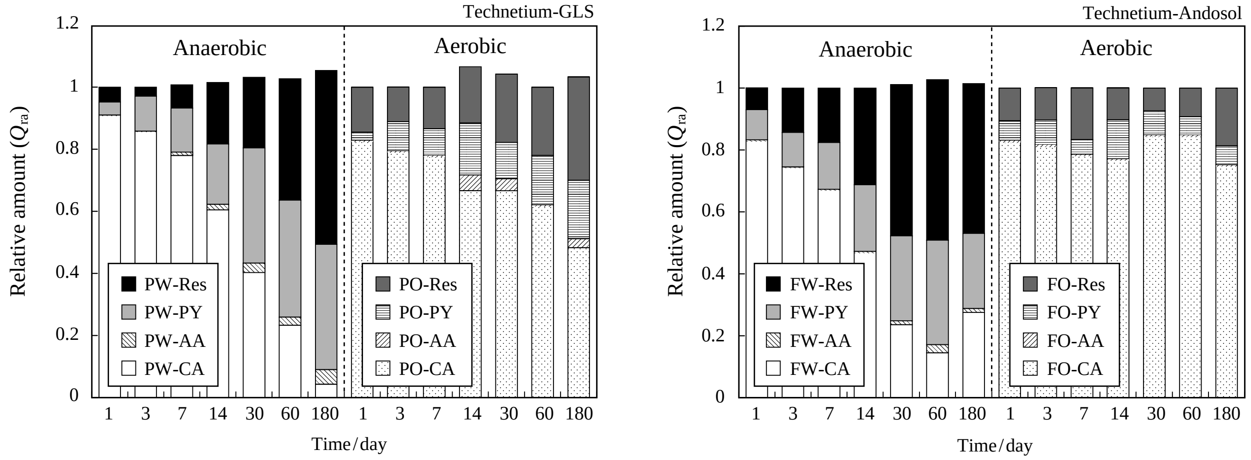

Figure 7. Time dependence on the amounts of CA-, AA- and PY-extractable Tc in GLS and Andosol under waterlogged and upland field water conditions. PW: GLS under waterlogged conditions, PO: GLS under upland filed conditions, FW: Andosol under waterlogged conditions and FO: Andosol under upland field conditions. CA, AA. PY and Res are explained in Table 3.

under upland field and waterlogged conditions. The relative amount (Q_{ra}) was defined as “the total activity in extracted solution from unit soil sample at each sampling time” divided by “ the total activity of the subjected unit soil sample”. The original extraction method was used sequential,[48, 50] however, in this study, the reagents were used individually because the single use showed less damage to the soils.[24] Thus, the extractions with AA and PY include CA and CA+AA, respectively. To calculate PW-AA, PO-AA, FW-AA, or FO-AA in Figure 7, the extracted fraction with CA (hereinafter this is designated as Q_{ra} of CA-Tc) was subtracted from the actually extracted fraction with acetic acid (Q_{ra} of AA-Tc) and, similarly, to get PW-PY, PO-PY, FW-PY, or PO-PY, Q_{ra}s of CA-Tc was subtracted from Q_{ra}s of PY-Tc. Residual part was calculated to subtract Q_{ra} of PY from 1. As can be seen from the Figure 7, the Q_{ra}s of ^{95m}Tc in soil samples under aerobic and anaerobic conditions differed. The Q_{ra} values of CA-Tc and AA-Tc were almost the same. It seems that the Tc which strongly adsorbed on the Andosol or GLS samples might be negligible. Under the aerobic condition, Q_{ra} of CA-Tc and Q_{ra} of AA-Tc for Andosol samples kept at a constant value of around 0.8 during the experiment while that for GLS dropped to about 0.5. Under the waterlogged condition, Q_{ra} of CA-Tc and Q_{ra} of AA-Tc for Andosol were decreased to about 0.2 and that for GLS decreased over time and became almost 0. One day after Tc was initially added to the aerobic and anaerobic soils, the Q_{ra} of PY-Tc was negligible compared to those of CA-Tc or AA-Tc. Then, in the anaerobic soils, the PY fraction gradually increased for 30 days then became almost constant, while no Q_{ra} of PY-Tc increments was found in aerobic soils. From the result, it was found that some part of the non-CA extractable Tc transformed to PY extractable, that is, organically bound forms.

These Tc reductions under the anoxic condition may be attributed to the transformation of Tc under the low redox potentials in the soil produced by waterlogging. The pertechnetate was transformed to lower oxidation forms, sulfates or organically bound. The sulfides might occur because H_2S gas can be produced in rice paddy fields under the waterlogged condition. As mentioned above, TcO_4^- is the most available form for plants.[11, 12] Thus, these changes of Tc in its chemical form under the anoxic condition affected less Tc transfer from soil to plants. This suggested that Tc transformation from soil to plants (not only rice but also any other higher plants grown under the anaerobic condition) became less with time after Tc addition to the soil.

4.3. Possibility of Change in Tc Extractability After Air-Drying. Technetium extractions in air-dried soils were carried out following 52 days of waterlogging of the soil. Q_{ra} values for extractions by CA as a function of time are shown in Figure 8. Extractions with AA and 1 M CH_3COONH_4 (pH=7) were also carried out to check the change of the amount of readily extractable Tc with time. The Q_{ra}s were approximately equal to that of CA, so that the data are not shown. Even though the soil was air-dried and kept in aerobic conditions, Tc extractability did not change significantly from the initial value, that is, the value at just the end of the waterlogging period. If all the Tc that adsorbed on to the soil was Tc(+4) oxides, such as TcO_2 and $TcO(OH)_2$, it could be transformed to a higher oxidation state, TcO_4^- though its rate would be slow. Even in the aerobic condition, other stable chemical forms of Tc, e.g. organically bound forms, sesquioxides bound forms and sulfides, probably were presented. The immobilized Tc might change to TcO_4^- in the presence of oxidants; however, such chemicals are never used in paddy field soils so that a quick reaction to TcO_4^- would not occur after the harvest.

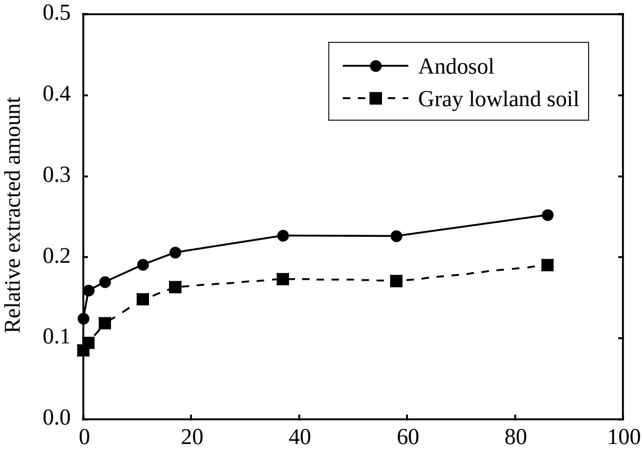

Figure 8. Time dependence on the amounts of CA-extractable Tc in the air-dried Andosol and GLS following waterlogging.
The soil samples were waterlogged for 52 days then air-dried for 86 days. Each extraction was carried out in duplicate.

From these radiotracer experiments, it is predicted that Tc transformation to lower oxidation states would be encouraged by waterlogging in an actual rice paddy field, and also microbial activity seemed to have an important role in Tc sorption reactions. Besides, the reaction of the immobilized Tc form to TcO_4^- should be slow.[32] When there is no potential process for removal of the ^{99}Tc from soil (leaching and harvesting), there was a possibility that Tc had been accumulating in the surface layer of paddy fields, although the fields would keep upland conditions from the harvest to the transplanting season (Figure 9).

Although paddy field soils could immobilize global fallout ^{99}Tc that was deposited directly onto them, the relatively high ^{99}Tc concentrations in paddy fields observed in our field study suggest other ^{99}Tc sources. Probably, the paddy field soils had trapped ^{99}Tc not only from deposition, but also from irrigation water through the mechanism as mentioned above. The average Japanese paddy field receives 1800 mm rainfall equivalent of irrigation water during the irrigation season, which is twice as much as the water supply from precipitation. The irrigation water would contain ^{99}Tc leached from other soil sites, e.g. forest soils. Some part of the ^{99}Tc in the water could be trapped onto the paddy field soil surface.

5. Transfer factors of Tc obtained in Chernobyl Area

For realistic assessment, it is necessary to obtain transfer parameters, such as TFs and K_ds, under natural conditions, but the data have been limited due to trace levels of ^{99}Tc. Obtaining TFs using global fallout ^{99}Tc in fields is difficult, because the concentration of ^{99}Tc is very low. Therefore, we focused on the Chernobyl site where ^{99}Tc concentration levels have already been shown to be higher than those from global fallout Tc.[33]

Soil and plant samples were collected by the Federal Office for Radiation Protection, Germany, in 1994 and 1995, assisted

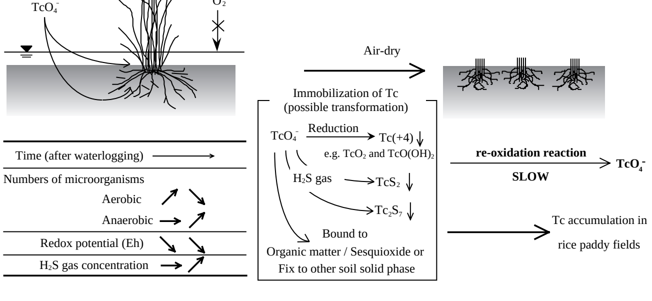

Figure 9. Immobilization mechanism of Tc in paddy field soil.

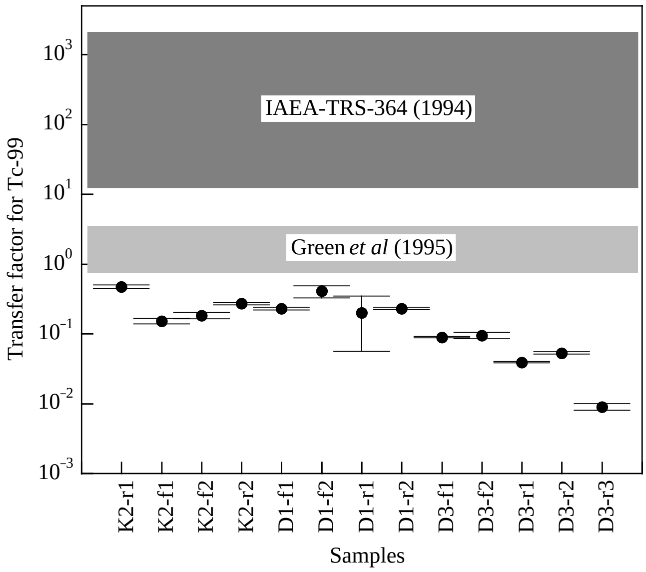

Figure 10. TFs of Tc from soil to strawberry and raspberry leaves collected from forest sites within the 30-km zone around the Chernobyl Reactor.

by Moscow State University, Russia, and the Research and Industrial Association 'Pripyat', Ukraine. The sampling was carried out in three forests around Chernobyl. Forests D1 and D3 were 28.5 km and 26 km to the south of the Chernobyl Reactor, respectively, while forest K2 was 6 km to the southeast of the Reactor. The sites D1 and D3 are mixed forests while K2 is a pine forest. Surface organic soil layers (L, Of and Oh) collected at each site were mixed and measured for their ^{99}Tc activity. The D1 samples, collected in 1994 and 1995, were mixed together, because of their small volumes. It is noted that forest understorey plants are expected to take up radionuclides mainly from the organic layers[53] and therefore, concentration of ^{99}Tc in organic soil would be important for estimation of its uptake. For this reason, we calculated TFs in terms of activity concentration in plant relative to activity concentration in organic soil. Plant samples used were strawberry and raspberry leaves since these species were found each year at each site, and possible differences of the TFs from different cites could be investigated.

The details of the ^{99}Tc concentrations in soils and plants were reported elsewhere,[34–36] therefore, only calculated TF is discussed. The expected TF values for grass and spinach are 7.6×10^1 and 2.6×10^3, respectively.[9] Comparing with the TF for Cs, that for Tc is about three to five orders of magnitude higher. For this reason, ^{99}Tc is one of the very important radionuclides for the assessment of internal dose by ingestion of the contaminated vegetables. However, attention should be paid to the fact that most of the TF values for Tc reported were obtained by tracer experiments in which Tc was applied to soil in a soluble form, e.g. as TcO_4^-. Because the chemical forms of Tc are variable under natural conditions, TF values obtained from laboratory experiments need not necessarily be the same as those obtained in the field.

The TF data for Tc obtained are shown in Figure 10. The TFs for Tc and Cs (not shown) obtained in this study are range from 0.09 to 0.45 and from 0.06 to 0.46, respectively, based on dry weight.[36] The obtained TFs for Cs are almost the same as those previously reported for strawberry leaves samples at the investigated sites.[53] The corresponding TFs for Tc are between factors two to five larger compared to those for Cs for the sites K2 and D1. On the contrary, at D3 the TF for Tc is lower by a factor of about 5 compared to that for Cs. This might be due to the fact that D3 is a so-called wet forest, and accordingly Tc might exist in the TcO_2 form, which is much less plant-available (see above).

For all sites, TFs for Tc observed in this work are two or three orders of magnitude lower than those reported for other plants.[9] However, recently Green et al.[54–56] performed uptake experiments using contaminated soil of marine origin in an area of reclaimed land to obtain Tc-TFs under the field conditions. The TFs they obtained were less than 2.0 for many kinds of vegetables based on dry weight of the vegetable, similar to those obtained in our study.

6. Summary

Tc is known to have high mobility and availability to plant in the soil environment because the dominant oxidation state of Tc is heptavalent, TcO_4^-. However, because Tc is a redox sensitive element, it might change to lower oxidation forms under anaerobic conditions. The behavior of Tc is expected to be different under upland field and rice paddy field conditions, but available data have been too limited to understand the Tc behavior under waterlogged conditions. Therefore, it was important to obtain some knowledge of ^{99}Tc in the soil-to-rice plant system.

To determine low-levels of ^{99}Tc in environmental samples, we developed a unique analytical procedure based on ICP-MS. Then, ^{99}Tc concentrations in Japanese rice paddy field soils were analyzed. The average concentration of ^{99}Tc in paddy fields was measured to be 34 mBq/kg-dry. The range of activity ratios of ^{99}Tc/^{137}Cs in the soil samples was $(2.0 – 5.2) \times 10^{-3}$; these ratios were one order of magnitude higher than the theoretical one, which is calculated now to be about 3.3×10^{-4}. Such high activity ratios indicated that ^{99}Tc had been accumulating in rice paddy soils like ^{137}Cs.

A series of radiotracer experiments were carried out to understand the accumulation mechanisms of Tc in soil. It was found that Tc transformed from TcO_4^- to other chemical forms because it was immobilized in soil under waterlogged conditions. The reaction of the immobilized Tc to TcO_4^- should be slow. On this Tc immobilization, microbial activity seemed to have an important role. We are working on radiotracer experiments to find out a possibility of Tc immobilization by aerobic bacteria under waterlogged conditions.[57] When Tc was immobilized, leaching and harvesting, those are thought to be main Tc removal paths, could only remove a small part of Tc from the soil and, thus, Tc had been accumulating in the surface layer of paddy fields. The results from the wet forest within 30-km zone from the Chernobyl Reactor can be a real example of this series of our experiments: the Tc in the forest was less available to plants than those in other two forests.

^{99}Tc would retain in the terrestrial and the marine environments for many generations, further studies on ^{99}Tc behavior in the environment is necessary, from the viewpoint of the long-term dose effect on humans.

Acknowledgement. The author is grateful to Dr. T. Sekine, Tohoku University, for kindly providing us with the Tc-95m tracer solution.

References

(1) A. Aarkrog, H. Dahlgaard, L. Hallstadius, E. Holm, S. Mattson, and J. Rioseco, in *Technetium in the Environment*, G. Desmet and C. Myttenaere, Eds. (Elsevier Appl. Sci. Pub., London, 1986), pp. 69.

(2) E. Holm, in *Low-Level Measurements and Their Applications to Environmental Radioactivity*, M. García-León and G. Madurga, Eds. (World Scientific, Singapore, 1987), pp. 443.

(3) BNFL: *Annual Reports on Discharges and Monitoring of the Environment in the United Kingdom, 2001.* (BNFL, Cheshire, 2002), p. 156.

(4) M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*. (Pergamon Press, Oxford, 1966), pp. 294.
(5) D.G. Brookins, *Eh-pH Diagrams for Geochemistry*. (Springer-Verlag, Berlin, 1988), pp. 97.
(6) R.E. Wildung, T.R. Garland, K.M. McFadden, and C.E.Cowan, in *Technetium in the Environment*, G. Desmet and C. Myttenaere Eds. (Elsevier Appl. Sci. Pub. London, 1986), pp. 155.
(7) E.R. Landa, L.J. Thorvig, and R.G.J. Gast, J. Environ. Qual. **6**, 181 (1977).
(8) J.M. Mousny and C. Myttenaere, Plant Soil **61**, 403 (1981).
(9) IAEA: *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Temperate Environments*. (IAEA, Vienna, 1994), Tech. Rep. Ser. No. 364.
(10) IAEA: *Generic Models and Parameters for Assessing the Environmental Transfer of Radionuclides from Routine Releases*. (IAEA, Vienna, 1982), Safety Ser. No. 57, p. 61.
(11) L.R. Van Loon, G.M. Desmet, and A. Cremers, in *Speciation of Fission and Activation Products in the Environment*, R.A. Bulman and J.R. Cooper Eds. (Elsevier Appl. Sci. Pub., London, 1986), pp. 352.
(12) G.C. Krijger, A.V. Harms, R. Leen, T.G. Verburg, and B. Wolterbeek, Environ. Exp. Bot. **42**, 69 (1999).
(13) R.G. Gast, L.H. Thorvig, E.R. Landa, and K.J. Gallagher, in *Environmental Cycling Processes*, D.C. Adriano and I.E. Brisbin Eds. (CONF-760429, 1978), pp. 550.
(14) R.E. Wildung, R.C. Routson, R.J. Serne, and T.R. Garland, in *BNWL-1950, PT2*. (CONF-741121-3, Richland, 1975) pp. 37.
(15) R.C. Routson, G. Jansen, and A.V. Robinson, Health Phys. **33**, 311 (1977).
(16) S. Takebe and X. Deying, *Studies on sorption behaviour of technetium in soils.* (JAERI-Research 95-024, 1995), p. 14.
(17) S. Uchida and K. Tagami, *in Abstracts of 6th International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere*,(Sendai, Japan, 1997), pp. 137.
(18) P.J. Coughtrey, D. Jackson, and M.C. Thorne, *Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems, A Critical Review of Data, Vol. 3*. (AA Balkema, Rotterdam, 1983), pp. 210.
(19) C. Wolfrum and K. Bunzl, J. Radioanal. Nucl. Chem. Articles **99**, 315 (1986).
(20) M.I. Sheppard, T.T. Vandergraaf, D.H. Thibault, and J.A.K. Reid, Health Phys. **44**, 635 (1983).
(21) C.T. Garten, F.O. Hoffman, and E.A. Bondietti, Health Phys. **46**, 647 (1984).
(22) C.M. Vandecasteele, J.P. Dehut, S. Van Laer, and C. Myttenaere, Health Phys. **57**, 247 (1989).
(23) K. Tagami and S. Uchida, Chemosphere **33**, 217 (1996).
(24) K. Tagami and S. Uchida, Toxicol. Environ. Chem. **56**, 235 (1996).
(25) K. Tagami and S. Uchida, Radiochim. Acta **63**, 69 (1993).
(26) K. Tagami and S. Uchida, Appl. Radiat. Isot. **47**, 1057 (1996).
(27) S. Uchida and K. Tagami, J. Radioanal. Nucl. Chem. **221**, 35 (1997).
(28) K. Tagami and S. Uchida, Radioact. Radiochem. **10**, 30 (1999).
(29) T. Sekine, M. Konishi, H. Kudo, K. Tagami, and S. Uchida, J. Radioanal. Nucl. Chem. **239**, 483 (1999).
(30) K. Tagami and S. Uchida, J. Radioanal. Nucl. Chem. **239**, 643 (1999).
(31) K. Tagami and S. Uchida, J. Nucl. Radiochem. Sci. **3**, 1 (2002).
(32) K. Tagami and S. Uchida, Chemosphere **38**, 963 (1999).
(33) S. Uchida and K. Tagami, J. Radioanal. Nucl. Chem. **240**, 357 (1999).
(34) S. Uchida, K. Tagami, E. Wirth, and W. Rühm, Chemospere **39**, 2757 (1999).
(35) S. Uchida, K. Tagami, W. Rühm, M. Steiner, and E. Wirth, Appl. Radiat. Isot. **53**, 69 (2000).
(36) S. Uchida, K. Tagami, W. Rühm, M. Steiner, and E. Wirth, in *Proceedings (CD) of International Conference on Radioactivity in the Environment*, P. Børretzen, T. Jølle, and P. Strand Eds. (Monaco, 2002).
(37) E. Holm, Radiochim. Acta **63**, 57 (1993).
(38) J.S. Crain and D.L. Gallimore, Appl. Spectroscopy **46**, 547 (1992).
(39) S. Morita, C.K. Kim, Y. Takaku, R. Seki, and N. Ikeda, Appl. Radiat. Isot. **42**, 531 (1991).
(40) S. Morita, K. Tobita, and M. Kurabayashi, Radiochim. Acta **63**, 63 (1993).
(41) C.K. Kim, S. Morita, R. Seki, Y. Takaku, N. Ikeda, and D.J. Assinder, J. Radioanal. Nucl. Chem. Articles **156**, 201 (1992).
(42) J.E. McAninch, I.D. Proctor, N.J. Stoyer, and K.J. Moody, *Viability of long-lived fission products signatures in forensic radiochemistry*, (UCRL-ID-126425, 1997) pp. 7.
(43) S. Nicholson, T.W. Sanders, and L.M. Blaine, Sci. Total Environ. **130/131**, 275 (1993).
(44) S.C. Sheppard, M.I. Sheppard, and W.G. Evenden, J. Environ. Radioact. **11**, 215 (1990).
(45) M.I. Sheppard and D. Thibault, Soil Sci. Soc. Am. J. **56**, 415 (1992).
(46) M. Kumata and T.T. Vandergraaf, Radioact. Waste Manag. Nucl. Fuel Cycle **17**, 107 (1993).
(47) Y. Takai, J. Korean Soc. Soil Sci. on Fertilizer **17**, 187 (1984).
(48) R.G. McLaren and D.V. Crawford, J. Soil Sci. **24**, 172 (1973).
(49) A. Tessier, P.G.C. Campbell, and M. Bisson, Anal. Chem. **51**, 844 (1979).
(50) K.L. Iu, I.D. Pulford, and H.J. Duncan, Plant Soil **59**, 317 (1981).
(51) A.S. Jeng and B.R. Singh, Soil Sci. **156**, 240 (1993).
(52) P. Quevauviller, G. Rauret, H. Muntau, A.M. Ure, R. Rubio, J.F. López-Sánchez, H.D. Fiedler, and B. Griepink, J. Anal. Chem. **349**, 808 (1994).
(53) D. Lux, L. Kammerer, W. Rühm, and E. Wirth, Sci. Total Environ. **173/174**, 375 (1995).
(54) N. Green and B.T. Wilkins, Sci. Total Environ. **173/174**, 385 (1995).
(55) N. Green, B.T. Wilkins, M.F. Davidson, and D.J. Hammond, J. Environ. Radioact. **27**, 35 (1995).
(56) N. Green, B.T. Wilkins, and D.J. Hammond, J. Environ. Radioact. **31**, 171 (1996)
(57) N. Ishii, K. Tagami, and S. Uchida, in *Abstract of International Symposium on Bio-Trace Elements 2002* (Wako, 2002).