

Soil-to-Plant Transfer Factors of Technetium-99 for Various Plants Collected in the Chernobyl Area

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Technetium-99 is thought to be highly soluble and rarely adsorbed onto soil, however, its mobility under natural environment is not well known because its scarcity and low levels in environmental samples has limited the available data. In this study, we determined ^{99}Tc contents in 27 plant samples collected in three forest sites in 1994 and 1995 around the Chernobyl area to obtain transfer factors (TFs) of Tc in the soil-plant system under environmental conditions. The samples were leaves of raspberry, strawberry and pink plants, black alder, birch, cowberry and oak trees, and ferns. After chemical separation, ^{99}Tc in the sample was measured by ICP-MS. Tc-95m was used as a yield tracer and the total recovery ranged from 0.48 to 0.92 with an average of 0.76. The determined ^{99}Tc concentrations in plants ranged from < 0.006 to 6.0 mBq g^{-1} (dry weight basis). TF values ranged from < 0.006 to 0.47, based on the ^{99}Tc contents of the soil organic layers. The highest TF was found in the leaves of raspberry plants. The observed TFs were much lower than the values of 8.1–2600 compiled by IAEA for grass, fodder and leafy vegetables.

1. Introduction

Technetium belongs to the Mn group and it has no stable isotopes. Among its radioactive isotopes, ^{99}Tc is of potential long-term importance in the environment like ^{137}Cs . Technetium-99 is a pure beta emitter ($E_{\text{max}} = 0.29 \text{ keV}$) and its radiological half-life is $2.11 \times 10^5 \text{ y}$. It is produced in the fissions of ^{235}U and ^{239}Pu at relatively high ratios of ca. 6%, which is similar to the values for ^{137}Cs and ^{90}Sr . Technetium-99 is widely distributed in the environment as a result of fallout from nuclear weapons testing and discharges from nuclear facilities. Nuclear medical use of $^{99\text{m}}\text{Tc}$ (half-life: 6.01h) which decays directly to ^{99}Tc is another source though the ^{99}Tc introduced into the environment via this route is negligible.

For a realistic long-term radiological assessment of the radionuclide, it is necessary to obtain transfer parameters, such as soil-to-plant transfer factors (TFs, concentration in plant/concentration in soil), under natural conditions. Generally, Tc is expected to be mobile in the surface soil environment because of its chemical form, TcO_4^- , which is the most stable chemical form under natural surface water conditions.¹ This chemical form is highly soluble in water, rarely adsorbed onto soil particle surfaces, and has a high availability for plants. Indeed, a TF of 5 in the edible parts of common plants (on a wet weight basis) was recommended by the International Atomic Energy Agency (IAEA) for Tc when assessing its behaviour.² Moreover, in Reference 3, soil to grass transfer factor for Tc was reported as 78 (on a dry weight basis), while those for Sr and Cs were 0.34–1.7 and 0.11–0.53, respectively. This highly mobile chemical form, TcO_4^- , however, changes with environmental conditions,^{4–7} consequently, TF values would also change. Unfortunately, TF data observed under natural conditions have been limited due to there being only trace levels of ^{99}Tc . Obtaining TFs using global fallout ^{99}Tc in agricultural fields is difficult, because the concentration of ^{99}Tc is very low.⁸ 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.⁹

In this study, we determined the concentrations of ^{99}Tc in plant leaves collected near the Chernobyl site to investigate the transfer of the nuclide in soil-plant systems under natural conditions. The samples were leaves of raspberry, strawberry and pink plants, black alder, birch, cowberry and oak trees, and ferns. Details of ^{99}Tc and ^{137}Cs data for soil samples collected at the same time were reported previously,⁹ thus, the data were used in this study to obtain TFs. Since TFs are usually high in leafy vegetables and grass as reported in Reference 3, leaves of raspberry, strawberry and pink plants are of the most interest in this study for comparison purposes.

2. Experimental

2.1. Reagents. Nitric acid used was ultra pure grade (Tama Chemicals, AA-100). A Tc-selective chromatographic resin (Eichrom Industries Inc., TEVA resin) was used for Tc purification. The grain size of the resin was 100–150 μm and the volume of the resin in the column was about 2 mL. Deionized water ($> 17.6 \text{ M}\Omega$) was used throughout the work. Technetium-95 m, which was obtained from an Nb foil using the reaction $^{93}\text{Nb} (\alpha, 2n) ^{95\text{m}}\text{Tc}$, was applied to determine the recovery of ^{99}Tc in the samples during the chemical separation procedure. The $^{95\text{m}}\text{Tc}$ was made at Cycrotron and Radioisotope Center, Tohoku University. In our previous work, we found that this reaction could not produce other long-lived Tc isotopes.¹⁰ A standard ^{99}Tc solution available from Amersham (Solution TCZ.44) was used for calibrating the ICP-MS.

2.2. Plant Samples. Twenty seven plant samples were collected at the Chernobyl site in 1994 and 1995 by the Federal Office for Radiation Protection, Germany, assisted by Moscow State University, Russia, and the Research and Industrial Association “Pripyat”, Ukraine. The sampling was carried out in three forests, D1, D3 and K2, around the Chernobyl Nuclear Power Plant. Forests D1 and D3 were 28.5 km and 26 km to the south of the reactor, respectively, while forest K2 was 6 km to the southeast. The sites D1 and D3 were mixed forests (D1: 50% oak, 30% pine, 20% birch; 55–60 years old; and D3: 50% alder, 40% birch, 10% pine; 50–75 years old), while K2 was a pine forest (about 50 years old).¹¹ Soil samples were

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also collected at the same sampling sites and the details were reported previously.⁹

The plant samples were leaves of various plants grown in the forests (Table 1). They were separated into three groups, that is, Fern, Herb (raspberry, strawberry and pink), and Tree (black alder, birch, cowberry and oak). After the samples were oven dried at 110 °C, they were thoroughly milled. Then they were transferred to plastic bottles and stored at room temperature.

TABLE 1: Chemical Recovery and Concentration of ⁹⁹Tc in Plant Samples Collected in Forests within the 30-km Zone Around the Chernobyl Nuclear Power Plant

Group	Sampling site	Sample	Plan	Dry weight (g)	Recovery	Technetium-99 (mBq g-dry ⁻¹)	
Fern	K2	94F-1a*		1.01	0.847	2.42 ± 0.18	
		94F-1b*		1.01	0.895	2.37 ± 0.29	
		94F-1c*		2.61	0.884	2.31 ± 0.26	
		95F-1		4.04	0.829	0.603 ± 0.045	
		95F-2		2.00	0.749	3.79 ± 0.35	
	D3	94F-1		7.02	0.661	< 0.040	
		95F-1		9.06	0.483	< 0.031	
		95F-2		4.03	0.844	< 0.069	
	Herb	K2	94G-1	Raspberry	4.04	0.599	4.04 ± 0.42
			94G-2a*	Strawberry	4.03	0.747	1.30 ± 0.17
94G-2b*				2.07	0.852	1.57 ± 0.16	
95G-1			Pink	3.99	0.739	6.02 ± 0.52	
95G-2			Raspberry	17.0	0.762	3.61 ± 0.33	
D1		94G-1a*	Strawberry	6.98	0.596	0.254 ± 0.022	
		94G-1b*		2.22	0.824	0.451 ± 0.090	
		94G-2	Raspberry	25.1	0.563	0.222 ± 0.017	
		95G-1	Raspberry	35.3	0.901	0.257 ± 0.021	
D3		94G-1a*	Strawberry	10.2	0.868	0.215 ± 0.016	
		94G-1b*		1.82	0.844	0.231 ± 0.025	
		94G-1c*		2.81	0.823	0.192 ± 0.029	
		94G-2	Raspberry	20.0	0.706	0.094 ± 0.008	
		94G-3	Raspberry	4.02	0.553	0.128 ± 0.011	
Tree		D1	94T-1	Oak	45.4	0.898	< 0.006
			95T-1	Oak	25.2	0.883	0.013 ± 0.001
		D3	94T-1	Birch	7.99	0.878	< 0.035
			94T-2	Oak	7.00	0.652	< 0.040
	94T-3		Cowberry	5.04	0.850	< 0.056	
	94T-4		Black alder	10.0	0.633	< 0.028	
	95T-1		Birch	10.0	0.685	< 0.028	
	95T-2		Black alder	12.1	0.543	< 0.023	
	95T-3		Oak	10.1	0.856	< 0.028	
	95T-4		Cowberry	8.06	0.843	0.094 ± 0.011	

*: Replicates.

The activities of ¹³⁷Cs in the samples were measured with a Ge detector (Seiko EG&G Ortec) coupled with a multi channel analyzer (Seiko EG&G, Model 7800) before the chemical separation for ⁹⁹Tc.

2.3. Chemical separation. A simple wet digestion method in combination with an extraction chromatographic resin separation method was applied for ⁹⁹Tc. About 1–45 g portions of the plant samples were incinerated at 450 °C in an electrical oven for 2 h to decompose organic matter. Then, in order to obtain the recoveries of ⁹⁹Tc, a certain amount of ^{95m}Tc was added and they were mixed uniformly. Next Tc was extracted with 4 M HNO₃ while heating the samples at 100 °C in a glass beaker covered with a watch glass. The residue was removed by filtration and the solution was diluted to obtain the acidity of ca. 0.1M HNO₃ and passed through a TEVA resin column to purify and concentrate Tc isotopes. Because ICP-MS cannot differentiate between ⁹⁹Ru and ⁹⁹Tc, it is necessary to remove all Ru from the final sample solution prior to ICP-MS mea-

surement. Ruthenium present in the sample solution is not effectively retained on the TEVA resin and passes directly through the resin, while almost all Tc is extracted on the resin.¹² The column was then washed with 2 M HNO₃ to remove any remaining trace Ru and other matrix elements which interfered with ⁹⁹Tc measurement by ICP-MS. Technetium adsorbed on the resin was eluted with 5 mL of 8 M HNO₃ solution. The volume of the ⁹⁹Tc fraction from the TEVA column solution was reduced to near dryness (< 70 °C) and then dissolved in 5 mL of 2% HNO₃ solution. Details of this method are in the literature.¹³

2.4. Measurements. Radiochemical recoveries of Tc plant samples were monitored with ^{95m}Tc activities in the final 2% HNO₃ solutions before ICP-MS measurements. The gamma-rays (204 keV), was measured with a NaI (TI) scintillation counter (Aloka, ARC-380) for 20 min. Then the solution was introduced into an ICP-MS (Yokogawa, PMS-2000) to measure ⁹⁹Tc for 10 min. The typical detection limit in solutions, calculated as three times the standard deviation of the blank, was 0.03 mBq mL⁻¹.

3. Results and Discussion

3.1. Technetium-99 concentrations in plant samples. Total chemical recoveries throughout the method with ^{95m}Tc are listed in Table 1, and they ranged from 0.48 to 0.92 with an average of 0.76. No relation was found between sample amount and recovery. Three replicates of samples K2-94F-1 and D3-94G-1 were used in amounts of 1–2.6 g and 1.8–10.2 g, respectively, and there were no differences between their recoveries. However, the recoveries of two sub-samples of K2-94G-2 and D1-94G-1 differed by about 0.1 and 0.2, respectively; when sample amounts increased, the recoveries decreased. Possibly, plant matrices, such as K, Ca and Cl, would affect the ⁹⁹Tc recovery, especially at the TEVA resin separation steps.

Technetium-99 concentrations in all samples are also listed in Table 1 and they ranged from < 0.006 to 6.0 mBq g⁻¹. For 11 samples, especially in the Tree group, it was hard to determine ⁹⁹Tc, because of its low concentration. Since K2 was closer to the reactor than the other 2 sites were, Fern and Herb groups showed higher ⁹⁹Tc concentrations in K2 than in D1 and D3. No Tree group samples were available from K2; however, we expected ⁹⁹Tc concentrations in tree leaves would be higher at K2 than at the other 2 sites as well, although the concentrations should be much lower than those of Fern and Herb groups.

Then, by calculating activity ratios of ⁹⁹Tc to ¹³⁷Cs in plant samples, we were able to compare uptake behavior of these elements. The results are shown in Figure 1. Previously, it was reported that the soil organic layer in these sites had ⁹⁹Tc/¹³⁷Cs activity ratios of between (0.37–1.24) × 10⁻⁴.⁹ These data were based on total activity ratio; the bioavailability of ¹³⁷Cs should be much smaller than that of ⁹⁹TcO₄⁻ due to their different chemistries and fixation mechanisms by soils. Consequently, higher activity ratios in the plants than in the soils were expected if Tc was in TcO₄⁻. At K2, the activity ratios for the Fern group were lower than that for the soils, while the Herb group showed higher activity ratios than soils did. It is well known that fern plants can adsorb much more Cs than more highly evolved plants can, and this could be the reason for their low activity ratios. For the samples at D1 and K2, the ratios for the Herb group were usually about 5–10 times higher than those for the soils, that is, bioavailability of Tc at D1 and K2 sites was 5–10 times higher than that of Cs. However the Tc bioavailability was smaller than expected from their reported TFs³ since TF of Tc was 150–800 times higher than that of Cs. There was no clear magnitude difference for the Tree group and soils. On the other hand, the ratios at D3 were usually lower than those in soils for Herb and Tree groups which implied that ⁹⁹Tc bioavailability there was much lower than expected. The results

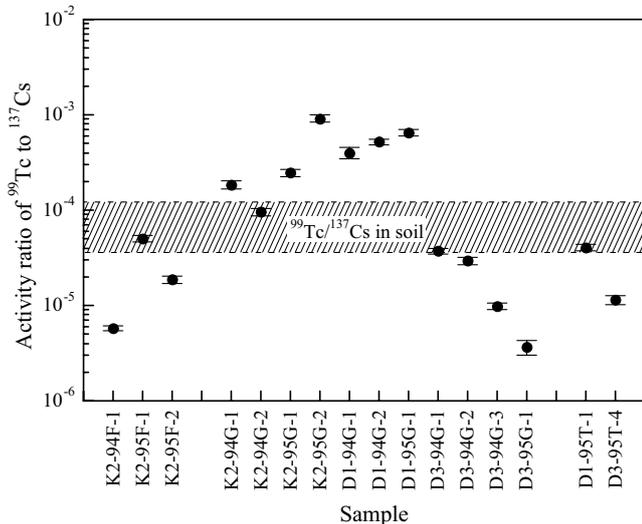


Figure 1. Activity ratio of ^{99}Tc to ^{137}Cs in plant samples collected in forests within the 30-km zone around the Chernobyl Nuclear Power Plant. Bars show counting error (1 sigma).

suggested that most part of the Tc was not pertechnetate form.

3.2. Transfer factor for ^{99}Tc . In general, TF is defined as the ratio of activity concentration in plant (in Bq g^{-1} dry weight (DW)) to activity concentration in soil (in Bq g^{-1} DW). It has been noted that forest under story plants are expected to take up radionuclides mainly from organic layers⁹ 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 a plant relative to activity concentration in organic soil. In the soils, as reported previously,⁹ concentrations of ^{99}Tc were $8.6 \pm 0.3 \text{ Bq g}^{-1}$ in 1994 and $13.4 \pm 0.2 \text{ Bq g}^{-1}$ in 1995 for K2 site, $1.1 \pm 0.02 \text{ Bq g}^{-1}$ (combined sample from 1994 and 1995) for D1 and $2.4 \pm 0.01 \text{ Bq g}^{-1}$ in 1994 and $1.72 \pm 0.05 \text{ Bq g}^{-1}$ in 1995 for D3 site.

Figure 2 shows the TFs of Tc for all the samples. They ranged from < 0.016 to 0.28 for Fern, 0.009 to 0.47 for Herb and < 0.006 to 0.05 for Tree groups based on the ^{99}Tc contents of the organic layers. The highest TF was found in the leaves of raspberry. The observed-TFs were lower than the IAEA-compiled values of 8.1–2600 for leafy vegetables, fodder and grass³; other reported values are as listed in Table 2. Comparing

TABLE 2: Transfer Factors for Tc Reported for Various Plants Grown in Soil

Crop	TF	Conditions	Reference
Soybean, Leaves	85–186	Silt loam, Pot	14
Wheat, Blade	312–476		
Herbaceous vegetation	6.7–22	Silt loam, Field	15
Radish	2.1, 9.5 9.5, 14.2	pH = 5.7 pH = 6.7	
Chard	2.6 6.3	pH = 5.7 pH = 6.7	4
Turnip	4.5 7.4	pH = 5.7 pH = 6.7	
		> 10y aged, Field	
Grass pasture mixture	6	3 y Lysimeter	5
Grass	0.91–3.02	Reclaimed land, Field	16
Green vegetables	1.2	Reclaimed land, Field	17
Rye grass	44–371	Cambisol, Pot	18
Herbaceous vegetation	0.009–0.47	Podzol, Peat-gley, Field	This study

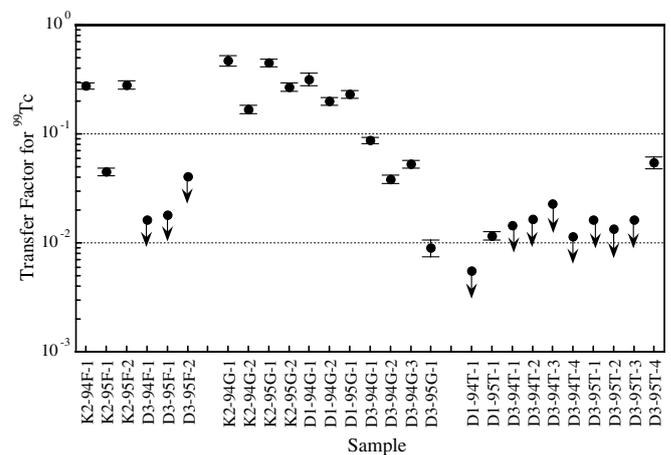


Figure 2. Soil-to-plant transfer factor of ^{99}Tc in plant samples. The ^{99}Tc concentration data are from reference 5. Error bars show counting error (1 sigma). Arrows indicate that TFs are lower than the values estimated from the detection limit for ^{99}Tc .

the TF for Tc reported for various plants grown in soil, the present results were almost the same as the data observed in reclaimed land,¹⁶ although the data from pot experiments^{14, 18} were much higher.

From these results, we concluded Tc bioavailability in the natural environment would be lower than the bioavailabilities obtained from laboratory studies that used TcO_4^- to obtain Tc TFs. Previously, we observed that there are three main paths for TcO_4^- uptake by plants.¹⁹ However, no clear path has been reported for the other Tc chemical forms. It is known that the most plant-available form of Tc is TcO_4^- , and other forms, such as Tc-cysteine, have less availability to plants.²⁰ Thus, as written above, TcO_4^- was not the only Tc chemical form in these forests. Possibly most Tc was in less soluble form, such as organically bound forms, sesquioxide bound and lower oxidation forms.⁶

Concerning the Herb group, the TFs were 0.17–0.47 at K2, 0.20–0.32 at D1 and 0.009–0.086 at D3. The TFs for the samples collected at D3 were lower than those at D1 and K2. This might be due to the fact that D3 was a so-called wet forest and reducing conditions might possibly exist. The bioavailable Tc was presumably influenced by the soil redox conditions. Since the anaerobic condition was established by waterlogging and activity of microorganisms, Tc would be transformed from to a lower oxidation and less available form such as TcO_2 , $\text{TcO}(\text{OH})_2$ or TcS_2 under a relatively low redox condition. Due to the relatively low redox conditions of the D3 site, the TFs were lower than those in K2 and D1 sites.

Thus, the low TFs we observed in this study implied that 8–9 years after ^{99}Tc release from the Chernobyl Nuclear Power Plant, Tc should have been transformed to insoluble or less plant-available forms. Technetium would not be in readily available form to plants in the environment.

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