Global Fallout Technetium-99 Distribution and Behavior in Japanese Soils

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In this study, concentrations of global fallout ^{99}Tc in twenty-one surface soil samples collected in Japan were determined by inductively coupled plasma mass spectrometry. The range of ^{99}Tc concentrations in rice paddy field, upland field and other soils were determined as 6 – 88, 4 – 8, and 7 – 29 mBq/kg-dry, respectively. The highest average activity ratios of ^{99}Tc /^{137}Cs were found in paddy field soils followed by upland field and other soils. The activity ratios in paddy field samples were one order of magnitude higher than the theoretical one estimated from nuclear fission yield, which was presently calculated as 3.3×10^{-4}. Not only the activity ratio in deposition samples, but also mechanisms of ^{99}Tc accumulation in paddy field soils from irrigation of surface water, can explain the high ^{99}Tc/^{137}Cs activity ratios in soils. The results of vertical distributions of ^{99}Tc and ^{137}Cs in undisturbed soils showed that the migration rate of ^{99}Tc would be slightly faster than that of ^{137}Cs, but most of ^{99}Tc would still be retained in the 0 – 20 cm layer from the surface.

INTRODUCTION

Environmental amounts of ^{99}Tc have been accumulating because of its long half-life of 2.1×10^5 y. This pure β-emitter (E_{max}= 0.29 MeV) is produced in the fission of ^{235}U or ^{239}Pu with a relatively high fission yield of ca. 6%, and it has been released to the environment through nuclear weapons tests and nuclear industries. The quantity of ^{99}Tc produced by atmospheric nuclear weapon explosions was estimated to be 140 TBq using an equal fission yield to that of ^{137}Cs and actual ^{137}Cs deposition data.[1] The release of ^{99}Tc by nuclear industries through 1986, as estimated by Luykx,[2] was of the order of 1000 TBq. This was mainly from 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; the reported total amount of ^{99}Tc was ca. 550 TBq in 1995-1999.[3] Compared to this, the amount introduced via nuclear medical use of ^{99m}Tc (half-life: 6.01 h) is negligible. For example, the amounts from ^{99}Mo/^{99m}Tc generators and ^{99m}Tc used during 2000 in Japan were 180 TBq and 285 TBq, respectively,[4] which corresponds to ca. 7 MBq of ^{99}Tc generation in total.

Technetium is known to exist in all valence states from +7 to –1 and the dominant species in natural aqueous solution in equilibrium with atmosphere is the highly soluble chemical form pertechnetate, TcO_4^-.[5] Thus, ^{99}Tc reaching the sea would remain in seawater for a long time. However, in the terrestrial environment, TcO_4^- has a high geochemical mobility[6] and availability for plants.[7-8] For this reason, it is thought to be one of the most important radionuclides for long-term dose assessment. From a radioecological viewpoint, analysis data on global fallout ^{99}Tc in environmental samples should give useful information for predicting the nuclide behavior. At present, however, due to very low concentration and analytical difficulties for determination of the nuclide in environmental samples, there is a general lack of data on ^{99}Tc levels in the literature. Therefore, the behavior of the nuclide in the terrestrial environment is not well understood.

In this study, we determined concentrations of ^{99}Tc in surface soil samples. Also ^{137}Cs was used as a comparative indicator for discussion of the sources of ^{99}Tc, because the fission yields from ^{235}U and ^{239}Pu are about the same (ca. 6%) for the two isotopes, and the behavior and distribution of ^{137}Cs in the environment is reasonably well understood. The activity ratio of ^{99}Tc/^{137}Cs was calculated to understand Tc mobility in the soil environment.

EXPERIMENTAL

Sample Pretreatment. Twenty-one soil samples were collected from the surface layer (< 20 cm) of paddy fields, upland fields and other areas (i.e., forests and orchards) in Japan (Figure 1). Table 1 lists the sampling sites and soil types. To
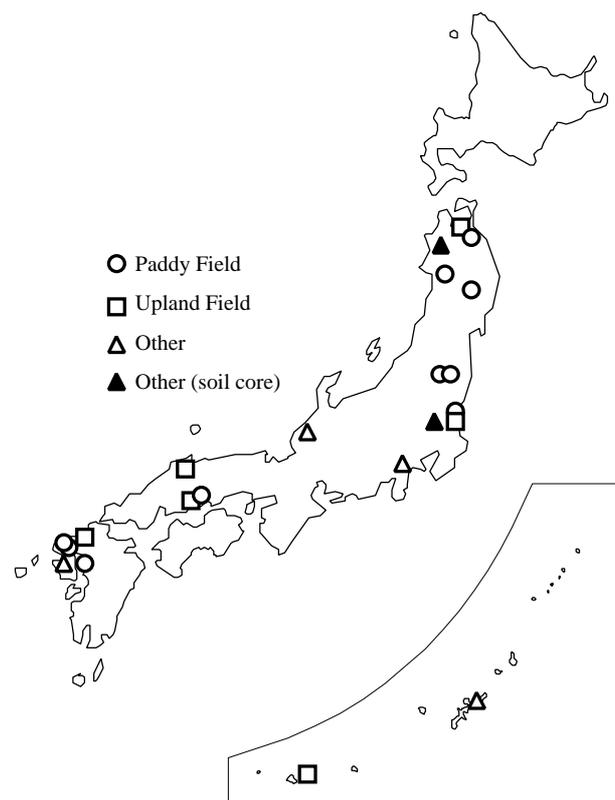

Figure 1. Soil collection sites in Japan.

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TABLE 1: Sampling Sites, Types, and Some Characteristics of the Soil Samples

Sample code	Sampling site Prefecture/City or Town	Soil type (FAO/UNESCO)	pH	CEC (meq/100g)	AEC (meq/100g)	Ex.-K$_2$O (g/kg)	Ex.-CaO (g/kg)	Act.-Al (g/kg)	Act.-Fe (g/kg)	Total-C (%)	Org.-C (%)	Total-N (%)
P-15	Ibaraki / Mito	Fluvisols	5.47	9.0	<0.05	0.14	1.18	4.5	9.5	2.40	2.16	0.26
P-16	Hiroshima / Fukuyama	Fluvisols	5.95	11.0	<0.05	0.24	1.76	0.9	4.2	1.46	1.37	0.15
P-18	Saga / Imari	Cambisols	6.06	16.0	<0.05	0.14	2.59	2.4	7.4	2.24	2.06	0.23
P-22	Saga / Kawazoe	Fluvisols	6.42	23.5	<0.05	0.22	4.56	1.6	6.0	2.42	2.00	0.19
P-28	Akita / Omagari	Fluvisols	5.92	18.4	<0.05	0.30	3.60	2.2	4.2	1.87	1.84	0.16
P-30	Aomori / Misawa	Andosol	6.70	36.5	0.10	0.19	2.89	39.8	22.0	9.48	8.92	0.59
P-32	Iwate / Morioka	Andosol	6.28	27.4	0.17	0.16	2.88	65.1	36.0	6.66	6.64	0.56
P-36	Fukushima / Koriyama	Cambisols	6.31	9.6	0.82	0.08	1.92	3.6	9.8	0.32	0.32	0.05
P-38	Fukushima / Koriyama	Fluvisols	6.36	15.4	0.10	0.19	2.42	2.8	12.8	1.54	1.42	0.15
F-21	Hiroshima / Fukuyama	Cambisols	5.36	6.0	0.09	0.19	0.79	0.9	1.5	0.90	0.82	0.10
F-23	Saga / Chinzei	Cambisols	5.98	14.4	0.36	0.83	1.74	4.0	5.7	1.26	1.15	0.12
F-31	Ibaraki / Asahi	Andosols	6.49	13.2	0.14	0.57	2.42	43.2	28.3	2.81	2.74	0.25
F-39	Aomori / Kamikita	Andosols	5.73	28.2	0.1	1.32	3.46	30.2	18.0	4.35	4.17	0.4
F-43	Shimane / Yokota	Cambisols	6.01	6.2	0.10	0.23	1.30	0.8	4.6	1.60	1.53	0.13
F-47	Okinawa / Ishigaki	Acrisols	8.29	15.6	0.06	0.27	6.19	5.4	11.7	1.11	1.00	0.13
O-10	Saga / Chinzei	Acrisols	4.72	18.1	0.17	0.42	0.97	4.4	4.5	1.69	1.38	0.17
O-14	Ibaraki / Tsukuba	Andosols	5.14	26.2	0.43	0.28	1.33	36.9	20.5	11.15	10.14	0.26
O-24	Okinawa / Ginoza-son	Acrisols	8.28	15.0	0.31	0.09	3.38	5.9	8.7	0.86	0.79	0.14
O-34	Shizuoka / Gotenba	Andosols	6.16	24.8	0.10	0.31	4.06	37.2	42.0	5.04	5.00	0.46
O-a	Fukui / Katsuyama	–	–	–	–	–	–	–	–	–	–	–
O-b	Akita / Akita	–	–	–	–	–	–	–	–	–	–	–

measure the depth profile of ^{99}Tc in undisturbed soil, two core samples were collected in Tsukuba (O-14) and Akita (O-b) cities. The samples were air-dried and passed through a 2 mm mesh sieve. Some amounts of the air-dried soil was used for the determination of soil characteristics, such as, pH, cation exchange capacity (CEC), anion exchange capacity (AEC), exchangeable-K$_2$O, exchangeable-CaO, active-Al, active-Fe, total C, organic-C, and total-N. The results are listed in Table 1 as well.

A 100 mL (85 – 140 g) portion of each sample was used for ^{137}Cs determination 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. For the ^{99}Tc determination, air-dried samples were incinerated for 8 h at 450°C to decompose organic matter before chemical separation.

Reagents. Nitric acid used was ultrapure-analytical grade (Tama Chemicals, AA-100). Deionized water (>17 MΩ) 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 separation of Tc. The column was pretreated with 5 mL of 8 M HNO$_3$ followed by 10 mL of 0.1 M HNO$_3$.

A standard ^{99}Tc solution available from Amersham (TCZ.44) was used for calibrating ICP-MS. A ^{95m}Tc solution (half-life: 61 d) was used as a yield monitor. It was prepared by irradiation of Nb in a cyclotron to avoid any ^{99}Tc contamination.[9]

Chemical Separation. The separation procedure used for ^{99}Tc determination in soil samples was reported previously,[10] hence, only a brief description of the experimental procedure is given here. Fifty to one hundred g of incinerated soil were thoroughly mixed with a known amount of ^{95m}Tc. Then, Tc was volatilized in a combustion apparatus for 3 h at 1000°C and Tc was collected in two vertical traps, each containing 150 mL of deionized water. After heating was completed, this sample was replaced with another 50 – 100 g batch of the same incinerated soil sample and the combustion procedure was repeated until the accumulated weight of the treated sample was 200 to 300 g. The volume of trap solution was reduced to approximately 200 mL by evaporation on a hot plate at 100°C.

Each solution obtained by the above mentioned extraction procedure was adjusted to 0.1 M HNO$_3$ and passed through a TEVA resin column to separate and concentrate Tc isotopes.[11] 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. Ruthenium present in the sample solution is not effectively retained on the TEVA resin. 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.

Measurement. 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 ^{99}Tc content of the sample solution was then determined by ICP-MS (Yokogawa, PMS-2000) with 180 s counting time at mass 99. Total measurement time was approximately 10 minutes per solution. A ^{99}Tc standard solution (Japan Isotope Association, NH$_4$TcO$_4$ in 0.1% ammonia solution) was used to determine detection efficiency. 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 average radiochemical recovery of ^{95m}Tc from the soil samples was 63 ± 6% by the present method. The instrumental detection limit for ^{99}Tc by ICP-MS was 0.03 mBq/mL of the sample solution which corresponds to 0.014 mBq/g-dry of soil sample under the operational conditions.

RESULTS AND DISCUSSION

Paddy field soils. The data for concentrations of ^{99}Tc and ^{137}Cs in paddy field soils are listed in Table 2. The ranges of ^{99}Tc and ^{137}Cs 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 concentrations of ^{99}Tc in paddy field soils are the same level as those we found previously.[12] Then, the concentration of ^{99}Tc was compared on the basis of several characteristics of the soils. The results are not listed here, but they showed that there is no correlation between ^{99}Tc concentrations and soil characteristics for paddy field soils. This

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TABLE 2: Concentrations of ^{137}Cs and ^{99}Tc in Paddy Field Soils in Japan on a Dry Weight Basis and Activity Ratio of ^{99}Tc to ^{137}Cs

Code	^{137}Cs (Bq/kg) Decay corrected to 2001.1.1	^{99}Tc (mBq/kg)	Activity ratio ^{99}Tc/^{137}Cs ($\times 10^{-3}$)
P-15	2.7 ± 0.3	8.4 ± 1.3	3.2 ± 0.6
P-16	1.4 ± 0.7	6.1 ± 0.5	4.4 ± 2.3
P-18	14.0 ± 0.6	88 ± 15	6.3 ± 1.1
P-22	4.1 ± 0.4	22 ± 3	5.4 ± 0.9
P-28	14.0 ± 0.5	34 ± 5	2.4 ± 0.4
P-30	6.3 ± 0.5	6.8 ± 0.7	1.1 ± 0.1
P-32	8.4 ± 0.5	52 ± 10	6.2 ± 1.3
P-36	1.7 ± 0.2	12 ± 1.7	7.0 ± 1.4
P-38	4.2 ± 0.4	29 ± 4	7.0 ± 1.1

Note) Error shows statistical errors in calculation (1σ).

agrees with our previous results obtained by tracer experiment.[13] We observed that Tc sorption ratios onto soil surface showed no correlation with any soil characteristics after a 3-day contact with the soils. Presumably, immobilization of Tc in soil was mainly controlled by redox conditions and was not affected by soil types.

The activity ratios of ^{99}Tc to ^{137}Cs are given in the last column of Table 2, and they range from 1.1×10^{-3} to 7.0×10^{-3} with an average of $(4.8 \pm 2.1) \times 10^{-3}$. 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 to now arises from fallout. Compared to the theoretical ratio, the activity ratios in the paddy field soils are one order of magnitude higher. However, the activity ratios in paddy field soils of this study are the same order of magnitude or one order of magnitude less than those in undisturbed soils in Japan reported previously as $(1.2 - 39) \times 10^{-3}$.[14–16] The ^{99}Tc/^{137}Cs activity ratio in soil is influenced by several factors: one of them is depositions containing rain and dry fallout. Ehrhardt and Attrep[17] reported that the range of the activity ratio in rain samples which were collected in the U.S.A. was $(0.11 - 2.5) \times 10^{-2}$ during $1961 - 1974$, those were already higher than the theoretical ratio. In Spain, García-León et al.[18] measured similar or higher values of $(0.3 - 12.3) \times 10^{-2}$ in rain samples collected during $1984 - 1987$. These ratios in the deposition samples are higher than those in soils obtained in this study. The activity ratio in atmospheric samples, except samples affected by the Chernobyl accident, seem to increase with time. However, it should be noted that the activity ratios in recent precipitations would not affect those in soil samples, because ^{137}Cs deposited on Japanese soil was derived from fallout of atmospheric nuclear weapons testing and the deposition level which peaked in 1963 had decreased to insignificant levels by the 1990's. The amounts of ^{99}Tc and ^{137}Cs deposited onto Japanese soils for the last two decades are negligible compared to total amounts already present in natural soils. One thing which is hard to explain is where the excess amount of ^{99}Tc comes from. Further studies are necessary to understand the ^{99}Tc behavior in the atmosphere.

The other Tc accumulation mechanisms in paddy fields are also explained by the change of Tc chemical form in soil under a waterlogged condition. The nuclide is expected to be in a soluble form as pertechnetate under an aerobic condition, such as in surface soils and 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.[19] The relatively low redox condition is common in paddy fields during the planting period. Indeed, when we previously did a test using three soils to measure Eh and pH changes with time under the waterlogged condition, the Eh values were 0.36 –

0.48 V and the pH values were $5.8 - 6.3$ just after becoming waterlogged, under which condition Tc should exist as TcO_4^-. Then after a 7-day waterlogged period, although hardly any pH values of the samples changed, the Ehs dropped to ca. 0.2V, which is close to the boundary between water-soluble TcO_4^- and other lower soluble Tc species in the pH-Eh diagram given by Brookins.[5] For a longer waterlogged period, the Ehs would drop near or lower than 0V due to microbial activity.[13] Probably, Tc is transformed from TcO_4^- to a lower oxidation form such as TcO_2, $TcO(OH)_2$, or TcS_2 under a relatively low Eh condition.[5, 20] Sulfides may be formed because H_2S gas can be produced in waterlogged soil when rice plants are growing. These lower oxidation forms of Tc have lower solubility and could possibly be sorbed onto soil. After harvesting rice from paddy fields, the fields are kept dry for the next several months until the next planting season to prevent plant diseases. In our previous radiotracer study, we found that most of the Tc immobilized onto the soil surface was not in a readily soluble form even under aerobic conditions.[21] When Tc was transformed from TcO_4^- to other chemical forms that have a low bioavailability, plants would not absorb Tc in the soil. Thus, ^{99}Tc would accumulate in the paddy field soils.

Although paddy field soils could immobilize global fallout ^{99}Tc that was deposited directly onto them, these relatively high ^{99}Tc concentrations in paddy fields suggest other ^{99}Tc sources. There is a possibility that the paddy field soils had trapped ^{99}Tc not only from deposition, but also from irrigation water through the mechanism as mentioned above. According to Watanabe,[22] the average Japanese paddy field receives 1800 mm 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, though there are no data on ^{99}Tc in water for irrigation.

Upland Field Soils and Other Soils. The data for concentrations of ^{99}Tc and ^{137}Cs in upland field soils and other soils are shown in Table 3. The averages of ^{99}Tc and ^{137}Cs concentrations in upland field soils are 5.9 mBq/kg-dry (range: 4.3 – 7.7 mBq/kg-dry) and 6.3 Bq/kg-dry (range: <1.1 – 7.7 Bq/kg-dry), respectively. Those in other soils are 16.4 mBq/kg-dry (range: 7 – 29 mBq/kg-dry) and 45 Bq/kg-dry (range: <1.1 – 144 Bq/kg-dry), respectively. The concentrations of ^{99}Tc in upland field soils are about one order of magnitude lower than those in paddy field soils but other soils are the same order as in paddy field soils. The activity ratios of ^{99}Tc/^{137}Cs in upland field soils and other soils are $(0.7 - 3.8) \times 10^{-3}$ and $(0.2 - 1.1)$

TABLE 3: Concentrations of ^{137}Cs and ^{99}Tc in Upland Field and Other Soils in Japan on a Dry Weight Basis and Activity Ratio of ^{99}Tc to ^{137}Cs

Code	^{137}Cs (Bq/kg) Decay corrected to 2001.1.1	^{99}Tc (mBq/kg)	Activity ratio ^{99}Tc/^{137}Cs ($\times 10^{-3}$)
Upland field			
F-21	3.4 ± 0.5	4.9 ± 0.5	1.5 ± 0.3
F-23	1.1 ± 0.4	4.3 ± 0.4	3.8 ± 1.4
F-31	3.1 ± 0.4	5.8 ± 0.8	1.9 ± 0.3
F-39	7.7 ± 0.6	5.6 ± 0.4	0.74 ± 0.08
F-43	<1.1	6.9 ± 0.4	–
F-47	2.7 ± 0.5	7.7 ± 1.2	2.9 ± 0.7
Others			
O-10	10.1 ± 0.4	7.0 ± 0.3	0.69 ± 0.04
O-14	56.1 ± 1.2	15.4 ± 0.5	0.27 ± 0.01
O-24	<1.1	12 ± 1.5	–
O-34	19.9 ± 0.8	20 ± 1.6	1.01 ± 0.09
O-a	143.8 ± 1.4	29.2 ± 3.2	0.20 ± 0.02
O-b	37.6 ± 0.4	13.9 ± 0.8	0.37 ± 0.02

Note) Error shows statistical errors in calculation (1σ).

$\times 10^{-3}$, respectively, with the averages of $(2.1\pm1.2) \times 10^{-3}$ and $(5.1\pm3.4) \times 10^{-4}$, respectively. Slightly high correlations $(r>0.5)$ between ^{99}Tc concentrations and some soil properties, such as CEC, act-Fe, total-C, org-C, and total-N, for upland field soils and other soils are found. No correlation appears for the paddy field soils. The relation has not been explained yet, though there was a possible influence from organic matter and microorganisms in the soils.

The average activity ratios found in this study for upland field soils are seven times higher than the theoretical ratio but those for other soils are close to the theoretical one. Among the soils used in this study, the average activity ratio for paddy field soils is the highest. 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.[13] 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 (Kd) of ^{99}Tc in Japanese soil samples generally showed low values,[23, 24] 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 the 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.
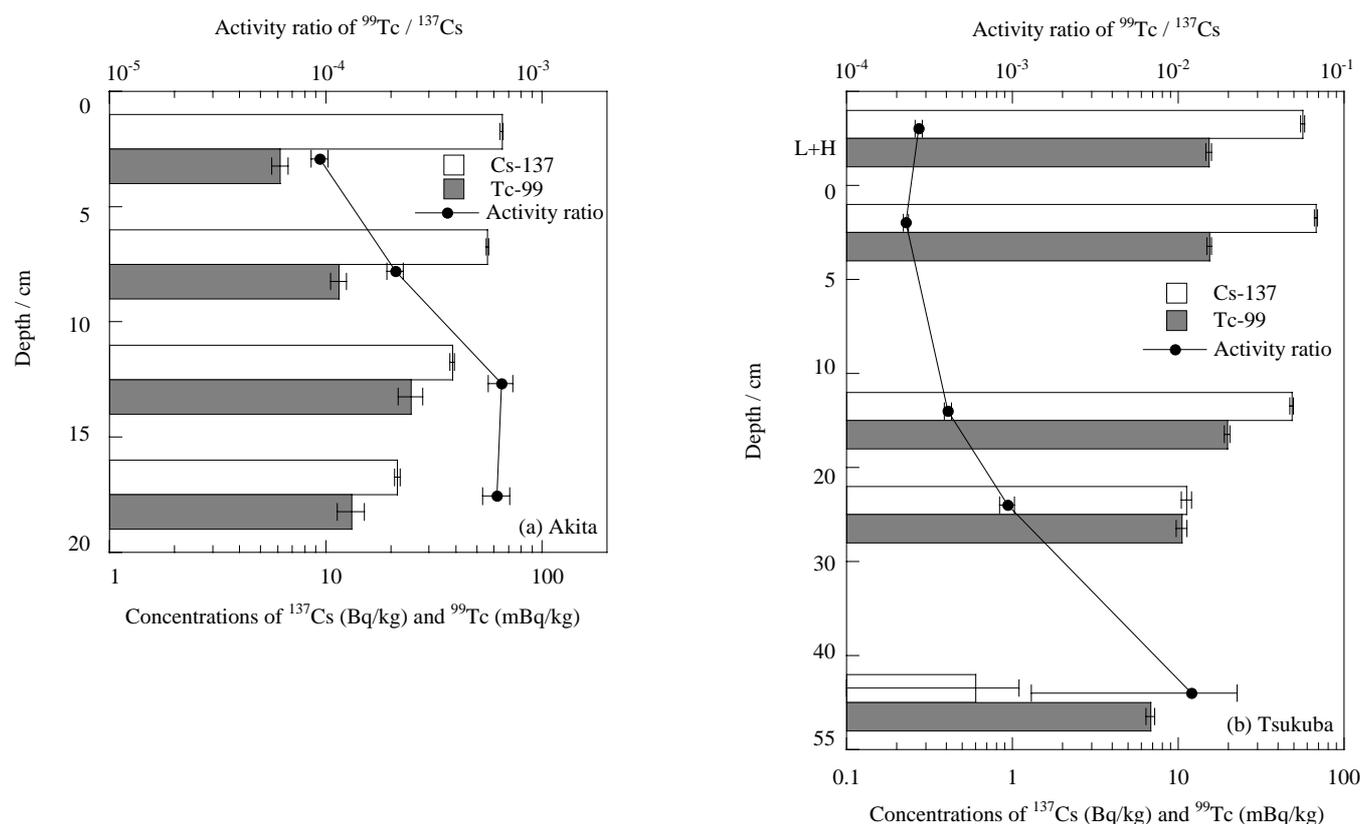
Vertical distributions in undisturbed soils. To know the details of ^{99}Tc and ^{137}Cs behaviors in other soils, 2 soil core samples were used for the measurement of vertical distributions of these radionuclides. The results are shown in Figure 2. Within 20 cm, the average activity ratios in both cores seem to be the same as the theoretical ratio. However, as it is clear from Figure 2 (a), the concentration of ^{137}Cs is highest in the first 5 cm while the highest ^{99}Tc concentration is found in the 10 – 15 cm portion. The same result is found in the Figure 2

(b), and, moreover, ^{99}Tc is determined at a soil depth of 40 – 55cm. ^{99}Tc migrates faster than ^{137}Cs, but the difference is smaller than expected because most of the ^{99}Tc was retained in the 0 – 20 cm portion.

Although local reduction conditions can be seen even in the aerobic surface soil, the mechanisms of Tc sorption onto the soil should not be explained by only redox factor. Some reports suggested that the soil organic fraction would play a role in immobilization of Tc, possibly through sorption by exchange mechanisms, reduction to less soluble forms and complexation.[7, 25] Moreover, Morita et al.[16] reported that there was a relatively good relationship between ^{99}Tc concentration and soil organic matter contents. Also, we found previously that there were high correlations between carbon contents and Tc adsorption rate at an early stage of the contact.[13] Technetium might combine with solid organic matter. As we found in this study, some soil properties would support TcO_4^- transformation into immobilized forms. However, the mechanism of how Tc is accumulated in the surface soil under aerobic conditions is not clear. Our results, at least, lead to a tentative conclusion that more Tc might have been fixed on soil as expected before. Further studies are needed to clarify the phenomenon of ^{99}Tc accumulation in surface soil layer, particularly, in an upland field environment.

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Figure 2. Vertical distributions of ^{99}Tc, ^{137}Cs and the activity ratio of ^{99}Tc/^{137}Cs in undisturbed soil core samples collected in Akita (a) and Tsukuba (b) cities, Japan. Error bar shows statistical error in calculation (1σ).

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