RICE UPTAKE AND LEACHING OF ^{99}TC IN DIFFERENT PADDY SOILS CONTAMINATED ACCORDING TO TWO CONTRASTING SCENARIOS

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Four different paddy soils collected around the Gyeongju nuclear site were treated with ^{99}TcO$_4^-$ solution under the assumption of two contrasting contamination scenarios. Scenario I (SN-I) is for a pre-transplanting deposition of ^{99}Tc followed by plowing, whereas SN-II is for its deposition onto the water surface shortly after transplanting. Rice plants were grown in lysimeters in a greenhouse. Plant uptake of ^{99}Tc was quantified with the TF$_{area}$ (m$^2 \cdot$kg^{-1}-dry). The SN-II TF$_{area}$ values for straws and brown rice, having been generally higher than the SN-I values, were within the ranges of 6.9x10^{-3}~4.1x10^{-2} and 5.2x10^{-6}~7.3x10^{-5}, respectively. Sorption onto clay seems to have decreased ^{99}Tc uptake in SN-I, whereas it may have had an insignificant effect in SN-II. A phenomenon characteristic of submerged paddy soil, i.e., the development of a thin oxic surface layer may have greatly affected the rice uptake of SN-II ^{99}Tc. The surface-water concentrations of ^{99}Tc were much higher in SN-II than in SN-I. For the percolating water, however, the opposite was generally true. At most 1.3% of the applied ^{99}Tc were leached through such percolation. The use of empirical deposition time-dependent TF$_{area}$ values was considered desirable in assessing the radiological impact of a growing-season deposition of ^{99}Tc onto paddy fields.

Keywords: Paddy soil; ^{99}Tc; Contamination scenario; Rice uptake; Leaching

1. INTRODUCTION

Rice is one of the most important food crops in the world [1-3]. It is a staple food crop in many Asian countries, where paddy rice fields occupy a large amount of national land [1,2,4,5]. Paddy fields are flooded with water during almost the entire period from sometime before transplanting rice seedlings until around maturity [1,2,6,7]. If soil is flooded, air supply from the atmosphere remarkably decreases and oxygen rapidly disappears due to the respiration of micro-organisms [6,8]. Under such an anoxic condition, many atom species are reduced and some changes occur in their mobility and phytoavailability [6-9].

It is well known that the most stable chemical form of Tc (technetium) in oxic soils is pertechnetate, TcO$_4^-$, but that Tc is reduced to lower valence-state forms such as TcO$_2$, TcO(OH)$_2$ and TcS$_2$ in anoxic soils [9-11]. TcO$_4^-$ is generally highly soluble and phytoavailable in soil, whereas the solubility of the reduced forms of Tc is very low, and thus they can be hardly absorbed by plants [9,10]. Accordingly, the uptake of soil Tc by paddy rice may be much lower than that by upland crops [12-14]. Nevertheless, the importance of paddy rice as a food crop makes it quite meaningful to produce parameter data for evaluating the uptake of soil Tc by paddy rice.

From an environmental point of view, ^{99}Tc is the most important isotope of Tc owing to a very long half-life and a comparatively high ^{235}U-fission yield [3,12,15,16]. Spent fuels and other radioactive wastes from nuclear installations are often stored permanently in underground repositories. Some failures may occur

in such disposal facilities after a long storage period, leading to a release of long-lived radionuclides into the environment [17,18]. The passage of radionuclides from waste containers into the biosphere through different types of barriers largely depends on the movement of underground water [17,18].

Paddy fields are generally located in lower lands [1] and, thus, they can be comparatively easily affected by underground water [19,20]. In addition, a large amount of underground water often needs to be used for irrigating paddy fields [21]. Therefore, it can be expected that the contamination of paddy fields with the ^{99}Tc released from an underground repository will be much more probable than that for upland fields. As occurred in the Chernobyl accident [3,22], a considerable amount of ^{99}Tc can be released by a severe reactor accident, possibly leading to a paddy field contamination with ^{99}Tc through direct fallout deposition, or indirectly, irrigation using ^{99}Tc-contaminated water.

Rice fields can be contaminated with ^{99}Tc either before or after transplanting rice seedlings. The rice uptake of ^{99}Tc from a pre-transplanting contamination can generally be evaluated using the traditional soil-to-plant transfer factor (TF, dimensionless) defined as the ratio of plant concentration to the soil concentration [23,24]. Such appropriateness of the use of the TF is based on the fact that rice fields are plowed before transplanting. It can be reasonable to assume that the top soil and ^{99}Tc are homogeneously mixed to an effective rooting depth through plowing. In contrast, the ^{99}Tc deposited onto a rice field after transplanting may be retained near the soil surface as rice fields are not plowed during the growing period. To evaluate the ^{99}Tc uptake following such a post-transplanting deposition, it may be appropriate to use the areal deposition-based TF (TF$_{area}$, m$^2 \cdot$kg^{-1}) defined as the ratio of plant concentration to the deposition density [25-27]. Even the uptake from pre-transplanting contamination with plowing can be quantified with the TF$_{area}$ only if the deposition density is known. For paddy rice, a few TF values of Tc are available [12,13,28], whereas almost nothing has been reported about the TF$_{area}$ except for Choi et al. [3]

In the present study, four different paddy soils collected around a nuclear site were labeled with ^{99}Tc in two different ways to cover two contrasting scenarios of the paddy-field contamination [3]. One is an entry of ^{99}Tc into rice fields followed by plowing and transplanting (Scenario I), and the other is an entry of ^{99}Tc into the surface water of flooded rice fields shortly after transplanting (Scenario II). For both scenarios, the rice uptake of ^{99}Tc was quantified with TF$_{area}$. The evolutions of the ^{99}Tc concentrations in the surface water and percolating water were observed to see the possibility of nearby water bodies being contaminated by drainage and leaching. The ^{99}Tc resolved in the surface water may be available for the uptake of ^{99}Tc through the plant base (shoot base) [25,27,29]. The data on the ^{99}Tc concentration in the surface water may be useful in estimating the magnitude of the plant-base uptake from the contaminated surface water. The uptake and leaching experiments were performed by means of lysimeter cultures in a greenhouse.

2. MATERIAL AND METHODS

2.1 Rice Culture in Lysimeters

Experimental soils (S1, S2, S3 and S4) were collected from four drained paddy fields located within a 5 km radius of the Gyeongju nuclear site in South Korea. This site is situated in a near-coastal area in the south-eastern part of the Korean peninsula, accommodating five operating nuclear reactors and a deep geological repository for low and medium level radioactive wastes. The locations of the paddy fields for collecting the soils were 35°45'04"N 129°29'34"E for S1, 35°44'41"N 129°27'46"E for S2, 35°41'35"N 129°28'29"E for S3 and 35°43'31"N 129°26'59"E for S4, and an associated map is given elsewhere [28]. Soil within a depth of about 20 cm was taken in bulk for each field and carried to a garden of the greenhouse. The soils were air-dried in the garden under natural conditions for two weeks. The physicochemical properties of the dried experimental soils are summarized in Table 1.

The lysimeters were made of stainless steel, and were 30 cm wide, 30 cm long, and 40 cm high with a tap for water discharge at the bottom level. They were flooded with tap water 17~18 d after they had been filled with the experimental soils. The filling each lysimeter with soil and the flooding had been made 22 to 23 d and 5 d, respectively, before rice seedlings were transplanted. This filling was done by putting a total of 30.4 kg of dry soil on small broken stones laid

Table 1. Physicochemical Properties of the Four Experimental Soils.

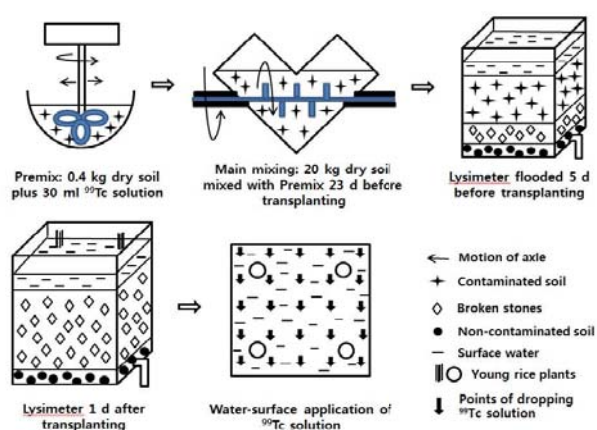| Soil	pH* (1:5)	OM† (%)	CEC‡ (cmol·kg⁻¹)	EC (cmol·kg⁻¹)§			Sand (%)	Silt (%)	Clay (%)	Texture‖
				Ca	Mg	K				
S1	5.5	3.7	14.5	4.5	1.9	0.3	50.6	38.4	11.0	L
S2	5.1	4.2	27.7	10.9	3.9	0.5	27.1	57.5	15.4	SiL
S3	5.6	3.1	17.0	6.1	3.2	0.5	38.7	34.4	26.9	L
S4	5.1	4.9	43.5	20.5	7.9	0.9	34.2	40.6	25.2	L

* 10 g dry soil vs. 50 mL distilled water
† Organic matter
‡ Cation exchange capacity
§ Exchangeable cation
‖ L: loam, SiL: silt loam.

Fig. 1. Schematic diagrams of the ⁹⁹Tc application for two different scenarios of paddy-field contamination. Upper row: Scenario-I for pre-transplanting contamination, Lower row: Scenario-II for post-transplanting contamination.

to a height of 4 cm from the bottom. The depth of the soil was settled to be about 28~29 cm after it was flooded. Fermented compost and slaked lime were supplied at doses of 90 and 10 g per lysimeter, respectively, and mixed with the topsoil, 2 d before transplanting. On the next day, 3.5 g of a composite fertilizer (N : P : K = 21% : 17% : 17%) was given to each lysimeter and mixed with the topsoil again. A total of 20 lysimeters were prepared. Of them, 16 were used to cover four experimental soils, two contamination scenarios and duplicate treatments, and the rest was used for controls.

On June 4, rice seedlings (*Oryza sativa* L. cv. Junam-byeo) were transplanted to the lysimeters at a density of 4 hills per lysimeter with 4 seedlings per hill. The lysimeters continued to be flooded until 119 d after transplanting except for an intermission for a week from 42 d after transplanting. The depth of the

surface water in a flooded lysimeter was around 2-7 cm during the irrigation period. Additional fertilizations were made with the composite fertilizer at a dose of 1.3 g per lysimeter each time 12, 51 and 84 d after transplanting. For ventilation, all windows and doors of the greenhouse were opened as widely as possible and powered fans were operated from the roof. Ear emergence started on August 13, i.e., 70 d after transplanting.

2.2 Application of ⁹⁹Tc

Two different ways of contaminating paddy soil with ⁹⁹Tc were adopted for two contrasting scenarios (I and II) of the paddy-field contamination. Figure 1 shows schematically the procedures of the ⁹⁹Tc application for the two scenarios.

For Scenario I (SN-I), 20 kg of dry soil per lysimeter was thoroughly mixed with a radioactive premix for 10 min using a V-shaped mixing machine (V-MIXER, KUKJE SCIENCE) 23 d before transplanting. The premix was made 3 d earlier by mixing 0.4 kg of dry soil and 30 ml of a ⁹⁹Tc working solution (247 kBq·ml⁻¹) using a semi-sphere-shaped mixer (Fig. 1). The working solution was made by diluting 40 ml of a purchased ⁹⁹Tc solution (148 MBq of ⁹⁹Tc as NH₄TcO₄ in H₂O, Eckert & Ziegler Isotope Products) with distilled water by a factor of 25. The mixture from the mixing machine was immediately added to 10 kg of unlabeled dry soil already put on the broken stones. This finally gave a lysimeter a total of 30.4 kg of dry soil. The depth of the labeled soil was estimated to be about 19-20 cm under the condition of flooding. For Scenario II (SN-II), 1 ml of the working solution was dropped to each of 25 points evenly distributed on the water surface of the flooded

lysimeter using a micropipette 1 d after transplanting. Each of the SN-II lysimeters was already filled with 30.4 kg of unlabeled dry soil.

2.3 Sampling and Sample Treatments

In the case of the surface water, the first sampling was made 6 d and 3 hr after the contamination of the lysimeter water in SN-I and SN-II, respectively, followed by seven more samplings at an interval of 4-28 d. In SN-I, the lysimeter water was regarded to be contaminated on the day when the lysimeter first became flooded, i.e., 5 d before transplanting. For each contaminated lysimeter, 20 ml of the surface water was taken using a micropipette. A composite water sample was made for each soil by putting the duplicate 20 ml samples into one bottle. For the control, 40 ml of surface water was taken from each of the four lysimeters. The surface water was pipetted at four or eight points per lysimeter with 5 ml taken at each point.

The percolating water was discharged almost every week from 14 and 8 d after the contamination of the lysimeter water in SN-I and SN-II, respectively, i.e., from 9 d after transplanting in both. For the weekly discharge, 3.4 L of the percolating water was drained from each lysimeter through the tap to simulate a daily water percolation of 5.5 mm, which is considered to be an average for Korean rice fields during the irrigation period [7,27]. Aliquots of the duplicate discharges from the contaminated lysimeters were put into one bottle to make a composite sample for each soil. The composite samples were made with one-week discharges for the first five weeks and with two-week discharges for the following 10 weeks. For the controls, 100 ml of water was taken from each weekly discharge and stored for analysis.

Rice plants were harvested 132 d after transplanting. They were cut at about 10 cm above the soil surface and divided into the ears and straws. These plant materials were dried in a glasshouse for a month. Grains were separated from the dried ears and gently ground in a mortar to obtain hulled rice, that is, brown rice. The dried straws were cut into small pieces using scissors. The brown rice and straw pieces were ground using a mortar and a mixer to obtain powder samples. The powder samples of brown rice were soaked in ammonium hydroxide (28% NH_3, SHOWA) for 1 d and evaporated to dryness at 70℃. The ammonia-treated samples of brown rice were incinerated for 12 hr in a muffle furnace (DF-4A, DAEHEUNG SCIENCE). The temperature inside the furnace was controlled to stay at 250℃ for 1 hr, increase from 250℃ to 500℃ over 5 hr and then stay at 500℃ for 6 hr. This procedure for incineration is based on the method by Wigley et al. [30]. They reported little loss of ^{99}Tc from ammonia-treated plant samples during their incineration at 450-550℃.

2.4 Analysis of [99]Tc Activity

The analysis of ^{99}Tc activity was performed by means of a total beta counting method [14,16,28]. For the surface and percolating waters, 10 ml of each composite sample was put in a stainless-steel planchet and evaporated to dryness under an infrared lamp. For the plant materials, 200 mg of ash (brown rice) or 100 mg of powder (straws) samples and a proper amount of distilled water were put in a stainless-steel planchet, uniformly mixed using a small glass rod, and then dried under the lamp. The dried ash and powder planchets were rewet with a collodion solution and dried again. An efficiency calibration was performed using the planchets prepared for different kinds of control samples in the same ways as mentioned above with known amounts of ^{99}Tc activity added. The efficiencies measured were in the ranges of 19.3~20.1% for brown rice, 22.0~23.1% for straws, 33.8~38.4% for surface water and 28.2~32.3% for percolating water. The efficiencies applied for the activity calculation were 19.6, 22.5, 35.0 and 30.0% for brown rice, straws, surface water and percolating water, respectively.

All of the prepared planchets were mounted in a low background alpha and beta counter (LB-5100 II, OXFORD-Tennelec), and the beta rays were counted for 0.5~1.0 hr. The net counts of the non-control and efficiency planchets were obtained by subtracting the counts of the corresponding control planchets from the total counts.

2.5 Calculation and Reporting

The values of areal transfer factor (TF_{area}, $m^2 \cdot kg^{-1}$) were calculated as follows [16,26]:

$$TF_{area} = \frac{\text{Concentraion of } [99]\text{Tc in mature rice plant}(Bq \cdot kg^{-1}\text{-dry})}{\text{Areal deposition density of } [99]\text{Tc}(Bq \cdot m^{-2})}$$

(1)

They were reported as the means and standard deviations for duplicate measurements. ANOVAs (analyses

Table 2. F Values Acquired from the ANOVA of the TF$_{area}$ Values for Each Compartment of Mature Rice Plants.

Source of variation	Degree of freedom	F value[*]	
		Brown rice	Straws
Contamination scenario (C)	1	74.85[##]	112.8[##]
Soil (S)	3	5.683[#]	3.738[†]
Interaction (CxS)	3	22.11[##]	18.69[##]
Treatment	7	22.60[##]	25.73[##]
Error	8	-	-

[*] One and two number signs mean that the values are statistically significant at P<0.05 and P<0.01, respectively.

[†] statistically significant at 0.05<p<0.1.

of variance) were performed for the produced TF$_{area}$ data, and Duncan's multiple range tests were followed when the F values for the treatments (different combinations of soil and scenario) were statistically significant [31,32]. Log-transformed data of the TF$_{area}$ values were used in the statistical analyses because of large variations in the original values from different treatments.

The activity level in water was expressed as the relative concentration (Rw, m^2·L^{-1}), which was determined as follows:

$$Rw = \frac{\text{Concentraion of } ^{99}\text{Tc in water (Bq·L}^{-1})}{\text{Areal deposition density of } ^{99}\text{Tc (Bq·m}^{-2})} \quad (2)$$

In both equations, the denominators were 7,400 kBq·m^{-2} and 6,167 kBq·m^{-2} for SN-I and SN-II, respectively.

3. RESULTS AND DISCUSSIONS

3.1 TF$_{area}$ Values of ^{99}Tc in SN-I and SN-II

Table 2 presents the results of the ANOVAs. For both brown rice and straws, the F values indicate statistically highly significant differences (p < 0.01) in the TF$_{area}$ value between the contamination scenarios, and among the treatments (different combinations of soil and scenario). A significant difference (p < 0.05) among the soils (Table 1) was indicated for brown rice, whereas the statistical significance of the F value was not high enough for straws (0.05 < p < 0.1). Highly significant interactions (p < 0.01) between the contamination scenario and soil were indicated in both compartments. Owing to these interactions, the tendencies of the difference among the soils differed distinctly depending on the contamination scenarios as explained below.
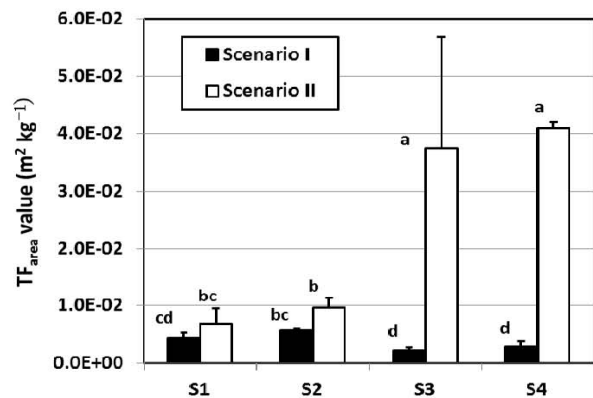
Fig. 2. TF$_{area}$ values of ^{99}Tc for rice straws in four different soils contaminated in two contrasting scenarios. Duncan's multiple-range test indicated significant differences (p < 0.01 or p < 0.05) between any two means that are marked with no common alphabet letter.
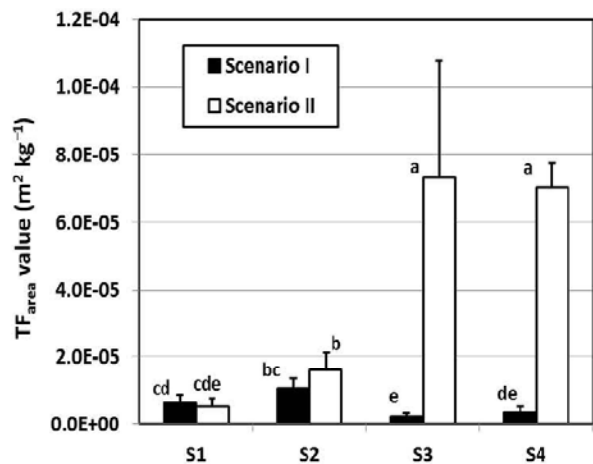
Fig. 3. TF$_{area}$ values of ^{99}Tc for brown rice in four different soils contaminated in two contrasting scenarios. Duncan's multiple-range test indicated significant differences (p < 0.01 or p < 0.05) between any two means that are marked with no common alphabet letter.

Figures 2 and 3 show the TF$_{area}$ values of ^{99}Tc for the straws and brown rice, respectively, in four differ-

ent paddy soils contaminated for two contrasting scenarios [3], and the results of Duncan's multiple range tests. The rice uptake of ^{99}Tc in SN-I can also be quantified with the traditional dimensionless transfer factor defined as the concentration ratio between plant and soil [28]. The values for straws were 2-3 orders of magnitude higher than those for brown rice, indicating that the mobility of absorbed ^{99}Tc from the vegetative part to the seed is very low. A similar trend had been found for rice by Yanagisawa et al. [12] and Yanagisawa and Muramatsu [13], and for other crops by Choi et al. [16], Denys et al. [33] and Wildung et al. [34]. These differences in the TF_{area} value of ^{99}Tc between straw and brown rice are much greater than those for radiostrontium [27], whose mobility in plants is also known to be very low.

In S3 and S4 soils, the TF_{area} values from SN-II were statistically significantly higher than those from SN-I, whereas in S1 and S2 soils, no statistically significant difference was found between the two scenarios. The significantly enhanced TF_{area} values in SN-II, as compared with SN-I, may be mainly attributable to a substantial increase in the contact of the root surface with ^{99}Tc in the form of TcO_4^{-1}, which is highly mobile and phytoavailable in soil [9,10]. Although paddy soil in the plowed zone quickly becomes anoxic after flooding, the topmost soil remains oxic owing to a continuous supply of oxygen from the surface water [1,6,7]. The thickness of the oxic layer may increase with time possibly up to 1~2 cm in general [1,7]. Therefore, a considerable amount of ^{99}Tc applied to the water surface after transplanting (SN-II) could stay in a thin layer of the surface soil in the form of TcO_4^{-1} for a comparatively long time. In addition, the distribution density of rice roots is known to be higher in the near-surface soil zone than in the deeper soil zone [6].

The above-mentioned conditions concerning the soil, radionuclide, and plants possibly combined to significantly increase the ^{99}Tc uptake in S3 and S4 soils. In S1 and S2 soils, however, an increase in the ^{99}Tc uptake in SN-II as compared with SN-I was insignificant. These different responses to the change in scenario may be explained with the thickness of the oxic zone developed. It may have been much greater in S3 and S4 soils than in S1 and S2 soils for some reason. The thicker the oxic zone is, the wider and longer the contact of rice roots with TcO_4^{-1} can be. In

addition, the roots may have been more densely distributed in the oxic zones of S3 and S4 soils than of S1 and S2 soils. The thickness of the oxic zone and the distribution density of the roots in there may depend on various soil parameters possibly including clay content. This possibility with clay is based on the fact that both S3 and S4 soils were considerably higher in clay than S1 and S2 soils (Table 1). Clay in mineral soils has a large and charged surface area so it plays important roles in many physical and chemical processes occurring in them[35]. However, the effects of clay on the thickness of, and the root distribution in, the oxic zone remain to be examined through further experiments. On the other hand, rice plants can also absorb ions through the plant bases, which are submerged in the surface water [25,27,29]. The plant-base uptake of ^{99}Tc may have been much higher in SN-II than in SN-I because of the direct application of TcO_4^{-} to the surface water in SN-II. This can partly account for the enhanced TF_{area} values in SN-II as compared with SN-I.

Owing to such different responses to the change in scenario, S3 and S4 soils produced significantly higher TF_{area} values than S1 and S2 soils in SN-II, whereas, in SN-I, the latter produced higher values than the former in general. This generally higher uptake of the SN-I ^{99}Tc in S1 and S2 soils than in S3 and S4 soils can be mainly attributed to the difference in the clay content (Table 1). Sheppard et al. [36] found in their experiment with various mineral soils that the soil sorption of Tc under anaerobic conditions tended to increase as the clay content increased. In contrast, they observed little sorption of Tc under aerobic conditions. In SN-I, therefore, the lower clay contents could lead to higher phytoavailability of soil ^{99}Tc, most of which possibly existed in the anoxic zone owing to the mixing of soil and the radioactive solution. In SN-II, however, the effect of the lower clay contents is likely to have been masked by the above-mentioned conditions. In addition, the presumed greater thickness of, and presumed higher root density in, the oxic zones of S3 and S4 soils seem not to have been very effective in enhancing the TF_{area} value for SN-I. This can be because the concentrations of SN-I ^{99}Tc in the oxic zones were likely quite low due to the activity dispersion over the mixing depth

According to Sheppard et al. [36], a higher soil pH and higher organic matter content can also give rise to

a higher soil sorption of Tc, and thus, lower root up-take in anoxic mineral soils. The differences in soil pH and organic matter content among the experimental soils cannot consistently explain those in the SN-I TF_{area} value. This may imply that the soil clay played a critical role in the differences in the SN-I TF_{area} value among the soils. Nevertheless, the statistically significantly higher SN-I TF_{area} values in S2 soil as compared with S3 and S4 soils occurred possibly by the combined effect of low clay content and comparatively low pH.

3.2 [99]Tc Concentrations in the Surface and Percolating Waters

Figures 4~7 show the changes of the ^{99}Tc concentrations in the surface and percolating waters with the elapsed time after water contamination in the two contrasting scenarios. The initial surface-water concentrations in SN-I can be reasonably considered to have been zero.

The surface-water concentrations of SN-I [99]Tc [3] as a whole increased rapidly for the first 5 d, followed by rather rapid decreases for about 10 d, and then much slower decreases during the remaining period (Fig. 4). In contrast, the surface-water concentrations of ^{99}Tc in SN-II [3] tended to decrease very rapidly for about 10 d from the beginning, followed by much slower decreases for about two months (Fig. 5). They remained rather constant during the last 1~2 months. Until the end of the flooding, the ^{99}Tc concentrations in the surface water decreased by factors of 50~800, and 2000~5000, depending on the soils in SN-I and SN-II,
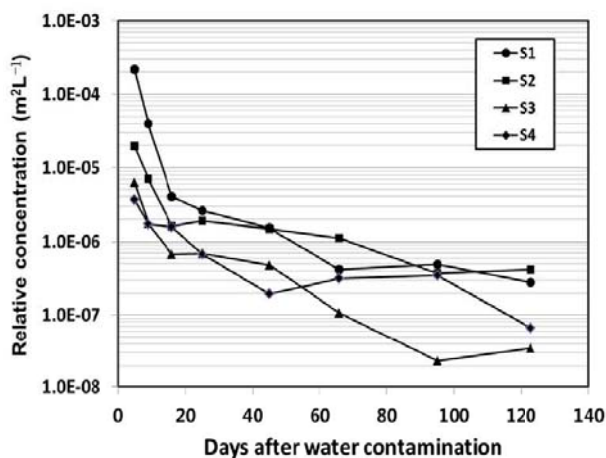

Fig. 5. Time courses of the relative concentrations of ^{99}Tc in the surface waters over four different soils in the SN-II lysimeters.

Fig. 6. Time courses of the relative concentrations of ^{99}Tc in the percolating waters discharged from the SN-I lysimeters of four different soils.

Fig. 7. Time courses of the relative concentrations of ^{99}Tc in the percolating waters discharged from the SN-II lysimeters of four different soils.

Fig. 4. Time courses of the relative concentrations of ^{99}Tc in the surface waters over four different soils in the SN-I lysimeters.
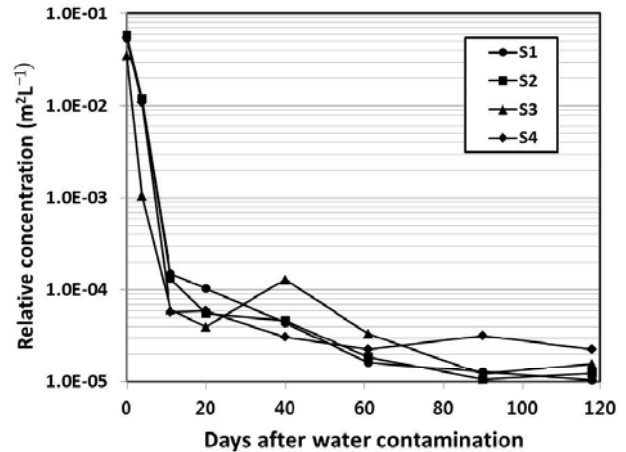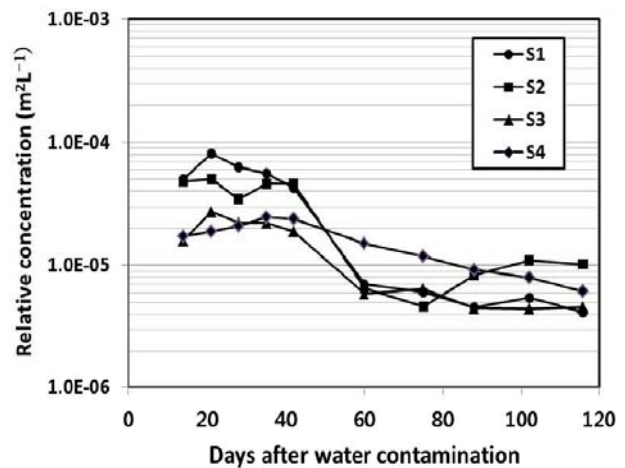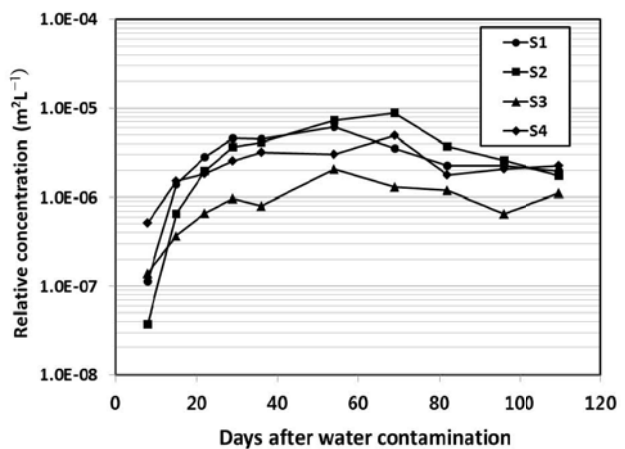
respectively. The temporal changes in the surface-water concentrations of ^{99}Tc in SN-II may indicate that, for a substantial decontamination of an SN-II paddy field, it needs to be drained within a couple of days after it is contaminated.

In SN-I, it is likely that the ^{99}TcO$_4^{-1}$ in oxic soil rapidly diffused out to the surface water immediately after flooding and that the supply of ^{99}Tc from the submerged soil decreased more and more as the soil became anoxic. Under anaerobic conditions, ^{99}TcO$_4^{-1}$ is reduced to insoluble and indiffusible forms of ^{99}Tc such as ^{99}TcO$_2$, ^{99}TcO(OH)$_2$ and ^{99}TcS$_2$ [9-11]. Small amounts of ^{99}TcO$_4^{-1}$ possibly having existed in the upper thin oxic layers of submerged soil may have rapidly disappeared owing to underground migration and plant uptake. In contrast, the rapid decrease from the beginning in SN-II may be attributable to a rapid diffusion of ^{99}TcO$_4^{-1}$ from the surface water into the soil-pore water. Subsequently, much retarded but generally continuing decreases occurred probably owing to a much slower diffusion into the underlying soil and plant-base uptake. At around 2~3 months after water contamination, the SN-II ^{99}Tc concentration in the surface water seems to have almost reached equilibrium with that in the pore water of the surface-soil zone.

The ^{99}Tc concentrations in the surface water varied with soils by factors of up to 60 in SN-I, whereas the corresponding variation in SN-II was generally much lower. In SN-I, S1 and S2 soils had higher surface-water concentrations than S3 and S4 soils in general. This may be a result of an increased supply of ^{99}Tc due likely to its lower soil sorption related to the lower clay contents in S1 and S2 soils as compared with S3 and S4 soils. Such an effect seems to have been insignificant in SN-II possibly because of the surface-water application of ^{99}Tc and its high distribution density in the oxic soil zone. The surface-water concentrations of the SN-II ^{99}Tc were higher than those of the SN-I ^{99}Tc by factors of several tens to several thousand depending on the soils and times after water contamination. The much higher surface-water concentrations in SN-II as compared with SN-I may have led to much higher plant-base uptake of ^{99}Tc in SN-II.

In SN-I, the percolating-water concentrations of ^{99}Tc as a whole tended to increase for the first 1~3 weeks, and then tended to gradually decrease until about a month before the end of water discharge (Fig. 6). In contrast, the percolating-water concentrations of the SN-II ^{99}Tc increased rapidly for about the first 30 d and slowly for about the following 30~40 d in general (Fig. 7). If the discharge had started shortly after the lysimeters had been flooded, there should have been rapid increases for a couple of weeks even in SN-I from the beginning. In this case, the surface-water concentrations of the SN-I ^{99}Tc may be slightly different from those shown in Fig. 3. For the last 40~50 d, the SN-II ^{99}Tc concentrations in the percolating water as a whole tended to slowly decrease.

The SN-I ^{99}TcO$_4^{-1}$ in the pore water of the mixed soil zone are likely to have rapidly moved down in the beginning after flooding. As the soils became anoxic, however, the downward movement of the SN-I ^{99}Tc seems to have been retarded more and more. Similarly, the SN-II ^{99}TcO$_4^{-1}$ having diffused into the pore water from the surface water may have rapidly moved down before the soils became anoxic, causing such rapid early-phase increases in the percolating-water concentrations. It is likely that, as the supply of ^{99}Tc from the surface water decreased and the soils became anoxic, much retarded increases, and subsequently, gradual decreases, occurred in the percolating-water concentrations of the SN-II ^{99}Tc.

In SN-I, the percolating-water concentrations were rather similar to the surface-water concentrations, whereas in SN-II, the former was 1~5 orders of magnitude lower than the latter depending on the soils and times. In contrast to the surface-water concentrations, the percolating-water concentrations were on the whole an order of magnitude higher in SN-I than in SN-II depending on the soils and times. This may be because SN-I ^{99}Tc had shorter distances to the discharge point owing to its being mixed with soil to a depth of about 20 cm.

Table 3 shows the fractions of the total applied ^{99}Tc activity that were leached out of the lysimeters through the percolating water during the whole periods of water discharge. About 5-10 times, depending on the soils, higher fractions were leached out in SN-I than in SN-II as indicated by the differences in its percolating-water concentrations. The leaching of contaminants from a paddy field can lead to a secondary contamination of nearby aquifers. The secondary contamination of nearby aquifers through the leaching of ^{99}Tc can be expected to be mostly inconsiderable in view of such low percentages of leaching (Table 3).

Table 3. Percent Leaching of the [99]Tc Activity from the Lysimeters of Four Different Soils through Percolating Water.

Contamination scenario	Percent leaching in different soils (%)			
	S1	S2	S3	S4
SN-I[*]	1.31	1.16	0.60	0.78
SN-II[†]	0.17	0.22	0.06	0.14

[*] The topsoil was homogeneously mixed with a $^{99}TcO_4^-$ solution 23 d before transplanting.

[†] A $^{99}TcO_4^-$ solution was applied onto the water surface 1 d after transplanting.

However, it needs to be noted that a severe pre-transplanting paddy field contamination with ^{99}Tc can cause a substantial secondary contamination of nearby aquifers. Not only in SN-I but also in SN-II, the fractions were higher in S1 and S2 soils than in S3 and S4 soils. This may imply that the leaching of ^{99}Tc, unlike its plant uptake, was decreased by soil clay even in SN-II. To be leached out, the SN-II ^{99}Tc as well as the SN-I ^{99}Tc had to pass through the anoxic soil zone, which is likely to have been comparatively thickly formed under the thin oxic layer [1,7]. The rate of this passage may greatly depend on the clay content of soil because ^{99}Tc is readily sorbed onto clay minerals under anaerobic conditions.

3.3 Implications in Food-Chain Dose Assessment

In most of the food-chain dose assessment models, radionuclide concentrations in the edible parts of the food crops are estimated using the soil-to-plant transfer factor (TF, dimensionless) defined as the ratio of plant concentration to soil concentration [23-26,37-39]. As mentioned above, the TF is applicable to the agricultural fields that are plowed after a radionuclide deposition [23,24]. Accordingly, its use is appropriate for the normal operation of nuclear facilities and an accidental deposition that precedes plowing. An extension of the use to an accidental deposition that occurs in the growing season is inappropriate because farmland is not plowed during plant growth [16,26,27]. In dynamic food-chain models, however, TF values are generally used for predicting radionuclide concentrations in food crops even after an acute growing-season deposition [38,39]. This use of TF values is accompanied by the assumption that plant uptake of radionuclides increases proportionally with an increase in the uptake duration (time from deposition to harvest) or in the plant biomass during uptake.

According to such an assumption, an SN-I deposition of some activity leads to a higher uptake than any SN-II deposition of the same activity provided decay-corrections are made. An opposite was found in the present study, which can be explained through two reasons [26,27,41]. One is that the use of TF is physically irrelevant for a growing-season deposition because the deposited activity is to be retained near the soil surface without being mixed with topsoil by plowing. The other is that plant uptake may greatly depend on the physiological activity and developmental stage of a food crop around the time of deposition rather than simply on the uptake duration or biomass increase. As a solution to these problems, the application of TF_{area} to an acute growing-season deposition can be considered [16,26,27]. An accidental deposition can occur at any time during plant growth. Therefore, experimentally obtained deposition-time dependent TF_{area} values may be greatly helpful in estimating the radionuclide concentrations in food crops after an acute growing-season deposition [27,40]. In the present study, only one deposition time was tested for the growing-season deposition. Further experiments need to be carried out for depositions at many different growth stages.

The SN-II TF_{area} values were significantly variable according to the soils. Soil in every field is likely to have its own physicochemical properties. Even in a field, soil properties may be considerably different from place to place. It can be expected that an accidental deposition affects simultaneously a number of fields in a region. It is impractical to establish a food-chain model that estimates radionuclide uptake in a particular field using TF_{area} data specific to the field. Therefore, it is necessary that TF_{area} values representative of a whole region or country should be determined for use in food-chain dose assessment models [41]. According to the IAEA [24], the geometric means of TF_{area} values from different soils can be used as a representative value. Table 4 shows the geometric means and geometric standard deviations of the TF_{area} values from the four different soils. Depending on the purpose of the assessment, the representative value

Table 4. Geometric Means (GMs) and Geometric Standard Deviations (GSDs) for the TF_{area} Values in the Four Different Soils.

Contamination scenario	Plant compartment	GM (Bq·kg-dry^{-1})	GSD
SN-I*	Brown rice	4.8×10^{-6}	1.9
	Straws	3.6×10^{-3}	1.5
SN-II†	Brown rice	2.6×10^{-5}	3.6
	Straws	1.8×10^{-2}	2.5

* The topsoil was homogeneously mixed with a ^{99}TcO$_4^-$ solution 23 d before transplanting.
† A ^{99}TcO$_4^-$ solution was applied onto the water surface 1 d after transplanting.

may need to be increased in relation to the statistical deviation. The SN-I TF_{area} values can be changed into TF values (dimensionless) by being multiplied by the effective soil density (kg-dry·m^{-2}) defined as the dry weight of the effective root-zone soil per unit area of farmland. In the present study, the effective soil density can be calculated to be 227 kg·m^{-2} (20.4 kg / (0.3 m x 0.3 m)). The representative TF values as geometric means have been reported elsewhere [28]. In view of the variability of the TF_{area} value with the soils, additional TF_{area} data need to be produced in many other paddy soils to reduce the uncertainty in the representative TF_{area} values.

From the next year following an acute growing-season deposition, the estimation of soil-to-plant transfer of radionuclides can be made using appropriate TF values because the contaminated farmland is plowed before planting. For this estimation, the soil concentrations of radionuclides need to be determined considering the previous activity loss in the effective root-zone soil due to plant uptake and downward migration. The present results indicate that the first-year losses of ^{99}Tc activity in the effective root zone of paddy soils following an SN-II deposition may be at most 5% given 0.4~1.0 kg-dry·m^{-2} as the yield of rice straws [42]. This estimation was based on the sum of the activity removal by rice plants and that by percolating water. For an SN-I deposition, the loss can be estimated to be much lower than 5% in general.

It is likely that rice straws were responsible for almost all of the activity removal by rice plants. The markedly lower TF_{area} values for brown rice than for straws indicate that the activity removal by hulled rice seeds (brown rice) was inconsiderable. Experimental data reported by Yanagisawa and Muramatsu [13] can make it possible to estimate that the TF value of ^{99}Tc for the chaffs of paddy rice was several times lower

than that for the straws. In addition, the dry yield of rice chaffs is around five times lower than that of rice straws [6,7]. These conditions may mean that the activity removal by rice chaffs was also insignificant as compared with that by rice straws. The activity loss due to ^{99}Tc removal by rice plants in the second year can be expected to be lower than in the first year in view of the lower TF_{area} values in SN-I (plowed soil) than in SN-II. Paddy fields are usually drained and air-dried after harvest, and resultantly the upper soil become oxic again [1,11]. According to Tagami and Uchida [11], however, the Tc once reduced and immobilized in paddy soil would hardly be re-oxidized and re-mobilized during the draining season. Therefore, the total loss of ^{99}Tc activity in paddy soils may generally be disregarded in a short-term dose assessment. In a long-term assessment, however, it may be desirable to consider the loss to avoid an unnecessary overestimation.

4. CONCLUSIONS

TF_{area} (m^2·kg^{-1}) values of ^{99}Tc for rice straws were markedly higher than those for brown rice, indicating a very low mobility of absorbed ^{99}Tc to the seed. The TF_{area} values in four different paddy soils as a whole were higher for the ^{99}Tc deposited onto the surface water shortly after transplanting (Scenario II: SN-II) than for the ^{99}Tc mixed with soil to a plowing depth before transplanting (Scenario I: SN-I). This increased uptake in SN-II, where most of the applied ^{99}Tc may have been retained near the soil surface for a considerable time, is mainly attributable to an increased contact of rice roots, which develop heavily there, with phytoavailable ^{99}Tc.

The ^{99}Tc concentrations in the surface water follow-

ing the SN-II deposition were much higher than those following the SN-I deposition, possibly leading to an increased plant-base uptake of ^{99}Tc. Larger fractions of the applied ^{99}Tc were leached out via percolating water after the SN-I deposition than after the SN-II deposition. However, these fractions were at most 1.3%, implying that the leaching of ^{99}Tc out of contaminated paddy fields would seldom result in a severe secondary contamination of the nearby aquifer.

It was indicated that sorption of ^{99}Tc onto clay minerals may have efficiently decreased the rice uptake of ^{99}Tc from the SN-I paddy soils, in which most of the activity likely existed in the anoxic zone formed after flooding. In contrast, the development of a thin oxic upper soil-layer caused by a continuous oxygen supply from the surface water was presumed to possibly have a great effect on the rice uptake of SN-II ^{99}Tc. The greater the thickness of the oxic layer, the wider and longer the contacts of rice roots with oxidized and highly phytoavailable ^{99}Tc (^{99}TcO$_4^{-1}$) may be. The two soils highest in clay content had the lowest TF$_{area}$ values in SN-I but the highest values in SN-II, possibly suggesting a positive effect of clay on the thickness of the oxic layer.

The present results show that the use of TF values (dimensionless) for assessing a growing-season deposition, which is a widely adopted practice in dynamic food-chain models, is inappropriate. An applicable alternative may be the use of empirical TF$_{area}$ values measured for several different times during the growing season. The geometric means of the TF$_{area}$ values in the four soils are proposed as representative values for temporary use in estimating the concentration of ^{99}Tc in rice following its pre-transplanting deposition and deposition shortly after transplanting. From the next year following a growing-season deposition of ^{99}Tc onto paddy fields, appropriate TF values can be used with attention to the loss of soil activity due to plant uptake and underground migration. It appears that such activity loss may need to be considered in a long-term assessment to avoid unnecessary overestimations.

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