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Tumbleweed and Cheatgrass Uptake of ^{99}Tc from Five Hanford Soils

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January 1977

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TUMBLEWEED AND CHEATGRASS UPTAKE OF ^{99}Tc
FROM FIVE HANFORD PROJECT SOILS*

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SUMMARY

The accumulation of technetium (Tc) by tumbleweed and cheatgrass was measured for five Hanford Project soils at the initial soil concentration of 1.0 pg/g of ^{99}Tc traced by $^{95\text{m}}\text{Tc}$ at one, two, and three months' harvest times. Tc was added to the soil as pertechnetate, the chemical form likely to predominate in aerobic terrestrial environments. Uptake of Tc at the three months' harvest time ranged from 23 to 82% and 10 to 69% of the added Tc for tumbleweed and cheatgrass species, respectively. The soil order of percent uptake by tumbleweed was Lickskillet < Burbank < Rupert < Warden < Ritzville. Shoot concentrations of ^{99}Tc ranged from 0.06 to 0.33 and from 0.05 to 0.36 ng/g for tumbleweed and cheatgrass, respectively. Shoot concentration generally decreased with increasing time of harvest. This may result from the rapid depletion of soil Tc concentration following plant uptake. Concentration ratios were calculated based upon the estimated average soil concentration during each harvest period. CR values ranged from 76 to 390 and from 54 to 421 for tumbleweed and cheatgrass, respectively. CR values were generally constant with increasing harvest time except for the Lickskillet soil which decreased from the first and second to the third month for both tumbleweed and cheatgrass. No definitive explanation of this result was found; however, some possibilities for this effect are discussed. In a separate experiment, tracer $^{95\text{m}}\text{Tc}$ was increased in the Burbank and Rupert soils by a tracer activity level factor of 50 over that used in the primary experiment. Good agreement was found when comparing the percent uptake values, shoot concentrations, and CR values between high and low $^{95\text{m}}\text{Tc}$ tracer concentrations.

for both soils. This demonstrated that ^{95m}Tc was an effective tracer for the ^{99}Tc and that the results were not influenced by either Tc toxicity or radiation effects.

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TUMBLEWEED AND CHEATGRASS UPTAKE
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INTRODUCTION

Technetium-99 (^{99}Tc), a low energy beta emitter (0.29 Mev E_{max}) with a half-life of 2.12×10^5 years is produced by the spontaneous fission of ^{238}U in nature and by ^{239}Pu and ^{235}U in nuclear reactors (Campbell, 1961). ^{99}Tc has an approximate fission yield of 6.1% from ^{235}U and 6.4% from ^{239}Pu . Nuclear fuel reprocessing plants can therefore be expected to encounter large quantities of ^{99}Tc ; Purex process raffinates, for example, have been estimated to contain about 41 mg/l of ^{99}Tc (Boyd, 1959, Campbell, 1961).

Although Tc can exist in various valence states from I to VII, Tc (VII) and Tc(IV) predominate in natural systems (Anders, 1960). The most stable chemical species in slightly acid, neutral, or basic aqueous solution in equilibrium with the atmosphere is TcO_4^- [Tc(VIII)] (Pourbaix, 1966). TcO_4^- can be slowly converted to the Tc(IV) oxidation state in the presence of reducing materials and by the thiocyanate ion, hydrochloric acid, anion exchange resins, organic impurities, and some organic solvents. In the presence of reducing agents in basic solution, Tc(IV) hydrolyzes to form insoluble TcO_2 which precipitates.

However, being a soft β emitter, ^{99}Tc is difficult to measure in environmental samples, and only limited data are available. Technetium-99 measured

in 13 rain samples in Texas, probably resulting from world-wide atmospheric testing of nuclear explosives, ranged from 0.14×10^{-2} - 1.7×10^{-2} pCi/l (Attrep et al., 1971). Assuming an average 20 in/yr rainfall over a 10 yr period, and total soil retention would result in a soil concentration of approximately 10^{-4} - 10^{-6} pCi/g. A recent report of Golchert and Sedlet (1969) found that 80% of 150 surface water analyses were below their detection limit for the analysis (0.5 pCi/l). The concentration of the remainder ranged from 0.5 - 49.4 pCi/l with an average of 4.6 pCi/l. Factors contributing to the higher Tc levels in 20% of the surface waters have not been evaluated.

A recent study of Tc mobility in soils showed that, under aerobic conditions over the short term, TcO_4^- was soluble, highly mobile, and sorbed in significant quantities only in high organic matter, low pH soils (Wildung et al., 1974b). This suggested that Tc may be available for accumulation by plants. Gast (1975) reported that Tc was almost totally "sorbed" by several high organic matter Minnesota soils. Sorption in these soils was at relatively high soil concentrations of 3×10^1 - 3×10^3 pCi/g, was several weeks to complete, and was independent of solution concentration of Tc. Gast suggested that Tc precipitated as the heptasulfide (Tc_2S_7). An equally plausible explanation is that Tc(VII) may have been slowly reduced by organic matter or microbial action to Tc(IV) and precipitated as TcO_2 or TcS_2 . In addition, some Tc may have been incorporated into microbial components.

Plant uptake of ^{99}Tc by soybeans and wheat was measured by Wildung et al., (1974a, 1976) and Cataldo et al., (1976). CR values as high as 1,000 were found. Gast (1975) also found high CR values for wheat (600-1150) even in the soils that "sorbed" Tc in long-term experiments. The objective of the present study was to obtain ^{99}Tc plant uptake data for typical plant species and representative soils from the Hanford Project.

MATERIALS AND METHODS

The plants used in the study were tumbleweed (Salsola kali) and cheatgrass (Bromus tectorum). Both tumbleweed and cheatgrass are introduced weeds which are well adapted to an arid climate. Tumbleweed, a deep-rooted plant, readily invades man disturbed sites where competition with native species is reduced on the Hanford Project. Cheatgrass, a shallow-rooted annual is ubiquitous on the Hanford Project, and being considered for revegetation of man-disturbed areas.

Five soils were used in the study to represent the range of soils found on the Hanford Project. The profiles of these soils were described by Hajek (1966). Chemical and physical soil properties are described in Table 1.

Plant uptake was measured using ^{99}Tc traced by $^{95\text{m}}\text{Tc}$, a gamma emitter that is detectable at several orders of magnitude lower solution concentration than is ^{99}Tc . The soils were amended to obtain a final ^{99}Tc concentration of 1.0 pg/g (1.7×10^{-2} pCi/g) of oven-dry soil. This concentration was chosen to be based on the maximum estimated environmental concentrations from fallout (Attrep et al., 1971) $^{95\text{m}}\text{Tc}$ was also amended to two soils at a concentration of 2.2×10^{-4} $\mu\text{Ci/g}$ $^{95\text{m}}\text{Tc}$ to determine if any radiation or toxicity effects occurred in the experiment as a result of the tracer addition. This activity level resulted in an increase of total Tc in the soil of about 47% to 1.47 pg/g.

Table 1. Properties of soil samples

Soil	Texture Class	Silt	Clay	Cation Exchange Capacity	pH	Organic Carbon
		%	%	meq100 g	units	%
Rupert	Loamy sand	8.5	7.4	~ 5.	6.8	0.42
Burbank	Loamy sand	17.9	4.0	5.5	7.0	0.52
Ritzville	Silt loam	43.9	12.5	14.4	6.2	0.54
Warden	Silt loam	37.6	8.5	13.4	5.7	0.63
Lickskillet	Loam	41.5	11.1	23.7	6.3	1.8

Approximately 4,400 g of oven-dry soil were quartered from a large sample of each soil type. Fifteen ml of solution containing the spikes were added to the 500 g subsample and thoroughly mixed by hand with a spatula. Sufficient water was previously added to the remaining 3,900 g of soil and mixed with a spatula to bring the soil moisture content to approximately 3%. Both the subsample and 3,900 g of soil were added to a V-blender and mixed for a minimum of two hours. Upon removal from the V-blender, sufficient water was added to the soil to bring the moisture content to about 13%, 13%, 21%, 23%, and 29% on an oven-dry basis for the Burbank, Rupert, Ritzville, Warden, and Licksillet soils, respectively. These moisture contents were selected to approximate the mid-points of available moisture for the respective soil textural types. The thoroughness of mixing by this technique was previously demonstrated with ^{85}Sr and ^{134}Cs (Routson, 1975).

One kg of soil was packed into a quart ice cream carton lined with a plastic bag. Ten tumbleweed or cheatgrass seeds were planted into the surface of the soil and a 2 cm layer (160 g) of coarse (No. 8 grit) distilled water-washed sand was added to cover the seeds and reduce evaporation. Four replicates of each treatment and a control were prepared and placed in a growth chamber (20 °C day and 12 °C night temperatures, 14 hr photoperiod, ambient humidity). Seedlings were thinned to three and four plants per pot for the cheatgrass and tumbleweed treatments, respectively, and irrigated on Monday, Wednesday, and Friday afternoons with distilled water to maintain soil moisture near the above percentages by weighing.

Tc removed from the system by thinning was negligible. Plants were grown for three months with one plant being harvested at one, two and three month intervals. In the tumbleweed treatment, plants were fertilized during the growing period with NH_4NO_3 solution added with the irrigation water. The total amount of N added was $84 \mu\text{g/g/soil}$. The harvest schedule for cheatgrass was the same as tumbleweed except that two plants were harvested the first month.

Above-ground plant material was harvested by parting the coarse sand and cutting the plants at the soil surface. The samples were placed in preweighed counting tubes and were wet-counted on a 400 channel analyzer with four inch NaI well crystal detector to obtain the activity per g of plant material. Plant tissue was subsequently dried in a forced draft oven at 60°C for 24 hr and weighed. Concentration ratios were determined for the tumbleweed and cheatgrass shoots. The concentration ratio (CR) is defined as

$$\text{CR} = \frac{\text{ng } ^{99}\text{Tc/g oven-dry plant}}{\text{ng } ^{99}\text{Tc/g oven-dry soil}}$$

Soil Tc concentrations for a given growth period were determined by averaging the estimated concentrations at the beginning and ending of each growth period. For example, the soil concentration for the one-month growth period was estimated by averaging the initial soil Tc concentration with the estimated soil concentration at one month. The soil concentration at one month was estimated by subtracting the estimated quantity of Tc in the plant from the initial quantity in the soil. The estimated Tc quantity in the plant was determined by multiplying the measured quantity of Tc in the one-month harvested plant by two and three for cheatgrass and tumble-

weed, respectively, since one-half and one-third of the plants were harvested at one-month for cheatgrass and tumbleweed treatments, respectively. In the case of most amended radionuclides, plant uptake from the soil removes a maximum of a few percent which tends not to limit uptake. Thus, since the soil concentration essentially remains constant throughout a single growth cycle experiment, the CR can be calculated using the added soil value. However, in the case of Tc, uptake from the soil is significant, which may limit uptake. Thus, it was necessary to estimate the soil concentration of Tc, using the above method to calculate the CR values at the one, two, and three month harvest times.

RESULTS AND DISCUSSIONS

Table 2 gives the shoot concentration of ^{99}Tc and concentration ratios calculated for tumbleweed grown on five Hanford soils for one, two, and three months. The order of uptake based upon percent uptake from soils was Lickskillet < Burbank < Rupert < Warden < Ritzville and ranged from 23-82% at the three month's harvest time. Percent uptake at one and two months harvest times, although only estimates based on the assumption that the unharvested plants are the same weight and activity as the harvested plants, shows that a large portion of the total uptake occurs in the first ($\sim 75\%$) and second months ($\sim 95\%$). Tumbleweed shoot concentration for these soils ranged from 0.065-0.33 ng/g and generally decreased from one month to the two and three month harvest times. This concentration decrease with increasing growth time is the reverse of that found for Sr and Cs (Routson, 1975). In the case of Sr and Cs, the percentage of uptake from the soil is small and the pool of these elements in the soil remains constant, never limiting uptake. In the case of Tc, uptake from the soil is large, reducing the soil pool which may limit plant uptake.

CR values for tumbleweed using Hanford soils, ranged from 76 to 390. Except for the Lickskillet soil, the CR values for all soils at the three harvest times are reasonably constant. This suggests that the reduction in plant Tc concentration observed during the latter two months resulted from a marked reduction of soil Tc following the rapid uptake of Tc during the first month. The lower CR values found with the Lickskillet soil during

Table 2. Plant uptake of ^{99}Tc by tumbleweed shoots from five Hanford soils traced by $2.2 \times 10^{-4} \mu\text{Ci/g}$ of $^{95\text{m}}\text{Tc}$ at one, two, and three months harvest times.

Soil	Uptake in Shoots			Shoot Concentration			Concentration Ratio ¹		
	Month			Month			Month		
	One	Two	Three	One	Two	Three	One	Two	Three
	-----%-----			-----ng/g-----					
Rupert	32	48	45	0.33 ± 0.02^2	0.22 ± 0.01	0.19 ± 0.001	357	342	315
Burbank	23	28	34	0.29 ± 0.01	0.19 ± 0.008	0.16 ± 0.005	225	232	213
Ritzville	73	81	82	0.22 ± 0.01	0.093 ± 0.005	0.078 ± 0.004	314	368	390
Warden	29	44	46	0.17 ± 0.01	0.11 ± 0.004	0.10 ± 0.004	183	155	169
Lickskillet	18	23	23	0.13 ± 0.01	0.087 ± 0.004	0.065 ± 0.003	127	99	76

¹CR = ng/g in the shoot divided by ng/g in the soil.

² $\bar{x} \pm \text{SD}$ (N = 4)

the latter two months may have resulted from a change of Tc to a form which is less available for plant uptake. This change in Tc form may be related to relatively high organic matter content of Lickskillet compared to the other soils studied. In fact, Wildung et al., (1974a) demonstrated that pertechnetate sorption by soils representing a broad range in properties, was a function of soil organic matter content and pH. Gast (1975) found that several Minnesota soils tended to sorb Tc, apparently because these soils were high in organic matter. Reduction of Tc to the IV valence state and precipitation as TcO_2 or TcS_2 by organic matter or microbial processes is one possible mechanism which may explain the reduced availability of Tc in both the Lickskillet and other high organic matter soils. Other factors which could affect the availability of Tc include complexation and assimilation into microbial tissues. These factors would also be expected to have the greatest effect in high organic matter soils.

Table 3 gives the plant uptake of ^{99}Tc by cheatgrass at one, two, and three month harvest times. The relative soil order to Tc uptake based upon percent uptake by soils was Burbank < Lickskillet < Rupert < Warden < Ritzville and ranged from 10-69% at the three month's harvest time. Cheatgrass shoot concentration ranged from 0.047 to 0.37 ng/g. The decrease in shoot concentration seen with tumbleweed was not as consistent in cheatgrass. There is a decrease in shoot concentration, with time, for plants grown on Ritzville, Warden and Lickskillet, while Burbank and Rupert exhibit some variation. Although the CR values are relatively constant with time of harvest for all soils except Lickskillet

Table 3. Plant uptake of ^{99}Tc by cheatgrass shoots from five Hanford Project soils traced by 2.2×10^{-4} $\mu\text{Ci/g}$ of $^{95\text{m}}\text{Tc}$ at one, two, and three months harvest times.

Soil	Uptake in Shoots			Shoot Concentration			Concentration Ratio ¹		
	Month			Months			Month		
	One	Two	Three	One	Two	Three	One	Two	Three
	-----%-----			-----ng/g-----					
Rupert	19	26	28	0.32 ± 0.009^2	0.36 ± 0.03	0.29 ± 0.02	357	421	357
Burbank	6	8	10	0.12 ± 0.01	0.11 ± 0.003	0.11 ± 0.006	112	104	112
Ritzville	76	77	69	0.17 ± 0.008	0.15 ± 0.03	0.055 ± 0.008	190	192	158
Warden	16	36	37	0.22 ± 0.02	0.14 ± 0.02	0.091 ± 0.01	220	180	130
Lickskillet	18	24	21	0.10 ± 0.004	0.10 ± 0.004	0.047 ± 0.007	103	114	54

¹C = ng/g in the shoot divided by ng/g in the soil.

² $\bar{x} \pm \text{SD}$ (N=4)

there is some variability in the data which results from the variability in shoot concentration.

Table 4 gives the percent uptake, shoot concentration, and CR values for the Burbank and Rupert soils amended with 50-fold excess of ^{95m}Tc . Good agreement was found for the percent uptake values, shoot concentrations, and CR values between the two (Table 2 and Table 4) activity levels which suggests that ^{95m}Tc is an effective tracer for ^{99}Tc . In addition, the increase in radiation dose (50-fold) and soil concentration (50%) indicates that there are no obvious radiation or chemical toxicity effects reflected in the data.

Although there are no literature values available for uptake of Tc by tumbleweed and cheatgrass, data are available for several agricultural plants including soybeans, corn, radishes, oats, barley, and wheat. CR values for the above plants and variety of soils range from 30-1,200, which is in general agreement with the values found in the present study (Gast, 1975; Wildung et al., 1974a; Wildung et al., 1976; Cataldo et al., 1976).

Table 4. Plant uptake of ^{99}Tc by tumbleweed shoots from Burbank and Rupert soils traced by $1.1 \times 10^{-2} \mu\text{Ci/g}$ of $^{95\text{m}}\text{Tc}$ at one, two, and three months harvest times.

Soil	Uptake in Shoots	Shoot Concentration			Concentration Ratio ¹		
		Month			Month		
		One	Two	Three	One	Two	Three
	%	-----ng/g-----					
Rupert	53	0.28 ± 0.01^2	0.18 ± 0.008	0.14 ± 0.03	362	341	294
Burbank	33	0.21 ± 0.01	0.16 ± 0.003	0.13 ± 0.004	248	223	178

¹CR = ng/g in the shoot divided by ng/g in the soil.

² $\bar{x} \pm \text{SD}$ (N=4)

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