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A POTENTIAL MECHANISM FOR UPTAKE AND TOXICITY

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INTRODUCTION

The isotope ^{99}Tc (T 1/2, 2.15×10^5 years) is produced by the spontaneous fission of ^{238}U in nature and by the slow neutron fission of ^{238}U in nuclear reactors. In the latter case, the potential exists for Tc entrance into the environment in emissions from nuclear reactors, nuclear fuel reprocessing plants, and other facilities which use Tc for commercial purposes.

Although published information on Tc uptake by plants was not available when this study was initiated, several factors suggested that Tc availability to plants should be investigated. The most stable chemical species of Tc in aqueous solution is the pertechnetate ion (TcO_4^{-1}), and it is this form which is most likely to enter surface soils. Recent studies by Wildung et al., (1974) indicated that at least over the short term, pertechnetate is soluble and highly mobile in most soils and is sorbed in significant quantities only in high organic matter, low pH soils. Plant availability normally increases with increased ion solubility in soil provided the ion is not discriminated against at the plant root level. Furthermore, the aqueous chemistry of pertechnetate is similar in several respects to permanganate and molybdate, compounds of elements essential in plant nutrition. For these reasons, a study was undertaken to assess the availability of Tc for plant uptake. As a preliminary phase in these studies, experiments were undertaken to

(i) determine if Tc, amended to soil as pertechnetate, was available to plants, (ii) obtain an estimate, for subsequent studies, of the soil concentrations required to result in detectable quantities of Tc in various structural components of the plant, and (iii) determine if anions likely to be present in the soil solution served as competitors for pertechnetate, influencing pertechnetate uptake by plants. Although these studies are preliminary, the results were quite marked and are summarized below.

MATERIALS AND METHODS

In an initial study to determine the uptake and distribution of Tc in plants as a function of time, soybeans (Glycine max cv. Clark) were grown in duplicate (4 plants/pot), using a split-root system of plant culture (Wildung and Garland, 1974), in a Ritzville silt loam (200 g) amended with ^{99}Tc (0.72 and 5.1 $\mu\text{g/g}$ of soil) and $^{95\text{m}}\text{Tc}$ tracer (0.001 $\mu\text{Ci/g}$ soil) as pertechnetate. Controls consisted of plants cultured in an identical manner except in the absence of Tc. On the basis of phenotypic development, plants were harvested 10, 13, and 25 days after emergence. Single plants from each treatment were harvested at 10 and 13 days and the remaining plants were harvested at 25 days. The plants were dissected, oven-dried (60°C), and the ^{99}Tc concentration determined by gamma spectroscopic techniques.

The preliminary studies suggested the need to examine Tc uptake at lower soil Tc concentrations and in larger soil volumes. Therefore, soybean and wheat plants were grown in pots containing Ritzville silt loam (400 g) amended with 0.001, 0.01, 0.1, 1 and 5 μg ^{99}Tc (as TcO_4)/g of soil. Controls

consisted of plants cultured in an identical manner except in the absence of Tc. Plants were harvested 30 days after emergence and analyzed by liquid scintillation techniques.

For preliminary evaluation of the mechanism of Tc accumulation by plants, the rate of uptake of ^{99}Tc by soybeans initially grown 28 days in Hoaglands solution (diluted 1:4, with H_2O) was measured in a pH 6.2, CaCl_2 (0.5m M) solution initially containing ^{99}Tc ($1 \mu\text{M}$) as TcO_4 and various potentially competitive ions ($10 \mu\text{M}$) including NO_3 , CrO_4 , SO_4 , MoO_4 , H_2PO_4 , WO_4 , and IO_4 . Plants were transferred from the nutrient solution to the CaCl_2 solution, and permitted to accumulate Tc for 2 hr. The plants were then removed from the solution, the roots washed three times (15 min) in a pH 6.2, CaCl_2 (0.5m M) solution, oven-dried, and analyzed by liquid scintillation techniques.

RESULTS AND DISCUSSION

Within five days of plant emergence in the split-root system, phenotypic responses to Tc were observed. At this time, the control plants exhibited fully-developed unifoliate leaves while plants growing in soil at both levels of ^{99}Tc exhibited only cotyledon expansion. Within nine days of germination, the terminal buds of all plants growing on treated soil were necrotic and growth appeared to have ceased. After 13 days, plants at the lowest ^{99}Tc level of amendment exhibited adventitious growth. After 25 days, plants were stunted, exhibited irregular leaf blade expansion, and reduced internode elongation.

Over the short growing period, the plants accumulated substantial quantities of the ^{99}Tc applied to soil and ^{99}Tc was mobile in the plant (Table 1). The accumulation ratios for the entire plant ranged from 181

to 473. The highest ^{99}Tc concentrations were present in the cotyledons. Cotyledons exhibited the highest ^{99}Tc concentrations at the 13 and 25 day harvest intervals whereas there was an overall decrease in ^{99}Tc levels in the stems from 13 to 25 days. Due to the toxicity of Tc, leaves did not develop except at the low Tc amendment level and only after 11 days of growth. The ^{99}Tc concentration in these immature leaves was $< 5.0 \mu\text{g/g}$. The formation of leaves at 11 days of growth at the low concentration level and the low concentration of Tc in the leaves relative to the stems likely resulted from a depletion of Tc in the soil and subsequent recovery of the plant from the toxic effects of Tc. Recovery may have been facilitated by the development of a major portion of the root biomass in the nutrient solution employed in the split-root system of plant culture. Roots contained < 1.0 and $25 \mu\text{g Tc/g}$ after 25 days of growth at the low and high soil Tc levels, respectively. At the low concentration, plants accumulated 95% of the Tc in the soil after 10 days of growth.

Due to the plant toxicity of Tc at Tc soil levels of $0.7 \mu\text{g/g}$, the recovery of plants after roots entered the nutrient solution and the depletion of Tc from soil at the low concentration level, a pot experiment was designed to determine Tc uptake at soil Tc levels as low as $0.01 \mu\text{g/g}$ in a sufficiently large soil volume to prevent depletion of Tc from the soil.

The growth characteristics of soybeans in the pot culture system at different soil concentrations are shown in Figure 1. At the $0.01 \mu\text{g/g}$ (or 10 ppb) level, the plants were similar in appearance to the controls. At the 0 and $0.1 \mu\text{g/g}$ level, chlorosis occurred at the leaf margins in the first trifoliolate and there was a browning of the buds and expanding second trifoliolate. At the $1.0 \mu\text{g/g}$ level, only the cotyledons developed. At the $5.0 \mu\text{g/g}$ level, growth ceased three days after emergence.

The growth characteristics of wheat at different soil concentrations are shown in Figure 2. As in the case of soybeans, toxicity symptoms were observed at the 0.1 $\mu\text{g/g}$ level and growth did not occur at the 1.0 and 5.0 $\mu\text{g/g}$ levels.

The uptake and distribution of Tc in soybean and wheat are shown in Table 2. The concentrations of Tc in the various plant tissues increased with soil concentration with highest concentrations in the cotyledon of the soybean and the leaf blade of wheat. A further breakdown of stem and leaf tissues (not shown in this table) showed a gradient in Tc concentration with highest concentrations in the oldest tissue.

The concentration of ^{99}Tc in different plant tissues and the accumulation ratios for the entire plant generally increased with increased soil concentration. This resulted from two phenomena. First, at the low concentration level, where plants appeared healthy, 83% of the Tc was removed from the soil limiting uptake. Secondly, at the higher soil concentration levels, plant yield was reduced limiting tissue dilution. Thus, it would appear that future studies of ^{99}Tc uptake should be directed at soil Tc concentration levels less than 0.01 $\mu\text{g/g}$.

Accumulation ratios for healthy soybean and wheat plants at the 0.01 $\mu\text{g/g}$ level were 138 and 145, respectively. In a recent research progress report, Gast (1975) reported Tc concentration factors for wheat seedlings ranging from 588 to 1,188 depending on soil type. Concentrations of Tc in the tissues of wheat seedlings were in the order of the concentrations found in the present study when grown on soils amended with ^{99}Tc to a level of approximately 1 $\mu\text{g/g}$. Toxic symptoms were not discussed. However, the ^{99}Tc was added to the soil surface in irrigation water at intervals over the 17-day growth period, perhaps reducing toxicity.

Comparatively, reported environmental plant:soil ratios for ^{131}I , also an anion, range from approximately 1×10^{-2} to 1 (Hanson, 1963) and concentration factors in growth chamber studies range from 5×10^{-2} to 609 (Cline and Klepper, 1975) for ^{125}I depending on soil type and plant species.

At the levels of Tc in the tissues, the possibility exists that damage to the growing tip resulted from radiation effects. However, if Tc, as suggested by the high plant affinity for pertechnetate, served as a nutrient analog, chemical toxicity might be a factor. For example, the known functions of Mo in plants are in the processes of nitrate reduction and nitrogen fixation. If Tc replaced Mo as the functional group in the enzymes responsible for nitrate reduction and led to a loss in enzyme function, or N fixation, amino acids would not be available for protein synthesis. The only source of reduced nitrogen in this case would be from that stored in the cotyledons and marked reduction in plant growth might be expected.

An insight into the mechanisms of Tc uptake and toxicity was provided by the anion competition studies. Addition of H_2PO_4 and IO_4 to nutrient solutions markedly reduced uptake of ^{99}Tc added as TcO_4 by both shoots and roots (Table 3). Similarly, SO_4 and CrO_4 reduced ^{99}Tc uptake by the shoots and roots, respectively, but to a lesser extent. It would appear that there is a real potential for Tc to function as a nutrient analog, particularly in the case of H_2PO_2 and SO_4 , which are present in relatively high concentrations in soils and are required in plant nutrition.

Detailed kinetic studies are required to firmly establish an anion as a competitor for a membrane carrier site and initial emphasis is being placed on these ions in kinetic studies now underway. The results of subsequent investigations should provide the basis for explanation of the

marked uptake and toxicity of ^{99}Tc in plants. Furthermore, identification of the principal competitive analogs would also provide a basis for establishment of remedial management practices and soil amendments to minimize ^{99}Tc uptake, should soil contamination occur.

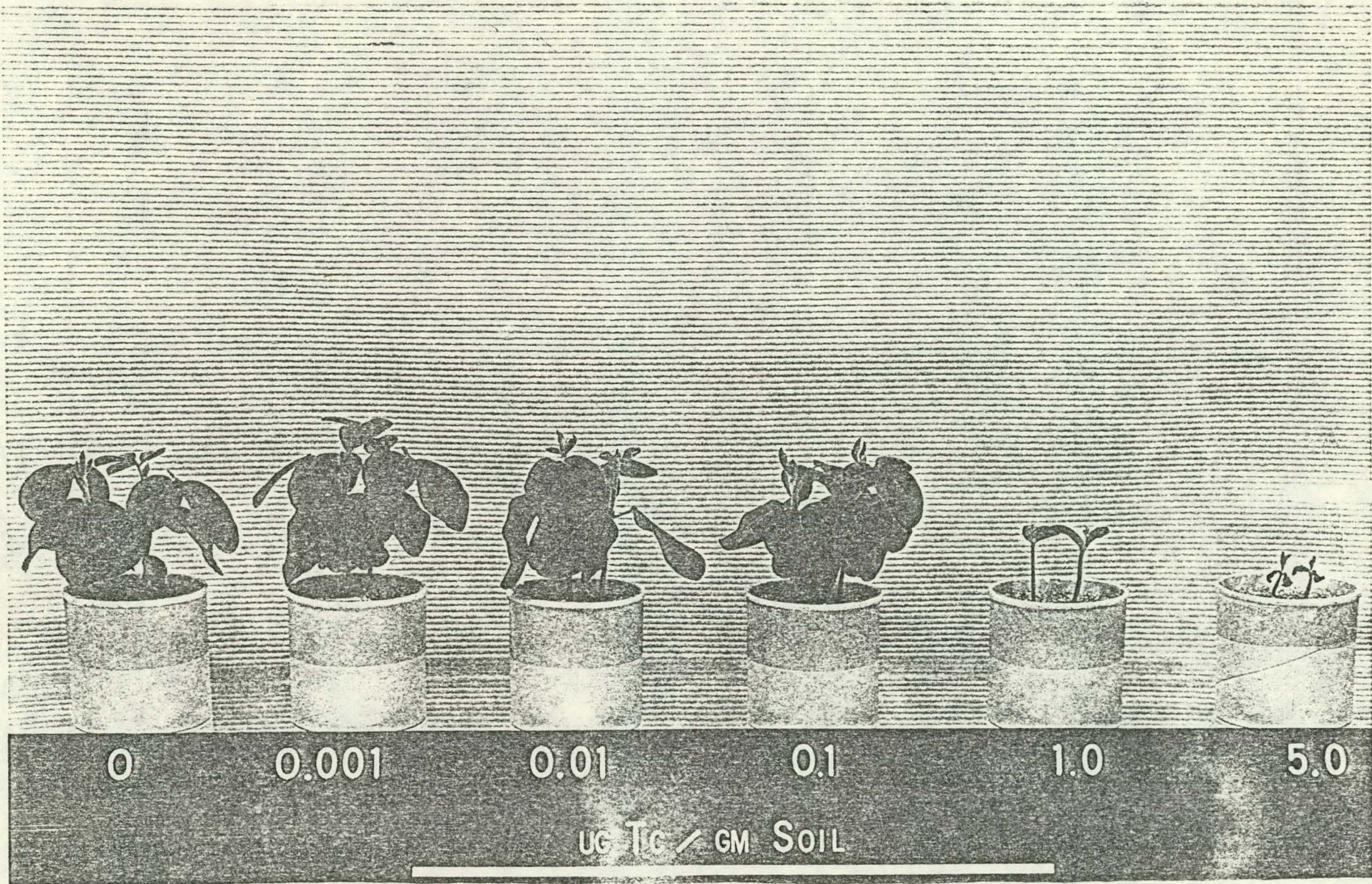


Fig. 1 Growth characteristics of soybeans at different Tc levels in soil

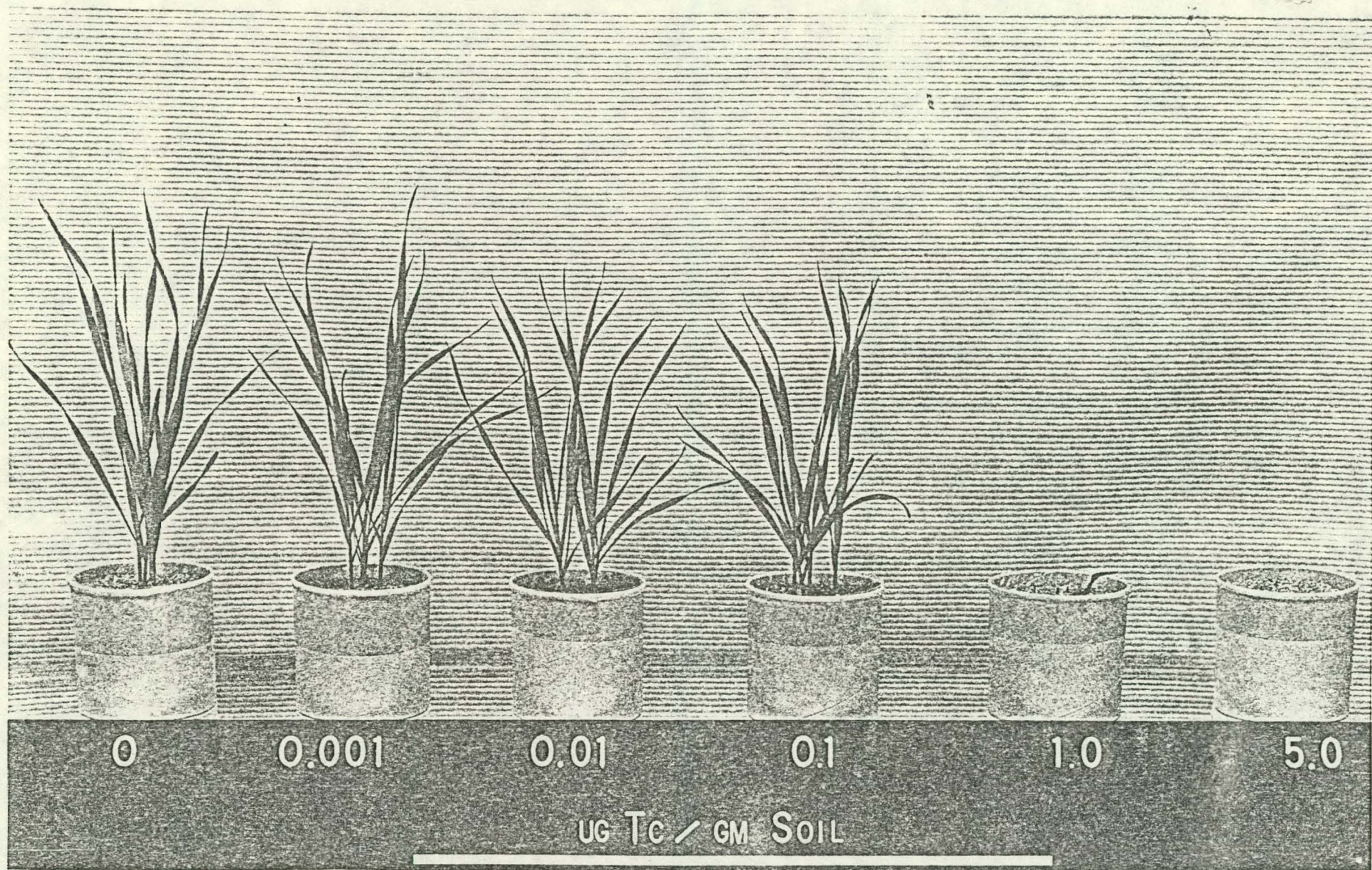


Fig. 7 Growth characteristics of wheat at different Tc levels in soil

Table 1. Distribution of ^{99}Tc in soybean plants during growth on soil at different ^{99}Tc levels.

Harvest Time (Days after Emergence)	Plant Concentration of ^{99}Tc at a Soil Concentration of					Accumulation Ratio - Entire Plant	
	0.73 $\mu\text{g/g}$		Accumulation Ratio - Entire Plant	5.1 $\mu\text{g/g}$			Accumulation Ratio - Entire Plant
	Stems	Cotyledons		Stems	Cotyledons		
----- μg -----		----- μg -----					
10	73	240	256	650	930	181	
13	83	260	282	920	1,400	249	
25	48	670	473	420	1,300	217	

Table 2. Distribution of ^{99}Tc in soybean and wheat plants grown on soil at different ^{99}Tc levels.

Soil ^{99}Tc Concentration	Plant Concentration of Tc^{99*}								Accumulation Ratio - Entire Plant
	Soybeans				Accumulation Ratio - Entire Plant	Wheat			
	Cotyledon	Stem	Leaves	Bud		Blade	Culm	Head	
----- $\mu\text{g/g}$ -----				----- $\mu\text{g/g}$ -----					
0.01	20.7	0.230	0.964	0.0134	138	3.12	0.0235	0.0235	145
0.1	50.4	1.25	8.46	0.225	67.0	39.7	0.130	0.130	173
1.0	484	202	131	132	376	N.G.	N.G.	N.G.	N.G.
5.0	342	640	202	N.G.	380	N.G.	N.G.	N.G.	N.G.

* At the 1.0 and 5.0 $\mu\text{g/g}$ soil Tc level, soybeans were stunted and wheat did not emerge from the soil.

Table 3. Effect of various anions in solution on the uptake of ^{99}Tc by soybeans grown in nutrient culture.

Anion added to solution	^{99}Tc uptake relative to control	
	Shoots	Roots
	----- % -----	
Nitrate	87	99
Molybdate	87	127
Chromate	75	64
Sulfate	68	83
Tungstate	52	80
Dihydrogen phosphate	45	11
Iodate	16	6.7