

Table IV. Degradation of EPTC, Butylate, and Vernolate by EPTC-Adapted Soil with and without the Addition of Dietholate^a

chemicals added	recovered, $\mu\text{g}/\text{mL}$	% degraded
EPTC	0	100
EPTC + dietholate	11.8	59
butylate	0	100
butylate + dietholate	9.5	65
vernolate	0	100
vernolate + dietholate	10.8	62
EPTC control (no soil)	33.2	
butylate control (no soil)	34.6	
vernolate control (no soil)	33.3	

^a 2 g of soil suspended in 10 mL of BMN medium was supplemented with 35 $\mu\text{g}/\text{mL}$ of EPTC, butylate, or vernolate \pm 15 $\mu\text{g}/\text{mL}$ dietholate.

sponding decrease in the amounts of dietholate. It is worth noting that the degradation of dietholate was dependent upon the cell density of the culture.

Effect of Dietholate on EPTC, Butylate, and Vernolate Degradation with EPTC-Adapted Soil. Dietholate inhibited the degradation of the three herbicides almost equally in the EPTC-adapted soil in 64 h (Table IV). The results suggest cross-adaptability of this soil to the three thiocarbamates, similar to the results obtained with the isolate TE1 from the EPTC enrichment culture of this soil.

Results of this study provide insight into the probable mode by which dietholate extends the efficacy of thiocarbamate herbicides in soils. Dietholate inhibits their degradation, thereby prolonging their persistence. The effect lasts until dietholate itself is degraded. This is consistent with the observation that dietholate increased the half-life of EPTC by 2.5-fold (Obrigawitch et al., 1983).

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Registry No. EPTC, 759-94-4; butylate, 2008-41-5; vernolate, 1929-77-7; dietholate, 32345-29-2.

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Absorption, Distribution, and Fate of Neptunium in Plants

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Soil-plant concentration ratios (CR) for neptunium (Np) in bushbean, measured over the range of 5.2×10^{-7} to 4.1 mg of Np/g of soil, are approximately 2 at soil concentrations below 4×10^{-4} mg/g and increase to 12 at higher soil levels. The CR values determined for soybean, bushbean, barley, and alfalfa range from 0.5 to 4 at a soil concentration of 2.6×10^{-6} mg/g. Root absorption by soybean seedlings of Np from solutions containing 7×10^{-7} to 473 mg of Np(V)/mL is generally proportional to concentration but exhibits some saturation in root absorption at higher concentrations. Seed concentrations in bushbean and wheat are a factor of 10 lower than vegetative tissues. Neptunium is transported within the plant in organic complexes containing one or more organic acid residues. Fractionation of plant tissues indicates that Np is substantially more soluble than plutonium, especially in seeds, with approximately 50% of the soluble Np in roots and leaves associated with plant ligands of less than 5000 molecular weight.

The continuing interest in the environmental and biological behavior of the transuranic elements is based on their long half-lives and their potential human toxicity. Studies addressing the transfer of transuranic elements from soils to plants have dealt primarily with plutonium

(Pu) and americium (Am), and only to a limited extent with the behavior of curium (Cm) and neptunium (Np), which are much more biologically available. Investigations have generally documented the transfer of the transuranic elements from soils to plants for specific field environs and assessed uptake over a range of elemental concentrations in soils, with a variety of plant species and growth conditions (Watters et al., 1980). The results of these efforts show that the transfer factors from soil to plant vary widely

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for a specific element, with the relative plant availability of transuranic elements to be $Np > Cm > Am > Pu$ (Watters et al., 1980; Romney et al., 1981a). However, investigations were generally not directed toward identifying the biological processes regulating the short- and long-term availability or chemical fate of these elements.

The characteristics of soils and associated processes that influence soil solubility and plant availability of transuranic elements have been evaluated. For Pu, a wide range in transfer factors have been reported, but correlations between soil physicochemical properties and plant availability have failed to define a predictive relationship (Hanson, 1980). In soil, the Pu(IV) state predominates, and its behavior is controlled by its propensity for hydrolysis and soil sorption of hydrolysis products at environmental pH values ($K_{sp} = 10^{-56}$). Soluble organic complexes of Pu have been implicated in increasing the availability of Pu for plant root absorption (Garland et al., 1981). In comparison, Np may exist in several valence states in soil, including NpO_2^+ , which can be expected to predominate in surface soils. The presence of Np(V) may account for the higher solubility and extractability (pH 8) of Np from a range of soils (Nishita et al., 1981) than Pu, Am, or Cm. The higher solubility of Np may account for its relatively higher plant availability and mobility in food chains (Trabalka and Garten, 1983). Romney et al. (1981a), using seven diverse soils and four plant species, performed pot studies that clearly showed both the influence of soil characteristics on the availability of Np to plants and the differences in uptake potential of different plant species grown in the same soils. However, little is known about the capacity for plant absorption of Np or its fate following uptake, each of which will influence the risk of ingestion to humans.

The present studies address those factors influencing the plant uptake of Np from solutions and soils, the distribution of Np in plant tissues following root absorption, and the chemical fate of Np in plant tissues.

MATERIALS AND METHODS

Plant Culture. Soybean (*Glycine max* cv. Williams), bushbean (*Phaseolus vulgaris* var. Tendergreen), barley (*Hordeum vulgare* var. Briggs), and alfalfa (*Medicago sativa* cv. Ladak) were grown from seed and maintained in either soil or hydroponic culture. Soil studies employed 8.5 × 8.0 cm plastic-lined pots containing 400 g of Ritzville silt loam, uniformly mixed with Np(V) and maintained at 18% moisture (Garland et al., 1981). Hydroponic procedures and nutrient solution composition have been described previously (Cataldo et al., 1983a). The pH of nutrient solutions was adjusted to 5.8, and solutions were changed three times per week. Plants were grown either for 60 days or to maturity in soil studies, and as noted below in hydroponic studies. All plants were maintained in controlled-environment chambers with a 16 h/8 h light cycle (approximately 500 $\mu E m^{-2} s^{-1}$, PAR, at leaf surface), a day/night temperature cycle of 26 °C/22 °C, and at 50% relative humidity.

Soil and Hydroponic Amendments. Stocks of $^{235}Np(V)$ and $^{237}Np(V)$ were prepared in water and amended to soils and nutrient solutions (Garland et al., 1981). Hydroponic studies employed either complete nutrient solution or 0.5 mM $CaCl_2$ (pH 5.8). The nutrient solutions were amended with sufficient Np to achieve concentrations required for concentration-dependent uptake studies. Studies of the chemical fate of Np in tissues were performed following 48-h uptake in complete nutrient solution containing ^{235}Np ($3 \times 10^{-2} \mu g/mL$), followed by 5-day equilibration in the absence of Np.

During the course of the experiments, no sorption of Np to glassware was detectable. In hydroponic studies with Np, intact root systems were immersed in 1 N HNO_3 for 5 min to remove surface-sorbed Np, following the absorption period.

Xylem Exudate Collection and Characterization. Xylem exudates were collected from 28- to 115-day-old hydroponically grown soybean plants (Garland et al., 1981). Exudates were employed either as whole exudates or as chemically separated class fractions. Class fractionation of whole exudates was performed by ion exchange as described previously (Cataldo and Berlyn, 1974). Whole exudates, or class fractions reconstituted to their original exudate volumes, were added to vials containing predried aliquots (50 μL) of Np(V), as NpO_2^+ to yield final Np concentrations of 0.6 mM. This method of addition assured that Np was in the V state when contacted with complexing ligands within the exudates, while avoiding partial dilution of the exudates, which may alter the solution concentration of ligands and subsequent complexation.

Elucidation of Np charge and the association of Np with complexing ligands contained within exudates was studied with electrophoretic methods. Inorganic forms of Np will have markedly different electrophoretic mobility. Neptunium(V), which exists as NpO_2^+ , will migrate to the cathodic pole, while Np(IV), which is prone to rapid hydrolysis and insolubilization, will remain at the origin. Complexes of Np(V or IV) with organic ligands will generally have an overall negative charge and migrate to the anodic pole.

Electrophoresis was performed on Brinkmann (MN 300, 20 × 20 cm × 0.1 mm) cellulose plates. Separations were performed using 0.1 M HEPES buffer, pH 7.5; potential was held constant at 400 V for 30 min. Components were visualized by autoradiography.

Tissue Fractionation. Root and leaf tissues were cut into approximately 5-mm sections, placed into 0.02 M ammonium acetate buffer at pH 6.9 (7.5 mL/g of tissue), and homogenized three times for 45 s each time with a Sorvall Omni-Mixer. The homogenate was centrifuged at 25000g for 15 min, the insoluble pellet was washed once, and the second supernatant solution containing less than 10% of the total solubles was combined with the first supernatant solution (soluble fraction). The insolubles were acid-digested and analyzed for residual Np. The soluble fraction was subjected to ultrafiltration using Amicon Diaflo YM30, YM5, and UM05 membranes, resulting in fractionation of the solubles into >30 000, 30 000–5000, 5000–500, and <500 equivalent molecular weight (MW) fractions (references to globular proteins).

Radioanalysis. Plant tissues and insoluble fractions were dried, acid-digested in concentrated HNO_3 for 12 h, ashed at 450 °C for 12 h, and resuspended in 1 mL of 1 N HNO_3 prior to neptunium analyses. Soluble fractions and solutions were analyzed directly; activity was determined by spectral analysis of the α peak (^{237}Np) or the 0.029-meV γ peak (^{235}Np) on a Beckman 9800 spectrometer. Concentration ratios (CR value) were calculated as micrograms of Np/gram of dry weight shoot tissue divided by micrograms of Np/gram of weight soil.

RESULTS AND DISCUSSION

The accumulation of inorganic elements by plants is controlled first by the concentration of available species in soil solution and subsequently by a series of plant processes that regulate not only root uptake but also transport within the plant and its subsequent chemical behavior. In order to understand the behavior of trans-

uranic elements such as neptunium and plutonium in soils and plants, consideration must be given to those processes governing inorganic plant nutrition. Cataldo and Wildung (1978) compared the plant availability of endogenous and amended trace element pools in soil. It was observed that, for elements such as cobalt, copper, manganese, and molybdenum, concentration ratios (CR values) are 2–3 orders of magnitude lower for total endogenous versus total amended soil pools, even though the former is 1 or more orders of magnitude greater in concentration than the latter. This result indicates that the available or soluble soil pool, and not the total soil pool, will control the rate of plant adsorption and, ultimately, the transfer from soil to plant.

This is clearly the situation with soils amended to similar concentrations with $\text{Pu}(\text{NO}_3)_4$ versus PuDTPA (Vyas and Mistry, 1983). In the case of $\text{Pu}(\text{NO}_3)_4$, Pu undergoes hydrolysis and is sorbed in soil, resulting in a relatively low soluble soil component and a low soil/plant CR value of 10^{-4} . PuDTPA , which is substantially more chemically stable in soil, results in soil/plant CR values of 1. This example serves to demonstrate the importance of soluble and/or biologically available versus total soil pools. Similarly, in the case of Np, increased soil solubility (Nishita et al., 1981) may account for the higher CR values (10^{-4} to 1) observed for Np supplied in the absence of complexing agents (Romney et al., 1981a,b), compared with Pu.

Once solubility constraints in soil are established for an ion, a series of plant processes (Cataldo and Wildung, 1983) regulate the flux to and across the root membrane via adsorptive and absorptive processes, ion compartmentalization within the root (whether for storage, metabolism, or transport), and the subsequent rate of ion transport to the shoot tissues. Each of these processes influences the ultimate CR value. The following studies examine the general behavior of Np with respect to these processes.

Influence of Np Concentration on Plant Uptake. Neptunium-237, because of its low specific activity compared with ^{238}Pu (7.05×10^{-1} versus 17.1 mCi/g), is usually employed experimentally at concentrations (0.4–3 $\mu\text{g/g}$ soil) far in excess of environmental fallout levels (approximately 3×10^{-6} $\mu\text{g/g}$) to permit detection in plants. It was hypothesized that the use of these necessarily high ^{237}Np soil concentrations would influence the observed CR values for plants grown under these conditions. This effect would arise from concentration effects on soil sorption and solubilization processes as well as plant root processes (e.g., saturation of cell wall sorption sites and membrane transport sites). In the present studies, the use of ^{235}Np with its higher specific activity (450 Ci/g, compared with 7×10^{-4} Ci/g for ^{237}Np) permitted evaluation of the influence of Np concentration on plant uptake over a wide range in concentration.

Preliminary studies indicated that Np could be detected in both exudates and shoot tissues of plants within 0.25 to 0.75 h at Np concentrations of 10^{-6} and 14 $\mu\text{g/mL}$ in the root bathing solutions. Uptake was found to be relative linear for up to 5 days at solution concentrations of 0.007 $\mu\text{g/mL}$, but growth of roots and shoots and the need to replenish the bathing solutions to maintain Np concentration, over this extended absorption period, resulted in increased variability in uptake and transfer to shoots with time. In addition, plant toxicity (chlorosis) was observed in plants supplied with Np in concentrations in excess of 14 $\mu\text{g/mL}$ for 48 h. On the basis of these results, hydroponic uptake studies were conducted for 24 h to limit the extent of Np depletion to <10–20% and alleviate any

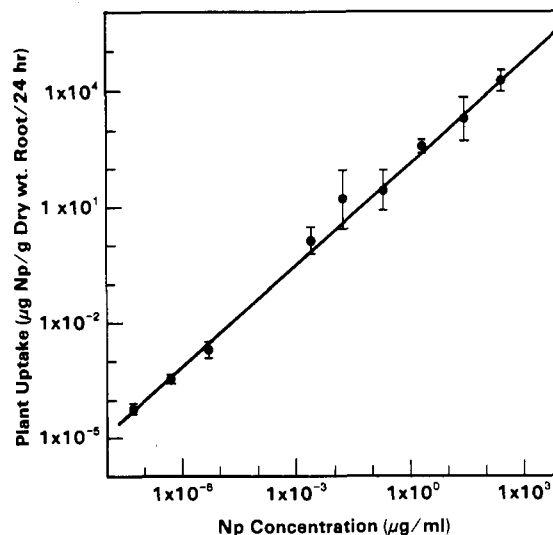


Figure 1. Influence of solution neptunium concentration on absorption of neptunium by soybean plants. Uptake from 0.5 mM CaCl_2 for 24 h.

apparent toxicity problems. Thus, under these conditions the effect of available Np concentration on root absorption and short-term transfer to shoots can be evaluated.

Studies with soybean plants grown hydroponically to allow examination of root processes and control of soluble Np concentrations were undertaken using 11-day-old soybean plants. These were placed in solutions containing 7×10^{-7} to 473 $\mu\text{g Np/mL}$, and whole plant uptake was determined after 24 h.

As shown in Figure 1, uptake rates, based on Np in roots and shoots, increased linearly with increasing Np concentrations. Since solution depletion of Np over the 24-h period was less than 20% of the total supplied, total absorption rates can be assumed to be at steady state over this period. Thus, in the absence of soil-mediating processes or controls on solubility, the potential for root absorption of Np is not limited.

In general, CR values used in dose assessment rely on the concentrations of an element in soils and aboveground tissues. There is ample evidence that rates of ion uptake by roots are not necessarily the same for transfer between roots and shoots. Short-term hydroponic studies with technetium (Cataldo et al., 1983b) showed that 10% of the intact plant technetium was transferred to the shoots at solution concentrations of 0.2 μM , increasing to 22% at solution concentrations of 0.18 μM , and remained constant to 10 μM . Similar 2-h uptake studies with Ni (Cataldo et al., 1978) showed transfer to shoot to be constant at 4–5% from 0.001 to 100 μM solutions. Ion partitioning between roots and shoots, which is a transport-regulated process (Cataldo et al., 1983a), is undoubtedly controlled by supply (concentration) and physiological demand. In addition to overall supply and demand constraints, other potential control mechanisms include the propensity of the ion for hydrolysis and binding to cell walls, and the extent of ion sequestering via root storage and/or metabolism.

The short-term partitioning or relative distribution of Np in roots and shoots following the 24-h absorption period is shown in Figure 2. At very low concentrations of Np (fallout), approximately 60% of the total plant content of Np was transferred to the shoot. At solution concentrations between 7×10^{-6} (3×10^{-5} μM) to approximately 3 $\mu\text{g/mL}$ (12.6 μM), transfer to shoots was reduced to 4–10% of the absorbed fraction, with the majority of the Np being retained by the roots. At solution concentrations in excess of 3 $\mu\text{g/mL}$, Np exhibits an increased transfer from root

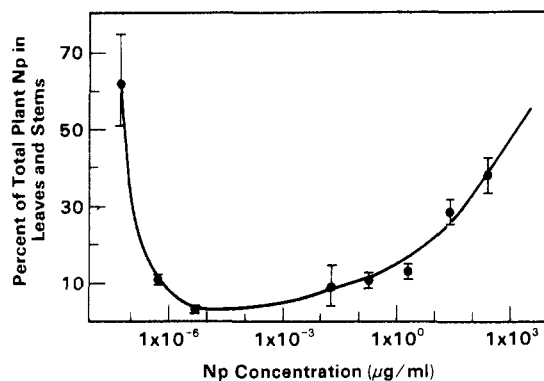


Figure 2. Influence of neptunium concentration in solution on transfer of root-absorbed neptunium to shoot tissues of soybean plants.

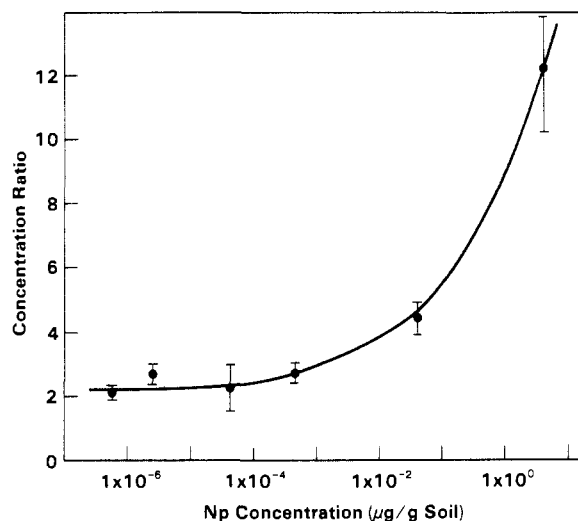


Figure 3. Influence of neptunium concentration in soil on CR values for bushbean plants.

to shoot (40%). The increase in Np transfer to shoots at the high concentrations is somewhat analogous to the reported behavior of technetium and may represent a saturation of sorption sites or saturation of storage compartments.

The increase in shoot transfer at very low concentrations ($3 \times 10^{-5} \mu\text{M}$), although not observed in previous ion absorption studies, was performed at concentrations generally not experimentally attainable except with very high specific activity tracers. The precise cause of this increase is difficult to assess but may simply be related to the lack of a sufficient concentration gradient between transport conduits and sorption sites and/or storage compartments. Although it is uncertain whether partitioning patterns will change over the life of the plant, the 24-h uptake data represent steady-state flux values. The overall importance of these data is that CR values based on shoot concentrations of Np may be dependent on Np concentrations surrounding the root and thus biased on the high side when employing low specific activity (high concentration) ^{237}Np amendments to the bulk soil.

Uptake studies, similar to those described above, were conducted with bushbean plants grown on soil amended with 5.2×10^{-7} to $4.1 \mu\text{g Np/g}$. Calculated shoot CR values showed a pronounced concentration effect as shown in Figure 3, similar to that observed in hydroponic studies (Figure 2). The CR values for bushbean plants sampled at postflowering were approximately 2 at soil concentrations below $4.1 \times 10^{-4} \mu\text{g/g}$; above this soil concentration CR values increased rapidly to approximately 12. Because

Table I. Concentration Rates for Various Plant Species Grown on Ritzville Silt Loam Amended with $2.6 \times 10^{-6} \text{ mg}$ of Np/g of Soil

plant sp.	tissue	concn ratio ^a
bushbean	leaves	2.7 ± 0.3
	seed	0.2 ± 0.1
barley	sheath and blades	0.5 ± 0.1
	grain	0.05 ± 0.01
soybean	leaves	1.5 ± 0.2
alfalfa	leaves	4.2 ± 0.2

^a Values are [mg of Np/g of dry weight tissue]/[mg of Np/g of dry weight soil]; average \pm SD, $n = 3$.

the majority of studies undertaken previously with ^{237}Np (Romney et al., 1981a; Schulz and Ruggieri, 1981; Schreckhise and Cline, 1980) employed soil concentrations of 0.4–42 mg/g, CR values currently used in dose assessments may be overestimated for most environmental Np concentrations. The extent of this concentration effect for different soils will depend on the soil properties that govern Np solubility.

Absorption and Partitioning of Np in Different Plant Species. Plants differ in their abilities to absorb specific ions and to partition these ions between roots and shoots and within tissues. Differences in Np uptake have been shown to occur for four plant species grown in seven soils (Romney et al., 1981a). In the current study, the absorption of Np by bushbean, barley, soybean, and alfalfa was determined on a Ritzville silt loam containing Np at near environmental concentrations ($2.6 \times 10^{-6} \mu\text{g/g}$ of soil). The order of Np availability/absorption was alfalfa > bushbean > soybean > barley (Table I). Bushbean plants grown to maturity exhibited a CR value of 2.7 for foliage and a CR value of 0.2 for seed. Barley exhibited the lowest accumulation, with CR values of 0.5 for foliage and 0.05 for grain. Both of these species exhibited a 10-fold reduction in CR value for seed that is also characteristic of Pu behavior. It is not uncommon for the concentrations of an ion in seed to be less than that in leaves, especially when the ion or organically complexed form of the ion is not remobilized or phloem mobile at seed filling or senescence. Soybeans grown to anthesis (60 days) exhibited a CR value of 1.5, somewhat lower than bushbeans grown for the same period of time. Alfalfa showed the highest CR value (4.2) of the four species tested. From these data, it is clear that Np is substantially more available than Pu, for which CR values range from 10^{-5} to 10^{-2} (Watters et al., 1980). While this is due in large part to the stability of Np(V) in soils, and its lower propensity for hydrolysis and sorption, differences in the chemical behavior of Np, compared with Pu, can also affect its mobility and chemical fate once absorbed by the plant.

Chemical Form of Np in Xylem Exudates. The uptake and mobility of Np in plants, particularly at high concentrations, would indicate either that Np persists in the soluble oxidized form (V) or that the reduced Np(IV), which is more subject to hydrolysis and precipitation, is present but is complexed and therefore sufficiently soluble for transport within the plant. Xylem exudate analyses were employed to determine the form of Np in transit between the root and the shoot tissues. Unfortunately, the concentration of Np in exudates (in vivo) was too low (0.01 mM) to permit chemical evaluation by TLE; therefore, in vitro amendments were employed. Whole exudates and class fractions from whole exudates collected from 28- to 115-day-old soybean plants were amended with NpO_2^+ to yield a final concentration of 0.6 mM, and Np-containing components were determined on the basis of overall charge (Figure 4).

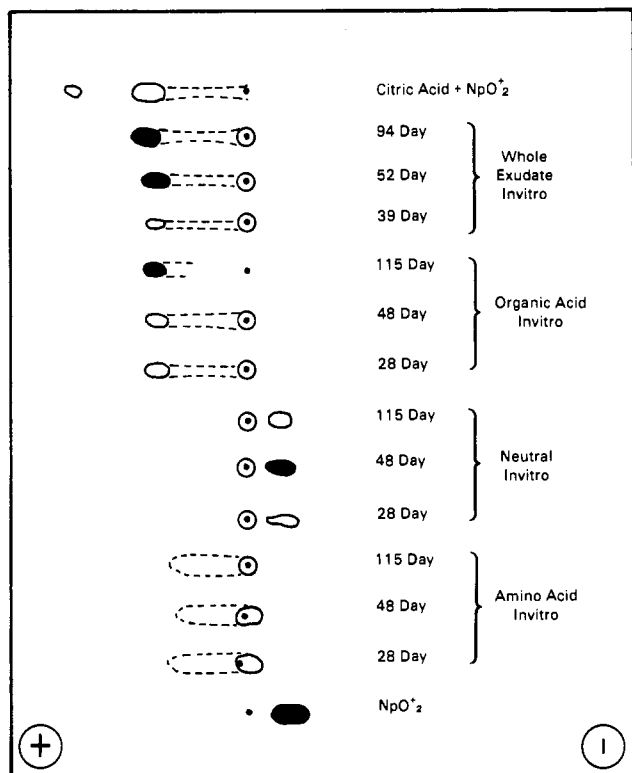


Figure 4. Electrophoretic behavior of neptunium in xylem exudates (in vitro) and xylem exudate fractions from 28- to 115-day-old soybean plants.

The Np amended in these studies was NpO_2^+ , as is evidenced by its cationic behavior and migration to the anode (Figure 4). In whole exudate of 39- to 94-day-old plants, Np is found at the origin, representing either neutral forms or reduced Np(IV), and as a single major anionic complex. The observed tailing between the origin and the anionic species of Np indicates some instability of the complex. The presence of the anionic Np complex is more prevalent with plant age. Prior to amendment with Np, whole exudates from 28- to 115-day-old plants were fractionated into their three chemical classes (amino acids, neutrals/sugars, organic acids) to determine which compound classes were effective in complexing Np. Electrophoresis of these fractions shows that only the organic acid fraction contains anionic components similar in mobility to those of the whole exudates. The overall electrophoretic behavior of Np indicates that Np is transported within the plant in an organically complexed, reduced form. This is based on the presence of neutral/hydrolyzed forms at the origin of exudate samples compared to the inorganic Np form. In addition, Np contained in exudates is maintained in soluble form as an organic acid complex. This complex has an R_f similar to that for Np in the presence of citric acid (Figure 4); citric acid is known to be an effective complexing agent for polyvalent cations such as Fe (Tiffin, 1966).

Chemical Fate of Np in Tissues. The solubility and distribution of Np in tissues was determined following root absorption from hydroponic solutions, followed by 5 days of metabolism in the case of soybean and bushbean plants, or after the first cropping in the case of alfalfa (60 days). The distribution of Np in the insoluble, soluble, and pellet or organelle fractions is shown in Table II. The Np associated with plant roots is primarily insoluble and may represent either reduced Np(IV) adsorbed to outer root surfaces and not desorbed by the acid leach or Np(IV) sorbed to insoluble cellular constituents within the root.

Table II. Distribution of Np in Homogenates of Alfalfa, Soybean, and Bushbean Tissues

tissue	fraction	treated plants, ^a % distribn		
		soybean	bushbean	alfalfa
root	residue	42.9 ± 2.2	56.1 ± 2.3	93.7 ± 1.1
	organelles	40.7 ± 2.2	10.7 ± 0.7	5.2 ± 0.3
	solubles	16.4 ± 0.2	33.1 ± 2.5	2.5 ± 0.0
leaves	residue	22.5 ± 3.5	31.0 ± 0.7	25.2 ± 1.9
	organelles	9.5 ± 2.8	15.8 ± 1.1	7.3 ± 1.8
	solubles	67.9 ± 2.8	53.2 ± 0.6	67.5 ± 0.1
seed	residue		26.1 ± 8.2	
	solubles		73.9 ± 8.1	

^a Mean, $n = 2$.

Table III. Distribution of Neptunium in Molecular Weight Fractions of Solubles Extracted from Alfalfa, Soybean, and Bushbean

plant	tissue	mol wt, ^a % distribn			
		>30 000	5000	5000-500	<500
soybean	leaves	39.6 ± 1.8	7.5 ± 0.5	28.1 ± 1.4	24.8 ± 2.7
	roots	32.9 ± 2.1	18.4 ± 1.7	21.4 ± 0.8	27.3 ± 1.1
bushbean	leaves	47.1 ± 4.1	13.7 ± 1.8	22.0 ± 3.2	17.1 ± 6.6
	roots	19.5 ± 0.5	23.4 ± 3.2	35.5 ± 0.2	21.6 ± 4.1
alfalfa	leaves	36.0 ± 3.3	7.9 ± 0.2	41.5 ± 0.9	14.5 ± 2.1
	roots	30.3 ± 7.3	6.1 ± 0.6	46.8 ± 12.6	16.6 ± 4.8

^a Mean, $n = 2$.

The solubles account for 3% of the total root content in alfalfa, 16% in soybean, and 33% in bushbean. Less than 11% of the activity in roots is found associated with the organelle fraction from bushbean and alfalfa, while accounting for 41% in soybean. Of the Np transported to and accumulated in the shoots of these plant species, more than 50% is soluble. The distributions of Np between solubles and the residue of soybean leaves and roots are comparable to those reported for Pu in soybean (Garland et al., 1981), although the latter studies combined the organelle and residue fractions. Only 7-16% of the Np associated with leaf tissue is isolated in the organelle fractions. The general increase in the proportion of Np associated with solubles of leaves compared with roots suggests a mechanism for both chemical stabilization of Np following root absorption and subsequent transport to shoots, either as complexed Np(IV) or as NpO_2^+ . The comparatively high solubility of Np (74%) associated with seeds of bushbean, compared with Pu (7%) in soybean seed (Garland et al., 1981), further supports the contention that mechanisms are present to chemically stabilize Np in plant fluids, although there are differences between Np and Pu.

The soluble tissue components were further fractionated by ultrafiltration to determine the molecular weight distribution of Np in each tissue and plant species (Table III). Distinct differences in the molecular weight distribution of Np are evident between plant species. In alfalfa roots and leaves, the majority of Np is associated with the >30 000 mW fractions (30 and 36%) and the 500-5000 MW fraction (42 and 47%). The np in the soluble fraction of soybean root tissue is relatively evenly distributed between each of the MW fractions. There is a decrease in the percentage of Np associated with the 5000-30 000 MW fraction (8%) in soybean leaves compared with roots (18%), while the >30 000 MW fraction contains 40% of the soluble Np. Of the Np associated with solubles of bushbean roots, 36% is contained in the 500-5000 MW fraction, with approximately 20% in each of the other MW fractions. In leaves of bushbean, 47% of the Np is associated with the >30 000 MW fraction, with 14-22% con-

tained in each of the other three fractions. Thus, soluble Np is associated with a broad range of MW fractions, with approximately 50% of the soluble Np contained in roots and leaves of all three species being associated with low-MW components (<5000 MW).

In contrast to the plant xylem, the chemistry of Np in roots and leaves is not analogous to that observed for Pu. The MW distribution of Np is markedly different from that previously reported for Pu in soybean tissues (Garland et al., 1981); these show 10% of the soluble Pu in soybean leaves to be associated with components of <5000 MW, only 4% of the soluble Pu in roots to be of <5000 MW, and >90% of the Pu to be associated with >10 000 MW components. It appears that the processes within the plant responsible for mobilization and immobilization of Np and Pu differ. This behavior may be related to the persistence of the more soluble, oxidized Np(V) in plant tissues or the relatively slow rate of hydrolysis of reduced Np(IV) compared with Pu(IV).

The differences observed in rates of plant uptake and subsequent chemical fate of Np compared with Pu can be placed into perspective by considering their solubility equilibria (Pourbaix, 1966). On the basis of pH (5.8–6.5) and E_h (+400–600 mV) conditions of the root bathing media in hydroponic studies and soil solutions of pot studies, Np(V) should predominate as NpO_2^+ , while disproportionation to Np(IV) occurs only at elevated pH (>5) when the E_h is <+100 mV. In comparison, at E_h values of <+1000 mV Pu exists primarily in the IV state and is prone to rapid hydrolysis. However, once reduced to the IV state, both Np and Pu have K_{sp} values of 10^{-56} . Thus, the solution equilibria of these two actinide elements, specifically the stability of Np(V), form the basis for their relative solubilities in soil and subsequent plant uptake rates.

Once these actinide elements are accumulated in plant tissues, they are found associated with widely different MW fractions. While it is presently not possible to define the speciation equilibria of Np and Pu in the presence of cell solutes, due primarily to a lack of thermodynamic data for these ions in the presence of complex organic ligands, one hypothesis is plausible. The observed differences in chemical behavior between Pu and Np may result from the ability of Np to exist in a relatively soluble V valence state and as soluble organic complexes of Np(IV) at the pH and E_h conditions in the plant. Pu solubility is likely the result of only organic ligand complexation in the IV state.

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Registry No. Np, 7439-99-8; ^{235}Np , 15700-37-5; ^{237}Np , 13994-20-2.

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