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FATE OF PLUTONIUM INTERCEPTED BY LEAF SURFACES: LEACHABILITY AND TRANSLOCATION TO SEED AND ROOT TISSUES[1]

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ABSTRACT

A low windspeed plant exposure chamber was employed for the generation and deposition of particulate plutonium-238, -nitrate, -citrate, and -oxide (fresh and aged) onto foliage of Phaseolus vulgaris. Physical deposition characteristics and particle sizing were routinely measured and deposition parameters calculated. At wind speeds of 0.42 cm sec^{-1}, deposition velocities for these compounds were of the order 10^{-3} cm sec^{-1} with deposition rates onto exposed foliage of 0.26 to 0.52 pg ^{238}Pu cm^{-2} sec^{-1}. The fate of surface deposited Pu compounds with respect to chemical modification and leachability was evaluated by leaching with synthetic "rainwater" and 0.1% HNO_3 solutions. Leaching of contaminated foliage with acidified solutions resulted in a 1-to-9 fold increase in Pu removal from foliar surfaces, depending upon chemical form, as compared to rainwater. Sequential leaching of foliage at 1, 7, 14, or 21 days after contamination indicated a reduced leachability of surface deposits with residence time on the leaf. The extent of leaching and concentration of soluble component was dependent on chemical form supplied (Pu-citrate > -nitrate > -aged oxide > -fresh oxide). The bioavailability of Pu as measured by translocation of foliarly deposited plutonium to root and seed tissue was markedly affected by the presence of a solution vector (i.e., simulated rainfall), and also the timing of its application. Accumulation ratios (AR) were increased by as much as three orders of magnitude when precipitation coincided with the time of maximum bean development. AR values for roots and seed tissue in the absence of a solution vector were from 10^{-5} to $< 10^{-6}$. In the presence of a solution vector, AR values were substantially increased (10^{-3} to 10^{-5}).

INTRODUCTION

Increasing reliance on the nuclear power cycle to meet future energy needs requires a better understanding of potential environmental effects. One aspect of this concern is the fate of airborne particulates such as plutonium. Although problems associated with direct inhalation of particulate contaminants by mammals are well-documented, little is known of the fate of foliarly-deposited contaminants, especially plutonium, with respect to entrance into the human food web. Folair contaminants such as plutonium can enter the food web by a number of routes including direct ingestion by herbivors, root uptake by other plants following resuspension or leaching and subsequent soil deposition, and direct ingestion by man of leafy vegetables, seed, or root tissues. The present study describes the fate of surface-deposited plutonium compounds with respect to chemical modification and leachability, and their availability for translocation to seed and root tissues.

MATERIALS AND METHODS

Aerosol Generation and Characterization: The low windspeed plant exposure chamber employed in these studies has been described previously [1]. The facility consists of a stainless steel wind tunnel fitted with a drawer for introduction of two potted plants into the air stream. Air movement is regulated by suction blowers, filtered through two high efficiency particulate aerosol (HEPA) filters and exhausted. Air entering the tunnel passes over the outlet of a RETEC^R Nubulizer[1] and aerosolized particles are carried in the air stream to the plant exposure section. For these experiments, wind speeds were maintained at 0.42 cm sec^{-1} which allowed larger particles to drop out of the air stream before reaching the plant canopy.

Particle size distribution for aerosolized compounds were determined using a Mercer Cascade Impactor [2]. Air concentrations were obtained from four filter paper samples located upstream and downstream of the plant exposure section. Deposition rates and velocities were calculated from air concentrations, leaf area, and quantity of plutonium deposited on foliage.

The "fresh" Pu-oxide was prepared by suspending the particles in triple-distilled water on the day of exposure. The "aged" oxide was obtained by aging a similar suspension for ten months. The freshly prepared and aged oxides had a soluble component equivalent to approximately 0.1 and 0.2% of the total activity, respectively (soluble component defined as passing a 0.01 μm mean pore size membrane filter). Pu-citrate was prepared by dissolving PuO_2 in 6N HNO_3 and 1M HF, bring the solution to dryness, and resuspending in 6N HNO_3. Citric acid (3.5 g) was then added to this Pu $(NO_3)_4$ solution (15 ml containing 5.53 mg ^{238}Pu) and slowly titrated to pH 5.8 using 0.6N NaOH containing 0.1 M Na citrate [3]. The resulting solution was > 99% soluble as defined by passing a 0.01 μm membrane filter. The pH 7.0 Pu-nitrate solution was prepared by rapid titration of $^{238}Pu(NO_3)_4$ in 6N HNO_3 with 6N NaOH. This solution was > 95% soluble at pH 7.0 for at least three weeks. These latter two solutions are stable and soluble at pH 7.0 as a result of the large molar excesses of their respective anions.

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[1] RETEC^R Nubulizer Model 7002, Burton Division of Cavitron Corporation, RETEC Development Laboratory, Portland, OR, USA

Plant Materials: Seedlings of Phaseolus vulgaris L. var 'Tendergreen' were grown in plastic-lined pint ice cream cartons containing fertilized Ritzville fine, sandy-loam soil. These were maintained in an environmental chamber with day/night temperature of 27/20°C and 14-hour photoperiod. Plants were exposed to aerosolized particles at 20 days of age, at which time they possessed fully expanded primary leaves and a partially expanded first trifoliate. Following exposure, plants were permitted to continue growth for an additional 28 days to allow for development of seeds and time for uptake and translocation of foliar deposits. Reproductive structures were initiated approximately five days after exposure and bean development was completed 28 days following exposure. At 28 days following exposure, plant tissues were separated into primary leaves, first trifoliate, seeds, roots, and all other shoot tissues (uncontaminated trifoliates, stem, and pods). Roots were washed free of soil by gentle agitation in 0.5 mM $CaCl_2$ solution. Tissues were subsequently oven-dried at 60°C, weighed, ashed at 425°C, the residue suspended in 6N HNO_3 and 1M HF, the solutions brought to dryness, resuspended in 6N HNO_3, an aliquot applied to planchets, and Pu alpha activity determined using a Beckman low background 2π counting system. Detection limits were approximately 0.4 dpm per sample aliquot. Data presented represents the average of four replicate samples for each treatment.

Leaching Procedures: Leaching studies were performed using a closed cylindrical chamber (25 cm dia. x 90 cm high) fitted with an atomizer head coupled to a metering pump. Separate groups of four plants were leached at 1, 7, 14, or 21 days following exposure. Only leaching solution passing over the canopy area was collected for analysis; wall runoff was collected separately and discarded. The leaching solution consisted of either a synthetic "rainwater" characteristic of the Central Washington area or 0.1% HNO_3 in "rainwater". The synthetic "rainwater" consisted of 9.21 mg $Ca(NO_3)_2 \cdot 4H_2O$, 4.47 mg $MgCl_2$, 3.62 mg $CaSO_4 \cdot 2H_2O$, 3.11 mg $NaHCO_3$, 1.80 mg $KHCO_3$, 3.57 mg $(NH_4)_2\ SO_4$, 0.23 mg $(NH_4)\ H_2PO_4$, and 1.26 mg $(NH_4)_2\ CO_3$ per liter of solution, and pH was adjusted to 5.8 with KOH. The leaching assembly can simulate a seven-minute rainfall equivalent to 0.4 cm and results in collection of 200 ml of leachate. Turbulence of the leaching mist and positioning of the plant in the assembly effectively eliminated shading effects by the uncontaminated trifoliate. Leachates were routinely analyzed to evaluate "soluble" and "insoluble" components (solubles are defined as passing a 0.01 μm membrane filter).

RESULTS AND DISCUSSION

Characterization of Aerosolized Particulates and Deposition Parameters:

The low wind speed aerosol exposure chamber employed in these studies provides a relatively consistent means of generating, characterizing, and depositing plutonium compounds onto plant foliage. Table 1 gives the physical characteristics for the aerosolized particles and deposition parameters for the four chemical forms of plutonium studied. A low wind speed was selected to allow larger particles to sediment prior to reaching the plant foliage and thereby shift the particle size distribution into the smaller size range. The air concentration was a function of the solution concentration in the generator and its homogeneity. Deposition rate and velocity were calculated from the quantity of material deposited on the leaves, leaf area and the air concentration. These deposition values are dependent on wind speed and particle size. The particle size distribution (characterized by the parameters of a log normal distribution AMAD and GSD)[2] not only affects deposition but is important in evaluating bioavailability as a function of environmental, chemical, and physiological variables, since the smaller the particle, the greater the surface area per unit mass. The AMAD of particles for these four compounds differ by less than a factor of three. The larger particle size distribution obtained with Pu-citrate and -nitrate result from the high molar concentration excess of citrate and nitrate anions, respectively.

<u>Availability of Surface Deposits for Leaching and Affect of Residence Time on Leachability</u>: Entrance into the food chain of foliarly deposited plutonium can occur by a number of routes, depending on whether it remains fixed to the leaves, is leached, or is translocated to plant tissues used as food. The following studies were designed to evaluate the leachability of foliar deposits as a function of time following exposure, the effect of leaching and residence time on the formation of soluble components, and finally the effect of leaching or the presence of a solution-vector on translocation to seed and root tissues.

Figure 1 shows the percentage of plutonium which is leached from foliage using a simulated rainfall of 0.4 cm in seven minutes. The actual amount of plutonium leached from foliage one day after exposure was dependent on chemical form, Pu citrate, >> -nitrate >> -fresh oxide > -aged oxide. Pu-citrate and -nitrate exhibit a 60 to 90% reduction in solubility,

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[2] AMAD = activity median aerodynamic diameter. GSD = geometric standard deviation.

respectively, compared to the original aerosolized solution. The apparent increases in solubility of the oxides results from a differential leaching of the soluble component and not from increased solubilization of insoluble components. All compounds exhibited a reduced availability for leaching over the 21 days following exposure. The difference seen between the citrate and nitrate forms may result from the lower stability of the nitrate form as compared to the citrate form. Assuming that shading is not a significant factor, and it was not especially at the one and seven-day periods, the reduced leachability observed could result from entrapment in crevasses on the leaf surface, engulfment by expanding epidermal plates, or by adsorption to unsatisfied surface valences.

The insoluble components for all of these compounds is most likely the oxide and hydrolysis products which are the most stable form of Pu in aqueous solution at biological pH. The "soluble" component of these leachates are of most interest since it is this component which should be most available for foliar uptake and subsequent translocation to other tissues. There appears to be a rapid decline in the soluble component for Pu-citrate, -nitrate, and -fresh oxide. The leachate from aged Pu-oxide treated foliage appears to have a relatively constant soluble component.

To evaluate the fate and retention mechanism of surface contaminants not leachable using a weakly ionic solution, 0.1% HNO_3 in synthetic rainwater was used seven days after exposure. The acid leach was employed to determine whether a significant fraction of the foliar surface plutonium was being immobilized by surface charge interaction [4]. The data presented in Table II indicate that a sizeable component of these foliar contaminants are immobilized by charge interaction and is acid leachable.

There is a variable increase in total plutonium leached for each of these compounds. Pu-citrate and fresh oxide show relatively small increases, 23 and 67%, while the aged oxide and nitrate exhibited a substantial increase in total plutonium leached (281 and 363%, respectively). The soluble component of the leachate was most affected by the acid leach; Pu-citrate, -fresh oxide, -nitrate, and -aged oxide exhibited increases of 64, 100, 486, and 650%, respectively. The quantity of plutonium leached using rainwater with or without 0.1% HNO_3 suggests that a major fraction of the foliar contaminants is not readily available for leaching. Whether this immobilization is the result of entrapment or engulfment of discrete particles is uncertain.

Plant Mobility of Foliar Plutonium in the Absence and Presence of a Solution Vector: The foliage of bean plants was contaminated with various chemical forms of ^{238}Pu at 20 days from planting and allowed to absorb and translocate ^{238}Pu for an additional 28 days. The target or sink tissues evaluated with respect to transport and bioavailability of folair deposits were seed and root, both of which were protected from aerosol contamination. The pot containing soil and root were double-bagged with polyethylene and sealed at the lower portion of the stem; the seed tissue was contained in pods formed after exposure.

Table III (Column A), shows the accumulation ratios (AR) of seed and root tissues following foliar contamination with the various chemical forms of ^{238}Pu. The AR value is defined as the pCi/g dry wt of seed or root pCi/g dry wt of primary leaves and first trifoliate. With the exceptions of root tissues in experiments using aged oxide and nitrate, little transport occurs and ^{238}Pu concentrations are below detection limits. The increased availability of the aged oxide as compared with the fresh oxide may result from the formation of hydrolysis products and radiolysis on aging of the oxide in H_2O solution. Pu-nitrate, which was employed in an attempt to optimize the formation of biologically available reaction products exhibited little increased availability. Although the aerosol solution of Pu-nitrate appears to be stable in the presence of excess NO_3, the particulates deposited on the leaves appeared to become rapidly insolubilized (Figure 1). These surface deposits, due to their chemical instability, would tend to form hydrolysis products on dilution and reaction with atmospheric or leaf surface moisture.

It has been shown that foliar plutonium in the absence of a solution vector is relatively immobile with respect to translocation to root and seed tissues, with plutonium concentrations in these tissues at or below the limit of detection. The possibility that environmental factors such as precipitation (rainfall) can affect foliar uptake and translocation does exist. To evaluate the effect of precipitation or a solution vector on transport, seed, and root tissues of plants employed in the previous leaching study (leached at 1, 7, 14, or 21 days) were analyzed and AR values determined 28 days after initial contamination. The data presented in Table III (Columns B and C) indicates that, with the exception of fresh oxide, the extent of translocation of foliarly deposited plutonium to root and seed tissue was markedly affected by not only the presence of a solution vector (i.e., simulated rainfall), but also the timing of its application with respect to stage of plant development. The fresh oxide, even in the presence of a solution vector exhibited availability below detection limits. However, the aged oxide, citrate, and nitrate exhibited

AR values from below detection limits of 10 to 1000-fold greater values. The higher values (Column C) were obtained for plant tissues leached at 7 and/or 14 days, while the lower AR values (Column B) were obtained from plants leached at 1 or 21 days. In effect, the presence of a solution-vector applied at time of maximum seed development (7-14 days after contamination) had a marked effect on the availability of a component of the foliar Pu contaminants. The data obtained for plutonium citrate and nitrate indicate that soluble forms of plutonium or situations favoring their solubility increase their potential for plant uptake and translocation. Another important aspect of these data is the increased availability of aged PuO_2 as compared to freshly prepared PuO_2. Obviously, Pu oxides can be introduced into solution situations in the environment, and based on these data, become increasingly available for biological transport. Whether this increased availability results from α-recoil and fragmentation of surface components of the oxide particle and/or formation of chemically stable and available forms as a result of radiolysis requires further study.

CONCLUSION

The use of a low wind speed plant exposure facility for generation, characterization, and deposition of aerosolized particles onto plant foliage enables the routine evaluation of suspended particle interactions and uptake in terrestrial plants.

Leaching studies indicate that the fate of foliarly deposited plutonium is dependent on chemical form and chemical stability. The order of leachability for the plutonium complexes studied was Pu-citrate > Pu-nitrate

> aged Pu-oxide > freshly prepared Pu-oxide. The component of the leachate defined as soluble was also dependent on the chemical form of plutonium used and followed a similar order. All plutonium compounds studied exhibited a reduced availability for leaching with respect to time following contamination (1 to 21 days). Acid leaching studies suggest that a sizeable fraction of foliar plutonium contaminants can be immobilized on leaf surfaces by charge interactions with unsatisfied leaf surface valences.

The extent of translocation of foliarly deposited plutonium to root and seed tissue was markedly affected by the presence of a solution vector (i.e., simulated rainfall), and also the timing of its application. AR values were increased by as much as three orders of magnitude when precipitation coincided with the time of maximum bean development. AR values for roots and seed tissue in the absence of a solution vector were from 10^{-5} to 10^{-6}. In the presence of a solution vector, AR values were substantially increased (10^{-3} to 10^{-5}).

REFERENCES

[1] CRAIG, D.K., KLEPPER, BETTY L., The design and calibration of a low speed windtunnel for studying the foliar deposition and uptake of aerosols, Amer. Ind. Hyg. Assoc. J. <u>36</u> (1975) In press.

[2] MERCER, T.T., TILLERY, M.I., NEWTON, G.J., A multi-stage low flow rate cascade impactor, J. Aersol. Sci. <u>1</u> (1970) 9.

[3] LINDENBAUM, A., WESTFALL, W., Colloidal properties of plutonium in dilute aqueous solution, Int. J. Appl. Radiat. Isot. <u>16</u> (1965) 545.

[4] LITTLE, P., A study of heavy metal contamination of leaf surfaces, Environ. Pollut. <u>5</u> (1973) 159.

Table I. Physical parameters of aerosolized plutonium-238 compounds deposited onto plant foliage.[1]

Physical Parameter	Pu-citrate	Pu-nitrate	Pu-oxide (fresh)	Pu-oxide (aged)
wind speed (cm sec^{-1})	0.42	0.42	0.42	0.42
air conc (pg cm^{-3})	57.4	34.7	80.7	68.0
deposition rate (pg $cm^{-2}sec^{-1}$)	0.28	0.48	0.52	0.26
deposition velocity (cm sec^{-1})	$4.9x10^{-3}$	$8.4x10^{-3}$	$6.4x10^{-3}$	$3.8x10^{-3}$
AMAD[2] (μm)	1.611±0.083	2.291±0.160	1.274±0.053	0.734±0.111
GSD[3]	1.86	1.91	1.63	2.16

[1] plants were exposed for 10 minutes

[2] activity median aerodynamic diameter, x ± sd

[3] geometric standard deviations

Table II: Effect of acid solution on leachability of foliar plutonium at seven days following exposure to plutonium compound.[1]

Compound	Leached Component	Leaching Compound Synthetic Rainwater	 0.1% HNO_3 in Synthetic Rainwater	% Increase in Plutonium Leached
		1%		
Pu-citrate	Soluble	28.0	46.0	64
	Insoluble	17.0	9.4	-45
	Total	45.0	55.4	23
Pu-oxide (fresh)	Soluble	0.5	1.0	100
	Insoluble	1.6	2.5	56
	Total	2.1	3.5	67
Pu-oxide (aged)	Soluble	0.6	4.5	650
	Insoluble	2.0	5.4	170
	Total	2.6	9.9	281
Pu-nitrate	Soluble	2.9	17.0	486
	Insoluble	1.4	2.9	107
	Total	4.3	19.9	363

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[1] Leachability expressed as μCi in leachate/μCi leached + μCi remaining on leaves X 100

Table III: Extent of translocation of ^{238}Pu from contaminated foliage in the absence and presence of a solution vector.

		A	B	C
			Accumulation Ratios in Presence of Solution Vector	
Compound[1]	Sink Tissue	Accumulation Ratios[2] in Absence of a Solution Vector	Leached at Day 1 or 21	Leached at Day 7 or 14
Pu Oxide (fresh)	Seed	$< 2.5 \times 10^{-6}$	$< 2.5 \times 10^{-6}$	$< 2.5 \times 10^{-6}$
	Root	$< 5.1 \times 10^{-6}$	$< 5.1 \times 10^{-6}$	$< 5.1 \times 10^{-6}$
Pu Oxide (aged)[3]	Seed	$< 8.6 \times 10^{-6}$	$< 8.6 \times 10^{-6}$	1.8×10^{-4}
	Root	2.4×10^{-6}	6.4×10^{-6}	3.0×10^{-5}
Pu Citrate	Seed	$< 4.2 \times 10^{-6}$	6.9×10^{-6}	1.0×10^{-4}
	Root	$< 5.4 \times 10^{-6}$	1.4×10^{-5}	1.6×10^{-4}
Pu Nitrate	Seed	$< 4.8 \times 10^{-6}$	2.8×10^{-6}	1.3×10^{-3}
	Root	3.0×10^{-5}	1.2×10^{-5}	2.6×10^{-4}

[1] All compounds supplied from solutions at pH 5.8 - 7.0.

[2] Accumulation Ratio = pCi/gm sink tissue/pCi/gm contaminated leaf tissue.

[3] Aged in H_2O at pH 7.0 for 10 months.

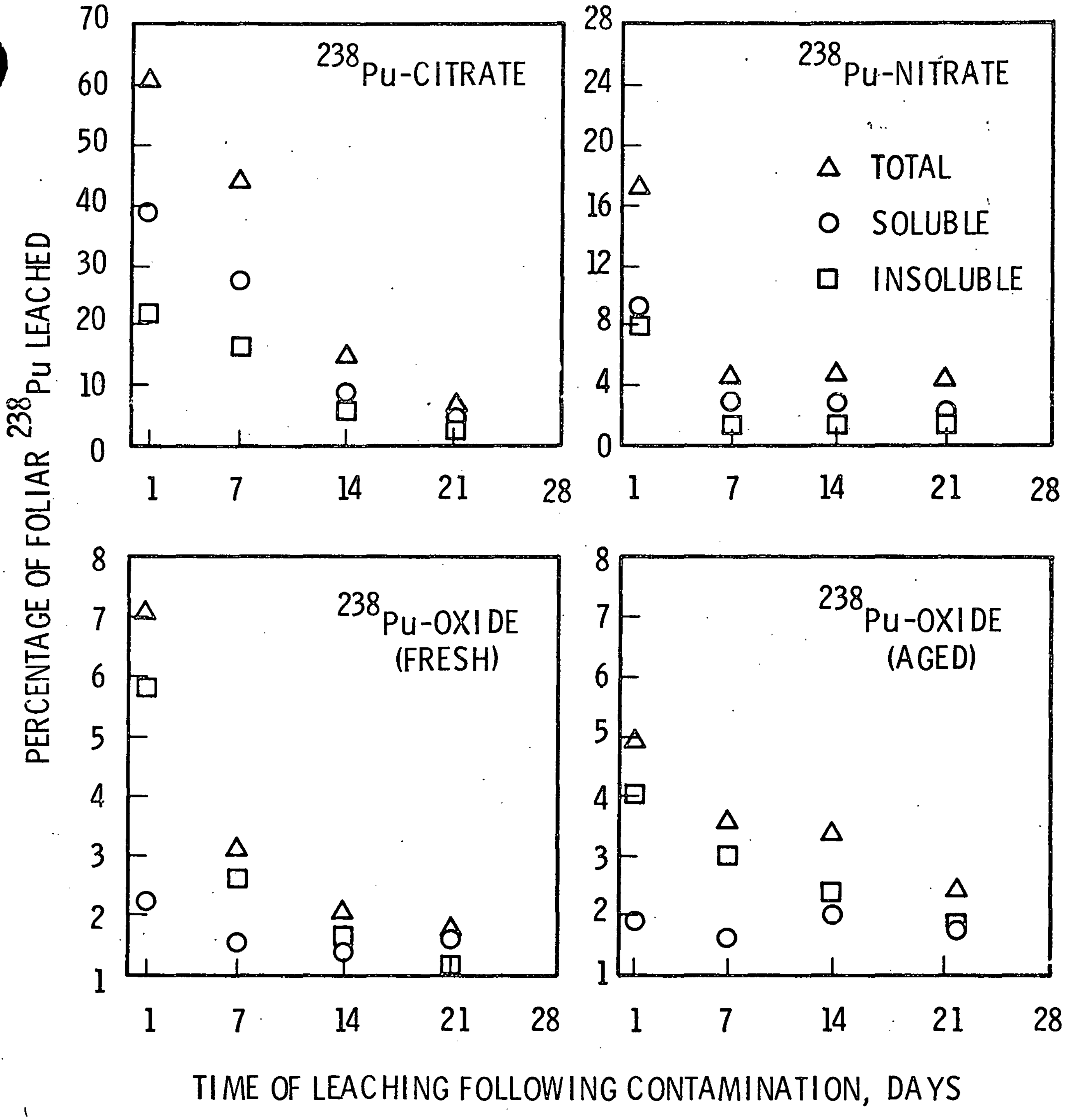

FIGURE 1: Leachability of foliar plutonium contaminants with respect to time following contamination.