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# Influence of soil factors on the vertical profile of plutonium physicochemical forms

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**Rūta Druteikienė,  
Benedikta Lukšienė,  
Rasa Gvozdaitė**

*Nuclear and Environmental  
Radioactivity Research Laboratory,  
Institute of Physics,  
A. Goštauto 12,  
LT-2600 Vilnius, Lithuania*

The dependence of Pu<sup>3+</sup> and Pu<sup>4+</sup> vertical distribution on soil characteristics in soddy and forest soil was investigated. Organic matter, pH, and the content of macroelements (Fe, Mg, K, Mn) in soil samples were determined. An analysis of soil samples showed that 81% of Pu<sup>4+</sup>, 44% of Pu<sup>3+</sup> and 82% of Pu<sup>4+</sup>, 61% of Pu<sup>3+</sup> were accumulated in the 0–5 cm layer of soddy and forest soil, respectively. Data on sequential extraction showed that plutonium was strongly fixed by organic substances and inorganic components of soil. It is evident that among the parameters affecting the behavior of various forms of plutonium, organic substances are very important, because organic matter contents affect the retention and migration of plutonium in the environment.

**Key words:** plutonium, soil factors, macroelements, organic matter, sequential extraction

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## INTRODUCTION

As a result of the overground nuclear weapon tests in the 1950s and 1960s and of the Chernobyl accident in 1986, long-lived radionuclides (plutonium isotopes among them) were deposited onto soil surface. When radionuclides are released from a source into a terrestrial environment, the assessment of long-term consequences to humans depends on information on the vertical distribution of the radionuclides in soil and their transfer to man via terrestrial pathways. On the other hand, the impact of trace metals and radionuclides in the environment is greatly dependent on their speciation in solution and solid phases, which determine their environmental availability, including bioavailability, toxicity, migration-accumulation phenomena, geochemical transfer and mobility pathways [5]. Therefore it is important to study the behaviour of radionuclides in geological media and to obtain some knowledge on the influence of soil factors on the fate of the radionuclides in ecosystems.

The parameters affecting the behaviour of plutonium in soil are organic substances, clay minerals, sesquioxides and the pH. On the other hand, the partitioning of plutonium among various soil constituents depends on its oxidation states and redox conditions. Also, plutonium has no stable counterpart and can exist simultaneously in several oxidation states. Organic matter represents a significant

proportion (70–80%) of total organic carbon in soils. Organic matter, due to its high cation-exchange capacity, is one of the most important geosystem characteristics, which influences the radionuclide dynamics. The second relevant property of humic substances is their ability to interact with metal ions and to form water-soluble, colloidal, and water insoluble complexes of various properties and widely differing chemical stabilities [5]. Organic acids and their complex salts connect plutonium into insoluble or poorly-soluble chemical compounds whose mobility is very low, and therefore they are concentrated in the topsoil layer [1]. The complex compounds of organic acids and iron determine the connection between ions of Pu and Fe. It is the prevailing hypothesis that plutonium cannot form self-sustaining chemical formations because of its low concentration ( $\sim 10^{-11}$  g/g) in soil. Consequently, plutonium integrates into chemical derivatives of non-isotopic carriers, and its behaviour depends on their behaviour. Therefore complex compounds of organic acids and Ca, Fe or Al ions and their hydroxides influence the plutonium migration in soil [4].

The main goal of the present investigation was to determine the influence of soil factors such as natural organic matter, pH, macroelements on the vertical distribution of <sup>239</sup>Pu (III) and <sup>239</sup>Pu (IV) and their physicochemical forms in soddy and forest soil horizons.

## MATERIALS AND METHODS

The investigation was carried out on soddy and forest soil artificially contaminated with  $^{239}\text{Pu}$  in different oxidation states. The association between plutonium and the soil components were determined by a sequential extraction procedure. Two columns (diameters 10 cm, length 20 cm) of undisturbed soddy and forest soil contaminated with  $^{239}\text{Pu}$  in chloride and nitrate forms were exposed to the action of natural meteorological conditions for about one year. After the exposition soddy and forest soil columns were divided into 4 layers, 5 cm each. The air-dried soil from each layer was sieved for the removal of stones and roots and mixed carefully.

For determination of total plutonium content in soil sample, 50 g of soil was heated at 550 °C overnight in a muffle furnace. The soil sample was spiked with  $^{242}\text{Pu}$  as a radiochemical yield tracer. Plutonium was isolated from the soil matrix by digestion with 8M  $\text{HNO}_3$ . Plutonium isotopes were separated and purified by means of strong basic anion exchange resin DOWEX 1 × 8 and then electrodeposited on a stainless steel disc from  $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$  electrolyte solution for 1 h, using a current density of 0.6 A · cm<sup>2</sup>.

Plutonium isotopes were determined by alpha-spectrometry, using a CANBERA PD type detector (area 450 mm<sup>2</sup>, resolution 17 keV (FWHM) at 4–6 keV). Alpha-efficiency was 25%, the detection limit for a counting time 86400 s was about 10<sup>-3</sup> Bq of  $^{239,240}\text{Pu}$ .

The organic matter content in soil sample was obtained by a loss-on-ignition analysis (550°). Atomic absorption spectroscopy (AAS) measurement was applied for Fe, K, Mg and Mn determination. The soil reaction (pH) was measured with a glass electrode in a 25 ml 1M KCl solution intensively agitated with 10 g of soil [6].

Association of  $^{239}\text{Pu}$  with various soil components was investigated in a layer (0–5 cm) of soddy soil (air-dried) by a sequential extraction procedure. Selective extractants were chosen basically according

to Tessier et al. [7]. The principal scheme and chemical phases leached by extractants are presented in Table 1.

A 20 g sample of soil was used for that purpose. All the extraction procedures were performed at room temperature by shaking on a water bath shaker. The extractant ratio was kept at 1:10.

Subsequently the suspension was filtered. The soil was then rinsed twice with distilled water. After filtration, this rinse water was added to the above solution phase for analysis. After addition of the yield tracers  $^{242}\text{Pu}$ , the solution was evaporated to dryness at low heat. The further analysis of plutonium was performed as above-mentioned.

## RESULTS AND DISCUSSION

The dependence of  $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$  vertical distribution on soil characteristics in soddy and forest soil was investigated. Organic matter, pH, and the content of macroelements (Fe, Mg, K, Mn) in soil samples were determined (Tables 2, 3).

Table 2. Physicochemical properties of the soddy soil

Depth, cm	Organic, %	pH	Fe, g/kg	Mn, g/kg	K, g/kg	Mg, g/kg
0–5	18.7	4.4	5.8	0.4	14.3	1.6
5–10	7.4	4.5	6.0	0.5	15.9	0.8
10–15	6.2	4.1	7.7	0.4	14.3	0.8
15–20	5.2	4.3	6.6	0.4	13.8	1.7

Table 3. Physicochemical properties of the forest soil

Depth, cm	Organic, %	pH	Fe, g/kg	Mn, g/kg	K, g/kg	Mg, g/kg
0–5	12.6	4.6	5.7	0.09	13.3	1.8
5–10	5.0	4.1	6.8	0.5	12.7	1.9
10–15	4.4	4.2	6.0	0.3	13.2	2.4
15–20	4.0	4.1	–	–	–	–

Table 1. Scheme of sequential extraction

Sequential extraction fractions	Chemical phase
Double-distilled water	Solubility of solids, trace elements in ionic phase and soluble complex compounds
1 mol/l ammonium acetate (pH 7)	Exchangeable ions
1 mol/l acetic acid	Carbonates, some Fe and Mn oxides
0.04 mol/l hydroxylamine chloride in 25% acetic acid (1:1)	Fe and Mn oxides (moderately reducible phase)
2 mol/l hydrochloric acid	Acid-soluble compounds
30% hydrogen peroxide, pH 2 with $\text{HNO}_3$	Organics, sulfide
$\text{HNO}_3$ and HF	Lithogenous fraction

The content of organic matter in the upper 0–5 cm layer of soddy and forest soil reached 18.7% and 12.6%, respectively. The organic content in the 5–20 cm layer reached about 4% in forest soil and varied in the range 7.4–5.2% in soddy soil. Both soddy and forest soil had a pH within 4.1–4.6 throughout all the profile of the horizons. The macroelement content in different soddy soil layers was 5.8–7.7 g/kg for Fe, 13.8–15.9 g/kg for K, 0.8–1.7 g/kg for Mg, and about 0.4 g/kg for Mn. The concentration values of macroelements in forest soil were similar to those in soddy soil, and the mean values were as follows: 6.1 g/kg for Fe, 13.1 g/kg for K, 2.0 g/kg for Mg and 0.3 g/kg for Mn. The content of Fe, Mn, K, Mg in the 15–20 cm forest soil layer was not determined. As can be seen, the physicochemical properties of both soddy and forest soils are nearly uniform, therefore it is obvious that there is no pronounced influence on the vertical distribution of plutonium in soil. On the other hand, small differences in the content of macroelements are observable for different soil layers.

An analysis of soil samples showed that 81% of  $\text{Pu}^{4+}$ , 44% of  $\text{Pu}^{3+}$  and 82% of  $\text{Pu}^{4+}$ , 61% of  $\text{Pu}^{3+}$  were accumulated in the 0–5 cm layer of soddy and forest soils, respectively (Fig. 1). It is evident that the organic matter content in soil affects the retention and migration of plutonium in the environment. From Table 4 we can conclude that there is a certain linear correlation ( $r = 0.99$ ) between the amount of organic matter and Pu concentrations in soil horizon (0–20 cm). These results mean that plu-

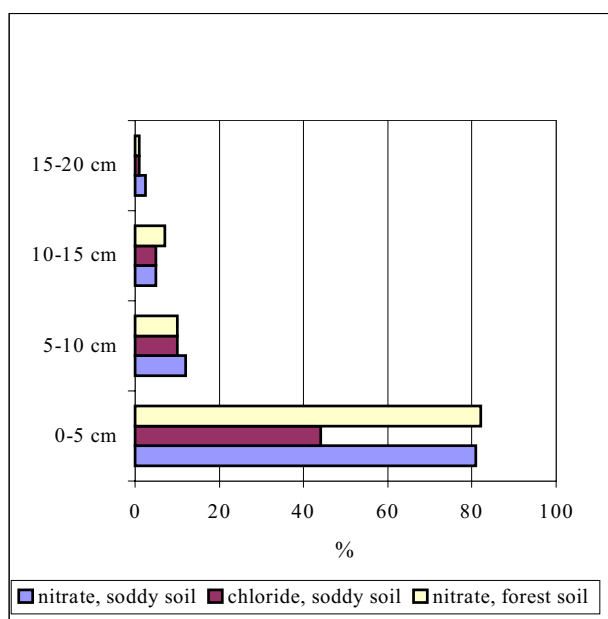


Fig. 1. Percentage distribution of  $^{239}\text{Pu}$  in the soil layers

Soil/chem. form of Pu	Organic matter	$\text{Fe}^{2+}/\text{Fe}^{3+}$	$\text{Mn}^{2+}$	$\text{K}^+$	$\text{Mg}^{2+}$
Soddy soil					
Pu nitrate	0.99	-0.62	-0.23	-0.19	0.44
Pu chloride	0.99	-0.61	-0.17	-0.12	0.36
Forest soil					
Pu nitrate	0.98	-0.68	-0.85	0.6	-0.65

tonium moves slowly into the deeper soil. A significant role of the downward movement of Pu can be ascribed to the presence of higher amounts of organic matter in the soil layers. In the soil environment, complex formations occur by the interaction of Pu with surface coatings, colloidal materials and complexing ligands. The complexation may influence the mobility of plutonium [3].

As presented in Table 4, there is a positive linear correlation between  $^{239}\text{Pu}$  amount in samples of each soil layer and the content of Fe, Mn and K in soddy and forest soils. However, a certain linear correlation between plutonium and magnesium in both soddy and forest soils was observed. The correlation coefficient reached  $r = 0.44$  for soddy soil and  $r = 0.36$  for forest soil. This result seems to show that the ions such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{K}^+$  do not affect the accumulation processes of plutonium in the present soil. Numerous investigations have shown that macroelements have affected the migration of radionuclides in soil. For instance, Fe reduction process can influence the parallel reduction of  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  [2]. We are of the opinion that a full-scale investigation of the influence of the pedological parameters, particularly of exchangeable bases  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  on the plutonium behaviour in soil should be carried out.

The direct impact of pH on mobility properties of plutonium in soil horizon was not determined, because in both soddy and forest soils the pH varied only within 0.5, i.e. pH values made up 4.1–4.6.

The data of sequential extraction showed (Fig. 2) that 0.2% of  $\text{Pu}^{4+}$  in soddy soil and 1.0% in forest soil were present in the water fraction. A significantly higher content of  $\text{Pu}^{3+}$  was found in the water fraction from soddy soil, it came up to 6.0%. The exchangeable Pu in all the samples studied varied from 0.5 to 15.8%. Percentage distribution of Pu bounded to Fe–Mn oxides was obtained in the order of 0.2–2.0%. The acid-soluble fraction contained from 4.0 to 17.0% of Pu. The largest percentage of Pu was determined in fixed fractions: 54.0% for  $\text{Pu}^{3+}$ , 55.0% for  $\text{Pu}^{4+}$  in soddy soil and 70.0% for  $\text{Pu}^{4+}$  in

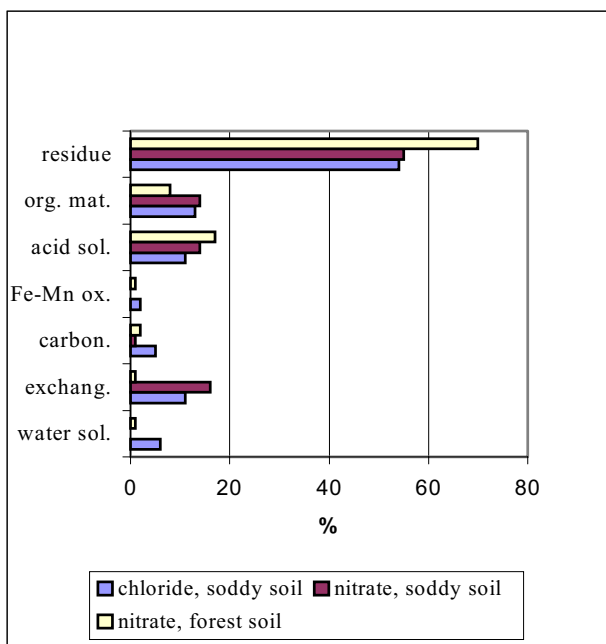


Fig. 2. Percentage distribution of <sup>239</sup>Pu activity in sequential extraction fractions

forest soil. The rather high values in the water-soluble fraction for Pu<sup>3+</sup> can be explained by the hydrolytic properties of these oxidation states. The differences between Pu<sup>3+</sup> and Pu<sup>4+</sup> solubility are connected with Pu<sup>4+</sup> ability to hydrolyze easily due to its low ion radius and high oxidation degree. In the process of hydrolysis Pu(OH)<sup>3+</sup> is formed, but the final product of hydrolysis is poorly-soluble Pu(OH)<sub>4</sub>. Transition from Pu(OH)<sup>3+</sup> ions to Pu(OH)<sub>4</sub> chemical forms is followed by the formation of plutonium polymers, which in colloidal state are sorbed on the mineral fraction [1]. A considerable increase in the Pu<sup>3+</sup> and Pu<sup>4+</sup> content in fixed fractions compared with the content in the other fractions of sequential extraction confirms that plutonium is strongly fixed by organic substances and inorganic components of soil.

## CONCLUSIONS

The downward movement of the plutonium deposited on soil surface depend on many parameters of the soil such as chemical forms of the radionuclides, physicochemical properties of the soil, and the biological and physicochemical processes in the natural environment. Among the parameters affecting the behavior of the various forms of plutonium, organic substances are very important, because the organic matter contents affect the retention and migration of plutonium in the environment. The largest part of released plutonium is accumulated in the

top soil layer, therefore the upper ground layer can be treated as a new potential source of this radionuclide in the biosphere. From the radioecological point of view, this part of the ecosystem plays a crucial role in the formation of the human irradiation dose.

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Rūta Druteikienė, Benedikta Lukšienė, Rasa Gvozdaitė

## DIRVOŽEMIO CHARAKTERISTIKŲ ĮTAKA PLUTONIO FIZIKINIŲ IR CHEMINIŲ FORMŲ VERTIKALIAI MIGRACIJAI

S a n t r a u k a

Plutonio izotopų, kaip ir daugumos kitų radionuklidų, akumuliaciją dirvožemyje nulemia jų pasiskirstymas kietoje ir skystoje fazėse. Kad būtų galima spręsti apie radionuklido elgseną dirvožemyje, svarbu žinoti jo sorbcijos tvirtumą ir įvairių aplinkos veiksnių įtaką jo migracijai. Svarbiausieji veiksniai, turintys įtakos plutonio migracijai dirvožemyje, yra organiniai kompleksiniai junginiai, molio mineralai (Ca, Mg, Al, Fe, K, Na), pH ir oksidacijos-redukcijos sąlygos. Ne mažiau svarbus veiksnys, nulemiantis plutonio elgseną dirvožemyje, yra jo cheminis individualumas ir cheminė forma.

Darbe pateikiami <sup>239</sup>Pu<sup>3+</sup> ir <sup>239</sup>Pu<sup>4+</sup> pasiskirstymo 20-ies cm velėninio ir miško dirvožemių sluoksniuose tyrimų rezultatai. Įvertinti dirvožemio geocheminiai parametrai ir jų įtaka skirtingų plutonio cheminių junginių vertikalijai

migracijai dirvožemio sluoksnyje. Nuosekliosios ekstrakcijos metodu nustatytos  $^{239}\text{Pu}$  neizotopinių nešėjų fizikinės-cheminės formos.

Tyrimų rezultatai parodė, kad didžiausias plutonio kiekis susikaupia viršutiniame 0–5 cm dirvožemio sluoksnyje, kuriame gausu organinių medžiagų – apie 19% velėniniame dirvožemyje ir apie 13% miško dirvožemyje. Abiejų tipų dirvožemių viršutiniame sluoksnyje aptikta 81%  $\text{Pu}^{4+}$  ir 44%  $\text{Pu}^{3+}$  (velėninis dirvožemis) bei 82%  $\text{Pu}^{4+}$  ir 61%  $\text{Pu}^{3+}$  (miško dirvožemis). Daroma išvada, kad dirvožemio organiniai junginiai „suriša“ plutonį ir yra stipriausiai jo migraciją sąlygojantis veiksnys. Dirvožemio makroelemen-

tų (Fe, Mg, K, Mn) įtaka plutonio vertikaliam pasiskirstymui įvertinta apskaičiavus koreliacijos koeficientus. Gauta, kad Fe, Mn ir K ryškios tiesioginės įtakos plutonio migracijai tirtuose velėniniame ir miško dirvožemiuose neturi. Išryškėjo tiesioginė priklausomybė tarp plutonio ir magnio: velėniniame dirvožemyje  $r = 0,44$ , miško dirvožemyje  $r = 0,36$ . Galima teigti, kad šių tipų dirvožemiuose magnis yra neizotopinis plutonio nešėjas. Nustatyta, kad  $\text{Pu(III)}$  junginiams būdingas didesnis mobilumas dirvožemyje nei  $\text{Pu(IV)}$  junginiams. Tai susiję su didesniu  $\text{Pu(IV)}$  polinkiu hidrolizuotis ir sudaryti stabilius netirpius cheminius junginius.