

Migration of ^{239}Pu in soluble and insoluble forms in soil

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A field experiment study was performed at the rural site of South-East Lithuania. The main tasks of the study included an evaluation of the peculiarities of partition of ^{239}Pu in soluble ($^{239}\text{Pu}(\text{NO}_3)_4$, $^{239}\text{PuCl}_3$) and insoluble ($^{239}\text{PuO}_2$) forms in soddy and forest soil horizons. The results of durable experiments (418 and 326 days) have shown that from 44.1% to 92.2% of ^{239}Pu of investigated chemical forms were accumulated in the top (0–5 cm) soil layer. Some share (5.7–39.2%) of plutonium from studied chemical forms was found in the 5–20 cm layers of studied soil samples (columns). Obtained distribution of plutonium in soil layers may be attributed to the consideration that the migration rate to the soil depth for plutonium is 0.1–1.0 $\text{cm}\cdot\text{y}^{-1}$ but for some part of plutonium 10 times higher migration rate is characteristic as well. Plutonium transfer factor (TF) to the grassland plants was calculated, the values ranged from 10^{-2} to 10^{-1} .

Introduction

Contamination of environment with plutonium is caused by the nuclear weapon tests, by the crash of installations with nuclear arrangements, by accidents at nuclear power plants and discharges of the nuclear fuel reprocessing plants as well. Besides, present in the context of environment protection and radioecological safety, storage of spent nuclear fuel plays a relevant role. The IAEA estimates that in 1997 about 10,500 ton of spent fuel was discharged from nuclear power reactors world-wide and this amount contained about 75 ton of plutonium. The cumulative amount of plutonium in spent fuel from nuclear power reactors world-wide is predicted to increase to about 1700 ton by 2010 year.¹ Radiochemists, radioecologists, geophysicists and other experts in Lithuania are focused on the studying of mechanisms of the transfer of radionuclides among the environmental compartments and strive for the prediction of peculiarities of a behavior especially of the artificial radionuclides. More or less, it is stipulated by the accident at Chernobyl NPP and the operating of two most powerful reactors (RBMK type) in Lithuania at Ignalina NPP. Our investigations are concentrated on the study of the behavior of plutonium in environmental systems as the most hazardous and radiotoxic element. Many authors pointed out on the diversity of the chemical forms of plutonium being released from different sources, from insoluble oxides to soluble inorganic salts and organic complex compounds. Because of the high temperature during the nuclear explosion, insoluble plutonium oxides, mixtures of oxides or compounds with the constructive elements ($\text{PuO}_x\cdot\text{MO}_x$; $\text{PuO}_x\cdot\text{U}_3\text{O}_8$) are dominant. Basically, the soluble forms of plutonium ($\text{PuO}_x\cdot n\text{H}_2\text{O}$; $\text{Pu}(\text{NO}_3)_x$; Pu organic complex compounds) are released to the environment from the nuclear technological cycle.^{2,3}

At present the largest part of global plutonium is distributed in soil and natural water reservoirs. Therefore, actually it is aimful to investigate the behavior of plutonium in soil which can be considered as a source of plutonium to the surface air and plants.

Processes of migration and accumulation of plutonium in that environmental system are in connection with the stability and change of its chemical compounds because of a reciprocity between components of investigative soil and plutonium chemical species.^{4–10}

Nevertheless, the continuation of an influence of various geochemical and geophysical factors plays a considerable role in the migration and accumulation of plutonium as well as other radionuclides when due to the different processes the chemical forms of radionuclide are restructuring. The majority of the investigation in this field were carried out with soil, naturally contaminated with fallout plutonium or plutonium from the reactors. The initial chemical forms of plutonium were unknown exactly in such kind of experiments and a fixation of existing chemical forms of plutonium without an assessment of their possible transformations took place.

The main goal of the present investigation was to determine the ability for the migration to the depth in soil of plutonium in soluble and insoluble forms ($^{239}\text{Pu}(\text{NO}_3)_4$, $^{239}\text{PuCl}_3$, $^{239}\text{PuO}_2$) and their transfer to the plants.

Experimental

Field experiments

The open-air ground with soddy soil and with mixed forest soil with poor leaf litter in rural locality in South-Eastern Lithuania were chosen for the field experiment.

Three plastic columns of 10 cm in diameter and 20 cm length were stuck into the soddy soil while the column surface came up with the soil surface and three analogous columns in the same manner were stuck in

the forest soil. Organic matter, pH and the content of macroelements Fe, Mn, K, Mg in each layer of soddy soil (Table 1) and forest soil (Table 2) were determined.

Table 1. Physicochemical properties of the soddy soil

Depth, cm	Organic, %	pH	Fe, g/kg	Mn, g/kg	K, g/kg	Mg, g/kg
0–5	17.1	4.4	5.8	0.4	14.3	1.6
5–10	3.6	4.5	6.0	0.5	15.9	0.8
10–15	3.0	4.1	7.7	0.4	14.3	0.8
15–20	3.6	4.3	6.6	0.4	13.8	1.7

Table 2. 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	–	–	–	–

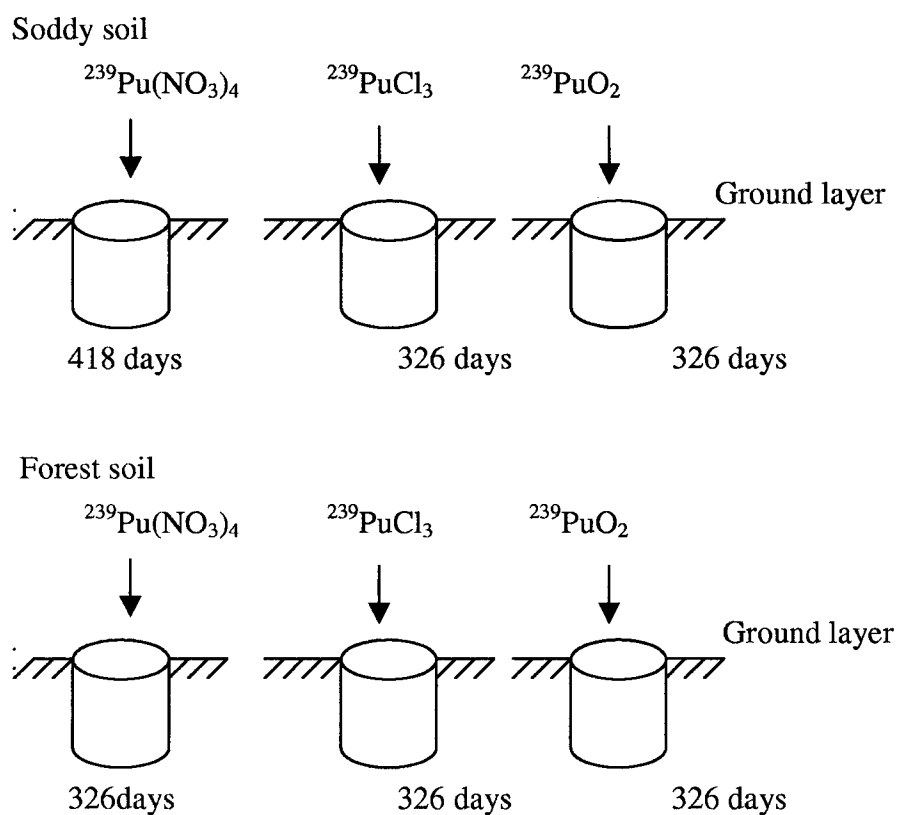


Fig. 1. Chart of field experiment

The soil surface of each column was contaminated with 30 Bq of ^{239}Pu , which was in the form of $^{239}\text{Pu}(\text{NO}_3)_4$, $^{239}\text{PuCl}_3$, and $^{239}\text{PuO}_2$ (Fig. 1).

The field experiment study with the $^{239}\text{Pu}(\text{NO}_3)_4$ started on the 23 July, 1996. The rest experiments were prepared on the 21 November, 1997. An outcome of all the experiments was done on the 22 September, 1998. Thus the columns with $^{239}\text{Pu}(\text{NO}_3)_4$ were exposed to an action of natural meteorological conditions for 418 days and the residual part of studied columns were exposed for 326 days.

After exposition each column was divided into 4 layers, 5 cm each. The soil was dried at room temperature, the plants and roots were separated from the soil. The soil was precisely grinded and mixed.

Preparation of the plutonium compounds

Plutonium oxide ($^{239}\text{PuO}_2$) was prepared by adding a solution containing 30 Bq of ^{239}Pu in nitrate form to 5 g of the respective soil and heated in platinum dish for 4 hours at 1000 °C.¹¹

Plutonium chloride ($^{239}\text{PuCl}_3$) was prepared in the following way. Hydrazine ($\text{N}_2\text{H}_2 \cdot \text{HNO}_3$) was added to the ^{239}Pu nitrate standard solution (30 Bq) until its concentration reached 0.3M. The mixture was heated on water bath (70–80 °C) for 30 minutes. Solution was evaporated to the wet salts then (conc.) HCl was added to it and the evaporation was done once more.^{12,13} The prepared salt ($^{239}\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$) was dissolved in 20 ml 0.5M HCl, mixed with the soil and dried at 100 °C.

$^{239}\text{Pu}(\text{NO}_3)_4$ compound was transferred to the required form by its mixing with the soil and drying at 100 °C.

Determination of plutonium, organic matter and stable elements

For the determination of total acid-soluble forms of plutonium, 50 g soil sample was heated at 550 °C overnight in a muffle furnace. After adding ^{242}Pu as a radiochemical yield tracer (received from the Risø National Laboratory, Denmark) the soil sample was digested repeatedly with 8M HNO_3 . Pu was separated and purified by means of Dowex 1X8 strong basic anion exchange resin and then electrodeposited on a stainless steel disk from the $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$ electrolyte solution for 1 hour using a current density 0.6 $\text{A}\cdot\text{cm}^{-2}$. Radiochemical analysis of plutonium oxide was carried out on an aliquot of 50 g soil according to the method described by HÖLGYE.¹¹

The organic matter content in the separate soil samples was determined using the loss-on-ignition method with ashing temperature of 550 °C for 24 hours. The pH was measured with a glass electrode in a 25 ml 1M KCl solution which was intensively agitated with 10 g of soil.¹⁴

The alpha-spectrometric measurement chain is composed of a Cambera PD detector (area 450 mm^2 , resolution 17 keV (FWHM) at 4–6 keV) coupled to a SES-13 spectrometer. Alpha-efficiency was 25%, the detection limit for a counting time of 86,400 seconds was about 10^{-3} Bq of $^{239,240}\text{Pu}$.

The analysis of macroelements was conducted by atom adsorption spectrometry.

Results and discussion

The distribution of ^{239}Pu in different chemical forms ($^{239}\text{PuCl}_3$, $^{239}\text{Pu}(\text{NO}_3)_4$, $^{239}\text{PuO}_2$) during the field research in 1996–1998 is shown in Figs 2 and 3.

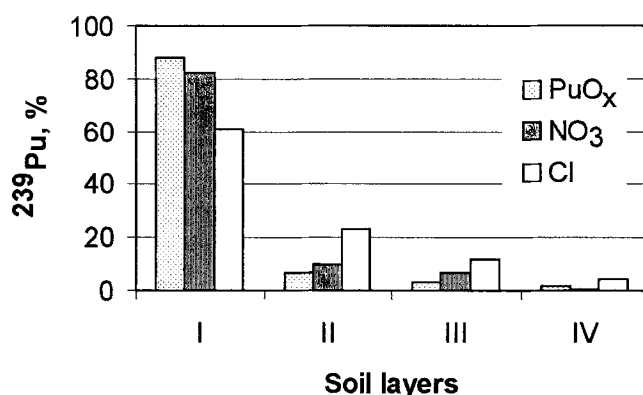


Fig. 2. Vertical migration of various chemical forms of Pu in forest soil (distribution in the horizons: I-0-5, II-5-10, III-10-15, IV-15-20 cm)

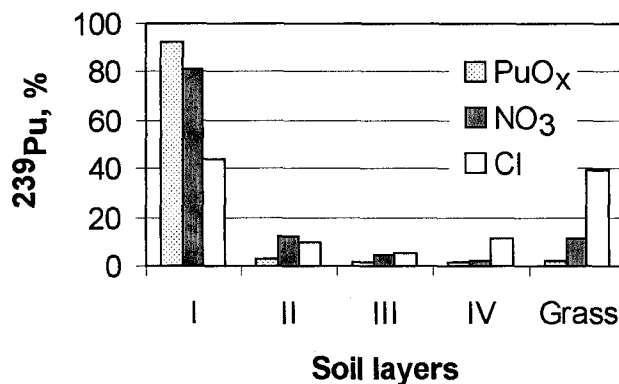


Fig. 3. Vertical migration of various chemical forms of Pu in soddy soil and grass (distribution in the horizons: I-0-5, II-5-10, III-10-15, IV-15-20 cm)

The largest quantity of ^{239}Pu released on the sample surface in each case was obtained in the upper 0–5 cm soil layer. Significant role for such dynamics of Pu can be attributed to the presence of higher amount of organic matter in the top soil layers. As can be seen, the content of the organic matter in the upper 0–5 cm layers changes in the range of 17–29.9%. A sudden decrease of the organic matter begins from the second 5–10 cm layer and further the consistent decrease is observed. The organic content in the 15–20 cm layer reaches only 2.6–5.2%. The link between the ^{239}Pu partition in the 0–20 cm soil layers and organic matter content is presented in Figs 4 and 5. The analysis of the soil samples indicated the decrease of plutonium with depth. An accumulation of plutonium nitrate in the top soil horizon of the soddy soil and grass came up to 81.0% and 11.7%, respectively, while in the 15–20 cm layer it reached only 2.5% (column B). ^{239}Pu of the same chemical form in the forest soil (0–5 cm) was found to be 82.2% and in the 15–20 cm horizon only 0.6% of it was distributed (column H). ^{239}Pu in soluble nitrate form with reduced mobility can be assumed. Insoluble products of hydrolysis and their interaction with the mineral and organic fractions takes place when Pu(IV) penetrate to the soil. Less amount of ^{239}Pu in chloride form (44.1%) was observed in 0–5 cm soddy soil layer and higher in grass (39.1%) and through the all deeper layers it quantity was very similar to that of ^{239}Pu in nitrate form. Bearing into mind that the similar partition of ^{239}Pu in chloride form was obtained for the forest soil (60.7% of ^{239}Pu 0–5 cm horizon and 4.1% in 15–20 cm horizon) it can be considered that ^{239}Pu chloride belongs to the compounds which are easier transferred to the plants and are more mobile in the soil. The explanation can be that Pu(IV) is the most stable valence form which forms stable complex compounds. According to PAVLOTSKAYA et al.³ the mobility of valence

forms decreases in the order of: Pu(V)>Pu(VI)>Pu(III)>Pu(IV). On the other hand the stability constants of complex compounds decrease in the cations (metals) line M(IV)>MO₂(II)>M(III)>MO₂(I) and in the anions line F⁻>NO₃⁻>Cl⁻>ClO₄⁻.²

Vertical migration of insoluble $^{239}\text{PuO}_2$ had an analogous tendency to the soluble ^{239}Pu compounds with the exception that its slight accumulation was observed in perennial grass. Partition of insoluble $^{239}\text{PuO}_2$ throughout all soil horizons the studied (0–20 cm) confirms the affirmation that insoluble and heavily mobile plutonium compounds released onto the soil and being for a long time in the soil and affected by various environmental factors are transformed to mobile forms^{2,15} and some part of them migrates to the depth.

But relevance of chemical form of plutonium and type of soil is evident as well. Thus, 0–5 cm forest soil layers contain from 9.4 to 12.6% organic matter, and 60.7% of $^{239}\text{PuCl}_3$, 82.2% of $^{239}\text{Pu}(\text{NO}_3)_4$ and 88.3% of $^{239}\text{PuO}_2$ were accumulated in this layer (Table 3, Fig. 2), respectively.

The top layers of undisturbed grass-land-soddy soil, where 17.1–29.2% organic matter was determined accumulated 92.2% of $^{239}\text{PuO}_2$, 81.0% of $^{239}\text{Pu}(\text{NO}_3)_4$ and 44.1% of $^{239}\text{PuCl}_3$ (Table 3, Fig. 3). According to Figs 2 and 3, the mobility of the ^{239}Pu compounds should be written in the following order: $^{239}\text{PuCl}_3 > ^{239}\text{Pu}(\text{NO}_3)_4 > ^{239}\text{PuO}_2$.

Plutonium migration rate to the depth of the soil is determined to change from 0.1 to 1.0 cm·y⁻¹.^{16–18} Also it was observed by PAVLOTSKAYA et al.³ that <35% of plutonium showed 10 times higher migration rate than the rest part of plutonium. Results of our experiments indicated that 16–39.9% of ^{239}Pu in soluble forms and from 5.7% to 11.6% of ^{239}Pu oxide was distributed through the 5–20 cm of different types of soil.

Table 3. Percentage distribution of ^{239}Pu and organic matter in the soil

Column (type of soil, contaminant)	Organic, %	^{239}Pu , %	Column (type of soil, contaminant)	Organic, %	^{239}Pu , %
B (soddy soil; $^{239}\text{Pu}(\text{NO}_3)_4$)			H (forest soil, $^{239}\text{Pu}(\text{NO}_3)_4$)		
Grass	12.7	11.7			
0–5	18.7	81.0	0–5	12.6	82.2
5–10	7.4	11.9	5–10	5.0	10.2
10–15	6.2	4.6	10–15	4.4	6.9
15–20	5.2	2.5	15–20	4.0	0.6
D (soddy soil; $^{239}\text{PuCl}_3$)			K (forest soil, $^{239}\text{PuCl}_3$)		
Grass	24.7	39.1			
0–5	29.9	44.1	0–5	9.4	60.7
5–10	5.2	10.2	5–10	4.4	23.5
10–15	11.0	5.4	10–15	4.4	11.7
15–20	2.6	1.2	15–20	3.6	4.1
F (soddy soil; $^{239}\text{PuO}_2$)			L (forest soil, $^{239}\text{PuO}_2$)		
Grass	10.7	2.1			
0–5	17.1	92.2	0–5	11.3	88.3
5–10	3.6	2.8	5–10	4.8	6.7
10–15	3.0	1.7	10–15	4.0	3.1
15–20	3.6	1.2	15–20	3.6	1.8

Such distribution could be induced by the presence of micro- and macroelements. For instance, Fe reduction process can influence the parallel reduction of Pu(IV) to Pu(III).² We suppose that one of the reasons of transport of comparable large amount of $^{239}\text{Pu}(\text{NO}_3)_4$ to the deeper soil layers can be related to the plutonium reduction process because the Pu(III) compounds are more mobile.

The mobility of ^{239}Pu in soluble and insoluble chemical forms was determined when the transfer of ^{239}Pu to the plant was analysed. The basic pathway of plutonium transfer from the environment to the vegetation are assumed to be through the leaves and roots. The decisive factor for the plutonium accumulation to the plants can be considered the solubility of plutonium compounds. The experiments have indicated that the complex forming compounds increases the solubility of plutonium and its transfer to the plants in 10–1000 times.² The transfer factor (TF) of ^{239}Pu from the first soil layer to the grassland vegetation is:

$$\text{TF} = \frac{\text{Pu concentration in plant (dry mass)}}{\text{Pu concentration in soil (dry mass)}}$$

Simulated TF values (Table 4) are comparable to TF for $^{239,240}\text{Pu}$ in grassland plants² which were found to be

in the order of 10^{-4} – 10^0 . The analysis of the data shows that the accumulation of Pu in grassland plants is conversely proportional to the sorption of Pu in soil (Table 3): 11.7% in grass, 81.0% in soil (column B); 39.1% and 44.2% (column D) and 2.1% and 92.2% (column F). The relatively small content of plutonium in plants in comparison to the soil can be explain by the influence of the sorption, followed by the decrease of mobile forms of Pu. TF for ^{239}Pu of nitrate and chloride forms to perennial grass was in the range of 10^{-1} – 10^{-2} what is in agreement to the results obtained by other authors. Such result of our field study may imply that ^{239}Pu uptake is not only through the roots but also in the way of its adsorption on the upper parts of plants.

The role of the pH which is relevant factor for the adsorption of radionuclides in soil was not observed and it is evident because both soddy soil and forest soil had a pH in the range of 4.1–4.6 throughout all the profile of the horizons.

Table 4. TF values for various ^{239}Pu chemical forms and exposition period

^{239}Pu chemical form	Exposition period, day	TF
Oxide	326	$2 \cdot 10^{-2}$
Nitrate	418	$1.8 \cdot 10^{-1}$
Chloride	326	$6 \cdot 10^{-1}$

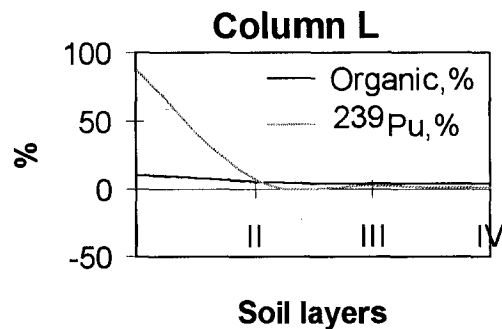
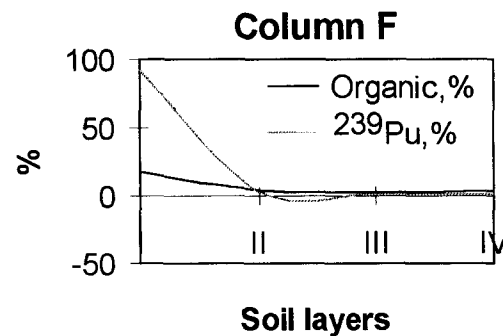
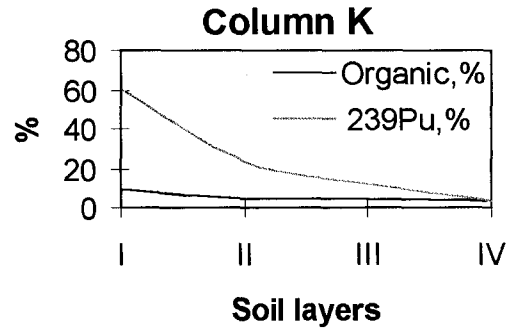
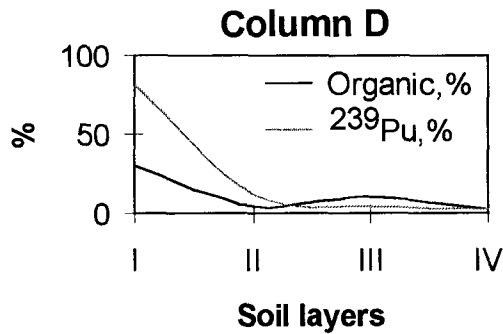
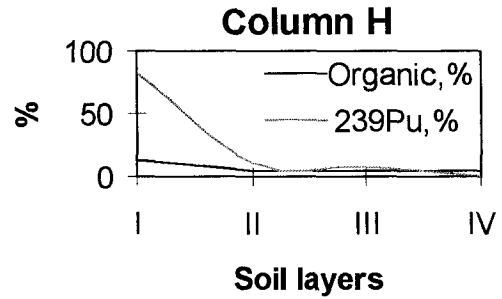
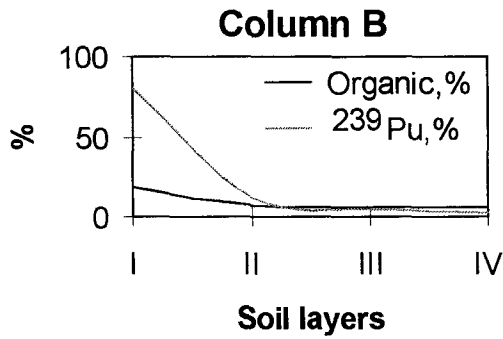


Fig. 4. Link between ^{239}Pu partition in the 0–20 cm soddy soil layer and organic matter content

Fig. 5. Link between ^{239}Pu partition in the 0–20 cm forest soil layer and organic matter content

Conclusions

Long-range field research study has shown that the soluble and insoluble forms of plutonium ($^{239}\text{PuCl}_3$, $^{239}\text{Pu}(\text{NO}_3)_4$, $^{239}\text{PuO}_2$) (from 44.1 to 92.2%) remained in the top (0–5 cm) layer of the undisturbed grassland, soddy soil and forest soil in significant extent, although the percolation present of ^{239}Pu in chloride form into the deeper soil was observed to be higher and insoluble $^{239}\text{PuO}_2$ showed the least mobility. It was strongly associated with the matrix of the upper soil layer and even the uptake of ^{239}Pu by plants was very negligible, only 2.1%.

The largest part of released plutonium to the environment is accumulated in the top ground layer. Therefore, the upper ground layer can be assumed as new potential source from which repartition of this radionuclide in the biosphere upon the influence of different mechanisms (vertical and horizontal migration, accumulation, resuspension) takes place. From the radioecological point of view this part of the ecosystem plays a critical role in the formation of the human irradiation dose. Evaluating the processes inducing plutonium redistribution in the environment, the most relevance can be shared to the resuspension which causes the plutonium return to the atmosphere. Thus, the inhalation is the fastest pathway of the plutonium occurrence in the human organism.

References

1. N. OI, Plutonium challenges. Changing dimensions of global cooperation. IAEA Bulletin No. 40, 1998.
2. W. C. HANSON (Ed.), *Transuranic Elements in the Environment. A Summary of Environmental Research on Transuranium Radionuclides Funded by the U.S. Department of Energy Through Calendar Year 1979, 1985* (in Russian).
3. F. I. PAVLOTSKAYA, B. F. MYASOEDOV, *Radiokhimiya*, 4 (1984) 554 (in Russian).
4. T. A. GORIČENKOVA, F. I. PAVLOTSKAYA, B. F. MASOEDOV, *J. Radioanal. Nucl. Chem.*, 147 (1991) 153.
5. K. BUNZL, W. KRACKE, W. SCHIMMACK, L. ZELLES, *J. Environ. Radioact.*, 39 (1998) 55.
6. F. R. LIVENS, M. S. BAXTER, *J. Environ. Radioact.*, 7 (1988) 75.
7. G. RIISE, H. E. BJORNSTAD, H. N. LIEN, D. H. OUGHTON, B. SALBU, *J. Radioanal. Nucl. Chem.*, 142 (1990) 531.
8. B. SALBU, H. E. BJORNSTAD, T. KREKLING, H. LIEN, G. RIISE, G. OSTBY, Determination of physicochemical forms of radionuclides deposited after Chernobyl accident, in: *Environmental Contamination Following a Nuclear Accident*, Vol. 1, IAEA-SM-306/35P, Vienna, 1990, p. 171.
9. G. SZABO, A. J. WEDGWOOD, A. BULMAN, *J. Environ. Radioact.*, 13 (1991) 181.
10. H. R. VON GUNTEN, P. BENES, *Radiochim. Acta*, 69 (1995) 1.
11. Z. HÖLGYE, *J. Radioanal. Nucl. Chem.*, 149 (1991) 275.
12. A. N. NESMEYANOVA, *Guide to the Practical Lessons in Radiochemistry*, Moscow, 1968, p. 457 (in Russian).
13. O. J. WICK (Ed.), *Plutonium Handbook: A Guide to the Technology*, Vol. 1, 1971, p. 67 (in Russian).
14. A. V. SOKOLOVA (Ed.), *Methods of Agrochemical Investigations of the Soils*, Nauka, Moscow, 1975 (in Russian).
15. I. G. KOCHAN, I. I. SHUKTOMOVA, *J. Radioanal. Nucl. Chem.*, 201 (1995) 371.
16. Y. MAHARA, S. MIYAHARA, *J. Geophys. Res.*, 89 (1984) 7931.
17. G. HARTMANN, K. BACHMANN, *J. Environ. Radioact.*, 8 (1988) 21.
18. G. HARTMANN, C. THOM, K. BACHMANN, *Health Phys.*, 56 (1989) 55.