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STUDY OF PLUTONIUM MIGRATION AND/OR ACCUMULATION IN SOIL UNDER FIELD AND LABORATORY CONDITIONS*

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This study investigated the dependence of Pu^{3+} and Pu^{4+} vertical distribution on the soil characteristics in soddy and forest soil. Soil samples were analysed for organic matter and pH. Special columns with contaminated (^{239}Pu) soil surface were kept for 326 days under field conditions. The analysis of the contaminated soil layers (5 cm each, totalling 20 cm) showed that 81 % of $^{239}Pu^{4+}$, 44 % of $^{239}Pu^{3+}$ and 82 % of $^{239}Pu^{4+}$, 61 % of $^{239}Pu^{3+}$ were accumulated in the 0-5 cm layer of soddy and forest soil. Sequential extraction of the soddy soil 30 days after surface contamination with ^{239}Pu, ^{137}Cs and ^{90}Sr showed the following differences in radionuclide distribution: the largest amount of ^{239}Pu (60 %) and ^{137}Cs (70 %) were extracted from the residual fraction while ^{90}Sr in this fraction reached only about 10 %.
This suggests that organic substances and some inorganic compounds, which usually are the main components of the residual fraction, affect the retention and migration of plutonium in the soil.

KEY WORDS*: chemical forms*, *^{137}Cs, forest soil*, *organic matter, ^{239}Pu, sequential extraction, soddy soil, ^{90}Sr*

Industrial nuclear technologies and their use for civilian or military purposes are always associated with a risk of radionuclide contamination. Because of global fallout or fallout after nuclear accidents, the upper soil layer is contaminated with long-lived radiotoxic, hazardous radionuclides (Pu isotopes, ^{90}Sr, ^{137}Cs, etc.). The assessed global background contamination level of soil and vegetation until 1990 was 2.4 kBq m^{-2} to 3.2 kBq m^{-2} for ^{137}Cs and 1.5 kBq m^{-2} for ^{90}Sr (1).$^{239,240}Pu$ background activity concentration in soil was 0.1 Bq kg^{-1} to 7.0 Bq kg^{-1} and in plants 0.3 Bq kg^{-1} to 2.0 Bq kg^{-1} (2). At present soil can be considered as one of the most contaminated environmental ecosystems.

Investigations of plutonium behaviour in the environment are of particular concern from several aspects. The first, radioecological, is related to the effects of ionising radiation caused by plutonium isotopes on living organisms including humans. The second important aspect is geophysical, and is related to the use of the distribution of radionuclides to investigate geochemical processes in lithosphere.

Contaminant migration and accumulation in soil depend on various factors. Numerous studies investigate radionuclide migration into the depth. The results of a study of the plutonium isotope vertical distribution dynamics in peaty-podzolic gley and mobile forms within the 30 km Chernobyl zone have shown that the greatest Pu activity was found in the upper soil layer (at the depth of 4 cm) (3). The authors assume that ^{238}Pu and ^{239,240} Pu were found in the layer of 5 cm to 10 cm in 1988 and in a layer of 10-15 cm in 1991 is due to migration of the most mobile plutonium forms. The measurements of soil samples taken in the 30 km area of the Chernobyl NPP in 1994 recorded ^{238}Pu, $^{239,240}Pu$, ^{241}Pu, ^{241}Am and $^{243,244}Cm$ activity in the layer of soil between 0 cm and 5 cm of depth (4). A similar situation for Chernobyl-

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*Preliminary report presented at the 6th Symposium of the Croatian Radiation Protection Association with international participation, Stubičke Toplice, Croatia, 18-20 April 2005 derived and fallout radionuclides has been observed in other regions. Ninety-six percent of plutonium accumulated in soil with a high humus content (5). The retention of plutonium in organic horizon may vary according to the content of organic matter, mineral composition and other geochemical and geophysical characteristics of soil. Moreover, the migration and accumulation of plutonium in soil depend on its initial chemical form. From the point of view of radiation protection, the risk of ground water pollution or radionuclide transfer via plant roots is decreased due to the slow migration of highly radiotoxic technogenic radioelements toward the deeper layers of soil. However, from the upper soil layer containing the largest number of radionuclides, radionuclides can get into the underground atmosphere because of erosion. Therefore, the upper soil layer can be regarded as the secondary source of the radioactive pollution.

The aim of this study was to determine the migration and/or accumulation of ^{239}Pu in soddy and forest soils in respect to its initial chemical form and to compare its binding to soil fractions with the binding of ^{137}Cs and ^{90}Sr.

MATERIALS AND METHODS

The outdoor field analysis included soddy soil and mixed forest soil with poor leaf litter in a rural locality of the southeast Lithuania. For this purpose we used special systems to create undisturbed soil blocks/columns. The soil surface of each column was artificially contaminated with ^{239}Pu (30 Bq) in three forms: $^{239}Pu(NO_3)_4$, $^{239}PuCl_3$ or $^{239}PuO_2$. The experiment was designed to preserve the original microbiological and mechanical properties of soil which was exposed to natural environmental conditions. The experiment lasted 326 days.

Laboratory experiments were carried out in three series in order to compare the behaviour of mobile forms of ^{239}Pu, ^{137}Cs and ^{90}Sr in soil. Model system columns were packed with the same soddy soil as in the field experiments. Soil surface was contaminated with $^{137}CsCl$ (^{137}Cs – $1.48 \cdot 10^2$ Bq), $^{90}SrCl_2$ (^{90}Sr - $1.46 \cdot 10^2$ Bq) and $^{239}PuCl_3$ (^{239}Pu – 30 Bq), each in three columns. Columns prepared in this way were left under laboratory conditions for 30 days.

After exposure each column was divided in four layers (5 cm). The soil was dried at room temperature, the plants and roots were separated from soil. The soil was finely ground and mixed. The amount of organic matter in the soil sample was obtained by a loss-on-ignition analysis (550 °C). The reaction (pH) of 10 g of soil, strongly shaken with a 25 mL 1 mol L^{-1} KCl solution, was measured using a glass electrode. Table 1 shows the organic matter content and pH values of the soddy and forest soils.

Table 1 *Amount of organic matter and pH values in soddy and forest soils*

Depth / cm	Soddy soil		Forest soil	
	Organic matter / %	pH	Organic matter / %	pH
0-5	17.1-29.9	4.4	9.4-12.6	4.6
5-10	3.6-7.4	4.5	4.4-5.0	4.1
10-15	3.0-6.2	4.1	4.0-4.4	4.2
15-20	2.6-5.2	4.3	3.6-4.0	4.1

To determine the total plutonium content in soil sample, 50 g of soil was heated in a muffle furnace at 550 °C overnight. The soil sample was spiked with ^{242}Pu as a tracer. Plutonium was isolated from the soil matrix by digestion with 8 mol L^{-1} HNO_3. Plutonium isotopes were separated and purified using a strong basic anion exchange resin DOWEX 1x8 and then electrodeposited on a stainless steel disc from the Na_2SO_4/H_2SO_4 electrolyte solution for 1 hour using the current density of 0.6 A cm^{-2}.

The sequential extraction method (6) was applied to separate water-soluble (deionised water) ion-exchangeable (1 mol L^{-1} CH_3COONH_4, pH 6.8), acid-soluble (1 mol L^{-1} HCl), and residual fractions of ^{239}Pu, ^{90}Sr and ^{137}Cs. Every fraction with ^{90}Sr and ^{137}Cs was evaporated and residual transferred into a dish of standard geometry for measurement. In the case of ^{239}Pu, before evaporation of each fraction ^{242}Pu tracer was added and residue dissolved in 8 mol L^{-1} HNO_3. Plutonium was separated through anion-exchange as described above.

The background ^{90}Sr activity, measured using a low-background beta detector in the UMF-1500 device, did not exceed 5 cpm. ^{137}Cs activity was determined using a gamma spectrometer with a semiconductor Ge(Li) detector with the registration efficiency of 0.26 % for ^{137}Cs. The minimum detectable activity (MDA) was 0.5 Bq per sample.

Plutonium isotopes were determined by alpha-spectrometry using a Canberra PD type detector (area 450 mm^2, resolution 17 keV (FWHM) at 4-6 MeV). Alpha-efficiency was 25 %, the detection limit to the counting time of 86400 seconds was about 10^{-3} Bq of $^{239,240}Pu$.

Statistical analysis was based on the number of replicate samples. Each type of soil had nine columns; three of them were polluted with $^{239}PuO_2$, the other three with $^{239}Pu(NO_3)_4$ and the remaining three with $^{239}PuCl_3$. The radiochemical analysis and the uncertainties of measurement yielded a 16 % error, which was taken into consideration in data presentation.

The sample set in laboratory experiments consisted of three columns run in triplicate. The data of those experiments were tested for normality before the Student's *t*-test. Laboratory data are presented as arithmetic mean ±SD.

RESULTS AND DISCUSSION

Figures 1 and 2 show the distribution of ^{239}Pu in different chemical forms [$^{239}PuCl_3$, $^{239}Pu(NO_3)_4$, $^{239}PuO_2$] recorded in the field study. The highest ^{239}Pu activity was measured in the top layer of both soils types, that is, 0 cm to 5 cm. The accumulation of $^{239}Pu(NO_3)_4$ in the top layer of soddy soil was 81.0 %, whereas in the 15 cm to 20 cm layer it dropped to 2.5 %. The data are presented as percentage of initial contamination. In the forest soil top layer(0 cm to 5 cm) $^{239}Pu(NO_3)_4$ activity was 82.2 %, only to drop to 0.6 % in the 15 cm to 20 cm horizon. A smaller amount of $^{239}PuCl_3$ (44.1 %) was observed in the 0 cm to 5 cm soddy soil layer, and through all deeper layers its quantity was very similar to that of ^{239}Pu in the nitrate form. $^{239}PuCl_3$ showed a similar in the forest soil (60.7 % in the 0 cm to 5 cm horizon and 4.1 % in the 15 cm to 20 cm horizon). Vertical migration of insoluble $^{239}PuO_2$ was similar to soluble ^{239}Pu compounds. The highest $^{239}PuO_2$ activity was measured in the top layer of soddy (92 %) and forest (88 %) soil. Plutonium activity concentration significantly dropped in the three lower layers and ranged from 1 % to 6 %.

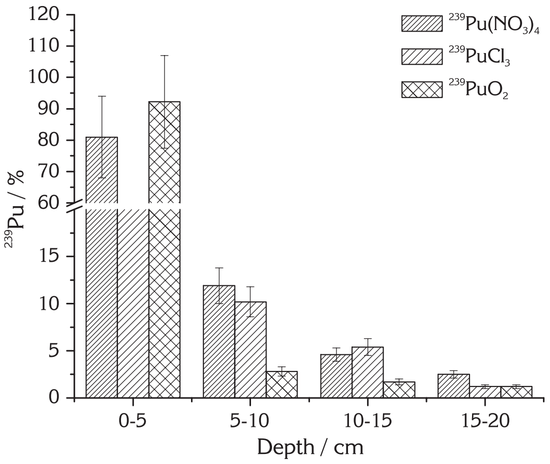

Figure 1 *Vertical distribution of different chemical forms of plutonium in soddy soil*

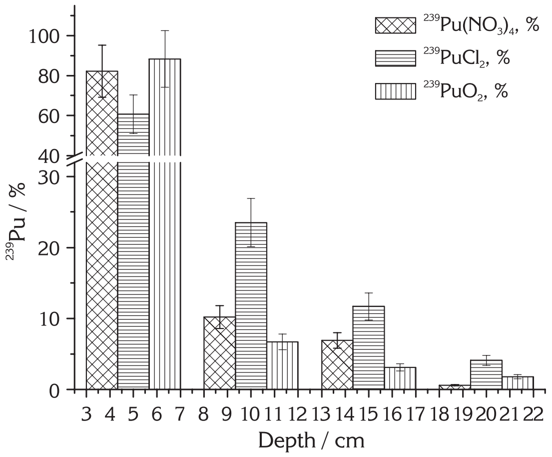

Figure 2 *Vertical distribution of different chemical forms of plutonium in forest soil*

During the long-term experiment under natural conditions the top soddy soil layer was covered with grass, and we analysed the transfer of ^{239}Pu from soil to grass. There the activity of plutonium nitrate, chloride and oxide was 11.7 %, 39 %, and 2 %, respectively.

The long-term field experiment has shown the relevance of the chemical form and of the type of soil for radionuclide migration and accumulation. A significant role in the vertical distribution of plutonium can be attributed to a higher amount of organic matter in soil. The content of organic matter in the top 0-5 cm layers ranges between 17 % and 30 % in soddy soil and between 9 % and 12 % in forest soil. It drops significantly as early as in the second 5-10 cm layer and throughout the column. In the bottom, 15-20 cm, layer of soddy and forest soil the organic content is only 2-5 % and 3-5 %, respectively. It can be assumed that the reduced mobility of ^{239}Pu in the soluble nitrate form can be related to the formation of insoluble products of hydrolysis and Pu(IV) interaction with mineral and organic fractions of soil. A smaller amount of ^{239}Pu (III) in the chloride form (44 %) was observed in the 0-5 cm soddy soil layer and a higher amount in grass (39 %). Through all deeper layers its quantity was very similar to that of ^{239}Pu in the nitrate form. As a similar activity of ^{239}Pu in the chloride form was measured in the forest soil (61 % of ^{239}Pu in 0 cm to 5 cm horizon and 4 % in 15 cm to 20 cm horizon), it can be assumed that ^{239}Pu chloride belongs to compounds which transfer to plants more readily and are more mobile in soil. We can also assume that Pu(IV) forms stable complex compounds which affect the vertical migration of this radionuclide. The mobility of valence forms in biocoenoses above ground decreases in the following order: Pu(V) > Pu(VI) > Pu(III) > Pu(IV). On the other hand, the constants of the stability of complex compounds decrease in the cation (metals) line M(IV) > MO_2(II) > M(III) > MO_2(I) and in the anion line F^- > NO_3^- > Cl^- > ClO^{4-} (7).

The distribution of ^{239}Pu from insoluble $^{239}PuO_2$ through all studied soil horizons (0 cm to 20 cm) confirms that insoluble and less mobile plutonium compounds transform to mobile forms under a variety environmental factors in soil. Because of this transformation, a part of insoluble $^{239}PuO_2$ migrates into the depth.

The distribution of plutonium can be influenced by micro and macro elements with reduction properties. The oxidation degree of plutonium and its behaviour in geochemical structures changes due to the interaction between plutonium and reductors. For instance, the oxidation of Fe^{2+} to Fe^{3+} causes parallel reduction of Pu^{4+} to Pu^{3+}. As a result, chemical compounds containing Pu(III) are more mobile in soil (7). We believe that one of the reasons for the migration of a relatively large amount of $^{239}Pu(NO_3)_4$ to deeper soil layers can be related to plutonium reduction, because Pu(III) compounds are more mobile.

Although relevant for the adsorption of radionuclides in soil, pH did not seem to play a role in either soddy soil or forest soil, that is, it ranged from 4.1 to 4.6 throughout the columns.

The second set of experiments allowed us to compare ^{239}Pu binding to soil geochemical fractions with that of ^{137}Cs and ^{90}Sr. After 30 days of artificial exposure, contaminated soil columns were analysed for ^{239}Pu, ^{137}Cs and ^{90}Sr using the sequential extraction method (8-11). The analysis showed a rather uneven distribution of ^{137}Cs, ^{90}Sr and ^{239}Pu between and within fractions (Figure 3). The largest amount of ^{239}Pu (60 %) and ^{137}Cs (70 %) was extracted from the residual fraction, while ^{90}Sr in this fraction reached only about 10 %. The sorption of plutonium and caesium in the crystal lattices of soil minerals is stronger and more irreversible if compared to the sorption of ^{90}Sr.

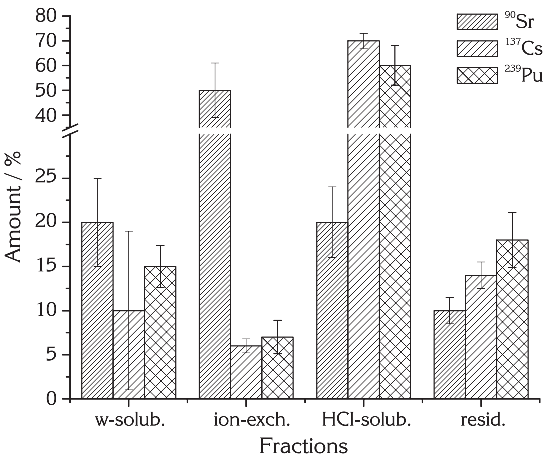

Figure 3 *The distribution of ^{239}Pu, ^{137}Cs, ^{90}Sr in geochemical fractions (water soluble; ion-exchangeable; HCl-soluble; residual)*

Binding to the organic part of soil and sorption into insoluble compounds or Fe, Al, Mn oxides are more characteristic of ^{239}Pu and ^{137}Cs. In our earlier study using simultaneous radioanalytical, alpha spectrometric and Mössbauer spectrometric analyses, we obsrved a linear correlation between ^{239,240}Pu and Fe_3O_4, Fe_2O_3 or FeOOH in environmental soil samples (12). Therefore, these iron compounds seem to affect plutonium accumulation and migration. Radionuclide compounds soluble in water were distributed as follows: 15 % of ^{239}Pu compounds, 10 % - of ^{137}Cs and 20 % - of ^{90}Sr. As much as 50 % of ^{90}Sr was found in the geochemical fraction characteristic of ion-exchange compounds compared to only 6 % of ^{137}Cs and 7 % of ^{239}Pu. The extraction of the soil in the fraction of 1 mol L^{-1} HCl (acid soluble fraction) showed the following distribution of the radionuclides: ^{239}Pu - 18 %, ^{137}Cs - 14 %, ^{90}Sr - 20 %.

The results of laboratory experiments help to explain ^{239}Pu accumulation in the top soil layer under field conditions. Furthermore, various iron compounds and other chemical substances in the organic matter in environmental soil can bind plutonium and make its downward migration more difficult.

CONCLUSIONS

Our long-term field study has shown that soluble and insoluble forms of plutonium [$^{239}PuCl_3$, $^{239}Pu(NO_3)_4$, $^{239}PuO_2$] were retained to a significant extent (from 44 % to 92 %) in the top layer (0 cm - 5 cm) of undisturbed soddy and forest soil. However, greater amounts of ^{239}Pu chloride percolated into the deeper soil layers than of the other two forms. Insoluble $^{239}PuO_2$ showed the lowest mobility. The mobility of ^{239}Pu compounds in our study was as follows: $^{239}PuCl_3 > {}^{239}Pu(NO_3)_4 > {}^{239}PuO_2$.

Our laboratory experiment showed that ^{239}Pu and ^{137}Cs basically bind with the same geochemical soil fractions. For these radionuclides, the residual fraction is of large relevance because averagely 60 % of plutonium and 70 % of caesium were determined in this fraction. Fifty percent of ^{90}Sr was found in the ion-exchangeable fraction. The results of the laboratory experiment should help to understand the reasons why the largest number of the radionuclides remains in the upper soil layer, as recorded in the outdoor experiments and natural surroundings.

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Sažetak

ISTRAŽIVANJE MIGRACIJE I/ILI AKUMULACIJE PLUTONIJA U TLU U TERENSKIM I LABORATORIJSKIM UVJETIMA

U istraživanju je promatran utjecaj svojstava tla na raspodjelu Pu^{3+} i Pu^{4+} po dubini uspoređujući travnato tlo sa šumskim tlom. Utvrđena je koncentracija organske tvari u tlu i pH-vrijednost uzoraka tla. Uzorci tla površinski su umjetno onečišćeni ^{239}Pu te su se u terenskim uvjetima držali u posebnim stupcima 326 odnosno 418 dana. Analiza onečišćenih slojeva tla (svaki debljine 5 cm) do dubine od 20 cm pokazala je da se u gornjem sloju do 5 cm dubine nakupilo 81 % $^{239}Pu^{4+}$ i 44 % $^{239}Pu^{3+}$ u slučaju travnatog tla, odnosno 82 % $^{239}Pu^{4+}$ te 61 % $^{239}Pu^{3+}$ u gornjem sloju šumskoga tla.
Primjenom metode sekvencijalne ekstrakcije utvrđena je raspodjela radionuklida u različitim geokemijskim frakcijama travnatoga tla 30 dana nakon površinskoga onečišćenja ^{239}Pu, ^{137}Cs odnosno ^{90}Sr u laboratorijskim uvjetima. Iz rezidualne frakcije najviše je ekstrahirano ^{137}Cs (70 %) te ^{239}Pu (60 %), dok je ^{90}Sr u ovoj frakciji bio zastupljen s tek 10 % početne aktivnosti. Stoga se može zaključiti da organski te neki anorganski spojevi, koji su uobičajeni sastojci rezidualnih frakcija, utječu na zadržavanje i migraciju plutonija u tlu.

KLJUČNE RIJEČI: *^{137}Cs, kemijski oblici, organska tvar, ^{239}Pu, sekvencijalna ekstrakcija, ^{90}Sr*, *šumsko tlo, travnato tlo*

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