

## Soil organic matter and migration properties of $^{239,240}\text{Pu}$ and $^{241}\text{Am}$

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**Abstract.** Humus influence on mobility of plutonium and americium in soil has been investigated. To do this the entrance of radionuclides into soil water solutions with different organic matter concentration and the distribution of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  between humus fractions of soil has been analyzed. The mineral and organic soils with distinct quantitative and qualitative composition of humus, contaminated by radionuclides of Chernobyl origin have been studied. The groups of fulvic (FA) and humic acids (HA) which differ in their composition and solubility in water were extracted from soils and the content of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in these organic fractions was detected. It was established that humus substances (HS) mainly promote the fixation of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in solid phase of soil. The humus of organic soils promotes the fixation of plutonium and americium to a greater extent than HS of mineral soils. That is one of the reasons of lower mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in organic soils. A higher ability of plutonium to form the difficultly soluble complexes with HS compare to americium may be a factor of higher mobility of americium in soil.

### 1. INTRODUCTION

The behavior of transuranic elements (TUE) in environment essentially depends on the ratio of mobile and heavy mobile radionuclide species in soil where up to now the main part of plutonium and americium of technogenic origin occurs. Plutonium and americium form different complexes with soil constituents, primarily, the complexes with HS of soil which influence significantly the migration of radionuclides in environment [1, 2]. The dispersion (i.e. molecular mass  $M$ ) of FA is 500 - 20 000 D and that of HA is 5 000 - 300 000 D [2, 3]. The components of HA are associated with clay ( $d < 2 \mu\text{m}$ ), Ca, stable hydroxides of Fe and Al more than FA and, as a rule, form less soluble complexes with TUE than FA. The competitive interaction of plutonium and americium with water-soluble components of FA and with insoluble components of HA which are specific sorbents of radionuclides considerably influences their mobility in soils. This paper is devoted to study of connection of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  with most important groups of organic substances of Belarusian soils. The aim of investigation is to analyze the effect of natural humus components on migratory properties of radionuclides in different types of soil.

### 2. OBJECTS AND METHODS OF INVESTIGATION

The objects of investigation were samples of (0-5)-cm layers of mineral and organic soils (Table 1). The points of observation are situated in Khoyniki district of Gomel region at the distance of 20-50 km from Chernobyl Nuclear Power Plant (CNPP). The extraction and separation of soil HS was carried out with the modified Tyurin's method [4]. It is based on the distinction in solubility of different groups of organic substances in water solutions of alkalis and acids. The following humus fractions of soil were obtained:

- $\text{FA}_I$  and  $\text{HA}_I$  — fulvic and humic acids, free and bound with mobile forms of Fe and Al hydroxides, soluble in 0.1 M NaOH;
- $\text{FA}_{II}$  and  $\text{HA}_{II}$  — fulvic and humic acids bound mainly with Ca, soluble in 0.1 M NaOH after treatment by 0.05 M  $\text{H}_2\text{SO}_4$  (decalcification of soil);

- **FA<sub>III</sub>** and **HA<sub>III</sub>** — fulvic and humic acids associated with soil clay minerals and stable forms of Fe and Al hydroxides, soluble in 0.02 M NaOH at temperature of 343 - 353 K;
- **HR** — humus of soil residue involving the slightly humified organic matter (OM) or most insoluble HS firmly associated with clay minerals of soil.

The content of HA and FA in solutions has been measured using the method of spectrophotometry [5]. The mass-molecular analysis of humus components in organic fractions and in soil solutions was carried out by method of gel chromatography using sephadexes G 25, G 100 and as filter gel G 10 [3]. The soil solutions with different concentration of OM were obtained from different types of water saturated soils by high-speed centrifuge SIGMA-4-10. The chemical characteristics of soil, solutions and activity of <sup>239,240</sup>Pu and <sup>241</sup>Am in the samples have been determined by standard methods of chemical and radiochemical analysis using <sup>242</sup>Pu and <sup>252</sup>Cf as the tracers for estimation of chemical yields of radionuclides [6, 7]. The radionuclides were detected by  $\alpha$ -spectrometer ALPHA-KING 676 A.

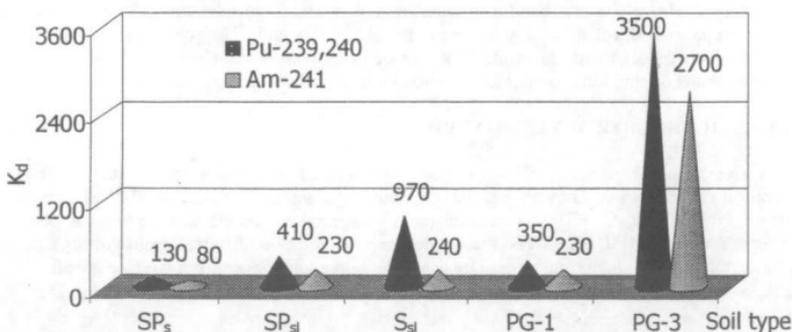
### 3. RESULTS AND DISCUSSION

The distribution coefficient  $K_d$  of <sup>239,240</sup>Pu and <sup>241</sup>Am between solid and water phases of soil (the ratio of activity concentrations of radionuclide in corresponding phases) was used as a measure of radionuclide mobility in soil. If the activity concentrations of radionuclide in the solid and liquid phases are expressed in the same units,  $K_d$  is a dimensionless value. A higher  $K_d$  corresponds to a lower mobility of radionuclide in soil. The distribution coefficients  $K_d$  of radionuclides for water saturated soils (Table 1, Fig. 1) show that the mobility of <sup>239,240</sup>Pu and <sup>241</sup>Am significantly depends on the properties of soil, in particular, the content of OM.

**Table 1.** The characteristics of dry soil samples (dried at 373-378 K)

Soil	Sampling date	pH <sub>KCl</sub>	OM, %	WC, %	C <sub>d,ex</sub>	CEC	A <sup>239,240</sup> Pu	A <sup>241</sup> Am
					meq/kg		Bq/kg	
SP <sub>s</sub> -2	1997, July	4.4±0.1	0.9±0.1	31.8±2.1	1.3±0.3	51.4±2.6	37.4±3.7	41.7±4.2
SP <sub>s</sub> -5	1997, July	4.0±0.1	1.3±0.1	30.1±3.0	1.5±0.3	29.0±2.9	67.2±3.4	75.1±3.8
SP <sub>sl</sub> -6	1995, May	5.0±0.1	7.5±0.4	59.2±1.4	54±5	166±8	27.7±2.8	29.2±2.9
S <sub>sl</sub> -2	1995, May	4.9±0.1	8.4±0.4	83.0±2.0	48±6	105±5	124±6	139±7
PG-1	1997, July	4.4±0.1	44±2	263±12	317±32	890±60	253±13	276±14
PG-3	1997, July	4.8±0.1	39±2	237±15	324±32	960±28	281±14	399±31

SP<sub>s</sub> — soddy-podzolic sand, SP<sub>sl</sub> — soddy-podzolic sandy loam, S<sub>sl</sub> — soddy sandy loam, PG — peat gley, OM — content of organic matter, WC — water capacity (total content of water kept solid phase of soil), CEC — cationic exchange capacity, C<sub>d,ex</sub> — content of exchangeable form of calcium.



**Figure 1.** The distribution coefficients of <sup>239,240</sup>Pu and <sup>241</sup>Am ( $K_d$ ) between solid and water phases of soils.

The highest mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  was found in soddy-podzolic friable sand,  $\text{SP}_{\text{f}-2}$  and  $\text{SP}_{\text{f}-5}$ , with content of OM in soil about 1% (an average distribution coefficient  $K_d$ : 80 - 130). In other mineral soils: soddy-podzolic and soddy sandy loam,  $\text{SP}_{\text{sl}-6}$ ,  $\text{S}_{\text{sl}-2}$ , with content of OM in soil about 8% the mobility of radionuclides is lower ( $K_d$ : 230 - 970). In organic soils, PG-1 and PG-3, with approximately equal content of OM (~40%) the mobility of TUE depends on the structure of HS. The content of water-soluble OM influences appreciably the mobility of plutonium and americium. In soil PG-1 with relatively high portion of OM in the water phase (2240 mg/l)  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  are much more mobile ( $K_d$ : 230 - 350) than in soil PG-3 ( $K_d$ : 2700 - 3500) with low content of such components in the water phase (190 mg/l, Table 2). The attention is drawn to the fact that there are essential distinctions not only between the concentrations of OM but also between the concentrations of iron in the water phase of different soils. In the peat gley soil, PG-1, the content of the mentioned components is much higher (more than factor 10) in comparison with PG-3. It seems likely that in such soils  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  enter into the water solution in composition of organomineral complexes with iron. A higher ratio between concentrations of OM and Fe in the water phase of soil,  $[\text{OM}]/[\text{Fe}]$ , corresponds to the higher distribution coefficient  $K_d$  of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$ . For example, the higher ratio  $[\text{OM}]/[\text{Fe}]$  in soddy-podzolic sandy loam,  $\text{SP}_{\text{sl}-6}$ , (26) corresponds to the lower mobility of radionuclides ( $K_d$ : 230 - 410) than in soddy-podzolic sand,  $\text{SP}_{\text{f}-2}$  and  $\text{SP}_{\text{f}-5}$ , (average  $[\text{OM}]/[\text{Fe}]=10$ ,  $K_d$ : 80 - 130). The same situation we see in peat gley soil: the higher ratio  $[\text{OM}]/[\text{Fe}]$  in PG-3 (54) corresponds to the lower mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  ( $K_d$ : 2700 - 3500) compare to PG-1, where mentioned ratio is 37 and  $K_d$ : 230 - 350.

Table 2. The characteristics of soil solutions

Soil	pH	$\text{Ca}^{2+}$	$\text{Fe}^{3+}$	OM	$\text{A}^{239,240}\text{Pu}$ and $\text{A}^{241}\text{Am}$	
		mg/l			Bq/kg	
$\text{SP}_{\text{f}-2}$	6.6±0.1	10.0±1.0	4.3±0.4	18±4	0.32±0.03	0.52±0.05
$\text{SP}_{\text{f}-5}$	6.2±0.1	10.0±1.0	4.9±0.05	70±4	0.46±0.04	0.90±0.09
$\text{SP}_{\text{sl}-6}$	7.0±0.1	65.1±6.5	22±2	574±29	0.07±0.01	0.13±0.03
$\text{S}_{\text{sl}-2}$	6.3±0.1	30.1±3.0	N.A.	300±15	0.13±0.02	0.61±0.02
PG-1	6.3±0.1	80.2±8.0	60±6	2240±100	0.72±0.07	1.21±0.12
PG-3	4.0±0.1	140±14	3.5±0.4	190±10	0.08±0.001	0.15±0.02

N.A. — samples were not analyzed.

To analyze the influence of OM on migratory properties of radionuclides in more detail the study of distribution of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  between different fractions of HS of mineral and organic soils has been carried out. The components of all extracted and separated fractions of soil humus can form complexes with plutonium and americium [1, 2]. The distribution of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  between organic fractions of soddy-podzolic sandy ( $\text{SP}_{\text{f}-5}$ ) and peat gley (PG-1) soils which differ significantly in quantitative and qualitative composition of OM has been found (Fig. 2). In composition of HS of mineral soil the total

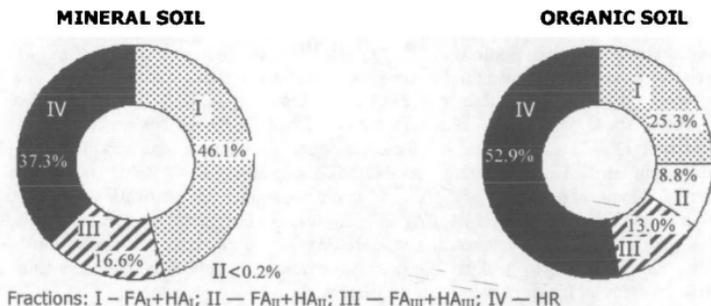
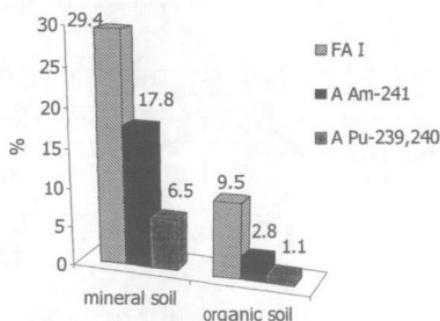


Figure 2. The content of organic fractions (I, II, III, IV, % of total mass of soil humus) in soils.

amount of FA ( $\Sigma$ FA) dominates over the total amount of HA ( $\Sigma$ HA) and the ratio  $\Sigma$ FA/ $\Sigma$ HA is 1.5. In organic soil it is the reverse of that and the ratio  $\Sigma$ FA/ $\Sigma$ HA is 0.5.

In sandy soil the portion of fractions  $FA_I$  and  $HA_I$  (46 % of total HS content in soil) is significantly higher than in peat soil (25 %, Fig. 2). The portion of the most mobile water-soluble fraction  $FA_I$  in mineral soil (29 %) is also higher compare to organic soil (9.5 %). The components of this  $FA_I$  fraction predominate in natural waters, the components of  $HA_I$  fraction are found there in insignificant amount [1]. Other organic fractions of soil ( $FA_{II}$ ,  $HA_{II}$ ,  $FA_{III}$ ,  $HA_{III}$  and HR) are insoluble in water and characterized by much lower mobility in soil.

It was found that in the both soils  $^{239,240}\text{Pu}$  is detected mainly in HR fraction of soil residue. It can be mentioned that in general the soil residue includes not only the most insoluble organic and organomineral complexes of TUE but also the insoluble products of their hydrolysis, radionuclides fixed by mineral components of soil and the fuel particles containing plutonium and americium. In studied soils the role of fuel particles in fixation of plutonium and americium is insignificant. In 1995 and later only at the areas near to CNPP ( $\leq 10$  km) can the fuel particles significantly influence the properties of TUE [7]. Plutonium and americium can form different complexes with organic and inorganic ligands of soil in wide limits of stability. The most stable complexes of plutonium and americium are formed with organic ligands of soil. Moreover, formation of organic complexes can suppress the hydrolysis of TUE and significantly influence their forms in soils and aquatic systems [1].

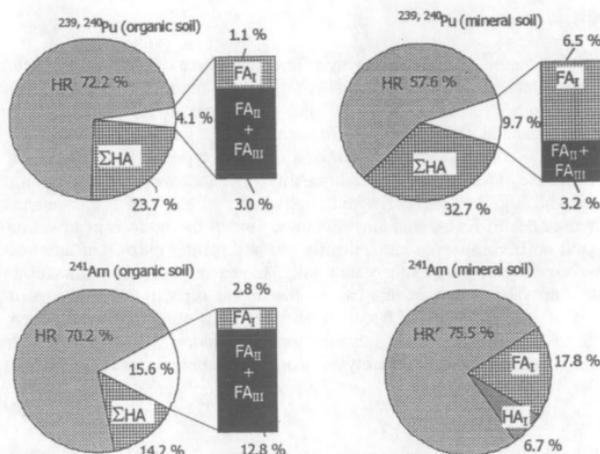


**Figure 3:** The portions of the most mobile fractions of soil fulvic acids ( $FA_I$ , % of total humus mass) and  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in the  $FA_I$  fraction of soils (A, % of total radionuclide content in the soil sample).

In organic soil HR fraction contained more  $^{239,240}\text{Pu}$  (72 %) than in mineral soil (58 %, Fig. 4). The remainder of the radionuclide in organic soil was found predominantly in HA fractions ( $HA_I + HA_{II} + HA_{III}$ ). In this soil the main part of  $^{241}\text{Am}$  was also found in HR (71 %) but the remainder of the radionuclide is almost evenly distributed between FA (15.6 %) and HA (14.2 %) fractions.

It was established that the portions of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in the most mobile fraction  $FA_I$  of mineral soil (6.5 and 17.8 %) are higher than in the same fraction of organic soil (1.1 and 2.8 %). The distinctions between humus composition of these soils can be the reason of different distribution of radionuclides between organic fractions of soils. As previously mentioned, in humus substances of mineral soil the portion of fraction  $FA_I$  is much higher than the corresponding fraction in organic soil (Fig. 3). In the both soils the portion of  $^{241}\text{Am}$  in fraction  $FA_I$  exceeds the portion of  $^{239,240}\text{Pu}$ . Because of noticeable hydrolysis of humus compounds of  $^{241}\text{Am}$  in acidic treatment (decalcification) of mineral soil its distribution among fractions  $HA_{II}$ ,  $HA_{III}$ ,  $FA_{II}$  and  $FA_{III}$  was not estimated. A lower stability of americium complexes than plutonium complexes and lack of OM in mineral soil to suppress the hydrolysis of americium compounds in acid medium is a possible reason of this phenomenon. In mineral soil humus residue HR' includes all fractions mentioned above (Fig. 4).

The results of gel chromatography analysis show that the organic substances of similar nature are present in aquatic solutions of all studied soils. The main part of water soluble organic substances in soil



**Figure 4:** The distribution of radionuclides between organic fractions of soils.  $\Sigma HA = HA_I + HA_{II} + HA_{III}$ , HR and HR' are humus of soil residues.

and natural waters are the components of  $FA_I$  fraction with molecular mass 600 - 800 D and only an insignificant amount of  $HA_I$  (few percents of soluble OM) are components with molecular mass 2000 D. The HS with greater molecular mass (5 000 - 30 000, 150 000, > 150 000 D) were found in composition of HS extracted from soil with 0.1 M NaOH after its decalcification at temperature 293 - 298 K and 0.02 M NaOH at temperature of 343 - 353 K.

The data on fractionation of HS and distribution of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  between organic fractions allow us to differentiate the soil with respect to humus influence on migration properties of radionuclides. It was shown that humus being the important part of the absorbing complex mainly fixes  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in the solid phase of soil. The insoluble part of OM of soil fixes plutonium to a greater extent than  $^{241}\text{Am}$ . The fixation of radionuclides in soil significantly depends on the quantitative and qualitative composition of HS. The mobility of radionuclides is essentially decreased as a result of formation of their difficultly soluble complexes not only with high molecular HA ( $M: \geq 30\ 000$  D) but also with relatively low molecular FA (5 000 - 20 000 D), associated with Ca, stable hydroxides of Fe, Al and clay minerals. The humus of organic soils is more favorable for fixation of radionuclides than humus of mineral soils and it can be one of the reasons of lower mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in these soils.

In the majority of soils  $^{241}\text{Am}$  is more mobile than  $^{239,240}\text{Pu}$ . The reason of this can be the higher capacity of plutonium to form the difficultly soluble complexes of low mobility with components of soil humus. Increasing the soil acidity causes the destruction of radionuclide complexes with HS associated with Ca similar to decalcification process. As a result an increase in content of relatively mobile forms of FA and corresponding actinide complexes in soil can occur. The content of  $^{239,240}\text{Pu}$  in fraction  $FA_{II}$  in organic soil is 1.4 % and in mineral soil — 0.1 %. The content of  $^{239,240}\text{Pu}$  in fraction  $HA_{II}$  is higher: 8.6 % in organic soil and 2.6 % in mineral soil.

In acid medium the hydrolysis of organic complexes of americium in mineral soil intensifies and the concentration of its cationic forms participating in migration processes increases. It should be emphasized that the stable cationic form  $\text{Am}^{3+}$  is found only in acid medium and the likelihood of its presence in soil solution at pH about 7 is low [1, 2].

#### 4. CONCLUSION

The mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in soils with different structure of the absorbing complex is different. The distribution coefficient of radionuclide between solid and liquid phases of soil ( $K_d$ ) varies from 80 to 2700 for  $^{241}\text{Am}$  and from 130 to 3500 for  $^{239,240}\text{Pu}$ . The values of  $K_d$  point at the higher mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in mineral soils ( $K_d$ : 80 – 970) compare to organic soils with minor portion of water-soluble OM ( $K_d$ : 2700 – 3500). It was established that in all types of soil HS mainly fix  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in the solid phase. The mobility of radionuclides is low owing to formation of their difficultly soluble complexes with high-molecular HS and components of HA and FA fractions of soil associated with Ca, stable hydroxides of Fe, Al and clay minerals. One of the reasons of lower mobility of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  in organic soils compare to mineral soils can be a greater portion of humus components fixing radionuclides in absorbing complex of organic soils. In the majority of soils the americium is more mobile than plutonium. The reason of this can be the higher capacity of plutonium to form difficultly soluble complexes of low mobility with components of soil humus in comparison with americium. Increasing in soil acidity promotes the higher radionuclide mobility, especially  $^{241}\text{Am}$ , as a result of destruction FA complexes with Ca and hydrolysis of organic complexes of americium in mineral soils.

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