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Geochemical fractionation and bioavailability of ^{241}Am , ^{60}Co and ^{137}Cs in Fluvisol soil after sharp temperature variation before the growing season

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This paper deals with the influence of sharp temperature variations on the geochemical fractionation and bioavailability of ^{241}Am , ^{60}Co and ^{137}Cs in Fluvisol soil. The study was performed using soil contaminated with aqueous solutions of ^{241}Am , ^{60}Co and ^{137}Cs in the laboratory and stored for three years at temperatures within the range of 10–18 °C and soil moisture from 20 to 30 wt %. Afterward the soil was divided into three equal parts and conditioned for one month at 10–18 °C, –18 °C and 40 °C temperature regimes, respectively. The impact of the storage conditions on geochemical forms of the radionuclides was investigated using single extraction of exchangeable ^{137}Cs with 1 M NH_4NO_3 and sequential extraction of ^{241}Am and ^{60}Co , and by gamma-spectrometric measurement. The influence of temperature rise up to 40 °C over a period of one month on the transfer factors (TFs) of the radionuclides from the investigated soil to orchard grass (*Dactylis glomerata* L.) was evaluated. The results showed that deep freezing and a sharp temperature increase continuing for one month led to re-distribution of ^{241}Am and ^{60}Co between the soil phases and provoked an increase of the exchangeable ^{137}Cs . Freezing led to a decrease of ^{241}Am in the residual fraction and an increase of oxide-bound americium. The storage at frozen conditions led to decrease of oxide bounded ^{60}Co and increased immobilization in the residual fraction. Conditioning at high temperature increased the migration ability of ^{241}Am and ^{137}Cs , while immobilization of ^{60}Co was registered. Conditioning at a sharp temperature increase before the growing season led to higher values of the TFs of all the studied radionuclides. This effect was highest for ^{137}Cs . The sharp temperature change of contaminated Fluvisol soil lasting one month was found to create a risk of increased migration and bioaccumulation of radionuclides.

Key words: radionuclides, geochemical forms, sharp temperature variation, Fluvisol soil, orchard grass, transfer factors

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Introduction

Understanding geochemical fractionation and bioaccumulation of radionuclides in nature are important tasks of radioecological studies, especially after a nuclear accident, when the radiological risk of their migration and transfer into the food chain is to be evaluated. Transfer factors of radionuclides are used to evaluate the biological uptake and the distribution of radioactive contaminants from soil to vegetation. They are defined as the ratio of the activity concentration (Bq/kg) of the radionuclide in a given plant species and its activity concentration in the soil. The TF values of the radionuclides vary significantly and were found to depend on soil characteristics and plant species (IAEA 2006, 2010). The main factors, which cause this variability for any particular radionuclide, are the type of crop and type of soil. The length of time the radionuclide has been in the soil is also important, particularly for ^{137}Cs . Other factors, such as crop variety, agricultural practice (especially fertilization) and weather variations during the growing season were also reported to be significant (IAEA 2006).

Numerous investigations summarized and discussed by Dowdall et al. (2008), showed that the sharp variations of the environmental temperature and precipitations may alter the soil properties and influence the geochemical fractionation of the radionuclides, thus changing their TFs.

The impact of the sharp changes of the environmental parameters is expected to be higher in the first months after contamination, when the radionuclides are not fixed to the soil matrix. Therefore, we performed several investigations on the effects of extreme environmental conditions on the geochemical behavior of radionuclides in non-equilibrium systems, shortly after their release into the soil. The influence of freezing on the migration ability and bio-availability of natural and technogenic radionuclides in the first weeks after their entry into Chernozem soil was studied; an increase in the potential migration ability of radiocobalt, radiocesium, radium, and thorium as a result of sharp temperature drop and subsequent thawing was registered (Kovacheva and Djingova 2014). The same soil type was used to investigate the influence of sharp changes in environmental temperature and soil drought on the physicochemical fractionation of Am, Th, and U in Chernozem during the first months after the contamination. Increased potential migration ability of Am and Th after three months of freezing was found and lack of changes after prolonged soil drought were registered. Immobilization of U and its redistribution between the soil phases after storage under freezing and water-deficient conditions were detected (Kovacheva et al. 2014).

The effects of the sharp drop of the environmental temperature and the soil drought on the geochemical forms of ^{241}Am , depending on soil characteristics, were also studied (Kovacheva et al. 2013). The changes of the geochemical fractionation of americium, driven by freezing and drought and continuing for one re-

spectively five months after its entrance into two soil types: Fluvisol and Cambisol were evaluated. Our data showed a risk of increased migration ability and bioavailability of americium in the Fluvisol soil, which has acidic pH, very low cation exchange capacity (CEC) and high sand content, while the opposite effects were observed in Cambisol soil.

Based on the obtained results, we considered carrying out a case study on Fluvisol soil, which is more sensitive to environmental conditions, to be aged for a longer period (three years) after its radioactive contamination. The study aimed at determining the geochemical fractionation and transfer factors of radionuclides after sharp changes of environmental temperature, simulating a very hot summer and a very cold winter.

This study presents the effects, during one month of deep freezing and temperature increase, on the geochemical forms and bioavailability of three of the most often-monitored technogenic radionuclides in Fluvisol soil. The experiment modelled the scenario where the soil was contaminated with an aqueous radioactive solution and aged for three years at temperatures in the range of 14–20 °C and soil moisture from 20 to 30 wt %. Afterward, a sharp increase and decrease of the environmental temperature, continuing for one month, was simulated and the geochemical fractionation of ^{241}Am , ^{60}Co and ^{137}Cs was determined.

Subsequently the initial temperature range was restored and the soil samples were planted with orchard grass (*Dactylis glomerata* L.) for determination of the TF values. Geochemical forms of ^{241}Am under different conditions were determined by the sequential extraction procedure proposed by Schultz et al. (1998) and recommended by the National Institute of Standards and Technology (NIST), USA, for fractionation of actinides in soils and sediments. The fractionation of ^{60}Co was studied using the three-stage sequential extraction procedure recommended by the European Community Bureau of Reference (BCR procedure) and described in Ure et al. (1993). This procedure has been widely applied to soil and sediment samples to study fractionation of heavy and toxic elements in environmental solids including soils, sediments, suspended particulate materials, as well as urban street dusts (Davidson et al. 1998; Usero et al. 1998; Feng et al. 2009). Single extraction of ^{137}Cs was obtained after extraction with 1 M NH_4NO_3 to determine its exchangeable forms and evaluate migration ability and bioavailability (Twining et al. 2006; Todorov et al. 2008).

Dactylis glomerata L. was chosen for the experiment because it is a fast-growing, medium- to long-lived, perennial bunchgrass, which is widely used for hay and pasture.

The aim of the study was to obtain data on the geochemical forms of ^{241}Am , ^{60}Co and ^{137}Cs and their transfer factors from soil to grass, when preceded by sharp variations of the ambient temperature.

Materials and methods

Soil, contamination, conditioning and greenhouse experiment

Fluvisol soil (FAO 2006) with the total weight of 1 kg was taken from the surface soil layer (0–5 cm) from the urban area in Sofia, Bulgaria. The soil was air-dried, cleaned from plant impurities and sieved through 2 mm-sieves.

The soil was classified as of loamy sand texture, containing 78.05% sand, 20.16% silt and 1.79% clay and 2.65% humus. The CEC of the soil was 5.89 cmol+/kg, and pH 5.5 in H₂O and 5.2 in 0.1 M KCl, respectively. The soil mineral composition, determined by X-ray diffraction analysis included feldspar (56%), quartz (25.4%), muscovite (10.4%), diopside (7.2%) and paracelsian (0.8%).

A soil sample with a weight of 50 g was homogenized in an agate mortar and measured by gamma-spectrometry. The activity concentration (*S*) of the radionuclides investigated prior to laboratory contamination, as determined by gamma-spectrometry, was as follows: $S < 0.7 \text{ Bq g}^{-1}$ for ²⁴¹Am; $S < 0.6 \text{ Bq g}^{-1}$ for ⁶⁰Co; $S < 0.5 \text{ Bq g}^{-1}$ for ¹³⁷Cs. Afterward, the rest of the bulk sample was divided into two subsamples and each of them was contaminated with aqueous solutions of radionuclides in chloride forms as follows: (i) ²⁴¹Am; and (ii) ⁶⁰Co and ¹³⁷Cs. The activity concentration of the contaminated samples was as follows: $S = 25 \pm 0.3 \text{ Bq g}^{-1}$ for ²⁴¹Am; $S = 10 \pm 0.01 \text{ Bq g}^{-1}$ for ⁶⁰Co; and $S = 15 \pm 0.01 \text{ Bq g}^{-1}$ for ¹³⁷Cs. The contaminated soil subsamples were homogenized, placed in plastic vessels and arranged in layers with a thickness of 5 cm. Thereafter the soil subsamples were conditioned for three years at $18 \pm 2 \text{ }^\circ\text{C}$ during the day and $10 \pm 3 \text{ }^\circ\text{C}$ during the night in open-air vessels in the laboratory. The soil was periodically watered, so that soil moisture varied within the range of 20–30 wt %. Subsequently, each subsample was divided into three equal parts, and conditioned for one month under the following conditions:

- A) $18 \pm 2 \text{ }^\circ\text{C}$ during the day and $10 \pm 3 \text{ }^\circ\text{C}$ during the night in open-air vessels in the laboratory. The sample was watered periodically so that the soil moisture varied within the range of 20–30 wt %;
- B) $-18 \pm 1 \text{ }^\circ\text{C}$ and soil moisture of $30 \pm 1 \text{ wt } \%$, achieved using closed plastic vessels in a freezer;
- C) $40 \pm 0.1 \text{ }^\circ\text{C}$ and relative air humidity of $50 \pm 0.1 \text{ wt } \%$, achieved by using a constant climate chamber Model HPP 108 (Mettmert GmbH, Germany). The soils were watered every two days and the soil moisture varied between 20 wt % and 30 wt %.

The experiments were carried out using three parallel samples of each storage condition. After conditioning, equal parts of the soil subsamples with a weight of 50 g each were taken; the frozen sample was thawed, all were dried at $30 \text{ }^\circ\text{C}$ for 24 h and processed by the sequential extraction procedure described below.

Thereafter the rest of the three conditioned soil subsamples were kept at condition A) for five days, then planted with orchard grass (*Dactylis glomerata* L.) and stored at the same conditions for two weeks until growing. The grass samples were collected by cutting at 0.5 cm above the soil surface, washed with tap and distilled water, air-dried, ground in a ball-mill and prepared for gamma-spectrometric measurements by packing in standardized geometry with a weight of 15 g.

Extraction procedures

The fractionation of ^{241}Am under different conditions was determined by the sequential extraction procedure proposed by Schultz et al. (1998). Four reagents: (1) 0.4 M MgCl_2 (pH 5), (2) 5–6% NaOCl (pH 7.5), (3) 1 M CH_3COONa in 25% CH_3COOH (pH 4) and (4) 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (pH 2) were applied for extraction of: (1) water soluble and exchangeable, (2) associated with the organic matter, (3) bound to the soil carbonates or specifically sorbed and (4) associated with Fe/Mn oxyhydroxide (sesquioxide) fractions.

The fractionation of ^{60}Co was studied using the three-stage sequential extraction procedure as described in Ure et al. (1993).

The exchangeable ^{137}Cs was determined after extraction with 1 M NH_4NO_3 as described in Kovacheva and Djingova (2014).

The relative contents (in %) of the radionuclides in the residual fractions were determined by the difference between their total radioactivity in the soil and the activity, extracted by the extractive reagents. Supernatants were separated from the solid phase by centrifugation at 3000 rpm at 20 °C for 20 min, followed by filtering through 0.2 μm cellulose nitrate filters using vacuum driven filtration, as performed in previous study (Kovacheva et al. 2013).

Measurement conditions

The crystal structure of the soil samples was studied by X-ray diffraction (powder diffractometer Siemens D500) using $\text{CuK}\alpha$ radiation filtered by a secondary monochromator (40 kV, 30 mA, $0.05^\circ 2\Theta/2\text{ s}$) for the 2Θ interval 3–60°. The phase identification and quantitative phase analysis of the soil minerals were performed by X'Pert HighScore Plus software.

The radioactivity of solid samples and leachates was determined using an HPGe detector Canberra 7229 (energy resolution of 1.9 and efficiency of 16% at 1332.5 keV) coupled to a 16000-channel DSA-1000 analyzer. The spectra were processed using Genie-2000 Basic Spectroscopy software. Efficiency calibration and measurements were performed as described in Kovacheva and Djingova (2014).

Table 1
Distribution of ^{241}Am , ^{60}Co and ^{137}Cs in various soil phases after their conditioning under different temperature regimes

Radionuclide	Soil fractions	Conditions of storage		
		(A) 18 °C, soil moisture 20–30 wt %	(B) –18 °C, soil moisture 20–30 wt %	(C) 40 °C, soil moisture 20–30 wt %
^{241}Am , %	Water soluble and exchangeable	2.20 ± 0.02	2.93 ± 0.03	4.87 ± 0.06
	Organic	8.80 ± 0.44	10.00 ± 0.51	4.47 ± 0.23
	Carbonate	24.7 ± 1.3	23.5 ± 1.2	48.6 ± 2.8
	Sesquioxide	1.00 ± 0.08	5.71 ± 0.46	6.66 ± 0.52
	Residual	63.3 ± 5.1	57.9 ± 4.2	35.4 ± 3.1
^{60}Co , %	Water-soluble, exchangeable and carbonate	42.0 ± 1.7	45.0 ± 1.8	28.0 ± 1.3
	Easily reducible oxides	40.0 ± 1.6	2.00 ± 0.08	40.0 ± 1.6
	Organic matter and sulfide	18.0 ± 0.78	22.0 ± 0.91	23.0 ± 0.86
	Residual	0.00	4.00 ± 0.2	9.00 ± 0.5
^{137}Cs , %	Exchangeable	6.5 ± 0.4	12.5 ± 0.7	10.7 ± 0.6

Results and discussion

Geochemical fractionation after sharp temperature variation

The results of the geochemical fractionation of the radionuclides after storage under conditions A, B and C (as described above) are presented in Table 1 and

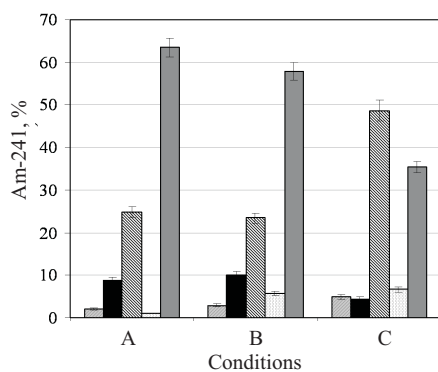


Fig. 1
Distribution of ^{241}Am in various soil phases after storage under different conditions: water-soluble and exchangeable fractions (□); organic matter fraction (▨); carbonate-bound fraction (■); sesquioxide-bound fraction (▤); residual fraction (▥)

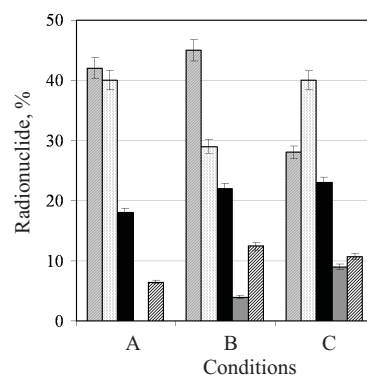


Fig. 2
Distribution of ^{60}Co in various soil phases: water-soluble, exchangeable and carbonates (▨); easily reducible oxides (□); organic matter and sulfides (■); residual fraction (▤) and exchangeable ^{137}Cs (▥) after storage under different conditions

Figs 1 and 2. The data represent the mean percentage of a radionuclide in each fraction \pm standard deviation calculated from triplicate determinations.

Deep-freezing for one month did not cause any significant changes in the distribution of ^{241}Am among the soil fractions, as can be seen from Fig. 1 (comparing the data at conditions A and B). The results showed an increase of the radionuclide fraction, bound to sesquioxides from 1 to 6% and a decrease of its relative content in the residual fraction. The same effects were observed in our previous study (Kovacheva et al. 2013), examining the changes of the geochemical fractionation of ^{241}Am as a result of one month freezing, occurring one week after its deposition in Fluvisol soil. It seems that the sharp temperature decrease has the same influence on americium fractionation in the studied loamy sand soil, both after short term and prolonged fixation of the radionuclide. These results can be ascribed to the impact of the deep freezing on the soil aggregates. Water expansion during the freezing process leads to the mechanical stress of its surroundings, which causes fracturing. The freeze-driven destruction of soil aggregates and dispersion could provoke partial elaboration of radionuclides from the solid phases and redistribution among the soil phases. Often clay minerals are covered by organic substances, impeding radionuclide interactions with soil oxides and carbonates. The registered increase of oxide-bound ^{241}Am can be explained by the increased surface of soil oxides due to organic matter desorption as a result of frost weathering.

This provoked an increased interaction between the soil solution and the mineral phase and enabled redistribution of the radionuclide between the fractions. Temperature increase up to 40 °C (condition C in Fig. 1) caused redistribution of ^{241}Am , provoked by increased weathering of the soil. A two-fold increase of americium content in the water-soluble, exchangeable, and carbonate-associated fraction, was registered compared to condition A. A decrease of the organic bound fraction and rise of the sesquioxide fraction were also registered. These effects could be due to desorption processes provoked by the temperature increase, which caused both mobilization of ^{241}Am and an increase of the concentrations of competitive ions at the surfaces of inorganic and humate-coated minerals, due to the increased solubility of numerous salts present in the soil. As a result, part of the desorbed ^{241}Am in forms of Am^{3+} , $\text{Am}(\text{CO}_3)_x^{3-2x}$ and $\text{Am}(\text{OH})_x^{3-x}$, AmSO_4^+ , AmNO_3^{2+} , AmCl^{2+} , etc., became associated with soil carbonates and sesquioxides; the rest remained in the water-soluble and exchangeable fraction. These changes led to a decrease of its content in the residual fraction from 63% to 35%. Accordingly, the sharp temperature change and its continuation for one month can induce liberation of Am fixed to the residual soil phases and increase its potential migration ability in the studied Fluvisol soil.

Freezing for one month caused a slight increase of the relative content of ^{60}Co , associated with the soil organic matter and sulfides and with the water-soluble, exchangeable and carbonate-bound fraction (Fig. 2; condition B). The rise of the labile fraction of the radionuclide can be attributed to the effects of the above-mentioned frost weathering of the soil. Simultaneously a decrease of the

oxide fraction from 40% to 29% and the appearance of a residual fraction of ^{60}Co were determined. Marion (1995) reported that solute exclusion during ice formation caused supersaturation of soil solutions, promoted precipitation of secondary minerals in soil and altered solution-phase compositions because of mechanical weathering. This could have caused an increased inclusion of the radionuclide in the residual fraction, e.g. due to co-precipitation of Co to Fe and Mn oxyhydroxides and sulphides, or an isotopic exchange of ^{60}Co with stable Co in cobalt-containing minerals. Such an effect of immobilization was observed in our previous investigations (Kovacheva et al. 2013) for ^{241}Am in Cambisol soil, frozen one week after its contamination and stored under this condition during 1 and 5 months, respectively.

The temperature rise during one month (condition C in Fig. 2) also provoked a redistribution of ^{60}Co between the soil fractions, which led to its immobilization. The water-soluble, exchangeable and carbonate-bound fraction of ^{60}Co decreased by 33%, while a slight increase of the organic-bound fraction and residual fraction, twice as much as for condition B was measured. Apparently, the higher temperature promoted the fixation of this radionuclide by transferring it from more mobile to less mobile geochemical fractions in the studied Fluvisol soil.

The data in Fig. 2 show an increase of the exchangeable ^{137}Cs , after conditioning of the soil both at decreased and increased environmental temperature. A similar effect of the freezing was registered in Chernozem soil in our previous investigations (Kovacheva and Djingova 2014). The sharp temperature variations were found to stimulate desorption of ^{137}Cs from the clay minerals. The effect, observed after storage at high temperature, could be explained by the increase of the concentration of competitive ions as a consequence of increased salt solubility caused by temperature rise. The rapid temperature decrease and storage at $-18\text{ }^{\circ}\text{C}$ promoted the destruction of clay minerals and the release of some portion of ^{137}Cs that was fixed in their structure. The expansion or contraction of the soil particles due to deep-freezing or temperature increase might have affected their aggregate stability, causing dispersion of the soil particles and increasing the specific soil surface.

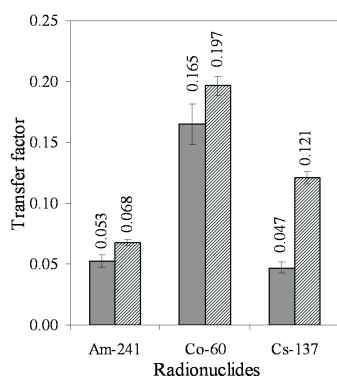


Fig. 3
Transfer factors of ^{241}Am , ^{60}Co and ^{137}Cs from Fluvisol soil to grass after storage during one month under conditions A (■) and C (▨), and planting at condition A

Transfer factors

Fig. 3 presents the TF values (calculated as the ratio Bq/kg dry grass to Bq/kg dry soil) from the greenhouse experiment with the soil subsamples, conditioned for one month under conditions A and C before the growing season. No grass grew on the soil stored at $-18\text{ }^{\circ}\text{C}$ (condition B). This could be explained by destructive effects of the month-long deep-freezing and thawing upon the soil aggregates. Frost formation causes mechanical weathering, which promotes destruction of soil compartments (e.g. clay minerals), leading to raised salinity of the soil solution after thawing. *Dactylis glomerata* L. tolerates low to moderate salinity and the above-mentioned soil alteration might have been the reason for the lack of vegetation.

The data in Fig. 3 show that the storage at increased temperature (condition C) for one month before planting led to higher bioavailability. This tendency is clearly expressed for the three investigated radionuclides although with different degrees of magnitude. The strongest effect is observed in TF of ^{137}Cs , where a relative increase of more than 150% is registered, compared to the TF obtained after constant storage at condition A. Apparently the temperature rise caused desorption of ^{137}Cs from the clay minerals of the soil, thus increasing its bioavailable forms. This is in agreement with the data presented in Fig. 2, where the relative percentage of exchangeable ^{137}Cs is shown to be 1.65 times higher after storage under condition C compared to condition A.

Smaller relative increases of the TF values were determined for ^{241}Am – 30% and ^{60}Co – 20%. Referring to the data for the geochemical fractionation of ^{241}Am (Fig. 1), showing that the temperature rise led to a nearly twofold relative content of its water-soluble and exchangeable forms, the observed effect on the TF follows the registered tendency. The data for geochemical fractionation of ^{60}Co do not directly resemble the obtained TF values. According to the results in Fig. 2, the migration ability of this radionuclide is expected to be lower at high temperature, as evaluated by the water-soluble, exchangeable and carbonate-associated fraction. However, the determined 20% increase of bioaccumulation after condition C corresponds to the 27% increase of the organic matter and sulphide-bound fraction of ^{60}Co . This can be attributed to the fact that Co is among the 17 elements, which are known to be essential for all plants and also be readily available through Co-organic chelates (Kabata-Pendias and Pendias 2001).

According to the IAEA (2010) the mean value and minimum and maximum TF values from soil to grass, summarized for the studied radionuclides for all soil types, are as follows:

$$^{241}\text{Am} \text{ (mean } 3.3 \times 10^{-2}, \text{ min } 4.2 \times 10^{-4}, \text{ max } 2.6 \times 10^{-1}); ^{60}\text{Co} \text{ (mean } 7.7 \times 10^{-2}, \\ \text{min } 4.0 \times 10^{-2}, \text{ max } 1.7 \times 10^{-1}); \text{ and } ^{137}\text{Cs} \text{ (mean } 6.3 \times 10^{-2}, \text{ min } 4.8 \times 10^{-3}, \\ \text{max } 9.9 \times 10^{-1}).$$

The comparison of the obtained TF values with the mean TF values shows that they are of the same order of magnitude. However, the present data are much closer to the maximal TF value determined by the IAEA, and for ^{60}Co it was even exceeded after conditioning at high temperature. Despite the variations in the soil types and biological characteristics of the grass samples, these results show that three years after the contamination, the studied Fluvisol soil still presents a high risk of bioavailability of the radionuclides and transfer within the food chain. The higher TF values, obtained after storing at conditions simulating a very hot summer, imply the need for further studies in this field in order to clarify the significance of basic climatic parameters in the radioecological investigations.

Conclusions

The results presented in this paper show that a sharp temperature increase or deep freezing for one month leads to different changes in the fractionation of ^{241}Am , ^{60}Co and ^{137}Cs in the studied Fluvisol soil, three years after its contamination. An increase of the potentially mobile forms of ^{241}Am as a result of the temperature variation was established. The same effects on the exchangeable forms of ^{137}Cs were measured. Increased migration ability of ^{60}Co after deep freezing and immobilization after temperature increase were registered.

The conditioning at 40 °C before the growing season caused increased bioaccumulation of the three radionuclides in orchard grass (*Dactylis glomerata* L.). This effect was higher for ^{137}Cs than for ^{241}Am and ^{60}Co . Further studies on the effects of sharp temperature change on bioaccumulation of radionuclides from different soils types would contribute toward a better assessment of the risk of their transfer in the food chain.

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