

THE IMPACT OF SHARP TEMPERATURE SHIFT ON THE WATER-SOLUBLE FORMS OF TECHNOGENIC RADIONUCLIDES IN DIFFERENT SOIL TYPES

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Abstract. Studying the impact of sharp temperature change on the migration ability of radioactive isotopes in nature is of significant importance when predicting the radioecological risk in case of nuclear contamination. The increase or decrease of the environmental temperature may affect the mobile forms of radionuclides and change their fate in the environment, especially in the first months after their release in the soils. This study presents the impact of freezing and sharp warming on the water-soluble forms of ^{241}Am , ^{60}Co , ^{137}Cs and ^{54}Mn in four soil types: Calcaric chernozem, Gleyic fluvisol, Salic fluvisol and Vertisol, classified according to World Reference Base for Soil Resources/FAO. The experiment is a case study, based on a scenario where the radionuclides have entered the soil in the form of aqueous solution, followed by a rapid change of environmental temperature. The soil samples, taken from the surface soil layer 0-10 cm were contaminated by radioactive solutions of ^{241}Am , ^{60}Co , ^{137}Cs and ^{54}Mn , separated into three subsamples and stored during two months at different temperature regimes: $-18\text{ }^{\circ}\text{C}$, $18\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ with the use of a freezer and a climate chamber. The water-soluble forms of the radionuclides were determined by single extraction and gamma-spectrometric measurements. The sharp temperature shift led to the decrease of the water-soluble forms of ^{241}Am , ^{60}Co , ^{137}Cs and ^{54}Mn in the Salic fluvisol soil with acidic pH. The increase of water-soluble ^{60}Co and ^{54}Mn after sharp warming or freezing was determined in Calcaric chernozem, Gleyic fluvisol, and Vertisol soils. Water-soluble forms of ^{241}Am and ^{137}Cs decreased in Salic fluvisol and increased in Vertisol soil as the result of sharp temperature increase or decrease. The storage at freezing or "hot summer" conditions caused the decrease of water-soluble forms of ^{241}Am in Calcaric chernozem. The increase of water-soluble ^{137}Cs was registered in Calcaric chernozem after sharp warming and in Gleyic fluvisol after freezing.

Key words: Radionuclides, soils, water-solubility, temperature change, freezing, hot summer

DOI: 10.21175/RadProc.2016.16

1. INTRODUCTION

Release of highly soluble radionuclides in the soils as a result of nuclear contamination poses serious environmental threats due to their ability to move with aqueous media in the subsurface. A variety of factors, including the solution pH, ionic strength, moisture content, competitive sorption, and complexation with inorganic and organic ligands, influence the type and extent of sorption onto soil particles, thereby affecting the environmental transport of radioactive contaminants [1]. Besides that, the equilibrium established between the soil and the solution or pore water is strongly influenced by the chemistry of the element, the properties of the solid matrix and the environmental conditions [2]. Substantial variations of basic climatic parameters, such as environmental temperature, precipitations, soil drought, wind etc. might cause changes of microbial activity and soil properties, such as pH, cation exchange capacity (CEC) and redox potential, thus leading to change in organic matter decomposition, element leaching or ion-

exchange processes. Such changes are likely to affect the geochemical forms and soil-to-plant transfer of radionuclides [3].

Investigations on the influence of increase or decrease of environmental temperature and soil drought on geochemical forms of different radionuclides were performed [4] – [8]. Studies on 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 showed increased potential migration ability of Am and Th after three months of freezing. Immobilisation of U and its redistribution between the soil phases after storage under freezing and water-deficient conditions were registered [5]. The impact of freezing on the migration ability of natural and technogenic radionuclides in the first weeks after their entry into Chernozem soil was studied and increase in the potential migration ability of radiocobalt, radiocesium, radium, and thorium as a result of sharp temperature decrease and subsequent thawing was found [6]. The results from the investigation of the influence of cooling, freezing and

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soil drought on the migration ability and potential bioavailability of ^{60}Co and ^{137}Cs in a fluvisol and a cambisol soils from Bulgaria are presented in [8]. High migration and potential bioavailability of ^{60}Co in the loamy-sand fluvisol soil, conditioned under freezing temperatures or arid conditions for period from one up to five months were detected. No influence of the investigated storing conditions on the water-solubility of ^{60}Co in the cambisol soil was established. The temperature drop caused redistribution of ^{60}Co among the fractions in both soil orders and increased the extractable forms of this radionuclide. The aging of loamy-sand and sandy-loam soils under freezing or arid conditions one week after their contamination led to double increase of exchangeable ^{137}Cs and indicated enhanced risk for its bioaccumulation [8].

The influence of sharp changes of basic climatic parameters on the migration ability of radionuclides has not been fully investigated. The results from studies on the impact of temperature increase or decrease on the water-soluble forms of the contaminants in different soil types may be essential for prediction of the consequences of nuclear pollution – an important aspect of radiological protection.

The aim of this investigation is to evaluate the influence of freezing and sharp warming on the water-soluble forms of ^{241}Am , ^{60}Co , ^{137}Cs and ^{54}Mn in four soil types: Calcaric chernozem, Gleyic fluvisol, Salic fluvisol and Vertisol, classified according to World Reference Base for Soil Resources/FAO [9]. The experiment is a case study, based on a scenario where the radionuclides have entered the soil in the form of aqueous solution (e. g. in case of flooding or heavy precipitation), followed by rapid change of environmental temperature for a period of two months. The influence of main soil characteristics on the water-solubility of the radionuclides of interest under the sharp temperature shift is considered.

2. MATERIALS AND METHODS

2.1. Soil sampling, contamination and conditioning

Calcaric chernozem, Gleyic fluvisol, Salic fluvisol and Vertisol soils [9] with weight of 1.5 kg each were taken from the surface soil layer (0–10 cm) from Bulgaria. The soils were air-dried, cleaned from plant impurities and sieved through 2 mm-sieves.

The general characteristics of the studied soils, including pH in H_2O (soil: water ratio 1:10) and relative content of sand, silt, clay were determined. The relative content of humus (including humic acids, fulvic acids, humans, humatomeanic acids and diverse products of microbial decomposition of organic residues) was determined according to the method of Tjurin [10].

CEC (cmol^+/kg) was determined after extraction with 1 M $\text{NH}_4\text{CH}_3\text{COO}$ (Trace Select, Sigma Aldrich), followed by centrifugation and subsequent analysis of the concentration of Na^+ , K^+ , Ca^{2+} и Mg^{2+} in the supernatant by ICP-MS (PerkinElmer DRCe).

The total element concentrations of the studied soils were determined by ICP-MS after acid assisted microwave digestion, using HNO_3 and HF were studied. The total digestion of the soil samples was performed as described in [4]. The mineral

composition of the crystal phase of the soil samples was investigated by X-ray diffraction.

Fifty-gram sub-sample of each soil was homogenized in an agate mortar and measured by gamma-spectrometry. The specific radioactivity (S) of the radionuclides in the soils investigated prior to laboratory contamination was $S < 0.4 \text{ Bq g}^{-1}$ for ^{241}Am , $S < 0.6 \text{ Bq g}^{-1}$ for ^{60}Co and ^{54}Mn ; $S < 0.5 \text{ Bq g}^{-1}$ for ^{137}Cs . Afterwards, 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) ^{241}Am and (ii) ^{60}Co , ^{137}Cs and ^{54}Mn in chloride forms. This was done in order to avoid the interferences of Compton scattered photons of ^{60}Co , ^{137}Cs and ^{54}Mn on the low energy gamma peak of ^{241}Am . The specific activity of the contaminated samples was $S = 50 \pm 0.01 \text{ Bq g}^{-1}$ for ^{241}Am , $S = 20 \pm 0.01 \text{ Bq g}^{-1}$ for ^{60}Co ; and $S = 25 \pm 0.01 \text{ Bq g}^{-1}$ for ^{137}Cs and $S = 14 \pm 0.01 \text{ Bq g}^{-1}$ for ^{54}Mn . The contaminated soil subsamples were homogenised and conditioned for one week at $18 \pm 1 \text{ }^\circ\text{C}$ in open-air vessels in the laboratory. The soils were watered so that the soil moistures were maintained between 20–24 wt %. Subsequently, each subsample was divided into three aliquots, placed in plastic vessels, arranged in layers with thickness of 5 cm and conditioned for two months under the following conditions:

- Temperate: $18 \pm 1 \text{ }^\circ\text{C}$ in open-air vessels in the laboratory. The soil moisture was maintained within the range of 22–24 % wt %;

- Hot: $40 \pm 0.1 \text{ }^\circ\text{C}$ 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 periodically and the soil moisture varied between 5 wt % and 50 wt %, aiming to simulate soil drought and intensive summer precipitations.

- Frozen: $-18 \pm 1 \text{ }^\circ\text{C}$ and soil moisture of $25 \pm 1 \text{ wt } \%$, achieved using closed plastic vessels in a freezer.

After the conditioning, the samples were dried at $30 \text{ }^\circ\text{C}$ for 24 hours. Three equal portions of 10 g each of the dry subsamples were extracted with water as described below.

2.2. Extraction procedure

A 1:10 (mass:volume) ratio was applied for extraction of the soil samples with distilled water (as performed in [2]). 10 g of the studied soil samples were mixed with 100 ml of distilled water. End-over-end extraction was performed by shaking at about $20 \text{ }^\circ\text{C}$ for 2 h, followed by vacuum filtration of the leachates through $0.2 \text{ }\mu\text{m}$ cellulose nitrate filters. The radionuclide content was measured in the supernatant, and the extraction yield was determined in respect to the initial radioactivity of the sample [8].

2.3. Measurement conditions

The radioactivity of solid samples and leachates was measured by using an HPGe detector Canberra 7221 (energy resolution of 1.9 and efficiency of 16 % at 1332.5 keV) coupled to a 16000-channel analyser DSA-1000. The spectra were processed using Genie-2000 Basic Spectroscopy software. The activity of the radionuclides was measured using the following gamma energies: ^{241}Am at 59.5 keV gamma peak; ^{60}Co at 1173.2 keV and 1332.5 keV; ^{137}Cs at 661.6 keV and

^{54}Mn at 834.8 keV. Efficiency calibration and measurements were performed as described in [6].

The crystal structure of the soil samples was studied by X-ray diffraction method (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 $3 - 60^\circ$. The phase identification and quantitative phase analysis of the soil minerals were performed by X'Pert HighScore Plus software.

3. RESULTS AND DISCUSSION

3.1. Soil characteristics

Selected general characteristics of the studied soils are presented on Figs. 1, 2.

Regarding to the relative amount of the particle sizes in the soils, shown on Fig. 1 the soil texture classes were determined as follows:

- Calcaric chernozem – Silt loam
- Gleyic fluvisol – Loamy sand
- Salic fluvisol – Loamy sand, and
- Vertisol – Sandy loam

According to the data on the CEC (cmol^+/kg), presented on Fig. 2, the soils were found to belong to the following two groups:

- Soils with very low CEC (from 0 to 10): Gleyic fluvisol and Salic fluvisol, and
- Soils with slightly low CEC (from 10 to 15): Calcaric chernozem and Vertisol.

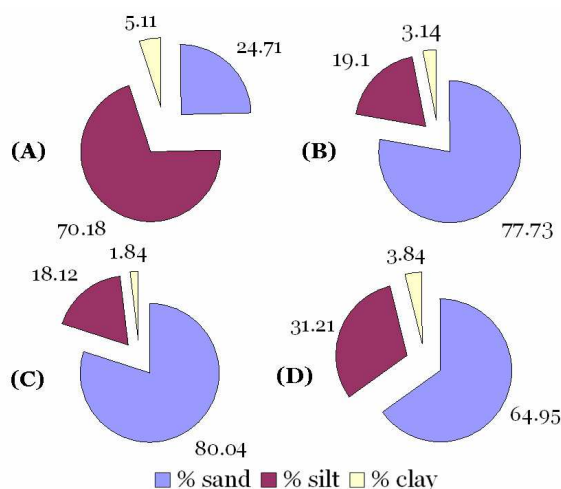


Figure 1. The relative content of sand, silt and clay in the investigated soils: (A) – Calcaric chernozem, (B) - Gleyic fluvisol, (C) - Salic fluvisol and (D) – Vertisol.

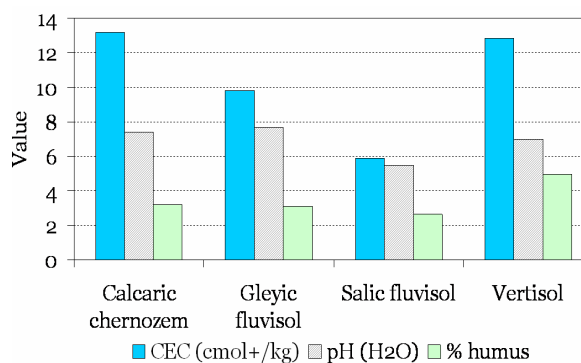


Figure 2. Cation exchange capacities (CEC), pH (H_2O) and relative humus content (%) in the investigated soils

Highest relative content of humus (%) was determined in the Vertisol soil (4.95 %) and lowest – in the Salic fluvisol (2.65 %). Gleyic fluvisol soil has slightly alkaline pH (7.7). Acidic $\text{pH}_{\text{H}_2\text{O}}$ (5.5) was measured in the Salic fluvisol, while the other two soils showed neutral pH.

3.2. Water-soluble forms of ^{60}Co and ^{54}Mn

The results for the water-soluble fraction of ^{60}Co and ^{54}Mn are presented in Fig. 3 as percentage from their total contents in the four soil types. The data represent the means \pm standard deviation of triplicate determinations.

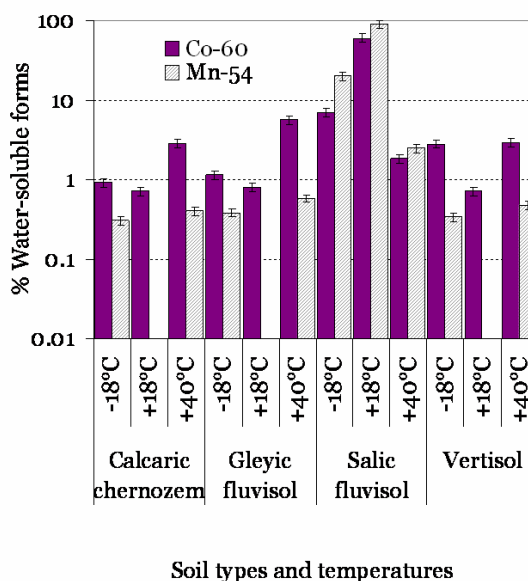


Figure 3. Water-soluble ^{60}Co (%) and ^{54}Mn (%) in the investigated soils, after conditioning at different temperature regimes for two months

The data showed that water-soluble forms of both radionuclides are highest in Salic fluvisol soil, conditioned at temperate temperature (60 % for ^{60}Co and 90 % for ^{54}Mn). Water-solubility of radiocobalt in the other three soils varied from 0.7 up to 5.7 %, while the solubility of ^{54}Mn did not exceed 0.6 %. Explanation of these results could be found, considering the geochemical properties of cobalt and manganese and the characteristics of the studied soils.

Cobalt may be retained by mineral oxides such as iron and manganese oxide, crystalline materials such as aluminosilicate and goethite, and natural organic substances in soil. Adsorption of cobalt onto iron and manganese increases with pH. The formation of insoluble hydroxides or carbonates of cobalt with increase of pH was also found to reduce cobalt mobility [11]. Investigation of King [12] on 13 soils from the southeastern United States, whose soil pH ranged from 3.9 to 6.5 have shown that cobalt sorption ranged from 15 to 93%; soil pH accounted for 84–95% of the variation in sorption.

Rapid increase of the adsorption of Co on maghemite coated quartz, and pure quartz with the raise of pH from 6 to 8 have been reported in [13].

The total concentration of iron in the investigated soils was found to decrease in the order:

Calcaric chernozem (27.9 mg/g) > Gleyic fluvisol (22.7 µmg/g) > Vertisol (16.9 mg/g) > Salic fluvisol (14.0 mg/g).

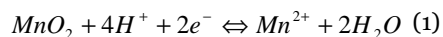
The relative content of quartz in the studied soils decreased in the order:

Gleyic fluvisol (41.1 %) > Calcaric chernozem (39.4 %) > Vertisol (33.4 %) > Salic fluvisol (25.4 %)

Considering the literature data and the above mentioned results, the highest water-solubility of ⁶⁰Co in Salic fluvisol soil can be explained by its lowest concentration of iron, lowest relative content of quartz and acidic pH, which differs it from the other three soils. The obtained data are in agreement with our previous results [8] which showed higher water-solubility of ⁶⁰Co in a fluvisol soil with acidic pH and very low CEC, compared to a cambisol with pH 7.6 and a normal range of CEC.

The solubility of Mn in soils is highly dependent on the pH and redox potential [14]–[16]; therefore, the most common reactions occurring in soils are oxidation-reduction and hydrolysis. In well-drained soils, the solubility of Mn has been found to increase with the increase of soil acidity. However, the ability of Mn to form anionic complexes and to complex with organic ligands may contribute to increased Mn solubility in the alkaline pH range [17].

The present results (Fig. 3) showed that in soils with neutral or slightly alkaline pH, no detectable ⁵⁴Mn (< 0.1%) was found when stored at temperate conditions for two months. The high content of water-soluble ⁵⁴Mn in Salic fluvisol soil can be ascribed to its acidic pH, which impeded manganese sorption and immobilization and favored the process:



The observed effects of sharp warming or freezing on the water-soluble forms of ⁶⁰Co are different for the acidic soil and the other three soils. Significant decrease of the water-soluble forms of both radionuclides in Salic fluvisol soil was registered. This might be explained by raise of pH, provoked by increase of salinity [18] as a result of supersaturation during solute-exclusion at freezing [19] or evaporation at hot conditions. Increase of water-solubility of ⁶⁰Co and ⁵⁴Mn was registered after storage of Calcaric chernozem, Gleyic fluvisol, and Vertisol soils at -18 °C or 40 °C (Fig. 3). It can be attributed to the destructive effect of the sharp temperature shift on the soil

aggregates, which might provoke desorption processes or generation of radiocolloids with lower size than the pores of the used cellulose nitrate filters (0.2 µm). The effects of freezing on the stability soil aggregates have been studied by Lehrs et al. [20], who noted a dependence on soil texture, organic matter, and water content.

The influence of the water-solubility on the migration of radionuclides in different soils and within the food chain can be evaluated if taking into account the water-holding capacity of the soils. Water-holding capacity is defined by the amount of water that a given soil can hold for crop use. It depends mainly on the soil texture and the soil organic matter content.

Considering the data on Fig. 1 and soil texture classes of the studied soils, their water-holding capacities decrease in the following order:

Calcaric chernozem (silt loam) > Vertisol (sandy loam) > Gleyic fluvisol (loamy sand) ≥ Salic fluvisol (loamy sand)

Salic fluvisol soil, which showed highest content of water-soluble forms of ⁶⁰Co and ⁵⁴Mn, has lowest water-holding capacity. Thus, in case of water excess (e. g. intensive precipitations or flooding), part of the radionuclides will migrate to the deeper soil layers, which will decrease their availability to the root systems of the vegetation and diminish their bioaccumulation.

3.3. Water-soluble forms of ²⁴¹Am and ¹³⁷Cs

Figure 4 presents the results for the water-soluble fraction of ²⁴¹Am and ¹³⁷Cs as percentage from their total contents in the four soil types. The data represent the means ± standard deviation of triplicate determinations.

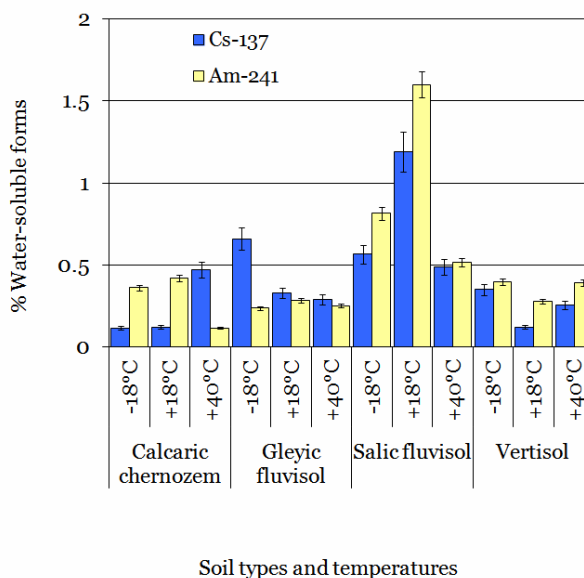


Figure 4. Water-soluble ²⁴¹Am (%) and ¹³⁷Cs (%) in the investigated soils, after conditioning at different temperature regimes for two months

The data showed that the relative contents of the water-soluble forms of ²⁴¹Am and ¹³⁷Cs in the soils at the studied temperature regimes do not exceed 1.7 %

and in most of the samples they are below 0.80 %. This indicates, that no danger of increased water-solubility can be expected after sharp temperature shift in the first two months after radioactive contamination with ^{241}Am and ^{137}Cs in the considered soil types. The obtained results are in agreement with our previous studies on geochemical fractionation of Am in soils after freezing and soil drought, where its water-soluble and exchangeable fractions did not exceed 2.5 % [4]-[5]. At neutral and slightly basic pH ranges, Am tends to form complexes with carbonate and hydroxide ions: $\text{Am}(\text{CO}_3)_{x^{3-2x}}$ and $\text{Am}(\text{OH})_{x^{3-x}}$, while in acidic environment (pH 5.5 in Salic fluvisol) it remains mainly as Am^{3+} . 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. associate to soil carbonates and sesquioxides [7] and become less mobile in the soil solution soon after their release in nature.

The measured low water-solubility of Cs is due to its ability to sorb strongly onto soil, especially micaceous clay minerals [21]. The present data are in good agreement with our previous investigations of two soil types, stored at temperate conditions, freezing and soil drought, where water-soluble ^{137}Cs varied from 0.4 to 4 % of its total content [8]. The highest relative content of radiocesium was determined in Salic fluvisol soil, probably due to its lowest clay content, as shown on Fig. 1 (C).

Effects of sharp temperature shift on the water-soluble forms of ^{241}Am and ^{137}Cs in Salic fluvisol were similar to those, observed for ^{60}Co and ^{54}Mn . Decrease their most mobile fraction after freezing or warming was registered, as shown on Fig. 4. This can be ascribed to the pH increase, which has favored their sorption on soil minerals. No changes of the water-soluble forms of ^{241}Am were found in Gleyic fluvisol soil, which has highest pH (7.7) among the studied soils. Slight increase of the water-solubility of ^{241}Am in Vertisol soil and decrease in Calcaric chernozem were determined after storing at freezing or sharp warming. Increase of water-soluble ^{137}Cs after sharp temperature variations was detected in Vertisol soil. Such effect was determined in Calcaric chernozem after sharp warming and in Gleyic fluvisol after freezing. These effects might be ascribed to the influence of temperature variations on the sorption processes and stability of soil aggregates, which provoked different changes in the soils with different textures.

4. CONCLUSION

The results from the study of the influence of freezing and sharp warming for a period of two months, on the water-soluble forms of ^{241}Am , ^{60}Co , ^{137}Cs and ^{54}Mn in Calcaric chernozem, Gleyic fluvisol, Salic fluvisol and Vertisol can be summarized as follows:

- The sharp temperature shift caused increase of water-soluble forms of ^{60}Co and ^{54}Mn in the soils with neutral and slightly alkaline pH and significant decrease of water-soluble forms of ^{60}Co and ^{54}Mn in Salic fluvisol soil with acidic pH.
- The storage at freezing or “hot summer” conditions caused decrease of water-soluble forms of ^{241}Am and ^{137}Cs in Salic fluvisol and decrease of

water-soluble ^{241}Am in Calcaric chernozem. Slight increase of the water-solubility of ^{241}Am and ^{137}Cs in Vertisol soil was determined after storing at freezing or sharp warming. Increase of water-soluble ^{137}Cs was registered in Calcaric chernozem after sharp warming and in Gleyic fluvisol after freezing.

Further investigations on the impact of sharp temperature variations on geochemical forms of radionuclides in different soil types are in progress in order to increase the knowledge on the change of their potential migration ability under sharp variations of climatic parameters.

Acknowledgement: This study was performed with the financial support of the National Science Fund, Ministry of Education, Youth and Science of Bulgaria, Contract No. DDVU 02-60/2010.

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