Impact of the rapid warming on the binding of ^{152}Eu with humic and fulvic acids in soils

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The study of the distribution of rare earth elements in the environment is necessary, given their widespread use and their toxic effects on living organisms. Europium is used in various materials and can contaminate the nature during the recycling processes. The rapid variations of climatic parameters like sharp temperature increase may change the geochemical fate of Eu and its distribution within the food chain. The application of radionuclides is an efficient approach to identify the changes of the geochemical forms of the elemental contaminants, caused by variations of the weather conditions. The present study aims to show the effect of the rapid environmental warming over a period of a month on the binding of Eu to humic and fulvic acids in soils. The research presents model experiments with soils taken from ten regions in Bulgaria and contaminated with ^{152}Eu in laboratory conditions. Hot summer and spring/autumn conditions were simulated for a period of a month, after which the fraction of ^{152}Eu associated with humic and fulvic acids was investigated. The extraction of humates and fulvates was performed with 0.1 M $Na_4P_2O_7$, followed by precipitation of the fulvates with H_2SO_4. Gamma spectrometry was used to determine the amount of the radionuclide extracted. The results showed that the rapid warming had highest impact on the humate and fulvate complexes of Eu in the alkaline Gleyic fluvisol soil with a very low cation exchange capacity and a loamy sand texture but lowest effect on the Chromic cambisol soil with loamy texture and normal cation exchange capacity.

Keywords: ^{152}Europium, rapid warming, soils, humic and fulvic acids.

INTRODUCTION

Europium (Eu) belongs to the group of light rare earth elements (LREE), possessing a 4f electron configuration and no paired electrons in the last electron shell. LREE have diverse applications in industry and modern technology, additives in steel, such as carbon arc lighting, cremes for lighters, surface polishing, rechargeable batteries in mobile phones and computers and even automotive catalytic converters [1, 2]. In addition, due to their stimulatory effects on nutrient uptake and/or chlorophyll biosynthesis, some REE are included in low concentrations in plant fertilizers [3].

The widespread and uncontrolled application of REE-containing fertilizers can cause, however, their accumulation in soils and plant organisms, contributing to their transfer through the food chain, thus endangering human health [4]. Various studies have evaluated the toxicity of REEs on bacteria [5], plants [6, 7], and human health [8, 9]. Europium can also enter the environment in the form of some of its radioactive isotopes. The radioactive isotopes of Eu: ^{152}Eu, ^{154}Eu and ^{155}Eu are mainly obtained as fission products. ^{152}Eu, however, can also be produced as a result of neutron activation of the control rods of nuclear reactors in which ^{151}Eu is added as a component due to its large neutron absorption cross section. ^{152}Eu can be released in the environment as a result of a nuclear accident, or in case of improper

management of radioactive waste. The use of radioactive europium as a tracer would allow to follow how the geochemical distribution of stable europium changes with time from the moment it enters the soil. In this way the geochemical forms of stable europium introduced as a pollutant can be distinguished from stable europium present in natural minerals in the soil. The geochemical behavior of radioactive europium after its release into the environment is a function of a number of factors, such as the type of soil and its characteristics: pH, cation exchange capacity (CEC), organic matter content, activity of microorganisms, mineralogical composition and morphology. The studies carried out so far on the binding forms of Eu in soil, however, do not take into account the possible influence of climatic conditions, for example changes in the temperature and the soil moisture. Such changes could have an impact, especially during the first weeks after the contaminants enter the soil, when their binding to soil components undergoes changes over time. Humic matters, including humic acids (HA) and fulvic acids (FA), are widespread compounds in the nature and comprise an important part of the organic carbon in soils and waters, both on the surface and underground [10, 11]. These naturally occurring organic substances have been found to exhibit polyelectrolyte properties observed for negatively

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charged and electrophilic colloids [10, 12]. In addition, humic and fulvic acids have strong complexing properties [12, 13] and thus have an impact on the geochemical migration of metal ions [14] and their subsequent bioaccumulation in plant species.

The aim of this study is to assess the impact of the rapid and abrupt increase of the environmental temperature for a period of a month, on the ability of Eu to bind to humic and fulvic acids in soils, soon after their contamination. Soils with different characteristics from ten regions in Bulgaria were selected. Model experiments were performed by contamination of soil aliquots with ^{152}Eu after that storing them at two temperature regimes, simulating hot summer and spring/autumn, followed by extractions of the humate and fulvate complexes of Eu.

MATERIALS AND METHODS

Materials

Soils from ten regions in Bulgaria were chosen for this study. Albic cambisol, two Calcaric chernozem soils, Chromic cambisol, Gleyic fluvisol, Eutric fluvisol, Haplic chernozem, Haplic luvisol, Salic fluvisol and Vertisol were selected, as classified according to World Reference Base for Soil Resources/FAO [15]. Soil samples with total weight of 5 kg each were taken from the surface soil layer (0–10 cm). The soils were air-dried, cleaned from mechanical and plant impurities and sieved through 2 mm-sieves.

Weight of 30 g of each soil was contaminated with an aqueous solution of ^{152}Eu^{3+} in chloride form, with specific activity of 100 Bq/g. The soil samples were homogenized and conditioned for two days at 18 °C $\pm$ 1 °C in open-air vessels. The soils were watered so that the soil moisture was maintained between 20–24 wt%. Afterwards, each contaminated soil was divided into two subsamples, and conditioned for a month under the following conditions:

✓ Temperature simulating spring/autumn: 18 $\pm$ 1 °C in open-air vessels in the laboratory. The soil moisture was maintained within the range of 22–24 wt %;

✓ High temperature, simulating hot summer: 40 $\pm$ 0.1 °C and relative air humidity of 50 $\pm$ 0.1 wt %, achieved by using a constant climate chamber Model HPP 108 (Memmert GmbH, Germany). The soils were watered every two days and the soil moisture varied within the range of 5–50 wt %, causing cycles of drying and wetting.

Methods

The general characteristics of the studied soils, including pH in KCl and in H$_2$O (soil: water ratio 1:10), humus and relative content of sand, silt, clay, needed to classify the soil texture, were determined.

The content of humus (%) was determined according to the method of Tjurin [16].

Soil texture was identified based on the size distribution of soil particles as follows: sand (2 mm - 0.05 mm), silt (0.05 mm – 0.002 mm) and clay (< 0.02 mm).

For measurement of CEC extraction with 1 M NH$_4$CH$_3$COO (Trace Select, Sigma Aldrich) was performed as described in [17], followed by centrifugation and subsequent analysis of the concentration of Ca^{2+}, K$^+$, Mg^{2+} and Na$^+$ in the supernatant by ICP-MS (PerkinElmer DRCe). CEC units are usually expressed as centimoles of positive charge per kg of soil [cmol$^+$/kg)], which is numerically equivalent to the previously used unit of milliequivalents per 100 g [18].

Extraction of the complexes of ^{152}Eu with humic and fulvic acids was performed. It was taken into consideration that HA are insoluble in water under acidic conditions (pH <2) because they are composed of predominantly hydrophobic units that are stabilized by weak attractive forces, but are soluble at higher pH values. The fulvic acids are known to be soluble in water at any pH conditions, as they consist of small hydrophobic molecules that contain a sufficient number of acidic functional groups [19]. Therefore, a solution of 0.1 Na$_4$P$_2$O$_7$ (Merck, purity > 99%) was used to isolate together humate and fulvate complexes, followed by acidification with H$_2$SO$_4$ (Merck, 96% Suprapur®), which caused precipitation of humate complexes. The procedures were carried out according to [20] as follows:

1. Extraction of humic and fulvic complexes: 15 ml of 0.1 M Na$_4$P$_2$O$_7$ were added to 5 g of soil and the mixture was shaken on a shaking machine for 1 h. The extract thus obtained was filtered with a membrane filter and collected in a plastic container, the solid residue was washed twice with 5 ml of 0.1 M Na$_4$P$_2$O$_7$ and the washing liquid was added to the extract. Another 15 ml of 0.1 M Na$_4$P$_2$O$_7$ was added to the residual solid phase and the procedure was repeated. The extracts were combined until a volume of 50 ml was reached. The radioactivity of ^{152}Eu was determined by gamma-spectrometry.

2. Separation of the humic and fulvic complexes: 2 ml of conc. H$_2$SO$_4$ was dropwise added to the 0.1 M Na$_4$P$_2$O$_7$ extract until precipitation of the complexes of the elements with humic acids. The precipitate obtained was separated from the mixture by centrifugation at 3000 rpm at 20 °C for 5 min and filtration through a cellulose-nitrate filter with a pore diameter of 0.20 μm. The filtrate was collected in plastic containers and measured by gamma-spectrometry.

Gamma spectrometric analysis was carried out using a HPGe detector Canberra – 7221, with an efficiency of 16% and a resolution of 1.9 keV for the ^{60}Co line at 1332.5 keV connected to a 16000-channel analyzer DSA – 1000 and Genie – 2000 Basic Spectroscopy Software. The activity of [152]Eu was measured by using the gamma peak at 121.78 keV. Efficiency calibration and measurements were performed as described in [21].

To quantify the effect of rapid warming, the relative change ($\Delta\%$) of the percentage of [152]Eu bound to humic and fulvic acids after storage under the two temperature regimes was calculated using the following formula:

$$\Delta\% = \frac{\%Eu\_HA\_FA(40^oC) - \%Eu\_HA\_FA(18^oC)}{\%Eu\_HA\_FA(18^oC)} \cdot 100$$

(1)

where % Eu_HA_FA is the amount of [152]Eu (%) associated with humic and fulvic acids (HA_FA) after conditioning at the given temperature regime.

RESULTS AND DISCUSSION

The characteristics of the soils selected for the experiments are presented in Table 1.

The data in Table 1 show that one of the soils is characterized by an acidic reaction (pH 5.5), two are slightly acidic (pH 6.3 – 6.4), one is alkaline, and the remaining six are neutral. The highest humus content determined was in the Vertisol soil (4.95 %) and the lowest in the Albic cambisol (2.03 %). Regarding the cation exchange capacity (CEC) values, soils are divided into the following groups [22]:

1. Very low CEC (meq/100 g soil): 0 – 10 indicating a very low nutrient retention capacity and low clay and organic matter content.

2. Low CEC (meq/100 g soil): 10 – 15, indicating a low capacity to retain nutrients and the presence of a larger amount of clay and mineral substances, compared to the previous group.

3. Normal CEC (meq/100 g soil): 16 - 40, corresponding to a high nutrient retention capacity and a high clay content.

Out of the studied soils, six had a normal CEC (soils 1-6), two had a low CEC (soils 7 and 10) and two had a very low CEC (soils 8 and 9). The selection of soils with different characteristics contributed to the study of the influence of certain parameters on the binding of europium to organic soil acids at both temperature regimes.

The results for the fraction of [152]Eu (%) bound to humic (HA) and fulvic acids (FA) in the soil samples, after conditioning for a period of a month at the two temperature regimes, are presented on Fig. 1.

The data show that in soils [152]Eu is predominantly associated with the humic acids (30 to 50%), while the amount of its complexes with fulvic acids vary from 10 to 20% (except for Salic fluvisol, where the amount of fulvates reached 30%).

The biggest amount of organically bound [152]Eu was measured in Salic fluvisol. Considering the high content of sand, the very low CEC and the acidic reaction of this soil, the obtained results can be explained by the presence of very weakly bound [152]Eu (including water-soluble and non-specifically sorbed), which was isolated in a soluble form, when extracted with 0.1 M $Na_4P_2O_7$.

It has been reported [23] that the association between a metal ion and a fulvate ligand is a function of the solution chemistry. Thus, a binding constant determined under a unique set of pH, metal ion, ionic strength, and fulvate concentrations cannot be translated to solutions whose chemical properties differ [23]. The content and the ion concentrations of the soil solution (the water surrounding the soil particles) depend on the soil characteristics, the soil humidity and can vary as a result of the temperature change. This would have a complex impact on the fulvate formation of the pollutant.

Table 1. Main characteristics of the soils

| №	Soil order/Texture class	Soil pH		CEC (meq/100 g)	% Sand	% Silt	% Clay	% Humus
		H₂O	KCl					
1	Haplic chernozem/Clay loam	7.5	6.8	30.3 ± 0.3	32.1	38.2	29.7	3.06
2	Chromic cambisol/Loam	6.6	6.3	32.0 ± 0.3	43	31.7	25.3	2.35
3	Haplic luvisol/Loam	7.0	6.4	23.2 ± 0.2	35.6	43.9	20.5	4.16
4	Eutric fluvisol/Loamy-sand	7.7	7.2	33.2 ± 0.3	74.3	21.5	4.2	4.50
5	Albic cambisol/Sandy-loam	7.6	7.4	31.1 ± 0.2	61.6	33.2	5.2	2.03
6	Calcaric chernozem (1)/Clay loam	7.8	7.1	38.1 ± 0.2	32.9	36.8	30.3	2.59
7	Calcaric chernozem (2)/Silt loam	7.8	7.4	13.16 ± 0.08	24.71	70.18	5.11	3.18
8	Gleyic fluvisol/Loamy sand	7.9	7.7	9.80 ± 0.10	77.73	19.13	3.14	3.09
9	Salic fluvisol/Loamy sand	5.2	5.5	5.89 ± 0.04	80.04	18.12	1.84	2.65
10	Vertisol/Sandy loam	7.3	7.0	12.82 ± 0.09	64.95	31.21	3.84	4.95
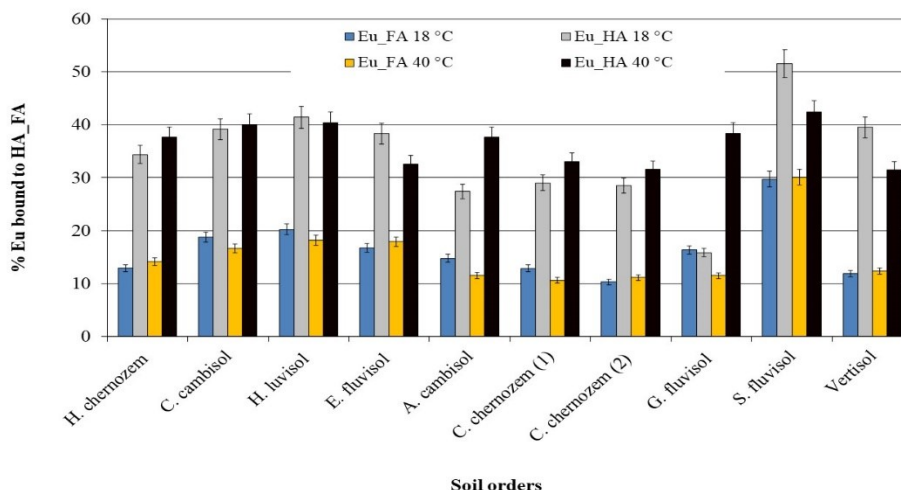
Fig. 1. Amount of ^{152}Eu (in %), bound to humic (HA) and fulvic acids (FA) after storage of the soil samples at 18 and 40 °C temperature regimes.

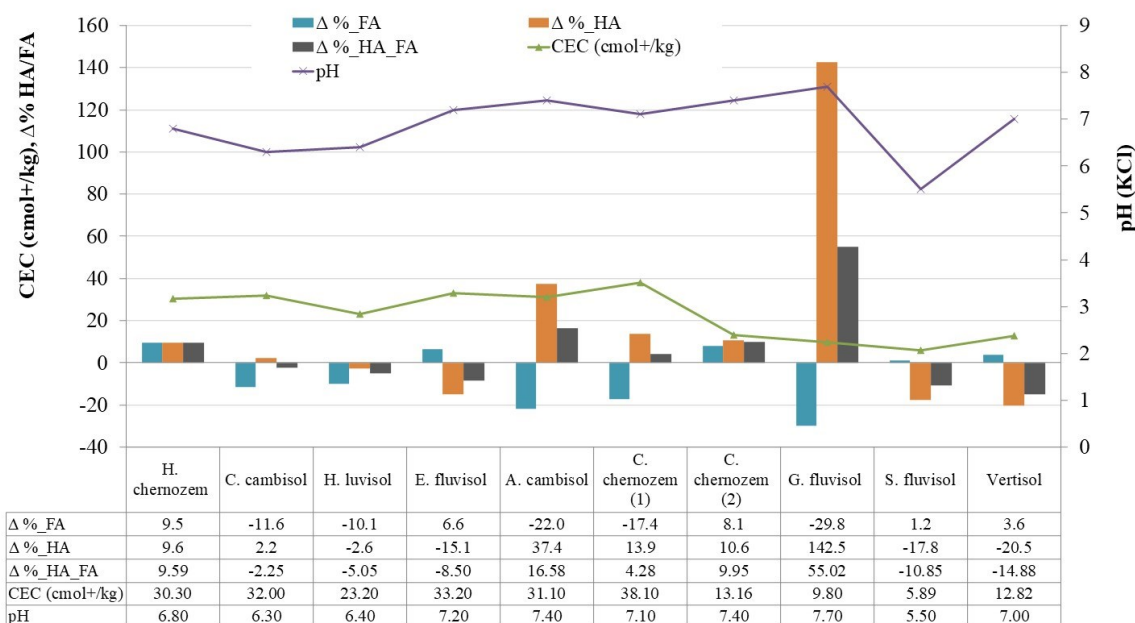|	H. chernozem	C. cambisol	H. luvisol	E. fluvisol	A. cambisol	C. chernozem (1)	C. chernozem (2)	G. fluvisol	S. fluvisol	Vertisol
Δ %_FA	9.5	-11.6	-10.1	6.6	-22.0	-17.4	8.1	-29.8	1.2	3.6
Δ %_HA	9.6	2.2	-2.6	-15.1	37.4	13.9	10.6	142.5	-17.8	-20.5
Δ %_HA_FA	9.59	-2.25	-5.05	-8.50	16.58	4.28	9.95	55.02	-10.85	-14.88
CEC (cmol+/kg)	30.30	32.00	23.20	33.20	31.10	38.10	13.16	9.80	5.89	12.82
pH	6.80	6.30	6.40	7.20	7.40	7.10	7.40	7.70	5.50	7.00

Fig. 2. Relative changes (Δ, %) of the fraction of ^{152}Eu, bound to humic (HA), fulvic acids (FA) and the total amount of humic and fulvic acids (HA_FA) after rapid warming, CEC and pH of the studied soils.

Humic acids, being hydrophobic, may bond to clay minerals, leading to their reduced migration and complex formation with the metal ions.

The values of the relative change of the fractions of Eu bound to humic and fulvic acids (Δ%) for the studied soils, as well as the values of CEC and pH (KCl) are presented in Figure 2.

The changes (Δ, %) that can be noticed, are of positive or negative value, indicating a redistribution of Eu between humate, fulvate and other soil fractions (such as carbonates, oxyhydroxides, etc. as mentioned in [24]). Since the temperature raise can cause complex competitive interactions between the

soil compartments and europium ions, one can distinguish some main effects to be mentioned:

✓ The greatest impact of the rapid warming on the total amount of europium humates and fulvates was registered at Gleyic fluvisol soil. An increase in the total fraction of humates and fulvates by 55% was measured, which was accompanied by a decrease in fulvate complexes by about 30 % in contrast to humate fraction, where Eu fraction increased by 142%. This soil differs from the others by its alkaline pH and very low CEC value.

✓ The Chromic cambisol soil had the least overall change (Δ% = -2.25). This soil was

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characterized by a slightly acidic pH (6.3) and with a normal CEC (32 cmol$^+$/kg).

✓ Increasing the soil pH to 7 and above 7 (as in Calcaric chernozem (1) and (2), Eutric fluvisol, Albic cambisol) caused an increase of the relative change as absolute values in soils with comparable CEC values (23-33 cmol$^+$/kg).

✓ The increase of the acidity of the soil solution accompanied by a very low CEC, as is the case with the Salic fluvisol soil (pH= 5.5 and CEC 5.89 cmol$^+$/kg) led to a mitigation of the effect of the rapid warming, as Δ% value amounts to about -11%. In Vertisol soil with a low CEC but neutral pH, the relative changes were greater than those in Salic fluvisol.

The importance of the acidity of the soil solution in the binding of radionuclides to humic and fulvic acids in the soil can be explained as follows:

Increasing the concentration of OH$^-$ in the soil solution (i.e. at pH > 7) increases the ionization of acids:

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

An increase in temperature can lead to an increase in the salt concentration in the soil solution, which causes an increase in pH as a result of hydrolysis of the anions present, as well as accelerate the complexation process, providing it with the necessary activation energy. When the soil has an alkaline pH (such as the Gleyic fluvisol soil), the rapid warming contributed to an increase in pH and increased binding of europium ions to organic soil acids. In the case of the acidic Salic fluvisol soil (pH 5.5), the effect of the rapid warming was much less pronounced, since the increase in pH was not large enough to cause alkalinization of the soil and subsequent deprotonation of organic acids.

CONCLUSION

The influence of the rapid increase in temperature over a period of a month on the binding of ^{152}Eu to humic and fulvic acids in soils from ten regions was investigated. According to the obtained results it can be summarized that the rapid warming:

✓ caused a change in the fraction of ^{152}Eu bound to humic and fulvic acids in soils with a loamy-sand or sandy-loam texture and had no significant effect on soils with a loam or clay-loam texture;

✓ primarily affected the humate complexes of ^{152}Eu in soils with high sand content and caused the greatest increase in its humate complexes in soils with very low cation-exchange capacity and alkaline pH.

The relative content of the water-soluble fulvate complexes of ^{152}Eu was found to be lower than the fraction of its humate complexes, which indicated a weaker mobility of the organically bound radionuclide among the soil horizons and through the soil to plant transfer.

The results obtained can be useful in further risk assessment of soil contamination with europium compounds (containing stable or radioactive Eu) in cases of a sharp increase in the temperature of the natural environment, which lasts several weeks.

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