VERTICAL DISTRIBUTION OF RADIONUCLIDES N SOILS OF VARYING PEDOCHEMISTRY

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Abstract

Natural gamma-emitting radionuclides (^{40}K, ^{226}Ra and ^{232}Th) and Chernobyl-derived radionuclide ^{137}Cs were determined in soil profiles representing typical soil types of Belgrade (Serbia). The influence of soil properties and content of stable elements on radionuclide distribution down the soil profiles (at 5 cm-intervals up to 50 cm depth) was analyzed. The relationships between soil properties and radionuclides suggested the association of ^{40}K, ^{226}Ra and ^{137}Cs with fine-grained soil fractions. The activity concentration of ^{137}Cs correlated significantly with organic matter content, cation exchange capacity, saturated hydraulic conductivity and specific electrical conductivity. The strong positive correlations between ^{226}Ra and ^{232}Th activity concentrations and Fe and Mn indicate their association with oxides of these elements in soil. The correlations observed between ^{40}K and Cr, Ni, Pb and Zn and also between ^{137}Cs and Cd, Cr, Pb and Zn could be contributed to their common affinity for clay minerals. The results of this study provide insight into the the main factors that affect radionuclide migration in the soil, which contribute to the understanding of radionuclide behaviour in the environment and factors governing their mobility within terrestrial ecosystems.

Introduction

Natural radioactivity in the soil arised mainly from primordial radionuclides formed in nucleosynthesis processes in stars before the early stage of the formation of the solar system is of special environmental concern because the majority of the total radiation dose to the world population is from natural sources. Anthropogenic radionuclides are derived from the radioactive fallout of nuclear fission products during nuclear weapon tests and from the Chernobyl accident in 1986. This accident resulted in significant deposition of

^{137}Cs on surface soils throughout Europe. An understanding of the pathways by which radioactivity reaches biota requires an assessment of the soil physical and chemical properties that affect the abundance and distribution of radionuclides. In this study the depth distribution of the natural radionuclides, ^{40}K, ^{226}Ra and ^{232}Th, and Chernobyl-derived ^{137}Cs, was studied in profiles representing typical soil types of the Belgrade area. To assess the pedogenic effect on the distribution of radionuclides and to gain insight into the biogeochemical behaviour of the radionuclides, the relationships between radionuclide specific activities and a number of soil properties were analysed.

Experimental part

Soil profiles were sampled in May 2008 at six locations where the soil types are representative for the territory of Belgrade (Fig. 1). According to the FAO (2006) the soils are classified as: Chernozems (A), Fluvisols (B), Humic Gleysols (C), Eutric Cambisols (D), Vertisols (E) and Gleyic Fluvisols (F).[1] Soil samples were collected every 5 cm from the uppermost layer down to 50 cm depth at each site. The samples were then dried at room temperature to constant weight, homogenized and passed through a 2 mm-sieve for radioactivity measurements and particle size analysis and ground in a mortar for other analyses. Radioactivity measurements were performed using an HPGe gamma-ray spectrometer (ORTEC-AMETEK, 34% relative efficiency and 1.65 keV FWHM for ^{60}Co at 1.33 MeV). The samples were then kept in hermetically sealed Marinelli beakers of 500 mL volume for about 4 weeks to allow equilibrium between ^{226}Ra and its daughters. The activity of each sample was measured for 60 ks. The specific activities of ^{40}K and ^{137}Cs were determined from their gamma-ray lines at 1460.8 keV and 661.6 keV, respectively. The specific activity of ^{226}Ra was assessed from the gamma-ray lines of ^{214}Bi (609.3 keV) and ^{214}Pb (295.2 and 352.0 keV). The specific activity of ^{232}Th was evaluated from the gamma-ray lines of ^{228}Ac at 338.4, 911.1 and 968.9 keV, assuming that a state of secular equilibrium exists between ^{232}Th, ^{228}Ra and ^{228}Ac. Gamma Vision 32 MCA emulation software was used to analyse gamma-ray spectra.[2] The traditional pipette method was used for particle size analysis.[3] Once the organic matter was removed, the remaining mineral sample was weighted and subjected to particle size analysis to determine the following fractions: sand (0.05-2 mm), silt (0.002–0.05 mm) and clay (<0.002 mm). Soil pH was measured in 1:5 soil-water suspensions.[4] Organic matter content was determined by dichromate digestion based on the Walkley–Black method.[5] Carbonates were measured volumetrically using Scheibler's calcimeter for $CaCO_3$ content.[6] The total cation exchange capacity of the sorptive complex was calculated as the sum of the hydrolytic acidity and total exchange bases, both measured according to Kappen (1929).[7] Dry bulk density was determined using undisturbed soil cylinders (100 cm^3).[8] Particle density was measured with a pycnometer.[8] Saturated hydraulic conductivity was measured by the falling-head method according to Klute and Dirksen (1986).[9] The specific electrical conductivity was measured in a 1:5 water suspension using a WTW inoLab ph/Cond 720 instrument.[10] For metal concentrations, samples were digested with HNO_3 and H_2O_2 in a microwave oven and then concentrations were determined using a Perkin Elmer PE3100/MHS-1 Atomic Absorption Spectrometer.[11] The SPSS 16.0 for Windows software package was used for evaluation of significant relationships between specific activities of radionuclides and soil physicochemical characteristics and stable element content.[12]

Results and discussion

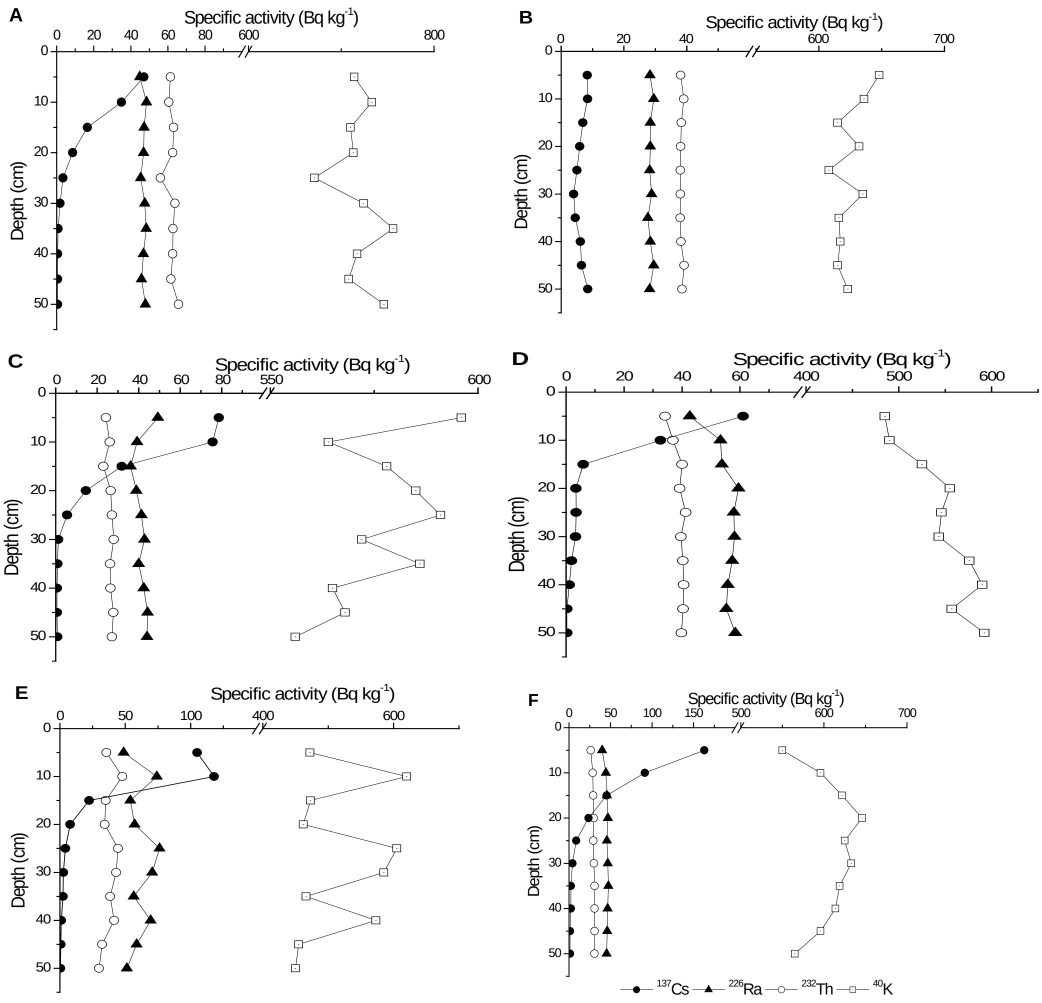
The mean values of natural radionuclide specific activities (Table 1) fell within the range for Serbian soils and those from the Belgrade area.[13, 14]

Table 1. Basic descriptive statistics for specific activities of radionuclides (Bq kg^{-1}) in analysed soils

Parameter	^{40}K	^{226}Ra	^{232}Th	^{137}Cs
Mean	600	38.9	46.6	18.5
Median	600	38.1	46.7	4.35
Mode	600	26.1	28.4	0.50
Standard deviation	74.4	11.8	11.5	33.2
Range	310	42.7	48.6	160
Minimum	450	23.0	27.6	0.30
Maximum	760	65.7	76.2	160

In all soil profiles specific activities of natural radionuclides showed homogeneous distribution (Fig. 1). The differences in ^{40}K depth distribution have generally been attributed to variability of organic matter and mineral composition of the soil and to soil biological activity including root distribution.[15] The ^{137}Cs specific activities in the surface soil layers showed a wide range of values (from 8.3 to 160 Bq kg^{-1} in the 0-5 cm layer and from 8.4 to 120 Bq kg^{-1} in the 5-10 cm layer), which could be attributed to non-homogeneous surface contamination after the Chernobyl accident.

Figure 1. Depth distribution of radionuclides in the 5 cm interval samples of the studied soil profiles



In profile B the specific activities of ^{137}Cs decreased with depth up to 25 cm and then slightly increased down the profile. Some other physical properties of the soil (pH, organic matter, carbonates, K) showed discontinuity at the 25 cm depth. This soil profile (Fluvisols) is collected in the alluvial plain of the Sava River which are flooded periodically. The physical and chemical characteristics of Fluvisols depend on nature and sequence of layers and length of periods of soil formation after or between flood events. The observed trend in the ^{137}Cs specific activities and other soil properties could be attributable to the different mechanical, mineralogical and chemical composition of layers in studied Fluvisols profile.

The effects on soil physicochemical characteristics and major and trace element contents on radionuclide specific activities were analysed through correlations and the results are summarized in Table 2.

Table 2. Pearson correlation coefficients between radionuclides and both soil properties and stable element content of the studied soils

	^{40}K	^{226}Ra	^{232}Th	^{137}Cs
Sand	0.05	-0.49**	-0.24	0.01
Silt	0.33**	0.49**	-0.11	0.28*
Clay	0.34**	0.28**	0.20	0.29*
pH	0.10	-0.30*	-0.59**	-0.13
Organic matter	-0.18	-0.19	0.09	0.73**
Cation exch. capacity	-0.27	-0.27	-0.25	0.41**
Carbonates	0.08	-0.67**	-0.73**	-0.13
Bulk density	-0.05	0.05	0.50	-0.52**
Particle density	0.15	0.11	-0.07	-0.61**
Sat. hidraulic conductivity	-0.04	-0.03	-0.19	0.68**
Spec. electrical conductivity	-0.09	-0.44**	-0.57**	0.61**
Al	0.19	0.13	-0.15	0.05
Ca	0.12	-0.57**	-0.75**	0.01
Cd	0.15	0.30*	0.11	0.41**
Co	0.18	0.32*	0.12	0.02
Cr	0.45**	-0.09	0.60**	0.68**
Cu	-0.06	-0.24	-0.16	0.06
Fe	0.31	0.48**	0.51**	-0.22
K	0.81**	-0.06	-0.16	-0.33*
Li	0.17	-0.04	-0.18	-0.26*
Mg	0.14	0.21	-0.28*	0.06
Mn	0.12	0.54**	0.37**	-0.16
Na	-0.01	0.17	-0.05	-0.21
Ni	0.35**	0.26*	0.54**	-0.14
Sr	-0.06	0.08	-0.13	-0.17
Pb	0.44**	0.36**	0.67**	0.56**
Zn	0.35**	0.60**	0.74**	0.48**
Ti	0.05	0.14	0.06	-0.16

Note:
**Correlation is significant at the 0.01 level
*Correlation is significant at the 0.05 level

The correlation analysis between radionuclide specific activities and particle size distribution confirmed results obtained world-wide showing that the fine-grained soil fraction has a higher tendency for radionuclide adsorption than coarse-grained soils since the soil particle surface area is larger.[16] The soil pH was found to be negatively correlated with ^{226}Ra ($p<0.05$) and ^{232}Th ($p<0.01$) specific activities. Positive correlations between ^{137}Cs specific activity and both organic matter content and cation exchange capacity ($p<0.01$) were found. Negative correlations ($p<0.01$) were observed between carbonate content and ^{226}Ra and ^{232}Th specific activities, which confirms suggests their binding in soils with minerals other than calcite, probably in silicates derived during weathering processes from parent rocks. Soil density was negatively correlated ($p<0.01$) with ^{137}Cs and ^{40}K, which is in accordance with the findings of Ligero et al. (2001).[17] Positive correlations ($p<0.01$) between ^{137}Cs specific activity and both saturated hydraulic conductivity and specific electrical conductivity were observed. Electrical conductivity was negatively correlated with ^{226}Ra and ^{232}Th specific activities. The correlations between radionuclides and major and trace elements revealed that ^{40}K was positively correlated ($p<0.01$) with K (as it is present in natural potassium with a constant abundance), Cr, Ni, Pb and Zn, which is in accordance with their common correlations to clay. Close positive correlations ($p<0.01$) were found between ^{226}Ra and ^{232}Th and Fe and Mn, which indicates association of these radionuclides with Fe and Mn oxides or deposition of Fe and Mn oxides on the surfaces of ^{226}Ra and ^{232}Th minerals. A positive correlation ($p<0.05$) between ^{226}Ra and Co was also observed, which agrees with the findings of Chao and Chuang (2011).[18] A negative correlation ($p<0.01$) between ^{226}Ra and ^{232}Th and Ca was found, which is in accordance with the negative correlation of these radionuclides with carbonates. The anthropogenic ^{137}Cs was found to be positively correlated ($p<0.01$) with Cd, Cr, Pb and Zn, which is in accordance with earlier results for soils from the Zlatibor area, Serbia.[19] These correlations could be attributed to the common affinity of these elements for clay minerals.

Conclusions

In this study the influence of a number of edaphic factors on radionuclide distribution down the depth profile was analysed. The distribution of ^{40}K, ^{226}Ra and ^{232}Th were found to be constant down the soil profile depth, while the large variability was observed for ^{137}Cs depth distribution. Clay and silt contents were positively correlated with ^{40}K, ^{226}Ra and ^{137}Cs. Close positive correlations were found between ^{226}Ra and ^{232}Th and Fe and Mn, which indicates association of these radionuclides with Fe and Mn oxides, supported also by strong positive correlations with Ni, Pb and Zn. A negative correlation between ^{226}Ra and ^{232}Th and Ca was found, which is in accordance with the negative correlation of these radionuclides with carbonates. The strong positive correlation was observed between ^{232}Th and Cr. The anthropogenic ^{137}Cs was found to be positively correlated with Cd, Cr, Pb and Zn, which confirmed their common affinity for clay minerals. As the large number of parameters which could influence radionuclide migration in soil were analysed, the findings of the study could be useful in the modeling of radionuclide migration in soils. The number of models are already developed to quantify radionuclide mobility of radionuclides in soils but they are not generally applicable because they require many input parameters that are specific for each site. The behaviour of radionuclides in soil is confirmed as a complex phenomenon that depends on a number of physical, chemical and biological properties of the soil.

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