Correlations of natural radionuclides in soil with those in sediment from the Danube and nearby irrigation channels

M. Krmar*, E. Varga, J. Slivka

Physics Department, Faculty of Science, University of Novi Sad, Trg Dositeja Obradovica 4, 21000 Novi Sad, Serbia

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ABSTRACT

The correlation between activity concentrations of some natural radionuclides (^{238}U, ^{226}Ra, ^{232}Th, ^{40}K) measured in soil and in sediment taken from the Danube River and nearby irrigation channels was studied. The soil samples were collected from the northern part of Serbia and the sediment from the Serbian part of the Danube River and from the surrounding irrigation channels. The correlation between ^{238}U and other natural radionuclides in irrigation channel sediments was not as good as in the Danube. One of the possible explanations for this weak correlation can be the different chemical dynamics of ^{238}U in the irrigation channel sediment or changes of the ^{238}U activity concentration in irrigation channel sediment due to some human activities. The evaluation of ratios of activity concentrations of some natural radionuclides could be a more sensitive method for the determination of contaminant, rather than the straightforward analysis of activity concentrations.

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1. Introduction

The level of soil natural activity (mostly from U and Th series and K) is related to the type of parent rock and to the soil genesis. The soil radioactivity is extensively studied because the assessment of possible gamma ray exposure of human population to natural radiation originating from soil. This is of particular importance for regions having elevated levels of natural radionuclides in the soil (Malanca et al., 1993; Narayana et al., 1995). The level of natural radioactivity of the soil is associated with the internal exposure of human population through ingested food because the major pathway for the transfer of most radionuclides to human body is the soil-plant-man chain (Pulhani et al., 2005).

The non-organic part of the river sediment is a specific mixture of different mineral components arriving into the river bed through weathering or erosion. The specific levels of natural radionuclides are mostly related to the types of rock or soil from which the sediment originates. Variation of the sediment composition can be result of the chemical and mineralogical evolution of sediment along the river stream, different properties of the watershed soils, influence of tributaries, etc. Radionuclides from the uranium and thorium decay series have been used for a long tome as tracers and chronometers in studies of weathering (Dosseto et al., 2006a;

Chabaux et al., 2006; Porcelli et al., 2001), as well as in studies of transport and the environmental dynamics of natural radionuclides (Dosseto et al., 2006b; Singh et al., 2003).

Enhanced concentrations of natural radionuclides can be found in river sediment as a result of industrial activities (Jurado Vargas et al., 1997; Perianez and Martinez-Aguirre, 1997). Processes of accumulation in sediment sometimes elevate concentrations of the ^{238}U family members more than one order of magnitude (Lozano et al., 2002).

Uranium series disequilibrium is powerful tool applied in earth science (Ivanovich and Harmon, 1982; Krishnaswami and Cochran, 2008), however ratios of concentration of radionuclides, members of two different series (or some other natural radionuclides, such as ^{40}K) were not frequently used in environmental studies. Some authors (Singh et al., 2005; Nageswara Rao et al., 1996) reported, without a detailed analysis, the direct correlation between the activity concentrations of ^{238}U (^{226}Ra) and ^{232}Th in soil. It suggests that some mean ratio of activity concentrations of two radionuclides for samples collected in one region can be established. The ratios of ^{238}U, ^{232}Th and ^{40}K in some areas should be dependent on mineral structure and origin of the soil and sediment. Possible deviations of the ratio can be an indicator that the concentration of one of the nuclides has increased because of industrial activities. The goal of this work was to measure a range of activity concentrations of natural radionuclides in the soil of Vojvodina (north Province of Serbia) and sediment in part of the Danube and surrounding irrigation channels through Serbia. From this, it should be possible to estimate if there are elevated concentrations of some

radionuclides (especially ^{238}U) in soil or sediment by comparing the ratios of the measured activities of ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K.

2. Sampling and measurements

Soil samples were collected from 50 locations which were evenly distributed over 21,506 km^2 of northern part of Serbia (agricultural region). Sampling sites were large farms with freshly ploughed soil, and samples were taken with a shovel directly from the surface layer (10 cm). This does not correspond to a natural depth distribution, but points out the layer used by young plants of the field crops. Additionally, 54 sediment samples were taken from 18 sites distributed along 314 km of the Danube route through Serbia, between the 1425th and the 1110th km of Danube. This part of the country is an agricultural region irrigated by a net of channels supplied by Danube water. A further 20 sediment samples were taken from irrigation channels. About 1 kg of wet sediment was collected from the Danube or irrigation channels at each sampling point. Sampling points were chosen at depositional areas, avoiding ones with pure sand, on the riverside at the water line in the period when the river dropped significantly. A sample consisted of four small shovel grabs of mud taken from the surface layer, at places 2 m apart following the water line. At irrigation channels the sampling time was random and a sample was composed only of two grabs. Collected samples of sediment and soil were dried at 105 °C to a constant weight. After homogenization, and after the removal of particles larger than 1 mm, the sample powder was packed in plastic containers (with a diameter of 6.70 cm and a height of 6.20 cm). The mass of dried soil and sediment samples packed in the standard laboratory geometry was up to 300 g. The containers were hermetically sealed and stored for more than 4 weeks in order to reach equilibrium between ^{222}Rn and daughter nuclei. The gamma spectra of the soil and sediment samples were collected up to 80,000 s by an HPGe detector, with a 32% relative efficiency, shielded by 25 cm of pre WWII iron. The integral background counting rate (between 30 and 3000 keV) was less than 1.2 counts s^{-1}.

The detection efficiency was established from certified calibration sources of various origin, geometry, and matrix, among others NBS Standard Reference Material 4350B (river sediment), and transformed to the sample specific geometry and matrix using the relative effective solid angle method (Moens et al., 1981) for known detector parameters (Jovanovic et al., 2010). Special attention was paid to the variation of sample density influencing possible changes of detection efficiency of low energy gamma lines. The detection efficiency uncertainty was combined by propagation of uncertainties of certified sources and counting statistics of calibration spectra. The sample final activity concentration uncertainty combined the above detection efficiency uncertainty with the sample counting uncertainty.

3. Results and discussion

The mean values and ranges of the measured activity concentrations in Danube and irrigation channel sediment samples, as well as the soil values, are presented in Table 1. It can be seen that

the maximum measured concentration of ^{238}U in Danube sediment was more than four times higher than the minimum concentration, which was also the case with the concentrations of ^{226}Ra. The range of measured activity concentrations of ^{232}Th was slightly lower, where the minimum and maximum values differed by a factor of 3.4. Concentrations of ^{232}Th, ^{226}Ra and ^{40}K in irrigation channel sediments had narrower ranges (3-fold) than the ranges of activity concentrations of the same radionuclides in Danube sediment. Only the activity concentration of the ^{238}U in irrigation channel sediment had a broader region of measured values than ^{238}U in the Danube sediment: the range was a factor 6.8. The activity concentrations of natural radionuclides in soil had a smaller range (Table 1) than the concentrations of radionuclides in Danube sediment. The frequency distributions of the measured activity concentrations of ^{238}U and ^{232}Th are presented in Fig. 1. It is interesting to notice that distributions of measured values of ^{232}Th in the Danube, irrigation channels and soil differ markedly. The frequency distributions of ^{238}U are more similar among the sample types. If we suppose that the distribution of the ^{238}U activity concentrations shown in Fig. 1 can be presented by a Gaussian function, a simple fit will give a mean value of 42 Bq/kg and a standard deviation of $\sigma = 28.7$ Bq/kg. Following the principle that a concentration having a value outside of the 3σ interval can be considered as increased, the distribution of ^{238}U measured values suggests that all values of activity concentrations higher than 128 Bq/kg were increased. This limit is three times higher than the mean value of the ^{238}U distribution. The activity concentrations of ^{238}U in channels had an even broader range than those in Danube sediment.

In the light of these data, it can be concluded that a small increase of some natural radionuclides cannot be easily noticed. For example, in the worse case, the concentration of ^{238}U in Danube sediment or soil can be increased by some human activities by a factor of 4 and even more and the overall activity concentration will still be in the range characteristic for the monitored part of the Danube.

The ratios of the activity concentrations of different natural nuclide pairs were calculated for all sediment and soil samples. The mean values and range of the values of some activity concentration ratios for Danube sediment, as well as for irrigation channel sediment and soil, are presented in Table 2. The distributions of ^{238}U/^{232}Th and ^{238}U/^{40}K activity concentration ratios are presented in Fig. 2. The most values of ^{238}U/^{232}Th ratio (except two of them) for Danube samples were grouped around the mean value of 1.15. The highest and lowest values of the ^{238}U/^{232}Th ratio in this group differed by a factor 1.7. This range is more than 3 times less than the range the in ^{238}U activity concentrations. If the distribution of ^{238}U/^{232}Th ratios is assumed to be Gaussian, without the two highest values presented in Fig. 2, the mean is 1.14 and σ has a value of 0.25. This means that a value just 66% higher than the mean of the ^{238}U/^{232}Th ratio distribution will be out of the 3σ range. Fig. 2 shows that two values of the ^{238}U/^{232}Th ratio are apparently out of the distribution. This means that two samples have values of ^{238}U which are higher than can be expected according the ^{238}U/^{232}Th

Table 1
Mean values and ranges of activity concentrations of natural radionuclides measured in sediment samples of the Danube and nearby irrigation channels, and in soils of the region.

Radionuclide	Danube		Irrigation channels		Soil	
	Mean [Bq/kg]	Range [Bq/kg]	Mean [Bq/kg]	Range [Bq/kg]	Mean [Bq/kg]	Range [Bq/kg]
^{238}U	42 ± 12	16–71	45 ± 21	13.5–92	52 ± 9	24–72
^{232}Th	36.0 ± 9.5	15.2–52	25.8 ± 6.5	12.5–34.7	53.7 ± 8.6	22–64
^{226}Ra	32.4 ± 8.4	14.2–59	25.3 ± 5.5	12.4–33.7	39.6 ± 7.6	19.7–51
^{40}K	445 ± 88	261–630	422 ± 95	242–550	553 ± 92	238–730