SHORT COMMUNICATION

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Behavior of long-lived radionuclides in the Danube river ecosystem in Serbia

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Radioactivity of water and sediments from the Danube river in its course through Serbia during 2001–2003 years has been tested by alpha- and gamma-ray spectrometry. Except for cesium originating from Chernobyl, the radioactivity level of water and sediment coincide with the content of natural radionuclides in the environment of rivers basin. No increase in the radioactivity of sediments, due to slowing down of the water flow, was observed. The obtained results were analyzed in accordance with the model which considers only naturally occurring radionuclides originating in river sediment. The distribution coefficients for natural radionuclides are determined.

Introduction

The ecosystems of the Danube river and its tributaries are the subject of investigations through many years.[1–4] The Danube river is an important international river and its average flow on entering Serbia at 1425.5 km from the sea, is 2400 m^3/s and on leaving the country, at 825 km, 5500 m^3/s. Serbian territory approximates 10% of the Danube river basin. Beside water supply other uses of Danube river and its surroundings include agriculture, forestry, power generation, recreation, etc. Furthermore, the tremendous changes in the water environment by human activity have affected ecological system of the Danube River.

The particular characteristic of the Danube on its course through Serbia, by all means, is the existence of the Djerdap hydro-energetic system along the Yugoslavian-Romanian border, and the lake of Djerdap with a dam which controls the level of the Danube between 21 and 35 meters. Because the nuclear power plants on its banks, there is a possibility of radioactive contamination of the river ecosystem.

In this work, natural and artificial radionuclides have been examined in a part of the Danube river, from Belgrade to Kladovo, in order to check the possible increase in radioactivity due to slow-down before coming to the dam at the hydroelectric power station. Previous investigations of the systems, especially after the Chernobyl accident in 1986, gave the possibility to observe the long-term behavior of radionuclides in the system.

Experimental

A 10 liter sample of water was used for analysis. It was evaporated to dryness. NH_4NO_3 and tracer solution of ^{232}U was added to the sample. Then the sample was heated to 550 °C for 6 hours. To dissolve the soluble salts 50 ml 5% HNO_3 was added and heated while stirring. Concentrated NH_4NO_3 was added to the sample solution until pH 9 while stirring, to precipitate. Supernatant was discarded. The precipitate was dissolved with 8M HCl and the sample passed through the column of anion-exchange resin Dowex 1x8 in chloride form. 1M HCl was used as eluent for uranium. Then the sample was evaporated to near dryness and transferred to 8M HCl, then the iron was removed by extraction with isopropylaether. Uranium was electrodeposited on a stainless steel disk, according to the method of TALVITIE[5] and determined by a Canberra 2004 alpha-ray spectrometer system with PIPS detector, with the following characteristics: area 300 mm^2, 20 keV resolution for ^{241}Am alpha-line, and 16% efficiency.

The activity of the natural and artificial gamma-ray emitters were analyzed by a multi-channel analyzer using a reverse electrode HPGe detector with relative efficiency of 23%. Sediment samples were dried at 105 °C in an oven. The radioactivity of the sediment samples was measured for the fraction of particles that passed through a 1.0 mm sieve, after establishing the radioactive equilibrium between ^{220}Rn and its daughter products.

Results and discussion

Table 1 shows the results of radioactivity measurement in the sediments of the Danube river, at five selected sites: 1145 km (1), 1116 km (2), 1062 km (3), 955 km (4) and 943 km upstream from mouth (5) in the course of a three-year period of 2001–2003, by means of gamma-ray spectrometry. ^{238}U, ^{232}Th and

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^{226}Ra are the most widespread radionuclides of natural origin and the most important ones from the point of view of impact to the environment.

Results from other authors[1] for the concentrations of natural gamma-emitting radionuclides in the Danube river sediments, from 1987 during the influence of the fall-out from Chernobyl, were of the similar character. Compared to the results of 15 years ago, there is no oscillations in the thorium content. Differences have been noticed in the results for uranium and radium, their concentration were higher after the Chernobyl accident.

Using alpha-ray spectrometry for the water samples, the concentration of uranium (^{238}U and ^{235}U) was determined (Table 2). The concentration of ^{235}U was near to the limit of detection, because of the rather high background of the apparatus (Fig. 1). The concentration of uranium was somewhat higher than found earlier.

Table 1. Radioactivity of sediments of the Danube river (in Bq/kg)

Sampling location	Year	^{238}U	^{232}Th	^{226}Ra	^{137}Cs
Danube No. 1	2001	22±5	36±4	31±3	33±3
(Belgrade)	2002	27±5	34±5	26±3	18±2
	2003	28±5	29±5	19±3	18±3
Danube No. 2	2001	23±6	36±4	49±4	31±3
(Smederevo)	2002	26±6	33±4	41±4	19±2
	2003	22±5	39±6	42±5	16±4
Danube No. 3	2001	28±7	35±4	44±4	27±2
(Gradište)	2002	30±7	41±5	39±4	22±5
	2003	22±5	32±5	42±5	13±4
Danube No. 4	2001	31±7	32±3	29±3	25±2
(Tekija)	2002	27±7	44±5	46±4	17±2
	2003	23±5	37±7	39±6	14±3
Danube No. 5	2001	21±5	43±5	38±4	25±2
(Kladovo)	2002	24±5	29±3	31±3	15±2
	2003	17±4	37±5	37±6	12±4

Table 2. Radioactivity of uranium in the Danube river water

Code	Location	Date of sampling, g	U, μg/l	^{238}U, mBq/l	^{235}U, mBq/l	^{234}U, mBq/l	^{234}U/^{238}U
18, Belgrade	Danube No. 1	06. 02. 2002	0.63	7.73±0.36	0.38±0.05	9.16±0.42	1.17
20, Tekija	Danube No. 4	06. 02. 2002	0.74	9.20±0.63	0.42±0.11	10.35±0.68	1.12
21a, Kladovo	Danube No. 5	06. 02. 2002	0.89	11.08±0.5	0.45±0.07	12.59±0.58	1.14
30, Tekija	Danube No. 4	10. 30. 2002	0.80	9.86±0.59	0.49±0.1	11.09±0.65	1.12
31, Kladovo	Danube No. 5	10. 30. 2002	0.90	11.18±0.6	0.58±0.1	11.01±0.6	0.99

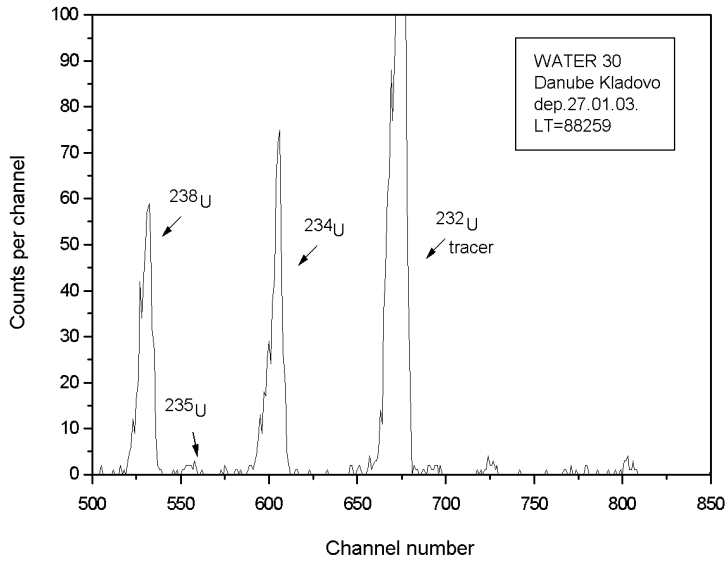

Fig. 1. Alpha-spectrum of uranium from the Danube river (Site No. 5)

The obtained concentrations were quite usual,[6] without any apparent influence of the Djerdap dam. No the measurable concentrations of artificial radionuclides could be identified by gamma-ray spectrometry, even ^{137}Cs was present less than 0.01 Bq·dm^{-3} level.

^{238}U concentration in the Danube water ranged between 7.0 and 11.1 mBq/l (Table 2) and the corresponding distribution coefficient between the solid and liquid phases (K_d) was (1–4)·10^3 l/kg. In the rivers of Spain this coefficient is approximately 1·10^3 l/kg.[7] The lower solubility of Th compounds in relation to the uranium compounds was reflected in the substantially higher K_d of (1.1–4.2)·10^5 l/kg. ^{226}Ra concentration increased in relation to the condition of the radioactive equilibrium with ^{238}U. The published K_d value for Ra is (0.6–2)·10^4 l/kg.[4]

The obtained results show, that the radioactivity of water and sediment of the Danube river reflects natural background.[8]

There are models developed for predicting the behavior and migration of radionuclides through rivers.[7,9] The model of RODRIGUEZ-ALVAREZ and SANCHEZ[7] is applicable to our results because it considers naturally occuring radionuclides (uranium, thorium and radium) originating in the river sediment itself.

The accumulation of radionuclides in sediments along the Bulgarian Black Sea coast near the mouth of the Danube river[10] shows clearly that ^{137}Cs is transported via sea currents rather than by river waters, i.e., river sediments contain lower Cs concentration than sea sediment. Rivers sediment imply high ^{137}Cs accumulation rate, its content has a falling down tendency (Table 1).

The nuclear power plants located on the bank of the Danube river do not contribute to the contamination of the river in its flow through Serbia.

Conclusions

The present work supplies quantitative information about the concentration of long-lived radionuclides in water and sediment of the Danube river through Serbia in three year period (2001–2003).

The model of RODRIGUEZ-ALVAREZ and SANCHEZ for the description of the behavior of radionuclides in river can be applied to our results for natural radionuclides because no external contamination source was observed. Due to the difference in the distribution coefficients (K_d) for uranium and thorium, the concentration of thorium slowly increases in relation to that of uranium in the sediment.

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