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^{226}Ra and ^{228}Ra in Croatian Rivers

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A B S T R A C T

The presence of natural radionuclides in Croatian rivers emphasizes the need for its continuous monitoring. Therefore results of ^{226}Ra and ^{228}Ra determination in Croatian river waters are presented in this paper. ^{226}Ra and ^{228}Ra were chosen as a possible source of human exposure due to their high radio-toxicity. Fifty liters of river water samples were collected from the Danube, Drava, Sava, Krka and Neretva rivers twice a year from 2002 to 2006. It is showed that activity concentrations of ^{226}Ra ranged from 6.54 mBq/L to 59.44 mBq/L and ^{228}Ra activity concentrations ranged from 2.57 mBq/L to 20.76 mBq/L. The highest values of both ^{226}Ra and ^{228}Ra were measured in the river Drava, and the lowest values in the river Sava. Statistically significant differences were not observed between radium concentrations from two watersheds (the Black Sea and the Adriatic Sea watershed), nor between ^{226}Ra/^{228}Ra ratio in rivers individually. The number of collected samples is insufficient to make more statistically significant conclusions. However the data obtained in this study could be the baseline for evaluating possible future changes.

Key words: *natural radioactivity, ^{226}Ra, ^{228}Ra, river water, monitoring*

Introduction

Croatia is a water-rich country and rivers in Croatia are important sources of water supply, along with underground water, wells and technical water supply systems. Therefore, the presence of natural radionuclides in the Croatian rivers emphasized the need for continuous monitoring. ^{226}Ra and ^{228}Ra were chosen as a possible source of human exposure to radioactivity due to their high radio-toxicity.

^{226}Ra is a member of the ^{238}U decay series and is an α-emitter with a long half-life of 1600 years. As a chemical homologue of Ca, an essential metabolic element, Ra follows Ca metabolism in man with eventual deposition in bones. Once deposited in bone tissue it continually irradiates the human skeleton for many years, and potentially induces bone sarcoma. It decays to ^{222}Rn (with a half-life of 3.8 days) which further decays into a series of short-living decay products. Closely following in toxic behavior is ^{228}Ra a β-emitter from the ^{232}Th decay series with a half-life of 5.77 years, which also has considerable significance in environmental radioactivity studies[1–4].

Decay of these radionuclides may cause significant exposure to radiation of the nearby tissue causing biological damage[1]. Moreover, the chemical and biological behavior of radium is similar to that of other alkaline earth metals (Ca, Sr, Ba) and so it can be easily incorporated into the bones of mammals and may cause an enhanced radiation dose to the public. Although environmental aspects of radioactivity and their possible effects on the population have been a subject of interest for several decades in Croatia, there are no reports on radium concentrations in river waters.

This paper presents the measurements of ^{226}Ra and ^{228}Ra activity concentration in the Danube, Drava and Sava rivers, which are a part of the Black Sea watershed, and the Krka and the Neretva River, which are a part of the Adriatic Sea watershed. According to The Water Classification Decree these rivers belong to the category of waters which can be used in industry and agriculture[5]. As for drinking, they have to be purified first using technological procedures for removing radionuclides from the water[6–8]. Monitoring of ^{226}Ra and ^{228}Ra presence in river waters is important because it provides better insight of radionuclide distribution in nature and quality control of waters that could be used for irrigation of agricultural areas, which are the possible sources of human exposure to radioactivity.

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Materials and Methods

Sample collection and analysis

River water samples were collected twice a year from 2002 to 2006 at the same seasonal period and at the same location using geographic coordinates, to reduce the uncertainty in sampling. The river water samples were: Danube-Vukovar, Drava-Osijek, Drava-Varaždin, Sava-Županja, Sava-Zagreb, Krka-Skradin and Neretva-Opuzen. Locations of sampling sites are shown in Figure 1.

Radiochemical separation of ^{226}Ra was performed on all samples. Precipitated $Ba(Ra)SO_4$ was determined by α-spectrometric measurement using Si detector (partially depleted PIPS detector: active area 450 mm^2, alpha resolution for ^{241}Am 19 keV) during at least 80,000 seconds[9].

After evaporating 50 L of each sample to volume of 1 L, all the samples were gammaspestrometrically analyzed in the laboratory using HP Ge and/or Ge(Li) detector (resolution 1.78 keV on 1.33 MeV ^{60}Co, relative efficiency 16,8%; resolution 1.56 keV on 1.33 MeV ^{60}Co, relative efficiency 18,7%) with electronic units and gammaspectromeric software on a personal computer. Samples were measured in Marinelli beaker. Measurement time was 170,000 seconds or longer. ^{228}Ra was calculated from ^{228}Ac which was measured gammaspestrometrically on 911.07 keV, 968.90 keV and 964.60 keV[10,11].

Results and Discussion

In most countries ^{226}Ra concentration in water is expressed through the gross α-activity of 100 mBq/L and gross β-activity of 1000 mBq/L[12–14]. Croatian law, i.e. The Hazardous Substances in Water Decree, recommends that water specific activity of ^{226}Ra should not exceed 500 mBq/L where gross alpha activity is maximally 250 mBq/L[15]. According to the World Health Organization (WHO) Guidelines for Drinking Water Quality, concentration should not exceed 1 Bq/L for ^{226}Ra and 0.1 Bq/L for ^{228}Ra[16]. Table 1 shows that total activity concentrations of ^{226}Ra and ^{228}Ra are in accordance with Croatian and WHO recommendations.

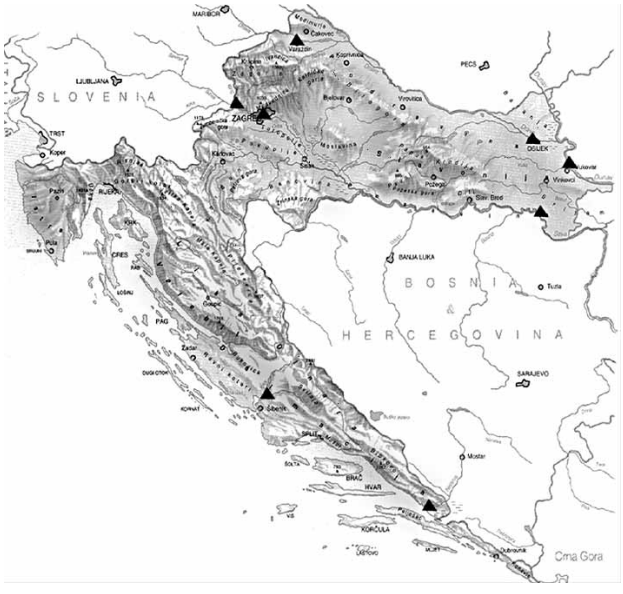

Fig. 1. Map of sampling sites of river water in Croatia.

TABLE 1
ACTIVITY CONCENTRATIONS OF ^{226}Ra AND ^{228}Ra IN RIVER WATER SAMPLES

	^{226}Ra	^{228}Ra	
Number of Samples	42	42	
Mean	22.44	10.23	
Median	19.57	10.22	
Minimum	6.54	2.57	(mBq/L)
Maximum	59.44	20.76	
Standard Deviation	13.09	5.10	
Standard Error	2.02	0.79	

As it is shown in Figure 2 and 3, activity concentraions of ^{226}Ra ranged from 6.54 mBq/L to 59.44 mBq/L and activity concentrations of ^{228}Ra ranged from 2.57 mBq/L to 20.76 mBq/L. It is also noted that the lowest values are measured in the Sava River, and the highest

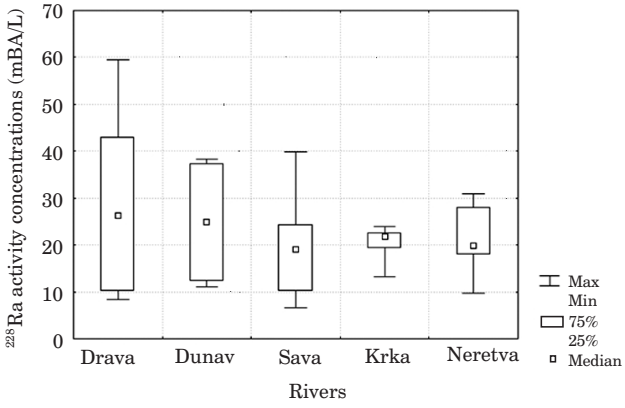

Fig. 2. ^{226}Ra activity concentrations in Croatian rivers.

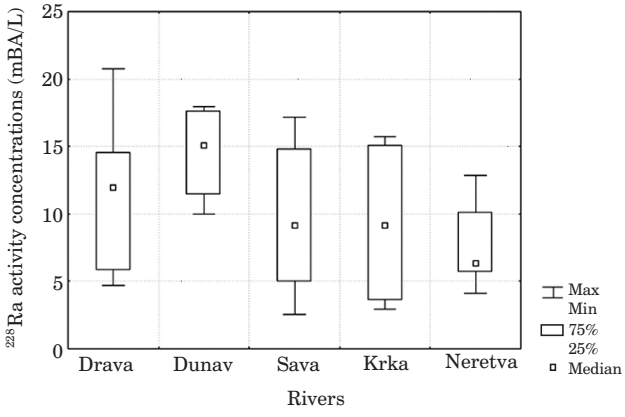

Fig. 3. ^{228}Ra activity concentrations in Croatian rivers.

values in the Drava River for both ^{226}Ra and ^{228}Ra. These results are in accordance with investigations of radium activity concentrations in the Sava River in Slovenia[14].

The activity concentrations of ^{226}Ra are higher than those observed in some French and Chinese rivers[17,18], but similar to those found in Portuguese, Spanish, Indian and Turkish rivers[19–22], although ^{228}Ra levels were slightly higher in Portuguese rivers than in Croatian. Very high natural radium concentrations are reported in Brazil (80–630 mBq/L for ^{226}Ra and 120–1520 mBq/L for ^{228}Ra)[23].

Figure 4 shows relations between activity concentrations of both radionuclides in all individual samples. Sign of bimodality in both ^{226}Ra and ^{228}Ra indicated some difference in activity concentrations between watersheds i.e. river waters. Large geological difference between Croatian rivers of the Black Sea watershed and the Adriatic Sea watershed suggested differences in radium concentrations, but radium concentrations of samples from both watersheds showed no statistical significant difference between them. There was also no statistical significant difference of ^{226}Ra/^{228}Ra ratio neither in the two watersheds, nor between rivers individually.

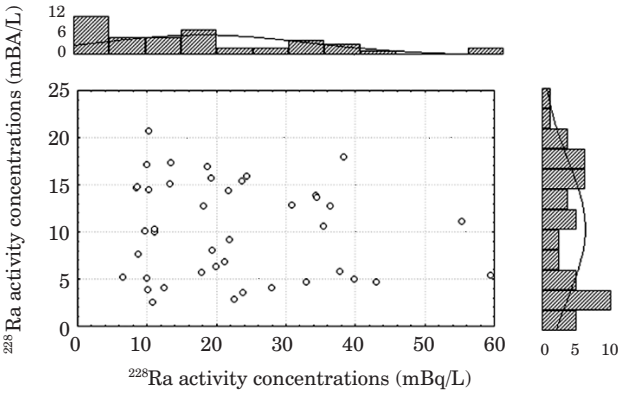

Fig. 4. Scatter plot with histograms showing relations between activity concentrations of ^{226}Ra and ^{228}Ra in Croatian rivers.

Conclusion

Determination of ^{226}Ra and ^{228}Ra content in river water is useful for the purpose of the prevention of unnecessary exposure of humans to natural radiation. All Croatian rivers flow through agricultural areas and are used for irrigation of crops, so monitoring of radium in river water is of great importance to prevent undesirable deposition into the human skeleton. The number of collected samples is insufficient to make conclusions on statistically significant level, however the data obtained in this study could be the baseline which can be used to evaluate possible future changes.

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^{226}RA I ^{228}RA U RIJEKAMA HRVATSKE

S A Ž E T A K

U ovom radu prikazani su rezultati mjerenja koncentracija ^{226}Ra i ^{228}Ra u rijekama Hrvatske. Zbog prisutnosti prirodnih radionuklida u rijekama potreban je neprestani monitoring. ^{226}Ra i ^{228}Ra su izabrani, zbog svoje visoke radio-toksičnosti, kao mogući izvor izlaganja ljudi radioaktivnosti. Mjerena je specifična aktivnost u 50 L uzoraka riječne vode iz Dunava, Drave, Save, Krke i Neretve. Uzorci su uzimani dva puta godišnje od 2002. do 2006. godine. Koncentracije aktivnosti ^{226}Ra varirale su između 6,54 mBq/L i 59,44 mBq/L, dok su koncentracije aktivnosti ^{228}Ra varirale između 2,57 mBq/L i 20,76 mBq/L. Najviše vrijednosti izmjerene su u rijeci Dravi, dok su najniže vrijednosti izmjerene u rijeci Savi za oba radionuklida. Nisu primijećene statistički značajne razlike između slivova (Crnomorski i Jadranski sliv), niti između odnosa ^{226}Ra/^{228}Ra u rijekama pojedinačno. Iako je premalo uzoraka za donošenje više zaključaka na statistički značajnom nivou, podaci iz ovog rada mogu biti korisni u procijeni stanja radioaktivnosti u okolišu, te mogućih promjena.