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Distribution of ^{103}Ru, ^{134}Cs and ^{137}Cs in Different Geochemical Media in the Bruvno Area in the Years 1985 and 1986

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In 1985 and 1986 (post Chernobyl) moss, stream detritus and soil were sampled in the region of the Bruvno brachy-anticline, in the carbonate terrains of south-western Yugoslavia. The necessity for continuous monitoring of the long-living radionuclides behaviour has been imposed for a longer time period, because of the radionuclides entering the whole geochemical cycle.

An insignificant presence of ^{137}Cs was determined in the samples taken in November 1985. Samples taken in June 1986 showed a significant presence of ^{103}Ru, ^{134}Cs and ^{137}Cs. On the basis of the measured specific activities, the values of the moss/stream detritus concentration factors were determined.

U karbonatnim terenima jugozapadne Jugoslavije na području bruvanjske brahiantiklinale uzimani su uzorci mahovine, dolinskog detritusa i tla u 1985. i 1986. godini. Radi ulaza radionuklida u cijeli geokemijski ciklus nameće se potreba za kontrolnim praćenjem ponašanja dugoživućih radionuklida u dužem vremenskom periodu.

U uzorcima 1985. godine utvrđeno je neznatno prisustvo radionuklida ^{137}Cs. U odnosu na 1985. godinu u 1986. godini sadržaj ^{103}Ru, ^{134}Cs i ^{137}Cs bitno je povećan. Na osnovi izmjerenih specifičnih aktivnosti određene su vrijednosti koncentracijskih faktora mahovina/dolinski detritus.

INTRODUCTION

Sampling of moss, stream detritus and soil from the nine springs in Bruvno brachy-anticline region, was carried out at November 1985. The aim was to analyse distribution of some trace elements. After the Chernobyl disaster, we found out that resampling the same localities would provide usefull data about degree of contamination caused by radionuclides originated only as fission products. In that case, content of the same elements in the samples collected in November 1985 could be considered as background values. Because of their relatively long half-life time, the specific activity of the radionuclides ^{103}Ru, ^{134}Cs and ^{137}Cs in samples of all three geochemical media was measured.

Bruvno brachy-anticline is built of paleosoic core covered by Mesozoic (Triassic) limestones and dolomites in the periclinal bedding. Subordinately clastics and tuffitic clastic are present.

Investigated region is characterized by the low karst type of relief with poor river systems. Water only circulates through the Triassic rocks. The existing springs are fed by gravity with capacity ranging from 1 to 10 liters per second. The soil is poorly developed, mainly on leveled areas and in stream valleys where mainly red soil and brown undifferentiated soil are present. Only a thin humus layer and a thin leached horizon are developed.

SAMPLING METHODS AND ANALYSIS

The following three geochemical media have been studied: moss and stream detritus from springs or within 20 m downstream, and soil nearest to the springs.

In field moss in contact with water was sampled by hand from about 10 places. The most frequently occurring species was sampled and was immediately washed in clean water.

Stream detritus samples were collected by compositing at least 10 handfuls of stream detritus from a different places. The samples were placed in small cloth bag.

The first soil sampling was made at a depth ranging from 15 to 30 cm from the surface, while the second one consisted in taking the 15 cm of the soil profile below the horizon A_1 (2—5 cm from the surface).

In the laboratory the moss samples placed in holders were, thoroughly rinsed in running water. When the water in the holders was completely clean, the moss was also considered to free of clastic dirt or other particles; it was then dried at 60 °C. The samples of the stream detritus and soil were dried at the same temperature and then sieved.

The material for the analysis was taken after sieving through a 83 μm sieve.

The radioactivity of the radionuclides ^{103}Ru, ^{134}Cs and ^{137}Cs in the samples was measured by the gammaspectrometric method using Canberra 4096 channel analyzer. Samples were analyzed in Marinelli holders of 250 to 500 g and in plastic holders of 100 g, depending on the amount of the samples available. The gammaspectrometric measurements were made with a Canberra »Closed and Coaxial« Ge(Li) detector with the sensitivity volume of about 50 cm^3, an efficiency of 15.7% and a resolution of 1.89 keV; the »peak to Compton« ratio was 41:1 for the ^{60}Co energy of 1332.5 keV.

Calibration for efficiency was made using a ^{152}Eu calibration source in the same geometry as that for the samples. The efficiency-curve error was about 5%.

The specific activity of radionuclides in the samples was determined by absolute measurements on a Ge(Li) semi-conductor detector. The measuring-time for one sample was from 1 000 to 10 000 s. The area of the characteristic spectral lines was determined by the following relation (W. B. Bowman and D. L. Swindle, 1976):

$$A = N_p - \frac{N_1\ N_2}{2} (N_2 - N_1 + 1)$$

where:

A — area of a spectral line,
N_p — total number of impulses below the photopeak of a spectral line,
N_1 — impulse number in the front-channel of the photopeak,
N_2 — impulse number in the end-channel of the photopeak.

The corresponding areas of the background radiation were subtracted from the area of the spectral lines of the sample. The measured areas of the spectral lines gave the specific radionuclids activity as follows:

$$A_s = \frac{A}{m \in I} \text{ Bq/kg}$$

where:

A_s — sample's specific activity for the measured radionuclides (Bq),
m — weight of a sample (kg),
$\in$ — detector efficiency for the given energy
I — intensity of the observed spectral line.

The statistical error of the specific activity is determined by the following relation:

$$\sigma_s = \sqrt{N_p + \frac{N}{M} L + (N_p - L)^2 Z^2}$$

where:

σ_s — standard deviation of the measured specific activity
N — number of channels included in the calculation of activity,
M — number of channels for the calculation of the basic radiation,
L — content of chanels for the calculation of the background,
Z — error related to the error in the estimation efficiency and the weight of the sample.

Low Level Detection (LLD) from the Table 2 to 4 was calculated by the following equation (A k i r a N a k a o k a e t al., 1980),

$$(LLD) = \frac{0{,}5}{C \in YW\, t} (1 + 2\sqrt{2C}\ \sqrt{tB})$$

where $\in$ is the detection efficiency of the radionuclide under consideration for the detector; C is the coefficient of variation (decided as 03); t is sample comuting time; Y is the γ-ray emission fraction of the radionuclide under consideration; B is the background comiting rate (cps), and W is the sample amount.

The half-life time, the energy and the absolute intensites of the measured gama-levels are listed in Table 1 (G. E r d t m a n n, and S. W e r n e r, 1979).

Table — Tabela 1.

Characteristics of the measured radionuclides

Karakteristike mjerenih radionuklida

Radinuclides Radionuklidi	Half-life time Vrijeme poluraspada (d)	Energy Energija (keV)	Intensity Intenzitet (%)
^{103}Ru	39.3	497.0	86.4—0.3
^{134}Cs	753.0	795.7	85.4—0.3
^{137}Cs	10723.0	661.6	84.6—0.5

RESULTS AND DISCUSSION

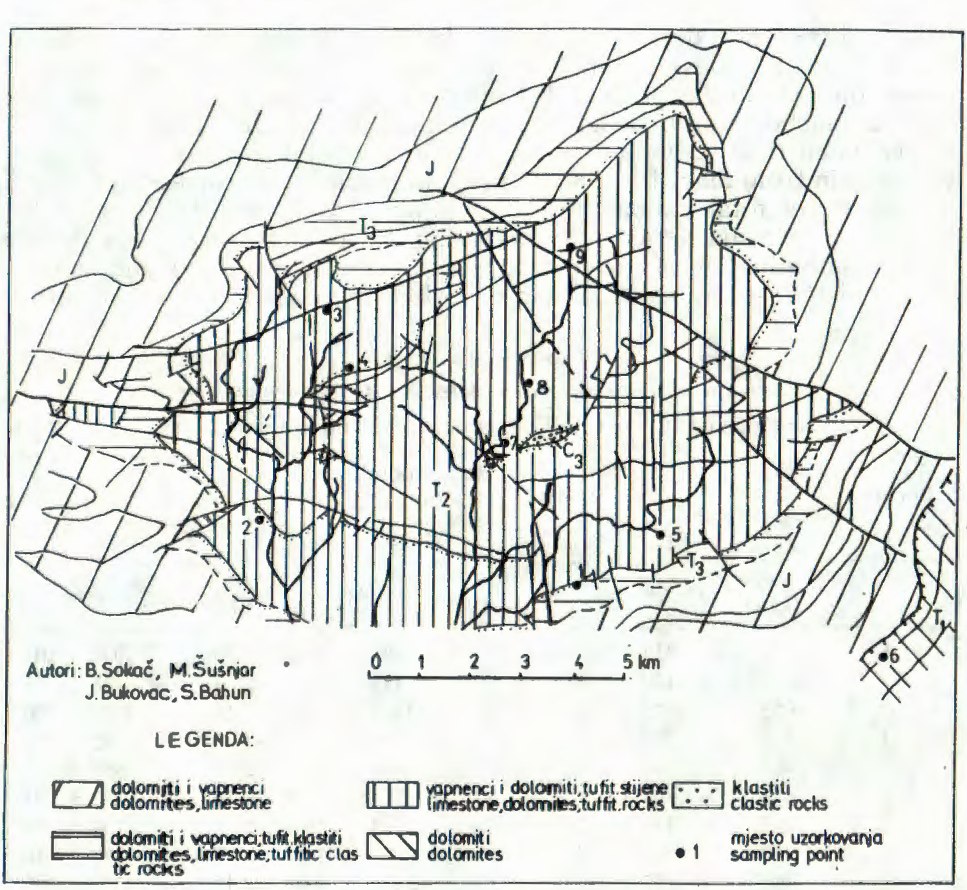
Four species of moss were collected from nine localities (Fig. 1). The species *Platyhypnydium riparioides* was determined in four samples, the species *Cratoneuron commutatum* in two samples, *Cratoneuron filicinum* in two samples, and *Brachythecium sp.* in one sample. Differences in the absorption of elements in various moss species have not been determined yet (S. Pirc, 1984). In moss, soil and stream detritus samples from Novembre 1985 only ^{137}Cs was present (Table 2—4). This radionuclid is remained in natural materials after the earlyer nuclear testings. Only the samples from June 1986 (moss, stream detritus and soil) contain all three radionuclides. The highest measured specific activities were found in moss (Table 2).

Table — Tabela 2.

Specific activity of moss (Bq/kg) dry weight

Specifična aktivnost mahovine (Bq/kg) suhe težine

Location Lokacija	Radionuclides Radionuklidi ^{103}Ru		^{134}Cs		^{137}Cs	
	1985 (LLD)	1986	1985 (LLD)	1986	1985 (LLD)	1986
1	< 5	3144 ± 181	< 6	913 ± 96	< 7	1913 ± 211
2	< 5	1808 ± 118	< 6	707 ± 62	< 6	1433 ± 155
3	< 5	15911 ± 936	< 6	7844 ± 750	< 7	14431 ± 1508
4	< 5	925 ± 86	< 6	735 ± 22	< 7	253 ± 60
5	< 5	2883 ± 167	< 6	398 ± 31	< 5	708 ± 79
6	< 5	4340 ± 241	< 6	709 ± 62	< 7	1681 ± 185
7	< 5	296 ± 26	< 6	66 ± 12	< 8	98 ± 15
8	< 5	770 ± 51	< 6	82 ± 7	< 4	178 ± 26
9	< 5	1033 ± 62	< 6	159 ± 16	< 7	269 ± 25



Slika 1: Shematska geološka karta bruvanjske brahiantiklinale

Fig. 1: Shematic geological sketch of the Bruvno brachy–anticline

It corresponds with data in literature (S. Pirc, 1984, and H. T. Shacklette, 1965). According to them the differences between low and high values of the content of elements in the moss are larger than in stream detritus and they better reflect anomalous regions, or in this case, the contaminated regions. These characteristics of moss are supported by the values of moss sediment concentration factors that, at the some localities, reach value of 12 (Table 5). If we consider the value of the measured radionuclides' radioactivity in samples from 1985 as background, a significant increase in the radioactivity in 1986 is noticable. This conclusion is in concordance with the estimation data on the contamination of the Croatian territory caused by the radioactive rainfalls (S. Lulić et al., 1986).

At the same locality where the samples of moss, stream detritus and soil were taken in the period from Aprill, 28th to May, 20th, 1986 the contaminated ground was defined by rain. The contamination of the ground by rain for the mentioned radionuclides (^{131}I, ^{132}Te, ^{132}I, ^{103}Ru, ^{137}Cs, ^{140}Ba,

^{140}La and ^{134}Cs in a decreasing order) that were released because reactor accident in Chernobyl contains 209000 Bq/m². By this level of contamination only about 9% of the total territory of Croatia was included. The six radionuclides, that caused the contamination of the ground and were evaluated take active part with 92% in the total measured radioactivity of rain from May, 4th 1986. Other radionuclides that take part in the rest of 8% of total radioactivity of rain are, ^{99}Mo, ^{106}Ru, ^{141}Ce, ^{95}Zr, ^{3}H, ^{125}Sb, ^{89}Sr, ^{90}Sr and ^{110m}Ag in a decreasing order. In the mentioned value of the contamination of the ground the contribution of the radionuclides ^{134}Cs and ^{137}Cs contains 11309 Bq/m², while the contributions of other

Table — Tabela 3.

Specific activity of stream detritus (Bq/kg) dry weight

Specifična aktivnost dolinskog detritusa (Bq/kg) suhe težine

Location	Radionuclides Radionuklidi					
	^{103}Ru		^{134}Cs		^{137}Cs	
	1985 (LLD)	1986	1985 (LLD)	1986	1985 (LLD)	1986
1	< 5	836 ± 44	< 6	565 ± 56	< 10	1030 ± 107
2	< 5	150 ± 35	< 6	158 ± 17	< 9	426 ± 47
3	< 5	3175 ± 143	< 6	1344 ± 130	< 14	2773 ± 290
4	< 5	223 ± 26	< 6	100 ± 15	< 8	282 ± 30
5	< 5	509 ± 41	< 6	366 ± 37	< 7	557 ± 60
6	< 5	707 ± 38	< 6	393 ± 40	< 14	752 ± 83
7	< 5	145 ± 12	< 6	83 ± 10	< 6	169 ± 19
8	< 5	196 ± 14	< 6	96 ± 11	< 7	152 ± 19
9	< 5	1877 ± 90	< 6	970 ± 93	< 12	1897 ± 200

Table — Tabela 4.

Specific activity of soil (Bq/kg) dry weight

Specifična aktivnost tla (Bq/kg) suhe težine

Location	Radionuclides Radionuklidi					
	^{103}Ru		^{134}Cs		^{137}Cs	
	1985 (LLD)	1986	1985 (LLD)	1986	1985 (LLD)	1986
1	< 5	31 ± 6	< 6	13 ± 1	< 10	99 ± 11
2	< 5	86 ± 8	< 6	29 ± 3	< 10	212 ± 22
3	< 5	209 ± 12	< 6	48 ± 5	< 8	82 ± 9
4	< 5	115 ± 11	< 6	34 ± 3	< 5	95 ± 10
5	< 5	119 ± 12	< 6	80 ± 8	< 4	153 ± 16
6	< 6	36 ± 5	< 6	7 ± 1	< 6	62 ± 7
7	< 6	33 ± 6	< 6	12 ± 1	< 10	52 ± 6
8	< 5	93 ± 8	< 6	23 ± 3	< 9	68 ± 7
9	< 5	135 ± 12	< 6	50 ± 5	< 10	156 ± 17

Table — Tabela 5.
Moss/stream detritus concentration factor
Koncentracijski faktor mahovina/dolinski detritus

Location	Radionuclides Radionuklidi		
	^{103}Ru	^{134}Cs	^{137}Cs
1	3,76	1,61	1,85
2	12,05	4,47	3,36
3	5,01	5,83	5,20
4	4,15	7,35	0,89
5	5,66	1,08	1,27
6	6,14	1,80	2,23
7	2,04	0,79	0,58
8	3,93	0,85	1,17
9	0,55	0,16	0,15

four radionuclides contains 52000 Bq/m^2 — all calculated on May, 20th 1986. As the statistical evaluation based on a rather small amount of data, there exists a possibility that the values obtained by the investigations do not need to be the maxima for this area.

Radionuclides from the radioactive rain entered into the whole geochemical cycle, so the necessity for a long-term monitoring of their behaviour was imposed. The moss will be used sa an indicator of radioactive pollution variations in this area, based on the presented results.

CONCLUSION

Moss, stream detritus and soil samples were collected from various springs at nine localites in the Bruvno brachy-anticline area during November 1985 and June 1986 (post Chernobyl period) and analyzed for the radionuclides ^{103}Ru, ^{134}Cs and ^{137}Cs by the gammaspectrometric method.

A significant increase in radioactivity was recorded in all the moss, stream detritus and soil collected in June 1986 relative to November 1985 samples. Radionuclides went through a complete geochemical cycle and still remained in higher or lower concentration in all the phases.

This imposed the need for a continuous monitoring of the radionuclides behaviour in order to study changes in specific geochemical media that give direct evidence of ecological alterations. The result of this work indicates that the most favourable indicator for such a monitoring is the specific activity of radionuclides measured on moss samples.

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Distribucija ^{103}Ru, ^{134}Cs i ^{137}Cs u različitim geokemijskim sredinama u okolini Bruvna u 1985. i 1986. godini

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U novembru 1985. godine sakupljeni su uzorci mahovine, dolinskog detritusa i tla s devet izvora u području bruvanjske brahiantiklinale, sa svrhom određivanja distribucije mikroelemenata. Nakon katastrofe u Černobilu zaključili smo da bi bilo korisno na istim mjestima ponoviti uzorkovanje u istim geokemijskim sredinama i analizirati uzorke sakupljene u novembru 1985. i u junu 1986. godine, na radionuklide koji nisu prirodnog postanka već su produkti fisije. Smatrali smo da uzorci iz 1985. godine odražavaju nulto stanje prije černobilske nesreće, dok će uzorci sakupljeni u 1986. godini pokazati intenzitet kontaminacije geokemijskih sredina koje su uzorkovane.

Kao najpogodniji elementi, zbog njihovog relativno dugog vremena poluraspada u odnosu na preostale radionuklide koji su stvoreni fisijom (^{131}J, ^{132}Te, ^{132}J, ^{140}Ba, ^{140}La), uzeti su ^{103}Ru, ^{134}Cs i ^{137}Cs. Specifična aktivnost ovih elemenata određena je gamaspektrometrijskom metodom.

Poznato je da je bruvanjska brahiantiklinala izgrađena od paleozojske jezgre (karbon) koja vrlo malim dijelom izlazi na površinu, oko koje periklinalno slijede mezozojski sedimenti predstavljeni vapnencima i dolomitima, podređeno s klastitima, a u gornjem trijasu i tufitičnim klastitima.

Teren se karakterizira niskim krškim reljefom s malim slivovima. Vode cirkuliraju samo u trijaskim naslagama. Izvori koji ovdje postoje su gravitacijski, kapaciteta 1—10 l/s. Tlo je vrlo oskudno razvijeno, uglavnom na zaravnjenim predjelima i u dolinama potoka. Pretežno je to zemlja crvenica, a podređeno smeđe nediferencirano tlo. Razvijen je samo tanki humusni sloj i isto tako vrlo tanak sloj izluživanja.

Rezultati i diskusija

U uzorcima mahovina, tla i dolinskog detritusa iz 1985. godine prisutan je samo radionuklid ^{137}Cs koji potječe od prijašnjih nuklearnih pokusa. Uočljivo je da samo uzorci iz 1986, mahovina, sedimenta i tla sadrže sva tri radionuklida. Najveće izmjerene specifične aktivnosti su određene u mahovinama što se slaže s literaturnim podacima o većem kontrastu koji daju mahovine u odnosu na dolinski detritus (S. Pirc, 1984). Ovu osobinu mahovina potkrepljuju i vrijednosti koncentracijskih faktora za odnos mahovine/dolinski detritus koji na pojedinim lokalitetima dostižu vrijednost i do 12. Ukoliko vrijednost izmjerene radioaktivnosti radionuklida u uzorcima iz 1985. godine uzmemo kao fon (pozadinu), uočavamo znatan porast radioaktivnosti u 1986. godini. Ovaj zaključak je u suglasnosti s rezultatima procjene kontaminacije područja SR Hrvatske putem radioaktivnih oborina (Lulić i sur., 1986). Željeli bismo istaći da prema statističkoj procjeni izrađenoj na osnovi ovog relativno malog broja podataka postoji mogućnost da vrijednosti koje su utvrđene izvedenim istraživanjima ne moraju biti i maksimalne za ovo područje. Radionuklidi iz radioaktivnih kiša ušli su u cijeli geokemijsk cklus i stoga se nameće potreba da se njihovo dalje ponašanje prati u dužem vremenskom periodu. Kao indikator kretanja (opadanja) radioaktivnog zagađenja na ovom području, a na osnovi iznesenih rezultata, poslužit će mahovina.