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STUDY OF RADIOACTIVE CONTAMINATION OF THE BIOSPHERE WITH A PARTICULAR EMPHASIS ON INFLUENCE OF DIETARY COMPOSITION UPON THE RADIOACTIVE MATERIAL INTAKE INTO ORGANISM

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Presented is the course of increases and decreases of the biospheric radioactive contamination following the nuclear explosions in the period from 1960 to 1966. Investigated was the effect of dietary composition upon the intake of Sr–90 in the organism. Presented is research conducted in two directions: 1) to study the factors affecting the environmental contamination, and 2) to develop more effective methods of experimental work.

I. BIOSPHERIC RADIOACTIVITY

Nuclear weapons experiments have produced widely differing radioactive fallout, resulting in the radioactive contamination of the entire atmosphere.

The biospheric contamination by the radioactive fission products caused the whole human race to become even more exposed to ionizing radiation. Sufficiently concentrated, so produced radionuclides can be hazardous for humans and animals as external sources, or internal ones if brought into the organism.

Because from the chemical standpoint there is no difference in the behavior of individual fission products as related to the identical inert material in the entire ecological cycle, it is important to determine, in all cycle phases, the hazards which might be caused by them.

First measurements in this country were initiated in 1960, on the territory of the Socialist Republic of Croatia. First, measurements were made of the total beta radioactivity in the air and in the precipitation (1, 2). Later on, the measurements were widened as to determine the total beta radioactivity in drinking and surface waters, and also to determine Sr-90 in radioactive precipitation, farm produce, human and animal bones, and in the sea and soils. Monitoring of Cs-137 started in 1964 (3–8).

Table 1 shows yearly averages of the total beta radioactivity in the air, as measured from 1962 through 1967.

Table 1

Yearly averages of the total beta radioactivity in the air

	pCi/m³					
	1962	1963	1964	1965	1966	1967
Zagreb	4.8	5.7	1.1	0.21	0.11	0.08
Zadar	—	—	—	0.26	0.13	0.08
Sljeme	4.8	6.1	—	—	—	—

Table 2 shows the total beta radioactivity of radioactive precipitation in selected localities.

Table 3 shows the total radioactivity of surface waters.

Table 3

The total radioactivity of surface waters

River	pCi/l					
	1962	1963	1964	1965	1966	1967
Sava	49	52	18	9	7	5
Kupa	37	40	13	6	5	3
Odra	34	47	—	—	—	—
Korana	32	34	—	—	—	—
Drava	—	—	17	9	6	5

The amount of Sr-90 in radioactive precipitation is shown in Table 4.

Table 4

The amount of Sr-90 in radioactive precipitation

Locality	^{90}Sr mCi/km²					
	1962	1963	1964	1965	1966	1967
Zagreb	15.5	28.5	20.3	8.59	3.37	1.7
Osijek	—	27.1*	19.2	7.28	2.82	1.3
Zadar	—	17.2*	21.8	7.85	5.41	1.9

* 9 months only

Table 2

Total beta radioactivity of radioactive precipitation in selected localities

	1962		1963		1964		1965		1966		1967	
	mCi/km²	mm of precipitation	mCi/km²	mm	mCi/km²	mm	mCi/km²	mm	mCi/km²	mm	mCi/km²	mm
Zagreb	1029	1154.3	625	954.9	339	1002.5	82.1	1105.9	32.6	1055.3	11.4	798.5
Osijek			906	674.7	157	680.5	51.9	771.6	19.5	640.9	11.6	616.8
Zadar			910	839.4	242	1000.8	56.0	744.4	42.2	1332.7	32.0	916.7
Pula					132	742.0	68.2	1010.2	26.6	1059.2	11.2	777.2
Bjelovar					74.9	816.9	57.2	1063.7	31.0	1019.1	13.4	826.3

As can be seen from the results of our measurements, the contamination level in all kinds of samples had been increasing till the end of 1963 when a slight decrease began, followed in 1965 by a fast decrease. This is obvious because from 1964 to 1967 there have been only a few Chinese nuclear explosions (9), which had only temporarily contributed to an upswing of radioactivity but did not influence the overall trend. Regarding such a situation it is of interest to take a look at the changes in the Sr-90 quantities in staple foodstuffs.

Table 5 shows the changes of Sr-90 amounts in wheat.

Table 5

Changes of Sr-90 amounts in wheat

Locality	^{90}Sr pCi/g Ca				
	1963	1964	1965	1966	1967
Zagreb	500	3175	675	258	121
Osijek	1246	6573	297	139	59
Zadar	516	2104	314	245	95

Changes of Sr-90 amounts in milk can be seen in Table 6.

Table 6

Changes of Sr-90 amounts in milk

Locality	^{90}Sr pCi/g Ca						
	1961	1962	1963	1964	1965	1966	1967
Zagreb	9.8	15.0	30.7	33.6	28.8	21.6	16.6
Osijek*	7.6	6.3	13.2	15.5	14.1	8.4	6.7
Zadar	—	6.4	21.9	23.3	23.9	8.1	6.0

* Dehydrated milk

A similar situation developed concerning cattle feed. Table 7 shows changes of Sr-90 amounts in alfalfa for the first and second mowings.

Other produce also demonstrate the virtually same tendency in their changes of the Sr-90 amount, in the period from 1962 to 1967.

By a comparison with the data in the Table 4, it is possible to say with certainty that surface contamination was predominant till 1964, and that Sr-90 has been infiltrating plants through their roots since then.

Table 7

Changes of Sr–90 amounts in alfalfa for the first and second movings

Locality		^{90}Sr pCi/g Ca					
		1962	1963	1964	1965	1966	1967
Zagreb	I	300	109	113	75	90	41
	II	46	—	137	73	40	30
Osijek	I	95	169	116	214	62	56
	II	41	—	156	166	46	45
Zadar	I	—	123	60	69	71	34
	II	—	59	67	81	42	32
Average		53	115	108	113	59	40

This can be best noticed in Diagram 1 presenting the changes of the Sr-90 amounts in milk and in atmospheric precipitation over the Zagreb milkshed.

As is visible in the diagram, the Sr-90 quantity in milk was a true reflection of the Sr–90 quantity in the radioactive fallout until 1964 when the relationship is no longer discernible, or is not so obvious (10, 11). That the relationship had really been obvious is evidenced also by the fact that types of cattle feed and the size of the milkshed are changed from year to year, which significantly influences (negatively) the relationship.

The Sr-90 amounts in the radioactive fallout were from 1963 to 1964 smaller by a factor of 1.4 (in the Zagreb area), from 1964 to 1965 by a factor of 2.4, from 1965 to 1966 by a factor od 2.5, from 1966 to 1967 by a factor of 2.

Concerning milk, this decrease is quite less evident because the quantity of Sr–90 in 1963, dropped from 30.7 pCi/g Ca to only 16.6 in 1967, which is less than a half, while at the same time Sr-90 quantity in radioactive precipitation decreased more than 16 fold.

The concentration of Sr-90 in soil has grown higher in virtually all sampled localities. The results of measurement are shown in Table 8.

The results somewhat differ, the reason being in a very small number of samples taken which were, moreover, not always possible to take from the same spot twice.

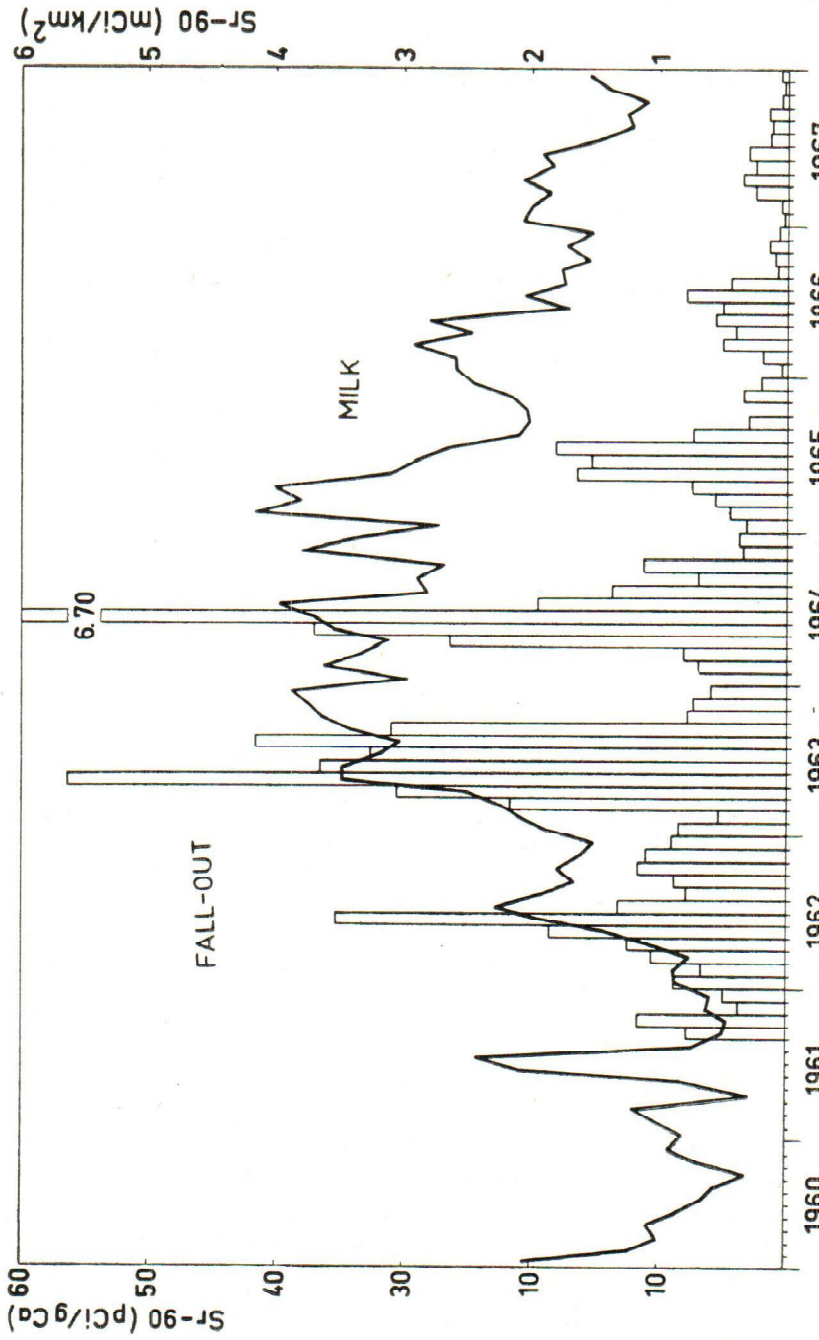

Diagram 1. *Changes of the Sr–90 amounts in milk and in atmospheric precipitation over the Zagreb milkshed*

Table 8

The results of measurement of the concentration of Sr-90 in soil

Locality	^{90}Sr pCi/g Ca				
	1963	1964	1965	1966	1967
Božjakovina	21	10	28	38	47
Osijek	17	11	18	13	22
Zadar	24	22	35	21	51
Pula	—	30	42	39	8
Delnice	—	62	101	118	32

All these results show that the radioactive contamination of the biosphere in Croatia can be compared with those in countries at the same geographic latitude, and having a nearly equal amount of atmospheric precipitation (12).

II. INFLUENCE OF DIETARY COMPOSITION ON Sr–90 INTAKE INTO THE ORGANISM

Contamination of human organism by means of fission products is done mainly through the intake of contaminated food and water. In order to ascertain the magnitude of the contamination created in this manner, it is necessary to know both, the amount of food and water taken into the organism, and concentrations of fission products contained either in individual foodstuffs and water, or in the whole amount of food taken daily or within any longer period.

In studying the influence of dietary composition on the intake of Sr-90 into the organism, two factors should be taken into account: (1) the amount of Sr-90 in each kind of foodstuff, and (2) the amount of the chemically similar calcium which by its total amount essentialy affects the metabolism of Sr-90 (13).

Considering the daily or yearly amounts of calcium taken in food into the organism, all countries might fall into 4 groups:

1st group – 800 mg Ca daily;	70–80% Ca from dairy products
2nd group – 600–700 mg Ca/day;	60–80% Ca from dairy products
3rd group – 300–450 mg Ca/day;	30–65% Ca from dairy products
4th group – 200–350 mg Ca/day;	grain is the main source of Ca.

Therefore, Yugoslavia would rank between the 2nd and 3rd groups, while in the amount of the dairy product derived calcium it would be closer to the 3rd group.

Table 9 shows the consumption per capita of foodstuffs in Yugoslavia, and the percentages of calcium and calories as well.

Table 9

Consumption per capita of foodstuffs in Yugoslavia

	Yearly kgs	Ca %	Calories %
Grain	182.1	17.99	59.6
Vegetables	131.2	16.47	8.6
Dairy products	79.9	58.97	6.6
Fruit	52.1	3.60	2.9
Meat	28.3	1.21	7.3
Eggs	3.1	0.76	6.4
Total	476.7	100.00	85.4

* Data from the Statistic Yearbook of SFRJ (1963)

Seen in the table is that nearly 60% of calories are received from grain, while at the same time it is the source of only 20% of calcium. Milk and dairy products supply approximately 60% of Ca but only 6.6% of calories.

Knowing that grain is one of the major carriers of Sr-90, it is clear that having the same level of biospheric contamination, more Sr-90 enters the organism in a country where grain consumption is higher.

On the other hand this means that even a small increase of Sr-90 concentration in grain can cause a significantly larger intake of Sr-90 into the organism, this in a very unfavorable ratio regarding calcium.

Therefore the ratio Sr-90/Ca changed from 1962 to 1964 very unfavorably just because the greatest part of Sr-90 arrived from grain. The ratio in 1962 was 57.6; in 1963 it was 76.9; and in 1964 it was 120.3. On the average, each person took into his organism 35 pCi of Sr-90 in 1962; 47 in 1964; 73 pCi in 1964. In following years this amount has been decreasing.

To make it more graphic, it is interesting to note that in New York City the ratio Sr-90/Ca was 28 in 1964.

The majority of Yugoslav population drink either tap water or spring water. But in certain parts of the country people drink cistern water. This being rainwater, e.i. soft water containing no calcium – and as it is known that rain is the main carrier of Sr-90 – the picture becomes considerably changed.

Moreover, taking into account (a supposition, for lack of exact information) that this segment of population consumes larger amount of grain, and lesser of dairy products, all the same drinking cistern water, makes quite a difference in the daily intake of Sr-90 and also to a large degree modifies the Sr-90/Ca ratio.

The daily intake of Sr-90 among these people amounted to 79 pCi in 1963; the Sr-90/Ca ratio being 189.4. In 1964, the daily Sr-90 intake climbed to 108 pCi, the Sr-90/Ca ratio to 254. Waterborne Sr-90 amounts to about 48% of the intake in 1963, or 36% in 1964. This means that water has become a major carrier of organism contamination.

Data for later years are not presented because the picture repeats itself. Namely, the amounts of Sr–90 in single foodstuffs were smaller in those years, so the daily intake has considerably decreased.

III RESEARCH ACTIVITY

Initial measurements and observations of the biospheric radioactivity brought along numerous problems, such as a scarcity of information needed for a wider evaluation of obtained results, and the inadequacy of the methods used. It has guided our laboratory work in two directions: a) in the direction of investigating the factors which were essential for a better understanding of the problems; and, b) in the direction of looking for, and introducing, more efective methods of experimental work.

a) *Study of essential factors*

The first phase of laboratory work over (1960–1962), research was started into the effects of various factors on fluctuations of the natural activity levels (15). Studied were daily fluctuations of beta activity, the influence of weather and geographic conditions upon the level fluctuations. It was observed that levels of total beta radioactivity, under identical conditions (same air flow speed, same type of filter paper, same volume of sampled air during a calendar year), varied within a given order of magnitude. Examined were the effects of air flow, its volume, and of the duration of pumping, as related to the levels recording.

In further efforts to determine the total contamination by fall-out, the Sr-90 measurements were continued, with efforts to determine the amounts of Cs-137 (16). In the 1965–1967 period, Chinese nuclear explosions (9) were tracked in precipitation and also in samples of alfalfa which is the best indicator for fast detection of new fission products in plants. Moreover, in precipitation we have investigated the contamination with cosmogenuous radionuclides, therefore Be-7 was measured for three years (17). Unlike data obtained for Sr-90 and Cs-137, which conformed with the world average, the amount of Be-7

was in this country somewhat higher than the world average (6.0×10^3 at/ml) (18), but in certain months agreed with findings in northern Italy (19), from which it can be deduced that there is a similarity of atmospheric conditions in this part of the continent.

Concerning the Cs-137 amount in foodstuffs, evident was the same decrease tendency as was with Sr-90 (6–8). A logical continuation in investigating the paths of fission products was our study of the amounts of soluble and insoluble Sr-90 in soils on the territory of the SR Croatia. It was found that the ratio soluble/insoluble was 1:2.5 to 1:1 (20), this being an essential information in evaluating the amounts of food contamination by Sr-90.These results are important because systematic examinations of fission product absorption in soils had not been done before then. It was also discovered that from the total amount of Cs-137, permanently fixed were 38–88% (21). These findings are within the limits of results obtained in the temperate climatic zone.

Study of marine organism contamination by fission products has not been undertaken in this country, although a good part of the population cat fish, but the concentration of Sr-90 in the Adriatic Sea was monitored. The work began (6) only in 1964, so the maximum is missing, but by comparing results with those received from Italy we were still able to reach a relatively precise evaluation of the Sr-90 amounts. Indeed, it was found that there existed a non-uniformity of sampling on the other coast of the Adriatic (22).

As the sea is recommended as the ultimate medium for an infinite disposal of hazardous radioactive materials (23), it is necessary to study the biologic cycle of radionuclides in sea (24) on account of the dangers involved in this solution (25). Therefore in our research we undertook to investigate how much adsorption of radionuclides Sr-90, Cs-137, Ce-144, Mn-54, Zn-65, and Sb-125 there is in the typical silty and sandy beds of the Adriatic Sea. Concurrently we are investigating the measure of desorption of sedimented radionuclides out of the sea bed in the presence of higher concentrations of hydrogen ions (26).

b) *Application of radiochemical and nuclear methods in determining traces of elements interesting from the viewpoint of biospheric contamination by radioactive materials*

In a number of biospheric radioactivity monitoring centers in this country, the total beta radioactivity of free waters is measured by the method of evaporizing a larger amount of water and then counting the ignited residue. This method being slow and inaccurate (27), we developed three new methods for determining the total beta radioactivity of water. For fast recording of larger radionuclide concentrations – we use the GM counter for liquids (28), this method being simple and fast. For measuring low levels of total radioactivity, developed were two methods. One is to evaporate a larger amount of water containing a certain amount of added complexing agents, then the residue is meas-

ured with a flow counter having a large area window (29). The other method consists of filtering a water sample throught a thin layer of an ion exchange resin which effectively retains present radionuclides (about 95%, and more). This layer of resin with the captured radionuclides can be counted with a normal flow counter (30). This method proved to be the most suitable for its simplicity and reliability, and is now in laboratory use for monitoring beta radioactivity of natural waters.

In monitoring the total beta radioactivity in natural waters, the amount of present K-40 must be ascertained, because when the radioactivity level of the sample is low, K-40 can represent the major part of the total beta radioactivity. Potassium is found out by flame spectrometry as a referential method, though as a fast field method we developed a gravimetric method of precipitation with sodiumtetraphenylborate (31).

Measurement of calcium in materials which so widely differ in their composition, as plant matter and soil, sometimes runs into difficulty. Therefore we developed a method of complexometric determination of Ca by means of a fluorexonemurexide mixture. The method is fully satisfactory for determination of Ca in seawater, soil, and in plant ashes (32).

While developing the methods examined were some reagents suitable for separation of individual fission products from the total sample mass.

Thus, parameters were found which affect the precipitation of stable cesium and potassium by means of sodiumtriphenylcyanoborate. The method was verified by the addition of tracer Cs-137 (33).

As sodiumtriphenylcyanoborate proved to be a selective reagent for cesium, it was used for separation of Cs-137 from biospheric samples.

Considering that there have been, as of now, little published material relating to radiochemical determination of Cs-137 in soil, we have separated the Cs-137 with sodiumtriphenylcyanoborate (34). This compound also proved useful in the separation of Cs-137 from seawater (35). An advantage of the method is in the possibility of determining the chemical yield what was impossible to achieve with ammonium phosphomolibdate determination of Cs-137 (35).

From plant material we precipitated Cs-137 with sodiumtriphenylcyanoborate when spectra stripping would not give acceptable results because of the presence of too many fission products (35).

Another reagent which had proved suitable for the radiochemical separations, is ammonium cinnamate. In efforts to determine the cosmic Be-7 in fall-out, ammonium cinnamate appeared to be an effective precipitant for Be-7 from the mass of fission products. Cs-137 from the same sample was separated throught precipitation by sodiumtriphenylcyanoborate (16).

Besides using organic reagents, we worked according to some already known methods modified because of our specific circumstances. So in investigating our soils we modified the *Vido* method (19), both, the extraction of the soluble Sr-90 with ammonium acetate, and the extraction with hydrochloric acid in measuring the total Sr-90 (36).

In developing the chemical methods we did not neglect physical methods, such as spectra stripping in determining gamma emitters. By this method we measured Ra-226, Ra-228, Zr-95, and Cs-137 in soils.

Continuing our research of the radionuclide biological cycle in the sea, we should find out the concentration of inactive isotopes of those radionuclides which are highly concentrated (25) in marine organisms. In the current research phase we are developing a method for determining traces of manganese, cobalt, and zinc in marine organisms by means of a substoichiometric radioisotope dilution (37).

Though outside of our strict laboratory problems, but because of a hazard of contamination of the human organism and biosphere, we developed a method for determining traces of thorium and uranium in human bones, blood, urine, and faeces (38).

Sensibility of the method is, in the case of thorium, better than in classic analytical methods, while in the case of uranium, it is equal to the otherwise most sensitive fluorescence method. The procedure itself of determining thorium by the activation analysis in biological matter is simpler than in all heretofore published processes. The method was developed in order to enable us to monitor the level of human contamination with the listed radiotoxic elements (39).

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