Population Exposure to Depleted Uranium in the Han Pijesak Region

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***Abstract*—In September 1995 the Han Pijesak area of Republic of Srpska was heavily attacked by Depleted Uranium (DU) ammunition. In this area, from 2003 to 2004, during one year, the components of natural ionizing radiation sources like radon, thoron, and gamma radiation were measured. In addition, during the same period, the samples of soil, moss, and lichen were collected in order to identify the content of technologically enhanced natural radionuclides in them and particularly their isotopic ratios, which determine radioactive contamination by depleted uranium. The paper presents techniques, methods, and results of the research carried out in Han Pijesak area on identification and quantification of depleted uranium being found in the environmental samples over the Han Pijesak region.**

***Index Terms*—Ammunition, contamination, depleted uranium, Han Pijesak, radionuclides, radon, thoron.**

I. Introduction

ENDOGENOUS and environmental pollutants (ionizing radiation, stable chemical elements, oxides of nitrogen, ozone, organic solvents, pesticides etc.) cause oxidative stress. The oxidative stress is the cause of many diseases and aging. The pollutants initiate the formation of free radicals, which even in small quantities endanger the health because of their high reactivity and possible damage of DNA, RNA, enzymes, and membrane lipid components. Ionizing radiation of various origin and properties is a fundamental characteristic of the environment. Man-made radioactivity occurs as a result of operation of nuclear power plants, or use of nuclear energy for military purposes, and lately from the use of ammunition and missiles with DU and transuranic elements. The wars in Iraq 1991 and 2003, in Kuwait, Bosnia and Herzegovina (bombing of Hažici, Lukavica, and Han Pijesak) 1995, Serbia (Kosovo and Metohija and south Serbia) 1999, and Afghanistan 2002, represent a series of dramatic events which have started the extensive investigation of the influence DU on environment and human health [1, 2].

Han Pijesak is a region of Republic of Srpska with population of about 5.500 inhabitants where in 1995 twelve military and civilian buildings were bombed with DU projectiles [3]. In total, more than 10.800 bullets were fired at different locations throughout Republic of Srpska (mainly in the area of Sarajevo), which corresponds to about 3.3 tonnes of scattered DU. Of these, Han Pijesak received 2.400 bullets which corresponds to about 730 kg of DU. The soil in this area is mainly limestone. In 2003, a one year research was carried out to study the ionizing radiation background level in the area, measuring radon, thoron activity concentration, and gamma radiation. The research was conducted by members of Electrochemical laboratory for developing nuclear track detectors (ECE Lab), Institute for nuclear sciences „Vinča“ [4]. Research included soil, moss, and lichen sampling. The analysis of the samples from Han Pijesak was conducted by two methods, gamma and alpha spectrometry, which had been developed in the ECE Lab in collaboration with the Institute of Nuclear Physics, PAN, Krakow, Poland [5,6]. The goal was to determine the content of natural and man-made radionuclides in the environment and to determine the level of DU contamination on the basis of their isotopic relations.

II. Method and Experimental Work

In order to identify the presence of DU in the samples in concentrations below 1 pg/g of material, or in a small sample a few grams, we used a very accurate radiochemical sample preparation and very sensitive analytical techniques. The research presented in this paper employed two methods the alpha and the gamma spectrometry. The samples analyzed are different types of moss, lichen and soil collected in April and November of 2000, eight years after the bombing of Han

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Pijesak with DU ammunition. From total number of collected samples following 25 were analyzed (Table I): 8 samples of soil, 6 samples of the lichen and moss, a sample of tree resign, and 4 mixed samples (bark with lichen, moss and soil and two samples of moss and lichen). Gamma and alpha spectrometry measurements were done at the Institute PAN in Krakow. For gamma spectrometric measurements all the samples of moss, lichen and soil were dried over night or longer at 105 ºC, homogenized, and inserted into the Marinelli vessels, on top of HPGe detectors protected with layers made of 10 cm Pb, 2 mm Cd and 18 mm Cu, associated with Silen gamma spectrometer (4096 channel). Spectrometer was calibrated at 662 keV (^{137}Cs), 911 keV (^{228}Ac) and 1461 keV (^{40}K) [7]. Efficiency calibration at 1001 keV (^{234m}Pa, which we assume to be in equilibrium with ^{238}U) was achieved by interpolation of the efficiency for the above enumerate radionuclides. The systematic error was well below of 10%.

Despite the complicated and long radiochemical sample preparation, alpha spectrometry technique is necessary for reliable measurements of DU activity concentration because this method reaches significantly lower limit of detection and directly determines the isotopic activity ratio ^{234}U/^{238}U.

Radiochemical preparation of samples for alpha spectrometry measurements [5] requires burning to ash at 600 ºC to remove the organic compounds. One gram of ash was placed in PTFE vessels in which acid mixture (9 ml of concentrated HNO_3, 3 ml of concentrated HCl, 3 ml concentrated HF) was added, independently into each vessel. Samples were then mineralized by heating to 200 ºC in microwave digester. After mineralization, each vessel was rinsed with 12 ml of 7M HNO_3. In the next step all the solutions used for individual samples were joined in 250 ml PTFE vessels and vaporized. Evaporation was repeated after adding of 30 ml concentrate HNO_3. This was followed by adding of 50 ml of concentrate HCl and heating, as well as 2 g H_3BO_3 in order to remove traces of fluoride [6].

As mentioned previously, for reliable identification of the presence of DU contamination we used alpha spectrometric analysis which was particularly useful for samples of low mass and very low intensity gamma lines (0.38%).

In these cases only the upper limit of uranium activities was established. For alpha spectrometry, it is necessary to make appropriate radiochemical separation and to measure ^{238}U, ^{235}U and ^{234}U activities as well as activity ratios ^{235}U/^{238}U, and

TABLE I
RESULTS OF GAMMA SPECTROMETRY MEASUREMENTS OF ENVIRONMENTAL SAMPLES COLLECTED IN HAN PIJESAK

Number and sample code	Sample weight [g]	Sample type and description of sampling	Activity concentration ^{137}Cs [Bq/kg]	Activity concentration ^{228}Ac [Bq/kg]	Activity concentration ^{40}K [Bq/kg]	Activity concentration ^{238}U [Bq/kg]
1/HP 1	193.5	Soil, house 1	47.9 ± 1.3	43.4 ± 1.8	328 ± 14	< 26
2/ HP 3	1.8	Lichen, house 2	68 ± 10	< 24	61 ± 100	< 1216
3/ HP 4	3.4	Lichen, house 2	88 ± 10	< 24	255 ± 94	< 1917
4/ HP 5	34.3	Bark with lichen, house 2	5.4 ± 1.2	2.6 ± 3.5	37 ± 20	< 99
5/ HP 5a	23	Tree resin, house 2	8.9 ± 0.8	2.4 ± 1.9	< 7.2	158 ± 87
6/ HP 6	9.7	Moss, house 2	76 ± 6	27 ± 13	200 ± 70	1190 ± 570
7/ HP 7	5.9	Moss, barracks	< 5	< 14	560 ± 160	< 926
8/ HP 8	14.4	Lichen, barracks	30.9 ± 2.7	29 ± 7	370 ± 390	< 476
9/ HP 8a	109.9	Moss and land, barracks	143 ± 4	29 ± 34	332 ± 20	< 116
10/HP 9	67.2	Moss, barrack, barracks	41 ± 1.6	16 ± 3	174 ± 17	1150 ± 130
11/ HP 10	110.7	Moss, barrack, barracks	38.8 ± 1.2	12.3 ± 1.3	151 ± 9	< 47
12/ HP 11	141.2	Soil, concrete, bullet hole, barrack	17.3 ± 1	9.9 ± 1.9	165 ± 13	5540 ± 170
13/ HP 16	45.6	Moss with lichen, barrack	209 ± 3	13 ± 3	87 ± 15	210 ± 80
14 / HP 17	70.2	Soil, barrack, barracks inside	38.7 ± 1.5	2.0 ± 1.7	46 ± 9	< 154
15/ HP 18	32.9	Soil, barrack, barracks inside	675 ± 8	11.2 ± 3.5	140 ± 20	2550 ± 210
16/ HP 20	3.3	Lichen with moss, house 3	27 ± 5	12 ± 15	236 ± 61	< 1301
17/ HP 21	14.6	Lichen, house 3	26 ± 3	< 6	81 ± 26	< 777
18/HP 22	14.4	Moss, house 3	128 ± 5	18 ± 10	347 ± 49	< 204
19/HP 23	106.5	Arable soil, garden house 3	98 ± 2	46 ± 3	446 ± 19	< 88
20/HP 24	81.1	Arable soil, garden house 4	113 ± 2	30 ± 3	495 ± 20	< 51
21/HP 26	18	Lichen, barrack, forest	152 ± 4		137 ± 20	< 215
22/HP 27	81.5	Moss, house 5	499 ± 14	33 ± 3	294 ± 19	< 137
23/HP 29	215.7	Soil, house 5	6.0 ± 0.6	45 ± 3	548 ± 27	133 ± 51
24/HP 30	13	Lichen, garden house 4	19 ± 3	11 ± 6	245 ± 38	< 660
25/HP 31	109.2	Arable soil, house 6	75 ± 2	61 ± 3	102 ± 9	< 65

$^{234}U/^{238}U$. If the ratio of isotope activities $^{234}U/^{238}U$ is below of 0.3, it clearly indicates the presence of DU in the sample.

III. Results

From a total of 25 samples analyzed, in five samples coming from the military barracks in Han Pijesak, (HP 9 – moss, HP 10 – moss, HP 11 – land, HP 16 – moss and lichens and HP 18 – land) the presence of DU was found. In papers [8-10] the lower value of isotope activity ratios was approximately 0.20, while in this paper, the lowest value was 0.117 + 0.001, determined in soil from the hole from the bullet that pierced a concrete barrack. To determine the homogeneity of the uranium distribution in the samples, we performed additional radiochemical separation and alpha spectrometry measurements of samples with high weight (HP 8, HP 10, HP 11 and HP 18), which resulted in 19 additional sub-samples, which were further analyzed.

It was found that only the sample HP 8 contained natural uranium while all others showed the presence of DU (Table I). Since the ratio between the highest and lowest measured ^{238}U activity was less than 2 (HP 11 and HP 18) and significantly lower for the HP 10, as was also observed in HP 8, which contained natural uranium, it was concluded that the distribution of uranium in the samples was uniform. The highest mean ^{238}U activity measured in the samples from Han Pijesak was 5630 ± 890 Bq/kg (sample 12/HP 11, Table II). Sansone et al. [11] reported the results of approximately 230.000 Bq/kg, which is two orders of magnitude greater value. Similar results on the presence of DU in samples of lichen and moss have been published in other publications [11-14]. This finding supports the knowledge of lichens and mosses as excellent indicators of DU contamination of the air.

IV. Conclusion

From the total of 25 analyzed samples (moss, lichen, soil, agricultural soil, and mixed samples) the presence of DU was

TABLE II
THE ^{238}U, ^{235}U AND ^{234}U ACTIVITY CONCENTRATION AND ACTIVITY RATIO $^{235}U/^{238}U$ GAINED BY ALPHA SPECTROMETRIC MEASUREMENTS

Number and sample code	Activity ^{238}U ($Bq \cdot kg^{-1}$)	Activity ^{235}U ($Bq \cdot kg^{-1}$)	Activity ^{234}U ($Bq \cdot kg^{-1}$)	Activity ratio ($^{235}U/^{238}U$)	Activity ratio ($^{234}U/^{238}U$)
1/HP 1	23.8 ± 3.1	< 0.33	26.8 ± 3.6	< 0.014	1.12 ± 0.11
2/HP 3	4.4 ± 0.5	0.86 ± 0.16	5.1 ± 0.6	0.20 ± 0.03	1.17 ± 0.10
3/HP 4	1.6 ± 0.3	0.29 ± 0.22	1.5 ± 0.3	0.19 ± 0.14	0.93 ± 0.22
4/HP 5	-	-	-	-	-
5/HP 5a	-	-	-	-	-
6/HP 6	2.4 ± 0.3	< 0.31	2.8 ± 0.3	< 0.13	1.14 ± 0.12
7/HP 7	5.8 ± 0.8	0.61 ± 0.40	5.4 ± 0.8	0.11 ± 0.07	0.92 ± 0.12
8/HP 8	27.0 ± 5.1	1.16 ± 0.84	26.9 ± 3.1	0.05 ± 0.04	1.01 ± 0.13
9/HP 8a	43.9 ± 6.6	2.2 ± 2.1	41.9 ± 6.4	0.05 ± 0.05	0.95 ± 0.09
10/HP 9	**590 ± 72**	**7.9 ± 1.7**	**83 ± 10**	**0.013 ± 0.002**	**0.140 ± 0.004**
11/HP 10	**234 ± 33**	**3.7 ± 1.5**	**50.9 ± 9.0**	**0.013 ± 0.005**	**0.22 ± 0.03**
12/HP 11	**5600 ± 900**	**66 ± 22**	**660 ± 110**	**0.013 ± 0.002**	**0.117 ± 0.001**
13/HP 16	**99 ± 11**	**1.47 ± 0.91**	**25.6 ± 3.0**	**0.015 ± 0.009**	**0.26 ± 0.01**
14/HP 17	1.6 ± 0.2	0.07 ± 0.04	1.4 ± 0.2	0.05 ± 0.03	0.89 ± 0.05
15/HP 18	**1500 ± 360**	**21.7 ± 7.9**	**189 ± 39**	**0.016 ± 0.004**	**0.13 ± 0.01**
16/HP 20	1.0 ± 0.3	0.51 ± 0.34	1.8 ± 0.4	0.53 ± 0.38	1.91 ± 0.67
17/HP 21	0.5 ± 0.1	< 0.10	0.4 ± 0.1	< 0.20	0.78 ± 0.20
18/HP 22	4.6 ± 0.7	0.57 ± 0.33	5.1 ± 0.7	0.13 ± 0.07	1.13 ± 0.14
19/HP 23	20.3 ± 3.8	< 2.50	34.6 ± 5.5	< 0.12	1.70 ± 0.26
20/HP 24	35.7 ± 4.2	1.35 ± 1.16	37.1 ± 4.3	0.04 ± 0.03	1.04 ± 0.06
21/HP 26	2.8 ± 0.4	< 0.28	2.8 ± 0.4	< 0.10	0.98 ± 0.12
22/HP 27	18.3 ± 2.7	< 0.59	15.2 ± 2.3	< 0.03	0.83 ± 0.09
23/HP 29	31.2 ± 4.0	< 0.92	30.5 ± 3.9	< 0.03	0.98 ± 0.09
24/HP 30	4.9 ± 0.7	< 0.27	4.9 ± 0.7	< 0.14	1.00 ± 0.14
25/HP 31	44.5 ± 7.0	< 1.53	58.3 ± 8.9	< 0.03	1.31 ± 0.13

Note: The results highlighted in bold print indicate the presence of DU in samples. Samples 4/HP 5and 5/HP 5a had very low masses, and it was not possible to prepare samples for alpha spectrometric measurements so the results were omitted.

identified in 5 samples collected near military barracks: HP 9, HP 10, HP 11, HP 16 and HP 18. In the samples of lichen and mosses collected in independent yards in Han Pijesak villages near the barracks (in houses 1, 3, 4, 5 and 6), no traces DU was found and this fact indicates that radioactive aerosols produced by the bombing did not contaminate the area.

Based on the results of this study and other work [11-14], the conclusion that biological samples of lichen and moss are good accumulators of radioactivity and therefore good bio-monitors of the presence of DU in the environment, is confirmed.

The detection of DU in samples from the environment by alpha spectrometric method is, compared to gamma spectrometric method, proved to be more accurate and reliable, as well as necessary because it provides significantly lower detection threshold and directly determines the activity ratio $^{234}U/^{238}U$.

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