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# Investigation of potentially contaminated areas in the Federation of Bosnia and Herzegovina with depleted uranium

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**Abstract:** During the war in Bosnia, depleted uranium was used on several - locations in Bosnia and Herzegovina, including the area of Hadzici. Estimated amount of used ammunition is close to three tons. Only a fraction of depleted uranium penetrator, detected in the surface ground layer was removed. A certain number of ground, moss and subterranean water samples have been collected in december 2013, for the purpose of evaluation of two decade long contamination from depleted uranium ammo usage. The colected samples were subjected to radiochemical separation and alpha-spectrometric analysis. The results of the examination showed that the uranium was present in the amount of 0.6 to 1.8 μg/kg in the ground samples, 0.2 to 7.0 μg/kg in the moss samples and 0.36 to 1.04 μg/L in the subterranean water. The activity ratio of $^{234}U/^{238}U$ in three moss samples, as well as one ground sample, showed the presence of depleted uranium. Analyzed water samples indicated a natural relation of uranium isotopes. Tests shows that the presence of depleted uranium deserves detailed examination of radioactivity, radioecology assessment and evaluation of population exposure.

## INTRODUCTION

During the last war in Bosnia, depleted uranium was used on several locations in Bosnia and Herzegovina, including the area of Hadzici. Estimated amount of used ammunition is close to three tons. The largest proportion of ammunition, whole penetrator or fragment, is buried deeper in the ground, where, depending on the chemical and other corrosive conditions, migrates into the environment and is a potential source of groundwater contamination. Only a fraction of depleted uranium penetrator, detected in the surface ground layer was removed. According to this, a certain number of surface soil, moss and groundwater samples were collected in December 2013. The purpose of that was to evaluate the contamination of this specific area, two decades following the use of depleted uranium ammo. Groundwater and surface water contamination has been identified as a major issue of concern for long-term testing. The size and chemical characteristics of the particles, as well as the local geochemical and hydrogeological characteristics exert a decisive influence on the migration of uranium. Also, the different chemical forms of radionuclides, present in the soil are available for plants and its absorption. Considering that, the tests are performed twenty years after the use of depleted uranium in the area tested, contamination of plants could be carried through radionuclide transfer from soil to plants via the root system. Bettencourt et al., (1988), have found that various factors, such as soil characteristics, climate, plants and their parts, the physical and chemical form of radionuclides and the effect of competing organism (organism that compete with plants for food) may affect the value of transfer factors.

The aim of this research is to determine uranium isotopes content in the collected samples of the ground,

moss and water, as well as to investigate the total alpha and beta activities of the selected samples. The collected samples were subjected to separation and alpha radiochemical analysis. Tests show that the presence of depleted uranium deserves detailed examination of radioactivity, radioecology assessment and evaluation of population exposure.

## EXPERIMENTAL

Ground samples were collected from nine different locations, water samples from three, and moss samples from five locations. The samples of the ground and moss were cleaned from mechanical impurities (stones, solid soil particles from moss) and then dried at room temperature, after which they were brought to the state of constant mass by application of the intermittent dry-heat procedure. Tracer ($^{232}$U) and mixture of acids (Aqua regia), were added to a specific amount of each sample, and together dried out. The dry residue was dissolved in concentrated HCl. The soultions were released through the ion exchange resin (Dowex 1x8), Cl-form, 100-200. Thorium was removed by releasing 8 mol/L HCl through ion exchange column, after which uranium was eluated by 25 mL 0.5 mol/L HCl. The samples were prepared for measurement by microprecipitacion with $NdF_3$, according to the HASL-300 procedure (EML, 28th Ed. 1997). The Nd-carrier, $TiCl_3$ as uranium reducer and concentrated HF was added to the solution containing uranium. Following that, the samples were kept in ice and then filtered through a membrane 0.22 μm filter paper. Filter paper was fixed to the planchete and then dried by UV lamp for fifteen minutes. The measurement was performed by alphaspectrometer (Alpha Analyst Canberra) equipped with silicium detectors (PIPS) with 450 mm$^2$ of active surface area. The measurement time was 172800 seconds and chemical yield was 20-98%. The lower limit of detection was 0.18–0.25 mBq/L for $^{238}$U, 0.12–0.17 mBq/L for $^{235}$U, & 0.20–0.28 mBq/L for $^{234}$U.

The collected water samples were taken to laboratory without acidification, were then filtered through 0.45 μm filter paper, and dry residue determined (105°C). Approximatelly 2 L of water were taken for the analysis from each sample. A uranium tracer $^{232}$U, approximately 15 mBq, was added to measured aliquotes of water samples in order to calculate chemical yield. Uranium was coprecipicated with $Ca_3(PO_4)_2$, according to the Eichrom procedure (Eichrom Technologies Inc. Ver 1.7.2011). After centrifuge, deposit $Ca_3(PO_4)_2$ was dissolved in 5 mL 8 mol/L HCl.

The further procedure with regard to water samples is identical to that of ground and moss as described above.

An isotope analysis of uranium was performed in the examined samples, as well as a total alpha-beta activity for moss and ground samples. The data of the analyzed samples of moss, ground and water are presented in the following tables and diagrams.

**Table 1**. Moss samples impulse responses measured by Alpha-spectrometry

| Moss samples | N ($^{238}$U) Imp | N ($^{235}$U) Imp | N ($^{234}$U) Imp | N ($^{232}$U) Imp |
|---|---|---|---|---|
| *1* | 441 | 39 | 183 | 495 |
| *2* | 534 | 16 | 386 | 546 |
| *3* | 100 | 12 | 106 | 286 |
| *4* | 1682 | 40 | 339 | 286 |
| *5* | 4350 | 71 | 671 | 328 |

The table clearly shows, based on the value of pulses for the $^{235}$U, that the analyzed samples of moss contain depleted uranium. Similar results were obtained for the analyzed samples of soil and water.

**Table 2**. Results of uranium radioisotopes activity obtained through Alpha-spectrometric analysis of moss samples

| Moss samples | A($^{238}$U) (Bq/kg) | A($^{234}$U) (Bq/kg) | Mass(U) (mg/kg) | Activity ratio $^{234}$U/$^{238}$U | Chemical yield |
|---|---|---|---|---|---|
| *1* | 5.17 | 2.03 | 0.4 | 0.39 | 77% |
| *2* | 8.51 | 6.02 | 0.7 | 0.71 | 73% |
| *3* | 2.74 | 2.71 | 0.2 | 0.99 | 39% |
| *4* | 45.31 | 8.84 | 3.6 | 0.19 | 34% |
| *5* | 86.57 | 13.13 | 7.0 | 0.15 | 36% |

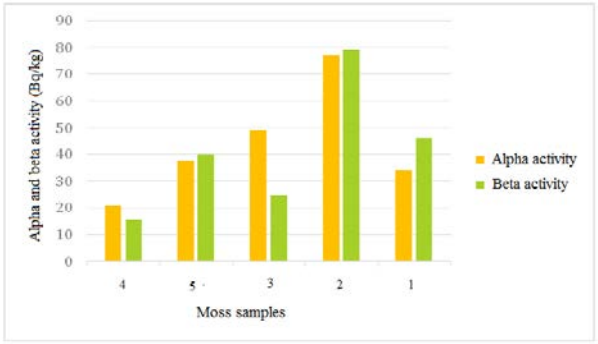


**Diagram 1.** Gross alpha and beta activity of analyzed moss samples

Determination of gross alpha and beta activity of the analyzed samples was performed in order to verify the presence of radioactive elements in analyzed samples. Results indicated the presence of alpha and beta emitters in moss and ground analyzed samples (Diagrams 1&2).

**Table 3**. Results of uranium radioisotopes activity obtained through Alpha-spectrometric analysis of ground samples

| Ground samples | A($^{238}$U) (Bq/kg) | A($^{234}$U) (Bq/kg) | Mass(U) (mg/kg) | Activity ratio $^{234}$U/$^{238}$U | Chemical yield |
|---|---|---|---|---|---|
| *1* | 18.1 | 17.3 | 1.5 | 0.95 | 30% |
| *2* | 11.3 | 11.4 | 0.9 | 1.01 | 56% |
| *3* | 7.7 | 8.3 | 0.6 | 1.07 | 37% |
| *4* | 19.6 | 20.7 | 1.6 | 1.06 | 21% |
| *5* | 13.4 | 15.8 | 1.1 | 0.69 | 20% |
| *6* | 22.3 | 18.8 | 1.8 | 1.10 | 27% |
| *7* | 16.1 | 11.1 | 1.3 | 1.17 | 25% |

The pulses value for two analyzed samples of the ground is at the lower limit of detection, so for them there was no need to count the active concentration of uranium isotopes.

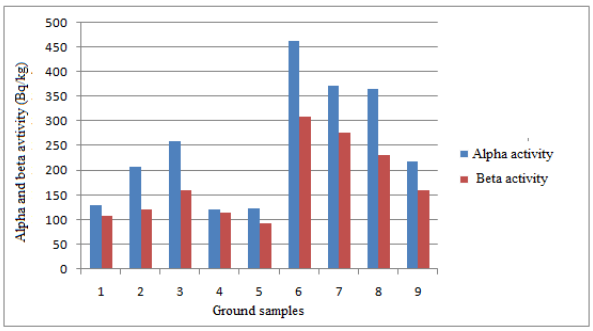


**Diagram 2.** Gross alpha and beta activity of analyzed ground samples

**Table 4.** Results of uranium radioisotopes activity obtained through Alpha spectrometric analysis of water samples

| Water samples | A($^{238}$U) (Bq/L) | A($^{234}$U) (Bq/L) | Mass(U) (μg/L) | Activity ratio $^{234}$U/$^{238}$U | Chemical yield |
|---|---|---|---|---|---|
| *1* | 0.0045 | 0.0049 | 0.36 | 1.09 | 72% |
| *2* | 0.0129 | 0.0175 | 1.04 | 1.35 | 94% |
| *3* | 0.0112 | 0.0160 | 0.90 | 1.43 | 98% |

The results of analysis show that the uranium content in the ground samples range from 0.6 to 1.8 mg/kg, in the moss samples from 0.2 to 7.0 mg/kg, and in the water samples, from 0.36 to 1.04 μg/L.

The analysed samples of water show presence of the natural ratio of uranium isotopes. Radioactivity of the examined water samples is relativelly low. The results for the investigated waters are considerably lower than World Health Organisation (WHO) drinking water guideline limit value of 30 μg/L for total uranium (WHO, 2011). The data obtained through analysis of the water samples are close to the date obtained in years 2003 (UNEP, 2003), (Jia G, et.al., 2006) and (Vidic A. et al., 2013). The same can be said for most of the surface ground samples, as well as for two of the moss samples. However, since uranium concentration can increase significantly within relativelly short period of time in case of contamination of water, a monitoring of uranium concentration in underground waters is necessary.

The ratio of $^{234}$U/$^{238}$U activity in four samles of moss, as well as in one sample of ground, show presence of depleted uranium. Similar results were obtained through analysis of vegetation and ground (several samples) performed by UNEP (UNEP, 2003). The obtained data shows that the contamination by depleted uranium in the surface layer has been present 20 years after the use of depleted uranium in this area.

## CONCLUSIONS

Radioactivity of water samples is relativelly low. Concentration of activity of uranium isotopes is low and ranges from 0.36 to 1.04 μg/L of uranium mass concentration.

The ratio of $^{234}$U/$^{238}$U activity in four samles of moss, as well as in one sample of ground, show presence of depleted uranium, which indicates the need of detailed survey (of greater number of samples of ground, water and vegetation), in order to obtain more accurate data on contamination of the examined area.

The analysis shows that the presence of depleted uranium points to the need to conduct a detailed analysis of radioactivity, radio-environmental evaluation, and evaluation of exposure of the population.

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## Summary/Sažetak

Tokom rata u BiH, osiromašeni uran je upotrebljen na nekoliko lokacija u BiH, uključujući područje Hadžića. Procjenjena količina upotrebljene municije iznosi približno 3 tone. Samo dio penetratora od osiromašenog urana, detektovan u površinskom sloju tla, je uklonjen. U decembru 2013. godine je prikupljen određen broj uzoraka tla, mahovina i podzemnih voda, u cilju procjene kontaminacije dvije decenije nakon upotrebe municije od osiromašenog urana. Prikupljeni uzorci su podvrgnuti radiohemijskoj separaciji i alfa spektrometrijskoj analizi. Rezultati ispitivanja pokazuju da sadržaj urana u uzorcima tla iznosi od 0.6 do 1.8 mg/kg, u uzorcima mahovina od 0.2 do 7.0 mg/kg, i uzorcima vode od 0.36 do 1.04 µg/L. Odnos aktivnosti $^{234}U/^{238}U$ u tri uzorka mahovina, kao i jednom uzorku tla ukazuje na prisustvo osiromašenog urana. Analizirani uzorci vode pokazuju prirodan odnos uranovih izotopa. Ispitivanja pokazuju da prisustvo osiromašenog urana zavređuje detaljno ispitivanje radioaktivnosti, radioekološku procjenu i procjenu izloženosti stanovništva.