

## URANIUM CONTENT FROM BOMB CRATERS

N. MILJEVIC<sup>a\*</sup>, M. MARKOVIC<sup>a</sup>, D. TODOROVIC<sup>a</sup>, M. CVIJOVIC<sup>b</sup>,  
D. GOLOBOCANIN<sup>a</sup>, M. ORLIC<sup>a</sup>, D. VESELINIVIC<sup>c</sup>

<sup>a</sup> *Vinca Institute of Nuclear Sciences, POB 522, 11 001 Belgrade, Yugoslavia*  
*E-mail: emiljevi@rt270.vin.bg.ac.yu*

<sup>b</sup> *The Copper Mill Sevojno, The Main Laboratory and Quality Control, 31 205*  
*Sevojno, Yugoslavia*

<sup>c</sup> *Faculty of Physical Chemistry, University of Belgrade, POB 137, 11 001*  
*Belgrade, Yugoslavia*

**Abstract.** Depleted uranium (DU) is a by-product of uranium enrichment process and its use is very dangerous and harmful. We measured uranium concentration in the surface soil (0-5 cm depth) from bomb craters caused by cruise missiles in which DU might have been used as counterweights during NATO attack. Total uranium concentration and isotopic ratio were determined using  $\gamma$ -spectrometry and inductively coupled plasma method. Obtained results were in the range 1.7 - 22 mg/kg dry soil that were comparable to the uranium values found in off-side locations of Serbian soils.

**Keywords:** depleted uranium (DU), soil,  $\gamma$ -spectrometry, inductively coupled plasma.

### AIMS AND BACKGROUND

NATO has used depleted uranium (DU) ammunition in Yugoslav conflict during its air campaign against the tanks and bunkers. Details about quantity, nature of weapons fired and locations of hit targets are military sensitive information. Some sources suggest that about 3000-10 000 of 30 mm DU rounds as armor-piercing shells fired from cannons fitted to A-10 aircraft<sup>1</sup> and probably a usage in some of 1500 launched Tomahawk Cruise missiles<sup>2</sup>. According to weight of rounds (roughly 300 g) and content in cruise missile (20 kg), estimated quantity of DU used could achieve 9-11 t. This ammunition has been previously used in the Gulf War<sup>3</sup> (940 000 DU aircraft rounds and 14 000 tank rounds) and in Bosnia<sup>4</sup>.

This paper is an attempt to determine uranium content in soil samples collected where a possibility exists of uranium introduction into the environment through detonation or by forceful impact. In order to obtain trustworthy results, we have compared the method of  $\gamma$ -spectrometry with inductively coupled plasma (ICP) regarding their specificity and sensitivity.

---

\* For correspondence.

## EXPERIMENTAL

### SOURCE AND PROPERTIES OF DEPLETED URANIUM

*Usage of depleted uranium.* DU is a by-product of uranium enrichments process that is largely depleted of the other two isotopes ( $^{234}\text{U}$  and  $^{235}\text{U}$ ) formed in naturally occurring uranium. Due to the gaseous diffusion process that is usually used by the American uranium enrichment companies, the US Department of Energy has in possession of about 734 000 metric tons stockpile of DU hexafluoride<sup>5</sup> with production rate of about 1900 metric t/year. Its high density ( $19.05\text{ g/cm}^3$ ) and low cost make it an effective material for military munitions and for civil purposes as aircraft counterweights<sup>6</sup>, shielding in some medical equipment, and ballast where volume constraints prohibit the use of less dense metals. DU is also placed into the tips of the BGM-109 Tomahawk land-attack cruise missiles (TLAM) during test flights to provide weight and stability<sup>7</sup>. Caliber of DU penetrators in the US arsenal is in the range between 20 and 120 mm (Ref. 8).

The Nuclear Regulatory Commission defines DU as uranium in which the content of the  $^{235}\text{U}$  isotope is less than 0.72%, while the military specifications designate that DU used by the Department of Defense (DoD) contains less than 0.3% of  $^{235}\text{U}$ . In fact, DoD uses only DU (Ref. 9) that contains approximately 0.2% of  $^{235}\text{U}$ .

*Properties of depleted uranium.* DU is both radioactive and toxic. Its total activity is 22% less and  $\alpha$ -activity 43% compared to the natural mixture of uranium isotopes. The specific activity of DU with daughter products is 39.42 MBq/kg while its  $\alpha$ -activity is 14.4 MBq/kg. It emits relatively strong  $\beta$ -radiation ( $E_{\text{max}}=2.29\text{ MeV}$  from  $^{234\text{m}}\text{Pa}$ ) and extremely low gamma emission (0.048 MeV) that yields from most of the six decay products.

When a DU bullet impacts on a hard object (armor or rock), it is crushed into fragments, burned (18-70%) and oxidized into dust. Thus, uranium oxides ( $\text{U}_3\text{O}_8$ ,  $\text{UO}_2$  and  $\text{UO}_3$ ) have been formed. The latter oxide is only one soluble in water, forming uranyl ( $\text{UO}_2$ )<sup>2+</sup> ions. The occurring oxide aerosol has 50-96% of respirable size particles (diameter less than  $10\ \mu\text{m}$ ) with air concentrations 5-780  $\text{mg/m}^3$  ( $\alpha$ -activity of 0.07-11.1  $\text{kBq/m}^3$ ), and 17-48% of these particles are soluble in water. The other particles became attached to soil particles by melting of the soils and formed a silicate glass. If the penetrators hit on soft ground (sand or clay), they will continue to penetrate into the soil (more than 50 cm in the depth of ground) remaining there for long time. Studies of DU penetrator weathering<sup>10</sup> has shown that they principally corrode into hydrated U(VI) oxides that are very soluble in water. The greatest danger to human health presents inhalation of insoluble DU dust and inhalation or ingestion of soluble one.

Investigations of DU fate and transport associated with dynamic weapons testing operations in both semi-arid (Los Alamos National Laboratory site, New

Mexico, 510 mm annual rainfall) and humid (Eglin Air Force Base, Florida, 1650 mm annual rainfall) environments<sup>11</sup> could help for making a strategy to obtain representative samples. Results for total uranium from 750 contaminant measurements<sup>12</sup> of atmospheric fall-out, soil, sediment, water and suspended sediments collected in the time period 1983-1990 in respect to background concentrations<sup>13</sup> have shown that about 90% of it remained in the proximity of the firing sites and 10% entered the watershed. Investigations were confined to one watershed called Potrillo Canyon, small size (5 km<sup>2</sup>), limited to public access. A conservative estimate of the total uranium source is about 35 t. These results could be the guideline in detection of uranium around the impact points.

1. Concentrations in soils and sediments decrease with increasing distance from the firing sites.

2. The greatest concentrations are in transported suspended sediments carried in runoff waters, followed by sediment present in stream banks.

3. Concentration in runoff in the dissolved and suspended sediment phases declines with downstream direction in the watershed.

4. Uranium moves vertically into the soil profile in regions close to the firing site with the largest concentrations in the upper 5 cm of soil, about 30 times higher than at 5-10 cm depth.

5. Uranium readily leached into the dissolved phase, often in a matter of a few hours, which is the time frame of most rainfall events.

6. Uranium concentration increases with decreasing particle size and it has a particular affinity for the fine silts and clays.

*Uranium natural background concentrations.* The natural background level for uranium in soils and sediments for particular sites are not available and can be quite variable. Geological settings of Serbia<sup>14</sup> include igneous rocks as granodiorite, crystalline shales and Neogene volcanics with uranium content up to 4.4 mg/kg. The scattering of ore refuses from uranium mine Kalna-Gabrovica had enriched its content (7.7-28.1 mg/kg) in the barren soil deposit with an average concentration of 17 mg/kg (from 32 samples)<sup>15</sup>. As the result of widespread phosphate fertilizer ( $P_{fert}$ ) utilization with very significant uranium concentration (30-300 mg/kg), the uranium concentration in Serbian soils<sup>16</sup> is in the range between 0.08 and 5.9 mg/kg.

#### EXPERIMENTAL

*Sampling.* Soil samples were collected from bomb craters in June based on information that they were caused by Cruise missiles in April and May, 1999 during bombardment of Yugoslavia. Selected locations were Belgrade, Smederevo, Nis, Bor, Prahovo, Kadinjaca, Jadovnik, Raska, and Sjenica. In addition, in the distance at least of 2 km away of those, on the unaffected sites sampling for uranium background concentration was performed. Soil sampling consists of randomly taken

shallow scoops of surface soil (0-5 cm depth, order of 1m<sup>2</sup>). After removing stones or cleaning the surface vegetation from the site, the sample has been wrapped in plastic bags and brought to the laboratory.

*Uranium analysis.* We used the outstanding advantage of  $\gamma$ -spectrometry to measure gamma emitters directly in soil samples<sup>17</sup>. After air-drying and mixing the sample aliquot was removed for analysis. Each sample was weighed and stored in a sealed polyethylene container (50 g) or Marinelli beaker (500 g capacity) for a 40-day ingrowth period. The analyses were carried out using Canberra HP Ge coaxial detectors (models GC1318-7500 and GC2018-7500) having a relative efficiency of 14.7% and 23%, energy resolution of 1.7 keV and 1.8 keV, respectively of the 1332 keV line from <sup>60</sup>Co. The background count rate was of 0.560 cps in the 20-2900 keV energy interval. Concentrations of <sup>238</sup>U and <sup>235</sup>U were determined via the photopeaks emitted by their daughters of <sup>234</sup>Th (63 keV) and <sup>235</sup>U (185 keV) decays, respectively. The range for the total relative errors for activity measurements was between 26 and 85%. The counting time for each sample was 86.000 s while background was measured for a longer period of time. The efficiency for sample counting configuration was determined with standard soil samples (Standard Reference Material 694, National Bureau of Standards) containing a known mixture of nine radionuclides.

In addition, as an alternative available method of the ICP/OES technique (ARL model 3580) was employed. A representative sample of soil was air-dried, grounded in the mill to be homogenized. A portion of sieved (3 mm) sample is weighted out (10 g) and placed in a high temperature furnace (550°C) during overnight to remove organics. It is then treated with concentrated HNO<sub>3</sub> / HCl in a platinum crucible followed by dilution and filtration<sup>18</sup>. The digestion of residue has been repeated 2-3 times until it becomes gray-white colour in order to yield the sample solutions. Measurements were made with standard addition of uranyl nitrate. Standard solutions were prepared and used to derive calibration curve. Standard reference materials were used to validate the analytical procedure. Decomposition and analysis were duplicated for each sample. The range for the relative standard deviation was 3-7%.

## RESULTS AND DISCUSSION

The primary objective of this survey was to locate DU used. There were almost no data on the levels of uranium in the environment around the analysed locations and undisturbed soil can be taken as background measurements.

A preliminary judgment of possible deposited uranium on the ground could be made on the basis that during one attack from A-10 aircraft 50-100 rounds are fired<sup>19</sup> and one of five bullets contains DU. Usually, three attack planes work together against a target and the amount of DU in the area hit (20×50=1000 m<sup>2</sup>)

might be 9-18 kg. If 10 kg of DU is spread, taking into consideration soil depth of 5 mm and specific gravity of 1.5 g/cm<sup>3</sup>, the uranium concentration of the soil would be estimated to be 1300 mg/kg. A similar evaluation could be performed for the cruise missile which contains DU. The dominant mechanism for uranium redistribution is the surface water pathway and due to high rainfall intensity happened in June (even 30-40 l/m<sup>2</sup> per day<sup>20</sup>), the resulting concentration might be low, much less than assumed. Although the estimation is very rough and it is only for the very place of action, it is suggested that the excess uranium in the surface soils would have a rather low enrichment. Therefore, it is very important which analytical method has been employed for quantitative analysis.

The results of measurements of our field investigation are summarized in Table 1 along with the description of soil origin. The individual isotopic uranium activity (<sup>238</sup>U) as well as the <sup>235</sup>U/<sup>238</sup>U isotopic ratio are presented. The concentrations in the surface soil (0-5 cm in depth) range from 1.7 to 14 mg <sup>238</sup>U/kg dry soil and up to 22 mg/kg of total uranium. The obtained isotope ratio from 0.0071 to 0.0075 corresponds to natural uranium abundance (0.00725) at the most locations. In contrast, high values between 0.0161 and 0.0085 were recorded for soil samples from bomb craters in Jadovnik, Raska, and Sjenica. It is worth mentioning that a relatively high ratio of 0.0105 was found in undisturbed soil on Jadovnik where we expected the control value. These markedly higher ratios could be rather explained by high counting errors (45-85%) than by the excess of non-natural uranium. The presence of only natural radionuclides <sup>226</sup>Ra, <sup>232</sup>Th, <sup>40</sup>K was identified at all locations under investigation.

**Table 1.** Uranium concentrations and its isotopic ratio in investigated soils in Serbia

Location	Concentration <sup>238</sup> U		Isotopic ratio <sup>235</sup> U/ <sup>238</sup> U	Description
	(Bq/kg)	(mg/kg)		
Belgrade	68 ± 18	5.5 ± 1.4	0.0074	bomb crater
Smederevo	32 ± 9	2.6 ± 0.7	0.0074	
	21 ± 6	1.7 ± 0.5	0.0073	
	86 ± 23	7.0 ± 1.9	0.0073	
	57 ± 15	4.6 ± 1.2	0.0071	
			background	
Bor	51 ± 14	4.1 ± 1.1	0.0073	bomb crater
Nis	61 ± 16	4.9 ± 1.3	0.0073	
Prahovo	53 ± 14	4.3 ± 1.1	0.0074	
	37 ± 10	3.0 ± 0.8	0.0075	
	55 ± 15	4.5 ± 1.2	0.0071	
			background	
Kadinjaca	53 ± 18	6.5 ± 2.2	0.0074	bomb crater
	41 ± 16	5.8 ± 2.2	0.0075	background
Jadovnik	22 ± 19	2.8 ± 2.4	0.0161	bomb crater
	30 ± 16	7.1 ± 3.7	0.0105	background
Raska	45 ± 21	14 ± 6	0.0143	bomb crater
Sjenica	60 ± 22	10 ± 4	0.0085	bomb crater

For comparison, Table 2 lists the total uranium concentration obtained by  $\gamma$ -spectrometry (measured  $^{238}\text{U}$  concentration data combined with the  $^{235}\text{U}/^{238}\text{U}$  ratio assuming that  $^{234}\text{U}$  and  $^{236}\text{U}$  have negligible concentration) and the results performed by ICP method. A good agreement for data for undisturbed locations on Kadinjaca and Jadovnik is evident. The reason for the significant difference between two corresponding samples taken at other locations is probably because of interference<sup>21</sup> from Si, Ca, Fe, and Al.

**Table 2.** Results of total uranium concentration by  $\gamma$ -spectrometry and inductively coupled plasma

Location	Total U concentration (mg/kg)	
	$\gamma$ -spectroscopy	ICP
Kadinjaca	$6.5 \pm 2.2$	$21.6 \pm 1.1$
	$5.8 \pm 2.2$	$5.0 \pm 0.4$
Jadovnik	$2.8 \pm 2.4$	$11.1 \pm 0.4$
	$7.2 \pm 3.7$	$10.7 \pm 0.6$

To confirm these results it would be necessary to carry out more advanced method with higher analytical precision like thermal ionization mass spectrometry<sup>22</sup> using isotope dilution spike. It is reasonable to suppose that the isotopic analysis can uniquely distinguish contamination by uranium from indigenous uranium present at background level.

## CONCLUSIONS

The presence of DU is difficult to detect directly in the environment unless its concentration is significantly above background. The wide range of uranium concentrations in the soils (2-22 mg/kg) at studied locations is due to the different type of soil, soil formation and soil transport process (geological origin). The values from bomb craters were comparable to those for undisturbed soils and data observed for Serbian soils indicating that there was not any evidence of the presence of DU at the locations analysed within measurement error limits.

## REFERENCES

1. J. J. RICHARSON: Depleted Uranium. Mother Jones, 23/6/99.
2. R. COGHILL: The Use of DU Bullets and Bombs by NATO Forces in Yugoslavia. Coghill Research Laboratories, <http://www.cogreslab.demon.co.uk> (April 1999).
3. Health and Environmental Consequences of Depleted Uranium Use in the US Army. US Army Environmental Policy Institute (AEPI), 1995.
4. D. RISTIC, R. BENDERAC, Z. VEJNOVIC, M. ORLIC, S. PAVLOVIC: NATO Ammunition Produced from DU Used in Bosnian War. Vinca Institute of Nuclear Sciences Bulletin, 4, 205 (1997) (in Serbian).
5. Final Programmatic Environmental Impact Statement for Alternative Strategies for the Long-

- term Management and Use of Depleted Uranium Hexafluoride. DOE/EIS-0269, Department of Energy, 1999.
6. P. LOEWENSTEIN: Industrial Uses of DU. Vol. I. American Society for Metals, 1989.
  7. G. BUKOWSKI, D.A. LOPEZ, F.M. MCGEHEE: III. Uranium Batterfields Home and Abroad: DU Use by the US Department of Defense. Rural Alliance for Military Accountability, Progressive Alliance for Community Empowerment, Citizen Alert, 1993.
  8. V. ZAJIC: Review of Radioactivity, Military Use and Health Effects of DU. SUC Report, July 1999, <http://members.tripod.com/vzajic>.
  9. Health and Environmental Consequences of Depleted Uranium Use in the US Army. US Army Environmental Policy Institute (AEPI), 1995.
  10. J. C. ELDER, M. C. TINKLE: Oxidation of DU Penetrators and Aerosol Dispersal at High Temperatures. LA-8610-MS, Los Alamos National Laboratory, 1980.
  11. N. M. BACKER, E. B. VARTA: Hydrological Transport of DU Associated with Open Air Dynamic Range Testing at Los Alamos Natural Laboratory, New Mexico and Eglin Air Force Base, Florida. LA-UR-95-1213, LANL, 1995.
  12. N. BECKER, J. IRVINE: Contaminant Signature at Los Alamos Firing Sites. LA-UR-95-670, LANL, 1996.
  13. N. M. BECKER: Influence of Hydraulic and Geomorphologic Components of a Semi-arid Watershed on Depleted Uranium Transport. Ph.D Thesis, 1991.
  14. R. JELENKOVIC: Uranium Mineralization in the Sumadija Metallogenic District (Serbia, Yugoslavia): Genetic and Morphostructural Types. Republic Fund for Geological Investigation, Belgrade, 1991.
  15. M. STOJANOVIC, M. SARIC, M. BABIC, D. ILES: Uranium Concentration in Pwood Plants Growing in the Vicinity of Closed down Uranium Mine in Kalna. In: Proceedings I Regional Symposium: Chemistry and the Environment, Vrnjacka Banja, September 25-29, 1995, 1007-1010.
  16. R. KLJAJIC, V. SIPKA, M. RADENKOVIC, R. MITROVIC: Coal and Fertilizers as a Source of Technologically Enchanted Natural Radioactivity. In: Ionization Radiation from Nature. JDZZ, Vinca Institute of Nuclear Sciences, 1995, 95-111 (in Serbian).
  17. A. S. MOLLAH, M. M. RAHMAN, S. R. HUSAIN: Distribution of  $\gamma$ -emitting Radionuclides in Soils at the Atomic Energy Research Establishment, Savar, Bangladesh. Health Phys., **50**, 835 (1986).
  18. Standard Test Method for Analysis of Total and Isotopic Uranium and Total Thorium in Soils by Inductively Coupled Plasma-Mass Spectrometry. Annual Book of ASTM Standards, vol. 12.01, 1999, 804-815.
  19. The Potential Effects on Human Health and the Environment Arising from Possible Use of Depleted Uranium during the 1999 Kosovo Conflict: A Preliminary Assessment. UNEP/UNCHS Balkans Task Force, October 1999.
  21. Hydrometeorological Institute of Serbia (personal communication).
  21. I. CAMIS, J. H. SHINN: Analysis of Beryllium and Depleted Uranium: An Overview of Detection Methods in Aerosols and Soils. LLNL, US Department of Energy, UCID-21400, 1988.
  22. A. M. VOLPE, J. A. OLIVARES, M. T. MURRELL: Determination of Radium Isotope and Abundances in Geologic Samples by Thermal Ionization Mass Spectrometry. Anal. Chem., **63**, 913 (1991).

*Received 24 November 2000*

*Revised 20 July 2001*