



Uranium content in the soil of the Federal Republic of Yugoslavia after NATO intervention

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Depleted uranium (DU) is a by-product of the uranium enrichment process. NATO has used DU ammunition in the Yugoslav conflict, in air strikes of tanks and bunkers. An estimated number of about 3,000-10,000 of 30 mm DU rounds of armor-piercing shells were fired from cannons fitted to A-10 aircraft and probably used in some of the 1,500 launched Tomahawk Cruise missiles. We measured the uranium content in the surface soil (0-5 cm depth) from bomb craters after NATO strikes. The selected locations were Belgrade, Smederevo, Niš, Bor, Prahovo, Kadinjača, Jadovnik, Raška, Sjenica, and Cape Arza. The total uranium concentration and isotopic ratio were determined using γ -spectrometry and the inductively coupled plasma method. The obtained values ranged from 21 to 762.000 Bq/kg of dry soil. At all locations, except Cape Arza, these values were comparable with the uranium content of soils measured at off-site locations.

KEY WORDS: Uranium; Spectrometry, Gamma; Soil Pollutants, Radioactive; Radiation, Monitoring, Yugoslavia; War; Nuclear Warfare

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INTRODUCTION

NATO has used depleted uranium (DU) ammunition in Yugoslavia in its air strikes against tanks and bunkers. Details about the quantity, nature of weapons fired and locations of hit targets, being militarily sensitive information, have not been fully disclosed. Some sources suggest that about 3,000-10,000 of 30 mm DU rounds were fired as armor-piercing shells from cannons fitted to A-10 aircraft (1). DU may have also been used in some of the 1,500 Tomahawk Cruise missiles launched (2). As based on the weight of the round (roughly 300 g) and the DU content in the cruise missile (20 kg), the estimated total mass of the deployed DU could amount to 9-11 tons (3). This type of ammunition has previously been used in the Gulf War (4) (940,000 DU aircraft rounds and 14,000 tank rounds) and in Bosnia (5).

The aim of this paper was to determine the uranium content in soil samples collected at locations where DU could have been be introduced into the environment through detonation or by impact. In order to obtain more reliable results, we have compared the

specificity and sensitivity of the γ -spectrometry and the inductively coupled plasma (ICP) methods.

SOURCE AND PROPERTIES OF DEPLETED URANIUM

DU application

DU has civilian and military applications. The typical civilian application is in the area of radiation protection as a shield because of its high density (19.07 g/cm³) and high atomic number (Z=92). A novel application is in isotope separation facilities for ²³⁵U re-extraction. DU is also used as a counterweight and ballast in aircraft and yachts, and as a catalyzer in chemical processes. The most important future application of DU could be in fast breeder reactors, for converting ²³⁸U into ²³⁹Pu as the demand for more nuclear fuel arises.

The military applications of DU are in ammunition and as an element of guided missiles. The main task of DU ammunition, which comes in different calibers, is to penetrate tank armour and concrete shelters. The important part of such ammunition is the so-called penetrator, made of DU doped with molybdenum and titanium, of high hardness.

DU is a by-product of the uranium enrichment process in which the abundance of two isotopes (²³⁴U and ²³⁵U), found in natural uranium, is enhanced. Due to the gaseous diffusion process which is most frequently used by the American uranium enrich-

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ment companies, the US Department of Energy is currently in possession of a stockpile of about 734,000 metric tons of DU hexafluoride (6), with a production rate of about 1,900 metric tons/y. Its high density (19.05 g/cm³) and low cost make it readily available for military munitions and for civil purposes, as aircraft counterweights (7), shielding in some medical equipment, and ballast where volume constraints prohibit the use of less dense metals. DU was also placed in the tips of the BGM-109 Tomahawk land-attack cruise missiles (TLAM) during test flights, to provide weight and stability (8). The caliber of DU penetrators in the US arsenal lies in the range between 20 and 120 mm (9). The Nuclear Regulatory Commission defines DU as uranium in which the content of the ²³⁵U isotope is below than 0.72%, while the military specifications designate that DU used by the Department of Defense (DoD) contains less than 0.3% of ²³⁵U. Actually, the DoD uses only DU containing approximately 0.2% of ²³⁵U (10).

Properties of depleted uranium

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

When a DU bullet impacts a hard object (armour or rock), it is crushed into fragments, burned (18-70%) and oxidized into dust. Uranium oxides (U₃O₈, UO₂ and UO₃) are being formed. The latter oxide is the only one soluble in water, forming uranyl (UO₂)²⁺ ions. The oxide aerosol resulting from impact has 50-96% of respirable-size particles (diameter less than 10 (m) with air concentrations 5-780 mg/m³ (α -activity of 0.07-11.1 kBq/m³), and 17-48% of these particles is soluble in water. The other particles become attached to soil particles by melting of the soil and form a silicate glass. If the penetrator hits soft ground (sand or clay), it will penetrate the soil (to a depth of over 50 cm) and remain there for long time. Studies of DU penetrator weathering have shown that they principally corrode into hydrated U(VI) oxides which are very soluble in water (11). The main pathway affecting human health is inhalation of insoluble DU dust and inhalation or ingestion of its soluble component.

Investigations of the migration of DU and its transport, following 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 could be useful in developing a strategy for obtaining representative samples (12). Assessments of the total uranium content from 750 site measurements (13) of

atmospheric fallout, soil, sediment, water and suspended sediments collected in the time period 1983-1990, related to background concentrations (14) have shown that about 90% of the uranium remained in the proximity of the firing sites and 10% entered the watershed. Investigations were confined to one watershed called the Potrillo Canyon, of small size (5 km²), and with no public access. A conservative estimate of the total uranium source was about 35 tons. These results could be used to develop the following guidelines in the detection of uranium around the impact points:

1. The concentration in soils and sediments decreases with increasing distance from the firing sites
2. The greatest concentration is to be found in transported suspended sediments carried in runoff waters, followed by sediment present in stream banks,
3. The 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 at regions close to the firing site with the largest concentrations in the upper 5cm of soil, about 30 times higher than at 5-10 cm depth,
5. Uranium is readily leached into the dissolved phase, often within a few hours, which is the time frame of most rainfall events,
6. Uranium concentration increases with decreasing particle size, having a particular affinity to fine slits and clays.

Measurement of DU

There are three types of measurements concerning the environmental impact of DU: territorial survey; measurements of samples of soil, water, air and food; and measurements in human body and excreta.

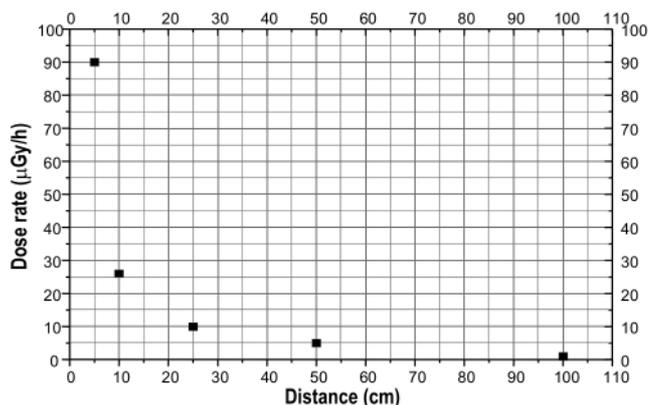


Figure 1. Depleted uranium ammunition caliber 30 mm external exposure of whole penetrator

The terrain is surveyed to rapidly locate sites where DU has been deposited. Surveying is performed on the basis of measurements of ionizing radiation. The most appropriate instruments, such as thin-window GM counters or scintillation detectors, have to detect

beta and gamma radiation. During the measurement the detectors have to be as close as possible to the ground. Even in that case it is very difficult to find the correct localisation. It is necessary to know the approximate location independently. As an example, the dose rate around a complete 30 mm caliber penetrator as a function of distance from the penetrator, is presented in Figure 1.

The radiological consequences of DU in humans can only be estimated by the effective dose from external or internal sources. To calculate dose from internal sources, applying respective conversion coefficients, it is necessary to measure the concentration of DU on the ground surface, in air, water, food and the human body. These measurements are based on samples of ground, food, water, air and excreta and can be performed only in specialized laboratories. There are two types of such measurements: nuclear (X, gamma and alpha spectrometry, neutron activation analysis, whole body counter) and non-nuclear (mass spectrometry).

Suitable preparation of samples is essential for all the above methods. The preparation can be very simple (gamma spectrometry) or more complicated (alpha spectrometry). Neutron activation analysis is the most sensitive method, but it is quite expensive, as it requires neutron sources, such as nuclear reactors.

DU activity or concentration measurements in air are performed indirectly by flowing large amounts of air through appropriate filters. These filters become sources of alpha, beta and gamma rays for further analysis using the above-described methods. Health effects of DU may result from its chemo- and radiotoxicity. Chemotoxicity could be the dominant effect in the immediate vicinity of the impact location. At larger distances both effects become negligible.

Uranium natural background concentrations

The content and activity of uranium in the environment are quite variable, as presented in Table 1.

Table 1. Uranium content in the environment

Sample	Content
Soil	0.5-5 ppm
Phosphate rocks	20-120 ppm
Fresh water	0.1-8 µg/l
Groundwaters	0.024-200 µg/l
Groundwaters in FRY	0.04-4.0 µg/l
Seawater	2.0-3.7 µg/l
Air	8·10 ⁻⁵ µg/m ³

The geological structure of Serbia's territory includes igneous rocks, such as granodiorite, crystalline shales and Neogene volcanics with an uranium content of up to 4.4 mg/kg (15). The scattering of ore refuses from the Kalna-Gabrovica uranium mine has enriched its U content (7.7 -28.1 mg/kg) in the barren soil deposit, with an average concentration of 17 mg/kg (as based on 32 samples) (16). As a result of widespread application of phosphate fertilizers (P-fert) with a very significant uranium concen-

tration (30-300 mg/kg), the uranium concentration in Serbian soils currently ranges between 0.08 and 5.9 mg/kg (17).

EXPERIMENTAL

Sampling

Soil samples were collected from bomb craters in June, based on information on these craters being caused by NATO Cruise missiles in April and May 1999. The selected locations were Belgrade, Smederevo, Niš, Bor, Prahovo, Kadinjača, Jadovnik, Raška, Sjenica, and Cape Arza on the Lustica peninsula. In addition, at a distance at least of two kilometers from the investigated craters, samples were gathered to assess the uranium content, in order to obtain a reference measurement of background uranium concentration. Soil sampling consists of randomly taken shallow scoops of surface soil (0-5 cm depth, order of 1 m²), after removing stones or cleaning the surface vegetation from the site. Soil samples were wrapped in plastic bags and brought to the laboratory.

Uranium analysis

We used γ -spectrometry to directly measure gamma emitters in soil samples (18). After air-drying and mixing the sample, an 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 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 ⁶⁰Co. The background count rate was 0.560 cps in the 20-2900 keV energy interval. The concentration of ²³⁸U and ²³⁵U was determined via the photopeaks emitted by their daughters: ²³⁴Th (63 keV) and ²³⁵U (185 keV), respectively. The total relative errors for activity measurements ranged between 26 and 85%. The counting time for each sample was 86.000 s, background being measured over a longer period. The efficiency for the sample counting configuration was determined with standard soil samples (Standard Reference Material 694, National Bureau of Standards, Budapest) containing a known mixture of nine radionuclides.

As an alternative, the technique of ICP/OES (ARL model 3580) was employed. A representative sample of soil was air-dried and ground in a mill to become homogenized. A 10 g portion of the 3 mm-sieved sample was placed in a high temperature furnace (550°C) overnight, to remove the organic components. The sample was then treated with concentrated HNO₃/HCl in a platinum crucible, followed by dilution and filtration (19). Digestion of the residue was repeated 2-3 times until it became gray-white in colour, in order to yield the sample solutions. Measurements

were made with standard addition of uranyl nitrate. Standard solutions were prepared and used to obtain the calibration curve. Standard reference materials were used to validate the analytical procedure. Decomposition and analysis were duplicated for each sample. The range of the relative standard deviation was 3-7%.

RESULTS AND DISCUSSION

The primary objective of this survey was to locate the deployed DU. As there were practically no data on the levels of uranium in the environment around the analyzed locations, undisturbed soil samples were taken to obtain natural background measurements. A preliminary judgement of the most likely amount of uranium deposited on the ground could be made assuming that during one A-10 aircraft engagement 50-100 rounds are fired and that one of every five bullets contains DU (20). Usually, three attack planes work together against a target and the amount of DU in the area hit ($20 \times 50 = 1000 \text{ m}^2$) might be 9-18 kg. If 10 kg of DU were spread, taking into consideration soil depth of 5mm and specific gravity of 1.5 g/cm^3 , the uranium concentration of the soil would be estimated to be about 1300 mg/kg. A similar evaluation could be made for the cruise missile that contains DU. The dominant mechanism for uranium redistribution is the surface water pathway and due to the high rainfall, which had occurred in June 1999 (up to 30-40 l/m² per day) (21), the resulting concentration, might be low, much less than assumed. Although the estimation is very rough and would apply only for the immediate vicinity of the target, it is suggested that the excess uranium in the surface soils would have a rather low enrichment. Therefore, the choice of the correct analytic method it is very important for quantitative analysis of DU concentration.

The results of our field investigation are summarized in Table 2, along with the description of the soil's origin. The individual isotopic uranium activity (²³⁸U) as well as the ²³⁵U/²³⁸U isotopic ratio are given. The concentrations in the surface soil (0-5 cm in depth) range from 1.7 to 14 mg ²³⁸U/kg dry soil and up to 22

Table 2. Uranium content and its isotopic ratio in the investigated soils

Location	Content ²³⁸ U		Isotopic ratio ²³⁵ U/ ²³⁸ U	Description
	(Bq/kg)	(mg/kg)		
Belgrade	68 ± 18	5.5 ± 1.4	0.0074	bomb crater
	32 ± 9	2.6 ± 0.7	0.0074	bomb crater
Smederevo	21 ± 6	1.7 ± 0.5	0.0073	bomb crater
	86 ± 23	7.0 ± 1.9	0.0073	bomb crater
	57 ± 15	4.6 ± 1.2	0.0071	background
Bor	51 ± 14	4.1 ± 1.1	0.0073	bomb crater
Niš	61 ± 16	4.9 ± 1.3	0.0073	bomb crater
	53 ± 14	4.3 ± 1.1	0.0074	bomb crater
Prahovo	37 ± 10	3.0 ± 0.8	0.0075	bomb crater
	55 ± 15	4.5 ± 1.2	0.0071	background
	53 ± 18	6.5 ± 2.2	0.0074	bomb crater
Kadinjača	41 ± 16	5.8 ± 2.2	0.0075	background
	22 ± 19	2.8 ± 2.4	0.0161	bomb crater
Jadovnik	30 ± 16	7.1 ± 3.7	0.0105	background
Raška	45 ± 21	14 ± 6	0.0143	bomb crater
Sjenica	60 ± 22	10 ± 4	0.0085	bomb crater
Cape Arza	344 525	(2.3 ± 0.2) × 10 ⁴	0.0011	bomb crater
	762 013	(6.1 ± 0.4) × 10 ⁴	0.0011	bomb crater

mg/kg of total uranium. The obtained isotope ratio from 0.0071 to 0.0075 corresponds to natural uranium abundance (0.00725) at most locations. In contrast, high values, between 0.0161 and 0.0085, were recorded for soil samples taken from bomb craters in Jadovnik, Raška, and Sjenica. It is worth mentioning that a relatively high ratio of 0.0105 was found in undisturbed soil on Jadovnik where we expected a control value. These markedly higher ratios could be explained rather by high counting errors (45-85%) than by any excess of non-natural uranium. On the other hand, the errors of measuring the ²³⁸U content for samples containing high activity from the Cape Arza location were small (about 7%). The obtained isotope ratios of 0.0011 in those samples indicate that a DU weapon was used at this site.

For comparison, Table 3. lists the total uranium concentration obtained by γ -spectrometry (measured ²³⁸U concentration data, combined with the ²³⁵U/²³⁸U ratio assuming that ²³⁴U and ²³⁶U have negligible concentration), and the results obtained with the ICP method. Good agreement between data obtained from undisturbed locations at Kadinjača and Jadovnik is evident. The reason for the significant difference between two corresponding samples taken at other locations is probably due to interference from Si, Ca, Fe, and Al (22).

Table 3. Results of total uranium concentration by γ -spectrometry and inductively coupled plasma

Location	Total U concentration [mg/kg]	
	γ -spectroscopy	ICP
Kadinjača	6.5 ± 2.2	21.6 ± 1.1
	5.8 ± 2.2	5.0 ± 0.4
Jadovnik	2.8 ± 2.4	11.1 ± 0.4
	7.2 ± 3.7	10.7 ± 0.6

To confirm these results a more advanced method with higher analytical precision, such as thermal ionization mass spectrometry using isotope dilution spike, should be applied (23). It is reasonable to suppose that the isotopic analysis can uniquely distinguish contamination by uranium from indigenous uranium present at background level.

CONCLUSION

The presence of DU is difficult to detect directly in the environment unless the concentration is significantly above background. The wide range of uranium content in the soils (2-22 mg/kg) at the studied locations is due to the different type of soil, soil formation and soil transport process (geological origin). The obtained values are comparable with those for undisturbed soils, indicating that there was no presence of DU at these sites within measurement error limits. Only once could deployment of a DU weapon be stated, at the studied Cape Arza location where the ²³⁸U content was between 23 and 61 kg/kg.

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