DETERMINATION OF URANIUM IN SOIL WITH EMPHASIS ON DOSE ASSESSMENT

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INTRODUCTION

Uranium is naturally occurring element and is found at an average concentration of 3mg/kg in the Earth's crust. Typical concentration range from 0.3 to 11.7mg/kg [1]. Naturally occurring uranium contains three isotopes, $^{238}$U (99.3% by weight), $^{235}$U (0.72%) and $^{234}$U (0.006%).

The major use of uranium is as a fuel for nuclear reactors and in nuclear weapons. $^{235}$U is fissile and for production of nuclear fuel the relative concentration of $^{235}$U has to be increased. A byproduct of this enrichment process is depleted uranium (DU). DU is distinguished from natural uranium by lower concentration of $^{235}$U (<0.7%, typically 0.2-0.3) and $^{234}$U. DU in civilian applications is employed in counterweights or ballasts in aircraft, radiation shields in medical equipment, as containers for the transport of radioactive material and as chemical catalysts. DU has also been used in glassware and ceramics and in dentistry. In military applications DU is used as kinetic energy penetrators due to its high density, its pyrophoric nature and its property of becoming sharper as it penetrates armour plating [2].

During conflict in Bosnia about 10,000 DU rounds (approximately 3 tons of DU) were fired during NATO air strikes in Bosnia and Herzegovina in 1994 and 1995, mainly around Sarajevo. 1500 of the 30-mm DU rounds were used at the location Tank Repair Facility near town Hadžići [3]. On impact of penetrator with target typically 10-35% (maximum 70%) becomes an aerosol and spread in the environment [2]. The majority of the penetrators that impact on soft targets (eg. sand or clay) penetrate the ground remaining intact for a longtime.

Inhalation of dust is considered the major pathway for DU exposure both during and after attack [2,4]. A possible exposure pathway for those working or living in DU affected areas after aerosols have settled is the inhalation of the DU particles in the soil that are resuspended through the action of the wind or human activities.
MATERIAL AND METHODS

During our mission former Tank Repair Facility was investigated. It is a large complex consisting of buildings, storage barns, workshops and yards. At the investigated site there were clear marks and holes caused by projectile impacts easily detectable visually and confirmed with hand held dose rate meters. Found penetrators at the surface had been removed at the time of the survey. Beside DU penetrators the area contained several hundred unexploded landmines.

The sampling campaign took place in April and September 2003. Ten samples of surface soil (0-5 cm) were collected. The selection of soil sampling sites can be roughly divided into two groups: undisturbed ground surfaces covered with grass within or close to the Facility; and contaminated debris containing dust and sand from the yards where tanks were hit and gama/beta radioactivity were detected above environmental levels with portable instrumentation.

Soil samples were collected using stainless steel coring sampler (a tube of diameter 5 cm and 15 cm length). Surface vegetation was removed and five cores of subsamples were taken. Debris samples were collected from five subsamples collected with metallic spatula. The subsamples were mixed and homogenized. The samples were dried at 105°C and then sieved. To remove organic carbon ~5 g of the sample were ashed at 500°C. Aliquots of 0.5 g were used for radiochemical treatment.

In all experiments analytical grade reagents and deionised water was used. The $^{232}$U tracer was obtained from Isotrac, AEA Technology, QSA. The $^{232}$U spike was added to serve as an internal tracer from which the chemical recovery could be determined. Total dissolution of the samples was done with sequential addition of mineral acids (HNO$_3$, then HNO$_3$ and HClO$_4$, and finally HNO$_3$, HClO$_4$, and HF). The residue, containing uranium, was dissolved in 7M hydrochloric acid and passed through an anion exchange column (DOWEX AG 1-x8). Thorium and iron were removed with 7M hydrochloric acid and 8M nitric acid respectively. Uranium was eluted from the column with 0.5M hydrochloric acid. Source preparation for counting was done by electrodeposition. The electrodeposition cell, produced by Tracerlab GMBH, was Teflon made of conical shape with active diameter of 19 mm. Platinum anode, circle shaped, was positioned in the centre of the cell, 0.5 cm from the SS planchet. The uranium solution is transferred to an electrolytic cell with 5.7% ammonium oxalate and electrodeposited on stainless steel disk. The electrolysis is maintained for 2 hours with current of 0.3A. After electrodeposition stainless steel planchet was heated for 30 seconds in the flame of the Bunsen burner.

Samples are counted on the alpha spectrometer “OASIS” - Oxford Alpha Spectrometry Integrated System (Tennelec) equipped with ULTRA ion-implanted silicon detectors with an active area of 450 mm$^2$ (resolution 25 keV FWHM at 5.486 MeV). The energy resolution and detection efficiency were determined using
a calibrated mixed source, consisting of $^{239}\text{Pu}$, $^{241}\text{Am}$ and $^{230}\text{Th}$ purchased from The Source Incorporated.

The exposure pathway included in the assessment was inhalation of soil resuspended by the action of the wind or by human activities. According to data for uranium found in soil and estimated in air we calculated the annual dose that could be received by an individual worker at the site and the people from the surroundings. Radionuclide concentrations in air due to resuspension were determined using a simple dust loading approach:

$$C_{\text{air},i} = SE \cdot C_{\text{soil},i}$$

(1)

Where:
- $C_{\text{air},i}$ is the activity concentration of radionuclide $i$ in air (Bq/m$^3$);
- $SE$ is the dust loading factor, $2.0E-6$kg/m$^3$ for wind driven resuspension, $3.0E-5$kg/m$^3$ for human made resuspension (kg/m$^3$) [5];
- $C_{\text{soil},i}$ is the activity concentration of radionuclide $i$ in soil from table 1 (Bq/kg);

Estimated doses are commited effective doses from inhalation and were calculated using a formula:

$$E = \left[ C_{\text{air},i} \cdot I_{\text{inh}} \cdot (1 - \text{Occ}) \right] + \left[ C_{\text{air},i} \cdot I_{\text{inh}} \cdot \text{Occ} \cdot I/O \right] \cdot DC$$

(2)

Where:
- $E$ is commited effective dose (Sv/a);
- $I_{\text{inh}}$ is inhalation rate; we used value of 7,300 [1] (m$^3$/a);
- $\text{Occ}$ is indoor occupancy; we used 0.5 and 0.75 values;
- $I/O$ is indoor/outdoor concentration ratio, for this report value of 0.5 was chosen;
- $DC$ is commited effective dose coefficients [7], we used coefficients for class S compounds, $8.0E-6$ for $^{238}\text{U}$, $8.5E-6$ for $^{235}\text{U}$, $9.4E-6$ for $^{234}\text{U}$, (Sv/Bq);
**RESULTS**

The results of the dose assessment are listed in Table 1.

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>$^{238}\text{U}$</th>
<th>$^{235}\text{U}$</th>
<th>$^{234}\text{U}$</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{235}\text{U}/^{238}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Soil</td>
<td>42.48±4.74</td>
<td>2.08±0.94</td>
<td>38.73±4.44</td>
<td>0.91</td>
<td>0.049</td>
</tr>
<tr>
<td>2</td>
<td>Soil</td>
<td>43.31±4.74</td>
<td>2.08±0.94</td>
<td>37.90±4.38</td>
<td>0.88</td>
<td>0.048</td>
</tr>
<tr>
<td>3</td>
<td>Sand</td>
<td>129.38±8.83</td>
<td>2.37±0.85</td>
<td>30.86±3.38</td>
<td>0.24</td>
<td>0.018</td>
</tr>
<tr>
<td>4</td>
<td>Sand</td>
<td>142.96±9.76</td>
<td>2.62±0.94</td>
<td>34.10±3.73</td>
<td>0.24</td>
<td>0.018</td>
</tr>
<tr>
<td>5</td>
<td>Soil</td>
<td>32.32±3.88</td>
<td>1.56±0.78</td>
<td>29.21±3.66</td>
<td>0.90</td>
<td>0.048</td>
</tr>
<tr>
<td>6</td>
<td>Soil</td>
<td>54.76±6.98</td>
<td>2.28±1.32</td>
<td>48.67±6.53</td>
<td>0.89</td>
<td>0.042</td>
</tr>
<tr>
<td>7</td>
<td>Soil</td>
<td>32.75±3.82</td>
<td>1.47±0.74</td>
<td>29.44±3.59</td>
<td>0.90</td>
<td>0.045</td>
</tr>
<tr>
<td>8</td>
<td>Sand</td>
<td>809.13±50.93</td>
<td>12.90±4.13</td>
<td>104.53±12.68</td>
<td>0.13</td>
<td>0.016</td>
</tr>
<tr>
<td>9</td>
<td>Soil</td>
<td>34.24±3.78</td>
<td>1.68±0.76</td>
<td>33.90±3.75</td>
<td>0.99</td>
<td>0.049</td>
</tr>
<tr>
<td>10</td>
<td>Soil</td>
<td>28.17±3.72</td>
<td>1.28±0.74</td>
<td>25.62±3.53</td>
<td>0.91</td>
<td>0.045</td>
</tr>
</tbody>
</table>

In Table 1 were summarized the results of the activity concentrations of $^{238}\text{U}$, $^{235}\text{U}$, $^{234}\text{U}$ and the values of $^{234}\text{U}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ activity ratios for analyzed soil samples. The errors reported were calculated according to Eurachem/Citac Guide 2000 and correspond to the propagation of statistical error and of the uncertainties associated with the sample and tracer masses, the tracer specific activity and the alpha detection efficiency [8]. The chemical yield varied from 30-50%. The detection limit, assessed using Currie’s method, was found to be 2.7 Bq/kg for $^{238}\text{U}$ and $^{234}\text{U}$, and 1.0 Bq/kg for $^{235}\text{U}$ in 86400 seconds of counting time [9]. Specific activities of $^{238}\text{U}$ found in the most soil samples (1,2,5,6,7,9,10) were 28.17±3.72 Bq/kg to 54.76±6.98 Bq/kg with mean value of 35.59±1.61 Bq/kg. The activity ratios $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ were in consistent with literature data of 0.046 and about 1 for natural uranium [6]. On the other side we found higher specific activities of some hot spots (3,4,8), in the range from 142.96±9.76 Bq/kg to 809.13±50.93 Bq/kg. Lower values of isotopic ratios for $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ clearly indicated presence of DU in those samples.

Based on measurements made, an assessment of the possible doses that could be received by individuals at the investigated sites was carried out. Assumptions were that uranium in air is associated with particles of dust and that size of particles are in respirable range, less than 10μm, which is reasonable to expect [10]. Since resuspended dust derives from a wide area for assessment purposes we used average values of activity concentration of uranium isotopes in soil. The annual dose of uranium from inhalation that could be received by an individual working at the site was 2.61μSv for a 2000 working hours per year ([8].
hours, 250days). While people residing in the area could receive doses of the order of 7.84 μSv/a assuming 50% indoor occupancy time.

CONCLUSION
The results for soil samples with $^{238}$U activity concentration below 54.76±6.98 Bq/kg were of natural origin since isotopic ratios were natural. Collected debris samples from concrete and cobblestone yards contained $^{238}$U up to 809.13±50.93 Bq/kg. Activity ratio of $^{235}$U/$^{238}$U were as low as 0.016 and 0.018 clearly indicating presence of DU. Accumulation of DU was result of washing out corroded fragments of DU penetrator and dust from the concrete surface and accumulating in the lowest part of yards. Generally, it can be concluded that there is not wide spread contamination which is in consistent with already published data. A conservative approach was adopted to estimate the possible annual doses that could be associated with DU. Annual doses that could arise to any members of the public residing in the area would be less than 10 μSv. Doses to workers in the Tank Repair Facility would be less then 5 μSv/y assuming that a person works continuously for one year (8 hours, 250 days) outdoors. The estimated doses in this assessment should be considered theoretical doses received in the areas investigated. Even with uncertainties of the assumed scenario it can be concluded that contribution to the annual dose from inhalation of uranium is insignificant for people working or spending time nearby.

REFERENCES
VI. simpozij HDZZ, Stubičke Toplice, 2005.


ABSTRACT

Uranium is present naturally in the earth crust and has three isotopes with long half-lives. These isotopes are $^{238}\text{U}$ (99.27% natural abundance), $^{235}\text{U}$ (0.72% natural abundance) and $^{234}\text{U}$ (0.006% natural abundance). Isotope $^{235}\text{U}$ is a valuable fuel for nuclear power plants. During the manufacture of nuclear fuel the concentration of $^{235}\text{U}$ is increased. Depleted uranium (DU) is a waste product of this enrichment process and typically contains about 99.8% $^{238}\text{U}$, 0.2% $^{235}\text{U}$ and 0.0006% $^{234}\text{U}$ in mass. Due to its high density and other physical properties, DU is used in munitions designed to penetrate armour plate. DU weapons were used during the Balkan war in Bosnia and Herzegovina. It was estimated, that nearly 10,000 projectiles were fired or 3 tonnes of DU used in B&H. The aim of this work was to determine uranium radioisotopes in soil and air collected in Hadžići (near Sarajevo). The investigated area is a former military base used for the production and maintenance of tanks and other heavy military vehicles. During a NATO attack in 1995, about 1,500 rounds were fired at the site. The specific activities of $^{238}\text{U}$ found in soil ranged from 28 Bq/kg to 55 Bq/kg. We found higher specific activities in some foci, in the range from 143 Bq/kg to 810 Bq/kg. The specific activities of uranium isotopes in the air were determined using simple dust loading approach. The results served to calculate the annual effective dose that could be received by individual workers at the site and by general population from the surrounding area. Radioactivity measurements in the environment of Hadžići showed that the annual effective dose for general population was less than 20 μSv.