# HEAVY METALS MOBILITY IN THE SOIL SAMPLES FROM DU CONTAMINATED AREAS

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**Abstract**

During the NATO air attacks in 1995 and 1999 some areas of ex- Yugoslavia have been contaminated in depleted uranium. Removal of projectiles and soil remediation started after a while, followed by detailed investigations of environmental contamination. Petrological and geochemical characteristics of particular terrain and local meteorological conditions have played a major role in determining influences of the pollution levels. Investigation has been made to define the correlation between macro-elements and heavy metals in soil samples obtained in contaminated areas. We applied five-step sequential extraction procedure in order to simulate environmental conditions for heavy metal mobility through the soil medium.

Concentratration of elements we were interested in had been determined by AAS, graphite and flame technique, as well as fluorescence spectroscopy.

Results indicated that all the areas from which the soil samples have been taken contained increased quantities of Cd, Pb and U. These elements are in such form that could be easily released to environment and made bioavailable and potential threat to the ground and drinking water.

**Introductions**

During the conflict in ex-Yugoslavia in 1990s NATO had used ammunition containing depleted uranium. Even today there are disagreement about the number of locations and quantities of DU dropped during the conflict. According to reports by the Army of Serbia and Montenegro it can be estimated that NATO forces fired about 3000 - 5000 projectiles from A-10A aircraft guns, containing depleted uranium (which is equivalent of 1 - 1.5 tones of U-238) onto the territory of Serbia and Montenegro, excluding the territory of Kosovo and Metohija. (7)

Geochemical and perological characteristics of particular terrain, as well as local meteorological conditions had determined behavior of uranium in contaminated areas. Our aim was to test the soil samples obtained in these areas and find out not only the total

contents, but also specific chemical forms of metals and their relation with macro-elements. The tests were to indicate substrates for heavy metals, including uranium, and predict the possibility of mobility and bioavailability of the contaminants at particular site.

In order to simulate natural conditions we performed modified version of Tessier's five-step sequential extraction procedure (1), based on defining exchangeable fractions (first phase), carbonate and Mn oxide (second phase), Fe oxide (third phase), organic (fourth phase) and residual fractions (fifth phase). Quantities of the elements we were interested in have been determined by AAS, graphite and flame technique and fluorescence spectroscopy.

## Experimental

During our tests we studied soil samples obtained in the following locations: Bratoselce in Southern Serbia (samples No. 1, 6, 9, 10, 11 and 12), Arza at Montenegro coast (samples No. 2, 3, 4 and 5), Han Pijesak (samples No. 8 and 12) and Veliki Zep (sample No. 7) in Republic of Srpska, Bosnia-Herzegovina.

Extraction procedure had been performed on 10,00 g of each sample, without drying to avoid chemical transformations such as oxidation processes, losing the water, etc. Moisture levels were determined before the procedure started. Extraction was performed at room temperature in a mechanical shaker. The solid / liquid ratio was 1:45 for all the phases.

The first step was to treat samples with 450 cm3 of 1M ammonium-acetate for 2 hours in the mechanical shaker, second step: 0,1 mol/dm3 $NH_2OH \cdot HCl$ and 0,01 mol/dm3 HCl for 9 hours, third step: 0,2M / 0,2M oxalic acid / ammonium - oxalate mixture for 7 hours. As a fourth step extraction was performed using 30% $H_2O_2$ in 0,01M $HNO_3$ at 85 degrees C. Metals that were eventually re-adsorbed have been deabsorbed by treating the sample with 3,2M ammonium - acetate solution for 30 minutes in the shaker. In the fifth phase a 6M HCl was applied for 9 hours at 85 degrees C. Remaining solid phase after every extraction step has been rinsed with three portions of water. That water has been joined to the extracts for analysis. Concentrations were determined by the absorption spectrophotometry, using graphite and flame techniques (Perkin - Elmer AAS 200, PE AAS 600). Uranium concentration has been determined by Lewandowski fluorimetric method (6).

## Results

The largest amount of Fe was evenly divided between ammonium-oxalate (third phase) and solutions of the high acidity (fifth phase). In summary, this is the case in more than 90% for all the samples, except sample No. 8 in which Fe is fairly well distributed between the second (32%), third (32,5%) and fifth phase (31,2%). This confirms the well-known fact that Fe is usually found in the form of its hydroxides.

Mn was mostly distributed between the second (oxide) and fifth phase.

The largest amounts of Ca were extracted in the first and the second phase, in summary more than 50% in samples from Arza, and more than 90% in other samples. This fact indicates that Ca is present in the form of carbonates. Ni and Zn were mostly extracted in the third and fifth phase, so it can be assumed that most of the extracted Ni and Zn were bound to the Fe hydroxides. In samples No. 10, 11 and 12 significant amounts of Zn

were extracted during the first and the second phase (Table 1).  This demonstrated very high Zn mobility in the nature.

**Table 1** Concentration of zinc found in extracts after extraction steps 1 and 2

|          | Values | 10   | 11   | 12   |
|----------|--------|------|------|------|
| 1st step | ppm    | 14.5 | 18.1 | 11.1 |
|          | %      | 23   | 29   | 15   |
| 2nd step | ppm    | 8.3  | 11.7 | 17.1 |
|          | %      | 13   | 19   | 24   |

Fig. 1 shows the lead distribution in sample No. 6 (Bratoselce) This sample shows the highest values after the first extraction phase, 26,7 ppm what is 58% of the total amount of extracted Pb. In samples No. 1, 7, 10, 11 and 12 lead was mostly extracted in the first two phases (Table 2).

**Table 2** Concentration of lead found in extracts after extraction steps 1 and 2

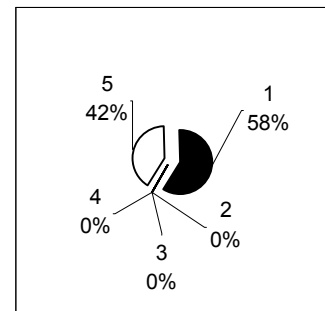|          | Sample | 1    | 7    | 10   | 11   | 12   |
|----------|--------|------|------|------|------|------|
| 1st step | ppm    | 27,2 | 23.5 | 9.3  | 25.5 | 45.2 |
|          | %      | 32   | 30   | 38   | 30   | 27   |
| 2nd step | ppm    | 0,0  | 20.6 | 2.07 | 24.1 | 24,1 |
|          | %      | 0    | 26   | 8    | 15   | 14   |



Fig.1 Pb distribution in sample 6

The largest amount of this metal is obviously non-selectively bound to various substrates in the soil.
Significant portions of cadmium were extracted in the first and second phase (samples No. 2,3,4,7,8, and 12) that points to the high potential for mobility of this element in the nature (Table 3, Figure 2)

**Table 3** Concentration of cadmium found in extracts after extraction step 1 and 2

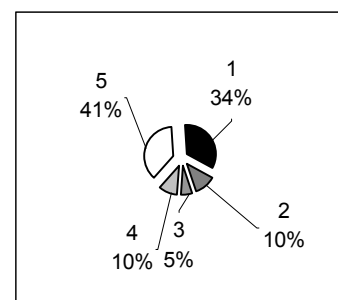|          | Sample | 2    | 3    | 4    | 7    | 8    | 12   |
|----------|--------|------|------|------|------|------|------|
| 1st step | ppm    | 0.00 | 0.31 | 0.24 | 0.00 | 0.00 | 0.00 |
|          | %      | 0    | 34   | 20   | 0    | 0    | 0    |
| 2nd step | ppm    | 0.19 | 0.09 | 0.19 | 0.13 | 0.18 | 0.19 |
|          | %      | 26   | 10   | 17   | 28   | 30   | 32   |



Fig.2 Cd distribution in sample 3

Analysis of uranium has been undertaken in samples obtained in locations in Bratoselce (No. 9 and 10) and Han Pijesak (No. 8 and 12).  Results from samples No. 9, 10 and 12

indicate that uranium was mostly extracted in the first and second phases. (Table 4; Figure 3, a, b, c) These phases have shown the greatest mobility and are the most relevant from ecochemical aspect. Facts are indicating that mobility of U is very high under natural conditions.

**Table 4.** Concentration of uranium found in extracts after extraction steps 1, 2, 3, 4 and 5

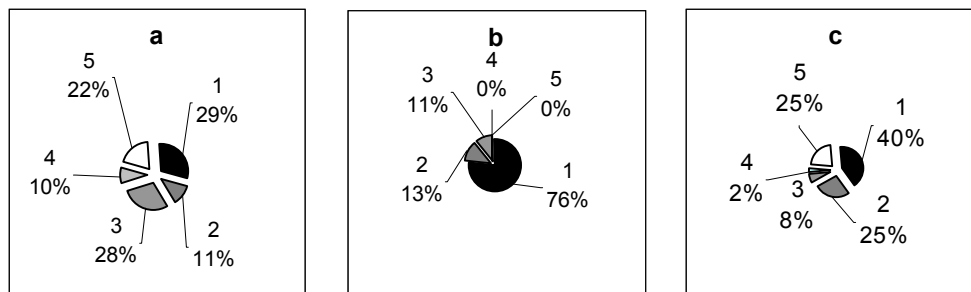| Sample | 1st step ppm | % | 2nd step ppm | % | 3rd step ppm | % | 4th step ppm | % | 5th step ppm | % |
|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 30.6 | 29 | 11.2 | 11 | 29.6 | 28 | 10.2 | 10 | 22.4 | 22 |
| 10 | 292.3 | 76 | 49.8 | 13 | 41.5 | 11 | 0 | 0 | 0 | 0 |
| 12 | 906.1 | 40 | 559.6 | 25 | 170.8 | 8 | 47.2 | 2 | 575.6 | 25 |



Fig. 3 U distribution in sample 9 (a); in sample 10 (b); in sample 12 (c)

**Discussion**

End results have shown that almost all samples contained increased contents of practically all elements analyzed.

In samples from Arza location almost all the elements (except Cd) were extracted in the first and fifth phase, in a form that is less dangerous for the environment. "Mobile phase" Cd extracted from the samples is most probably adsorbed in an ion-exchangeable manner and bounded by carbonate bounds. On the other hand, samples obtained on Bratoselce location have shown increased levels of all heavy metals in the first and second phase. These phases, as the most mobile ones, are most relevant from the electrochemical point of view. Increased values of metals are indicating to significant potential for mobility to ground waters, as well as the influence of metals to biopotential.

The most interesting sample was the one obtained at location in Han Pijesak (No. 12) that has shown high percentage of "mobile phases" for all the elements, including uranium. This can be explained by direct pollution of the soil during the conflict. Situation with uranium is very disturbing because large amounts of this element have been extracted in the first and second phase in the samples obtained on locations in Bratoselce (No. 9 and 10) and Han Pijesak (No. 12). Uranium is most probably bounded by carbonate bounds in these samples. This element is bioavailable on these locations and had entered the food chain.

## Conclusions

Results for samples obtained on these locations are showing increased levels of Ni, Zn, Cd, and Pb that are easy mobile, indicating contamination in the recent past.

Uranium is found in significant amounts and it is still very mobile, even it has been several years since bombing.

High levels of heavy metals, including uranium, and their presence in highly mobile phases are indicating that these metals represent hazard for ground waters and biopotential of the region.

## Acknowledgements

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