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HEAVY METALS AND ARSENIC IN SOILS FROM GRASSLANDS IN BULGARKA NATURE PARK

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Abstract

KARATOTEVA, D., E. TSVETKOVA and D. BEZLOVA, 2014. Heavy metals and arsenic in soils from grasslands in Bulgarka Nature Park. *Bulg. J. Agric. Sci.,* 20: 73-78

In a recent study, we detected elevated content of heavy metals in medicinal plants and pasture grasses of Bulgarka Nature Park. In the present work, we have investigated the content of lead (Pb), arsenic (As), cadmium (Cd) and mercury (Hg) in the soils of these grasslands. The highest concentrations were found in soils from the grassland in Malusha site. The mean value for Pb content was very high (183±141 $mg.kg^{-1}$DW), while the value for As content was 78±18 $mg.kg^{-1}$DW. Both elements exceeded the maximum permitted level for grasslands. The maximum concentrations of Pb and As (497 $mg.kg^{-1}$DW and 112 $mg.kg^{-1}$DW, respectively) were detected only in the eastern part of the grassland of Malusha site. Thus, it is recommended to perform soil mapping and limit grazing within definite parts of the site. A source of risk to the environment could be considered the enhanced soil levels of As in the grasslands of Ispolin Peak site (17-74 $mg.kg^{-1}$ DW), the village Ezeroto (107 $mg.kg^{-1}$DW) and the grasslands near Gabrovo hut (43 $mg.kg^{-1}$ DW).

Key words: grassland, protected areas, maximum permitted level, risk assessment

Abbreviations: nature park (NP), maximum permitted level (MPL)

Introduction

The content of total forms of heavy metals in soils of forest lands in Bulgaria have been a subject of survey within the network for large-scale and intensive monitoring. Results on soil resistance to contamination (Malinova, 2001) have been published and studies on the profile distribution of heavy metals and their biogenic accumulation in the surface soil layers have been conducted (Malinova et al., 2004; Malinova , 2012). Some relations between different parameters in soils of forestlands were established as well (Tzvetkova, 2006; Tzvetkova, 2009). Summarized results were presented in two monographs (Kolarov et al., 2002; Pavlova et al., 2006). The content of mobile forms of heavy metals was investigated mainly in the stationary sample plots for intensive monitoring (Malinova, 2002).

Studies on the content of highly toxic elements such as As, Cd and Hg in forestland soils are limited. Detailed investigations of soils conducted on the slopes of the Balkan Mountain and Sredna Gora Mountain in the region of Pirdop-Zlatitsa and part of the Central Balkan National Park (Malinova, 1997; Bezlova et al., 2001) have shown elevated content of As in the litter (up to 230 $mg.kg^{-1}$) whereas total As content was up to 65 $mg.kg^{-1}$, 80 $\mu g.kg^{-1}$ of which being in a mobile form. Hg in soils of this region was under detection limit. Increased levels of As have been found in forestland soils in the region of Ada tepe-Rhodopi mountain (up to 314 $mg.kg^{-1}$) (Malinova, 2004).

Investigations conducted in forest landscapes of Bulgarka Nature Park by Malinova (2010) showed that As content in single soil samples was above the maximum permitted level (MPL), which according to the criteria of Regulation 3 (MoEW, 2008) under definite conditions could disturb the soil functions thus leading to a threat to the environment and human health. In a recent study on the content of Pb, Cd, As and Hg in medicinal plants and grasslands on the territory of Bulgarka Nature Park we have detected exceedances for Pb, As and Cd content in *Festuca valida, Viola tricolor, Mentha pulegium, Holcus lanatus, Thymus* sp.*, Fragara vesca* , etc. (Bezlova et al., 2012). The elevated levels of heavy metals in

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these plants could be due to the natural geochemical background as no soil contamination because of aerosol depositions was established (Malinova, 2010).

The aim of the present pilot study was to determine sites with high soil content of heavy metals and As, which may lead to a risk to the environment and humans due to the translocation of these elements to other media.

Materials and Methods

Subject

Soils on the territory of Bulgarka Nature Park were analyzed. Samples were collected from sites where in a recent study we have detected elevated content of heavy metals in medicinal plants and pasture grasses. The grasslands are located in the flat ridge part of the park occupying altitudinal range 1250-1500 m –Ispolin Peak site (around 200 ha), Malusha site (14 ha) and Uzana site. The areas near the villages Potok and Ezeroto as well as Voditsi holiday village have limited possibilities for grazing due to the steep slopes of the Balkan Mountains and the small area of the grasslands.

Sampling sites

Mixed samples were taken from soil layers depending on the soil depth. The layers of the shallow soils (*Rendzic Leptosols)* were 0-10 cm or 0-20 cm whereas for deeper soils (*Haplic Luvisols* and *Cambisols*) they were 0-20 cm and 20-40 cm. In the largest grasslands, Malusha site and Ispolin Peak site, mixed samples were collected from points which were located 50 m far from each other in a transect with a total length of 400 m in east-west direction. A total of 21 samples were collected and analyzed. Sampling sites were coordinated by means of GPS. Sampling was carried out in late June, 2010 and 2012.

Analytical methods

For decomposition of the samples, we applied closed microwave digestion under pressure with acids ($HCl + HNO_3$, 3:1). The analyses were done using an atomic emission spectrophotometer with inductively coupled plasma. They were conducted in the licensed Central Laboratory for Chemical Testing and Control of the Ministry of Agriculture and Food in compliance with Bulgarian State Standards EN 14084:2003 and EN 13806:2003. The results were calculated on a soil dry weight basis.

Statistics

The parameters of the descriptive statistics (mean value, standard deviation, median, low 25% quantile and upper 25% quantile) were calculated using Microsoft® Office Excel 2003.

Results and Discussion

Malusha site occupies the flattest ridge part of the park and is a preferred place for grazing. Soil was *Rendzic Leptosols* developed on limestone. Its depth varied between 3 and 20 cm depending on the slope and the erosion processes which have had occurred. The major morphological characteristics of the soil include dark color (7.5YR 3/2 in a fresh state), fine granular structure, and sandy-clay soil texture. The soil material did not react with 10% HCl. Effervescence was observed only on the rock fragments.

The soil solution was neutral (pH_{H2O} = 7.08). The content of heavy metals and As is presented in Figure 1.

The mean value for Pb content in the soil was very high (183±141 $mg.kg^{-1}$DW). It exceeded both the background concentration for non-contaminated soils in our country (26 $mg.kg^{-1}$) and the maximum permitted levels for permanent grassland (130 $mg.kg^{-1}$) determined for soils with $pH_{(H2O)}$ 6.0 - 7.4 according to Regulation № 3 “Standards for admissible content of harmful substances in soils” (2008). There was considerable variability of the values for the 400 m transect which was evident from the big difference between the minimum (106 $mg.kg^{-1}$DW) and maximum (497 $mg.kg^{-1}$DW) measured values. The minimum value was very high and the maximum value was close even to the intervention concentration (500 $mg.kg^{-1}$) according to Regulation № 3, which suggests a risk to the environment and humans. The soil formation process in the undeveloped soils like *Rendzic Leptosols* is greatly influenced by the chemical composition of the bedrock. As no soil contamination as a result of aerosol depositions was established in the studied areas (Malinova, 2010), it can be concluded that this soil contains elevated nat-

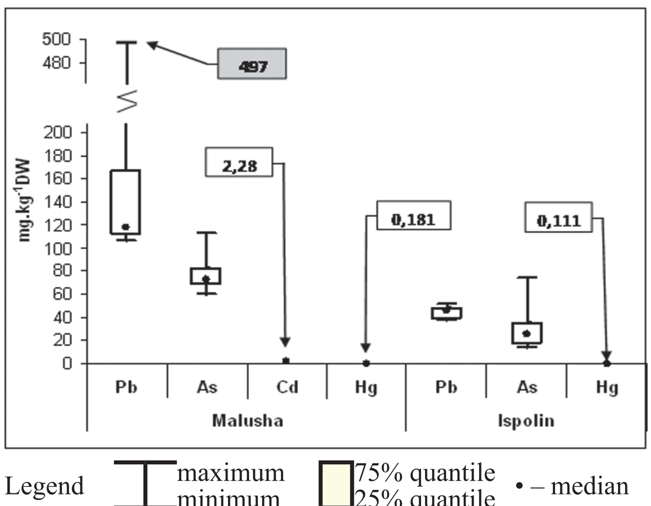

Fig. 1. Content of heavy metals and As in soils from Malusha site and Ispolin Peak site

ural content of Pb and the measured high Pb concentrations can be considered as naturally inherited from the bedrock. The standards for admissible content of harmful substances in soils defined in Regulation № 3 (2008) do not refer to soils with elevated natural content of heavy metals. This aspect of the Regulation should be interpreted in terms of the presence or absence of soil contamination by anthropogenic sources. It is also appropriate to use it as a criterion for assessment of the risk to the environment and humans in soils with elevated natural content of heavy metals, as this could make soil a potential source for contamination of other media due to the possibility for translocation of contaminants along the food chain leading to disturbances in its sanitary state.

The content of As in soils from Malusha grassland was also very high. The variability of the results was high with a mean value of 78±18 $mg.kg^{-1}$DW. In all sampling points the content of As exceeded 1.9-3.6 times the maximum permitted levels which may lead to a risk to the environment (Figure 1).

The content of Cd and Hg in Malusha site was below the detection limit with the exception of sample 1 taken from a sample point with the highest values for Pb and As. The content of Cd (2.3 $mg.kg^{-1}$DW) in this sample point almost reached the value for the maximum permitted level of 2.5 $mg.kg^{-1}$. In the same sample the content of Hg exceeded 2.5-fold the precautious value, but not the maximum permitted one. Our results showed accumulation of heavy metals in soils from definite parts of the grassland, the highest content being detected in its eastern part. Pb and As can be considered as sources of risk to the environment (Figure 2). It is recommended to perform soil mapping in this area and limit grazing within definite parts of the grassland.

The soil from the grassland on Ispolin Peak site is *Rendzic Leptosols* developed on limestone. The average profile depth was about 20 cm. The morphological characteristics of the soil profile were similar to those of Malusha grassland. Soil was dark in color (7.5YR 3/4 in a fresh state), with fine granular structure, sandy-clay soil texture. Effervescence in the presence of 10% HCl was observed only on the rock fragments. The soil solution was neutral. The mean Pb content in soil was 44±6 $mg.kg^{-1}$DW. It exceeded almost twice the background concentration for non-contaminated soils in our country. On the other hand, it was lower than the maximum permitted level (90 $mg.kg^{-1}$) for permanent grasslands. The variability of the values was less expressed compared to Malusha grassland (Figure 1). We did not detect concentrations of Pb higher than the maximum permitted levels in either of the sampling points on Ispolin Peak site. The mean value for As content in the soil (31±21 $mg.kg^{-1}$DW) was close to the maximum permitted levels (30 mg/kg^{-1} DW). The variability of the values was high (14-74 $mg.kg^{-1}$DW) (Figure 1). The measured values in three of the sampling points exceeded 1.1-2.4 fold the maximum permitted levels. Cd was under the detection limit while Hg was detected in only one sample with a value under the maximum permitted levels. For Ispolin Peak site, As can be considered a major source of risk to the environment and humans (Figure 3).

The content of heavy metals and As was determined in *Rendzic Leptosols* in Uzana site and the village Ezeroto (Figures 4 and 5). The profile depth in Uzana site was greater, at an average of 40 cm, which permitted sampling from two depths. In the surface soil layer the reaction was highly acidic (pH_{H2O} = 5.12), while at a greater depth soil was weakly acidic (pH_{H2O} = 6.42). Among the elements studied only As content was increased although in the surface soil layer it was below the maximum permitted level.

The concentration of As increased 1.7-fold in depth thus confirming our conclusion about the existence of enhanced natural geochemical background levels (Figure 4). In support of this conclusion were also the results for the region of the village Ezeroto where *Rendzic Leptosols* of 20-cm depth inherited As content of 107 $mg.kg^{-1}$DW from the bedrocks. The measured value was higher than the intervention level and was assessed as a threat to the environment. The content of Pb in the same region was also high although it was below the maximum permitted level (Figures 4 and 6).

On the territory of the park, *Cambisols* are also widespread. They are mostly occupied by forests, but can be also found in open spaces. Soil profile was established in natural

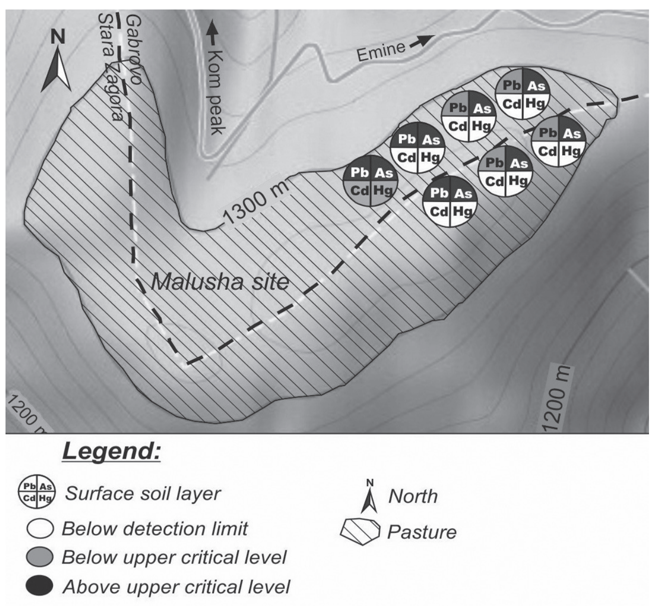

Fig. 2. Areas with elevated content of heavy metals and As in soils from Malusha site

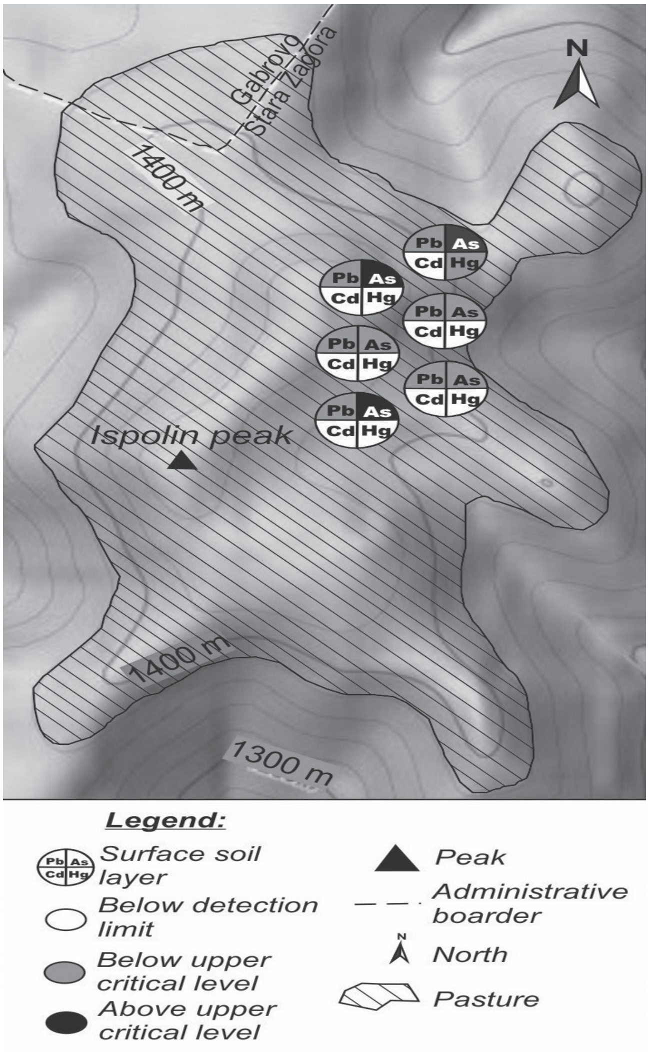

Fig. 3. Areas with elevated content of heavy metals and As in soils from Ispolin Peak site

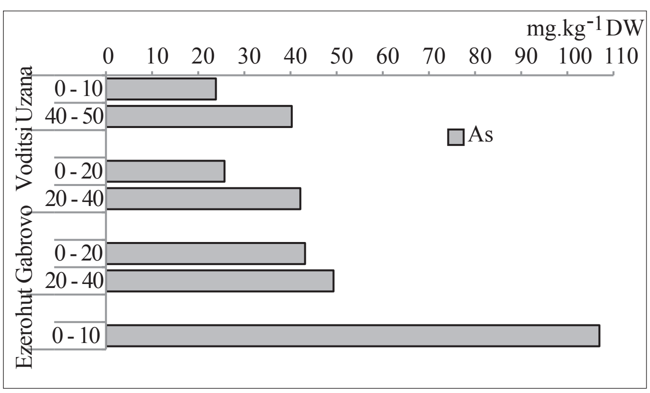

Fig. 4. Profile distribution of As content in soils

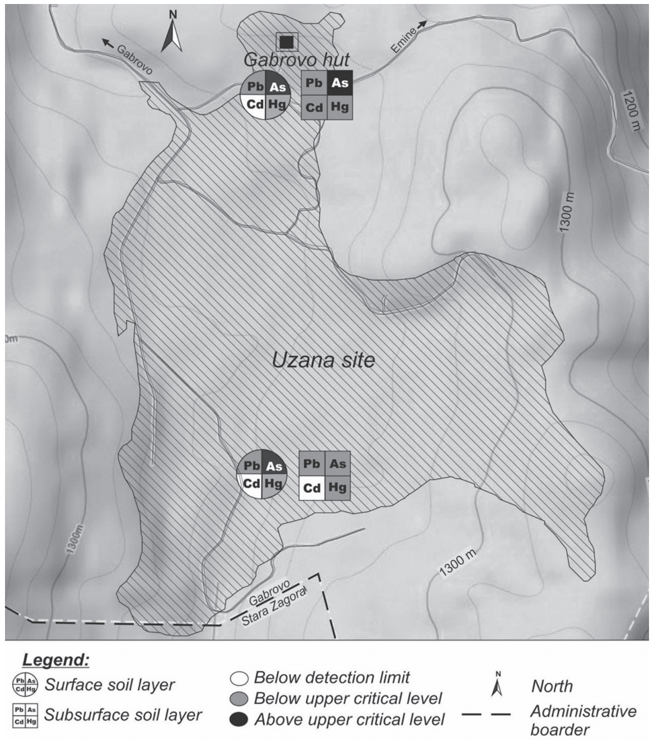

Fig. 5. Areas with elevated content of heavy metals and As in soils from Uzana site and in the region of Gabrovo hut

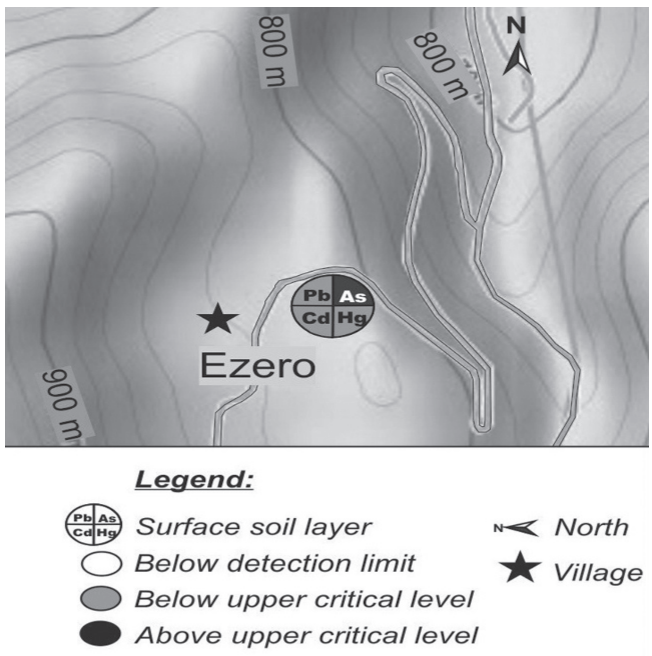

Fig. 6. Areas with elevated content of heavy metals and As in soils from the region of the village Ezeroto

grassland in the region of Gabrovo hut. The humus-accumulating horizon depth was about 20 cm. The color was light brown (7.5YR4/4). Soil was slightly moist, lacking soil structure, sandy-clay soil texture. The metamorphic horizon depth was about 35 cm. The soil color was lighter (7.5YR4/6). It has sandy-clay soil texture. Effervescence in the presence of HCl was not detected. The surface soil layer was highly acidic ($pH_{(H2O)}$ - 4.90). The only element exceeding the maximum permitted level in this profile was As (1.4-fold), (Figure 5).

Haplic Luvisols were also found on the territory of the park. They occupied a relatively small area in the lower forest belt. To investigate the content of heavy metals and As, soil profile was established near Voditsi holiday village. Soil sampling was done in *Haplic Luvisols* developed on limestone. Soil was eroded, but the soil profile was complete. The surface horizon was present and its depth was about 10 cm. Fresh soil was light brown in color (7.5YR4/4), with sandy-clay soil texture and well shaped granular structure. Effervescence in the presence of 10% HCl was observed only on the rock fragments. The alluvial horizon was above 40 cm in depth. It was thick with clay soil texture. The soil solution reaction was neutral (pH_{H2O} = 7.24). The content of all studied elements was below the maximum permitted level (Figure 7).

Similar to the other regions, the concentration of As increased with soil depth (Figure 4). In the surface 20-cm soil layer As concentration was 26 $mg.kg^{-1}DW$ whereas it increased to 42 $mg.kg^{-1}DW$ in the 20-40-cm layer.

The analysis of the profile distribution of the elements in soils with greater depth showed that Pb content in Voditsi holiday village did not change considerably with depth whereas in the other two sites, Uzana site and Gabrovo hut, it increased in the surface layers due to biogenic accumulation processes (Figure 8).

The assessment of the multiple enrichment of soils with heavy metals and As showed that in most regions high content of both elements was detected. In most cases the concentration of As was higher than that of Pb (Figure 9).

This is in contrast with the normal concentrations of these elements detected in non-contaminated soils. The observed trend confirms the leading role of As in soils as a source of contamination of the environment. The easy access to the regions studied and the use of plants grown on the park territory for medicinal and other purposes increases the risk for translocation of the toxic elements along the food chain. Further investigations are needed to confirm this conclusion including potential contamination of animal products.

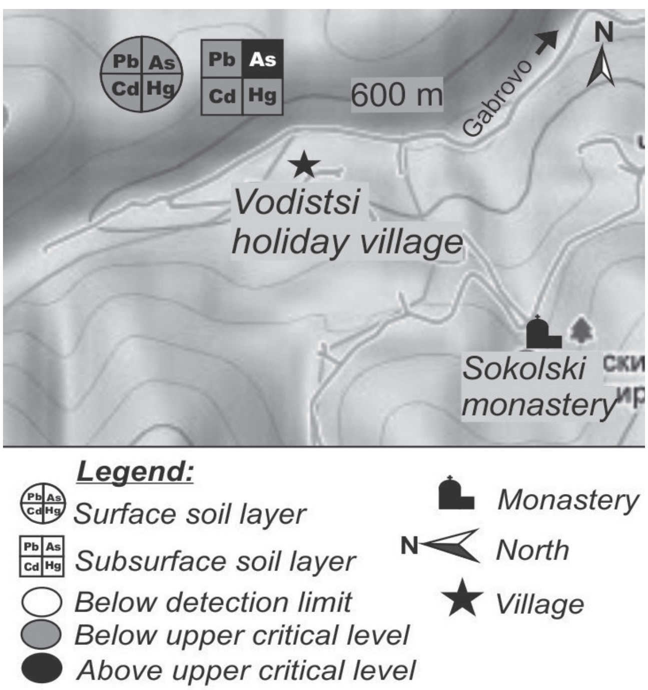

Fig. 7. Areas with elevated content of heavy metals and As in soils from the region of Voditsi holiday village

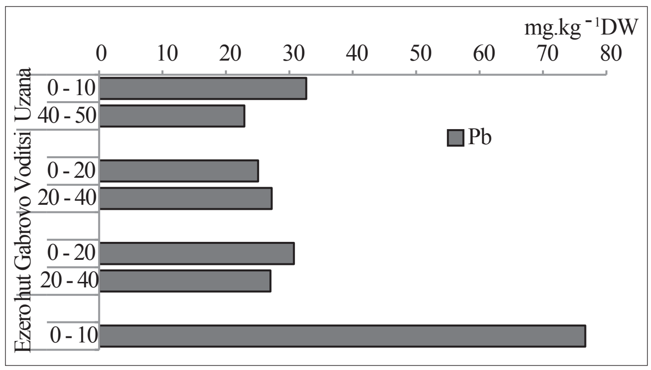

Fig. 8. Profile distribution of Pb content in soils

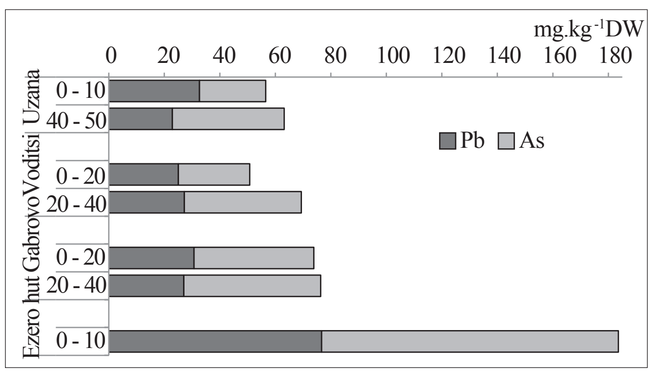

Fig. 9. Profile distribution of Pb and As content (in total) in soils

Conclusions

The analysis of the content of heavy metals and As in soils on the territory of Bulgarka Nature Park confirms the assumption that soils can be a source of contamination of medicinal plants and pasture grass species.

- The soils from Malusha site in whose eastern part the highest content of Pb, As and Cd was detected represent the greatest risk to the environment
- A source of risk to the environment could be considered also the elevated content of As in soils from the grasslands of Ispolin Peak site, the village Ezeroto as well as near Gabrovo hut.
- The results obtained in this study are new for Bulgarka Nature Park. They indicate the need for soil mapping in the large areas occupied by grasslands and application of restrictive land use regulations in definite sites.

Acknowledgements

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