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POLLUTION WITH ARSENIC AND HEAVY METALS OF SOILS AND SOME COMPONENTS OF THE FOOD CHAIN IN THE ENVIRONMENT OF GOLIAM BUKOVETS MINE TAILINGS IMPOUNDMENT, CHIPROVTSI MINING AREA, NW BULGARIA

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Abstract: The Chiprovtsi mining area is contaminated as a consequence of past mining. The 20-year existing of Goliam Bukovets mine tailings impoundment has affected all elements of its surroundings. As a result elevated concentrations of arsenic and heavy metals in upper soil layers and in grass are established. The low distributions of arsenic and heavy metals in depth allow assuming their low mobility which restricts their unfavourable environmental impact. The sheep's milk has elevated Zn and Cu contents and so it transfers them to the humans. The carry-over of Pb, Cd and As from grass to the milk is low. Metal concentrations in livestock's excrements are low and seem not to pose risk for secondary soil contamination if used as organic fertilizer. Although the tailings impoundment is almost recultivated and the dust pollution is finished the contaminated soils of the surroundings contain arsenic and heavy metals and continue to transfer them trough the food chain. Besides, the soil cover of the impoundment is not sufficient to avoid the penetration of grasses root to the mine tailings.

Keywords: arsenic, heavy metals, soil, plants, milk, Chiprovtsi mining area.

1. Introduction

Heavy metals and metalloids released from the mine wastes in mining areas are among the most important sources of environmental pollution.

The Chiprovtsi mining area is located in NW Bulgaria, 30 km W from Montana town (Fig. 1). The area is situated at an altitude from 900 to 400 m. The mean annual precipitation in the region is 756 mm/m^2 per year with maximum in the spring and minimum in the autumn (Koleva and Peneva, 1990). The mean temperature is 10.4^{o}C, the spring is wet and the winter is mild (Climatic reference book, 1983). The major soil type is strongly eroded grey forest soil (Koinov et al., 1998). The bedrock consists mostly of the rocks of the metamorphic diabase-phillitic complex (DPC) and comprises an alternation of diabase, diabasic tuffs, phillites, marbles, chlorite-sericite- and quartz-chlorite schist and diorite porphyrite. Diabasic tuffs and phillites are the most widespread rocks of this complex (Nikolaev and Tonev, 1961).

The mines in Chiprovtsi region are known to be exploited from Roman times, through Middle Ages, but most intensively from 1950 to 1999, when the last mine ceased its activities. Three types of deposits containing minerals of As, Pb, Zn and Cu have been exploited here: Pb-Zn-Ag Chiprovtsi deposit with main minerals galena, chalcopyrite, tetrahedrite and arsenopyrite (Dragov and Obretenov, 1974;Atanassov and Pavlov ,1982) has produced 4789.1 thousand t of Pb-Zn ore in the period 1951-1995 (Milev et al., 1996); Fe-As-Au Govezhda and Kopilovtsi deposits with main minerals arsenopyrite, galena, sphalerite, tennantite, proustite (Nikolaev and Tonev, 1961; Mladenova et al., 2003) have produced 1105.6 thousand t of ore with average Au content of 3.5 g/t, and 3863 kg pure gold (Milev et al., 1996); Fe-Mo Martinovo deposit with main minerals arsenopyrite, löllingite, chalcopyrite, molybdenite with 79 thousand t of Mo-ore production (Velchev, 1974, Tarasova,

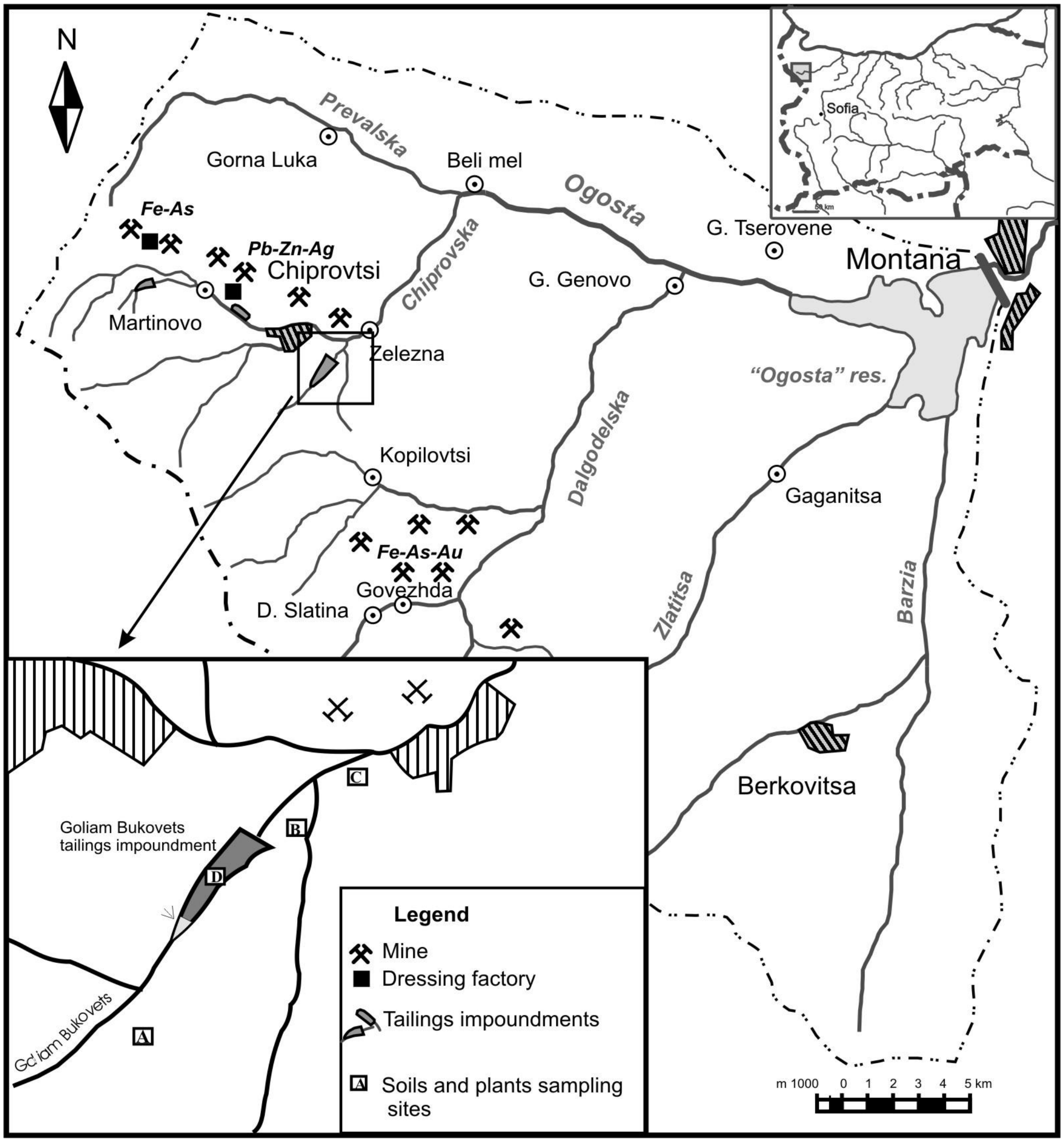

Fig. 1. The Ogosta River catchments and schematic map of the study area with location of sampling sites.

1987; Milev et al., 1996). As a result numerous waste rock dumps and 3.5 million tones mill tailings stored in 3 tailings impoundments are available in the region.

Remediation activities have been carried out in the region since 2000 year, which covered the three tailing impoundments, as well as numerous mine waste dumps. At present almost all mine waste dumps are partially or completely remediated.

The Goliam Bukovets mine tailings impoundment is the biggest one. It occupies a natural negative relief and has surface of approximately 0.16 km^2, volume of about 3.0 million tones and a maximal depth of about 70 m. The impoundment was the main place for the waste storage from the ore processing from the 3 types of deposits. The upper layer is composed only from the wastes of Martinovo deposit because it was the last closed mine in the region. The wall of the tailings impoundment is built up from the oreless massive waste produced by the dry magnitic separation of the iron ore in Martinovo factory (Vesselinov et al., 1996). The main minerals in the impoundment are calcite, siderite, quartz, chlorite, amphibole and magnetite. The sulphide minerals are less 5%, the most abundant are pyrite and arsenopyrite, and galena, sphalerite, chalcopyrite and fahl ore are rare (Mladenova and Zlatev, 2004).

The tailings in the impoundment remained dry and uncovered until 2001. The emission of dust from Goliam Bukovets tailings with high concentrations of mineral phases with As and heavy metals has impacted waters and river sediments and the agricultural fields and meadows used for farming and livestock breeding. In 2001 Goliam Bukovets tailings impoundment was covered with coating of a slowly soluble, non-reactive synthetic precipitate and about 30 cm of uncontaminated soil and Dutch clover was plant.

The aim of this study is to provide data concerning the contamination with As and heavy metals of soils, plants and some components of the food chain in the surroundings of Goliam Bukovets mine tailings impoundment in Chiprovtsi mining area, NW Bulgaria. The determination of their concentrations is important in assessing of their potential environmental impact.

2. Sampling and analytical methods

Sampling sites were chosen to include sites with background concentrations and sites with expected pollution. Samples were collected in August 2005. Figure 1 shows the location of the sampling points. Samples of primary ores as well as of the tailings were studied to assess the specific pollution sources.

Four soil profiles differing in their position and therefore metal concentration were sampled. The locations of the profiles are given in Figure 1.

The first profile (A) is located in meadow between agricultural fields at about 500 m SW from the impoundment and is considered as unpolluted background reference. It was sampled to a depth of 30 cm from three soil horizons in the following depths: A1- 0-2 cm, A2 - 2-12 cm; A3- 12-27 cm.

The second profile (B) is located at the water shed 100 m NE from the impoundment. It is situated on the main wind directions in the area and was affected by dust pollution during 20 years. The sampling was performed to a depth of 46 cm from four soil horizons in meadow without indication of tilling at least several decades. The following depth intervals have been studied: B1 - 0-3 cm; B2 - 3-13 cm; B3 - 13-23 cm; B4 - 23-34 cm; B5 - 34-46 cm.

The third profile (C) refers to an alluvial terrace on the right bank and 100 m far from Ogosta River and is located in an orchard 800 m NE from the impoundment and is supposed to be polluted through dust emissions as well as through the polluted river waters especially in the period before 1979 when the impoundment has been not yet constructed. The profile is sampled to a depth of 42 cm from three soil horizons. The depth intervals 0-5 cm, 5-12 cm, 12-18 cm, 18-30 cm and 30-38 cm have been analysed.

The forth soil sampling site (D) is from the soil cover of the impoundment and is considered as unpolluted one but its composition is important because it is a growth environment for the plants.

Stems of heterogeneous grasses from all points of soil sampling as well as Dutch clover stems from the surface of the recultivated impoundment were collected. In order to follow the contamination of the food chain livestock milk and excrements from the polluted areas were collected.

The bulk soil samples, grass and excrements were dried naturally. Soils were homogenized and dry sieved at 2 mm then at 63 μm mesh sizes in order to separate two soil fractions – less than 2mm (bulk sample) and less than 63 μm (fine fraction). The samples were then analysed by X-ray fluorescence spectrometry (XRFS) and by ICP- AES, AAS for their major-, minor and trace element contents. The grass and excrements were milled to powder and then analysed by ICP-OES.

The 500-ml raw milk samples were collected and held at 4^0C and arrived at the analytical laboratory within 48 h after their collection. The concentrations of arsenic, cadmium and lead were made by means of absorption spectrophotometer VARIAN AA220Z. Copper and zinc are analysed by IVP-AES. As a references the whole powder milk (RM 8435, National Institute of Standards and Technology, USA) were used.

The mineralogical compositions of selected samples from both soil fractions of the two contaminated soil profiles were determinate by powder X-ray diffraction.

A selected samples of polish samples of primary ores as well of tailings and soil were examined under the optical microscopy in order to characterize the mode of occurrence of As and heavy metals in the ore and in the tailings and the occurrence of secondary minerals concentrating the studied elements.

The pH values of soil samples were measured in the leachates consisting of boiled distilled water and soil in ratio 20 g soil:100 ml H_2O. The composite was shaken 30min and then leached for 1h.

3. Results and discussion

3.1. Soils

3.1.1. Bulk chemical composition

Soil's compositions reflect the composition of the parent rocks and are important of viewpoint for precipitation of secondary phases which potentially might concentrate the heavy metals and metalloids. MnO and P_2O_5 in all of the samples from the 3 profiles are below 1 wt %.

Fe_2O_3 contents in the samples from the two contaminated profiles are almost the same (mean 7.5 wt. % for profile B and 7.9 wt.% for profile C) and these contents are lower than Fe_2O_3 in the background profile (mean 10.13 wt.%).

Significant differences are established in the CaO content also. The two contaminated profiles show lower content (mean 0.9 wt. % for profile B and 1.9 wt. % for profile C) than the background profile (mean 3.6 wt.%).

SO_3 content in the samples from the three profiles is almost the same despite the two contaminated profiles should show higher concentration because of their air pollution with tailings dust.

The loss of ignition (LOI) reflects the content of free and fixed water in minerals and varies in the samples from profile B between 6.6 and 15.0 wt.% (mean 8.8 wt.%), in profil C – between 5.2 and 12.7 wt.% (mean 8.2 wt.%) and in the background profile-between 6.7 and 15.7wt.% (mean 6.8wt.%).

The contents of SiO_2, TiO_2, Al_2O_3, MgO, Na_2O and K_2O vary in narrow range. A close relation with the parent rocks is difficult to obtain because of the complex composition of the metamorphic complex.

3.1.2. As and heavy metals

The soils in the region have high As, Pb and Zn background contents because of the rocks and ore deposits.
The contents of Pb and Zn in the background profile (A) are lower than the maximum accepted concentrations (MAC) for soils with pH 6.2-7.0 by Bulgarian legislation; As vary around the MAC (MAC in mg/kg: As-25; Pb-80; Cu-255; Zn-330) (Instruction Nr.3 2004) (Fig. 2.A).

Arsenic in the two contaminated profiles and in the sample from the impoundment is over the MAC (Fig.2A, 2B). In profile B it varies between 515 and 65 ppm in the bulk sample and between 460 and less than 30 in the fine fraction. In profile C As contents in bulk sample are between 335 and less than 40 ppm and between 295 and 85 in fine fraction.

Cu is below the MAC values for Bulgaria in the both fractions from the two profiles and in the river bank sample and its concentrations vary between 101 to 58 ppm for profile C and between 92 and 69 ppm for both fractions of profile B (Fig. 2B, 2C).

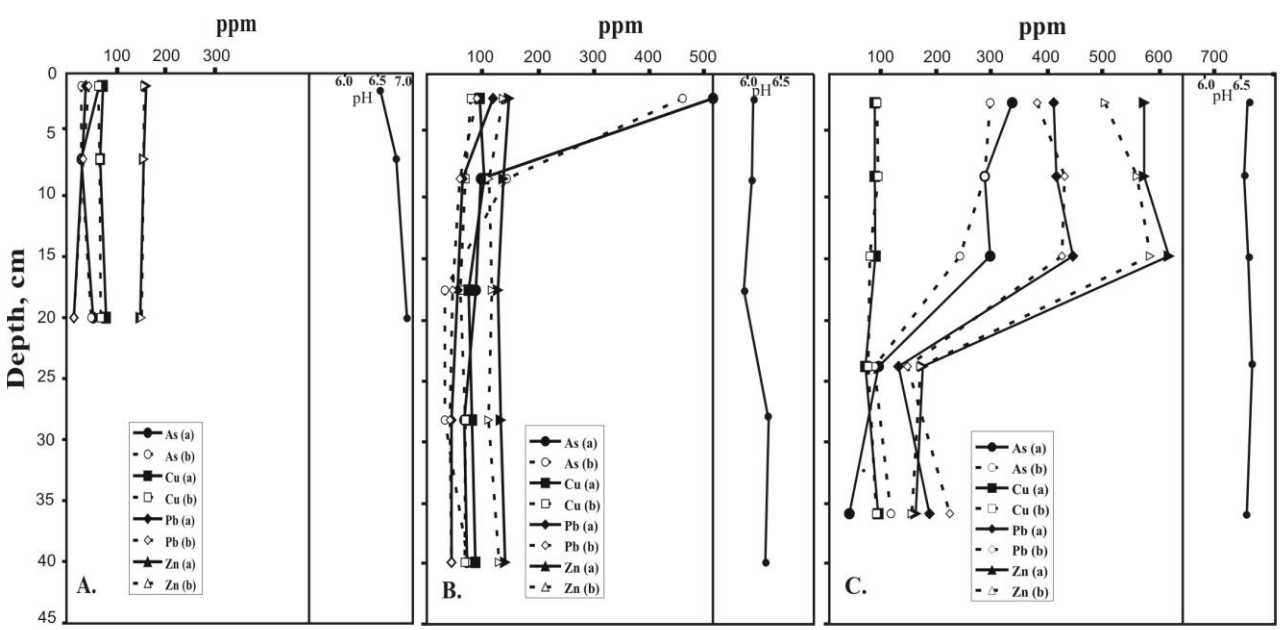

Fig. 2. As and heavy metals distributions and pH changes with depth in bulk (a) and fine (b) soil fractions: A. – *profile A* (background); B.- *profile B* (in meadow at the water shed 100 m NE from the impoundment); C. - *profile C* (in orchard 800 m NE from the impoundment).

Pb in both fractions of profile B is under and close to MAC (from 117 to 42 ppm in bulk sample and 88-39 ppm in fine fraction) (Fig. 2B). The concentrations in profile C are higher and above MAC in the range 445-129 ppm for bulk sample and 430-145 ppm for fine fraction (Fig. 2C).

Zn in the both fractions of profile B is under MAC (in the range 146-126 ppm for bulk sample and 135-109 ppm in the fine fraction (Fig. 2B). In profile C its contents are from 619 to 160 ppm for bulk sample and from 585 to 153 in fine fraction (Fig. 2C).

The two contaminated profiles show enrichment of As and heavy metals in the upper layers. In profile B the highest concentrations are found out in the upper 5 cm, because the contamination was performed by dust and the meadow has not been cultivated. In the alluvial river terrace (profile C) high concentration are established deeper (to 15-20 cm) probably because of the tilling or flooding by the contaminated Ogosta River. In depth 5-40 cm the values of the elements in profile B are almost constant and have concentration close to that in the background profile, while in profile C the values in the depth are higher.

3.1.3. pH and mineral composition

The pH values of soils are nearly neutral with some differences for each of the studied profiles (Fig.2A, 2B, 2C). In background profile (A) the pH values in the 3 sampled depths are as follow: A1-6.6, A2 – 6.7, A3 – 6.9. In the first profile with pollution (B) the pH values in the 5 depths are: B1 -6.0, B2 – 6.0, B3 – 5.9, B4 – 6.3, B5 – 6.3. In the second profile with pollution (C) the pH in the sampled are: C1 – 6.6, C2 – 6.6, C3 – 6.6, C4 – 6.7, C5 – 6.6. The highest pH values have the soil from the cover of the impoundment (between 7.8 and 7.9) which comes not from the surroundings.

The main minerals are quartz, K-feldspar, plagioclase and micas; montmorillonite and chlorite are less abundant. Organic matter occurs in all samples.

In the interval 30-38 cm of soil profile C solid brownish spots were observed. Optically well-shaped oxidised pyrite grains and iron oxides minerals were seen (Fig. 3a, b). No secondary arsenic and heavy metals-bearing minerals have been established. Arsenic in small amount has been determined by microprobe analyses in the iron oxides minerals.

3.2. Grass, milk, excrements

Arsenic and heavy metals can enter the food chain through the plants. Their concentrations in the grass of the background area (profile A) are (mg/kg): As - 0.6, Cd -0.17, Cu -4.64, Zn - 17.33, Pb - 0.6. The concentrations in the heterogeneous pasture grass from the surroundings of the contaminated profiles are (mg/kg): As - 7.0 in profile B, 16.2 in profile C, 3.8 in sample D; Cu - 6.3 in profile B, 14.6 in profile C, 5.2 in sample D; Pb - 1.2 in profile B, less than 0.5 in profile C, 0.5 in sample D; Zn - 27.6 in profile B, 52.5 in profile C, 9.0 in sample D; Cd content is under the detection limit of 0.05 mg/kg in all profiles. The Dutch clover from the recultivated beach of the impoundment contains As-1.7, Cu-6.1, Pb-1.4, Zn-13.6 and Cd - less 0.05. These concentrations are higher compared to their contents in Dutch clover from the polluted with heavy metals Zlatiza-Pirdop region in Srednogorie zone in Bulgaria (As-0.08, Cu-

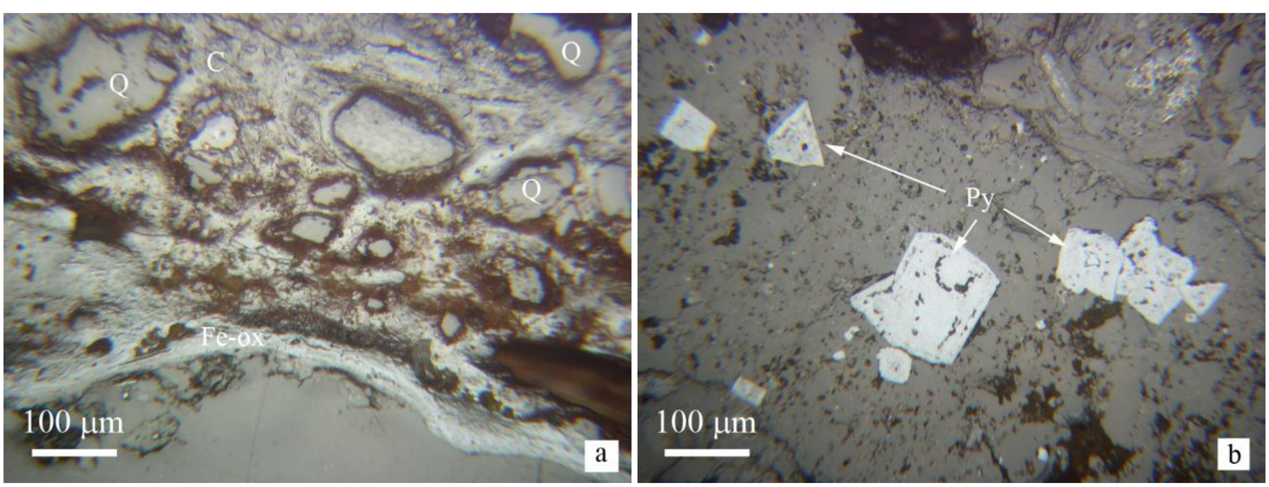

Fig. 3. Microphotographs of polish sections from brownish dense part of soil profile C (depth 30-38 cm). a. Iron oxides minerals (Fe-ox) embracing quartz (Q) and clay (C) particles; b. Well-shaped oxidised pyrite (Py) grains.

2.14, Pb-0.41, Zn-6.96, Cd-0.02) (Stojanov 1999).

As a link between soil and man sheep milk yielded from 200 sheep has been analyzed. The concentrations (in mg/kg) of Zn (6.75±0.11) and Cu (2.75±0.08) are higher than the MAC in foods according Bulgarian legislation (Instruction Nr.31 2004) (Zn-5.0; Cu-0.4). As (0.037±0.005), Pb (0.077±0.008) and Cd (0.005±0.001) are lower than MAC (As-0.05; Pb-0.1; Cd -0.01). These values are higher compared to the sheep's and goat's milk in the area (Kotsev et al. 2009). The low Cd concentration in milk is due to the low concentration of the element in soils as well as to its accumulation in liver and kidney (Prankel et al. 2004) and to the low carry-over to the milk (Blüthgen 2000). Lead concentrations in milk are usually much lower than blood levels and animal tissues with the highest concentrations of Pb are liver, kidney and bone (Biehl and Buck 1987).

The excrements are an integral part of the bio-circle. The concentration of the studied elements in the excrements of the same sheep is (in mg/kg): As -13.2±0.8; Zn - 61.7±0.6; Cu – 20.4±1.9; Pb – 4.9±0.3; under the detection limit are Sb (0.5) and Cd (0.05). The concentrations of the elements in the cow's excrements collected on the recultivated beach are: As (8.1±0.5); Zn - (45.9±0.4); Cu – (22.6+2.0); Pb – (4.6+0.3); Sb and Cd are under the detection limit, too. According to EFSA (2005) in mammalian species inorganic arsenic is converted into methylated metabolites, which are rapidly excreted compared to other organic arsenic compounds. The high As contents in sheep's and cow's excrements and the ratios $C_{es}(C_{ec})/C_{soils}(C_{grass}, C_{Dutch\ clover})$ support these statement (Tab. 1). Metal concentrations in both cow's and sheep's excrements are lower than MAC for soils and much lower than the local background and seem not to pose risk for secondary soil contamination if used as organic fertilizer.

The real risk for human health is connected with the plants capability to extract elements from the contaminated soil and to deliver it to milk. The calculated ratios are given in table 1. They show that As is absorbed with low intensity from grass which restricts its transfer to the next element of the food chain.

The grasses and the Dutch clover have extracted most intensively Zn, Cu and Pb and the relations C_{soil}/C_{grass} and $C_{soil}/C_{dutch\ clover}$ give an idea for their bio-absorption capability. The absorption capability of grasses in background part and of Dutch clover on the beach decreases as follows: Zn>Cu>Pb>As and Zn>Cu>As>Pb for the grass of the pasture grounds in the contaminated areas and the beach, relatively.

According to Sirotkin et al. (2000) the ratio $C_{milk}/C_{soil}(C_{grass}, C_{Dutch\ clover})$ indicate the rate of transfer of As and heavy metals from soil and grasses to the milk. The calculated transfer capability in this study decreases in the following order: Zn>Cu>Pb>Cd>As.

Table 1. Ratio between the concentrations of elements in soil, milk, plants and livestock's excrements.

Ratios		***As***	***Cu***	***Pb***	***Zn***	***Cd***
Cgrass/Csoil	bulk	0.02	0.05	0.006	0.05	n.d.
	fine	0.03	0.06	0.006	0.06	n.d.
Cdc/Csoil	bulk	0.01	0.06	0.02	0.08	n.d.
	fine	0.01	0.07	0.02	0.09	n.d.
Ces/Csoil	bulk	0.07	0.19	0.063	0.37	n.d.
	fine	0.09	0.23	0.06	0.43	n.d.
Cec/Csoil	bulk	0.05	0.22	0.06	0.28	n.d.
	fine	0.05	0.26	0.06	0.32	n.d.
Ces/Cgrass		3.47	3.92	9.8	6.86	1
Ces/Cdc		7.76	3.34	3.5	4.54	1
Cec/Cgrass		2.13	4.35	9.2	5.11	1
Cec/Cdc		4.76	3.70	3.29	3.38	1
Cmilk/Csoil (x100)	bulk	0.020	2.67	0.1	4.11	n.d.
	fine	0.024	3.13	0.09	4.72	n.d.
Cmilk/Cgrass (x100)	-	0.97	52.9	15.4	75.1	10
Cmilk/Cdc (x100)	-	2.18	45	5.5	49.7	10

Abbreviations: C- concentrations, dc- Dutch clover, es – sheep's excrements, ec-cow's excrements, n.d. – not detected.

4. Conclusions

The 20 years existing of Goliam Bukovets mine tailings impoundment has affected all elements of its surroundings. As a result elevated concentrations of arsenic and heavy metals in upper soil layers and grass are established.

The low distribution of arsenic and heavy metals in depth of soil profiles indicate their low mobility which restricts their unfavourable environmental impact.

Although the tailings impoundment is almost recultivated and the dust pollution is finished the contaminated soils of the surroundings contain arsenic and heavy metals and continue to transfer them to the food chain. The sheep milk has elevated Zn and Cu contents and so it transfers them to the humans. The carry-over of Pb, Cd and As from grass to the milk is low. Metal concentrations in livestock's excrements are low and seem not to pose risk for secondary soil contamination if used as organic fertilizer.

The soil cover of the impoundment is not sufficient to avoid the penetration of grasses root to the mine tailings and this causes the contamination of the grasses on the surface of the recultivated impoundment. A favourable circumstance is the presence of carbonate minerals in the ore (in the host rocks and as gangue) as well as in the tailings and in soils which increases the pH and avoids acid mine drainage.

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