Environmental impact of the Golyam Bukovets tailings pond on the soils, plants and some elements of the food chain, Chiprovtsi mining area, NW Bulgaria

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Introduction

Mine waste containing heavy metals and metalloids is one of the main sources of environmental pollution. Soils are known to accumulate heavy metals and metalloids transferring them further into the grasses and through the livestock into the people. The aim of this study is to provide data concerning the contamination with As and heavy metals of soils, grasses and some components of the food chain in the surroundings of the Golyam Bukovets tailings pond from the Chprovtsi mining region.

Site description

Mining activity in the Chiprovtsi region from 1951 to 1999 left waste rock dumps and 3.5 Mt of waste stored in 3 tailings ponds. The Golyam Bukovets tailings pond is the largest one. It is the main site for waste storage from the ore processing of 3 types of deposits: *Pb-Zn-Ag, Fe-As* and *Fe*. It is situated at an altitude of 500 m between Chiprovtsi and Zhelezna and located in a natural negative relief. Its area occupies approximately 0.6 km^2 and the total amount of waste is about 30 Mt. In 2001 the Golyam Bukovets tailings pond was covered with a coating of an insoluble, non-reactive synthetic precipitate and about 30 cm of uncontaminated soil and Dutch clover was plant.

Sampling and analytical methods

Sampling and description of soil profiles

The dust emissions from the Golyam Bukovets tailings pond, containing high concentrations of phases enriched in As and heavy metals, have impacted agricultural areas and meadows used for farming and livestock breeding, waters and river sediments. Soils and grasses from the background and contaminated areas in the surroundings of the tailings pond were sampled for the aims of the present study.

Three soil profiles differing in their position and therefore metal concentration were sampled.

The **first** profile (1) is located in a meadow between agricultural fields at around 500 m SW from the tailings pond and is considered to be unpolluted background reference. It was sampled to a depth of 30 cm from three soil horizons.

The **second** profile (2) is located at the water shed between two neighbor hills 100 m NE from the tailings pond. It is situated on the main wind directions and has been affected by dust pollution during the last 20 years. The sampling was performed to a depth of 30 cm from four soil horizons in the meadow which has not been tilled more than 40 years.

The **third** profile (3) refers to an alluvial terrace on the right bank and 100 m far from Ogosta River. It is located in a fruit-tree garden 800 m NE from the tailings pond and is supposed to be polluted by dust emissions and impure river waters especially in the period before 1979 when the tailings pond had not been constructed yet. The profile was sampled to a depth of 40 cm from three soil horizons.

The **forth** sample (4) is from the soil cover of the tailings pond and is considered to be unpolluted. Being a growth environment of the grasses, it is important as reference for the present study.

The bulk soil samples were dried naturally, homogenized and dry sieved at 2 mm and 63 μm mesh sizes in order to be separated two soil fractions — less than 2 mm and less than 63 μm. The first fraction will be referred as a bulk sample and the second one — as a fine fraction.

Heterogeneous grasses from the four points of soil sampling as well as Dutch clover from the beach of the tailings pond were collected. In order to follow the contamination of the food chain, livestock's milk and excrements from the polluted areas were collected.

Analytical methods

The mineralogical compositions of the selected soil samples were determined by a powder X-ray diffraction. Chemical analyses of the both fractions from the four profiles were determined by X-ray fluorescence spectroscopy (XRF). Heavy metals and metalloids in soils and milks were analyzed additionally by ICP-AES and AAS.

Results and discussion

Soils

The soils from the region are characterized by high As, Pb and Zn background contents due to the adjacent rocks and ore deposits. The contents of these elements in the **background profile** (1) are higher than the maximum accepted concentrations (MAC) for soils with pH 6.2-7.0 by the Bulgarian legislation (MAC in mg/kg: *As*-25; *Pb*-80; *Cu*-255; *Zn*-330) (Instruction No 3, 2002) (fig. 1A).

As in the two contaminated profiles and in the beach sample exceeds the MAC. In profile 2 it varies between 515 and 65 ppm, in the bulk sample, and between 460 and less than 30, in the fine fraction. In profile 3 the *As* content in the bulk sample is between 335 and less than 40 ppm, and in the fine fraction — between 295 and 85 ppm.

Cu is below the MAC values for Bulgaria in both the fractions from the two profiles and in the beach sample. Its concentrations vary between 101 and 58 ppm, for profile 3, and between 92 and 69 ppm, for both fractions of profile 2.

Pb in both fractions of profile 2 is below and around the MAC (from 117 to 42 ppm, in the bulk sample, and 88-39 ppm, in the fine fraction, respectively). The concentrations in profile 3 are higher and exceed the MAC values (445-129 ppm, for the bulk sample, and 430-145 ppm, for the fine fraction).

Zn in both the fractions of profile 2 is below the MAC (146-126 ppm, for the bulk sample, and 135-109 ppm, in the fine fraction). In profile 3 the *Zn* contents vary from 619 to 160 ppm (bulk sample) and from 585 to 153 (fine fraction).

The two contaminated profiles showed enrichment of As and heavy metals in the upper layers (fig. 1B, C). In profile 2 high concentrations were found in the upper 5 cm because of dust contamination and absence of cultivation of the meadow during the last 40 years. In the alluvial terrace (profile 3) high concentrations were established at a deeper level (up to 15-20 cm) probably because of tilling or flooding by the contaminated Ogosta River. At a depth of 40 cm the concentrations of the elements in profile 2 are almost constant and close to the background values, while in profile 3 they are higher in depth.

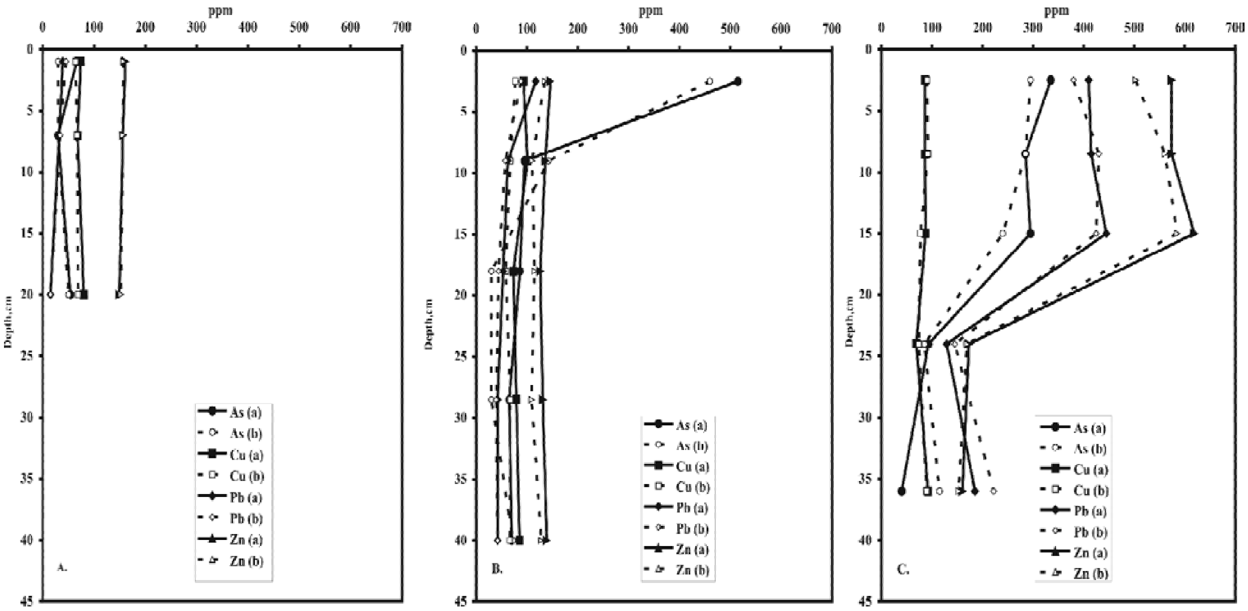

Fig. 1. As and heavy metals distributions in: **A)** — *profile 1* (background); **B)** — *profile 2* (meadow at the water shed, 100 m NE from the tailings pond); **C)** — *profile 3* (fruit-tree garden, 800 m NE from the tailings pond)

Table 1. Elemental ratios in the studied samples from the region of the Golyam Bukovets tailings pond

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

Abbreviations: s — soil; es — sheep's excrements; ec — cow's excrements; g — grasses; m — milk; dc — Dutch clover; n.d. — not detected

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

A number of secondary As- and heavy metals-bearing minerals have been established. As in small amounts has been determined also in iron-oxide minerals.

Grasses, milk, excrements

As and heavy metals can be involved in the food chain through the **plants**. Their concentrations in the grass from the background area (profile 1) are, as follows (mg/kg): *As* — 0.6, *Cd* — 0.17, *Cu* — 4.64, *Zn* — 17.33, *Pb* — 0.6. The values in the heterogeneous pasture grass from the surroundings of the contaminated profiles are (mg/kg): ***As*** — 7.0, in profile 2; 16.2, in profile 3; 3.8, in sample 4; ***Cu*** — 6.31, in profile 2; 14.64, in profile 3; 5.2, in sample 4; ***Pb*** — 1.2, in profile 2; less than 0.5, in profile 3; 0.5, in sample 4; ***Zn*** — 27.6, in profile 2; 52.5, in profile 3; 8.99, in sample 4; ***Cd*** content in all profiles is lower than the detection limit of 0.05 mg/kg. The Dutch clover from the reclamed beach of the tailings pond contains *As* — 1.7, *Cu* — 6.11, *Pb* — 1.4, *Zn* — 13.58, and *Cd* — less than 0.05. These concentrations are higher than in the Dutch clover from the Zlatitsa—Pirdop region (*As* - 0.08, *Cu* — 2.14, *Pb* — 0.41, *Zn* — 6.96, *Cd* — 0.02) (Stojanov, 1999).

As a link from the soil to the man, a sheep's **milk** from a herd of 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 (*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).

The **excrements** are an integral part of the biocircle. The concentrations of the studied elements in the sheep's excrements, the milk of which was analyzed, are (in mg/kg): *As* — 13.2±0.8; *Zn* — 61.7±0.59; *Cu* — 20.41±1.90; *Pb* — 4.9±0.3; *Sb* (0.5) and *Cd* (0.05) — under the detection limit. The concentrations of the elements in the cow's excrements, collected from the reclamed beach, are, as follows: *As* — 8.1±0.5; *Zn* — 45.94±0.41; *Cu* — 22.61±2.05; *Pb* — 4.6±0.3; *Sb* and *Cd* — under the detection limit. The metal concentrations in both cow's and sheep's excrements are lower than the MAC values for soils and much lower than the local background, so it seems to be not dangerous for a secondary soil contamination if used as an organic fertilizer.

The real risk for men's health is related to the plants capability to extract elements from the contaminated soil and to transport them into the milk. The calculated relations are given in Table 1. They show that *As* is absorbed with a low intensity from the grass which restricts its transfer to the next element of the food chain. The grasses and the Dutch clover extracted most intensively *Zn, Cu* and *Pb*, and the *Cs*/*Cg* and *Cs*/*Cdc* ratios give idea for their bioabsorption capability. The adsorption capability of grasses in the background part and the Dutch clover from the beach decrease, as follows: *Zn*>*Cu*>*Pb*>*As*. For the grasses from the pasture-grounds of the contaminated parts and the beach the relation is: *Zn*>*Cu*>*As*>*Pb*.

According to Sirotkin et al. (2000) the *Cm/Cs(Cg, Cdc)* ratios indicate the transfer rate of *As* and heavy metals from soil and grasses to the milk. The calculated transfer capability in this study decreases, as follows: *Zn>Cu>Pb>Cd>As*.

Conclusions

During its 20 years existence, the Golyam Bukovets tailings pond has affected all elements of its surroundings. As a result, elevated concentrations of As and heavy metals in the upper soil layers and in grasses are established.

The low distribution of *As* and heavy metals in depth allows to assume their low mobility, thus restricting their unfavorable environmental impact.

The sheep's milk is characterized by elevated *Zn* and *Cu* contents transferred further into the men.

Although the tailings pond is almost reclamed and the dust pollution is stopped, the contaminated soils around contain *As* and heavy metals and continue to transfer them into the food chain. Besides the soil cover of the tailings pond is not sufficient to avoid the penetration of the grasses root to the mine waste.

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Екологично влияние върху почвите, растенията и някои елементи от хранителната верига на хвостохранилище Голям Буковец, Чипровски минен район, СЗ България

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Резюме. Анализирани са геоекологичните последствия от въздействието на хвостохранилище Голям Буковец върху прилежащите му ландшафти и ефекта от извършената рекултивация. Изследвано е замърсяването на почви и растителност в 4 пункта (един фонов, 2 със замърсяване и един от плажа на хвостохранилището), както и на мляко и екскременти от овце и крави на паша в района.

Анализирани са концентрациите на елементи в две фракции на почвите: валова проба (под 2 mm) и фина фракция (под 63 μm). Съдържанията на ***As*** в двата профила със замърсяване и в плажа са над максимално допустимите концентрации (ПДК). ***Cu*** е под ПДК, ***Pb*** е под и малко над ПДК, ***Zn*** в профил 2 е под ПДК, а в профил 3 съдържанията варират и достигат стойности над ПДК. В условията на замърсяване на хвостохранилището по въздуха максимални концентрации на елементите са налице в първите няколко сантиметра на почвения профил и не е установено придвижването им в дълбочина. Под въздействието на праховото замърсяване и заливането или поливането със замърсени речни води в профила от заливната тераса на р. Огоста (профил 3) се наблюдават високи съдържания и на по-голяма дълбочина при рязко понижение под 15—20 cm, което е признак за слаба подвижност на вредните компоненти и в речната тераса.

В овчето мляко концентрациите на *Zn* и *Cu* са над ПДК, а на *As*, *Pb* и *Cd* — под ПДК.

Опасността за човешкото здраве е свързана със способността на растенията да извличат елементи от замърсената почва и по този начин да ги включват в хранителната верига. Коефициентът на биологично поглъщане показва слабо до много слабо захващане на изследваните елементи от тревната растителност. Редът на биологично поглъщане за тревите от фоновия участък и бялата детелина от плажа е с последователност *Zn>Cu>Pb>As*, а на интегралната тревна растителност от замърсените участъци и от плажа — *Zn>Cu>As>Pb*.

Степента на предаване на *As* и тежки метали от почвата към тревите и млякото намалява в реда *Zn>Cu>Pb>Cd>As*.