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ASSESSMENT OF THE AGRICULTURAL SOILS POLLUTION BY HEAVY METALS IN PROBISHTIP REGION, REPUBLIC OF MACEDONIA

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SYNOPSIS

The fact is that the metallurgical activities cause the most serious impact on the environment as whole (air, water, soil).

Within this paper we present the data after inspection of the soil quality in the surrounding of the metallurgical complex “Zletovo”, Probishtip. The attention was focused on the presence of the heavy metals in as-explored agricultural fields that actually provide different nutrition products for the local population as well as the wider population in the country.

Content of Pb, Zn, Al, Cr, Cd, Cu, Hg, Ni and As was continuously determined by ICPA-AAS method, on 18 controlling points in the investigated region pointed to the enormous soil pollution i.e the multiple transgression of the values prescribed by the EU rules for the soil quality.

INTRODUCTION

The Dangerous Substances Directive of the European Union (76/464/EEC) [1] defines all toxic, persistent or/and bio-accumulative substances as dangerous substances. Having in mind that heavy metals are elements (cannot be broken down) they persist in the environment for unlimited period showing tendency towards accumulation in the environment. The main anthropogenic source of heavy metals is metallurgical activities that can give rise to elevated concentration of metals relative to the natural background values. Heavy metals exert their toxic effects entering biochemical reactions in the organisms and typical responses are growth inhibition, suppression of oxygen consumption as well as the reproduction cycle impairment.

Site description and investigations poinst determination

The community of Probishtip enlarges on 3;25 km2 in eastern part of the Republic of Macedonia. The population (16 193 inhabitants or 50 c/ km2) is mainly engaged by agriculture products production - 40% from the total land is agricultural

soil while 38% belongs to pastures. The other activities of the populatiin is seen their work within the mine complex “Zletovo”, the biggest producer of lead-zinc concentrate in Balkan Peninsula. Despite the immanent business success of the mine complex the obvious unvanted impacts on the surrounding environment could not be neglected.

The pollution by waste from hydro-flotation stage at mining complex “Zletovo” dates from the very start of mine exploitation (1945), when the production activities were characterized by the most expressed capacity, however the existing acts prescribing waste disposal were not properly respected. Existing regulations determining disposal of the techno-gene waste material were not very clear thus, subsequently, global environmental problems appeared. Furthermore, monitoring and prescription for techno-gene waste disposal were inadequate. Preliminary investigations of serial of soil samples point to very high concentration in Pb, Zn, Cd, Cu, Ag and Hg [2].

Analysis of the soil quality on the bands down-stream of the Kiselicka river points to high concentration in heavy metals. The main source of this degradation is passive waste site by mining complex “Zletovo” but the non-controlled application of agrochemicals could be taken as pollution contributors as well. The fact that the disturbance in the soil quality is caused by non-controlled action of as-deposited flotation waste is manifested by the yellowish color of the Kiselicka river waters.

The general consideration on the high pollution of land and soil along the river Kiselicka and Zletovska river is visible through the change in soil color to orange-brown that outlines the effects of pollution after the big accident at the flotation waste material release 1975) [3, 4].

The real area of soil pollution extends on surface of ~ 500-700 ha, along the Kiselicka river, from the waste-site Kiselica to its entry to Zletovska river, in the length of ~5,5 km and wide 200-500 m. The high concentration in heavy metals in the Valley of Zletovska River is evident on the surface area of 4 km2 approximately. In this region we constructed the investigations network locating 17 measuring points (MP’s) in the distance between Lozovo to Zletovo.

EXPERIMENTAL

Multiple samples have been collected on a standard way and further analyzed. All analyses were performed according to the ISO 11047 standard, while concentration of particular element were determined by procedure of AAS and ICP-AES. The amount of element As in the soil texture have been determined according to ISO 11 466 standard.

RESULTS

All obtained results in regard to the actual soil contamination by heavy metals are presented in Table 1, as average values.

Table 1. Presence of heavy metals in agricultural soils in the Probistip region (mg/kg)

MP	Pb	Zn	Cu	Co	Ni	Fe	Cd	As	Cr	Mn
Lozovo	30.0	61.0	32.0	21.0	161.0	31330	1.0	5.0	235.0	1370.0
Puzderci	92.0	60.0	17.0	15.0	29.0	40600	2.0	5.0	80.0	979.0
Topolo	45.0	61.0	17.0	13.0	28.0	41610	2.0	-	47.0	447.0
Bosilkovec	50.0	72.0	26.0	17.0	90.0	33870	2.0	-	197.0	1010.0
Casa	32.0	66.0	15.0	14.0	25.0	44520	2.0	-	30.0	905.0
Pat: Petrisino-Neokazi	180.0	130.0	27.0	14.0	23.0	42920	2.0	-	65.0	1172.0
Pat:..Buciste-. Petrsino	202.0	55.0	15.0	18.0	20.0	42570	2.0	-	46.0	1277.0
Petrisino	49.0	79.0	59.0	19.0	22.0	46960	2.0	-	33.0	952.0
Strmos	90.0	54.0	24.0	12.0	32.0	26940	2.0	5.0	54.0	1317.0
Naskazi-Rastavci (1)	60.0	8.0	38.0	15.0	23.0	45780	3.0	6.0	26.0	1290.0
.Naskazi-.Rastavci (2)	74.0	966.0	30.0	18.0	23.0	37110	2.0	120.0	25.0	1385.0
Ratavci-Strmos (1)	157.0	102.0	94.0	23.0	23.0	52130	2.0	52.0	23.0	2125.0
Rastavci- Strmos (2)	223.0	102.0	87.0	20.0	24.0	51850	3.0	10.0	29.0	1510.0
Ratavici-Zletovo (1)	53.0	59.0	49.0	10.0	22.0	35280	2.0	5.0	44.0	725.0
Ratavici-Zletovo (2)	61.0	80.0	41.0	11.0	78.0	41610	1.0	5.0	55.0	770.0
Ratavici-Z;letovo (3)	61.0	121.0	42.0	27.0	190.0	39770	2.0	138.0	364.0	1132.0
.Rtavici-Zletovo (4)	53.0	73.0	55.0	9.0	23.0	35160	2.0	5.0	37.0	910.0

^Symbols from (1)- (4) assign the different points at the same location within the investigation network

The presented data point to the very high concentration in Ni and Cr in soils at MP: 1, 4 and 18, traditionally known as agricultural fields for vegetables and vineyards.

On the terrains between Lozovo and Strmosh (MP: 1,6, 8, 10, 13, 14), exceeding amount of Pb was evident. The higher amount of As was considered only at the MP's: 12 (120 mg/kg) ; 13 (52 mg/kg) and 18 (138 mg/kg).

According to data presented in Table 1. , we could consider followings:

- The concentration level for Al on the soil surface shows small difference at the investigated site, however around the mine complex "Zletovo" Al concentration is much higher. The Al amount on the waste - site "Kiselica" is relatively low because the silicate minerals are insignificantly present in flotation waste sediment;

- The concentration of Sb is very similar to those of Al. In the flotation waste material the concentration of both of these elements is lower than MAV;

- The region of the surrounding of the mine complex "Zletovo" and down-stream of the Kiselicka river manifest high amount of heavy metals- higher than 100 mg/kg. It seems that the mine surrounding is most possibly affected by mineralization, while the soil profile along Kiselicka river is disturbed by the ecological catastrophe (flotation waste material overflow (1972));

- The concentration value of Be is several times lower comparing to the lower detection limit (LDL) as it is the case with Bi;

- The investigated region (mining complex “Zletovo” and along the Kiselicka river) is characterized by high values in Zn concentration ranging from 500 – 956 mg/kg, most possibly due to mineralization and recent accident. The soil along the Zletovska river contains as well high concentration of Zn (488 mg/kg);

- The concentration values for Cd in the region of the mine complex “Zletovo” and along the Kiselicka river exceed the lower detection limit (LDL), reaching the numbers of same magnitude as stated for Zn;

- Although the values of Co concentration in the soil and barren do not differ significantly, the highest value of 29 mg/kg has been considered in the area of the town of Kotchani;

- The amount of Fe in barren on the waste-site is slightly higher comparing to those in the soil;

- Generally, the soil exhibits Mn in the amount of 0,01%, that suggests that the whole location is naturally reach in Mn;

- The highest value in Ni concentration (101 mg/kg) has been registered in the town of St. Nikole, however this fact proves the similar distribution as it was previously discussed for Co, Fe and Cr;

- The soil, generally, contains high concentration of lead (Pb). The effect is especially pronounced in the surrounding of the mine-complex “Zletovo” and along the Kiselicka river where the Pb content ranges to relatively high values up to 487 – 2.241 mg/kg, undoubtedly as the result of mineralization including the consequences of the overflow of the flotation barrens. These registered high value are typical to the values characteristic to Cd, Cu, Mn, Mo and Zn;

- The Ag content in the soil around the mines as well as along the Kiselicka river is relatively high (1-6 mg/kg), that could be ascribed to the mineralization and flotation barrens overflow, however comparable to Zn, Cgd, Cu, Mn and Pb distribution;

- All registered values of Tl concentration in the soil are lower than the LDL;

- Ti content is in the range of <3 – 21 mg/kg. Higher values are not registered even in the mine surroundings and are of magnitude order comparable to Al content;

- V, Se and Hg are present in low amount, lower than the LDL;

- As could be found evident in the soil along the Kiselicka river where the concentration ranges between 49 and 169 mg/kg that is most probably due to the mineralization and flotation barren overflow. This situation could be compared with the values considered for Zn, Cd, Cu, Mn, Mo, Pb, Ag and Hg.

Since the presence of lead and zinc in agricultural soils in Probistip region is of the most crucial importance, we turned the further attention to these two heavy metals illustrating their distribution in Figures 1 and Figure 2, respectively.

It is obvious that peak concentration value for Pb is registered at the MP’s Puzderci (92 mg/kg); Petrisino-Neokazi (180 mg/kg); Buciste-Petrisino (202 mg/kg); Ratavici-Strmos (1) (167 mg/kg) and Ratavici-Strmos (2) (223 mg/kg), usually agricultural fields for production vegetables and vineyards. According to presented data we could asses these soils as practically inadequate for agricultural production due to the very high Pb content (Figure 1).

Similar situation was met in regard to Zn presence in agricultural soils in the investigated region (Figure 2). The elevated concentration was considered at the position of Petrisino-Neokazi (130 mg/kg); Ratavici-Strmos (102 mg/kg) and Ratavici-Zletovo (121 mg/kg) that point to the serious agricultural soil threat.

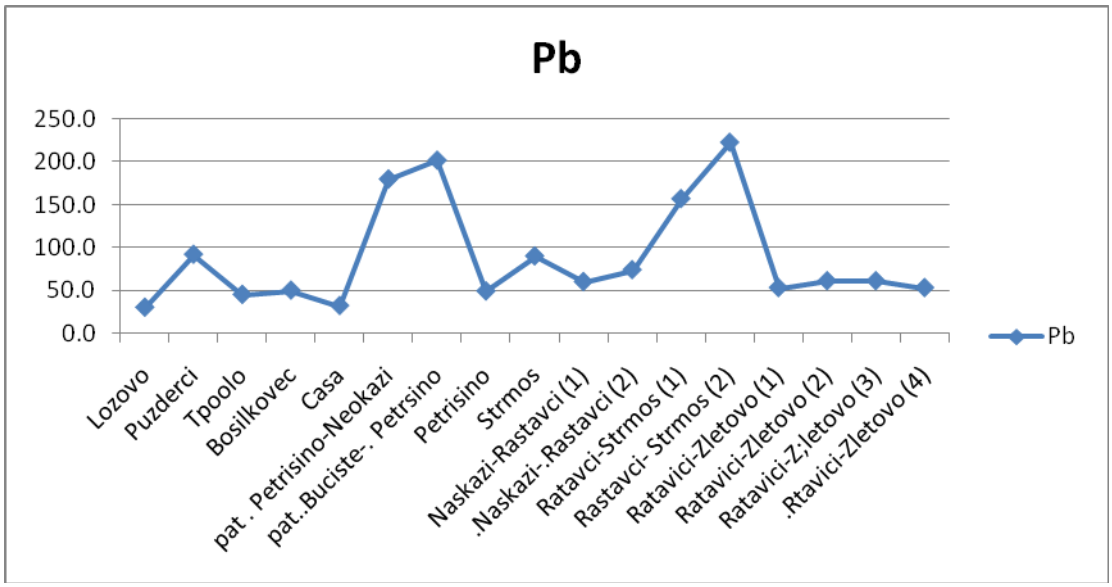

Figure 1. The distribution of lead (Pb) on investigated measuring points

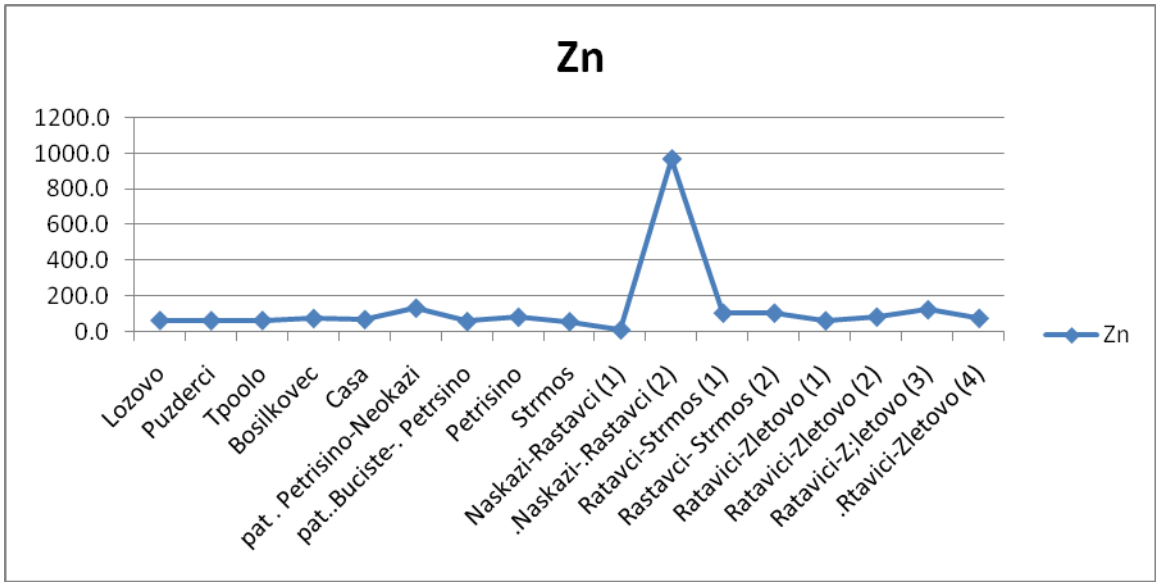

Figure 2, Disposition of zinc (Zn) on the points of investigations

In the absence of the national legislative for the available heavy metals content in agricultural soils, we used data appearing in soil standard in Nederland and Bulgaria (West European and South-East European country, respectively).

Our investigations showed that the most critical heavy metals – Pb and Zn in agricultural soils in the surrounding of the mine-complex “Zletovo”, exhibit concentration values although high but not exceeding values considered within the Nederland soil quality standard (Pb: 530 mg/kg; Zn: 720 mg/kg), i.e Pb concentration is 42 %, lower, while Zn concentration is 40% lower than values appearing in Nederland standards for heavy metals in agricultural soils in the Probishtip region.

The comparison to the Bulgarian standard (70 mg/kg for Pb) points to 77 % higher value in Probistip agricultural soil. Zn concentration in the agricultural soils in the surrounding of metal complex “Zletovo” is 55,6 % higher than the value appearing in Bulgarian standard (200 mg/kg) .

CONCLUSIONS

The problem of agricultural soils contamination by technogene waste materials is a crucial problem in all over Europe. In that context we conclude the enormous an abnormal soil contamination by heavy toxic metals (primarily lead and zinc) in the surrounding of thee mine complex “Zletovo”, Probistip, Republic of Macedonia. The Republic of Macedonia does not have any national standard on soil quality management, but the efforts to adopt European standards in order to make possible soil quality control are intensively progressed. The soil quality monitoring is necessary to ensure proper and clean production of nutrition products for the population.

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