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# Heavy Metals Content in Soil Near Non-ferous Metals Production Facility and Domestic Wastes Landfill in the Area of Kardzhali Town

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Abstract. The predominant soil types in the region of Kardzhali are maroon forest soils - highly leached and poorly podzolized. Most of the soils have medium to high erosion ability - II-III degree, and the pH is neutral to slightly alkaline (7-7,8). Few are weak and moderate acidic pH (6,7-5). Soils are mostly shallow to moderately deep, poor in nutrients. In the region of Kardzhali main pollutants are heavy metals from mining-processing and metallurgical business activities of "Gorubso-Kardzhali" - AD and LZC - AD, Kardzhali. In the paper are presented results of soil contamination mainly with lead, cadmium, copper and zinc, showing concentrations of lead in the soil over the MAC, according to Ordinance N $_{0}$  3/2008 Standards for acceptable content of harmful substances in soil.

Key words: soil, heavy metals, pollution, Kardzhali. Bulgaria.

#### Introduction

The predominant soil type in District Kardjali is maroon forest soils - highly leached and poorly podzolized. There are also smaller brown forest soils rendzinas (humus-carbonate), alluvial, maroonpodzolic, delluvial and insignificant amount other soil types. The most fertile soils are in the valleys of the Arda River and its tributaries in the northern area of the Haskovo region border.

Most of the soils have medium to high erosion - II-III degree, and the pH is neutral to slightly alkaline (7-7,8). Few are weak and moderate acidic pH (6,7-5). Soils are mostly shallow to moderately deep, poor in nutrients. Arable lands are scattered and small. Characteristic in this region is that the arable area does not form compact areas, as in other regions of the country and is divided into many units, different size, shape and position (YANCHEV *et al.*, 2005).

In the region of Kardzhali main pollutants are heavy metals from mining and metallurgical processing business of "Gorubso-Kardjali" - AD and LZC-AD Kardzhali (STAYKOVA, 2009).

In this publication are presented the results of soil contamination mainly with lead, cadmium, copper and zinc.

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#### Material and methods

Sampling of soil samples was performed in accordance with the requirements of ISO 10381-1 and BSS 17.4.5.01-85 for analysis of heavy metals. Depending on the accepted practice in hygienic criteria are defined points. Their representative sampling number is 21 and are located near sources of pollution, to the over traffic road junctions away from pollutants and near kindergartens and schools.

Soil samples were taken according to "Method of diagonals", with conditional splitting territory for sampling of plots of 0,5 ha, with an analysis of 5 samples from each plot. Samples from each sampling point are mixed with spot shaping random sample of 1 kg. Average samples consist of 5 single samples taken uniformly from the area of the fixed site. Sampling was conducted from a depth 0-10 cm.

Determination of toxic elements in mineralizatite was conducted through the methods of atomic absorption spectroscopy flame AAS according using to ISO 11047:1998, after appropriate sample preparation - mineralization by BSS 17.4.4.01-79 (MECHKUEVA, 2003).

Preparation and analytical determination of the studied elements was made according to standardized methods (Table 1).

Element	Method of analysis	Analytical technique	Detection Limit, mg/kg
Cadmium	BSS 17.4.4.04-80, ISO 11047	FAAS	0,25
Copper	BSS 17.4.4.03-80, ISO 11047	FAAS	0,30
Zinc	BSS 17.4.4.05-80, ISO 11047	FAAS	0,32
Lead	BSS 17.4.4.02-80, ISO 11047	FAAS-2	2,5

Table 1. Used laboratory methods for analysis of heavy metals.

#### **Results and Discussion**

The main industrial pollutants in soil near the town of Kardzhali are: Lead-zinc complex (LZC AD), "S & B Industrial Minerals" AD (ex Bentonit AD) and tailings of "Gorubso-Kardzhali" AD. The heavy metals fall in the soil through the emitted into the air emissions from those industries.

Anthropogenic pollution from industrial activity depends on the direction of prevailing winds, which are for the region north and northwest of the city.

Besides the direction of prevailing winds and the ambient elevation, soil acidity is of great importance, since it depends on the MAC of heavy metals in soils (Ordinance № 3/01.08.2008 for the standards of acceptable content of harmful substances in the soil).

Soils in the region of Kardzhali are calcareous humus-resinous, average power and light clay. Soil composition and reaction factors are relatively active migration of heavy metals in soil vertical profile.

In Table 2 are presented data on the content of heavy metals (cadmium, copper,

zinc and lead) in soil, averaged over the period 2008-2010. From those data in Table 2 and Figure 1-4 was found that the cadmium content in the soil into a research area does not exceed the MAC, under Ordinance 3/2008 (MEW, MH, MAF, 2008). The highest cadmium concentration (2,40 mg/kg) was recorded in the sampling point № 7 - Vocational School "Vasil Levski", which is located near the factory for the extraction and processing of lead-zinc ores – "Gorubso-Kardzhali" - AD.

The content of copper and zinc is bellow the MAC at all locations. Limit of copper were specified in sampling point № 9 square "Studen Kladenets" Street "Dospat" № 1A (182,66 mg/kg), and zinc (387,27 mg/kg) again at sampling point № 7 - VS "Vasil Levski". Approximately in 50% of the sampling points a lead content is above the MAC (200 mg/kg) from 1.10 to 3.44 times. The most massive lead contamination of soil samples was examined in the region of VS "Vasil Levski". High average values for the period are recorded in sampling point - the Railway station. The probable accumulation of lead is not only LZC-AD, and from the tailings pond of "Gorubso-Kardzhali"-AD by the transport of lead concentrate near this point and traffic from the adjacent boulevard. The average total lead concentration for the 21 sampling points does not exceed the MAC.

N⁰	Sampling Doint	Heavy metals content, mg/kg			
IN⊻	Sampling Point	Cd	Cu	Zn	Pb
1	Kardzhali, Baykal District, 2 "Gen. Vladimir Stoychev"Street	1,38	9,87	127,85	222,56
2	Kardzhali, exit to Haskovo		11,64	122,59	114,65
3	Kardzhali, Belomorski Blvd., yard of Kindergarten "M. Gorki"		25,78	198,25	289,50
4	Kardzhali, Studen Kladenets District, "Veslets" Street		42,09	99,58	31,11
5	Kardzhali, Studen Kladenets District, RRM		41,64	200,12	405,31
6	Kardzhali, Railway Station, Block 81		22,89	205,23	441,28
7	Kardzhali, Vocational School "Vasil Levski", the yard		27,68	387,28	688,67
8	Kardzhali , MSCH	1,82	22,28	115,20	221,03
9	Kardzhali , Studen Kladenets District, 1A "Dospat" Str.	1,06	182,66	103,38	239,54
10	Kardzhali , Studen Kladenets District, "St. Kliment Ohridski" High School	1,21	19,51	113,82	293,95
11	Kardzhali , FHL Kindergarten	0,79	17,79	116,72	49,58
12	Kardzhali, Vazrozhdentsi District, P. R. Slaveykov High School	1,33	17,36	95,73	132,36
13	Kardzhali, Veselchane District, 9 "Victory" Street	0,80	21,05	115,42	38,67
14	Kardzhali,Gledka District, 4 "Tina Kirkova" Street	0,53	21,08	99,64	27,08
15	Kardzhali, Gorna Gledka District, 17 "K. Lyatifova" Street	0,86	15,33	78,85	35,94
16	vil. Ostrovitsa, municipality Kardzhali	1,66	24,98	164,27	64,27
17	Kardzhali - exit to Ardino	0,59	10,15	78,06	22,88
18	Kardzhali, Prileptsi District opposite PWPS	0,74	12,97	51,33	21,61
19	vil. Vishegrad, municipality Kardzhali	0,67	23,98	54,30	25,83
20	vil. Gluhar, municipality Kardzhali	0,81	13,98	193,07	36,15
21	vil. Enchets, municipality Kardzhali	0,50	16,13	134,88	375,00
	Toatal Average value	1,35	1,07	28,61	135,98

**Table 2.** Heavy metal content, averaged over the period 2008-2010 in (mg/kg).

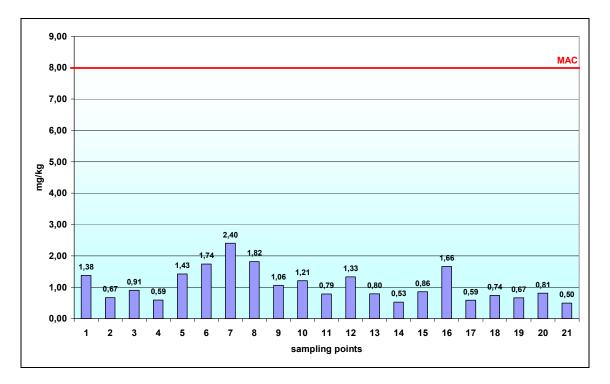


Fig.1. Cadmium content in soils – average to the period 2008-2010.

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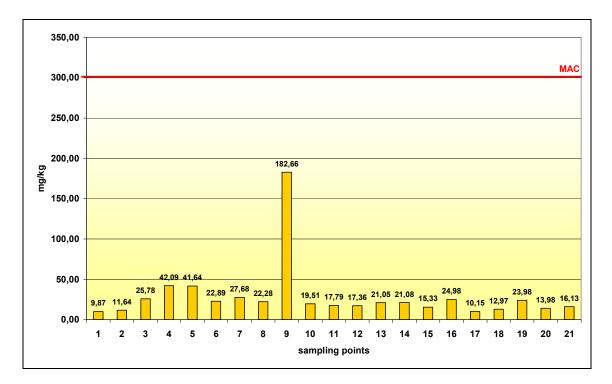


Fig. 2. Copper content in soils – average to the period 2008-2010.

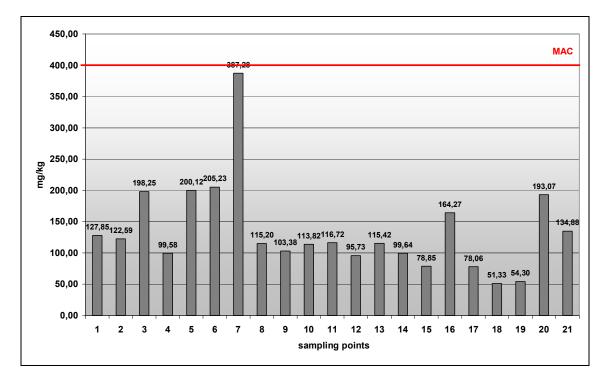


Fig. 3. Zinc content in soils – average to the period 2008-2010.

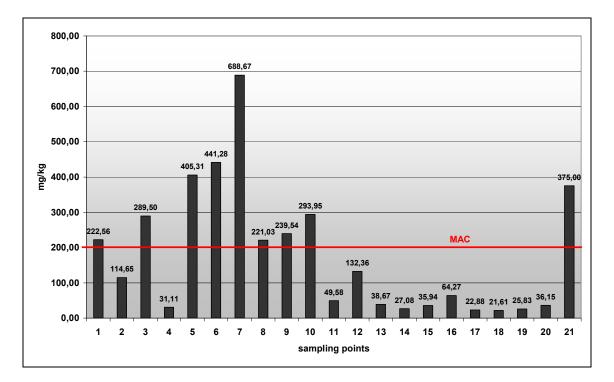


Fig. 4. Lead content in soils - average to the period 2008-2010.

*Index of variety among seasons and* Comparing the data content of heavy metals (cadmium, copper, zinc and lead) in the soil of the region of Kardzhali for the period 2008-2010 was found significant higher concentration at the end of the study, which confirms the conservative properties and cumulative soil as a media. The results are presented in Table 3.

Table 3. Averages, medians and standard deviations of heavy metals					
in soils for the period 2008-2010					

		Statistical indicator			
Heavy metals	Year	Average value	Median	Standard deviation	
	2008	0,500	0,400	0,138	
Cd	2009	0,465	0,280	0,631	
	2010	1,516	1,250	0,868	
	2008	44,150	39,500	20,559	
Cu	2009	7,102	0,870	15,533	
	2010	17,143	14,000	9,873	
	2008	168,600	173,000	32,107	
Zn	2009	42,143	16,880	60,520	
	2010	201,357	180,000	133,312	
	2008	36,950	38,000	5,889	
Pb	2009	19,853	2,750	42,232	
	2010	70,626	48,000	52,256	

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## Conclusions

• The soil secondary contaminated by the atmosphere is a depot facility for heavy metals exceeding the statutory limits could be a potential source of groundwater contamination, plant and animal products with a local origin.

• For the observed period (2008-2010) was found that approximately 50% in the sampling points a lead content of soils over the MAC (200 mg/kg) from 1,10 to 3,44 times. Cadmium, copper and zinc is bellow the MAC.

• At the regional level institutions with responsibilities for the management of environmental quality and public health in the region need to fit together to successfully achieving of effective solutions to issues concerning:

- Aerosol pollution from tailings pond of "Gorubso – Kardzhali" AD;

- Optimization of treatment facilities and LZC – AD and "S & B Industrial Minerals" AD in their proceedings;

- Promotion among private farmers growing crops with little potential for

accumulation of heavy metals and appropriate planting.

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