ASSESSMENT OF SOIL CONTAMINATION WITH ZINC IN THE AREA OF KARDZHALI LEAD-ZINC PLANT

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The Kardzhali region, Southeastern Bulgaria, is an area at environmental risk associated with local manufacturing industry, and poor management of the increased domestic and production waste disposal. The main industrial production processes are related to the operation of the Lead-Zinc Complex Plc smelter, Gorubso-Kardzhali tailings, Bentonite Plc., Monek Yug Plc., and S&B Industrial Minerals Plc. Zinc content was determined in 113 soil samples, collected over an area of about 220 km^2, ranging 12 km to the North and South and 10 km to the East and West from the smelter chimneys. Total Zn concentrations were determined in accordance with ISO 11047 by *aqua regia* digestion (ISO 11466), concentrations of mobile forms of the element were determined in compliance with ISO 14870. Samples were analyzed using atomic absorption spectrophotometer 'Varian Spektra AA 220', Australia, at a wavelength of 213.9 nm. Results show that for the majority of soil samples, values were within the norms defined by the judicial documentation for interventional and maximum permissible concentrations. It was found that zinc pollution is greatest in the vicinity of the lead-zinc complex and the tailings area. Statistically significant regression dependence between the total concentration of the element and the mobile forms was determined through regression and correlation analyses. The exponential model adequately describes the dependence between soil organic matter content and zinc mobile forms in the sample set. The determined associations warrant total concentrations of the element to be used in conjunction with DTPA-extractable contents (mobile forms accessible to plants) for risk assessment of heavy metal contaminated soils.

INTRODUCTION

Within Kardzhali municipality pollutants have frequently been above the standards in place for atmospheric air quality in Bulgaria. This has been linked to the operation of the Lead-Zinc Complex Plc smelter, Gorubso-Kardzhali tailings, Bentonite Plc., Monek Yug Plc., and S&B Industrial Minerals Plc.

Weather and geographical conditions in the municipality favour the retention of incoming atmospheric pollution. The number of days with fog and calm weather predetermines the poor dispersion of local pollutants and, therefore, their increased concentration. As the predominant wind directions are north and south, the region is characterized by a bidirectional wind rose.

The wide variety of soil types found on the territory of the municipality is determined by the diversity of the relief, vegetation, soil forming bedrocks and characteristics of climatic conditions. Much of the soil is eroded, especially in arable lands on steep slopes. The scarcity of arable land is clear, as the state agricultural lands are damaged to varying degrees [1, 4, 5, 6]. The main source of income of the population in the Kardzhali region is tobacco production. Soil studies provide information on atmospheric emissions of heavy metals and other toxic elements during the operation of the Lead and Zinc Complex.

The aim of this study is to assess the content of the environmentally significant element zinc in soils near LZC-Kardzhali.

SAMPLES AND METHODS

Object of study

The study area of about 220 km^2 is located in southeast Bulgaria, in the vicinity of LZC, Kardzhali. The smelter is located on the northern shore of the Studen Kladenets pond. In this region there are cinnamon forest soils (the majority of which strongly leached), alluvial-meadow, diluvial and diluvial-meadow, pseudopodzolic, and humus carbonate soils.

For the purpose of the study, 113 soil samples were obtained; with a distance ranging from 12 km to the north and south and 10 km to the east and west from the smelter chimney. The sampling was performed in accordance with the requirements of Ordinance number 3 for permissible contents for harmful substances in the soil [3] and ISO 10381 [10]. A map of the sample collection sites is presented in Fig. 1. Coordinates were determined using GPS.

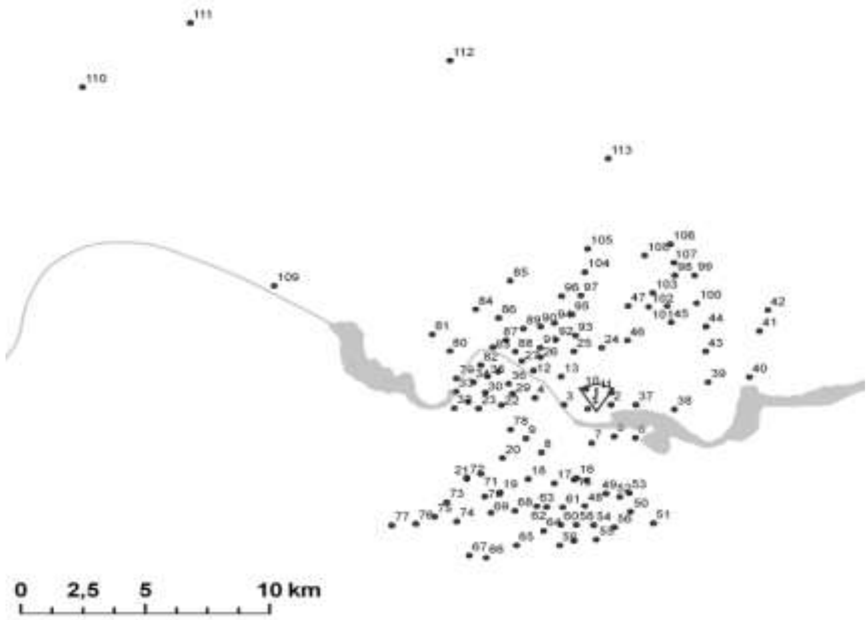

Fig. 1. Sampling sites

Methodology and equipment

Soil sample preparation was carried out in accordance with ISO 11464 [11].

The following indices were determined:

1. Total zinc content via *aqua regia* digestion, ISO 11466 [7];
2. Mobile form of zinc – extraction with 0.005M DTPA + 0.1M TEA, pH 7.3, ISO 14870 [9];
3. Organic matter content in Turin;
4. pH in H_2O – potentiometrically, ISO 10390 [12];
5. Soil separates – pipette method (in Wigner).

Total zinc concentration was determined in accordance with ISO 11047 with the use of an atomic absorption spectrophotometer ‘Varian SpektrAA 220’, Australia, with operating wavelength 213.9 nm [8].

RESULTS AND DISCUSSION

Summarized results of the statistical analyses on the determined pH levels, organic matter and clay contents are presented in Table 1. Soil reaction (pH levels) ranges between 4.60 and 8.05 (from strongly acidic to weakly alkaline). 50 % of the soil samples are acidic; 33% of which are weakly acidic, 14% have moderate acidity and 2% are strongly acidic (Fig. 2). It is known that in an acidic medium, zinc exhibits higher mobility than in neutral or alkaline medium [2]. Acidic soil reactions have been determined in soil samples from the area of the villages Glouhar (to the west of the village), Opalchensko, Panchevo, Zhelezni Vrata, Shiroko Pole, Letovnik, Volovartsi, Dangovo, Chenoochene. In the town of Kardzhali and the vicinity, soil reactions are alkaline. There is a great diversity in terms of soil acidity in some of the sampled areas. On the territory of a singular settlement, areas with weakly acidic, neutral and weakly alkaline reactions are present.

Table 1. Determined pH level, organic matter and clay (<0.02 mm)

Statistical data	pH	Organic matter [%]	Clay [%]
Arithmetic mean [mg/kg]	6.86	5.00	32.40
Standard deviation [mg/kg]	0.73	2.67	24.08
Minimal value [mg/kg]	4.60	0.75	7.20
Maximal value [mg/kg]	8.05	12.00	86.60
Coefficient of variation [%]	10.64	53.40	74.32

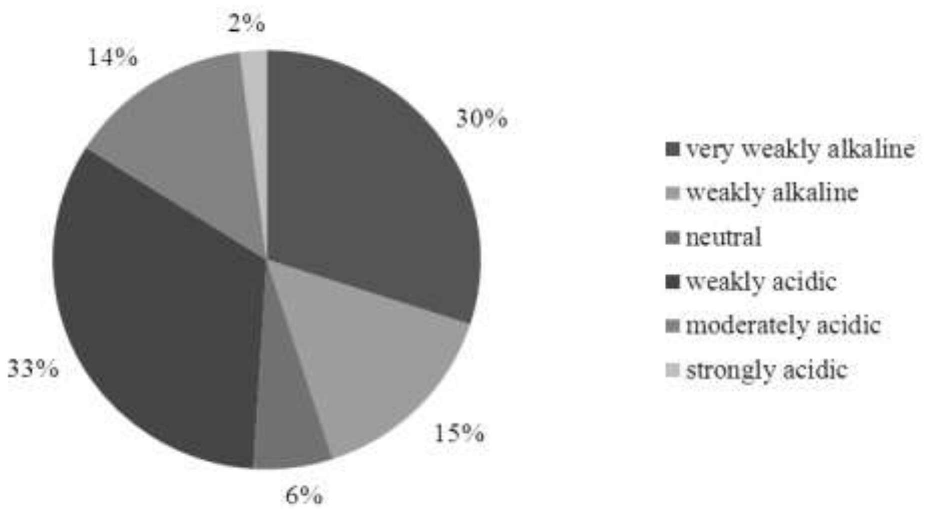

Fig. 2. Soil reaction (pH)

Organic matter concentration varies considerably: from 0.75% to 12%. The highest values were determined in samples obtained in parks and gardens. Clay content (particle size <0.02 mm) also varies greatly, from 7.20 to 86.80%. Light sandy clay soils are dominant in the sample set, followed by moderate clay and moderate sandy clay (Fig. 3).

In 4% of the sampled soils, the determined elemental content was above the interventional concentration levels (Fig. 4); and in 12 % of the samples, the maximum permissible concentration was exceeded. Maximum permissible concentration (MPC) is defined as the content of a harmful substance in soil [mg/kg], which, if exceeded, under certain conditions could potentially inhibit soil functions and pose danger to the environment and human health. Interventional concentration (IC) is the content of a harmful substance in the soil [mg/kg], above which inhibition of soil functions and danger to the environment and human health are present [3], meaning that these soils have inhibited functions and pose risk to the environment and human health.

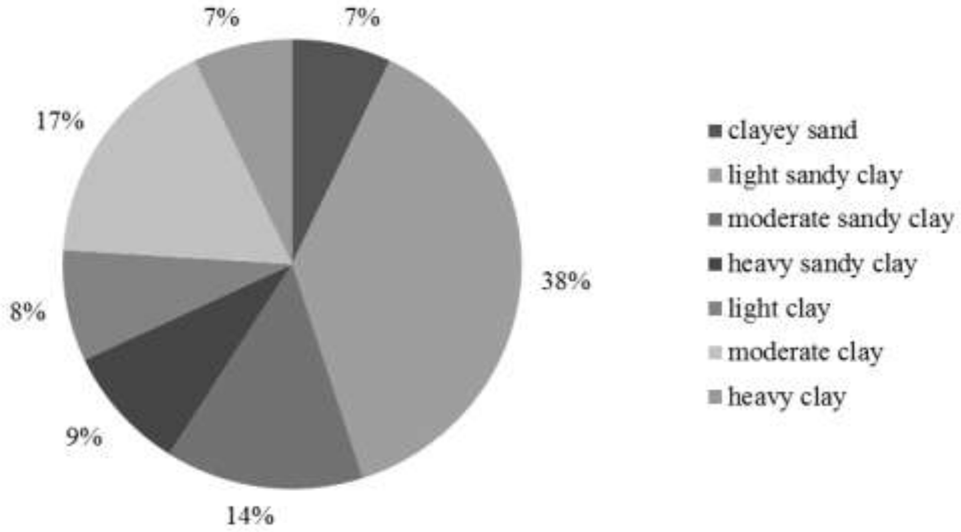

Fig. 3. Soil texture

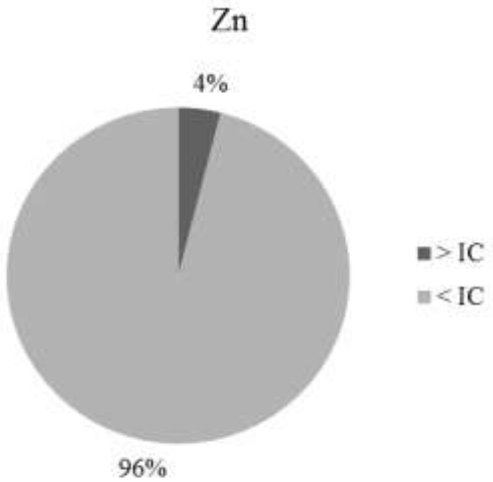

Fig. 4. Zn concentration according to IC

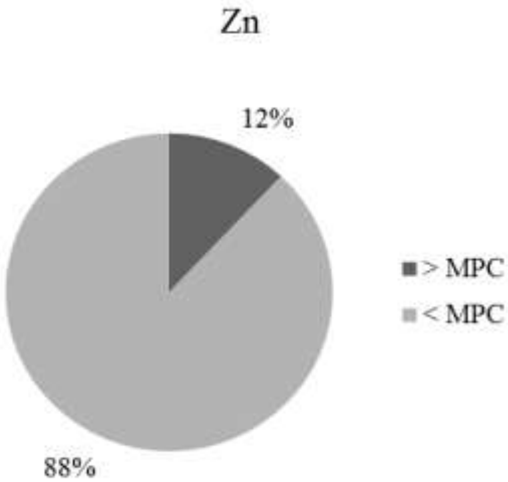

Fig. 5. Zn concentration according to MPC

Table 2. Total Zn concentration and mobile forms

	Zn total	Zn mobile form
Arithmetic mean [mg/kg]	868.93	39.29
Standard deviation [mg/kg]	3631.15	77.43
Minimal value [mg/kg]	33.67	1.00
Maximal value [mg/kg]	34487.00	510.42
Coefficient of variation [%]	415.61	197.07

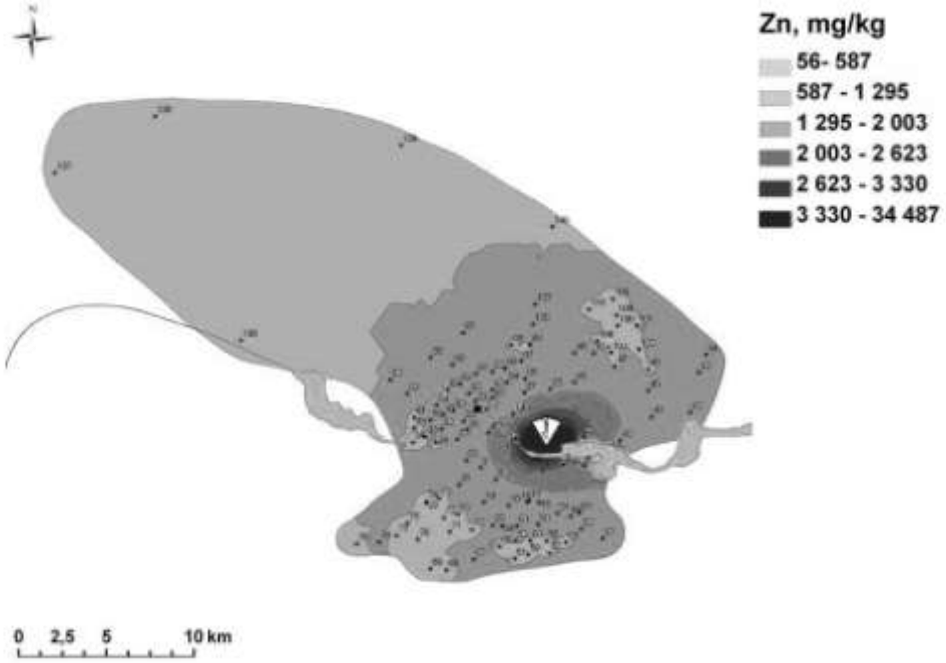

Fig. 6.Atmospheric deposition pattern for Zn

Zinc MPC was surpassed in sample sites closest to the LZC, Ostrovitsa, Propast, park Gorubso, Zhelezni Vrata, Balabanovo, Kalinka. MPC varies between 220 and 600 mg/kg. The determined Zn concentrations ranges from 33.67 mg/kg, in Chernoochene, to 34487 mg/kg, in sample 1 – the closest to the ZLC (Fig. 6). The determined total Zn concentration in sample 1 exceeded the MPC by a factor of 57, and in sample 2 – by a factor of 30.

Table 3 contains regression equations which describe the relationship between total Zn concentration and mobile form content determined in the soil samples; and between soil characteristics and the mobile forms of the element. The second column shows the correlation coefficient R. The significance of the correlation coefficient was tested at a significance levels $\alpha = 0.05$ and $\alpha = 0.01$. Asterisks to the right of the R values (* and **) mark statistical significance at $\alpha = 0.05$ and $\alpha = 0.01$. The observed level of significance in the regression model α_s is presented in the third column. The null hypothesis is rejected if $\alpha_s < \alpha$, i.e. the regression model is adequate at the respective level of significance ($\alpha = 0.05$, $\alpha = 0.01$).

The Power model adequately describes the relationship between the determined total zinc content and its mobile forms; and the relationship between organic matter content and zinc mobile forms is described by the exponential model. In Table 3 the observed levels of significance (α_s) are less than the critical value 0.01, so the correlation coefficients are statistically significant.

Table 3. Regression analysis and significance results

Regression equations	R	α_s
$Zn_{mobile\ formи} = 0.073 . Zn_{total}^{\ 1.069}$	0.816**	0.000
$Zn_{mobile\ form} = 4.541 . e^{0.255 organic\ matter}$	0.539**	0.000
$Zn_{mobile\ formи} = - 348.98 . pH + 3047.78$	0.005	0.460

** and ** mark statistical significance at α = 0.05 and α = 0.01*

The results of the regression and correlation analysis indicate that with an increase of the pH levels of the soil, the content of mobile zinc forms is reduced, but no statistically significant correlation is found.

CONCLUSIONS

It was found that in most soil samples, zinc content meets the regulations for interventional and maximum permissible concentrations.

Zinc contamination is highest in the vicinity of the lead-zinc complex and the tailings area. Concentric zones with varying concentrations of zinc are formed from the source of contamination to the periphery; and MPC and IC are exceeded severalfold in the central zone.

Statistically significant relationship between the total concentration of the element and the mobile forms was determined through regression and correlation analyses. The exponential model adequately describes the dependence between soil organic matter content and zinc mobile forms in the sampled soil.

The determined associations warrant total concentration of the element to be used in conjunction with DTPA-extractable contents (mobile forms accessible to plants) for risk assessment of soils contaminated with heavy metal.

Appropriate land use and implementation of ameliorative measures for soil recovery are needed in the polluted areas in order to restrict the entry of heavy metals in agricultural production.

ACNOLEDGEMENTS

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