ASSESSMENT OF SOIL CONTAMINATION WITH Pb AND Cu IN THE AREA AFFECTED BY KARDZHALI LEAD-ZINC SMELTER

S. Marinova[1], P. Zaprianova[2], R. Bozhinova[3], H. Hristov[1],
G. Hristozova[1], M.V. Frontasyeva[4]

[1]Faculty of Physics and Engineering Technologies,
"Paisii Hilendarski" University, Plovdiv, Bulgaria
[2]University of Agriculture, Plovdiv, Bulgaria
[3]Tobacco and Tobacco Products Institute, Plovdiv, Bulgaria
[4]Joint Institute for Nuclear Research, Dubna, Russia

ABSTRACT

The contents of Pb and Cu in 113 soil samples collected in the area of the lead-zinc smelter in the town of Kardzhali, Bulgaria, were determined. The sampled area was about 480 sq. km, ranging 12 km to the north and south and 10 km to the east and west from the factory chimney. The coordinates of the sampling sites were determined by GPS. Atomic absorption spectrometry was used as the analytical technique ("Varian SpektrAA 220", Australia). Sample preparation was performed in accordance with ISO 11464. Extractions were made with aqua regia in accordance with ISO 11466. The content of heavy metals was determined in accordance with ISO 11047. The following wavelengths were used: Pb – 217.0 nm and Cu – 324.8 nm. The results from the study demonstrate that the concentrations of Pb and Cu in the majority of the soil samples were within the norms defined by the judicial documentation for interventional and maximum permissible concentrations. Therefore, for most of the sampled locations measures for soil remediation are not necessary. Application of land improvement is needed in the polluted zones, where Pb and Cu concentrations exceed 90 mg/kg and 80 mg/kg respectively.

INTRODUCTION

Amongst the numerous substances entering the atmosphere as a result of anthropogenic activity, particular attention is paid to heavy metals as they are hazardous toxicants. Their involvement in irreversible geochemical and biochemical processes leads to disturbances of the ecological balance and consequently, diseases in humans [4]. The most dangerous sources of local pollution by heavy metals are powerful technological facilities which have not been renovated and reconstructed. One of these is the lead-zinc smelter in the town of Kardzhali, Bulgaria ('Lead-Zinc Complex' (LZC) Plc.). The smelter's atmospheric emissions associated with the production of non-ferrous metals through the years inflicted serious environmental damage to the surrounding rural areas, and are directly related to the present issue of human health protection in a number of villages in the Kardzhali region [1, 6, 7]. Soil surveys provide information about atmospheric emissions of heavy metals and toxic elements during production processes.

The aim of this study is to assess the content of the environmentally significant elements lead and copper in soils near LZC-Kardzhali.

SAMPLES AND METHODS

Object of study

The study area of about 480 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.

The area has a low-mountain relief with a rugged terrain, and much of the soil is eroded.

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 have been determined using GPS.

Methodology and equipment

Soil sample preparation was carried out in accordance with ISO 11464 [11]. Aqua regia digestion procedure was performed in accordance with ISO 11466 [8]. Heavy metal content was determined according to ISO 11047 [9] with the use of an atomic absorption spectrophotometer ‘Varian SpektrAA 220’, Australia, under the following operating wavelengths: Pb – 217,0 nm and Cu – 324,8 nm. Soil reaction (pH level) was determined in compliance with ISO 10390 [12].

Fig. 1. Sampling sites

RESULTS AND DISCUSSION

The summarized results of the statistical analyses on the determined pH and concentration values for lead and copper are presented in Table 1.

Table 1. Statistical data on pH, Pb and Cu concentrations in the soil samples

Statistical data	pH	Pb	Cu
Number of samples	113	113	113
Average, mg/kg	6.86	504	77
Standard deviation, mg/kg	0.73	3817	422
Minimum value, mg/kg	4.60	17	6
Maximum value, mg/kg	8.05	40413	4296
Coefficient of variation, %	10.64	757	547

The data from Table 1 shows that the pH levels of the studied soil samples range 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, copper and lead exhibit a higher mobility than in neutral or alkaline medium [2, 5]. 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. The majority of these soils are present in pastures and meadows. In the town of Kardzhali and the vicinity, soil reactions are alkaline. In some areas, the soils are very diverse in terms of acidity. On the territory of a singular settlement, areas with weakly acidic, neutral and weakly alkaline reactions are present.

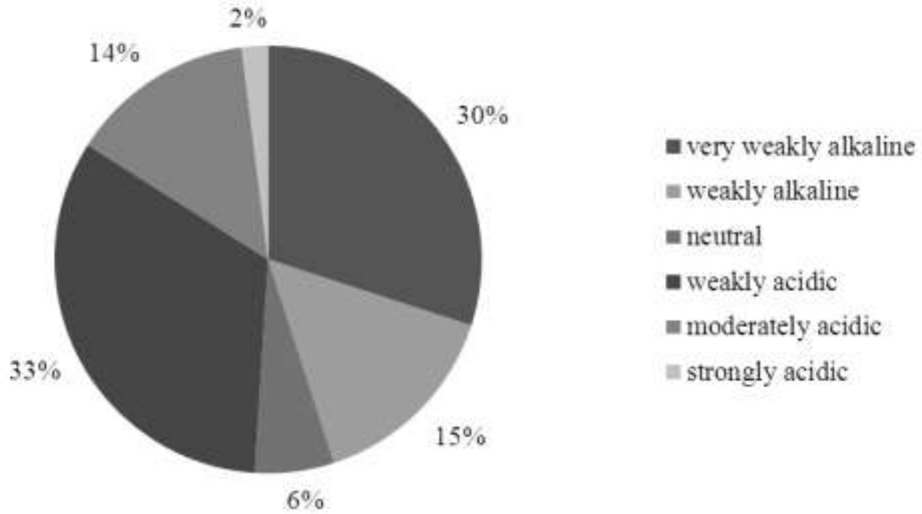

Fig. 2. Soil reaction (pH)

Pb concentration varies considerably - from 17 mg/kg to 40413 mg/kg (Table 1). The variation coefficient for this element reaches 757%. The highest values were determined in samples obtained from sites in close proximity to the LZC - samples 1 and 2. The lowest concentration was found near the village of Bolyarci - northeast of the smelter. In the majority of the studied soil smaples (86%) lead content does not exceed the maximum permissible concentration (MPC) (Fig. 3). Maximum permissible concentration is defined as the content of a harmful substance in soil [mg/kg], which, if exceeded, under certain conditions could inhibit soil functions and pose danger to the environment and human health [3]. 5% of the determined elemental concentrations were above the interventional concentration levels (IC, interventional concentration, 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]). Therefore, these soils have inhibited functions and pose risk to the environment and human health (Fig. 4).

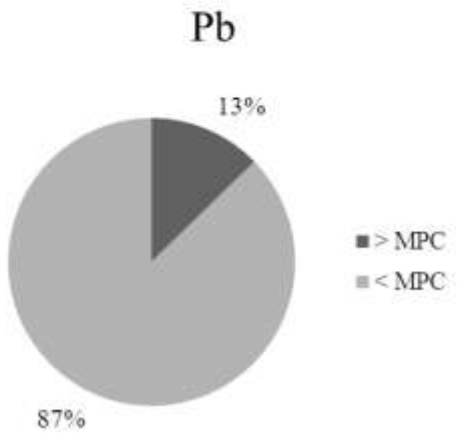

Fig. 3. Pb concentration according to MPC

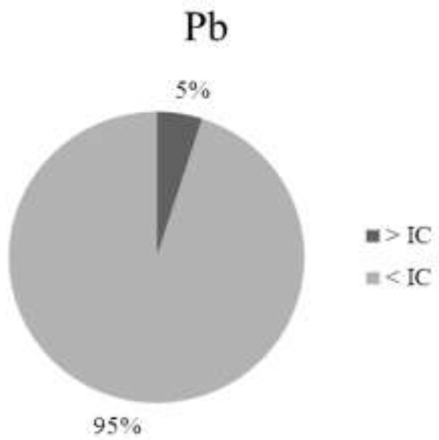

Fig. 4. Pb concentration according to IC

As with lead, the highest copper content was determined in the soil sample obtained in the town of Kardzhali, near the fence surrounding the chimney of the smelter. The maximum determined value was 4296 mg/kg, and the minimum - 6 mg/kg. For the majority of the surveyed points the Cu content was within the safety standards, i.e. the element content in the soil does not result in an inhibition of the soil functions or endangerment of the environment and human health. For locations in which this standard level was surpassed, Cu content was still lower than the maximum permissible concentration (MPC). Exceeding of the MPC and IC was observed only in 2 % of the samples (Fig. 5 and Fig. 6).

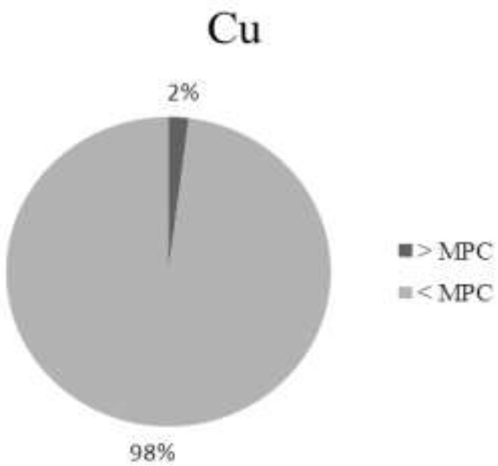

Fig. 5. Cu concentration according to MPC

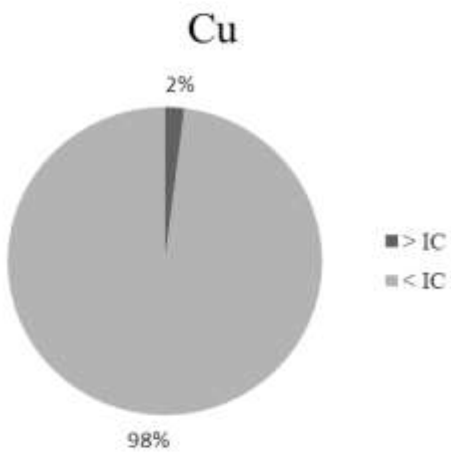

Fig. 6. Cu concentration according to IC

CONCLUSIONS

The results demonstrate that in the majority of the soil samples the concentrations of the two studied elements, Pb and Cu, meet the standards for interventional and maximum permissible concentrations. Therefore, in most locations, adoption of measures to better and restore the soil condition is unnecessary.

The locations in which the determined concentrations of the elements surpass MPC and IC can be regarded as contaminated. These are found in soil primarily in the close vicinity of the LZC. Lead contamination is particularly pronounced.

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.

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