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# Effect of Historical Zinc Processing on Soil: A Case Study in Southern Poland

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***Abstract*** **-** The present study focuses on the geochemical hazard in the soil system affected by the historical zinc processing in Jaworzno, Southern Poland. We measured pH, total sulphur and total carbon values as well as total Zn, Pb and Cd content (ICP-OES) for soil samples and waste material. Essential information about the heavy metal bioavailability and toxic impact on the natural environment was delivered by the modified three-steps sequential extraction method (BCR). The application of soil enzyme activity analysis and the bioassay test with *Vibrio fischeri* allow us to assess the effect of heavy metal toxicity/bioavailability on active soil environment. We conclude that after 40 years since Zn processing was abandoned, the total content of Zn, Pb and Cd in the investigated soil is extremely high, ca.8 to 28 times larger than in the European topsoils and about twofold above the values of geochemical background for the Southern Poland. In view of above statements and results of bio-tests, we note that the area of current study is strongly affected by the historical zinc industry and the topsoil is heavily contaminated or even toxic.

***Keywords*****:** Zn smelting, ZnO processing, heavy metals, waste, soil toxicity

## 1. Introduction

Our study focuses on the geochemical hazard in the soil system affected by the historical zinc processing in Jaworzno, Southern Poland. We measured physical properties (pH, total sulphur and total carbon values) as well as total heavy metals (Zn, Pb and Cd) content (ICP-OES) for soil samples and leftover material. Essential information about the heavy metal bioavailability and toxic impact on the natural environment was delivered by the modified three-steps sequential extraction method (BCR). The application of soil enzyme activity analysis (dehydrogenase analysis – DHA) and the bioassay test with *Vibrio fischeri* allow us to assess the effect of heavy metal toxicity/bioavailability on active soil environment.

## 2. Material and methods

The research was conducted in an industrial and anthropogenically altered city space of Jaworzno, located in the NE part of the Upper Silesia, Southern Poland. The Zn-Pb ore mining and smelting started here in 12th and lasted to 20th century. In the area of the study, the Zn smelter was established in 1822. Then it was transformed to white zinc (ZnO) plant in the 1865, which was finally closed in the 1976. Non-sulfide Zn ore from local mines served as the raw material for Zn smelting. Nowadays, the relics of the Zn historical metallurgic processes are represented by tailings deposited on the old heap situated in close vicinity of residential area and community gardens.

The study was conducted on 4 forest soil profiles of the podzol and 5 waste samples collected from 3 waste locations. Each soil profile was divided into separate horizons, what gave 22 soil samples. Soil pH was obtained using pHmeter ELMETRON CP-315m. Concentration of total carbon (TC), total sulphur (TS) and total inorganic carbon (TIC) were determined by an Eltra CS-530 IR-analyzer with a TIC module. The chemical fractionation forms of the studied metals were obtained using the modified BCR sequential extraction given by Rauret et al.[1]. Exchangeable, reducible, oxidizable and residual fractions were separated and the heavy metals contents in each fraction were determined using ICP-OES. Microbial activity in the analyzed soil, was conducted based on the Casida et al. [2] method with the use for reduction 2, 3, 5- triphenyltetrazolium chloride (TTC) to the creaming red-colored formazan (TPF). The red methanolic solutions of the formazan were read at 485 nm with the use of Spectrophotometer UV-Vis, DU 640. The toxicity assessment of soil and waste was performed with Microtox M500 Analyzer. In the test, decrease in luminescence in *Vibrio fischeri* was measured, which is an effect of metabolic inhibition in the bacteria after exposure to a toxic substance.

## 3. Results and discussion

Values of soil pH fluctuate between 3.85 and 7.59, with median 5.55. The waste samples show mostly very low-pH characteristic (values vary from 2.83 to 7.41). It means that examined materials are ultra-acidic to neutral, mostly very strong acidic. Generally, pH value decreases with depth. TOC values obtained for the soil range from 0,1 % to 22.07 %, with a mean 1,57 %, while amount of TS vary from 0 to 0,17 %. Both parameters mostly decrease with depth. In waste samples TOC value fluctuate between 0,42 % and 8,86 % whereas TS change in the range from 0,09 % to 0,78 %. Higher content of the sulphur in the waste may be connected with sulfides naturally occurred in Zn-Pb ores used in smelting process.

Investigated soil samples contain 9.53 – 2307.52 mg . kg-1 d.m. of Zn, 3.07 – 531.09 mg . kg-1 d.m. of Pb and 0.16 – 17.62 mg . kg-1 d.m. of Cd, with geometrical means 91.76 mg . kg-1 d.m., 38.45 mg . kg-1 d.m. and 1.31 mg . kg-1 d.m., respectively. Load of the same elements in the waste ranges as follows: 25.89 – 4625.82 mg . kg-1 d.m. (Zn), 60.21 – 3932.94 mg . kg-1 d.m. (Pb) and 0.11 – 14.64 mg . kg-1 d.m. (Cd), with geometrical means 173.56 mg . kg-1 d.m., 269.41 mg . kg-1 d.m. and 0.93 mg . kg-1 d.m., correspondingly. The total contents of Zn, Pb and Cd in the soil are definitely above the values of geochemical background for the Southern Poland [3]. The levels of metal concentrations in the topsoil are over 2- and even 3-fold higher than the baseline concentrations. In the comparison with European soils [4], the studied soil is severely contaminated. The Zn, Pb and Cd contents exceed median value 8-fold, 11-fold and 28-fold, respectively. However, compared to the Zn–Pb ore long-lasting mining and smelting sites in Poland [5-8] and all over the world [9-11], the heavy metal contents in the studied topsoil are at least 2-times lower.

The sequential extraction procedure (SEP) delivers information on the mobility of heavy metals in soil profiles [12]. Zn in the topsoil is related to the exchangeable (49.8%), reducible (20.2%) and organic/oxidizable (18.4%) phases. The residual (11.7%) fraction is of minor importance. The Zn fractionation in the whole soil profiles Zn looks slightly different, with depletion of exchangeable (42.2%) and reducible (15.9%) phases as well as with enrichment of residual (21.7%) and organic (20.1%) fractions. The largest amount of Pb is associated with the reducible fraction, accounting for about 44.5% for topsoil and 43.5% for whole profiles. The next most substantial phase is the organic/oxidizable with 37.4% and 29.7%, respectively. Residual and exchangeable phases reached lower lead accumulation ca. 10% and 14.3% also 8.1% and 12.5%, correspondingly. The cadmium is mainly extracted in the exchangeable fraction (53% and 55.6%, accordingly from the topsoil and whole profile) and in the reducible fraction (31.1% and 22.9%). The organic/oxidizable and residual fractions, getting about 10%, are of the minor importance.

Our results suggest that the mobility and bioavailability of Zn, Pb and Cd in the topsoil decline in the order Cd > Zn > Pb. It is also seen, that generally, the participation of the residual fraction increased with depth. These findings are in line with those of Ullrich et al. [6], Li & Thornton [13] and Gruszecka & Wdowin [14]. Moreover, when compared with Chrastný et al. [8], they follow Ettler's [15] announcement that the proportion of contaminants in the "labile" fractions of sequential extraction procedures, and subsequent vertical mobility, is generally higher for forest than for agricultural soils.

The results of toxicity assessment of study soil and waste samples by bacteria V. fischeri are presented below. In the soil samples the luminescence inhibition of V. fischeri is between: 51 to 84% for profile 1, -10 to 54% for profile 2, 52 to 89% for profile 3 and between 17 to 77% for profile 4. Depending on the studied waste samples, V. fischeri luminescence inhibition was from 66 to 95% (sample I), 43% (sample II) and 46% (sample III). The toxicity classification developed by Persoone et al. [16] was used to estimate soil and waste sample toxicity. According to the classification, soils collected from sampling sites 1 and 3 are toxic (class III). Toxicity of soil sampled from profile 4 vary from class III (deeper parts) by II to I (topsoil). Soil collected from profile 2 shows the lowest toxicity to the test organisms. Most samples in this profile are intoxic (class I), but upper horizons are still classified into toxicity class III. Waste samples were classed as III (toxic, sample I) and II (low toxic, samples I and II).

## 4. Conclusion

After 150 years since Zn smelter was closed and 40 years since ZnO plant was abandoned, the total content of Zn, Pb and Cd in the investigated soil is extremely high, ca.8 to 28 times larger than in the European topsoils [4] and about twofold above the values of geochemical background for the Southern Poland [3].

The total heavy metal concentration (from ICP-OES) in topsoil does not describe bioavailability well. The BCR procedure brings more useful details. According to BCR results, over the half of total Zn, Pb and Cd content can be easily transferred from topsoil downward and to the other parts of environment.

In view of above comments and results of bio-tests, we note that the area of current study is strongly affected by the historical zinc industry and the topsoil is heavily contaminated or even toxic.

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