

Joanna Świdwa-Urbańska¹, Marcin Zalewski²

Assessment of Selected Heavy Metals Content in Soil of Agricultural Activity

Abstract: A representative sample of agricultural soil was studied for assessing the level of toxic heavy metals that could be passed on to crops; this can be the first step towards determining the possibility of its further use, especially in areas where strong industrialization progress is visible. The soil texture, pH, and bulk density along with the total amount of lead (Pb), cadmium (Cd), and nickel (Ni) were analyzed for characterizing the status of the soil at two depths: TOP (a composite sample from 0–30 cm deep) and BOTTOM (a composite sample from 30–60 cm deep). The sampling scheme was a square grid with 16 regularly spaced points. The heavy metals concentration values were below legal limits but higher than the regional geochemical background level, suggesting an anthropogenic origin. The pollution load index (PLI) was implemented as a tool for computing the generalized heavy metal pollution status. A geostatistical analysis of the data shows a spatial variation on a detailed scale, both in the horizontal and vertical dimensions, with the TOP soil showing higher average Pb and Cd concentrations.

Keywords: heavy metals, pollution load index, agricultural soils

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¹ AGH University of Science and Technology, Faculty of Mining Surveying and Environmental Engineering, Department of Environmental Management and Protection, Krakow, Poland, email: jurb@agh.edu.pl
ORCID ID: <https://orcid.org/0000-0003-0297-8435>

² Student AGH University of Science and Technology, Faculty of Mining Surveying and Environmental Engineering, Department of Environmental Management and Protection, Krakow, Poland

1. Introduction

Heavy metals are considered to be one of the most dangerous soil contaminants. Anthropogenic sources are an increasingly frequent cause of heavy metals making their way into the environment. As a result of industrial development and pollution, the soil is heavily exposed to pollution by heavy metals accumulation. Investigating, monitoring, and measuring heavy metals pollution is a general concern worldwide [1–4]; however, it is especially important for areas devoted to agricultural purposes [5–7], as there is a high risk of heavy metals entering the human food chain in excessive quantities [5]. Plants generally accumulate heavy metals in quantities proportional to their concentrations in the soil [3]. Their accumulation may be different due to the intrinsic soil characteristics and the influence of various environmental factors. The type of soil, clay minerals, or organic matter content have an impact on the retention of metals in the sorption complex. One of the most influencing factors in the mobility, concentration, and distribution of heavy metals is soil pH [3, 4, 8]. In acid soils or in soils susceptible to acidification, the mobility of heavy metals can be high due to their higher solubility at acidic pH [3, 7].

This subject was studied using different approaches and variate analytical tools, including a statistical interpretation of the results as well as a spatial visualization. The pollution index used in this research is treated as a powerful tool for assessing the quality of the soil and ecological geochemistry [9, 10].

2. Characteristics of Studied Area and Sample-Collection Method

Soil samples were taken from an agricultural area located in the neighborhood of an industrial city – Stalowa Wola (Podkarpackie Voivodeship, Stalowa Wola District, Pysznica Community) (Fig. 1).



Fig. 1. Location of studied area

This city has been associated with industry since its location as a result of the development of the Central Industrial Region in Poland during the first half of the 20th century. Included in the first industrial facilities was the Stalowa Wola Steelworks (current name – HSW S.A.) and a coal-fired power plant (current name – ESW). Over the following years, industrial plants developed activities and productions that are still working nowadays.

The surveyed area can be regarded as representative of the neighborhood because of its similar agricultural practice to other land use in studied region as well as a similar type of soil. The investigated site is square-shaped (50 × 50 m) with the following corner coordinates: (50°33'39.14"N, 22°6'8.27"E), (50°33'37.78"N, 22°6'6.78"E), (50°33'36.85"N, 22°6'8.94"E), (50°33'38.20"N, 22°6'10.42"E). The area was formerly used for agricultural purposes as a pasture land. Nowadays, the area is prepared for the future planting of potatoes and wheat sowing.

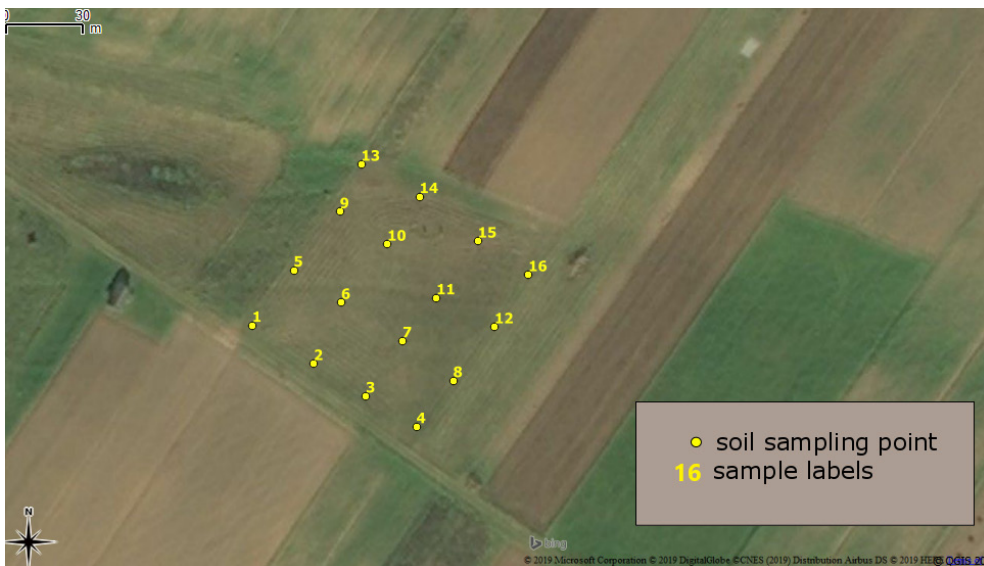


Fig. 2. Location of sampling points

The soil sampling was systematically designed for screening purposes in a regular grid, whose nodes were evenly spaced at 16 × 16 m (Fig. 2), resulting in 16 nodes that were selected as sampling positions. The soil sampling was performed at two depths (from 0 to 30 cm [TOP] and 30 to 60 cm [BOTTOM]) using composite sampling within an area of approximately 1 square meter. Each of the 32 samples weighed approximately 2 kg and were placed in bags, referenced, and transported to the laboratory. The coordinates of each of the 16 points was fixed by long record, averaged position from Global Navigation Satellite System (GNSS) and a mobile topographer application with a position accuracy of < 1 meter.

The analyses described in this paper were performed at the soil laboratory at AGH UST, Faculty of Mining Surveying and Environmental Engineering. The total concentration of heavy metals (Pb, Ni, Cd) was analyzed by the ASA method after mineralization in a mixture of perchloric and nitric acids (4:1). Other basic soil parameters were analyzed as well: pH in 1 mol/dm³ KCl and pH in H₂O by the potentiometric method, texture analysis by the Cassagrande method, and bulk density by the paraffin covering method.

3. General Characteristics of Soil

The analyzed soil samples are characterized by low pH levels (Tab. 1).

Table 1. Basic statistics of selected parameters of soils

Statistics	pH _{KCl}	pH _{H₂O}	Sand [%]	Loam [%]	Clay [%]	Bulk density [g/cm ³]
TOP (0–30 cm)						
Min.	4.29	5.27	10.00	37.00	15.00	1.44
Max.	5.05	6.07	43.00	70.00	30.00	1.79
Mean	4.62	5.72	20.69	57.06	22.25	1.60
Median	4.56	5.74	17.00	59.50	21.50	1.60
Variance	0.0443	0.0515	95.9625	86.3292	23.9333	0.0080
Standard dev.	0.21	0.23	9.80	9.29	4.89	0.09
25 th percentile	4.50	5.57	14.50	47.50	18.50	1.57
75 th percentile	4.73	5.89	24.50	63.50	26.50	1.66
BOTTOM (30–60 cm)						
Min.	4.29	5.82	1.00	36.00	21.00	1.39
Max.	5.18	6.86	37.00	76.00	37.00	1.59
Mean	4.80	6.34	16.19	57.63	26.19	1.51
Median	4.88	6.35	15.00	60.50	25.50	1.54
Variance	0.0688	0.0728	115.7625	138.1167	20.8292	0.0043
Standard dev.	0.26	0.27	10.76	11.75	4.56	0.07
25 th percentile	4.64	6.21	7.50	51.50	22.00	1.45
75 th percentile	4.97	6.51	23.50	64.50	29.00	1.56

The average values of pH in the BOTTOM layer are higher than in the TOP (measured in the KCl and H₂O). The lowest pH value (4.29) can be observed in the KCl at both depths, while the highest is 5.05 for the TOP and 5.18 for the BOTTOM layers. The minimum pH in the H₂O at the 0–30 and 30–60 cm depths are 5.27

and 5.82, respectively, while the maximums are 6.07 and 6.86, respectively. The dispersion of the results around the mean value is greater for the TOP layer and for the measurements in the H₂O. For 25% of the soil samples from the TOP layer, the pH in the KCl is less than 4.50 (a very acidic level).

The Shapiro–Wilk test was performed for both parameters and showed that the pH data approaches a normal distribution (at both depths). To compare the pH data between the TOP and BOTTOM layers, the t-student test was applied (all assumptions for this test [the group equivalence, distribution normality, and homogeneity of variance] were confirmed earlier). For an applied level of significance of $\alpha = 0.05$, the test confirmed statistically significant differences between the pH in the two layers (pH KCl: the *t*-value is -2.1852 , and the *p*-value -0.0368 ; pH H₂O: the *t*-value is 6.9423 , and the *p*-value $-1.04 \cdot 10^{-7}$)

The soil texture (Tab. 1) is described using the USDA classification. All soil samples from the TOP layer are heavy-textured soils (silt loams, clay loams, and loams), with a domination of silt loams (75% of the samples). The soils from the BOTTOM layer were classified as silt loams, silty clay loams, and loams, with a domination of silt loam texture (62.5%). The average value of the bulk density measured in the set of 32 measurements was 1.55 g/cm^3 . In the upper layer (TOP), the range of the determined values was within a range of $1.44\text{--}1.79 \text{ g/cm}^3$. In the BOTTOM layer, the data range was smaller.

4. Total Content of Pb, Cd, and Ni in Soil

The range of each heavy metal is shown in Table 2 and Figure 3. The average concentration of Pb and Cd are higher in the 0–30-cm layer, whereas higher-than-average Ni concentrations are observed in the 30–60-cm layer. The values of standard deviation indicate a larger spread of the results around the averages in the BOTTOM layer (30–60 cm).

Table 2. Basic statistics of content of selected heavy metals in soils

Statistics	Pb [mg/kg] TOP	Ni [mg/kg] TOP	Cd [mg/kg] TOP	Pb [mg/kg] BOTTOM	Ni [mg/kg] BOTTOM	Cd [mg/kg] BOTTOM
Min.	16.71	38.18	0.45	10.78	28.68	0.19
Max.	23.30	55.41	0.80	22.32	64.38	0.61
Mean	20.23	46.78	0.58	15.83	48.555	0.40
Median	20.25	45.06	0.56	16.46	48.56	0.39
Variance	4.285	24.948	0.009	10.592	100.594	0.011
Standard dev.	2.07	4.99	0.10	3.25	10.03	0.10
25 th percentile	19.07	43.95	0.50	13.68	39.99	0.34
75 th percentile	21.92	50.55	0.64	17.49	55.81	0.46

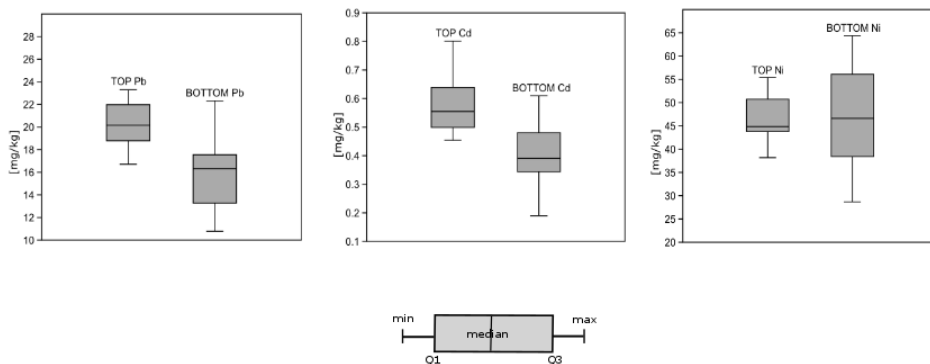


Fig. 3. Distribution of selected statistics of content of Pb, Cd, and Ni in soil samples from TOP and BOTTOM levels

More than 50% of the samples from the BOTTOM layer are characterized by lower lead concentration than the minimum value in the TOP layer. This was also the case for cadmium, where the percentage of the samples was about 50–75%. On the other hand, the concentrations of nickel in the BOTTOM layer exceeded the maximum value for the TOP layer in more than 25% of the cases.

In order to compare the average content of the heavy metals between the TOP and BOTTOM layers, the parametric *t*-student test was used for the lead and cadmium (due to the fulfilled statistical test requirements), and the non-parametric U-Mann Whitney test was used for the nickel data (due to the heterogeneity of the variance for nickel checked by the Levene test). The distribution of the measured values for lead (Pb) and cadmium (Cd) differs greatly for the TOP and BOTTOM data sets. The *t*-student test statistics for Pb (*t*-value of 4.5615, *p*-value of 0.00008) and Cd (*t*-value of 5.1351, *p*-value of 0.00016) for the TOP and BOTTOM sets confirmed statistically significant differences. The U-value of the test for Ni concentration for the TOP and BOTTOM sets is 106, and the *p*-value is 0.41648. For applied level of significance 0.05 test not confirmed statistically significant differences in Ni concentration between two layers.

Based on the results of spatial variability (Figs. 4–6), an increase in the concentration of nickel and lead in the studied area can be observed in the BOTTOM layer along the southwestern direction. Impacting factors on such a distribution of heavy metal concentration can be the frequent southwest-direction wind blowing in this region and the unpaved access road sharing borders with the studied area. For testing the statistical significance trend between the concentration and spatial location, the Mann–Kendall trend test was applied. For a level of significance of $\alpha = 0.05$, the test confirmed a statistically significant trend in all of the investigated heavy metal distribution in southwest to northeast direction in the BOTTOM layer: there is a statistically significant decreasing trend in the lead (*z*-value of 3.7368, *p*-value of 0.000186), cadmium (*z*-value of 3.4254, *p*-value of 0.000614), and nickel (*z*-value of 4.0482, *p*-value of 0.0000516).

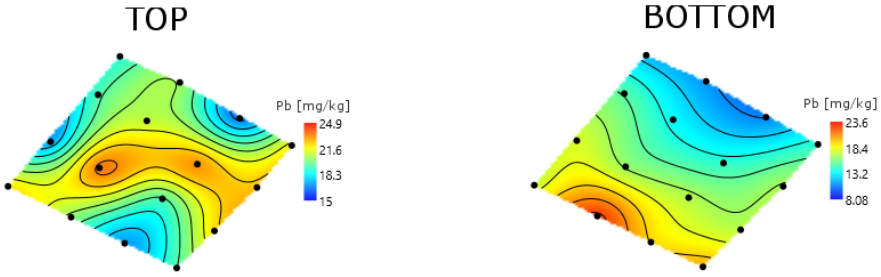


Fig. 4. Distribution of content of Pb in soil

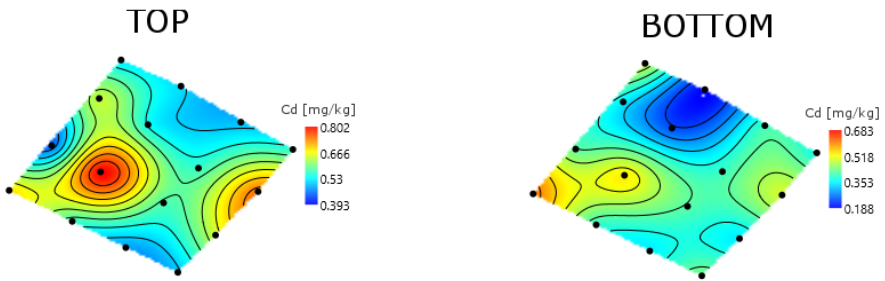


Fig. 5. Distribution of content of Cd in soil

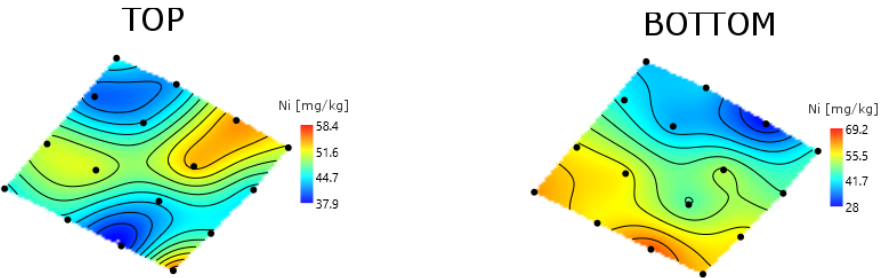


Fig. 6. Distribution of content of Ni in soil

To check the variability in depth, the differences were calculated between the TOP and BOTTOM layers in the studied heavy metal concentrations. The spatial distribution of the differences between the layers is presented in Figure 7. The highest levels of contamination in the TOP layer over the BOTTOM is visible in the north-eastern part of the studied area for lead and nickel. In the case of cadmium, all values are higher in the upper set of the data.

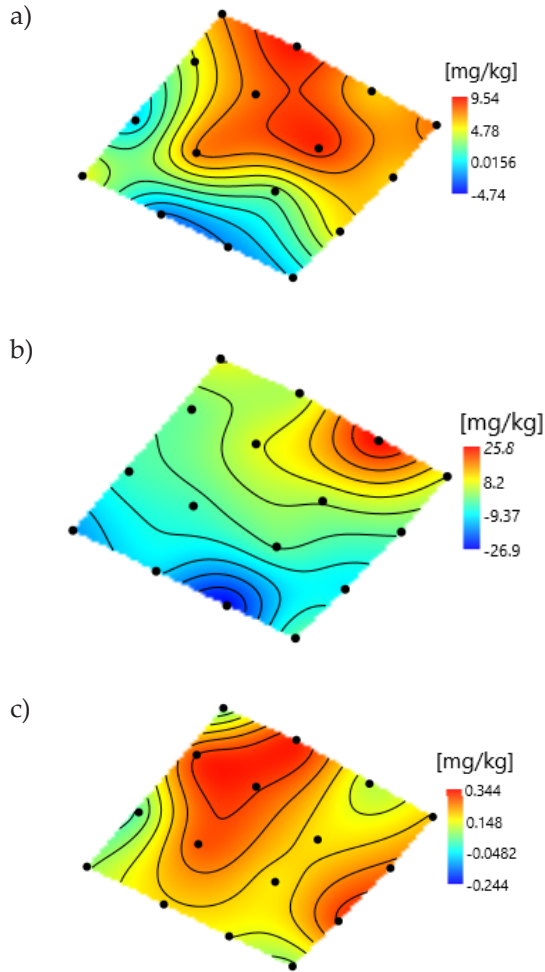


Fig. 7. Distribution of difference between TOP and BOTTOM layer in concentrations of lead (a), nickel (b), and cadmium (c)

To evaluate the summarized heavy metal contamination on the investigated area and compare the TOP and BOTTOM layers, a pollution load index (PLI) was calculated by Formula (1) [11]:

$$PLI = \sqrt[n]{CF_1 \cdot CF_2 \cdot CF_3 \cdot \dots \cdot CF_n} \quad (1)$$

where CF is the contamination factor of the sampling site ($CF = C_{\text{metal}}/C_{\text{background value}}$), and n is the number of contamination factors.

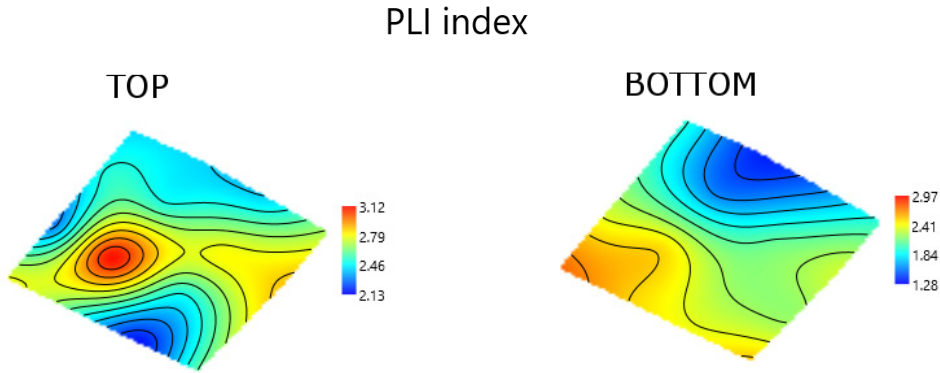


Fig. 8. Distribution of PLI index in TOP and BOTTOM soil

The results of the spatial analyses of the PLI indices in both layers are presented in Figure 8; these show a similarity to the cadmium distribution. This correspondence could be caused by the highest contamination factors calculated for Cd. Using background levels as reference data, PLI index values >1 indicate pollution due to the influence of external sources.

5. Summary

It was hypothesized that the existence of the nearby location (located about 2 km from the sources of emission) of industrial plants has impacted the quality of the agricultural land. Special attention was paid to the study of heavy metal content in the soil due to the types of industrial plants in the neighborhood (the energy and metallurgy sectors). The object of the research was to evaluate the content of heavy metals using different methodologies.

The article has led to the following conclusions:

1. The limit values contained in the national regulations [12–14] for heavy metal content in areas useful for agricultural use have not been exceeded.
2. The PLI index values for the whole investigated area based on a high enrichment contamination factor for each point suggest an anthropogenic origin of the heavy metals in the soil.
3. A low pH level can determine the high heavy metal solubility and availability for plant uptake. Under such conditions, there is a high risk of the bioaccumulation of heavy metals in plants and passing them on to humans by the ingestion of agricultural crops.
4. The statistical tests confirmed statistically significant differences in Pb and Cd concentration between the two soil depths.
5. An increase in the concentration of Pb, Ni, and Cd in the BOTTOM layer of the studied area was observed along the northeastern to southwestern direction.

6. A statistical significance trend between the concentration and spatial location were confirmed for all of the studied heavy metals in the BOTTOM layer.
7. The highest levels of lead and nickel contamination in the TOP layer over the BOTTOM were detected on the northeastern part of the studied area. In the case of Cd, all of the TOP values are higher in the upper set of the data.

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Ocena zawartości wybranych metali ciężkich na przykładzie gleb użytkowanych rolniczo

Streszczenie: W pracy przedstawiono badania gleb reprezentatywnego obszaru użytkowanego rolniczo w celu oceny poziomu toksycznych metali ciężkich, które mogłyby przedostać się do upraw. Może to stanowić pierwszy krok do określenia możliwości dalszego wykorzystania gleb, zwłaszcza na obszarach, na których widoczny jest silny postęp industrializacyjny. W celu scharakteryzowania stanu gleby na dwóch głębokościach analizowano strukturę gleby, pH, gęstość objętościową oraz całkowitą zawartość ołowiu (Pb), kadmu (Cd) i niklu (Ni): TOP (próbka 0–30 cm) i BOTTOM (próbka 30–60 cm). Schemat pobierania próbek był oparty na kwadratowej siatce z 16 punktami rozmieszczonymi regularnie. Wartości stężenia metali ciężkich były poniżej prawnych limitów, ale wyższe niż regionalny poziom tła geochemicznego, co sugeruje ich pochodzenie antropogeniczne. Indeks PLI został wdrożony jako narzędzie do obliczania ogólnego stanu zanieczyszczenia metalami ciężkimi. Analiza geostatystyczna danych pokazuje zmienność przestrzenną w szczegółowej skali, zarówno w wymiarze poziomym, jak i pionowym, przy czym poziom TOP gleby wykazuje wyższe średnie stężenia Pb i Cd.

Słowa

kluczowe: metale ciężkie, indeks PLI, obszary użytkowane rolniczo