The pollution indices of trace elements in soils and plants close to the copper and zinc smelting works in Poland’s Lower Silesia

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Abstract

The quality of soils polluted by trace elements around the facilities with the Cu and Zn smelting activities and the post-flotation tailings pond from copper industry were assessed. The level of the contamination of soils was determined on the basis of the contamination factor and the geoaccumulation index. The geoaccumulation index allows to distinguish more degrees of soil contamination and simplifies the assessment of the useable value of soil. The degrees of soil contamination and the pollution load index were shown. It has been shown that the pollution indices are a useful tool in describing the soil quality and planning corrective actions in the areas contaminated as a result of industrial activity. Histograms of pollution indices were used in order to detect the distribution of trace elements in soils. The content of metals in biomass was assessed using bioaccumulation indices. Triticum L. and Brassica napus L. show low bioaccumulation of studied metals in cereal plants. The correlations were used in order to detect the relationship among trace elements in soil as well as the relationship of metal (soil)-metal (plant) and metal bioaccumulation (plant)-metal (soil). The highest values of indices were recorded for the Ołaawa smelter, presumably due to the long operation period before technological changes limiting the emission of pollutants were introduced. This research area was classified as very highly contaminated with all trace elements. Soils around other facilities are at least moderately contaminated.

Keywords Toxic elements · Soil quality · Contamination factor · Geoaccumulation index · Degree of contamination · Bioaccumulation index

Introduction

The metallurgical industry of non-ferrous metals is particularly oppressive to the environment and human health (Mukhacheva 2017; Kim et al. 2016; Kalinovic et al., 2016; Jamshidian et al. 2015). In Poland, this industry dynamically develops mainly in Upper and Lower Silesia, significantly changing the quality of the environment near the smelters (Kapusta and Sobczyk 2015; Skubała and Zaleski 2012; Damek-Poprawa and Sawicka-Kapusta 2003). Many authors confirm that long-term emission of gaseous pollutants and metal-bearing dusts is the source of the enrichment of soils with metals around the emitter of pollutants. The impact of copper smelters was considered by Vorobeichik and Kaigorodova (2017); Nikolić et al. (2011); Medyńska-Juraszek and Kabala (2010); Kabala et al. (2008); Martley et al. (2004); and Adamo et al. (2002). Strong influence of zinc smelters on the environment was reported by Ćuske et al. (2013); Filzek (2004); Goodarzi et al. (2002); and Sterckeman et al. (2000 and 2002). An additional source of the emission of pollutants into the environment is the landfills of slag from the ore smelting process and the tailings pond with the post-flotation wastes of ores (Karczewska et al., 2017, Kalinovic et al. 2016; Medyńska-Juraszek and Kabala 2012; Medyńska et al. 2009; Cabala et al. 2009; Krzaklewski et al. 2004).

The richest deposits of copper in Europe occur in the Legnica-Glogów Copper District, in the Lower Silesia region of Poland. All mines located here extract both sandstone ore and shale-carbonate ore with the copper mineralization—a series of Permo-Triassic sediments. Copper mineralization occurs mainly in the form of small grains of sulfides, most often distributed evenly, but in some places concentrated in the form of smudges and extended pockets. Locally, there are coarse-
Grain forms of mineralization in the shape of veins of varying thicknesses or irregularly located pockets. Simple copper sulfides: chalcocite and digenite predominate in these types of copper ores. The accompanying chemical elements are lead, silver, cobalt, zinc, and nickel. The average copper content is 1.9% of Cu, while the average silver content is equal to 61 g/mg.

The copper ores are sent to the nearby smelting facilities: chalcocite and digenite predominate in these types of mineralization in the shape of veins of varying thicknesses or irregularly located pockets. Simple copper sulfides: chalcocite and digenite predominate in these types of copper ores. The accompanying chemical elements are lead, silver, cobalt, zinc, and nickel. The average copper content is 1.9% of Cu, while the average silver content is equal to 61 g/mg.

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The wastes after flotation of copper ores with a mass of up to 26 million Mg/year are deposited in the Żelazny Most reservoir. The ongoing reconstitution of the facility is aimed at achieving a capacity of 1.1 billion m³. The Legnica copper smelter has been in operation since 1953 and is located on the outskirts of the city, about 4 km from the city center. It uses the shaft furnace technology and its production capacities of the electrolytic copper amount to approx. 111.1 thousand Mg/year. The smelter is surrounded with agricultural areas where mainly wheat and rape are grown. The Głogów copper smelter comprises two branches. Since 1971, the Głogów I smelter was operated with the traditional technology of shaft furnaces with production capacity of 160 thousand Mg Cu/year. Between 2014 and 2016, the existing installation was replaced with the flash furnace and electric furnace technology. The Głogów II smelter commenced operation in 1978 with a flash furnace installation with production capacity of 150 thousand Mg Cu/year. In 1999, a protection zone around the Głogów copper smelter was established and the recultivation of lands was carried out. The zone was liquidated in 2005 and currently, the agricultural production near the smelter includes mainly the cultivation of wheat, potatoes, and sugar beets. The Olawa zinc smelter has been operating since 1845 and is the largest producer of cadmium, lead, and zinc oxides. It is located in the south-eastern part of the city in the immediate vicinity of family houses and blocks of flats. At a distance of less than 1 km to the west from the site, the city park is located, followed by arable lands and garden plots. Maize, rapeseed, wheat, rye, potatoes, and sugar beets are the main crops growing there.

In assessing the content of trace elements in the soil, the index of geoaccumulation, the contamination factor, and the degree of metal contamination are most commonly used. These indicators are used to assess the intensity of anthropogenic pollutants deposition in surface layers of soil (Kowalska et al. 2018). It is possible to assume the global background coverage for the studied chemical element, referring to the average content of the element in the earth’s crust (Yaylali-Abanuz 2011; Loska et al. 2004; Taylor and McLennan 1995). The reference level of the chemical element may also mean the world average concentration of the metal in the clayey sediment, the so-called average shale value (Zahran et al. 2015; Rahman et al. 2012; Müller 1969). Rubio et al. (2000) recommend using a regional background because significant differences in the chemical composition of the soil can occur locally. Depending on the parent material, the metal concentration in soil can change even up to 2–3 rows of magnitude according to Blaser et al. (2000). Furthermore, Blaser et al. (2000) and Sutherland (2000) recognized that the concentration of elements from the deeper layers of the soil profile can be considered the local background for the upper soil layers. Manna and Maiti (2018) assumed as the background the content of metals in the soil sample from the uncontaminated area outside of the influence of anthropogenic activity.

This study aims at as follows: (1) assessment of the condition of soils in the immediate vicinity of the copper smelters in Legnica and Głogów and the post-flotation copper ore tailings pond, and the zinc Olawa smelter in Lower Silesia, Poland, (2) assessment of the suitability of soils for the cultivation of cereal plants, and (3) assessment of the utility of pollution indices for the comprehensive evaluation of the degree of soil contaminated with metals.

Materials and methods

Sample collection and analytical procedure

Environmental samples were collected in June and July 2017. The sampling points were located at a distance of up to 2.5 km from the borders of industrial facilities: the copper and zinc smelters and the Żelazny Most reservoir with the post-flotation copper ore tailings pond, and the zinc Olawa smelter in Lower Silesia, Poland. (2) assessment of the suitability of soils for the cultivation of cereal plants, and (3) assessment of the utility of pollution indices for the comprehensive evaluation of the degree of soil contaminated with metals.
The preparation of samples for the elemental analysis using atomic absorption spectroscopy included weighing approx. 0.2 g of homogeneous dry material (soil or plant) and digestion in nitric acid of 65% (8 ml) according to PN-ISO 11465 (1999). The mineralization process was conducted in a closed Microwave Digestion System using Start D Milestone equipment, in conditions of a linear temperature increase of 220 °C with the use of microwave power of 800 W. The measurements of zinc, copper, and lead content were performed through the FAAS and the GFAAS instrumental method using the Thermo Solaar iCE 3500 device (PN-ISO 11047, 2001). In the trace metal analysis were applied the certified reference materials (CRM) from Sigma Aldrich. The reagent blank samples were used to check the instrument readings. The limits of detection were estimated based on three times the standard deviation for digestion blanks. The accuracy of the determination was controlled using the method of the standard addition. The percentage of the recovery was 94–98%. The pH and the electrical conductivity measurements in soils with a stoichiometry of 1:2.5 (m:v) were conducted according to PN-ISO 10390 (1997).

The AAS measurement results were verified through the standard deviation, the coefficient of variation, and the confidence interval. The accepted results of the determination for a given point were within 10%. Statistical analysis was made based on the Student test with the number of degrees of freedom equalling 5 and the p value of 0.05. Chemical analyses have been carried out in the certified Laboratory of Toxicology and Environmental Research in the Faculty of Environmental Engineering at the Wrocław University of Science and Technology.

The content of metals in soil and plant was calculated as the average value with the standard deviation for six independent environmental samples from one location. The average values of pollution index for a given location were used.

The statistical analysis was carried out using the program Statistica ver. 13.1 and Microsoft Excel 2013. The data was checked for normal distribution (Shapiro-Wilk’s W test). The Mann-Whitney U test was used for the data which did not show normal distribution. Spearman’s rank correlation coefficients were calculated for elemental concentrations for all samples. Correlations were considered strong when higher than 0.7, and p value was 0.05.

**Pollution indices**

The contamination factor \( C^i_f \) defines the ratio of the mean content of metal in soil from six sampling sites \( C^i_0 \) to the preindustrial concentration of individual metal \( C^i_n \) (Hakanson 1980). In our work, we applied the concentration of elements in the Earth’s crust as a reference value similarly to Loska et al. (2004). The average content of copper, zinc, lead, and cadmium in the Earth’s crust is respectively, in mg/kg: 39 (Cu), 67 (Zn), 17 (Pb) (Tylor and McLennan 1995).

\[
C^i_f = \frac{C^i_0}{C^i_n}
\]

\( C^i_f \) value

| Soil quality | Low contamination | Moderate contamination | Considerable contamination | Very high contamination |
|--------------|-------------------|------------------------|---------------------------|------------------------|
| 1 ≤ \( C^i_f \) < 3 | \( C^i_d \) < 8 | 8 ≤ \( C^i_d \) < 16 | 16 ≤ \( C^i_d \) < 32 | 32 ≤ \( C^i_d \) |

The degree of contamination in soil \( C_d \) is defined as a sum of contamination factors for all trace elements \( C^i_f \).

Four classes of the \( C_d \) parameter were categorized by Hakanson (1980). Zahran et al. (2015) introduced a modification of earlier defined ranges of the degree of contamination, assuming as \( n \) the number of trace elements to be determined.

\[
C_d = \sum_{i=1}^{n} C^i_f
\]

According to Abrahim and Parker (2008), Machender et al. (2011), and Rahman et al. (2012), the modified degree of contamination \( mC_d \) is the average value of pollution indices for all trace elements \( C^i_f \), provided that at least three chemical elements \( n \) are used in the calculations.

\[
mC_d = \frac{C_d}{n}
\]

\( mC_d \) value

| Soil quality | Nil to very low degree of contamination | Low degree of contamination | Moderate degree of contamination | High degree of contamination | Very high degree of contamination | Extremely high degree of contamination | Ultra high degree of contamination |
|--------------|--------------------------------------|-----------------------------|---------------------------------|-----------------------------|---------------------------------|-----------------------------------|----------------------------------|
| 1.5 ≤ \( mC_d \) < 2 | 2 ≤ \( mC_d \) < 4 | 4 ≤ \( mC_d \) < 8 | 8 ≤ \( mC_d \) < 16 | 16 ≤ \( mC_d \) < 32 | 32 ≤ \( mC_d \) |
The pollution load index (PLI) is the geometric average of the impurity coefficients ($C_{f}^{i}$) and determines the contribution of all metals in a given place (Tomlinson et al. 1980; Jorfi et al. 2017). This parameter allows to assess the level of environmental contamination in order to undertake monitoring or repair activities aimed at improving soil quality.

The index of geoaccumulation ($I_{geo}$) applies a logarithm operation of the data set and the constant equal 1.5, which allows for the elimination of possible differences in the content of the studied element in the soil due to the possible variation in the background ($B_{n}$) (Stoffers et al. 1986; Ruiz 2001) and a small influence of anthropogenic activity (Muller 1981). In this work employed a modified $I_{geo}$ index to make calculations because the background value was denoted of the concentration of trace elements in the Earth’s crust (Tylor and McLennan 1995).

In the worldwide studies, there is a lack of consistency in the application of geochemical background values (unification) and the selection of a standardized (universal) indicator describing the contamination of soils. The diversity in the ways of assessing the degree of soil contamination makes it impossible to compare soils around industrial facilities, even with a similar kind of production. During the work, we have chosen indices: $I_{geo}$ and $C_{f}$ with the reference background, and $C_{f}/mC_{d}$ and PLI, which made it possible to easily compare them with each other, which is confirmed statistically by the linkage distances between clusters according to Kowalska et al. (2018). So far, no comprehensive analysis of the environment with the use of pollution indices around non-ferrous metallurgy works and tailings pond with metal ore post-flotation waste has been carried out. Therefore, in this work, an effort was made to look at the indices of pollution in the assessment of soil quality. We point out that environmental pollution indices are a useful tool in assessing the quality of soils. In contrast, elemental concentrations inform about the exceeding of the permissible standards, without taking into account the geochemical level of the element in soil and not distinguishing between the degrees of soil pollution.

In order to monitor the content of these elements in plants, the bioaccumulation coefficient ($BAC$) is used. This parameter compares the concentration of the trace element in biomass (plants aboveground parts, $P_{i}^{t}$) with its content in the soil ($C_{0-1}$). It further enables categorization of plants as accumulators ($BAC > 1$) or excluders ($BAC < 1$) of trace elements (Olowoyo et al. 2010).

$$BAC = \frac{P_{i}^{t}}{C_{0-1}}$$

The assessment of total accumulation of all trace elements in plants is based on the metals accumulation index of MAI (Liu et al. 2007), where $n$ is the total number of trace elements to be determined and $I_{i}$ is the subindex for variable $i$. The parameter $I_{i}$ is obtained by dividing the average concentration value of each metal in biomass ($P_{i}^{t}$) by the standard deviation ($\delta P_{i}^{t}$).

$$MAI = \left(\frac{1}{n}\sum_{i=1}^{n} I_{i}; I_{i} = \frac{P_{i}^{t}}{\delta P_{i}^{t}}\right)$$

The comprehensive bioconcentration index ($CBCI$) is based on fuzzy synthetic and allows to assess the overall performance of plant species in the phytoremediation of soils contaminated with many trace elements (Zhao et al., 2014).

$$CBCI = \left(\frac{1}{n}\sum_{i=1}^{n} I_{i}; I_{i} = \begin{cases} 0 & BCAC = BAC_{\text{min}} < BAC < BAC_{\text{max}} \\ 1 & BAC = BAC_{\text{max}} \end{cases}\right)$$

### Results and discussion

The studied soils were mainly slightly acidic (pH 5.6–6.5) and neutral (pH 6.6–7.2), which is confirmed by the data from Medyńska-Juraszek and Kabala (2012 and 2010), Kabala et al. (2008), and Cuske et al. (2013). No alkaline soils were found near the copper smelters in Legnica and Głogów. Soils around all facilities were poorly salted. The electrical conductivity was basically below 25 mS/m
(92% of samples in Żelazny Most, 75% in Głogów, 100% in Legnica, and 67% in Oława).

**Trace element contents**

The content of trace elements in the top layer of soils around the smelting works and the Żelazny Most copper ore tailings pond is presented in Table 1. A high value of the coefficient of variation (CV > 0.90) means high extent of spatial variation and indicates high degree of anthropogenic contribution (point pollution). Other CV values, except for copper in Oława, also indicate that studied areas have undergone anthropogenic influence with moderate level of spatial inhomogeneous. Such results can also be achieved from the p value of the normal distribution test. All elements have p values below 0.05, which implies that they cannot pass the normal distribution test. It may also suggest that the elements have anthropogenic source. When the data did not show normal distribution, the Mann-Whitney U test was used and showed that the differences between the medians of the concentrations of two elements are statistically significant (p < 0.05).

The positive values of skewness mean that most of the results are below the average value, whereas the positive values of kurtosis inform about the existence of a large pool of results close to the average value and at the same time a small number of outcomes with the extreme values. For the studied areas, the arithmetic average value is significant influenced by the single very high concentrations of a given trace element. A special situation occurs in Legnica, where the largest spread between the concentrations of a given metal was observed, with a small arithmetic average value at the same time. The maximum concentrations of trace elements were greater than the average values of 8.5-fold for copper and 6-fold for lead. In Głogów, a large spread of results for zinc concentrations in soil samples was observed. The maximum value was almost 7 times higher than the average value. A large dispersion of results for zinc was observed in Oława as well. The average value was 3 times lower than the maximum value, but at the same time similar to the median.

The values of Spearman’s rank correlation coefficient (p value of 0.05) indicate strong correlation between Cu and Pb (0.73) and moderate correlation between Zn and Pb (0.59) in Głogów. Moderate correlations were also recorded for pairs of Cu-Pb (0.54) and Zn-Pb (0.59) in Oława, for pairs of Cu-Zn (0.66) and Cu-Pb (0.42) in Legnica, and also between Cu and Zn in Żelazny Most (0.69), which may suggest the metals originated from industrial activity.

When comparing obtained concentrations of metals in soils with the literature data from previous years, from 5 to 10 years back for studied industrial facilities (Table 2), no significant reduction of metals content in the top of soil profile is still observed. High levels of metals in topsoils within a distance of up to 2.5 km from the studied facilities are noticed. For other facilities in the world with similar activities, the comparable and sometimes even much higher concentrations of trace elements than in Poland were observed (Ettler 2016).

**Pollution indices and soil quality**

The $C_F$ index values usually suggest a higher degree of soil contamination with metals in comparison with the $I_{geo}$ index. Applying the logarithmic transformation of the initial data

| Metal | Range  | Avg.  | SD   | Q1   | Med.  | Q3   | Skewness | Kurtosis | CV  |
|-------|--------|-------|------|------|-------|------|----------|----------|-----|
| Żelazny Most, n = 30 | | | | | | | | | |
| Zn    | 32.78–92.97 | 48.28 | 17.98 | 34.76 | 38.47 | 55.81 | 1.28 | 0.71 | 0.37 |
| Cu    | 36.47–337.11 | 93.61 | 90.50 | 40.47 | 51.92 | 84.04 | 1.80 | 2.09 | 0.97 |
| Pb    | 2.71–82.93  | 19.67 | 21.03 | 9.62  | 13.64 | 17.24 | 2.30 | 4.64 | 1.07 |
| Głogów, n = 30 | | | | | | | | | |
| Zn    | 29.75–836.03 | 124.28 | 215.04 | 42.93 | 58.73 | 78.76 | 3.02 | 7.48 | 1.73 |
| Cu    | 23.56–250.97 | 130.12 | 69.49 | 72.80 | 118.00 | 186.35 | 0.20 | –1.29 | 0.53 |
| Pb    | 10.44–89.52 | 43.49 | 21.09 | 28.00 | 37.32 | 53.78 | 0.82 | –0.30 | 0.48 |
| Legnica, n = 30 | | | | | | | | | |
| Zn    | 24.33–241.52 | 59.46 | 54.70 | 31.31 | 37.93 | 72.86 | 2.63 | 6.28 | 0.92 |
| Cu    | 51.18–2476.30 | 290.38 | 559.62 | 84.27 | 102.86 | 118.53 | 3.11 | 9.24 | 1.93 |
| Pb    | 50.00–685.77 | 124.92 | 149.97 | 66.06 | 80.98 | 102.10 | 3.31 | 10.14 | 1.20 |
| Oława, n = 30 | | | | | | | | | |
| Zn    | 190.81–2535.63 | 825.70 | 617.48 | 270.15 | 717.32 | 1024.57 | 1.30 | 1.64 | 0.75 |
| Cu    | 28.89–44.79  | 36.51 | 4.44  | 33.19 | 36.50 | 39.81 | 0.06 | –1.12 | 0.12 |
| Pb    | 90.34–1168.51 | 329.02 | 305.77 | 120.92 | 161.04 | 405.26 | 1.45 | 0.99 | 0.93 |
narrow the $I_{geo}$ index compartments down to the range between the minimum and maximum values for a given population of results. For this reason, the $I_{geo}$ index makes a distinction between a bigger number of different degrees of soil contamination. It allows to verify the quality of soils without classifying them equally. This is particularly important in the case of heavily contaminated soils around industrial facilities. However, the $C_f$ index provides the basis for the calculation of complex indices group and the degree of soil pollution with all analyzed heavy metals. Shapiro-Wilk’s $W$ test conducted for the $C_f$ and the $I_{geo}$ indices confirmed the lack of normal distribution ($p < 0.05$). The Mann-Whitney $U$ test showed that the differences between the $C_f$ and $I_{geo}$ indices are statistically significant ($p < 0.05$) with the exception of the Zn-Pb pair in Żelazny Most ($p$ value of 0.16).

**Żelazny Most tailings pond**

The median of $I_{geo}$ for analyzed metals does not indicate contamination of soils around the Żelazny Most reservoir (Table 3). Despite that fact, the median of $C_f$ shows moderately contaminated soils with copper because some sampling point soils are heavily or considerable contaminated with this element (Fig. 1).

**Głogów copper smelter**

According to the $I_{geo}$ classification, 50% of the population of samples are moderately contaminated with copper, with division into the 2nd class and the 3rd class (Fig. 1). The median of $C_f$ for copper confirms enrichment of soils (Table 3). For zinc and lead, the medians of the $I_{geo}$ indices do not indicate contamination of soils. The average of $C_f$ for zinc is 2 times higher than median of $C_f$ which confirms the heterogeneity of the distribution of metal content in soils.

**Legnica copper smelter**

The median of $I_{geo}$ does not indicate contamination of soils with copper (Table 3); however, the median of $C_f$ shows moderate contamination of soils. The average of $C_f$ is much higher than the median value because very highly contaminated soils with copper are noticed in the border area of the smelter at a distance below 100 m from the facility border (5th and 6th classes of $I_{geo}$) (Fig. 1).

The median of $I_{geo}$ index for lead classifies soils as moderately polluted. Soils closer to the smelter belong to the 5th class of $I_{geo}$ (heavily to extremely contaminated). The median of $C_f$ confirms a considerable contamination of soils with lead. According to the median of $I_{geo}$ and $C_f$ indices, zinc is not a pollutant of soils. Only in the border area of the smelter a moderate pollution of soils with zinc was recorded (2nd class of $I_{geo}$).

**Oława zinc smelter**

The medians of $I_{geo}$ for zinc and lead show accumulation of metals in soils in the immediate vicinity of the Oława smelter. The $I_{geo}$ classification allows to assign the soils into classes between the 3rd and the 5th for zinc and from the 3rd up to the 6th class of soils for lead (Fig. 1). High medians of $C_f$ for both metals.
Table 3: Descriptive statistics of pollution indices in soils

|                | Avg. | SD    | Med.  | Q1  | Q3   | Avg. | SD    | Med.  | Q1  | Q3   |
|----------------|------|-------|-------|-----|------|------|-------|-------|-----|------|
| Żelazny Most   |      |       |       |     |      |      |       |       |     |      |
| Zn             | 0.72 | 0.27  | 0.57  | 0.52| 0.83 | -1.14| 0.47  | -1.39 | -1.53| -0.86|
| Cu             | 2.40 | 2.33  | 1.33  | 1.04| 2.15 | 0.23 | 1.04  | -0.18 | -0.53| 0.41 |
| Pb             | 1.16 | 1.24  | 0.80  | 0.57| 1.01 | -0.92| 1.21  | -0.90 | -1.43| -0.57|
| Cₙ       | 4.28 | 3.57  | 2.63  | 2.31| 4.22 | -    |       |       |     |      |
| mCd          | 1.40 | 1.20  | 0.87  | 0.77| 1.34 | *2.45/3.61|       |       |     |      |
| PLI           | 1.15 | 0.81  | 0.82  | 0.73| 1.04 | *2.11/3.47|       |       |     |      |
| Glogów        |      |       |       |     |      |      |       |       |     |      |
| Zn             | 1.85 | 3.21  | 0.88  | 0.64| 1.18 | -0.52| 1.20  | -0.78 | -1.23| -0.35|
| Cu             | 3.34 | 1.78  | 3.03  | 1.87| 4.78 | 0.89 | 0.94  | 1.00  | 0.32 | 1.67 |
| Pb             | 2.56 | 1.24  | 2.20  | 1.65| 3.16 | 0.60 | 0.71  | 0.55  | 0.13 | 1.08 |
| Cd             | 7.75 | 4.67  | 6.52  | 3.83| 9.51 | -    |       |       |     |      |
| mCd           | 2.58 | 1.56  | 2.17  | 1.28| 3.17 | *1.31/1.14|       |       |     |      |
| PLI           | 2.16 | 1.24  | 1.98  | 1.17| 2.52 | *1.45/1.62|       |       |     |      |
| Legnica       |      |       |       |     |      |      |       |       |     |      |
| Zn             | 1.05 | 1.02  | 0.54  | 0.48| 0.98 | -0.97| 1.02  | -1.48 | -1.66| -0.66|
| Cu             | 9.13 | 15.40 | 2.80  | 2.19| 4.29 | 1.38 | 1.54  | 0.90  | 0.54 | 1.44 |
| Pb             | 9.69 | 11.42 | 5.41  | 4.12| 6.64 | 2.30 | 1.09  | 2.02  | 1.63 | 2.31 |
| Cd             | 13.37| 20.26 | 7.45  | 5.82| 9.55 | -    |       |       |     |      |
| mCd           | 4.46 | 6.75  | 2.48  | 1.94| 3.18 | *2.86/7.06|       |       |     |      |
| PLI           | 3.09 | 4.31  | 1.83  | 1.43| 2.30 | *2.92/7.86|       |       |     |      |
| Oława         |      |       |       |     |      |      |       |       |     |      |
| Zn             | 12.32| 9.22  | 10.71 | 4.03| 15.29| 2.63 | 1.12  | 2.88  | 1.43 | 3.35 |
| Cu             | 0.94 | 0.11  | 0.94  | 0.85| 1.02 | -0.69| 0.18  | -0.68 | -0.82| -0.56|
| Pb             | 19.35| 17.99 | 9.47  | 7.11| 23.84| 3.19 | 1.15  | 2.66  | 2.25 | 3.99 |
| Cd             | 32.61| 22.91 | 23.00 | 11.85| 53.66| -    |       |       |     |      |
| mCd           | 10.87| 7.64  | 7.67  | 3.95| 17.89| 0.76 | 0.69  | 0.76  | 0.69 | 0.69 |
| PLI           | 5.54 | 2.69  | 4.63  | 2.81| 8.43 | *0.39/1.46|       |       |     |      |

*Skewness/kurtosis

Table 3 indicate very high or considerably contamination of soils. Copper is not a pollutant of soils around the Oława smelter.

Kabir et al. (2012) presented the values of the Igeo index for the zinc smelters in China, Slovenia, and the UK. Compared with our results, the indicated areas were more lead-polluted (heavily to extremely contaminated): 4.85 Slovenia; 3.98 China; 2.18 the UK. The Igeo value of zinc at China smelter (2.67) was similar to the values in Oława zinc smelter. In Slovenia, high level of copper contamination was recorded (3.39) which was not noticed around the Oława smelter.

The soil quality near the copper smelter in Albania (Rubik) shows extreme soil contamination with copper (4.24) and zinc (4.63) according to Shallari et al. (1998). The Igeo index for lead of 2.40 was close to the value measured for Legnica smelter in Poland. The area around the copper smelter in Spain was moderately contaminated with lead (1.50) according to Kabir et al. (2012).

**Total level of soil pollution**

According to Zahran’s et al.’s classification (2015), the sum of the pollution indices for all trace elements (med Cd) indicates a very high degree of the pollution of soils around zinc smelter and considerable degree of pollution around both copper smelters (Table 3). Particularly high Cd values were recorded for the area around the Oława smelter (73% of samples). At the Glogów and Legnica copper smelters, the value of Cd exceeded the limit of 12 (ca. 16% of samples population). The degree of the contamination (med Cd) of soils around the Żelazny Most reservoir is low for studied chemical elements.

According to Hakanson’s classification (1980), studied soils have low degree of contamination (med Cd) close to the copper smelters of Legnica and Glogów and the tailing pond of Żelazny Most. In the Oława smelter, 43% of soil samples were identified as very highly polluted (Table 3).

The percentage shares of individual metals in contaminated soils are presented as the ratio of Cₙ to Cₙ indices. The soils enrichment with metals near the copper smelters and the Cu post-flotation tailings pond was shown in descending order: Legnica Pb (49%) > Cu (46%) > Zn (5%), Glogów Cu (46%) > Pb (33%) > Zn (24%), and Żelazny Most Cu (56%) > Pb (27%) > Zn (17%). Around the zinc smelter in Oława trace elements comprised the following order: Pb > Zn > Cu.
Fig. 1 Percentage of samples in the $C_f$ and $I_{geo}$ classes.
The share of lead and zinc in soils in Oława was significant and amounted to, respectively, 59% and 38%.

The medians of \( m_{Cd} \) indicate lack of soil contamination for Żelazny Most, moderate degree of soil contamination for Legnica and Głogów, and high degree in Oława. The soil quality assessed with the use of \( PLI \) index coincides with the assessment of contamination degree of soils using \( C_d \) median (Table 3). Thus, all indices of \( C_d, m_{Cd} \) and \( PLI \) similarly determine the quality of soil in the investigated areas.

A large asymmetry in the frequency distribution of \( m_{Cd} \) and \( PLI \) was observed in locations connected with copper smelting and tailing pond. Positive skewness values of the right-skewness distribution confirm the predominance of soils with low contamination for the studied areas (Table 3). At the Oława smelter, the soils are very heavily contaminated with metals and there are few results close to the average (negative kurtosis) (Fig. 2).

Due to a similar type of industrial activity (copper ore processing) and the use of the individual (\( C_d \)) and complex (\( C_d, m_{Cd}, PLI \)) contamination indices by Demková et al. (2016), we can compare the level of contamination of studied areas in Poland with the area of mining and processing of copper and mercury in Central Spiš in Slovak Republic. The authors used the contamination indices to compare the soil pollution degree in 1997 and 2015. Despite extremely high pollution, an improvement in the quality of soil was noticed after 18 years when the mining activity was stopped and the processing activity of copper was limited at the beginning of the twenty-first century. Comparison of the complex contamination indices for three trace elements (Cu, Zn, Pb) shows similar degree of soils contamination in Oława (Table 3) and in Spiš, Slovakia for 2015 (Avg. \( C_d \) 30.5, \( m_{Cd} \) 10.2, \( PLI \) 8.38). In the Legnica-Głogów Copper District area in Poland, the values of these indicators are much lower: 7 times in Żelazny Most, 4 times in Głogów, and 2 times in Legnica. The lower pollution of soils can be attributed to conducting the study outside of the border industrial plants.

In Poland, the first indices analysis of soils’ quality for the comprehensive evaluation of the degree of soil contamination in the industrial area was performed by Loska et al. (2004). The Upper Silesian Industrial Region of Poland is an area exposed to the emission of pollutants from the main industrial center of Poland, the Trzyńiec steel smelter in the Czech Republic, and local coal mining. Analysis of the \( C_d, m_{Cd} \) and \( PLI \) indices for the three elements does not show contamination of soils with lead, zinc, and copper. The higher values of parameters (Table 3) for copper and zinc smelters we studied indicate the impact of industrial activity on the soil environment in the immediate vicinity of these industrial plants.

**Plants’ response to the quality of soils**

The cereal plants are grown within a radius of up to 2.5 km from the copper smelters under consideration. The dominant species is *Triticum L.* in Głogów and *Brassica napus* L. in Legnica. The area around the Żelazny Most post-flotation tailings pond from the copper industry is significantly wooded, that is why grasses without specifying of the species and *Taraxacum officinale* were picked up in the foreground of the tailings pond. The Oława smelter is located within the city; therefore, the same plants were collected from the green areas as from the area of Żelazny Most.

Metal concentrations observed in biomass in the studied areas show high levels of trace elements close to the industrial facility and a decrease in metal concentrations along with the increase of the distance from its borders (the lack of normal distribution, \( p < 0.05 \) and statistically significant differences between medians of concentrations, \( p < 0.05 \)). Particularly high levels of trace elements in biomass (Fig. 3) were observed in Oława. The median of zinc in grasses and *Taraxacum officinale* are almost 9 times and 4 times higher as in the analogous plant biomass in Żelazny Most. Lead is almost 7 times higher in *Taraxacum officinale* in Oława.
Copper values are over 2 times higher in the plant biomass in Żelazny Most.

Zinc values in the cereal biomass of *Triticum* L. in Głogów are 1.5 times higher than in *Brassica napus* L. in Legnica, although more copper (1.5 times) and lead (2.5 times) in *Brassica napus* L. were observed.

The values of the *MAI* index for the *Taraxacum officinale* demonstrate this species’ good capability to adsorb trace elements in biomass from the contaminated soils.

Trace elements’ uptake in plants (*MAI*) was the highest around the Żelazny Most tailing pond, with 52.05 for grasses and 192.86 for *Taraxacum officinale*. Around the Oława smelter, 50.92 and 65.71 were reported, respectively, for the same plants. The lower values of the *MAI* index were obtained for the cereal plants of *Triticum* L. in Głogów (29.93) and *Brassica napus* L. in Legnica (10.54).

Giacomino et al. (2016) and Levei et al. (2017) obtained low of the *MAI* values of 1.61–2.25 for *Taraxacum officinale* in the traffic-impacted areas in Italy (Cuneo province in Piedmont) and of 1.4 for the mine tailings in the Metaliferi Mountains in Baia Mare County in Romania. Much higher *MAI* values in *Taraxacum officinale* were presented by Nadgórska-Socha et al. (2017) from Poland. The values of metal accumulation indices ranged from 4.68 to 28.1 for the area connected with the industry emitters (iron smelter, coking plant, and waste processing plant) in the Dąbrowa Górnicza city in the Upper Silesia.

Strong and very strong degrees of positive correlations between metal content in soil and metal content in plant are
observed for copper: grasses Żelazny Most (0.89), *Triticum* L. Głogów (0.60); for zinc: *Taraxacum officinale* Żelazny Most (0.76); and for lead: grasses Żelazny Most (0.73), *Triticum* L. Głogów (0.91). Other correlation coefficients confirm moderate or weak relationship.

The activity of industrial facilities may affect the content of metals in biomass in a reason of the mobility of trace elements from the soil solution. If the BAC values are higher than the unit, the plants are classified as hyperaccumulators, while if the BAC values are lower than the unit, plants are considered to be tolerant in relation to the trace element (Antonijević et al. 2012). Based on this principle, *Taraxacum officinale* and grasses can be considered good indicators of metals. The bioaccumulation of zinc and copper was observed for *Taraxacum officinale* and grasses in Żelazny Most and for grasses in Oława (Fig. 4). The bioaccumulation of the abovementioned metals in grasses was greater than in *Taraxacum officinale*. In addition, strong correlations between the bioaccumulation and the concentration of metals in soil were observed in Żelazny Most (grasses, Cu and Zn; *Taraxacum officinale*, Cu) and Olawa (grasses and *Taraxacum officinale*, Zn).

In the cereal plants, no bioaccumulation of metals in biomass was observed. For *Triticum* L. in Głogów, bioaccumulation of zinc was reported in 25% (upper quartile) of the samples population. In Legnica, median values of the BAC index do not indicate an increasing level of metals in the biomass of *Brassica napus* L. The soils in the vicinity of the Legnica and Głogów copper smelters may be used for cultivation of cereal crops due to low bioaccumulation of studied trace elements.

Despite the observed bioaccumulation of individual trace elements in *Taraxacum officinale* and grasses, the multi-metal
accumulation is not observed in tested plants at the same time (CBCI of 0.28 to 0.57).

In the leaves of Taraxacum officinale within the city of Dąbrowa Górnicza in the industrial region of Upper Silesia in Poland, the average value of the BAC index for zinc was 2.36 (Nadgórńska-Socha et al. 2017). It was considered that Taraxacum officinale is suitable for using in areas with significant soil and air pollution, especially with trace elements.

In the plant biomass from the Głogów copper smelter and the Żelazny Most copper ore tailings pond, strong correlations of copper with zinc: 0.87 for Triticum L./0.82 grasses/0.93 Taraxacum officinale, and also correlations of copper with lead: 0.56/0.53/0.91, were observed. At the same locations, a positive moderate correlation of zinc with lead (0.51/0.53/0.75) was also noticed. In Olawa, moderate correlation was noted for copper and lead in grasses (0.59).

Conclusions

The worldwide research publications mainly show that the contents of trace elements in soils vary along the distance from the site or the depth in the soil profile. Therefore, comparing the environment around objects with similar industrial activity is often impossible due to different permissible content of a given element in soil, applicable in a regulation of a given country. The advantage of using pollution indicators is the possibility of comparing different objects in the world directly, provided that the reference geochemical background values are used. Thus, the indicators provide information directly on the quality of the soil environment. For objects associated with the smelting of colored metals, there is still a lack of information on the quality of the soil environment based on pollution indices.

The pollution indices are an objective tool for assessing the real enrichment of soils with trace elements. The individual indices were used to obtain information on the level of soil pollution by each of the analyzed metals. The complex indices were used to determine the total pollution of the examined areas. The simultaneous use of several indicators allows us to more accurately assess the pollution of soil with heavy metals.

The use of the $C_f$ indicator resulted in the soil being classified as very contaminated with copper and lead in Legnica and zinc and lead in Olawa. Thanks to use of the $I_{geo}$ parameter, other classes—from 2nd to even 6th—have been assigned, specifying degrees of soil pollution from moderately to heavily contaminated. And so the assessment of soil quality using the $I_{geo}$ index allows to identify soils with less pollution as compared with assigning soils to a common $C_f$ class.

The quality of soils within a distance of up to 2.5 km from the studied facilities is poor due to the high values of pollution indices for trace elements: copper and lead in the Legnica smelter and in some sampling points at the Głogów smelter, and lead and zinc in the Olawa smelter. The complex indices integrate and average all available analytical data and allow comparison of the degree of general pollution in different places. The complex indices of $C_{fa}$, $mC_{fa}$, and $PLI$ assessed the soil around the Olawa smelter as very highly contaminated with trace elements. Soils around copper smelters were moderately contaminated with metals. The individual and complex pollution indices do not indicate contamination of soils with copper, zinc, and lead around the Żelazny Most reservoir.

The research on accumulation of metals in biomass with the use of the BAC and the MAI indices shows that grasses and Taraxacum officinale accumulate larger amounts of trace elements as compared with the biomass of the cereal plants. Additionally, strong correlations between the content of the trace element in the soil and the amount of metal in grasses and Taraxacum officinale were recorded. The multielemental bioaccumulation in plants around the examined industrial facilities was not observed. Cereals can be harvested from the areas of the Głogów and Legnica smelters, but with periodic control of the trace elements content in biomass.

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Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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References

Abraham GMS, Parker RJ (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Environ Monit Assess 136:227–238

Adamo P, Dudka S, Wilson MJ, McHardy WJ (2002) Distribution of trace elements in soils from the Sudbury smelting area (Ontario, Canada). Water Air Soil Pollut 137(1–4):95–116

Antonjević MM, Dimitrijević MD, Milić SM, Nujkić MM (2012) Metal concentrations in the soils and native plants surrounding the old
flotation tailings pond of the copper mining and smelting complex Bor (Serbia). J Environ Monit 14(3):866–877
Barlett SC, Burgess H, Djamantović B, Gowans RM, Lattanazi CR (2013) Technical report on the copper-silver production operations of KGHM Polska Miedź S.A. in the Legnica-Głogów Copper Belt area of southwestern Poland. Bay Street, Toronto, Canada
Blaser P, Zimmermann S, Luster J, Shotyk W (2000) Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. Sci Total Environ 249:257–280
Cabala J, Krupa P, Misz-Kennan M (2009) Heavy metals in mycorrhizal rhizospheres contaminated by Zn-Pb mining and smelting around Olkusz in southern Poland. Water Air Soil Poll 199:139–149
Cuske M, Marcinkiewicz M, Szopka K., Karcewzka A, Pora E (2013) The influence of Olawa zinc smelter on soil environment of adjacent areas in the light of total content of heavy metals in surface levels of Olawa soils. Paper of Uni Zielona Góra / Environ Eng Series 149(29):42-50 (in Polish, with English summary)
Damek-Poprawa M, Sawicka-Kapusta K (2003) Damage to the liver, kidney, and testis with reference to burden of heavy metals in yellow-eyed mice from areas around steelworks and zinc smelters in Poland. Toxicology 186:1–10
Demkošová L, Jezny T, Bobulska L (2016) Assessment of soil heavy metal pollution in a former mining area - before and after the end of mining activities. Soil Water Res:1–8
Etter V (2016) Soil contamination near non-ferrous metal smelters: a review. Appl Geochem 64:56–74
Filzek P, Spurgeon D, Broll G, Svendsen C, Hankard P, Kammenga J, Donker M, Weeks J (2004) Pedological characterisation of sites along a transect from a primary cadmium/lead/zinc smelting works. Ecotoxicology 13:725–737
Giacomino A, Malandrino M, Colombo ML, Miaglia S, Maimone P, Blancato S, Conca E, Abollino O (2016) Metal content in dandelion (Taraxacum officinale) leaves: influence of vehicular traffic and safety upon consumption as food. J Chemother:1
Goodarzi F, Sanei H, Garrett RG, Duncan WF (2002) Accumulation of trace elements on the surface soil around the Trail smelter, British Columbia, Canada. Environ Geol 43:29–38
Hakanson L (1980) An ecological risk index for aquatic pollution control. J Environ Qual 9:106–123
Jaramihan MK, Saboori A, Akrami MA, van Straalen NM (2015) On-farm site contamination in a commercialised site with combined land use pattern. Sci Total Environ 536:139–149
Kabala C, Chodak T, Szerszeń Ł (2008) Influence of land use pattern on the content of zinc in soil near copper smelter, based on a 34-year monitoring cycle. Žemės ūkio mokslo 15(3):8–12
Kabir E, Ray S, Kim K-H, Yoon H-O, Jeon E-C, Kim YS, Cho Y-S, Yun S-T, Brown RJC (2012) Current status of trace metal pollution in soils affected by industrial activities. Sci World J 2012:917605:1–18
Kalinskas T, Serbula SM, Radojevic AA, Kalinskas JV, Steharnik MM, Petrovic JV (2016) Elder, linden and pine biomonitoring ability of soil and plants for heavy metals. Geochemical restoration and reclamation of mining influenced soils, Academic Press, pp 149–202
Kim YD, Eom SY, Yim DH, Kim IS, Won HK, Park CH, Kim GB, Yu SD, Choi BS, Park JD, Kim H (2016) Environmental exposure to arsenic, lead, and cadmium in people living near Janghang copper smelter in Korea. J Korean Med Sci 31:489–496
Kowalska JB, Mazurek R, Gasiorek M, Zaleski T (2016) Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination-a review. Environ Geochem Health 40(6):2395–2420
Krzaklewski W, Barszcz J, Malek S, Kozioł K, Pietrzykowski M (2004) Contamination of forest soils in the vicinity of the sedimentation pond after zinc and lead ore flotation (in the region of Olkusz, southern Poland). Water Air Soil Poll 159:151–164
Lever L, Andrei ML, Hoaghaia MA, Ozanu A (2017) Assessment of metals content in dandelion (Taraxacum officinale) leaves grown on mine tailings. AIP Conference Proceedings 1917:020001–020004
Liu YJ, Zhu YG, Ding H (2007) Lead and cadmium in leaves of deciduous trees in Beijing. Chian: development of a metal accumulation index (MAI). Environ Pollut 145:387–390
Loska K, Wiechula D, Korus I (2004) Metal contamination of farming soils affected by industry. Environ Int 30:159–165
Machender G, Dhakate R, Prasanna L, Govil PK (2011) Assessment of heavy metal contamination in soils around Balanagar industrial area, Hyderabad, India. Environ Earth Sci 63:945–953
Manna A, Maiti R (2018) Geochemical contamination in the mine affected soil of Raniganj Coalfield – a river basin scale assessment. Geoscience Frontiers (GSF) 9:1577–1590
Martley E, Gulson BL, Pfeifer HR (2004) Metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembia, NSW, Australia. Sci Total Environ 325(1–3):113–127
Medyńska-Juraszek A, Kabala C (2012) Heavy metal pollution of forest soils affected by the copper industry. J Elem 17:441–451
Medyńska-Juraszek A, Kabala C (2010) Heavy metals concentration and extractability in forest litters in the area impacted by copper smelter near Legnica. Ecol Chem Eng A 17(8):981–989
Medyńska A, Kabala C, Chodak T, Jezierski P (2009) Concentration of copper, zinc, lead and cadmium in plants cultivated in the surroundings of Zielonka Most copper ore tailings impoundment. J Elem 14:729–736
Mukhaicheva VS (2017) Long-term dynamics of heavy metal concentrations in the food and liver of bank voles (Myodes glareolus) in the period of reduction of emissions from a copper smelter. Russ J Ecol 48:559–568
Muller G (1981) Die Schwermetallbelastung der sediments des Neckars und seiner Nebenflüsse: Eine Bestandsaufnahme. Chemiker-Zeitung:105:156–164
Muller G (1969) Index of geoaccumulation in sediments of the Rhine River. Geosystem 2:108–118
Nadgórska-Socha A, Kandziora-Ciupa M, Trzeciaki M, Barczyk G (2017) Air pollution tolerance index and heavy metal bioaccumulation in selected plant species from urban biotopes. Chemosphere 183:471–482
Nikolić D, Milošević N, Živković Ž, Mihajlović I, Kovacević R, Petrović N (2011) Multi-criteria analysis of soil pollution by heavy metals in the vicinity of the Copper Smelting Plant in Bor (Serbia). J Serb Chem Soc 76:625–641
Olowoyo JO, van Heerden E, Fischer JL, Baker C (2010) Trace metals in soil and leaves of Jassacura mimosafolia in Tshwane area, South Africa. Atmos Environ 44:1826–1830
PN–ISO 10390, 1997. Polish version. Soil quality - determination of pH
PN–ISO 11047, 2001. Polish version. Soil quality - determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in soil extracts with aqua regia - flame and electrothermic atomic absorption spectrometry methods
PN–ISO 11465, 1999. Polish version. Soil quality - determination of dry matter content of soil and water on the basis of dry matter - weight method
Rahman SH, Khanam D, Adyl TM, Islam MS, Ahsan MA, Akbor MA (2012) Assessment of heavy metal contamination of agricultural soil
around Dhaka Export Processing Zone (DEPZ), Bangladesh: implication of seasonal variation and indices. Appl Sci 2:584–601
Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution. Mar Pollut Bull 40:968–980
Ruiz F (2001) Trace metals in estuarine sediments from the south western Spanish coast. Mar Pollut Bull 42:482–490
Shallari S, Schwartz C, Hasko A, Morel JL (1998) Heavy metals in soils and plants of serpentine and industrial sites of Albania. Sci Total Environ 209:133–142
Skubala P, Zaleski T (2012) Heavy metal sensitivity and bioconcentration in oribatid mites (Acari, Oribatida): gradient study in meadow ecosystems. Sci Total Environ 414:364–372
Sterckeman T, Douay F, Proixa N, Fourrierb H (2000) Vertical distribution of Cd, Pb and Zn in soils near smelters in the north of France. Environ Pollut 107:377–389
Sterckeman T, Douay F, Proixa N, Fourrierb H, Perdrix E (2002) Assessment of the contamination of cultivated soils by eighteen trace elements around smelters in the north of France. Water Air Soil Pollut 135(1–4):173–194
Stoffers P, Glasby GP, Wilson CJ, Davis KR, Watter P (1986) Heavy metal pollution in Wellington Harbour. New Zeal J Mar Fresh 20:495–512
Sutherland RA (2000) Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ Geol 39(6):611–627

Tomlinson DL, Wilson JG, Harris CR, Jeffrey DW (1980) Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index. Helgel Mearesunsters 33:566–575
Tylor SR, McLennan SM (1995) The geochemical evolution of the continental crust. Rev Geophys 33:241–265
Vorobeichik EL, Kaigorodova SY (2017) Long-term dynamics of heavy metals in the upper horizons of soils in the region of a copper smelter impacts during the period of reduced emission. Eurasian Soil Sci 50:977–990
Yaylal-Abanuz G (2011) Heavy metal contamination of surface soil around Gebze industrial area, Turkey. Microchem J 99:82–92
Zahran MAE, El-Amier YA, Elaggar AA, Mohamed HAE, El-Alfy MAE (2015) Assessment and distribution of heavy metals pollutants in Manzala Lake, Egypt. J Geosci Environ Protect 3:107–122
Zhao X, Liu J, Xia X, Chu J, Wei Y, Shi S, Chang E, Yin W, Jiang Z (2014) The evaluation of heavy metal accumulation and application of a comprehensive bio-concentration index for woody species on contaminated sites in Hunan, China. Environ Sci Pollut Res 21:5076–5085

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