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ORIGINAL ARTICLE

Trace metals in surface soils under different land uses in Kielce city, south-central Poland

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Abstract
This work presents the influence of land use in Kielce on the spatial differentiation of heavy metals in the near-surface soil layer. The aim is to determine the amounts of ten trace elements (As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) contained in soil samples of five land use categories (residential areas, roads, urban greenery, allotment gardens, agricultural areas) in the city and to evaluate the contamination using geochemical indicators. The Clarke values of Earth's crust and the average content of the elements in Poland's soils are exceeded only for Pb and Zn ($N=60$). Soils of urban greenery and residential areas stand out in this respect. Particularly noteworthy is the fact that a high content of As has been documented in the soils of allotment gardens and confirmed by high values of the geoaccumulation index (moderate to high pollution) in relation to the Clarke values and to average contents in Poland's soils. The highest average Pb content has been found in the areas of urban greenery and residential areas. The integrated pollution index (IPI) in terms of maximum values indicates high level of metal pollution of soils in all forms of land use, except for agricultural areas (moderate). On average, IPI and potential ecological risk index are low.

Keywords Metal pollution · City · Land use · Index of geoaccumulation · Integrated pollution index · Potential ecological risk index

Introduction

Cities are generally characterized by an increased content of many metals, especially in the surface layer of ground. They come mostly from atmospheric and communication pollutants and their presence is the effect of many years of intensive industrialization and urbanization. This issue has been the subject of many works concerning cities in both highly developed countries (including Imperato et al. 2003; Chen et al. 2007; Liebens et al. 2012; Rodríguez-Seijo et al. 2017) as well as in developing ones (including Mireles et al. 2012; Al-Obaidy and Al-Mashhadi 2013; Benhaddya and Hadjel 2014; Darko et al. 2017). An extensive review of the results of the study on the content of seven selected trace elements in soil samples from cities around the world was presented by Ajmone-Marsan and Biasioli (2010).

Many authors point out that there is a large spatial variation of metal content mainly due to ways of development and functioning of the city area (Chen et al. 2005; Wei and Yang 2010; Wiłkomirski et al. 2011; Xia et al. 2011; Luo et al. 2012; Iwegbue 2014; Tahmasbian et al. 2014; Doležalová Weissmannová et al. 2015; Ferreira et al. 2016; Hołtra and Zamorska-Wojdyła 2018; Kosheleva et al. 2018; Świercz and Zajęcka 2018). In recent years, the content of toxic metals in soils of residential and recreational areas has been increasingly analyzed since they can potentially pose a threat to the environment and human health (Madrid et al. 2002; Lu and Bai 2010; Chabukdhara and Nema 2013; Szolnoki et al. 2013; Praveena et al. 2015).

Kielce (Poland) is the city in which these threats were noticed many years ago. The city's geological substratum is characterized by naturally increased contents of heavy metals, which is additionally intensified by anthropogenic pollution (Lenartowicz 1994; Lis et al. 2012). The city is located

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within structures and geological formations belonging to the Paleozoic core of the Holy Cross Mountains (HCM). Sedimentary rocks representing all periods of the Paleozoic era are cut by a dense network of faults, which were the migration paths of solutions containing dissolved compounds, among which those harmful to people's health may occur (Filonowicz 1973). An increased content of trace elements was found around some faults and their related historical sites (XIV–XX centuries) of lead ore (galena) within the city (Karczówka) and of copper and iron ore in the immediate vicinity (Miedziana Góra) (Gałuszka et al. 2015, 2018). In this area, there was a primary center of strongly developed mining of mineral resources, working for the needs of the Old-Polish Industrial District.

In Kielce, anthropogenic soil pollution with metals comes from two main sources. Atmospheric pollution is the first one of them (mainly suspended dust). It is captured by precipitation and deposited on the surface of the ground. An important source of these pollutants, especially in the second half of the twentieth century, was a former mining and processing plant of carbonate raw materials, a part of the "White Basin". This area was classified as of high ecological hazard (Kozłowski 2013). After the privatization and modernization of the plants operating here (among others, by the Dyckerhoff concern, Cement Roadstone Holding) and the implementation of a system of efficient filters and alternative fuels, there was included in the group the most environment-friendly plants of this type in Poland. This has resulted in a significant reduction of dustiness in Kielce in the last dozen or so years (Air quality assessment in the Świętokrzyskie Province in 2017 2018). A significant source of dust in the air of Kielce was "Heat and Power Plant Kielce", operating on hard coal. Fly ashes emitted into the atmosphere in the combustion process were many times richer in heavy metals than the coal from which they were formed. At the beginning of the twenty-first century, introduction of efficient devices limiting the emission of dust (with an efficiency of 99.5%) resulted in measurable effects (in 2002 emission of 452 Mg of dust, in 2017—107 Mg). Another source of soil contamination with metals in Kielce is car traffic. This type of pollution, which is deposited in the road lane, is easily washed away during rainfall and thaw in the surface flush process. Pollutants also come with air masses from the SW direction. They come from the combustion of fuels by the energy sector located in the Upper Silesia Industrial Region and Czech Republic (Kozłowski and Jóźwiak 2013).

As mentioned before, the main purpose of the field and laboratory research was to determine the spatial variation of the content of ten heavy trace elements (As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in soils of five different land uses (residential areas, roads, urban greenery, allotment gardens, agricultural areas) in Kielce city in 2016. Data analysis was conducted to assess (1) the level of concentration of trace elements and their potential source of origin, using various statistical methods, and (2) the contamination using geochemical indicators (index of geoaccumulation—I_{geo}, integrated pollution index—IPI, potential ecological risk index—PERI) with reference to the Clarke values of selected metals in the upper continental crust and their average content in Poland's soils. Particular attention was paid to allotment gardens, because earlier studies showed high concentrations of toxic trace elements in these areas (Ciupa and Biernat 2000; Świercz and Smorzewska 2015).

Materials and methods

Study area

The city of Kielce (109.4 km^2), inhabited by about 198 thousand people (2017) is located in central Poland, 200 km south of Warsaw (Fig. 1). Kielce is located in a large tectonic depression, surrounded by mountain ranges, whose slopes' gradients locally exceed 15°, forming an "amphitheatrical" arrangement of the main forms of terrain relief. It determines the course and directions of many natural, settlement-related and transport-related phenomena, including the movement of pollutants. The morphological location of the city and its spatial layout are also conducive to the formation of atmospheric air depots containing pollution. In combination with the existing emission of pollutants from local emitters, it leads to the formation of smog, especially in autumn and winter. Examination of lichens as bioindicators for the assessment of air pollution showed that the highest environmental burdens from selected heavy metals, in hierarchical terms, are as follows: Zn–Pb–Cu–Cr–Cd (Jóźwiak and Jóźwiak 2009). Kielce soils, developed in large part on the limestone material, have been additionally strongly alkalized due to long-term accumulation of dust emitted from the nearby cement plants, as mentioned above, but also due to using building materials (cement, concretes, etc.) containing $CaCO_3$, salt for winter road maintenance (Gałuszka et al. 2010), etc. The excess of calcium in soils increases their pH (Kozłowski 2013) and this is not conducive to the process of leaching metal from them (Kabata-Pendias 2010). It is worth noting that changes in management structure in Kielce, including technological processes, at the beginning of the twenty-first century resulted in reduction of various types of pollution. Express roads, which took over a significant part of vehicular traffic of a transit nature, including the cumbersome transport of rock raw materials and products of the cement and lime industry, are of significant importance in relieving the city from traffic pollution.

In the functional–spatial structure of the city, built-up areas (including residential areas) constitute 29.3%, transportation areas—9.2%, agricultural areas (arable land, fallow

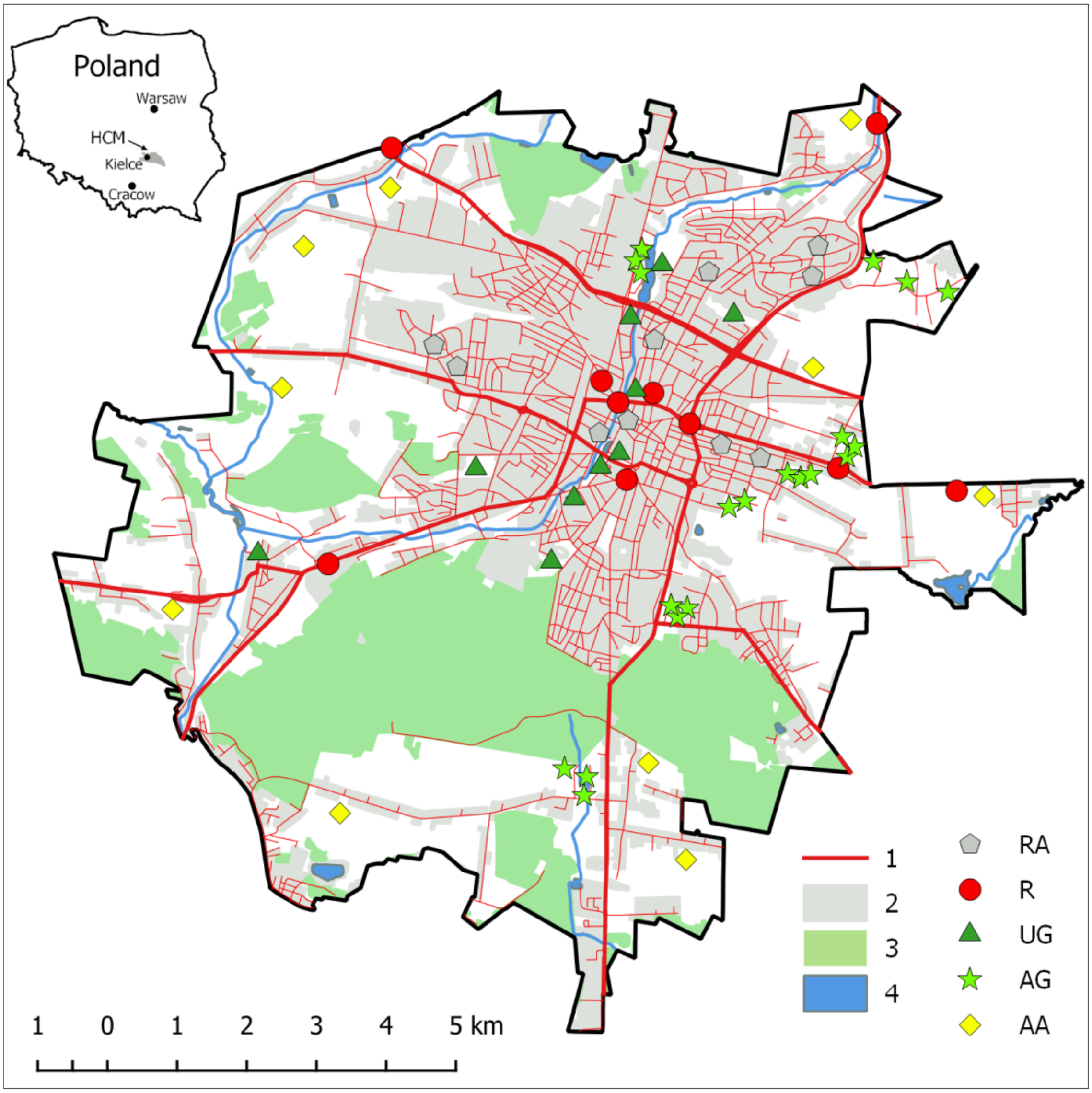

Fig. 1 Location of sampling sites superimposed on land use in Kielce. Land use: 1—roads, 2—built-up areas, 3—forests, 4—surface water. Sampling sites: RA: residential area, R: road, UG: urban greenery, AG: allotment garden, AA: agricultural area. HCM: Holy Cross Mountains

land, and gardens)—37.0%, forests and woodlots (including urban greenery)—23.0%, and other—1.5% of the total area. Kielce is distinguished by a very large share of legally protected areas (about 51%), including two being part of the NATURA 2000 network.

Soil sampling and laboratory analysis

Soil samples with a mass of approx. 1000 g each were taken from the depth of 0–20 cm in July 2016. Each of them consisted of soil coming from five points within a 100 × 100 cm sampling site. They were taken from 60 sites, including: ten from residential areas (RA), 10 from along transportation routes (R), 10 from urban greenery areas (UG), 20 from allotment gardens (AG), and 10 from agricultural areas (AA) (Fig. 1). The largest number of samples was taken from the surface layer of soils in allotment gardens, which form in Kielce one of the largest complexes of this type (346 ha) in European cities. The samples were stored in a separate room and dried at room temperature. Then they were sieved to obtain a particle size of < 2.0 mm.

The trace elements (As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) have been identified using an ICP MS TOF spectrometer (Optimass 9500 GBC). The calibration curve was based on the CLMS 2AN standard. All solutions have been prepared on the basis of Suprapur 1% nitric acid. The following concentrations have been prepared for calibration: 0 (blank), 1, 10, 50, 100, and 1000 µg/dm^3. To verify the correctness of the obtained results, a sample of the certified reference material has also been analyzed (Table 1).

Meanwhile, it should be pointed out that the authors took samples from the same places in 2000 using identical techniques. However, identification of a few selected elements (including As, Pb, Zn) was then carried out using X-ray fluorescence spectrometry (XRF) (Ciupa and Biernat 2000).

Quantification of metal pollution

A descriptive statistical analysis (arithmetic mean, standard deviation, median, minimum, and maximum) has been performed using the Statistica 13 software. Analyzed data have been tested for normal distribution using the Shapiro–Wilk test. In the situation of not fulfilling the criterion, to verify the hypothesis about the insignificance of differences between the medians of a tested variable in samples from different types of land use, the non-parametric *U* Mann–Whitney test has been used and the Spearman's rank correlation coefficient has been calculated. In addition, the correlation coefficient (R) and the determination (R^2) have been calculated and regression analysis between the contents of selected metals has been carried out, with the determination of regression p values. Additionally, multivariate analysis (PCA—principal component analysis) has been used for the interpretation of soil contamination (Li et al. 2013; Doležalová Weissmannová et al. 2015).

Among many indicators used to assess the degree of soil contamination with metals (Doležalová Weissmannová and Pavlovský 2017), three have been selected: the index of geoaccumulation, the integrated pollution index, and the potential ecological risk index. The calculations assume the Clarke values of selected metals in the upper continental crust (McLennan 2001) and their average content in Poland's soils, calculated based on the register in the Geochemical Atlas of Europe (Salminen et al. 2005) (Table 2).

The index of geoaccumulation (I_{geo}) was introduced by Müller (1969) and in this work, it has been calculated for each metal using the modified equation (Loska et al. 2004):

$$I_{\text{geo}} = \log_2 \frac{C_i}{1.5B_i},$$

where C_i the measured concentration of the element i (mg/kg) in the soil (particle size < 2.0 mm), B_i Clarke value of the element i (mg/kg).

The degree of soil contamination has been determined on a 7-level scale (Müller 1969; Zhiyuan et al. 2011; Barbieri 2016): practically uncontaminated ($I_{\text{geo}} \le 0$), uncontaminated to moderately contaminated ($0 < I_{\text{geo}} \le 1$), moderately contaminated ($1 < I_{\text{geo}} \le 2$), moderately to heavily contaminated ($2 < I_{\text{geo}} \le 3$), heavily contaminated ($3 < I_{\text{geo}} \le 4$), heavily to extremely contaminated ($4 < I_{\text{geo}} \le 5$), extremely contaminated ($I_{\text{geo}} > 5$).

Integrated pollution index (IPI) has been calculated using the following (Sun et al. 2010; Taghipour et al. 2013):

$$\text{IPI} = \frac{(\text{PI}_1 + \text{PI}_2 + \cdots + \text{PI}_n)}{n},$$

where $\text{PI}_{1,2,\ldots,n}$ pollution index for each element:

$$\text{PI}_i = \frac{C_i}{B_i},$$

N the number of metals.

Table 1 The concentration of elements in the certified ERM-CC141 reference material produced by the Institute for Reference Materials and Measurements, Belgium

Metal	ERM-CC141		ICP MS TOF		Difference[a] (%)
	Concentration (mg/kg)	Uncertainty (mg/kg)	Concentration (mg/kg)	Standard deviation	
As	7.5	1.4	6.6	±0.7	− 12.0
Cd	0.25	0.04	0.27	±0.1	9.5
Co	7.9	0.9	7.0	±0.5	− 11.8
Cr	31.0	4.0	31.5	±1.8	1.5
Cu	12.4	0.9	13.3	±2.8	7.4
Mn	387.0	17.0	392.9	±8.8	1.5
Ni	21.9	1.6	23.0	±1.4	5.1
Pb	32.2	1.4	33.6	±2.7	4.3
Zn	50.0	4.0	46.0	±2.0	− 7.7

[a] Relative difference between measured and certified concentration $100\% \cdot (c_z - c_c)/c_c$

Table 2 Clarke values and average content of determined elements in Poland's soils

Extent	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
World[a]	1.5	550	0.098	17.0	83.0	25.0	600	44.0	17.0	71.0
Poland[b]	2.6	251	0.172	3.2	36.8	4.9	245	9.1	18.7	23.4

[a] Upper continental crust after McLennan (2001)

[b] Own calculations based on Salminen et al. (2005)

The pollution level of all the considered elements has been determined on a 4-level scale: low ($\mathrm{IPI} \le 1$), moderate ($1 < \mathrm{IPI} \le 2$), high ($2 < \mathrm{IPI} \le 5$), very high ($\mathrm{IPI} > 5$).

The potential ecological risk index (PERI), which is a comprehensive indicator reflecting the impact of metals on the environment, has been calculated using the following formula (Xu et al. 2008):

$$\mathrm{PERI} = \sum_{i}^{n} \left(\mathrm{Tr}_i \cdot \frac{C_i}{B_i} \right),$$

where Tr_i biological index of the toxicity of metal i; $\mathrm{Ba} = \mathrm{Mn} = \mathrm{Zn} = 1$, $\mathrm{Cr} = 2$, $\mathrm{Co} = 5$, $\mathrm{Cu} = \mathrm{Pb} = 5$, $\mathrm{Ni} = 6$, $\mathrm{As} = 10$, $\mathrm{Cd} = 30$ (Håkanson 1980).

The degrees of potential ecological risk (Håkanson 1980; Jiang et al. 2014) are as follows: low ($\mathrm{PERI} < 150$), moderate ($150 \le \mathrm{PERI} < 300$), considerable ($300 \le \mathrm{PERI} < 600$), and very high ($\mathrm{PERI} \ge 600$).

Results and discussion

Element concentrations

Characteristic (extreme and average) content of ten trace elements in Kielce soils of different land uses is presented in Table 3. Only the average content of two metals in soils of Kielce, i.e. Pb (25.6 mg/kg) and Zn (79.7 mg/kg), is higher than the Clarke values given by McLennan (2001) and the average content calculated for Poland (after Salminen et al. 2005). The obtained contents were lower than the average Pb and Zn contents in the soils of 34 European cities (102 and 130 mg/kg, respectively) and 21 cities in China (55 and 109 mg/kg, respectively) (Luo et al. 2012), but higher than, for example, in the Hungarian cities of Szombathely and Sopron (Horváth et al. 2018). In Kielce, the highest average Pb content has been found in the soils of: urban greenery, residential areas, and roads (from 35.9 to 28.8 mg/kg, respectively). In Poland, similar but slightly higher average Pb content has been documented in urban greenery areas in the center of Kraków 54.6 mg/kg (Gąsiorek 2011) and in Rabka-Zdrój 40.0 mg/kg (Kicińska and Klimek 2015), similarly in Athens (45.0 mg/kg Argyraki and Kelepertzis 2014), and much lower than in other European cities, e.g. in Madrid 161 mg/kg, Sevilla 137 mg/kg (Madrid et al. 2002). In Lublin, (Poland) Pb concentration in road dust has reached only 23.3 mg/kg (Kiebała et al. 2015).

As far as in 2000, the highest Pb content in Kielce was documented along transportation routes (79.3 mg/kg), which was associated with pollution originating mainly from car exhausts. The over threefold reduction in Pb pollution along roads in Kielce in the period 2000–2016 was a positive effect of the mandatory use of unleaded petrol (since 2005) and improvement of its combustion efficiency in vehicle engines, which largely resulted from the adjustment of fuel quality requirements to the European standards. It is worth noting that at the same time the content of Pb decreased in urban greeneries and residential areas only by about 35%. The lowest average Pb concentration in 2016 has been found in samples taken in agricultural areas (9.9 mg/kg).

In 2016 the highest average Zn content has been found in grounds of allotment gardens (107.4 mg/kg), residential areas (90.9 mg/kg) and roads (86.8 mg/kg). A similar value of Zn concentration in automobile workshop area (Ghana) was found by Appiah-Adjei et al. (2019). With reference to 2000, as in the case of Pb, the highest decrease in concentration (almost twofold) took place within transportation areas, and the lowest in residential areas and allotment gardens.

The maximum concentration of Pb and Zn in 2016 has been found in samples taken from allotment gardens (102.6 mg/kg and 290.3 mg/kg, respectively). The obtained results confirm earlier interpretation (Świercz and Smorzewska 2015). Significantly higher maximum Pb and Zn contents were found in soils from allotment gardens of Wrocław (Pb—659 mg/kg, Zn—2103 mg/kg) (Kabala et al. 2009) and from selected urban parks of the Silesian agglomeration (Pb—789 mg/kg, Zn—365 mg/kg) (Kicińska 2016). The high content of Pb and Zn in residential areas, urban greenery and allotment gardens of Kielce is largely conditioned by natural factors. Namely Paleozoic rocks, which are found in the substratum, contain fissure-intrusive deposits of Pb and Zn ores, locally exploited from the fourteenth century (Lenartowicz 1994). An additional source of Zn in residential areas is associated with the operation of motor vehicles (abrasion of brake linings, car body wear). In the case of allotment gardens, the Zn accumulation also results from the use of agrochemicals (fertilizers and pesticides) and composting (Romic and Romic 2003). The Clarke values were also exceeded within allotment gardens in Kielce—in the content of As (2.7 mg/kg), Cd (0.182 mg/kg) and Mn (616 mg/kg). Such high concentrations of the first two elements are not accidental here, because they are components of plant protection chemicals and fertilizers used often in excess for many years. The average content of As in soils of allotment gardens in Kielce was also the highest in 2000 (1.15 mg/kg). The maximum content of As was at a similar level in 2000 and 2016 (9.13 mg/kg and 10.0 mg/kg, respectively). At the same time, these are the highest concentrations of this toxic metal found in Kielce, but still lower than the average content in the ground of several dozen cities in China and Europe (Luo et al. 2012).

In addition, compared to the Clarke value in the world's continental crust, the average content of trace elements is exceeded by: As in residential areas and urban greenery, Cd in residential areas and roads, Mn in residential areas. In relation to typical content in Poland's soils, the exceedance

Table 3 Extreme and average content of trace elements in grounds of different land uses in Kielce in 2016 in relation to Clarke values and their average content in soils of Poland

Area	As (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
World[a]	1.5	550	0.098	17.0	83.0	25.0	600	44.0	17.0	71.0
Poland[b]	2.6	251	0.172	3.2	36.8	4.9	245	9.1	18.7	23.4
Kielce										
Min–max										
Residential areas	1.1–3.4	11.7–129.5	0.000–0.234	0.5–3.0	3.2–12.9	1.8–12.3	84–1804	2.0–13.7	6.4–94.9	18.6–273.8
Roads	0.5–2.8	22.8–58.3	0.032–0.368	0.5–1.9	3.8–12.5	8.7–22.7	96–711	3.1–9.9	9.1–45.1	38.8–234.8
Urban greenery	0.3–8.4	7.4–170.9	0.001–0.215	0.2–2.5	1.4–19.1	0.9–24.1	39–1308	1.2–11.7	1.2–102.3	7.2–192.5
Allotment gardens	0.3–10.0	16.4–135.3	0.079–0.486	0.5–3.7	2.6–18.4	3.1–41.9	122–1674	1.5–9.8	7.3–102.6	26.8–290.3
Agricultural areas	0.5–3.7	7.7–168.5	0.001–0.195	0.2–1.6	0.8–6.8	0.6–11.1	99–1303	0.6–5.9	4.7–28.9	8.9–49.8
Mean (SD)										
Residential areas ($N=10$)	2.3 (0.7)	52.1 (15.6)	0.104 (0.086)	1.5 (0.46)	7.9 (2.8)	8.2 (3.2)	657 (385)	6.4 (3.2)	33.6 (31.7)	90.9 (77.1)
Roads ($N=10$)	1.2 (0.6)	39.3 (12.5)	0.141 (0.090)	1.0 (0.37)	6.8 (2.2)	13.8 (4.0)	330 (206)	5.2 (1.8)	28.8 (13.5)	86.8 (56.2)
Urban greenery ($N=10$)	2.5 (2.4)	42.7 (45.4)	0.081 (0.073)	1.1 (0.74)	6.9 (5.6)	9.9 (6.3)	365 (361)	5.2 (3.5)	35.9 (28.8)	58.0 (52.0)
Allotment gardens ($N=20$)	2.7 (2.6)	55.3 (25.8)	0.182 (0.091)	1.7 (0.92)	7.9 (4.0)	11.5 (5.0)	616 (394)	5.0 (2.3)	22.8 (20.0)	107.4 (74.5)
Agricultural areas ($N=10$)	1.3 (1.0)	40.3 (44.4)	0.050 (0.058)	0.8 (0.41)	3.6 (1.7)	4.7 (3.7)	441 (381)	2.5 (1.4)	9.9 (6.8)	27.7 (12.0)
Weighted mean ($N=60$)	2.1 (2.0)	47.5 (33.4)	0.124 (0.096)	1.3 (0.78)	6.8 (4.0)	9.9 (6.5)	504 (410)	4.9 (2.8)	25.6 (23.2)	79.7 (68.2)

[a] Upper continental crust after McLennan (2001)

[b] Own calculations based on Salminen et al. (2005); values in brackets—standard deviation (SD)

of Mn has been found in the ground of all analyzed forms of land use and Cu in four of them (excluding agricultural areas). The content of other analyzed metals (Ba, Co, Cr, Ni) does not exceed typical contents in the upper continental crust, even in the maximum content in individual samples. The average Ba and Cr content in Poland's soils was not exceeded in Kielce even within the maximum measured concentrations. It should be emphasized that the highest average concentration of as many as six elements (As, Ba, Cd, Co, Cr, Zn) and the maximum concentrations seven elements (except for Ba, Mn, Ni) have been found in allotment gardens. These studies confirm earlier results saying that in the ground of this form of land use, the content of metals has remained high for many years, especially in case of maximum values and is generally higher than in other forms of land use (Ciupa and Biernat 2000; Świercz and Smorzewska 2015). The research carried out has shown that from among the identified metals Mn has emerged as the dominant one, while Cd has shown the lowest concentration in grounds of all the considered types of land use. The average values of metal content in Kielce soils are sequenced as follows: Mn (504 mg/kg), Zn (79.7), Ba (47.5), Pb (25.6), Cu (9.9), Cr (6.8), Ni (4.9), As (2.1), Co (1.3), Cd (0.124).

The high average concentration of Mn in surface soils in Kielce is due to the geological structure. In the substrate, there are carbonate rocks and within their outcroppine, rendzinas were formed, which are a natural, rich source of Mn, as indicated by Wedepohl (1978). This is confirmed by the study by Lenartowicz (1994) who found that the average concentration of this element in Kielce was of 638 mg/kg and locally exceeded 10,000 mg/kg. The geochemical anomaly of trace elements (including Mn) within the soils in Kielce has recently been indicated by Gałuszka et al. (2018).

Relationships between the content of particular elements in the soils of Kielce result from their geochemical relations and may also inform about the sources of their origin. It has been found that the Spearman's rank correlation coefficient between particular pairs of metals in Kielce soils ($N = 60$) is statistically significant at the level of $\alpha = 0.01$ and only for two pairs at the level of $\alpha = 0.05$ (As–Cu; Cu–Mn) (Table 4).

The correlation coefficient at the significance level of $\alpha = 0.01$ indicates very strong relationship between analyzed data pairs. The largest positive correlations are between As and Co ($R = 0.88$), Cr and Ni ($R = 0.87$), and Co and Ni ($R = 0.85$). These results may reflect the fact that these metals come from similar or even common sources.

The relationships between content of selected elements in individual samples, taken from the soil of various land uses, are described by power and linear equations. Determination coefficients (R^2) reach high values (maximum from 0.85 to 0.92) at the significance level of $\alpha = 0.01$ (Fig. 2a).

The strongest relationship has been identified between Ni and Zn in the samples taken from roads, which certainly

Table 4 Spearman's rank correlation coefficient and p values (in brackets) matrix for concentration of heavy metals in Kielce city in 2016 ($N = 60$, significance level: $\alpha = 0.01$, $^*\alpha = 0.05$)

	As	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
As	1.0									
Ba	0.63 (<0.001)	1.0								
Cd	0.48 (<0.001)	0.64 (<0.001)	1.0							
Co	0.88 (<0.001)	0.77 (<0.001)	0.60 (<0.001)	1.0						
Cr	0.72 (<0.001)	0.74 (<0.001)	0.62 (<0.001)	0.84 (<0.001)	1.0					
Cu	0.31* (0.017)	0.51 (<0.001)	0.62 (<0.001)	0.44 (<0.001)	0.53 (<0.001)	1.0				
Mn	0.75 (<0.001)	0.68 (<0.001)	0.57 (<0.001)	0.84 (<0.001)	0.64 (<0.001)	0.30* (0.018)	1.0			
Ni	0.75 (<0.001)	0.72 (<0.001)	0.59 (<0.001)	0.85 (<0.001)	0.87 (<0.001)	0.66 (<0.001)	0.65 (<0.001)	1.0		
Pb	0.51 (<0.001)	0.52 (<0.001)	0.66 (<0.001)	0.55 (<0.001)	0.60 (<0.001)	0.63 (<0.001)	0.47 (<0.001)	0.71 (<0.001)	1.0	
Zn	0.39 (0.002)	0.70 (<0.001)	0.73 (<0.001)	0.58 (<0.001)	0.69 (<0.001)	0.72 (<0.001)	0.47 (<0.001)	0.72 (<0.001)	0.65 (<0.001)	1.0

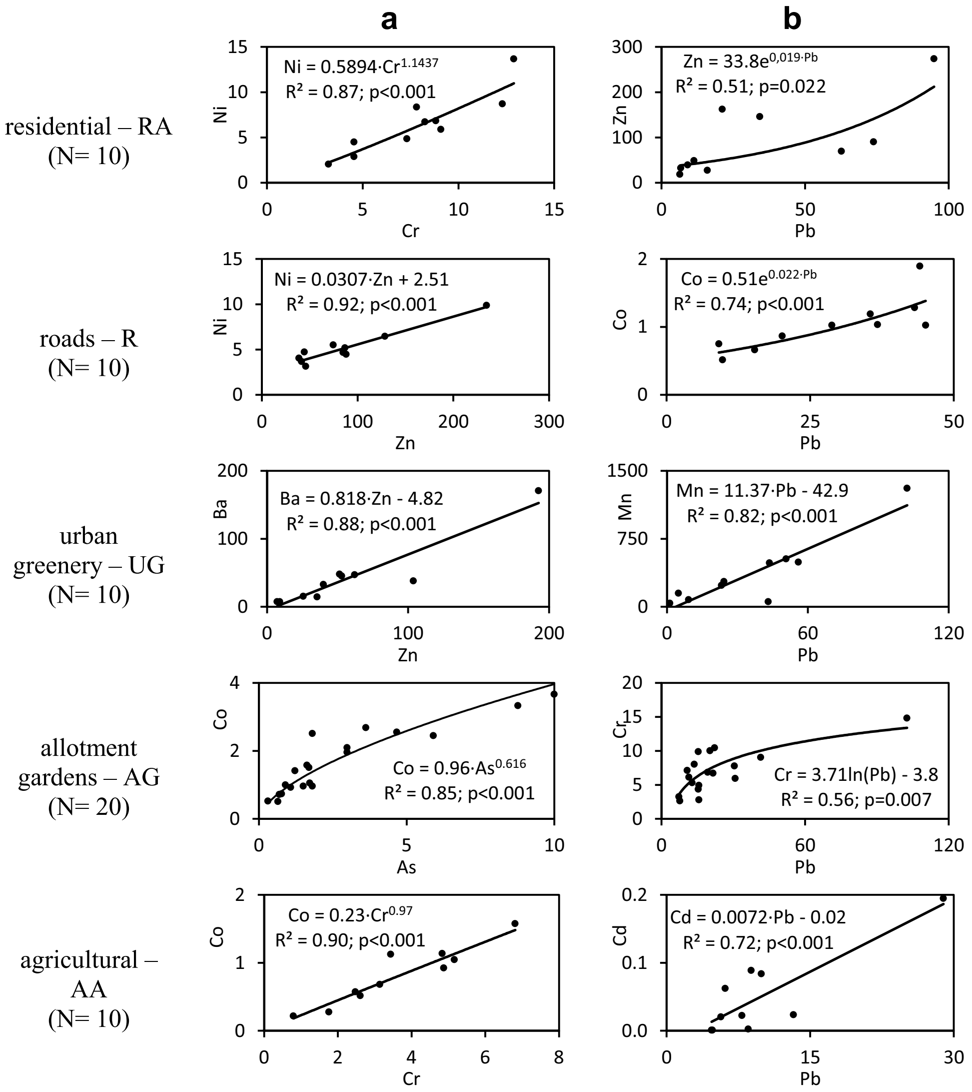

Fig. 2 Best-fit relationships between: **a** metals, **b** Pb and metals, in soil samples of different land use. *N* number of pairs, R^2 coefficient of determination, *p p* value

shows their common origin associated with car pollution. A lower level of statistical significance (p value < 0.05) has been discovered by analyzing only the relationship between the Pb content and the concentrations of other metals (Fig. 2b). The highest degree of fit is from $R^2 = 0.51$ (p value = 0.022) to $R^2 = 0.82$ (p value < 0.001). It is interesting that Pb has shown relationships with other metals in all types of land use. The best fit has been found between Pb and Mn in samples taken from the urban greenery areas.

With the use of the PCA (principal component analysis) method, four main components have been distinguished—PC1–PC4 (Table 5). Together they generated 83% of the cumulative total variance of trace elements in soil samples in Kielce, regardless of the form of land use. They take into account both natural (PC1) and anthropogenic conditions (PC2–PC4).

The first component (PC1), representing the impact of natural conditions of the geological substrate, has generated

Table 5 PCA analysis of heavy metals in Kielce city

Variable	Component			
	PC1	PC2	PC3	PC4
As	– 0.71[a]	– 0.42	– 0.43	– 0.02
Ba	– 0.65[a]	– 0.07	0.60[a]	0.26
Cd	– 0.77[a]	0.30	– 0.22	0.27
Co	– 0.88[a]	– 0.38	– 0.12	0.05
Cr	– 0.83[a]	– 0.04	0.28	– 0.11
Cu	– 0.73[a]	0.36	– 0.33	0.27
Mn	– 0.65[a]	– 0.50	0.14	– 0.11
Ni	– 0.88[a]	– 0.04	0.04	– 0.13
Pb	– 0.54	0.38	– 0.04	– 0.70[a]
Zn	– 0.63[a]	0.60[a]	0.17	0.09
% of variance	54	13	8	8
Cumulative %	54	67	75	83

[a] PC1 and PC4 ≤ – 0.7; PC2-PC3 ≥ 0.6

54% of the total variance and showed high weights (≤ – 0.7) for Co, Ni, Cr, Cd, Cu, and As (Table 5). In turn, the second component (PC2) has shaped 13% of the total variance with the highest weight for Zn (Fig. 3a) and moderate for Mn and As. The analysis of PC3 (8% of variance) is also significant. It has shown a high weight for Ba and a moderate for As (Fig. 3b). This applies especially to allotment gardens, where plant protection products and fertilizers are used. Also, 8% of the total variance has been explained by the PC4 component (Fig. 3c), which has shown the highest weight for Pb (– 0.70) whose source has anthropogenic origin, including communication. It is worth noting that As was related to three main components, i.e. PC1 (– 0.71), PC2 (– 0.42), and PC3 (– 0.43) and this indicates the multi-directional sources of this trace element.

The analysis of the Mann–Whitney *U* test result concerning the content of metals in samples across all the analyzed forms of land use has shown that a set of statistically significant differences existed only between the content of metals in samples from allotment gardens and agricultural areas. The value of the obtained probability indicates that the difference in the medians of the content of eight determined metals (Table 6) in these forms of land use was statistically significant at the level of $\alpha = 0.05$, and for two of them, i.e. As and Mn, was statistically not significant at this level. The results clearly indicate that intensive use of land in allotment gardens in terms of enriching soil humus with peat or its substitutes might have contributed to a considerable increase in the content of metals. This is due to the fact that, in humus-rich soils, most metals form complex compounds, which is supported by the presence of numerous functional groups of humic and fulvic acids (Stevenson 1994). Research on the mechanisms of interaction of metal ions with humic and fulvic acids and their interaction in the soil environment are not fully explained in the subject literature and are still very complex (Boguta and Sokolowska 2013). In addition, many years of irrational use of plant protection chemicals and artificial fertilizers, often in unjustified doses, has resulted in statistically significant changes in relation to their content in agricultural areas.

Assessment of environmental risk

The results of calculations of the index of geoaccumulation for the entire city of Kielce and for different forms of land use, in reference to the maximum ($I_{\text{geo\_max}}$) and mean ($I_{\text{geo\_avg}}$) content of individual elements, are presented in Fig. 4.

The calculations has indicated positive $I_{\text{geo\_max}}$ values in individual samples for six elements (As, Cd, Cu, Mn, Pb, Zn) regardless of the comparison to the Clarke values of the continental crust and average content in Poland's

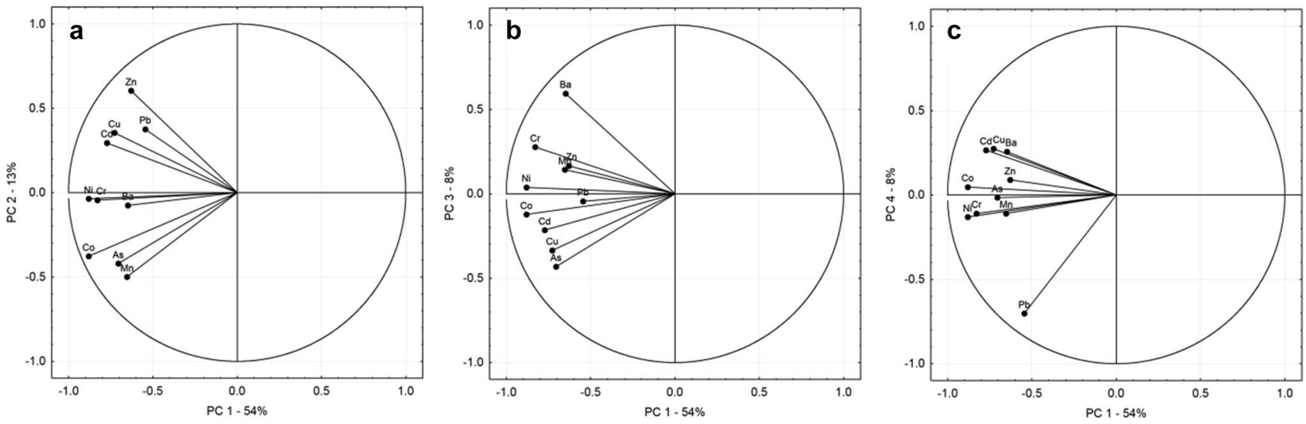

Fig. 3 Graphical image of the relationship between PC1 and PC2, PC3 and PC4 components

Table 6 The Mann–Whitney *U* test results concerning the content of metals determined within ground samples from allotment gardens ($N = 20$) and agricultural areas ($N = 10$) at the significance level of $\alpha = 0.05$

	As	Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Ranks total gardens	349	367	395	363	383	381	352	374	381	402
Ranks total agriculture	116	98	70	102	82	84	113	91	84	63
U	61	43	15	47	27	29	58	36	29	8
p value	0.091*	0.011	< 0.001	0.019	< 0.001	0.001	0.067*	0.004	0.001	< 0.001

*Relationship statistically not significant

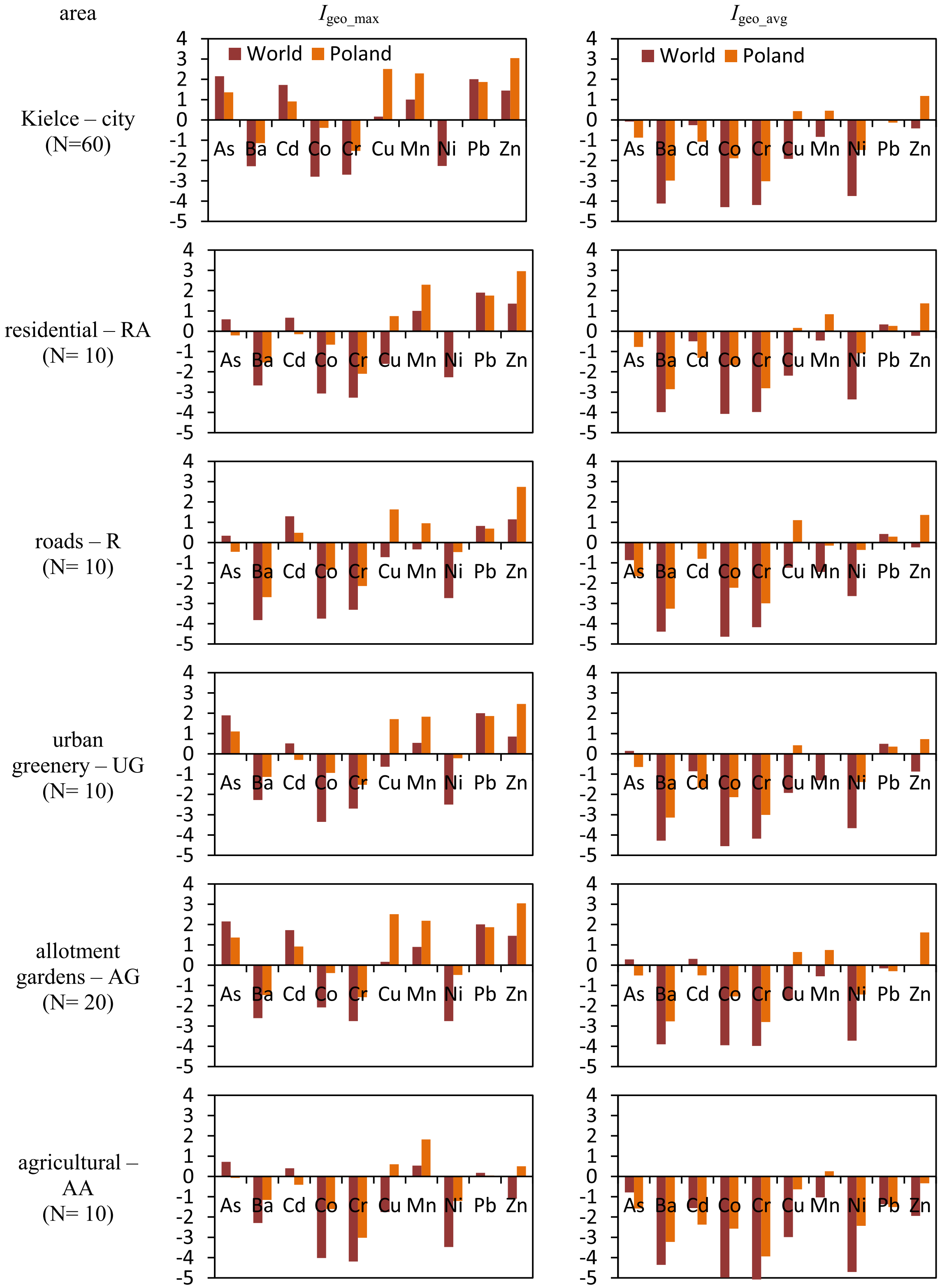

Fig. 4 Index of geoaccumulation (I_{geo_max}, I_{geo_avg}) characterizing grounds of different land use in Kielce in 2016 in relation to the Clarke values in upper continental crust and to the average content in Poland’s soils

soils. When compared to the Clarke values, in individual samples collected in allotment gardens, moderate to heavy As ($I_{geo\_max} = 2.15$) and Pb (2.01) soil contamination and moderate Cd and Zn contamination (1.73 and 1.45, respectively) has been found. Furthermore, considering the average content of the elements in Poland's soils, heavy Zn ($I_{geo\_max} = 3.05$) and moderately to heavy Cu (2.51) and Mn (2.30) soil contamination has been found.

The index of geoaccumulation (I_{geo_avg}) calculated from the average content of elements in the soil of the Kielce city has had negative values for almost all the metals (except for Pb—$I_{geo\_avg} = 0.007$) in relation to Clarke values in the upper continental crust. Positive values of this index for Pb have been obtained in urban greenery (0.492), roads (0.425), and residential areas (0.339). As for the average content of elements in Poland's soils, moderate soil contamination in Kielce concerned Zn ($I_{geo\_avg} = 1.18$), and in the category of uncontaminated to moderately contaminated ($0 < I_{geo\_avg} \leq 1$) Cu and Mn. Within the allotment gardens, positive but low values of I_{geo_avg} have been obtained for Zn (0.01 Clarke value, 1.61 average content in Poland's soils). Definitely the lowest values of I_{geo_avg} have been calculated for soils of agricultural areas (practically uncontaminated).

The IPI indicates that on average and regardless of the form of land use, the ground in Kielce is little contaminated with metals (IPI = 0.69) in relation to Clarke values. The highest average value has been obtained for samples coming from allotment gardens (IPI = 1.43) and only in agricultural areas the pollution level is low (0.61). Maximum IPI values for individual samples have been obtained for allotment gardens (2.71) and urban greenery areas (2.05), which indicates high levels of pollution. In other types of land use, these values remain moderate (Fig. 5a). In turn, considering the geochemical average content of elements in Poland's soils, the IPI is considerably higher in Kielce. In case of maximum values, it ranges from 2.54 (transportation areas) to 4.32 (allotment gardens), which indicates high level of pollution and in agricultural areas, it is the lowest (1.58) indicating a moderate pollution level (Fig. 5b).

The average values of the PERI indicate low pollution with heavy metals across all types of land use in Kielce, both in relation to the Clarke value and the average content in Poland's soils (Fig. 6).

The maximum PERI value for an individual sample has been found in allotment gardens, both in relation to the Clarke values and the average content in Poland's soils

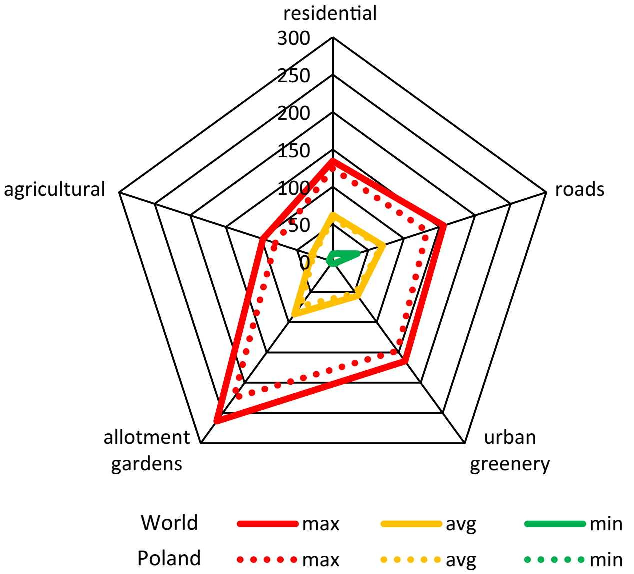

Fig. 6 Extreme (max, min) and average values of the potential ecological risk index (PERI) for areas of different land uses in Kielce in 2016, in relation to the Clarke values and the average content of elements in Poland's soils

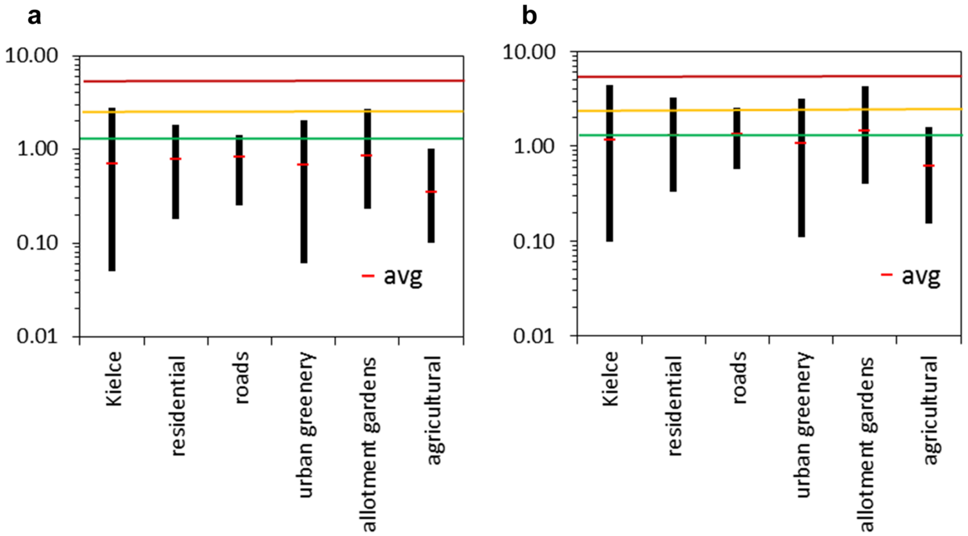

Fig. 5 Extreme and average values (avg) of the integrated pollution index (IPI) characterizing grounds of various land uses in Kielce in 2016, in relation to the Clarke values for Earth (**a**) and Poland's soil (**b**). The lines indicate the upper limits of pollution levels: green—low (1), yellow—moderate (2), red—high (5)

(263.7 and 225.1, respectively), which indicates a moderate level of potential ecological risk ($150 \leq \mathrm{PERI} < 300$). In relation to the Clarke values, this threshold has also been exceeded for samples taken from roads and urban greenery. Even higher values of this index for the areas of city parks in Poland were obtained in Bydgoszcz (Dąbkowska-Naskręt et al. 2016) and in Kraków (Gąsiorek et al. 2017).

Such results were determined by high Cd content, as it is the element with the highest biological toxicity index ($\mathrm{Tr}_{\mathrm{Cd}} = 30$). It comes mainly from the abrasion of car tire treads (Ferreira et al. 2016) and car exhausts (Ajmone-Marsan and Biasioli 2010). Cadmium and its compounds have been listed in a strategic European document as the most dangerous substances as early as in the 1970s (Council Directive 76/464/EEC 1976).

Conclusions

The analysis of the heavy metals content in the topsoil in the Kielce area has shown some regularities in terms of their occurrence within five categories of land use, in relation to Clarke values and average content of elements in the soils of Poland. These levels are exceeded by the average concentration of two heavy metals in the Kielce soils, i.e. Pb and Zn. Particularly, high content has been found in the ground of urban greenery areas and in residential areas. Noteworthy is the threefold decrease of the average Pb content and the twofold decrease of the average Zn content in the ground along major transportation routes in the city comparing to year 2000. In turn, the maximum concentration of Pb and Zn in 2016 was found in samples taken from allotment gardens, which might have resulted from the fact that the soils had been formed directly on the outcrops of Paleozoic rocks containing Pb and Zn ores.

It is surprising that the highest content of toxic elements, i.e. As and Cd (both maximum and average) has been found in soils of Kielce's allotment gardens. This is probably a consequence of the long term and intensive use of plant protection products and artificial fertilizers. The highest average concentration of four other metals (Ba, Co, Cr, Zn) has also been documented there.

The average content of elements in Kielce soils, regardless of the form of land use, is sequenced as follows: Mn–Zn–Ba–Pb–Cu–Cr–Ni–As–Co–Cd. The correlation coefficient between individual pairs of the abovementioned metals is mostly statistically significant. High correlation values at the significant level of $\alpha = 0.01$ between As and Co, Cr and Ni, Co and Ni indicate their common source. This is additionally confirmed by the principal component analysis, pointing to the natural and multidirectional anthropogenic sources of trace metals.

Indicative, relative assessment of the degree of soil contamination with metals in Kielce, in relation to the Clarke value, as well as the average content in Poland's soils has shown that:

- the index of geoaccumulation was positive only in individual samples ($I_{\mathrm{geo\_max}}$) for six elements (As, Cd, Cu, Mn, Pb, Zn) and it reached the highest values within allotment gardens both compared to the Clarke values (As—moderately to heavily contaminated, Cd and Zn—moderately contaminated), as well as the average content in Poland's soils (Zn—heavily contaminated, Cu and Mn—moderately to heavily). The average values of $I_{\mathrm{geo\_avg}}$ were negative for almost all metals (except for Pb) in relation to the Clarke values and in relation to the average content in Poland's soils they were positive only in a few cases (Zn—moderately contaminated, Cu and Mn—uncontaminated to moderately contaminated);
- the IPI, in relation to the Clarke values, as well as the average content in Poland's soils, in terms of maximum values, showed high level of soil pollution in Kielce in almost all the considered forms of land use, except for agricultural areas, where it was moderate; in terms of average values, the documented pollution was one level lower, with the preservation of the structural system;
- the PERI, on average, informs about a low level of metal pollution among all types of land use in Kielce; in relation to the Clarke values and to the average content in Poland's soils, a moderate level of potential ecological risk has been identified in individual soil samples coming from allotment gardens and in relation to the average content in Poland only—in samples from roads and urban greenery. The concentration of cadmium, the element with the highest biological toxicity index, had the biggest influence on this result.

The discovery of elevated toxic concentrations of trace elements (As, Cd) in allotment gardens in Kielce is of great importance, not only cognitive, but also practical. The results obtained are reported to the services related to environmental protection at the City Hall in Kielce and this knowledge is already used in ecological education of children and adults, including gardeners (18 thousand families). In addition, this information can be valuable in the process of repair and remediation of these lands. The Kielce research community and the city authorities recognize the need to continue monitoring of trace metals in the soils of these areas, taking into account the diversity of the soils. At the same time, the authors are well aware of the limitations resulting from a low number of soil samples taken and the lack of metal speciation analysis. The soil samples used were taken from the exact same places as those analyzed during a similar research conducted in 2000 and thus, their number was limited. It allowed, however, for making a comparative analysis of the concentration of the selected trace metals under five land uses in Kielce in the years 2000 and 2016. The authors plan to increase the number of soil samples to be used in the following research series and to extend the scope of methods used by including the analysis of trace elements content in several particle size fractions and by metal speciation analysis. This will allow to illustrate potential human health risk assessment of trace metals in allotment gardens (carcinogenic and non-carcinogenic hazard index) for child and adult, as well as cumulative risk, which reflects the contemporary directions of research on the subject (Chrzan 2016; Gupta et al. 2019).

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