Carpathian Journal of Earth and Environmental Sciences, February 2018, Vol. 13, No. 1, p. 249 – 266; DOI:10.26471/cjees/2018/013/022

ACCUMULATION OF HEAVY METALS IN THE URBAN SOILS OF THE CITY OF SKARŻYSKO-KAMIENNA (POLAND) WITH REGARD TO LAND USE

Anna ŚWIERCZ[1] & Ewelina ZAJĘCKA[2]
[1]*Chair of Environmental Protection and Modelling, Jan Kochanowski University, ul. Świętokrzyska 15, Kielce, Poland, e-mail: swierczag@poczta.onet.pl*
[2]*Institute of Biology, Jan Kochanowski University, ul. Świętokrzyska 15, Kielce, Poland, e-mail: ewelina.smorzewska@gmail.com*

Abstract: This article raises the issue of heavy metal concentrations in urban soils. Soil samples were collected from the surface layers of urban soils located in industrial areas, urban allotment garden areas as well as urban green areas in the city of Skarżysko-Kamienna which has chiefly industrial origins. The soil samples collected in Skarżysko-Kamienna indicated slightly acidic pH_{KCl} in the range of 3.48-6.97. The highest average pH_{KCl} value was reported for the industrial areas. The analyses indicated varied concentrations of heavy metals. The maximum values were reported for the soil samples coming from the industrial areas, except for Cd whose highest values were noted in the soils of urban allotment gardens. The results in comparison to the geochemical background defined for the soils of Skarżysko-Kamienna demonstrated higher concentrations of Pb, Cu, and Zn in the soils. This was confirmed by the analysis of the contamination degree determined through the geoaccumulation index (Igeo); however, the Igeo values were very differentiated within each group of land-use types. The study does not indicate a direct relationship between heavy metal concentrations and types of land use, except for Cr in the case of which such relationships were statistically proved. The degree of contamination of the city is especially affected by the locations having outlying concentrations of heavy metals as showed by the spatial presentation of the obtained results by means of the kriging method.

Keywords: urban soils; heavy metals; soil properties; Skarżysko-Kamienna; geoaccumulation index

1. INTRODUCTION

The issue of the origins of heavy metals in soils is widely analysed by many researchers (Czarnowska et al., 1983; Chen et al., 1997; Kabata-Pendias & Pendias et al., 1992; Madrid et al., 2002; Imperato et al., 2003, Salminen et al., 2005). Contamination of soil surface layers with heavy metals is particularly visible in urban areas which are intensively managed by humans (Walczak et al., 2011). Progressing urbanisation makes soils structurally altered and that results in their degradation (Wu, 2014; Mao et al., 2014). In urban areas, a wide range of substances being produced through combustion of fuels, industrial processes, road de-icing, and abrasion of vehicle exploitation materials (mainly tyres) are emitted to the environment. These are toxic gases and dust enriched with heavy metals. Such contamination undergoes deposition and penetrates into soils (Shang, et al., 2012; Mcbride et al., 2014). Transformed structure and chemistry of soils may lead to serious disturbances in their biological activity and impoverishment of vegetation cover (Mireles et al., 2012; Hu et al., 2013). The problem of the impact of urban contamination on soils concerns the whole urban centre, including urban allotment gardens and recreation areas (Bielicka et al., 2009). As cities intensively develop, their recreational areas, including allotment gardens lying typically at their peripheries, are nowadays within their centres. This is important because allotment gardens are commonly used for amateur cultivation of seasonal vegetables and fruit. Areas located closely to communication routes are especially vulnerable to contamination. This poses a real threat to human health due to the accumulation of these elements in crops (Huang et al., 2012; Schwarz et al., 2012; Szolnoki et al., 2013; Niewiadomski & Szubert al., 2014).

The analysis of spatial presentation of results is becoming more important in determining the causes of contamination of urban soils with heavy metals. By means of this analysis, it is possible to determine the source of contamination or to designate areas for further monitoring studies (Santos-Francés et al., 2017). It is a method which, in conjunction with the analysis of indicators of soil contamination and environmental hazards, is very useful for evaluation of soil quality and further monitoring studies. Multiple factor analysis of the problem together with the spatial presentation of the results may have a practical approach and will be used to model the variation of soil properties (Santos-Francés et al., 2017; Lee et al., 2006). This is even more useful when taken into consideration that soil studies are costly and time-consuming, and that covering the entire city with such studies is a long-term process and involves a lot of financial effort. The works are being conducted mainly locally. In order to determine the origins of heavy metals, it is necessary to recognise the lithology of a given area, its spatial structure and potential emitters. High concentrations of heavy metals are not always associated with anthropogenic factors, but are often the result of the content of these chemical elements in parent rocks.

The aim of this study was to identify the soil environment in terms of the content of selected heavy metals, as well as to identify its physicochemical properties. By analysing the spatial distribution of heavy metal concentrations in relation to the correlations among these elements, it may be possible to assess the contamination of the soils, and to designate the areas for further and detailed monitoring studies. The city of Skarżysko-Kamienna was selected as a study area due to the fact that no soil studies have been conducted in the area of the city so far.

2. MATERIALS AND METHODS

2.1. Study area

Skarżysko-Kamienna is a medium-sized county city with an entire area of 64.2 km^2, located in the central part of Poland (N: 51^{o}119’, E: 20 879’). Nowadays, the city has nearly fifty thousand inhabitants. The beginnings of settlement in the area of the contemporary city are directly connected with the development of metallurgical craftsmanship in the early medieval period. At that time, industrial colonies with mining and metallurgical plants had been established along the Kamienna river valley. Those colonies then gave rise to the Staropolski Industrial District – the eldest and largest mining, metallurgical and lead-silver-copper processing district on the Polish lands. Skarżysko-Kamienna was granted with its city rights in 1923, and in 1936 it was incorporated into the functional area “A” of the newly-formed Central Industrial District. As a result, the city underwent a strong and rapid concentration of defence, railway and chemical industries. After World War II there was a period of further intensified industrialisation of the city. During the systemic transformation, initiated in 1989, the industrial plants found themselves in a difficult economic situation – a significant part of them became bankrupt. Nowadays, Skarżysko-Kamienna still remains an important industrial centre on the Polish map. There are such dominant types of industries as: electromechanical (including production of weapons and ammunition, mechanised equipment for households and gastronomy, light fixtures, agricultural and forestry machines), food, clothing, and building materials (Zemeła & Kardyś, 2013).

The area of the city and its geological and tectonic structures are located at the northern border of the Świętokrzyskie Mountains, built out of the Mesozoic formations (the so-called Mesozoic layers of the Świętokrzyskie Mountains). The basis for the Mesozoic formations is constituted by the Paleozoic sediments – Carboniferous greywackes interbedded with mudstones and claystones whose thickness amounts to 870 m. Much younger – Permian sediments belong to sea formations – the Zechstein dolomites with marl, limestone and conglomerate deposits whose thickness is up to 230 m (Fig. 1).

The state of the natural environment in Skarżysko-Kamienna is determined on the basis of standard monitoring studies conducted within regional environmental monitoring (SEMP, 2012). According to these studies, the concentrations of SO_2, NO_3 and PM10 in the air for Skarżysko-Kamienna indicate class A, which means that no exceeding has been recorded for determined contamination levels. The Chemical composition of PM10 is not, in turn, analysed in terms of heavy metal concentrations. In the case of surface waters within the city boundaries, their ecological state is determined as either moderate or weak. Ground waters, after little treatment, fulfill the requirements for waters intended for human consumption. Chemistry monitoring of agricultural soils includes basic studies of soil abundance with macroelements, pH and concentrations of selected heavy metals.

2.2. Sample collection

The soil samples were mainly collected in the eastern and central part of the city, where there are a developing urban centre as well as main roads and railways (Fig. 2).

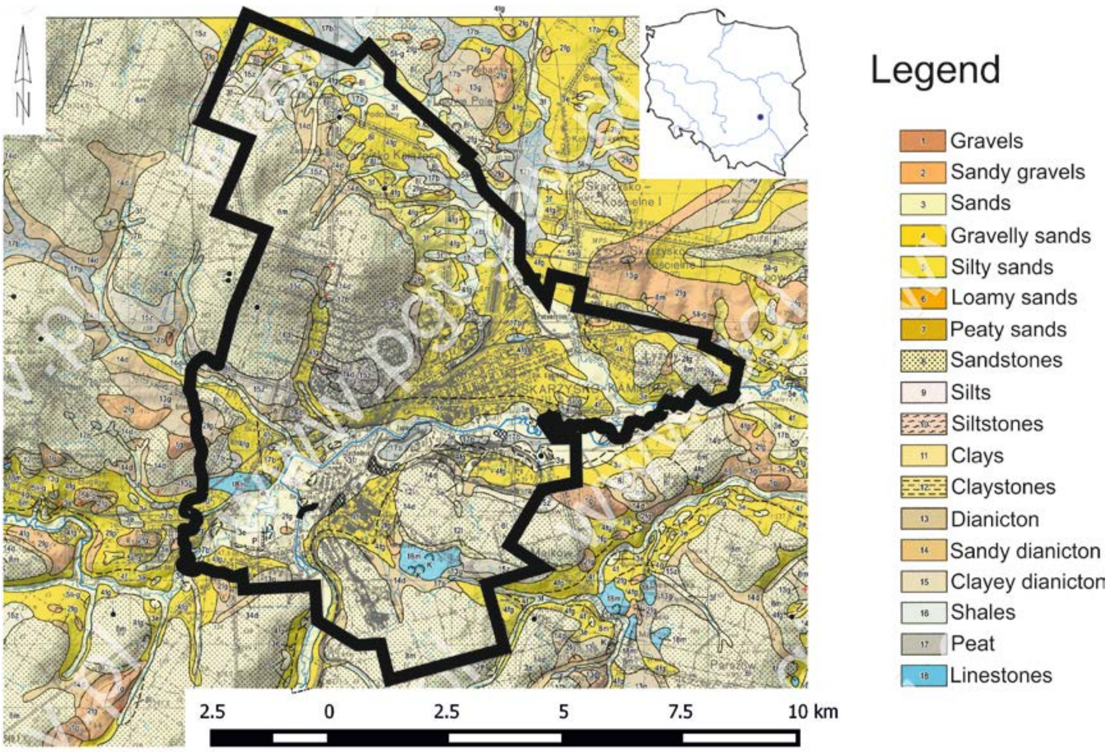


Figure 1. Lithological composition on the basis of the lithological map of Poland sheet 779 Skarżysko-Kamienna, with an indication of the city area and the study area.

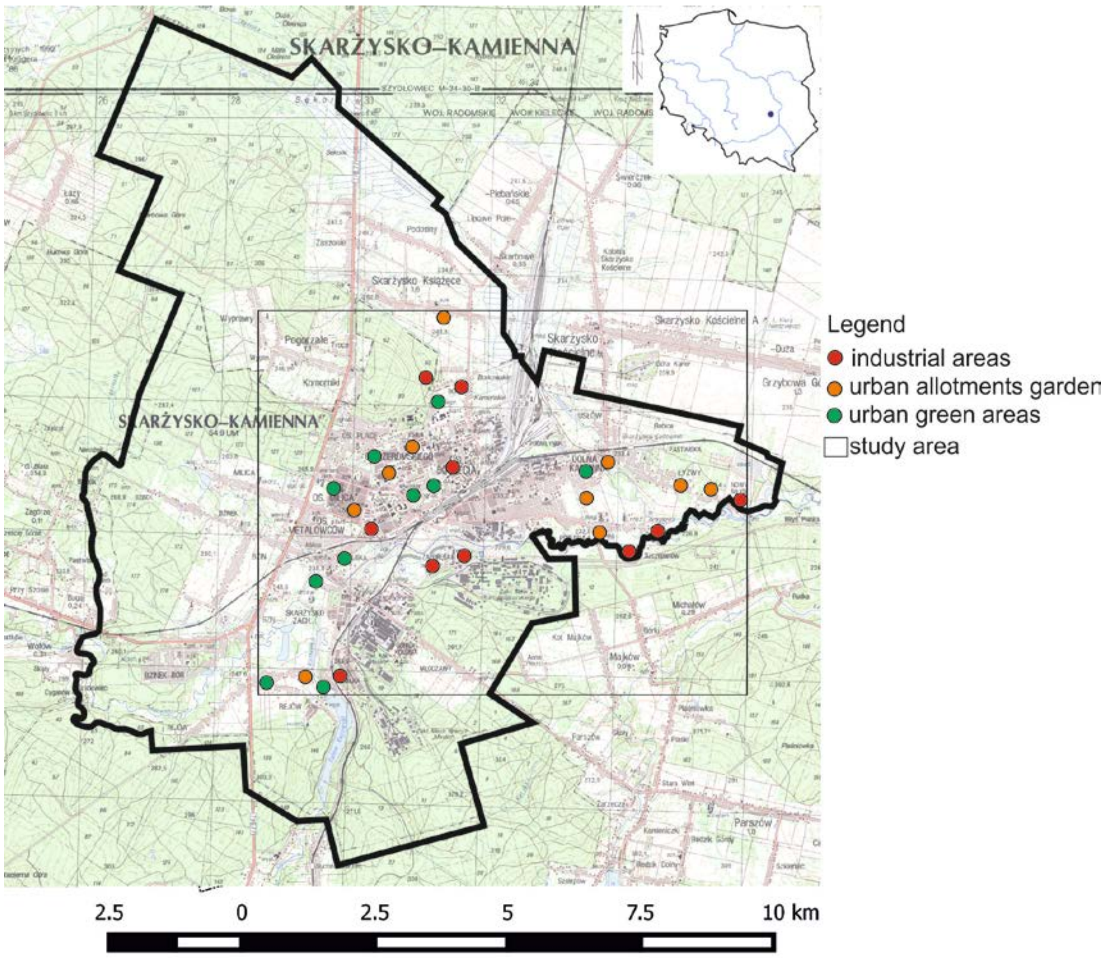


Figure 2. Area of the city of Skarżysko-Kamienna on the geoenvironmental base map, with an indication of soil sampling plots.

The northern part of the city is poorly developed and is covered mainly with forests. The soil was collected using the Egner's sampling stick from the surface layer up to 25 cm. One mixed sample was made up of the soil material weighing 1 kg. Each mixed sample consisted of the soil material coming from 5 points of puncture by the Egner's sampling stick within one 300x300 cm plot.

2.3. Laboratory analyses

The soil samples were deprived of non-humificated organic matter and then dried at room temperature. Afterwards, they were ground in an agate mortar and sieved through a 2 mm mesh sieve. In the soil samples, the total content of selected heavy metals, i.e. Pb, Cd, Cu, Ni, Zn, and Cr was determined, after 24-hour digestion in *aqua regia* (a mixture of concentrated acids HCL and HNO_3 in a molar ratio of 1:3), by the flame atomic absorption spectrometry (FAAS) method with an atomic absorption spectrometer. Also, the following physicochemical properties of soils were analysed (Ostrowska et al., 1991):

(A) grain-size composition by the Cassagrande's aerometric method in Prószyński's modification;

(B) Ph_{KCl} by the potentiometric method with using a pH meter and Elmetron electrode in a ratio of 1:2.5, 1M KCL-soil;

(C) hydrolytic acidity H_h by the Kappen's method;

(D) adsorption capacity by the Kappen's method.

In order to analyse the content of heavy metals in the soil, the measurement uncertainty was determined, consisting of: volumetric vessel uncertainty, uncertainty of standards, relative standard deviation of repeatability, as well as relative standard deviation of recovery. Two independent reference curves were designated using the Merck and Sigma's certified reference materials. Measurement uncertainty was 25%. In order to determine the accuracy of pH meter and electrode's indications, the electromotive force was defined – the linearity of pH meter's indications in the analysed range was checked. Standard buffers with pH: 4.01, 7.00 and 9.21 were used. Uncertainty in $pH_{KCl}$was 5%.

2.4. Statistical analysis

Statistical analysis was performed using the Statistica v. 13 software. Descriptive analysis was obtained using the following variables: arithmetic mean, median, range, standard deviation, and coefficient of variation. In addition, the geoaccumulation index (Igeo) was calculated, which was helpful to assess the level of soil contamination. In order to check the normal distribution of collected data, such statistical tests as: Kolmogorov-Smirnov test, Shapiro-Wilk test and Lilliefors test were used. The compilation of the empirical histogram with the normal distribution density curve for heavy metals with regard to land-use types is shown in Figure 3.

Then, the one-way analysis of variance (ANOVA) was performed in order to check whether the content of heavy metals in soils is determined by the type of land use and whether the land-use type determines the physicochemical properties of analysed heavy metals. The analysis of spatial variability was performed using the Surfer software. The kriging method was used as well. Geostatistical kriging procedure is one of the most common interpolation methods used in recent years. The kriging method is characterised by numerous advantages, such as: basing the interpolation procedure on the variation model of interpolated parameters; taking into account the mutual position of the observation with respect to each another and with respect to the point in which the parameters are made (or predicted); minimising an interpolation error; possibility of estimating the values of parameters in the points and their mean values in assumed-size plots; as well as assessing the magnitude of errors associated with any variant of the interpolation (Santos-Francés et al., 2017; Goldsztejn & Skrzypek, 2004).

3. RESULTS

3.1. Heavy metal concentrations in the soil

The average content of heavy metals in the soil together with descriptive statistics parameters are included in Table 1. The highest average content of such heavy metals as Pb, Cu, Ni, Zn and Cr in the analysed soils was reported for industrial areas. The highest average content of Cd was recorded for urban allotment gardens. The soils of industrial areas were characterised with the highest coefficient of variation for the analysed heavy metals, except for Cd – the highest variation of this heavy metal was found in the soils of urban allotment gardens.

The highest coefficients of variation were noted for Pb. Comparing to the maximum geochemical background specified for Skarżysko-Kamienna, the average content of heavy metals was exceeded in the cases of: Pb (industrial areas, urban green areas); Cd (urban allotment gardens); Cu (industrial areas, urban green areas); Ni (industrial areas, urban green areas, urban allotment gardens); Zn (industrial areas); Cr (industrial areas, urban green areas).

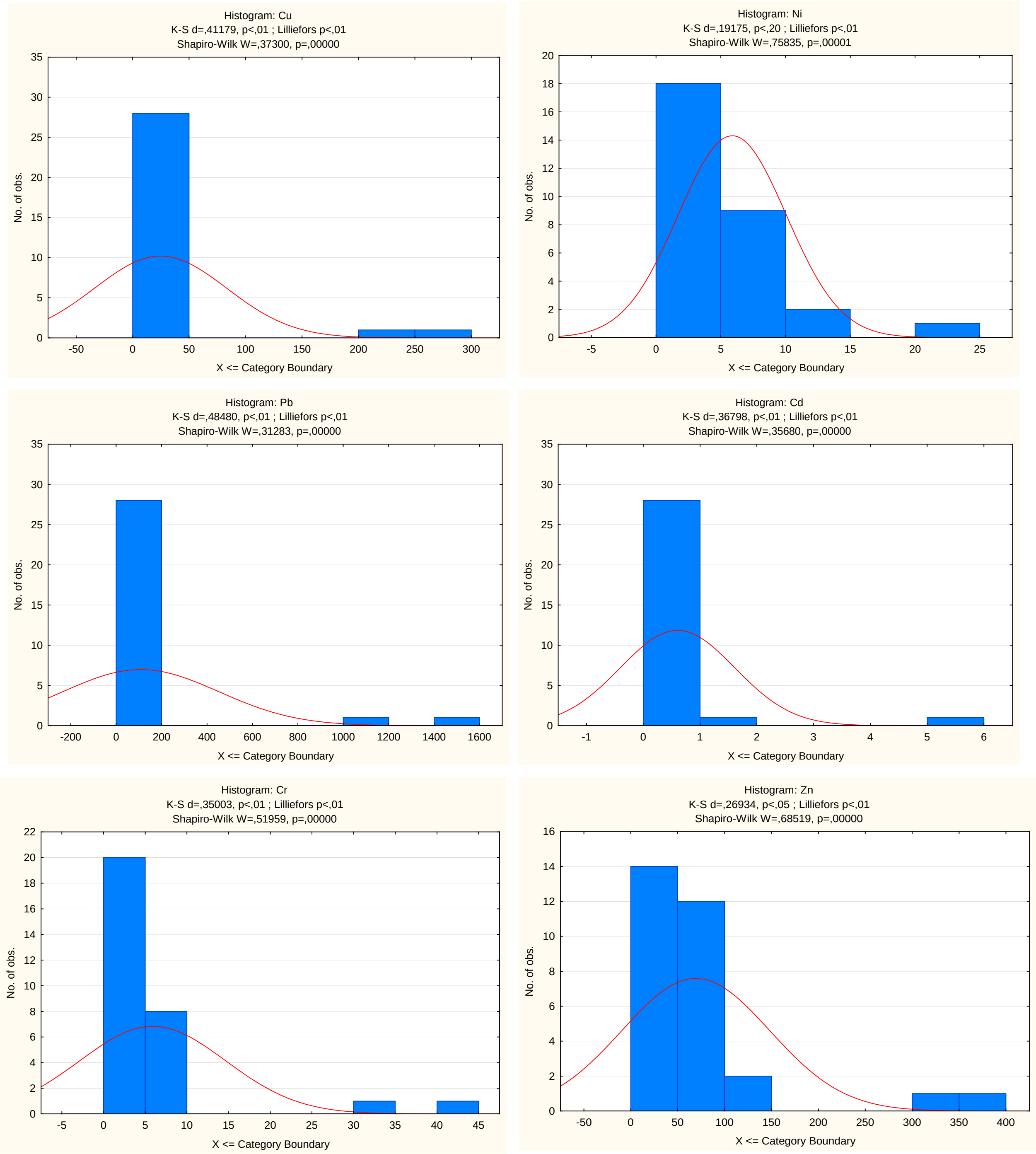


Figure 3. Frequency histograms of heavy metal concentrations for Pb, Cd, Cu, Ni, Cr, and Zn

The results of the analysis indicated that the soils had a tendency to accumulate heavy metals. The analysed soils were characterised with the pH ranging from 5.53 to 6.43 which indicated that they had slightly acidic pH (Table 2). The lowest pH was reported for the soils of urban green areas, and the highest – for the soils of industrial areas. The soils were characterised with a small pH variation as evidenced by the calculated coefficients of variation. The average values of hydrolytic acidity were comparable for the soils of urban green areas and urban allotment gardens, and amounted to 4.48 and 4.90, respectively. Much lower average values were noticed for the soils of industrial areas – 2.71. The coefficients of variation for the soils of industrial areas, urban green areas and urban allotment gardens were comparable and amounted to 0.77, 0.84 and 0.80, respectively.

The average values of adsorption capacity were comparable for the soils of industrial areas and urban allotment gardens, i.e. 24.57 and 23.34, respectively. Such values were lower for the soils of

Table 1. Statistical analysis of the content of heavy metals in the soils of Skarżysko-Kamienna with regard to different types of land use (mg/kg d.m.)

Statistical parameters	**Pb**	**Cd**	**Cu**	**Ni**	**Zn**	**Cr**
Industrial areas						
Mean	181.1	0.45	55.9	8.03	105.15	10.9
Median	24.5	0.3	11.0	5.6	55.25	4.5
Min	2.0	0.1	2.0	2.3	9.0	2.0
Max	1600	1.3	261	21.8	352	42
Standard deviation	499	0.37	96.9	6.28	125	13.9
Coefficient of variation	2.75	0.82	1.73	0.78	1.18	1.27
Geochemical background for Skarżysko-Kamienna	13-25	0.5-0.5	5-9	2-4	35-64	2-4
Geochemical background for Poland	0.5-21	0.03-1	0.4-23.5	0.5-28.5	5-59	2-64
Urban green areas						
Mean	125.8	0.37	10.2	4.69	62.75	5.4
Median	17.5	0.4	8.5	4.45	64.35	6.0
Min	8.0	0.2	2.0	1.4	11.2	2.0
Max	1092	0.5	23	7.3	134	7.0
Standard deviation	340	0.116	6.84	1.74	32.7	1.51
Coefficient of variation	2.70	0.31	0.67	0.37	0.52	0.28
Geochemical background for Skarżysko-Kamienna	13-25	0.5-0.5	5-9	2-4	35-64	2-4
Geochemical background for Poland	0.5-21	0.03-1	0.4-23.5	0.5-28.5	5-59	2-64
Urban allotment gardens						
Mean	18.3	0.99	8.1	4.93	39.98	1.4
Median	18.0	0.45	7.0	4.0	41.05	1.0
Min	7.0	0.3	3.0	2.4	2.1	1.0
Max	33.0	5.8	15.0	9.5	99.0	3.0
Standard deviation	8.26	1.70	4.48	2.49	32.2	0.70
Coefficient of variation	0.45	1.71	0.55	0.51	0.80	0.50
Geochemical background for Skarżysko-Kamienna	13-25	<0.5-0.5	5-9	2-4	35-64	2-4
Geochemical background for Poland	0.5-21	0.03-1	0.4-23.5	0.5-28.5	5-59	2-64

urban green areas and amounted to 18.79. The coefficient of variation was in the range of 0.33-0.68. The analysed soils were classified with regard to grain-size composition. The most dominant were sandy clay and loamy clay. A few individual samples (17%) were grouped as loose sand and slightly loamy sand. The soils were characterised with low values of coefficients of variation for sandy fractions and significantly higher ones for silty and loamy fractions.

3.2. Assessment of environmental risk

In order to determine the origins of heavy metals and the anthropological impact on the analysed soils, a geoaccumulation index Igeo was provided for each land-use type. This index was proposed by Müller (1969) in order to assess contamination of sediments with heavy metals. Nowadays, it is used to assess a degree of soil contamination as well (Zhiyuan et al., 2011; Faiz et al., 2009; Chen et al., 2005). Geoaccumulation index is calculated using the equation:

$$Igeo = \log_2(C_n/1.5B_n)$$

where: C_n – content of a given heavy metal in the soil; Bn – geochemical background for a given heavy metal; 1.5 – natural variations of the content of a particular heavy metal in the environment resulting from differences in the geological structure.

The degree of soil contamination may be assessed with using a 5- or 7-point scale (Table 3) (Zhiyuan et al., 2011). The 7-point scale is useful for assessing the contamination degree of soils characterised with slightly differentiated Igeo values. Appropriate selection of geochemical background values is crucial for the results of Igeo calculations. Although a correction coefficient used in the formula, inappropriate selection of geochemical

Table 2. Statistical analysis of the physicochemical properties of the soils of Skarżysko-Kamienna with regard to different types of land use

Statistical parameters	pH_{KCl}	Hydrolytic acidity H_h	Adsorption capacity T	Granulation		
				Sand content	Clay content	Loam content
	-	cmol(+)/kg		%		
Industrial areas						
Mean	6.43	2.71	24.57	74.9	11.9	13.2
Median	6.46	2.50	20.12	72.5	11.5	11.0
Min	5.37	0.60	4.82	58.0	2.00	1.00
Max	6.97	6.60	49.67	90.0	30.0	30.0
Standard deviation	0.49	2.09	16.87	10.8	8.88	8.00
Coefficient of variation	0.08	0.77	0.69	0.14	0.75	0.61
Urban green areas						
Mean	5.53	4.48	18.79	76.5	11.6	11.9
Median	5.64	3.60	17.96	78.0	12.5	14.5
Min	3.48	0.70	5.42	59.0	1.00	0.00
Max	6.54	12.80	27.37	90.0	23.0	19.0
Standard deviation	0.91	3.76	6.13	9.89	6.67	7.00
Coefficient of variation	0.16	0.84	0.33	0.13	0.57	0.59
Urban allotment gardens						
Mean	5.65	4.90	23.34	64.0	19.7	16.3
Median	5.57	4.90	20.77	63.0	18.5	13.0
Min	3.97	0.60	14.17	39.0	2.00	5.00
Max	6.74	12.00	42.77	89.0	45.0	46.0
Standard deviation	0.87	3.91	8.85	16.3	11.24	12.01
Coefficient of variation	0.15	0.80	0.38	0.25	0.57	0.74

Table 3. Value classes of Igeo

Seven grades			**Five grades**		
Igeo	Class	Soil quality	Igeo	Class	Soil quality
Igeo ≤ 0	1	Practically uncontaminated	Igeo ≤ 0	1	Uncontaminated /Slightly contaminated
0 <Igeo< 1	2	Uncontaminated to moderately contaminated	0 <Igeo< 1	2	Moderately contaminated
1 <Igeo< 2	3	Moderately contaminated	0 <Igeo< 3	3	Moderately / Strongly contaminated
2 <Igeo< 3	4	Moderately / Strongly contaminated	3 <Igeo< 5	4	Strongly contaminated
3 <Igeo< 4	5	Strongly contaminated	Igeo< 5	5	Extremely contaminated
4 <Igeo< 5	6	Strongly / extremely contaminated			
Igeo< 5	7	Very strong contamination			

background values may result in wrong values and misinterpretation of Igeo. The average values of geochemical background regionally specified for the analysed area of Skarżysko-Kamienna were used for the calculations (Lis & Piaseczna, 1995). The results of Igeo calculations are presented in Table 4. The analysis of Igeo for the soils indicated the points of high heavy metal concentrations in the analysed area as evidenced by the high Igeo values at the level of >3. This concerned especially the soils of industrial areas where the high soil contamination was recorded for Pb (20% of samples), Cu (60% of samples) and Zn (10% of samples).

Table 4. Geoaccumulation index Igeo for the heavy metals with regard to land-use types

	Pb	Cd	Cu	Ni	Zn	Cr
Industrial areas						
Mean	-0.28	-1.13	3.88	0.48	-0.45	0.46
Median	-0.36	-1.32	3.46	0.29	-0.45	-0.01
Min	-3.83	-2.91	1.00	-0.97	-3.03	-1.17
Max	5.81	0.79	8.03	2.28	2.26	3.22
Standard deviation	2.65	1.11	2.40	1.06	1.82	1.49
Urban green areas						
Mean	-0.20	-1.09	-0.35	-0.06	-0.46	0.16
Median	-0.75	-0.91	-0.31	-0.02	-0.19	0.42
Min	-1.83	-1.91	-2.39	-1.68	-2.71	-1.17
Max	5.26	-0.58	1.13	0.70	0.87	0.64
Standard deviation	2.05	0.51	1.04	0.68	0.98	0.56
Urban allotment gardens						
Mean	-0.79	-0.42	-0.58	-0.02	-0.02	-1.81
Median	-0.67	-0.75	-0.60	-0.17	-0.17	-2.17
Min	-2.03	-1.32	-1.81	-0.91	-0.91	-2.17
Max	0.21	2.95	0.51	1.08	1.08	-0.58
Standard deviation	0.73	1.27	0.83	0.67	0.67	0.60

High soil contamination with Zn was also noted for the soils of urban allotment gardens (20% of samples). In the case of urban green areas, there were no extreme Igeo values apart from Pb (10% of samples). The above Igeo values were differentiated as evidenced by the calculated values of standard deviation. The Igeo values calculated for the soils of urban allotment gardens and urban green areas were characterised with the lower spread of results than those calculated for the soils of industrial areas.

3.3. Statistical analysis

The Pearson correlation coefficients calculated for each land-use type indicated statistically significant ($p<0.05$) relationships among the content of analysed heavy metals and physicochemical properties of the soils (Table 5). In the case of industrial areas, the results indicated the relationships among Ni and other analysed heavy metals, which may suggest that there were lithological relationships among these elements. Positive relationships were recorded for Cr, Zn and Cu as well. However, the relationships reported for Pb and Cd were insignificant, which may indicate anthropogenic enrichment of the soils with these elements. The trend for heavy metal relationships in the soils of urban green areas and urban allotment gardens was comparable, except for Ni for which less significant relationships were found than in the case of other analysed heavy metals. The analysis of correlation among the content of heavy metals and physicochemical properties of the soils indicated that there were significant relationships among concrete properties and soil lithology. This mainly concerned the adsorption capacity in the case of the soils of industrial areas and urban green areas, in which a positive correlation was found for Cd, Cu and Ni (industrial areas) and Ni, Zn and Cr (urban green areas). There were no significant relationships among the content of heavy metals and the soil pH (except for Cr in the soils of urban allotment gardens), as well as the content of clay fraction.

3.4. One-Way Analysis of Variance ANOVA

In order to determine whether the content of heavy metals in the soils of Skarżysko-Kamienna was determined by the type of land use, the one-way analysis of variance ANOVA was performed. On such basis, two scientific hypotheses were formulated:

H_0: Content of individual heavy metals is not conditioned by the type of land use

H_1: Content of individual heavy metals is conditioned by the type of land use

In order to verify the above hypotheses, the one-way analysis of variance ANOVA was performed. If the F value (test statistics) is higher than the F test value (critical value for a given significance level and a given number of degrees of freedom), then there are grounds for rejecting the null hypothesis and accepting the alternative hypothesis for the given element (Table 6).

Table 5. Pearson correlation coefficients with regard to land-use types

	Industrial areas (underlined results were significant at the level of $p<0.05$)									
Variable	**Pb**	**Cd**	**Cu**	**Ni**	**Zn**	**Cr**	**KCl**	**Hydrolytic Acidity H_h**	**Adsorption Capacity T**	**Loam content**
Pb	1.000	0.177	0.601	**0.791**	0.579	0.519	0.387	-0.346	0.503	-0.043
Cd	0.177	1.000	**0.762**	0.447	0.210	0.018	-0.109	0.223	**0.728**	-0.064
Cu	0.601	**0.762**	1.000	**0.819**	0.528	0.388	0.262	-0.081	**0.767**	0.126
Ni	**0.791**	0.447	**0.819**	1.000	**0.865**	**0.785**	0.382	-0.207	**0.750**	0.370
Zn	0.579	0.210	0.528	**0.865**	1.000	**0.980**	0.208	-0.024	0.481	0.585
Cr	0.519	0.018	0.388	**0.785**	**0.980**	1.000	0.243	-0.069	0.340	0.635
KCl	0.387	-0.109	0.262	0.382	0.208	0.243	1.000	**-0.944**	0.407	-0.044
H_h	-0.346	0.223	-0.081	-0.207	-0.024	-0.069	**-0.944**	1.000	-0.256	0.193
T	0.503	**0.728**	**0.767**	**0.750**	0.481	0.340	0.407	-0.256	1.000	0.074
Loam content	-0.043	-0.064	0.126	0.370	0.585	0.635	-0.044	0.193	0.074	1.000
	Urban green areas (underlined results were significant at the level of $p<0.05$)									
Variable	**Pb**	**Cd**	**Cu**	**Ni**	**Zn**	**Cr**	**KCl**	**Hydrolytic acidity H_h**	**Adsorption capacity T**	**Loam content**
Pb	1.000	0.113	0.570	-0.259	0.051	0.146	0.396	-0.356	-0.066	-0.139
Cd	0.113	1.000	**0.666**	0.230	**0.828**	0.458	0.467	-0.417	0.487	-0.073
Cu	0.570	**0.666**	1.000	0.261	**0.807**	0.477	0.438	-0.370	0.529	0.063
Ni	-0.259	0.230	0.261	1.000	0.549	**0.799**	-0.256	0.231	**0.671**	-0.222
Zn	0.051	**0.828**	**0.807**	0.549	1.000	0.617	0.374	-0.323	**0.737**	0.153
Cr	0.146	0.458	0.477	**0.799**	0.617	1.000	0.077	-0.077	**0.651**	-0.112
KCl	0.396	0.467	0.438	-0.256	0.374	0.077	1.000	**-0.989**	0.240	0.223
H_h	-0.356	-0.417	-0.370	0.231	-0.323	-0.077	**-0.989**	1.000	-0.182	-0.164
T	-0.066	0.487	0.529	**0.671**	**0.737**	**0.651**	0.240	-0.182	1.000	0.120
Loam content	-0.139	-0.073	0.063	-0.222	0.153	-0.112	0.223	-0.164	0.120	1.000
	Urban allotment gardens (underlined results were significant at the level of $p<0.05$)									
Variable	**Pb**	**Cd**	**Cu**	**Ni**	**Zn**	**Cr**	**KCl**	**Hydrolytic acidity H_h**	**Adsorption capacity T**	**Loam content**
Pb	1.000	0.065	**0.806**	0.544	-0.046	0.304	-0.289	0.370	0.386	0.296
Cd	0.065	1.000	0.567	0.586	0.619	-0.193	0.200	-0.251	0.371	0.155
Cu	**0.806**	0.567	1.000	**0.851**	0.166	0.163	-0.083	0.151	0.580	0.231
Ni	0.544	0.586	**0.851**	1.000	0.194	-0.027	0.291	-0.212	0.630	0.025
Zn	-0.046	0.619	0.166	0.194	1.000	-0.071	0.223	-0.385	0.406	-0.243
Cr	0.304	-0.193	0.163	-0.027	-0.071	1.000	**-0.717**	**0.731**	-0.232	-0.254
KCl	-0.289	0.200	-0.083	0.291	0.223	**-0.717**	1.000	**-0.965**	0.580	-0.257
H_h	0.370	-0.251	0.151	-0.212	-0.385	**0.731**	**-0.965**	1.000	-0.528	0.355
T	0.386	0.371	0.580	0.630	0.406	-0.232	0.580	-0.528	1.000	-0.210
Loam content	0.296	0.155	0.231	0.025	-0.243	-0.254	-0.257	0.355	-0.210	1.000

The results of one-way analysis of variance ANOVA indicated no grounds for accepting the hypothesis saying that the content of heavy metals is conditioned by the type of land use. For each analysed heavy metal, the F test value was lower than the F value, except for Cr. In the case of Cr, there were statistical premises to state that the content of this heavy metal was conditioned by the type of land use.

3.5. Spatial distribution of heavy metal concentrations in the soil

In order to present the spatial variability in distribution of heavy metals, the geostatistic method was used. The method of spatial estimation was applied as well. By means of the spatial methods, it is possible to estimate the values at unsampled locations by using the values from adjacent points. Kriging is one of the most commonly used methods. The advantage of kriging is that the average estimation error is equal to zero, while the variance of the estimation error is being minimised. Figures 4 and 5 present spatial interpolation maps.

In the study area, there were clear points with high heavy metal concentrations diverging from other results obtained for the analysed area. In the case of Pb, its variability in the city was determined by the maximum values obtained for the soils of industrial areas (1092 and 1600 mg/kg d.m. at an average value of 181.1 mg/kg d.m.).

Table 6. Results of the One-Way Analysis of Variance ANOVA for heavy metal relationships in the analysed soils with regard to land-use types

Pb						
Groups	Counter	Sum	Mean	Variance		
Industrial areas	10	1811	181.1	248928.8		
Urban allotment gardens	10	183	18.3	68.23333		
Urban green areas	10	1258	125.8	115332.4		
Source of variance	SS	df	MS	F	P-value	F test
Among groups	137060.6	2	68530.3	0.5643	0.575323	3.354131
Within groups	3278965	27	121443.1			
Total	3416025	29				
Cd						
Groups	Counter	Sum	Mean	Variance		
Industrial areas	10	4.5	0.45	0.136111		
Urban allotment gardens	10	9.9	0.99	2.881		
Urban green areas	10	3.7	0.37	0.013444		
Source of variance	SS	df	MS	F	P-value	F test
Among groups	2.274667	2	1.137333	1.125866	0.339129	3.354131
Within groups	27.275	27	1.010185			
Total	29.54967	29				
Cu						
Groups	Counter	Sum	Mean	Variance		
Industrial areas	10	559	55.9	9397.211		
Urban allotment gardens	10	81	8.1	20.1		
Urban green areas	10	102	10.2	46.84444		
Source of variance	SS	df	MS	F	P-value	F test
Among groups	14592.47	2	7296.233	2.3128	0.118273	3.354131
Within groups	85177.4	27	3154.719			
Total	99769.87	29				
Ni						
Groups	Counter	Sum	Mean	Variance		
Industrial areas	10	80.3	8.03	39.38678		
Urban allotment gardens	10	49.3	4.93	6.213444		
Urban green areas	10	46.9	4.69	3.029889		
Source of variance	SS	df	MS	F	P-value	F test
Among groups	69.41067	2	34.70533	2.140978	0.13707	3.354131
Within groups	437.671	27	16.21004			
Total	507.0817	29				
Zn						
Groups	Counter	Sum	Mean	Variance		
Industrial areas	10	1051.5	105.15	15510.34		
Urban allotment gardens	10	399.8	39.98	1034.191		
Urban green areas	10	627.5	62.75	1067.738		
Source of variance	SS	df	MS	F	P-value	F test
Among groups	21877.87	2	10938.94	1.863292	0.174569	3.354131
Within groups	158510.4	27	5870.757			
Total	180388.3	29				
Cr						
Groups	Counter	Sum	Mean	Variance		
Industrial areas	10	109	10.9	193.8778		
Urban allotment gardens	10	14	1.4	0.488889		
Urban green areas	10	54	5.4	2.266667		
Source of variance	SS	df	MS	F	P-value	F test
Among groups	455	2	227.5	3.470927	0.045549	3.354131
Within groups	1769.7	27	65.54444			
Total	2224.7	29				

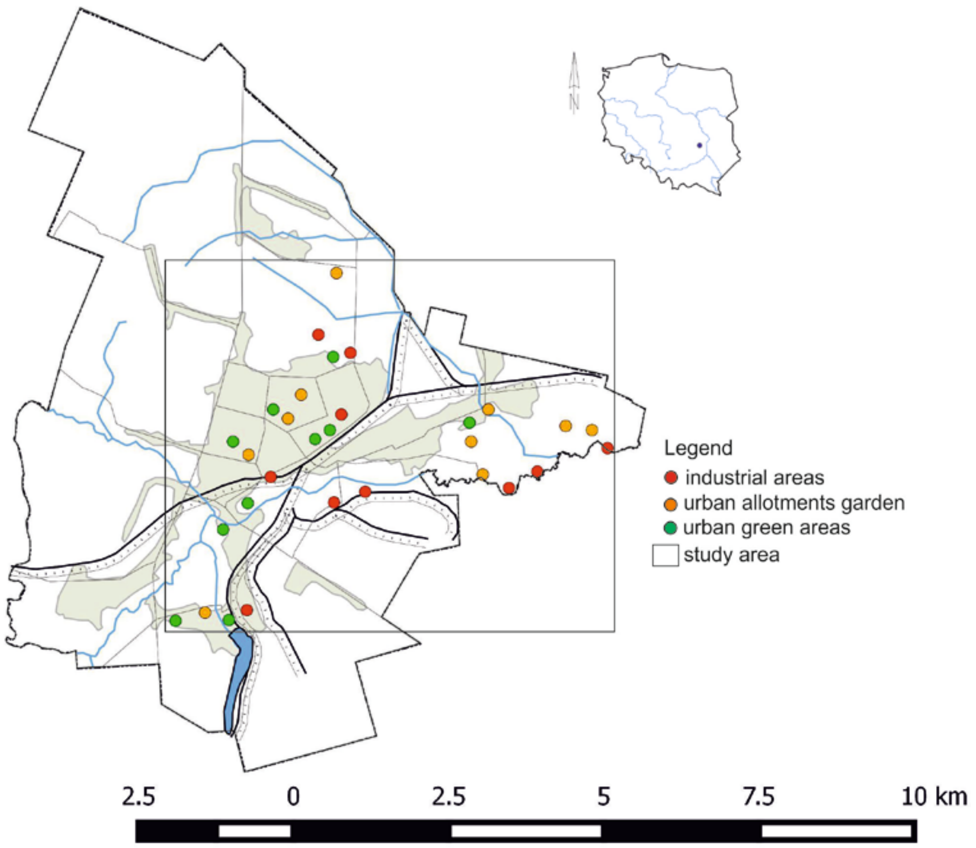
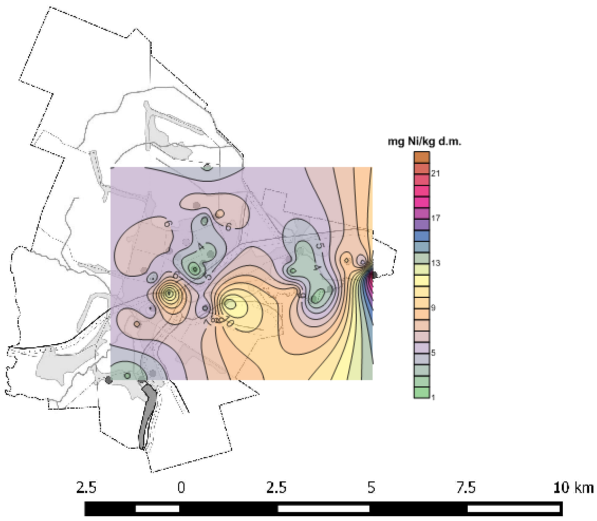


Figure 4. Study area covered by the kriging method, with an indication of soil sampling plots

After rejecting the extreme values, the soil samples were characterised with a lower level of variance. A similar situation was recorded for Zn, Cr, Cu and Cd, where the spatial distribution of values was determined by the single extreme values in the study area. Maximum values were obtained for the soils of industrial areas, except for Cd whose highest concentrations were noted in the soils of urban allotment gardens. High and point concentrations of heavy metals did not concern all analysed heavy metals, which indicated that the origins of extremely high values of these elements were differentiated. Similar distribution of values was found only for Zn and Cr, which was determined by the study results of the soil samples from the industrial areas (correlation coefficient for the analysed heavy metals at the level of 0.98). Regular distribution, without any clearly outlying points, was observed for Ni, which indicated the lithological origins of this element in the analysed soils.

4. DISCUSSION

Physicochemical properties of soils reflect the state of the natural environment and have a direct impact on satisfying nutritional requirements of plants, and thus determine their quality and condition. In urban areas, specific characteristics of urban environment often lead to degradation of soils (Golcz et al., 2014; Li, 2014). Nevertheless, it is very difficult to determine an unequivocal impact of the human economy on the urban environment.



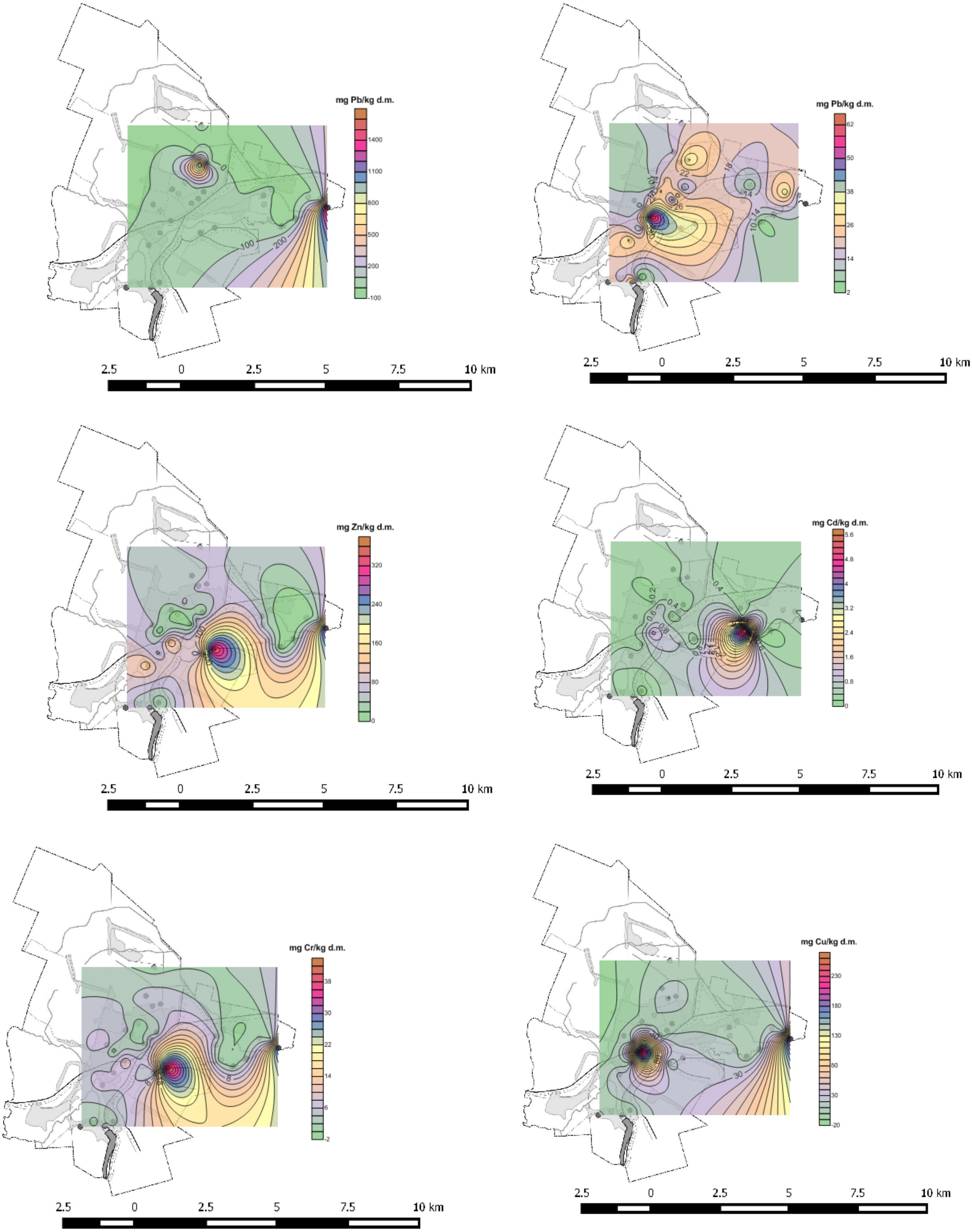


Figure 5. Spatial distribution of the content of heavy metals in the soils of Skarżysko-Kamienna** for Pb, two spatial distribution maps cover all soil sampling plots and those without outlying values.

This depends on many variables, including the intensity of human activities and development of the urban centre. The impact of increasing urbanisation on urban soils is reflected in high variations in their physicochemical properties (Greinert, 2015).

Physicochemical properties of urban soils are dependent on the characteristics of geological substrate as well as the conditions and structure of the urban environment (Greinert, 2015). As noted by Park et al., (2010), physicochemical properties of soils are derivatives of the city age and spatial structure. It is caused by the factors influencing soils in various stages of urban development and concerns both industry and transportation growth, as well as the intensity of urbanisation. Moreover, soils are subject to numerous land-use treatments and thus unequivocally transform their structure and physicochemical properties. Urban soils may often be characterised by the presence of skeletal particles (rubble and stones) as well as rubbish. This is one of the main factors which distinguishes anthropological soils from natural ones (Greinert, 2015). Therefore, urban soils do not have a homogeneous structure, and their properties, as well as transformation levels depend on the type of land use. This fact makes the studies on urban soil properties, including heavy metal concentrations, be conducted with regard to land-use types. Multiple factor analysis of land development parameters in relation to city's genesis and age, and presence of potential contaminating emitters is crucial for making a proper assessment of environmental changes occurred in the soil environment. A pH is a basic parameter considered in terms of urban soil monitoring. It is the key factor that determines the forms of heavy metal occurrence in soils (Cappuyns & Swennen, 2008). Under natural environmental conditions, the soil pH is dependent on the characteristics of parent rocks and the type of vegetation. It is therefore the parameter which often indicates differences between soils of natural and anthropogenic origins. The soil samples collected in the area of Skarżysko-Kamienna had rather a neutral pH (50% of samples); however, some samples were characterised with low pH values being either slightly acidic. The minimum pH_{KCl} values were in the range of 3.48-5.37. The highest average pH value was reported for the soils of industrial areas – it was oscillating at the pH_{KCl}level of 6.41. The soils of allotment gardens and green areas were characterised by the same pH values. The highest variation in pH levels was recorded for the soils of urban green areas (coefficient of variation CV: 16%). However, there were no unvarying trends in the distribution of pH values observed for each part of the city. Golcz et al. (2014), as well as Dzierżanowski and Gawroński (2011) point out, based on literature data, that urban areas have either neutral or alkaline pH. This thesis was only partially confirmed by the results of the studies conducted in Skarżysko-Kamienna − the maximum pH_{KCl} values remaining at the level of 6.93-6.98 in relation to the specificity of substrate indicated the other, probably anthropogenic, processes influencing the growth in pH values. The soils in Skarżysko-Kamienna were indeed largely developed on the Lower and Upper Triassic sandstone (Rhaetian). There are mainly poor, sandy podsolic and acid brown soils formed of clays, clay sands, and to some extent, loams. They are characterised with relatively high natural acidification. Low soil pH is important for the amateur cultivation of vegetables and fruit in urban allotment gardens, which is very popular among city inhabitants, because it may facilitate the solubility and migration of heavy metals in soils. The hydrolytic acidity H_h values in the analysed soils were differentiated. The coefficient of variation (CV) was in the range of 77-84%. The largest spread of this characteristic was found in the soils of allotment gardens and urban green areas. The soils of urban green areas were characterised by the highest average hydrolytic acidity $H_{h.}$ High variation in the distribution of the values of hydrolitic acidity H_h in the soils of allotment gardens could be the result of applied agricultural treatments. Malczyk and Rydlewska (2011) note that systematic liming and fertilisation of soils with manure, being very popular in these areas, contribute to reducing soil acidification and, at the same time, decreasing hydrolytic acidity H_h. In spatial terms, such situation causes a large spread of results. Greinert (2009) argues in his studies that soil adsorption properties affect the bioavailability of contamination accumulated in urban soils. High soil adsorption capacity permanently inhibits the migration of contaminants accumulated in soils as well as affects the leaching of nutrients (Bielińska & Mocek, 2010; Ge & Hendershot, 2005). The analysed soils were characterised by adsorption capacity at the level of 2.02-45.9 cmol (+)/kg, while the highest variation of this characteristic was reported for the soils of industrial areas (CV value at the level of 89%). High variability of the analysed characteristic may be related to the transformation of the soil profile as a result of conducted urbanisation or agricultural works. A typical result is the irregular distribution of soil material or admixture, such as building rubble which has high adsorption capacity and thus artificially increases adsorption properties of soils. The highest variation in the value of adsorption capacity was noted for the soils of industrial areas, which indicated the intensity of mechanical treatments conducted in these areas. The maximum adsorption capacity values were comparable to those determined for the urban soils in the city of Poznań (Poland) (Golcz et al., 2014); whereas Bielińska and Mocek (2010) in their studies of urban park soils conducted in large Polish cities indicate a high degree of variation in the values of adsorption capacity, and that was also observed for the analysed soils of Skarżysko-Kamienna. Grain-size composition determines adsorption properties of soils and degree of heavy metal migration. Silt and clay fractions are of a particular importance as well (Rejman et al., 2001). Grain-size composition of urban soils may significantly differ from that of soils free from mechanical transformations. The analysed soils were characterised with a slightly differentiated share of sand fraction and greater share of silt and clay fraction which determined the grain-size groups. Mihailović et al., (2015) in their studies in the city of Novi Sad (Serbia) recorded similar grain-size types of urban soils. Skarżysko-Kamienna is a city of industrial genesis, where mining and metallurgy of heavy metals were developing well. High concentration of industrial plants in the past could exert significant pressure on the soils. Skarżysko-Kamienna has a well-developed network of roads and railways, which is also a factor posing a risk of soil contamination. Heavy metals which frequently contaminate urban centres are Cu, Zn, Cr, Ni, Pb, and Cd. The content and origins of these heavy metals are widely analysed in numerous scientific studies (Osma et al., 2013; Xia et al., 2011). Studies conducted by Falta et al., (2008) indicate that the emission of industrial dust containing heavy metals, which contaminates soils due to its deposition, is a real problem in urban areas. The presence of heavy metals in dust is conditioned by the size of its particles. PM10 mainly contains Zn and Pb, and PM 2.5 has, in turn, bioavailable forms of Cu, Ni, Zn, Cd, and Pb. Lead belongs to those toxic chemical elements which are released due to emission of car exhaust fumes (Ferreira et al., 2016). Geochemical background for the soils of Skarżysko-Kamienna with regard to Pb was determined at the level of 13-25.0 mg/kg d.m. (Lis & Piaseczna, 1995). It was found that 30% of all analysed soil samples were characterised by higher concentrations of Pb than its geochemical background values. The values significantly higher than the other results were reported for two soil samples (soils of industrial areas). The values recorded for the areas located in the city centre were similar to those observed for its suburbs and were not determined by the type of land use. The average values of all soil samples for Pb were comparable to the median value specified for the urban soils from 34 European cities (102 mg/kg d.m.) (Luo et al., 2012); while the average values for the soils of industrial areas and urban green areas were higher than this median. Cadmium is a chemical element which enters the natural environment due to abrasion of car tyre treads (Ferreira et al., 2016; Sansalone & Buchberger, 1997). Its origins may also be the result of specific forms of industry in a given area. With regard to Cd, the value of geochemical background was oscillating at the level of <0.5-0.5 mg/kg d.m. (Lis & Piaseczna, 1995). In the analysed soils, the content of this heavy metal did not differ significantly from its geochemical background values, except for one soil sample collected from allotment gardens (the accumulation of Cd in the soil samples was ten times higher than the threshold value of its geochemical background, i.e. 5.8 mg/kg d.m.). Copper is a chemical element widely existing in nature, and its content in urban soils is involved in many processes. The main sources of this heavy metal are emission of car exhaust fumes as well as abrasion of car tyre treads and road surfaces (Ferreira et al., 2016). The content of Cu for the soils of Skarżysko-Kamienna was recorded at the average level of 8.10-55.9 mg/kg d.m. Outlying values were noted for the soils of industrial areas (215 and 261 mg/kg d.m.) and the high average content of Cu was determined by exactly these values. The geochemical background value was ranging between 5 and 9 mg/kg d.m. (Lis & Piaseczna, 1995); whereas the median value for the European cities was at the level of 46 mg/kg d.m. (Luo et al., 2012). With regard to nickel, the geochemical background value was oscillating at the level of <2-4 mg/kg d.m. (Lis & Piaseczna, 1995); while the median in the European cities was at the level of 22 mg/kg d.m. (Luo et al., 2012). The average Ni concentrations recorded at the level of 4.69-8.03 mg/kg d.m. indicated its natural content in the soils, except for the exceeded point values in the soils of industrial areas − 30% of the soil samples had the content of Ni at a higher level than that specified for other land-use types. The soil samples no. 7 and 8 were collected in close proximity to a railway. According to the studies conducted in Warsaw (Poland) by Radziemska et al., (2016), this heavy metal has exceeded values if occurs in the vicinity of railways. Its origins are related to the abrasion of steel parts out of which wheels are built. Similar conclusions were reached by Mazur et al., (2013). The average Zn concentrations were ranging from 39.98-105.15 mg/kg d.m.; while the median for the European cities amounted to 130 mg/kg d.m. (Luo et al., 2012). In the case of analysed soils, the enrichment in this element was higher for the soils of industrial areas and urban green areas than those of allotment gardens. The geochemical background value for Zn was oscillating at the level of 35-64 mg/kg d.m. (Lis & Piaseczna, 1995). It was exceeded in 30% of the soil samples collected in the industrial areas and in 10% of the soil samples coming from the urban green areas. The highest concentrations of Zn occur, as in the case of Ni, in close proximity to railways. Higher content of such heavy metals in these areas may indicate that they have the same origins. Zinc may be released from anti-corrosion coatings applied to steel railway sleepers, as well as directly from transported goods (Ferdeous & Manalo, 2014). Anthropogenic enrichment of areas lying along railways in Zn is also noted by Wiłkomirski et al., (2011) in the studies conducted in the areas of a railway station in the town of Iława (Poland). The scientists report the enrichment in this heavy metal at the level of 1438 mg/kg d.m. The concentrations of Cr being higher than its geochemical background value were observed for three soil samples collected in the industrial areas (2-4 mg/kg d.m.). The location of samples with high content of this element referred to the results of studies on Zn concentrations. This may indicate the similar origins of these elements and the high emission of contaminants in close proximity to railway lines and selected industrial areas. The content of Cr in other soil samples was low. The lowest values were noted for the soils of allotment gardens – the average value was oscillating at the level of 1.40 mg/kg d.m. and was several times lower than the average value determined for the soils of industrial areas and urban green areas (10.9 and 5.40 mg/kg d.m). High variations in the obtained results, i.e. coefficient of variation CV at the level of 0.27-275, may give evidence for anthropogenic enrichment of the soils in heavy metals. This concerns especially the concentrations of Pb and Cu which were characterised by the highest spread of values. Accumulation of these heavy metals in urban soils is closely related to emission of car exhaust fumes and abrasion of brake components (Doležalová Weissmannová et al., 2015). The highest average values for the soils of industrial areas were noted in the case of Cu, Ni, Zn, and Cr. These values were higher than those reported for the soils of urban allotment gardens and urban green areas. Higher concentrations of heavy metals in the soils of industrial areas indicated point sources of contamination emission. Similar observations are presented by Świercz and Smorzewska (2015) in their studies on the urban soils of the city of Kielce. Analysis of correlation coefficients may contribute to identification of relationships among the analysed heavy metals, as well as indicate their sources and common origins (Salah et al., 2015). Coefficient of correlation at the level of > 0.7 indicates extremely strong relationships among the analysed pairs of data (Pam et al., 2011). The studies conducted by Salah et al., (2015) suggest that Cu, Pb and Zn belong to the group of lithologically related heavy metals. Significant correlation among these heavy metals may indicate their natural origins associated with the chemistry of parent rocks. For the soils of Skarżysko-Kamienna, very strong and strong relationships among the above-mentioned heavy metals were determined. However, Doležalova Weissmannova et al., (2015) and Hu et al., (2013) point out that the given linear relationships among heavy metals in urban soils may be a derivative of environmental pressure and anthropogenic enrichment in heavy metals. Doležalova Weissmannova et al. (2015) notice strong relationships among Cu-Cd and Pb-Zn-Cu in the soils of Ostrava (Czech Republic), while Hu et al. (2013) obtain relationships among Cu-Zn, Pb-Cd and Zn-Pb in the soils of Guangdong Province (China). The degree of soil contamination with heavy metals was analysed in reference to the indices of geoaccumulation Igeo. This method, elaborated and introduced by Müller (1969), is based on the comparison between heavy metal content in the soil before and after being contaminated, and whose reference constitutes the geoaccumulation index value with respect to adopted grading scale. The calculated indices of geoaccumulation demonstrated various origins of heavy metals in the analysed soils. The maximum Igeo values determined for the analysed heavy metals were recorded in the soils of industrial areas, except for Cd, which adopted the maximum values in the soils of urban allotment gardens. Wei and Yang (2010) report the highest Igeo values, in their studies conducted in the area of China, for Pb and Cu. The Igeo values were oscillating at the level of 3.54 for Pb and 1.22 for Cu on average. Similarly, the highest Igeo values for Pb (2.0) and Cu (2.5) are indicated by Doležalová Weissmannova et al. (2015). These two heavy metals were characterised with maximum Igeo values in the soils of Skarżysko-Kamienna as well. The comparison of Igeo values with the values of Pearson linear correlation coefficients indicated anthropogenic enrichment of the urban soils in Skarżysko-Kamienna in lead and zinc. Considering the spatial distribution of the analysed heavy metals, it should be stated that enrichment in these chemical elements was inhomogeneous. Locations with outlying concentrations were noted, indicating point sources of anthropogenic land contamination with a given heavy metal. This concerned each analysed heavy metal. However, the least differentiation in the values was reported for Ni, while the greatest one − for Pb. The analysis of obtained Igeo values showed that the overall degree of contamination of urban soils in Skarżysko-Kamienna was affected by the locations with outlying concentrations of heavy metals. The presence of such locations with high heavy metal concentrations, mainly Cu and Pb, confirms the industrial character of the city as well as directed and point anthropogenic pressure exerted on the soils.

5. CONCLUSIONS

The soil samples collected in Skarżysko-Kamienna indicated neutral or slightly acidic pH which may mean that the soil environment in the city is not homogeneous as far as pH values are concerned. The highest mean pH value was noted for the industrial areas. The soils of allotment gardens and green areas were characterised with the same lower pH values. Naturally, the soils of Skarżysko-Kamienna are classified as acidic soils. Higher pH values found in the urbanised area of the city indicated the influence of anthropogenic factors, including mechanical alterations of the soil profile structure as well as dust precipitation alkalising the soils. Grain-size composition, hydrolytic acidity and cation exchange capacity were characterised with a high degree of variation, regardless of the type of land use. The studies on the soils of Skarżysko-Kamienna suggest that the content of heavy metals in the soils was not directly determined by the type of land use. The relationships between the type of land use and heavy metal concentrations were found only for Cr. The studies indicated the exceeded values for heavy metal concentrations, especially Pb and Zn, which may have an anthropogenic background, as suggested by the obtained Igeo values. The analysis of the content of heavy metals indicated point sources of contamination of the analysed soils with these chemical elements in the locations with outlying concentrations of heavy metals. At the same time, higher concentrations of heavy metals were reported for the soils of industrial areas, rather than for those of urban allotment gardens and urban green areas. In Skarżysko-Kamienna, clear points with high heavy metal concentrations were found, which have an impact on the overall state of the urban environment. High hydrolytic acidity, as well as unfavourable adsorption conditions may pose a real threat due to elution of heavy metals and their accumulation in plants. Moreover, high values of hydrolytic acidity made the analysed soils susceptible to acidification. This issue is significant due to growing popularity of amateur cultivation of vegetables and fruit in urban allotment gardens.

REFERENCES

Bielicka A., Ryłko R. & Bojanowska I., 2009. *Contents of Metals in Soils and Vegetables from Gdansk and Straszyn Allotments*. Environ. Protect. Natur. Res., 40, 209-216.

Bielińska E.J. & Mocek A., 2010. *Sorption Properties and Enzymatic Activity of Municipal Park Soils in Regions of Varying Impact of Anthropologic Pressure*. J. Res. Applic. Agricult. Eng., 55, 20-23 (in Polish).

Cappuyns V. & Swennen R., 2008. *The Application of pH (stat) Leaching Tests to Assess the pH-dependent Release of Trace Metals from Soil, Sediments and Waste Materials*. J. Hazard. Mater., 158, 1, 185-195.

Chen T., Zheng Y., Lei, M., Huang Z.C.H., Wu H., Chen H., Fan Ke Yu K., Wu X. & Tian Q., 2005. *Assessment of Heavy Metal Pollution in Surface Soils of Urban Parks in Beijing. China.* Chemosphere, 60, 4, 542-551.

Chen T.B., Wong J.W.C., Zhou H.Y. & Wong M.H., 1997. *Assessment of Trace Metal Distribution and Contamination in Surface Soils of Hong Kong*. Environ Pollut., 96, 1, 61-68.

Czarnowska K., Gworek B., Kozanecka T., Latuszek B. & Szafrańska E., 1983. *Heavy Metals Content in Soils as Indicator of Urbanization*. Pol. Ecol. Stud., 9, 1-2, 63-79.

Doležalová Weissmannová H., Pavlovský J., & Chovanec P., 2015. *Heavy Metal Contaminations of Urban Soils in Ostrava, Czech Republic: Assessment of Metal Pollution and Using Principal Component Analysis*. Int. J. Environ. Res., 9, 683-696.

Dzierżanowski K. & Gawroński S., 2011. *Analysis of Heavy Metals Content in Soil and Dandelion Leaves in the Vicinity of a Busy Urban Street Using a Handheld xrf Spectrometer*. Environ. Protect. Natur. Res., 50, 202-211 (in Polish).

Faiz Y., Tufail M., TayyebJaved M., Chaudhry M.M. & Siddique N., 2009. *Health Risk Assessment of Heavy Metals in Road Dusts in Urban Parks of Beijing. China*. Microchem. J., 92, 186-192.

Falta T., Limbeck A., Koellensperger G. & Hann S., 2008. *Bioaccessibility of Selected Trace Metals in Urban PM2.5 and PM10 Samples: A Model Study*. Anal. Bioanal. Chem., 390, 4, 1149-1157.

Ferdeous A. & Manalo A., 2014. *Failures of Mainline Railway Sleepers and Suggested Remedies – Review of Current Practice.* Eng. Fail. Anal., 44, 17-35.

Ferreira A.J.D., Soares D., Serrano L.M.V., Walsh R.P.D., Dias-Ferreira C. & Ferreira C.S., 2016. *Roads as Sources of Heavy Metals in Urban Areas. The Covões Catchment Experiment, Coimbra, Portugal*. J. Soils Sediments, 16, 11, 1-18.

Ge Y. & Hendershot W., 2005. *Modelling Sorption of Cd, Hg and Pb in Soils by the NICA [Non-Ideal Competitive Adsorption] – Donnan Model*. Soil Sediment Contam., 14, 1, 53-69.

Golcz A., Kozik E., Golcz-Polaszewska M., Kościelniak K. & Musił N., 2014. Soils and Plants in the Nadolnik Park in Poznań. Part I Physical and Chemical Properties of Soils and the Content of Macroelements in Plants. Sci. Natur. Technol., 8, 3, 1-13 (in Polish).

Goldsztejn P. & Skrzypek G., 2004. *Applications of Numeric Interpolation Methods to the Geological Surface Mapping Using Irregularly Spaced Data*. Pol. Geol. Rev., 52, 3, 233-236 (in Polish).

Greinert A., 2009. *Sorption Capabilities Improvement as a Condition of Maintaining the Municipal Green in Good State*. Soil Sci. Ann., 60, 75-83 (in Polish).

Greinert A., 2015. *The Heterogeneity of Urban Soils in the Light of their Properties*. J. Soils Sediments, 15, 8, 17-25.

Hu Y., Liu X., Bai J., Shih K., Zeng E.Y. & Cheng H., 2013. *Assessing Heavy Metal Pollution in the Surface Soils of a Region that Had Undergone Three Decades of Intense Industrialization and Urbanization*. Environ. Sci. Pollut. Res., 20, 9, 6150-6159.

Huang Z.Y., Chen T., Yu J., Qin D.P. & Chen L., 2012. *Lead Contamination and its Potential Sources in Vegetables and Soils of Fujian. China.* Environ. Geochem. Health, 34, 1, 55-65.

Imperato M., Adamo P., Naimo A.D., Arienzo M., Stamzione D. & Violante, P., 2003. *Spatial Distribution of Heavy Metals in Urban Soils of Naples City (Italy).* Environ. Pollut., 124, 2, 247-256.

Kabata-Pendias A. & Pendias H., 1992. *Trace Elements in Soils and Plants. Second Edition.* CRC Press: Boca Raton, USA, 1992.

Lee C.S.L., Li X., Shi W., Cheung S.C.N. & Thornton I., 2006. *Metal Contamination in Urban, Suburban, and Country Park Soil of Hong Kong: A Study Based on GIS and Multivariate Statistics*. Sci. Total Environ., 356, 1-3, 45-61.

Li X., 2014. *Distribution of the Heavy Metal in Urban Soils*. J. Chem. Pharm. Res. 2014, 6, 6, 2260-2263.

Lis J. & Pasieczna A., 1995. *Geochemical Atlas of Poland 1:2500 000*. Polish Geological Institute: Warsaw, Poland, 1995.

Luo X.S., Yu S., Zhu Y.G., & Li H.D., 2012. *Trace Metal Contamination in Urban Soils of China*. Sci. Total Environ., 421-422, 17-30.

Madrid L., Diaz Barrientos F. & Madrid F., 2002. *Distribution of Heavy Metal Contents of Urban Soils in Parks of Seville*. Chemosphere, 49, 10, 1301-1308.

Malczyk P. & Rydlewska M., 2011. *Spatial Variability of Total Mercury Content in Surface Horizon of Soils of Gnieznieńskie Lakeland Area*. Ecol. Chem. Eng., 18, 8, 1087-1092.

Mao Q., Huang G., Buyantuev A., JianguoWu J., ShanghuaLuoS. & KemingMa K., 2014. *Spatial Heterogeneity of Urban Soils: The Case of the Beijing Metropolitan Region. China*. Ecol Process. 2014, 3, 23, 23-28.

Mazur Z., Radziemska M., Maczuga O. & Makuch A., 2013. *Heavy Metal Concentrations in Soil and Moss (Pleurozium Schreberi) near Railroad Lines in Olsztyn (Poland)*. Fresen. Environ. Bull., 22, 4, 955-961.

Mcbride M.B., Shayler H.A., Spliethoff H.M., Mitchell R.G., Marquez L.G., Ferenz G.S., Russel, J.M., Casey A.L. & Bachman S., 2014. *Concentrations of Lead, Cadmium and Barium in Urban Garden-Grown Vegetables: The Impact of Soil Variables.* Environ. Pollut., 194, 254-261.

Mihailović A., Budinski-Petković L.J., Popov S., Ninkov J., Vasin J., Ralević N.M. & Vučinić Vasić M., 2015. *Spatial Distribution of Metals in Urban Soil of Novi Sad, Serbia: GIS Based Approach*. J. Geochem. Explor., 150, 104-114.

Mireles F., Davila J.I., Pinedo J.L., Reyes E., Speakman R.J. & Glascock M.D., 2012. *Assessing Urban Soil Pollution in the Cities of Zacatecas and Guadalupe, Mexico by Instrumental Neutron Activation Analysis*. Microchem. J., 103, 158-164.

Müller G., 1969. *Index of Geoaccumulation in Sediments of the Rhine River*. Geo. J., 2, 109-118.

Niewiadomski A. & Szubert Ł., 2014. *The Quality of Soils of Selected Allotment Gardens in Łódź*. Folia Geogr. Phys., 13, 51-65 (in Polish).

Osma E., Serin M., Leblebici Z. & Aksoy A., 2013. *Assessment of Heavy Metal Accumulations (Cd, Cr, Cu, Ni, Pb, and Zn) in Vegetables and Soils*. Pol. J. Environ. Stud., 22, 5, 1449-1455.

Ostrowska A., Gawliński S. & Szczubiałka Z., 1991. *Methods of Analysis and Evaluation of Soil Properties and Plants – Catalogue*. Institute of Environmental Protection: Warsaw, Poland, 1991.

Pam E., Akiti T., Osae S., Ganyaglo S. & Gibrilla A., 2011. *Multivariate Cluster Analysis of Some Major and Trace Elements Distribution in an Unsaturated Zone Profile, Densu River Basin, Ghana*. Afr. J. Environ. Sci. Technol., 5, 155-167.

Park S.J., Zhiqiang C., Hanbae Y., Morris E.E., Sutherland M., Mcspadden Gardener B.B. & Grewal P.S., 2010. *Differences in Soil Chemical Properties with Distance to Roads and Age of Development in Urban Areas*. Urban Ecosyst., 13, 4, 483-497.

Radziemska M., Fronczyk J., Mazur Z. & Vaverková M., 2016. *Impact of Railway Transport on Soil and Pleurozium Schreberi Contamination with Heavy Metals*. Infr. Ecol. Rural Areas, 1, 45-57 (in Polish).

Rejman J., Iglik I., Brodowski R., Turski M. & Smarz M., 2001. *Evaluation of Spatial Variability of Soil Texture and Organic Content in Soil in a Loess Landscape*. Acta Agr., 18, 409-419.

Salah E.A., Turki A.M. & Mahal S.N., 2015. *Chemometric Evaluation of the Heavy Metals in Urban Soil of Fallujah City, Iraq*. J. Eniron. Protect., 6, 11, 1279-1292.

Salminen R., (Chief-Editor), Batista M.J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris, M., Gilucis A., Gregorauskiene V., Halamic J.,

Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P. J., Olsson S.Å., Ottesen R.-T., Petersell V., Plant J.A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A. & Tarvainen T.,** 2005. *Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps*. Espoo, Geological Survey of Finland, 526 pages, 36 figures, 362 maps.

Sansalone J.J. & Buchberger S.G., 1997. *Partitioning and First Flush of Metals in Urban Roadway Storm Water*. J. Environ. Eng., 123, 134-143.

Santos-Francés F., Martínez-Graña A., Zarza C.A., Sánchez A.G. & Rojo P.A., 2017. *Spatial Distribution of Heavy Metals and the Environmental Quality of Soil in the Northern Plateau of Spain by Geostatistical Methods*. Int. J. Environ. Res. Public Health, 14, 1-19.

Schwarz K., Pickett S., Lathrop R.G., Weathers K.C., Kouyat R.V., Cadenasso M.L., 2012. *The Effects of the Urban Built Environment on the Spatial Distribution of Lead in Residential Soils*. Environ. Pollut., 163, 32-39.

Shang L.Y., Sun R.H., Wang Z.M., Ji Y.H. & Chen L.D., 2012. *Assessment of Heavy Metal Pollution in Surface Sediments of Rivers in Northern Area of Haihe River Basin*. China J. Environ. Sci., 33, 606-611.

State Environmental Monitoring Programme for the years 2013-2015. Chief Inspectorate for Environmental Protection: Warsaw, Poland, 2012 (in Polish).

Świercz A. & Smorzewska E., 2015. *Variations in the Zinc and Lead Content in Surface Layers of Urban Soils in Kielce (Poland) with Regard to Land Use*. J. Elem., 20, 2, 449-461.

Szolnoki Z., Farsang A. & Puskás I., 2013. *Cumulative Impacts of Human Activities on Urban Garden Soils: Origin and Accumulation of Metals*. Environ. Pollut., 177, 106-115.

Walczak B., Greinert A., Gosk Ł., Gorka K., 2011. *Influence of Soil Geomechanical Transformations in Urban Communication Areas on their Physicochemical Properties*. Soil Sci. Ann., 62, 2, 412-419 (in Polish).

Wei B. & Yang L., 2010. *A Review of Heavy Metal Contaminations in Urban Soils. Urban Road Dust and Agricultural Soils of China*. Microchem. J., 94, 99-107.

Wiłkomirski B., Sudnik-Wójcikowska B., Galera H., Wierzbicka M. & Malawska M., 2011. *Railway Transportation as a Serious Source of Organic and Inorganic Pollution*. Water Air Soil Poll., 218, 1-4, 333-345.

Wu J., 2014. *Urban Ecology and Sustainability: The State-of-the-Science and Future Directions*. Landsc. Urban Plan., 125, 209-221.

Xia X., Chen X., Liu L. & Liu H., 2011. *Heavy Metals in Urban Soils with Various Types of Land Use in Beijing, China*. J. Hazard. Mater., 186, 2-3, 2043-2050.

Zemeła K. & Kardyś P., 2013, *The History of Skarżysko-Kamienna. Monograph on the occasion of the 90th Anniversary of City Rights*. City Hall: Skarżysko-Kamienna, Poland, 2013 (in Polish).

Zhiyuan W., Dengfeng W., Huiping Z. & Zhiping Q., 2011. *Assessment of Soil Heavy Metal Pollution with Principal Component Analysis and Geoaccumulation Index*. Procedia Environ. Sci., 10, 1946-1952.

Received at: 01. 07. 2017
Revised at: 20. 09. 2017
Accepted for publication at: 22. 09. 2017
Published online at: 28. 09. 2017