

## VARIATIONS IN THE ZINC AND LEAD CONTENT IN SURFACE LAYERS OF URBAN SOILS IN KIELCE (POLAND) WITH REGARD TO LAND USE

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### Abstract

The article presents an overview of the results of a study concerning the zinc and lead content in urban soils of Kielce with regard to different land use. 61 topsoil samples were collected in the industrial areas (I), urban green areas (Z), urban allotment gardens (O), as well as parks and forests (P). The maximum values for zinc and lead were observed in the industrial zone, i.e. 181.3 mg kg<sup>-1</sup> and 112.6 mg kg<sup>-1</sup>, respectively; whereas the average content in the soils of Kielce oscillates at the level of 134.2 mg kg<sup>-1</sup> for zinc and 92.85 mg kg<sup>-1</sup> for lead. Geochemical indices, such as the geoaccumulation index ( $I_{geo}$ ), contamination factor (CF) and accumulation index (AI) indicated that areas located in close proximity to the main roads of the city, especially in the city centre and the former industrial estate called Białogon, are characterised by the highest concentration of the analysed heavy metals. Generally, the enrichment of soils in zinc and lead decreases further from the city centre. In most cases, the content of the analysed heavy metals in surface layers of urban soils considerably exceeded values considered as geochemical background and valid legal norms of the Ordinance of the Minister of Environment on soil quality standards and land quality standards (Journal of Laws of 2002, No. 165, item 1359). The exceeded values of the analysed metals are caused mainly by deposition of contamination from car exhaust emissions and broadly defined industry.

**Key words:** urban soils, heavy metals, zinc, lead.

## INTRODUCTION

The main characteristic of the chemical composition of urban soils is their considerable enrichment in heavy metals, which has been investigated by many researchers (IMPERATO et al. 2003, CIESIELCZUK et al. 2011, XINGHUI et al. 2011, DU et al. 2013, SALAH et al. 2013). Apart from the chemistry of the ground, the content of heavy metals is a result of several factors, of which a major role is played by the atmospheric deposition of pollutants caused by a variety of human activities, including industry and transportation (MCALISTER et al. 2006, DABKOWSKA-NASKRĘT, RÓŻAŃSKI 2009, SADEJ, NAMIOTKO 2010). Excessive content of these elements implicates a negative human impact on soils (LI et al. 2009, DU et al. 2013). Heavy metals are not biodegradable and because they persist in the environment, they enter a complex system of dependencies and may pose a serious threat to human health (WEI, YANG 2010, AL-FARRAJ et al. 2013). This necessitates studies to identify the ecological state of soils. Therefore, the aim of this research project was to determine the content of the most common heavy metals, i.e. zinc and lead, in urban soils of Kielce and to correlate the findings to the type of land use. Even small amounts of lead are considered to be harmful to plants; in addition, lead is scarcely mobile and becomes immobilised at alkaline pH. Lead, especially in acidic soils, is highly soluble, which significantly raises its phytotoxicity (KICIŃSKA 2011). Zinc is very mobile in the soil environment. Just like lead, it shows elevated solubility in acid soils and its excess may result in poorer microbial activity (KICIŃSKA 2011, BHATTACHARYA et al. 2013).

## MATERIAL AND METHODS

The study covered the area of Kielce, the capital of a province, with a population of nearly 200,000. In total, 61 soil samples were collected from industrial areas – petrol stations, road edges and industrial estates (I), urban green areas (Z), urban allotment gardens (O) as well as parks and forests (P) – Figure 1.

The soil samples were collected from surface layers, to a depth of 30 cm, with the use of an Egner's sampler. One aggregate sample consisted of the material obtained from 15 to 20 cores. Such physicochemical properties as the particle-size distribution by the hydrometer method, pH in 0.1 M KCl  $\text{dm}^{-3}$  by the potentiometric method and the content of total organic carbon ( $C_{\text{TOT}}$ ) by the wet oxidation method were determined in the soil material. The content of zinc and lead was determined after mineralisation in *aqua regia* ( $\text{HCl-HNO}_3$  at 3:1) by flame atomic absorption spectroscopy (FAAS) on a Perkin-Elmer Avanta spectrometer (the procedure according to PN-ISO 11047:2001 standard). The analyses were conducted in the Chemical-Agricultural Station in Kielce.

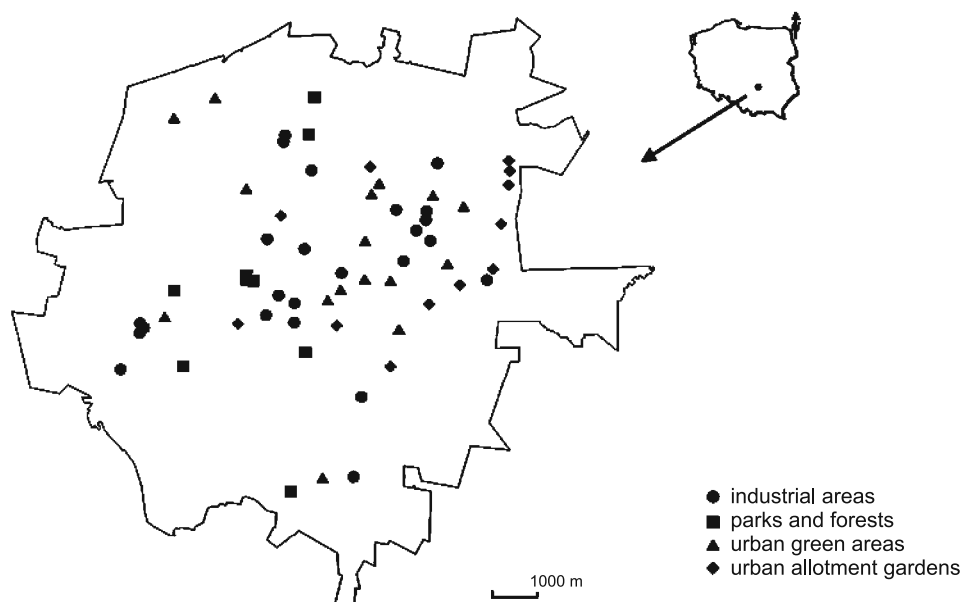


Fig. 1. Soil sampling sites in the area of Kielce

Soil contamination with zinc and lead was assessed on the basis of geochemical indices (CHEN et al. 2005, FAIZ et al. 2009), i.e. the geoaccumulation index ( $I_{geo}$ ):

$$I_{geo} = \log_2 (C_n / 1.5B_n),$$

where:  $C_n$  – concentration of the analysed metal in soil;  $B_n$  – the geochemical background for the analysed metal (CZARNOWSKA 1996); 1.5 – natural variation of the content of the metal in the environment resulting from some slight differences in the geological structure.

The contamination factor (CF) for the study area was calculated from the formula:

$$CF = C_1 / C_n,$$

where:  $C_1$  – the arithmetic mean of the metal concentration in at least five measurement points;  $C_n$  – the geochemical background. There is also an accumulation index (AI), which is a quotient of the geometric mean of the content of a particular heavy metal ( $\bar{x}_g$ ) and its content in the parent rocks – geochemical background ( $C_n$ ).

$$AI = \bar{x}_g / C_n.$$

The data were analysed statistically, and the spatial variability of distribution of the analysed heavy metals as well as selected geochemical indices were presented using the Surfer v. 10 program.

## RESULTS AND DISCUSSION

The humus layer of urban soils was characterised by diverse texture (Table 1). The content of fine-earth fractions  $\Phi < 0.02$  oscillated around the same level in all analysed land-use types. The lowest mean values were observed in soil samples collected from parks and forests (P) as well as industrial areas (I). The apparent low contribution of fine-earth fractions  $\Phi < 0.02$

Table 1

Basic properties and metal content in the urban soils of Kielce with regard to land use

Soil properties	Functional zone	Min.	Max.	$\bar{x}$	$\bar{x}_g$	SD
pH	I	5.66	8.33	7.09	7.05	0.76
	Z	5.55	8.13	7.29	7.25	0.79
	O	5.90	7.53	6.66	6.64	0.56
	P	4.15	7.02	5.52	5.44	0.99
$C_{TOT}$ (%)	I	0.89	29.55	4.63	2.55	7.70
	Z	0.89	4.53	1.85	1.59	1.12
	O	1.22	6.44	2.97	2.71	1.39
	P	0.79	3.53	1.30	1.16	0.85
Zn (mg kg <sup>-1</sup> )	I	17.20	1646	181.3	92.94	337.0
	Z	15.90	293.1	112.95	87.12	80.61
	O	28.60	377.8	144.94	112.69	80.60
	P	28.40	160.5	97.77	77.38	71.11
Pb (mg kg <sup>-1</sup> )	I	10.40	428.0	112.6	50.65	282.9
	Z	10.40	141.5	47.82	36.87	35.39
	O	16.70	78.90	42.69	38.90	19.85
	P	22.80	590.0	168.7	77.19	233.2
$\Phi < 0.02$ (%)	I	6	30	15.08	13.86	6.31
	Z	9	37	18.25	16.45	8.99
	O	12	25	19.17	18.75	4.00
	P	4	24	14.60	12.68	7.16
Dominant soil texture classification by the Polish Society of Soils Science (PSSS)						
	I	loamy sand (pg) / sand (ps)				
	Z	loamy sand (pg)				
	O	sandy loam (gl) / loamy sand (pg)				
	P	sand(ps) / sandy loam (gl)				

Explanation: I – industrial areas, Z – urban green areas, O – allotment gardens, P – parks and forests

in the industrial areas arises mainly from human activity and numerous mechanical changes to soils, as well as large amounts of sand scattered on icy pavements in winter. The pH values determined in 1 M KCl ranged from 4.15 to 8.33. The acidic pH was noted only in soil under parks and forests (P), where the average value oscillates around 5.52 versus 6.64 for soils of whole Kielce. Slightly higher pH values in soils of Kielce were noted by GALUSZKA et al. (2011). In other types of land use, the observed pH was neutral, which is characteristic for cities and results from a specific character of urbanised areas. High pH values are principally caused by alkaline airborne dust, snow removal, contamination with construction waste and intensive liming (CHUDECKA 2013, KABAŁA et al. 2009).

The content of  $C_{TOT}$  is in the range of 0.89÷29.55% (Table 1). The higher values noted in urban allotment gardens (O) are related to the use of organic fertilizers, whereas in industrial areas (I) they appear because of a more extensive area overgrown with shrubs and turf on road verges. Moreover, the high mean content of  $C_{TOT}$  noticed in industrial estate is caused by the organic soils originating from fluvial deposits in the area of former Białoński Pond, which had been created for the needs of a metallurgical plant and a machine building factory (ŚWIERCZ, PRAŻAK 2014). The content of heavy metals in urban soils varies in a wide range and results from the character and specific purposes of a particular area, as well as the diverse density of industrial facilities and transportation routes in urban areas (CHUDECKA 2013). As far as the analysed soil material is concerned, zinc occurred in a range of 15.90-1647 mg kg<sup>-1</sup> (Table 1). The total content of zinc in industrial areas (I) was considered to be the most diversified and the maximum values were considerably higher than 30 mg kg<sup>-1</sup>, corresponding to the geochemical background of Polish soils (CZARNOWSKA 1996) or to standard values specified by *The Ordinance of the Minister of Environment* (2002) for industrial areas (Figure 2). In order to show the degree of soil contamination, the results were referred to the maximum permissible values in industrial areas specified by the Ordinance (2002) for a depth of 0-2.0 m b.g.l. For better elucidation and comparison of the spatial variability of the analysed heavy metals, soils samples were collected from surface layers to a depth of 30 cm according to the same methodology in all parts of the city.

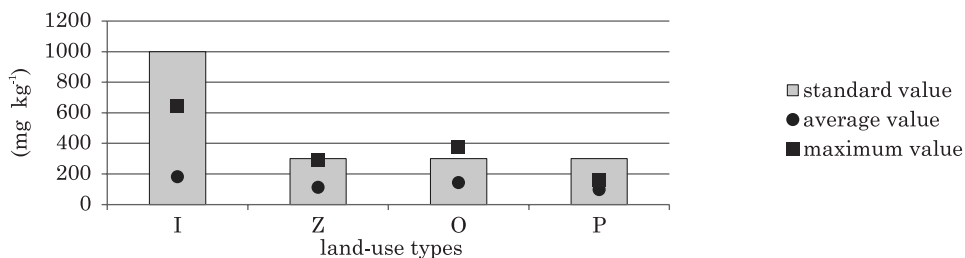


Fig. 2. Content of zinc in the soils of Kielce as compared to the standard values in *The Ordinance of the Minister of Environment* (2002): I – industrial areas, Z – urban green areas, O – allotment gardens, P – parks and forests

The high soil enrichment in zinc clearly had a local character and concentrated in the close proximity of main roads and petrol stations in the northern as well as central and eastern parts of the city (Figure 3). Moreover, extremely high values were found at a site previously occupied by metallurgical and machine building plants, located in the south-east of the city (Figure 3). This was due to the long-lasting deposition of dusts and metalliferous compounds originating from the anthropogenic activity pursued for over two-hundred-year near Białogoński Pond, i.e. the Alexander Metalworks (since 1817), Machinery Manufacturing Plant, Mechanical Plant and Cast-Ironworks and, opened in 1997, Białogon JSC Kielce Pump Manufacturing Plant (ŚWIERCZ, PRAŻAK 2014).

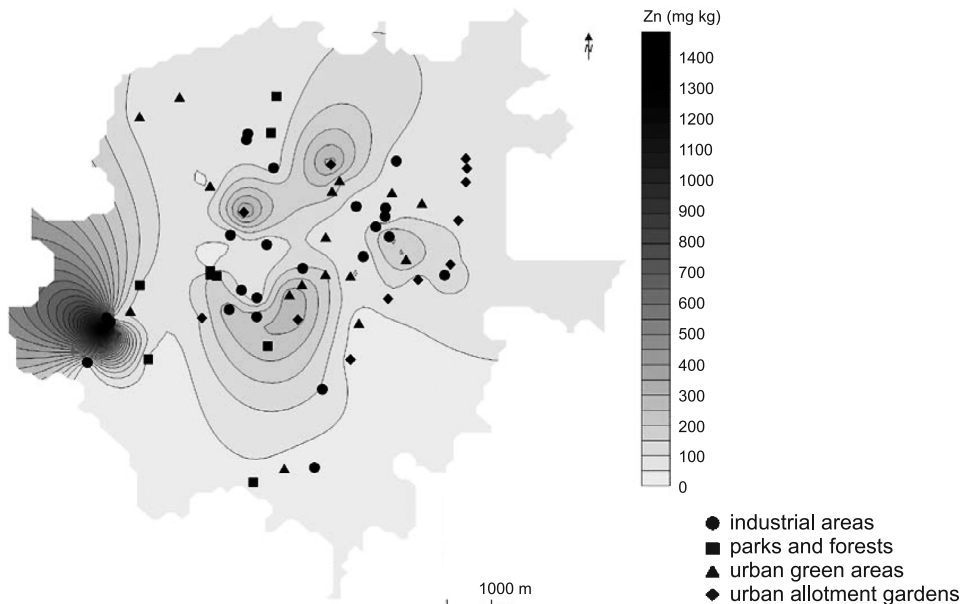


Fig. 3. Spatial variability of the zinc content in the soils of Kielce

The elevated content of zinc up to  $377.8 \text{ mg kg}^{-1}$  was found in the soils of urban allotment gardens located mainly in the city centre, which also emerged in the research by ŚWIERCZ and SYKAŁA (2009). The current values are similar to those noted in allotment gardens in Gdańsk (BIELECKA et al. 2009), Seville and Glasgow (HURSTHOUSE et al. 2004), but were much higher than the values in urban soils of Wrocław (KABAŁA et al. 2009). Admittedly, the soils of urban green areas (Z) have a lower *albeit* still significant level of enrichment in zinc. The minimum values of zinc were reported in the soils of parks and forests (P). The permissible values specified by *The Ordinance of the Minister of Environment* (2002) were not exceeded in any of the analysed parks or forests.

Parks and forests located in the western part of the city, particularly in Karczówka Nature Reserve, are characterised by the maximum values

of lead (559.9 and 590.0 mg kg<sup>-1</sup>). The soil enrichment in lead resulted from geological conditions, such as the presence of limestone rocks rich in lead minerals, galena ores that used to be extracted extensively (URBAN 2010). High lead concentrations significantly above the level of 9.8 mg kg<sup>-1</sup>, i.e. the geochemical background in soils of Poland (CZARNOWSKA 1996), were detected especially frequently in the industrial areas (I) – Figure 4. For both lead and zinc, there was a relationship between the maximum soil enrichment in the heavy metals and the industrial character of the area.

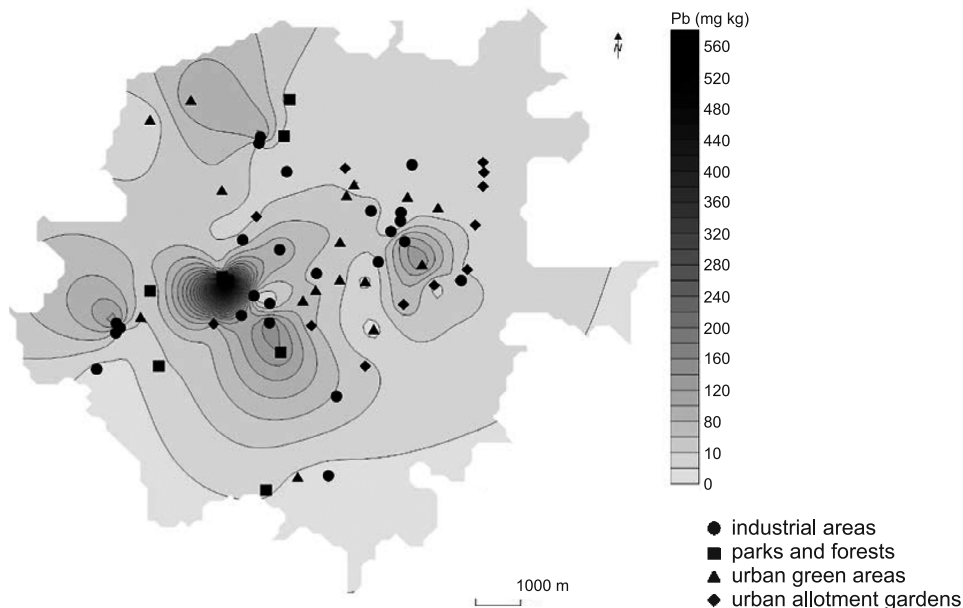


Fig. 4. Spatial variability of the lead content in the soils of Kielce

Similarly to zinc, the highest soil enrichment in lead is observed in the industrial estate called Białogon. Also, areas located along the main streets of the city (I) abound in large amounts of lead due to its deposition from traffic fumes. Urban allotment gardens (O) are less rich in lead and the minimum values determined in soils of urban green areas (Z) oscillate around a similar level. The average content of lead exceeds standard values specified by *The Ordinance of the Minister of Environment* (2002) only in the case of parks and forests (P) (Figure 5), which is caused by the highest but natural values found in soils of Karczówka Nature Reserve.

The high values of correlation coefficients indicate significant relationships between the content of heavy metals and physicochemical properties of the soils. The data presented in Table 2 show a positive relationship between the content of zinc, lead, fine-earth fractions  $\Phi < 0.02$  and organic carbon content. These correlations were verified in the soils of industrial areas (I) and urban garden allotments (O). As far as parks and forests (P), there is a

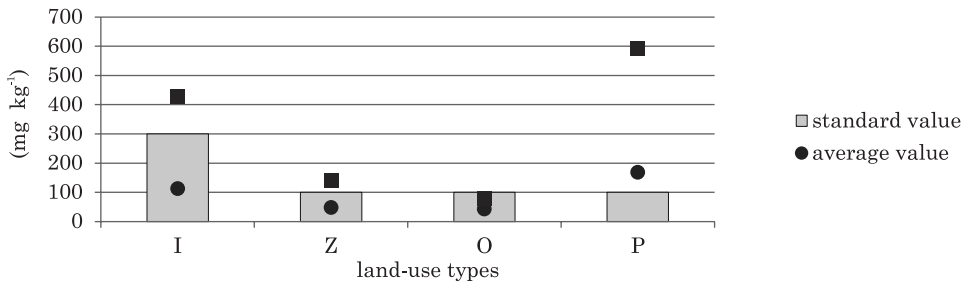


Fig. 5. Content of lead in the soils of Kielce as compared to the standard values in the Ordinance of the Minister of Environment (2002): I – industrial areas, Z – urban green areas, O – allotment gardens, P – parks and forests

Table 2

Significant correlation coefficients among the analysed parameters ( $p < 0.05$ )

Functional zone	Pairs of variables	Correlation coefficient
I	$\Phi < 0.02 - \text{Zn}$	0.68
	$\Phi < 0.02 - \text{Pb}$	0.49
	$C_{\text{TOT}} - \text{Zn}$	0.66
Z	$\text{Zn} - \text{Pb}$	0.51
O	$\Phi < 0.02 - \text{Zn}$	0.52
	$\Phi < 0.02 - \text{pH}$	0.68
	$C_{\text{TOT}} - \text{Pb}$	-0.53
	$\text{pH} - \text{Zn}$	0.56
P	$\text{pH} - C_{\text{TOT}}$	0.61
	$\text{pH} - \text{Zn}$	-0.53
	$\text{pH} - \text{Pb}$	-0.51
	$\text{Zn} - \text{Pb}$	0.59
In general	$\text{pH} - C_{\text{TOT}}$	0.64
	$\Phi < 0.02 - \text{Zn}$	0.42

Explanation: I – industrial areas, Z – urban green areas, O – allotment gardens, P – parks and forests

negative relationship among the pH and the analysed heavy metals. Similar tendencies were noted for the soils of garden allotments ( $C_{\text{TOT}} - \text{pH}$ ). MANTA et al. (2002) and SALAH et al. (2013), who conducted studies in Al-Fallujah and Palermo, respectively, conclude that car exhaust emissions as well as local urban emitters are the sources of an excessive heavy metal content in urban soils. They also claim that the degree of its deposition is influenced mainly by microclimate conditions.



The soil studies conducted in Kielce show an elevated concentration of heavy metals in the city centre, where heavy road traffic dominates. Dust and aerosols emitted by vehicles may lead to an excessive accumulation of metallic elements in soils. As can be expected, the heavy metal values decrease further from the city centre. Such a tendency for distribution of heavy metals, including zinc and lead, was also indicated by CHEN et al. (2005) and WEI, YANG (2010). The actual degree of soil contamination depends on the duration and nature of anthropogenic pressure (MEDYŃSKA-JURASZEK, KABALA 2012). In Kielce, this may be confirmed by the results of analyses of soils from the industrial estate Bialogon, from locally contaminated premises occupied by petrol stations and from roadsides, where soil contamination with zinc and lead is the most severe, as indicated by the geoaccumulation index ( $I_{geo}$ ).

With respect to the accumulation index (AI) and contamination factor (CF), all the calculated values are higher for lead than for zinc. Moreover, the variability of the geochemical indices for lead was definitely much greater – the highest values were calculated for the soils of parks and forests (P) as well as industrial areas (I). As far as the other types of land use are concerned, i.e. urban green areas (Z) and allotment gardens (O), these values seem to be comparable to the ones obtained for zinc (Figure 6).

Table 3 shows that in many cases the mean content of zinc and lead in the urban soils of Kielce was similar to levels observed in other large cities worldwide.

The accumulation of zinc and lead in the soils of Kielce is significantly higher than the average values obtained for Beijing, Al-Fallujah, Turku and

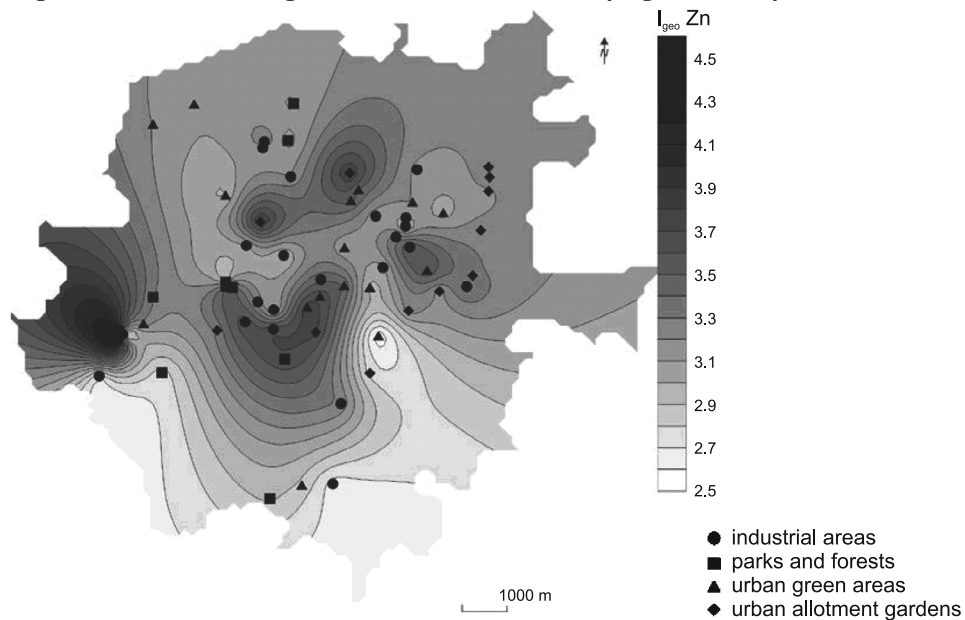


Fig. 6. Spatial variability of the  $I_{geo}$  value for zinc in the soils of Kielce

Mean content of zinc and lead in the urban soils of selected cities in the world (mg kg<sup>-1</sup>)

City	Zn	Pb	Reference
Al-Fallujah (Iraq)	5.50	3.82	SALAH et al. (2013)
Hong Kong (China)	168	93.40	LI et al. (2001)
Madrid (Spain)	210	161	DE MIGUEL et al. (1998)
Naples (Italy)	251	265	IMPERATO et al. (2003)
Palermo (Italy)	138	202	MANTA et al. (2002)
Beijing (Chinese)	157	49.4	KHAN et al. (2008)
	89.63	39.50	XINGHUI et al. (011)
	70.7	23.9	BAO et al. (2014)
Seville (Spain)	145	137	MADRID et al. (2002)
Turku (Finland)	72.50	20	SALOMEN, KORRKA-NIEMI (2007)
Poznań (Poland)	72.98	30.59	GRZEBISZ et al. (2002)
Kielce (Poland)			
I	181.31	112.55	Present study
Z	112.95	47.83	
P	97.77	168.73	
O	144.94	42.69	
Average	134.24	92.95	

Explanation: I – industrial areas, Z – urban green areas, O – allotment gardens, P – parks and forests

Poznań (GRZEBISZ et al. 2002, SALOMEN, KORRKA-NIEMI 2007, KHAN et al. 2008, XINGHUI et al. 2011, SALAH et al. 2013, BAO et al. 2014). This is due to many factors, such as the geological conditions promoting concentration of heavy metals in parent rocks, but also local heavy contamination of soils within the industrial estate of Białogon and in close proximity to the main streets in the city. Studies conducted by other scientists (MADRID et al. 2002, MANTA et al. 2002, CHEN et al. 2005) corroborate the spatial distribution pattern of zinc and lead observed in Kielce. For instance, the content of the analysed heavy metals decrease further from the strongly transformed city centre. MADRID et al. (2002), MANTA et al. (2002), and CHEN et al. (2005) also point out that the concentration of heavy metals is greater in the areas older in terms of land development, particularly that of an industrial character. In the case of Kielce, this may explain the heavy soil contamination of the former industrial district of Białogon.

## CONCLUSIONS

1. The urban soils in Kielce are excessively enriched in heavy metals, which may pose a threat to the natural environment due to their non-biodegradability.

2. The elevated content of zinc and lead in the analysed soils is limited only to the city centre and local industrial areas. The contamination decreases with the distance from the city centre, and generally higher enrichment is noted in areas of long-lasting anthropogenic impact.

3. The concentration of zinc and lead is spatially variable and depends chiefly on the density the city's street grid and on the location of industrial sources of contamination. Additionally, the chemistry of parent rocks has an impact on the high content of lead.

4. The soil enrichment in zinc and lead is not explicitly determined by the land use, but is affected by many factors, such as the historical land use and current presence of industrial sites and transportation routes, intensity of human activity, as well as the bedrock geology.

5. The values of the geochemical indices  $I_{geo}$ , contamination factor (CF) and accumulation index (AI) confirm the impact of human activity on the chemistry of urban soils.

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