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Geochemical Assessment of Heavy Metals Pollution of Urban Soils

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Abstract

Metals associated with urban soils are of environmental concern because of their direct and indirect effects on human health. The main purposes of this study undertaken in the city of Poznan (Poland) were to identify heavy metals with dangerous environmental load and to define areas of their environmental impact. Measured concentrations of cadmium, lead, copper and zinc in surface horizon and background soils were used to estimate the geochemical load indices and their spatial distribution in urban soils. It was found that concentrations of heavy metals were higher than geochemical background in 61% of the samples for Cadmium, 47% of samples for Lead, 49% of samples for Copper, and 61% of samples for Zinc. Contaminated areas by heavy metals are concentrated around industrial plants and in the center of the city as well as along highways.

Keywords: heavy metals, geochemical load index, spatial distribution, urban soils

Introduction

Heavy metals are natural constituents of the Earth's crust. Human activities have drastically altered the balance and biochemical and geochemical cycles of some heavy metals. Therefore, the concentration of heavy metals in soils has been an issue of great interest in the past few years not only to ecologists, biologists and farmers but also environmentalists. An assessment of the environmental risk due to soil pollution is of particular importance for agricultural and non-agricultural areas, because heavy metals, which are potentially harmful to human health, persist in soils for a very long time. In addition and according to soil parameters they may enter the food chain in significantly elevated amounts [3, 11, 12,15].

The tests performed by Terelak et al. [17] indicate that arable soils are contaminated with heavy metals at a low percentage. However, greater soil contamination may be present in heavily industrialized regions and in large city agglomerations [6]. The city environment forms a mosaic of soils with different levels of mechanical surface transformations which makes the cause and effect analysis of soil contamination very difficult. The majority of studies on the contamination of soils with heavy metals comes down to the determination of their content in a few soil samples without considering the specificity of their random and systematic variations [16, 8]. A good indicator of environmental pollution of soils by heavy metals is their geochemical load index (GLI).

The aim of the study described here was to perform a quantitative determination of the spatial distribution

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(random and systematic variation) of the geochemical load indices (GLI) of lead, cadmium, copper and zinc in surface soil horizons in the city of Poznan.

Materials and Methods

The present administrative Poznan municipality was the system boundary used for the investigation. The total area of the city is 261.3 km^2 of which 38.1% is under agricultural use, 33.7% is covered by buildings and roads (23.1% and 10.6% respectively), 4.2% - parks and green belts, 14.2% - forests and parks, 3.1% water and 6.7% is classified as being under various other uses, but is mostly wasteland.

In order to determine spatial variability in the content of Cd, Pb, Cu and Zn, soil samples for laboratory tests were taken from 350 sites in a random system (Fig. 1) from 0-20 cm depth. The metals content was assayed in "aqua regia" (3:1 HCl:HNO$_3$ by vol.) solution using the AAS method.

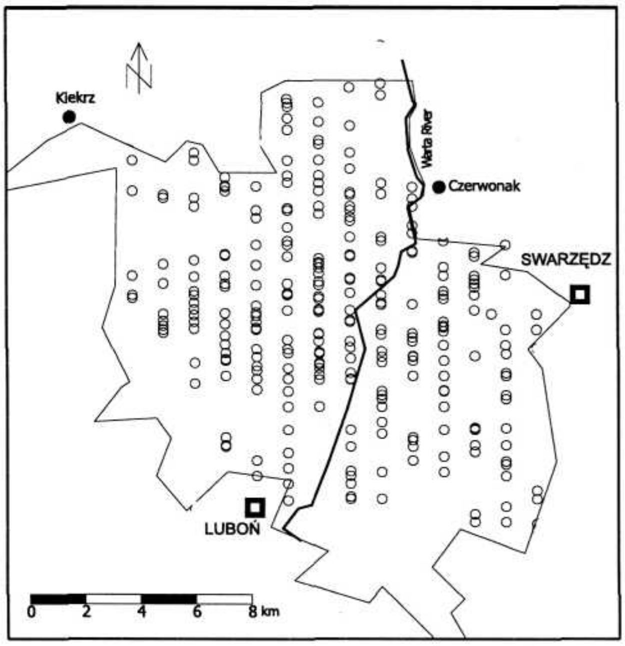


Fig. 1. Scheme of sample spots distribution.

For evaluation of soil contamination by heavy metals a geochemical load index (GLI) was calculated [1]:

$$GLI = \log_2 \frac{C_i}{B \cdot 1.5} \tag{1}$$

where: Ci - concentration of an element in surface horizons, mg/kg of soil dry weight, B - natural background concentration of heavy metal - estimated for glacial till (soil parent material) after elemental analysis of samples. The total concentrations of Cd, Pb, Cu and Zn were determined after digestion with HF [9] by ICP method and were found to be 0.3, 16.8, 10.0 and 31.7, respectively. The estimated natural background concentrations of Cd, Pb, Cu and Zn were similar to values reported by Kabata-Pendias [4].

The spatial variability of heavy metal content in soils was determined by means of geostatistical methods in which semi-variance is the basic function ($\gamma_{(k)}$) defined as the square of the difference between a soil property in point Xj and the same property in a point at a distance of x_{i+k} [19, 5]:

$$\gamma_{(k)} = \frac{1}{2 \cdot n(k)} \cdot \sum_{i=1}^{n(k)} [Z(x_i) - Z(x_{i+k})]^2 \tag{2}$$

where: n(k) - number of pairs of observation; Z(xi) - soil property measured in point x, and in point x + k.

The parameters of spatial variability of heavy metals GLI were performed using the "VARIOWIN", v. 2,21 program [14]. By plotting the semi-variance $\gamma_{(k)}$ values versus distance k, semivariograms of the spatial variability of the geochemical load index of Cd, Cu, Pb and Zn in soils were drawn. On the basis of the spatial variation structure contour maps of the geochemical load index of Cd, Cu, Pb and Zn were drawn by means of the Kriging method for point interpolation [19]:

$$Z^*(x_0) = \sum_{i=1}^{n} \lambda_i \cdot Z(x_i) \tag{3}$$

where: Z*(xo) - interpolated value of variable Z at location xo, Z(xi) - values measured at location xi, λi; - weighed coefficients calculated on the basis of the semivariogram when:

$$\sum_{i=1}^{n} \lambda_i = 1 \tag{4}$$

The weights, calculated in this way, make it possible to obtain non-biased interpolated values, that is, the expected value: E[Z*(xo) - Z(xo)] = 0 and the estimated variance Var. [Z*(xo) - Z(xo)]= minimum.

Results and Discussion

Most soils in the territory of the City of Poznan vary greatly from arable and forest soils. Due to relatively deep transformations related to the city's infrastructure, the natural morphological features of many soils have been considerably disturbed and the surface horizons often contain such impurities as rubble, brick or peat. Therefore, part of the soils under investigation should be classified as Humi-Arenic Anthrosols [2] and those in which the natural genetic horizons have remained are classified as a Luvisols, Arenosols, Gleysols and Histosols [7]. Their soil texture, organic matter content and soil reaction indicates the significant transformation of surface horizons in the investigated soils. In the surface horizons, around 25% of soils exhibited sandy texture, 65% - loamy sand, and only 8% exhibited sandy loam texture. The content of organic carbon ranged between 0.7 and 19.8%; however, in about 50% of samples, the organic carbon content ranged between 5-9%. In most of the samples, the investigated soils exhibited a neutral reaction. The descriptive statistics of basic physical and chemical properties of the investigated soils are summarized in Table 1. The data indicate that not only the basic soil properties show great variation but also the heavy metal content in soils. The mean content of lead was 30.6 mg/kg of soil, whereas the difference between the lowest and the highest lead content was 51 times, and the variation coefficient was 85%. The expected range for lead was from 27.85 to 33.33 mg/kg. The greatest variation was present in the content of cadmium, which can be demonstrated by the variation coefficient, which reached 107%. The mean content of cadmium in the soils of the city of Poznan was 0.755 ± 0.086 mg/kg, and it is around 3.5 times higher than the mean content of this metal in the soils of Poland, and 1.5 times higher than its mean content in world soils [18]. A slightly smaller dissipation in contents was showed by zinc and copper (Table 1).

This great variation in the content of Pb, Cd, Zn and Cu in the soils of the City of Poznan makes it difficult to analyse their degree of contamination without taking into account the spatial variability of metals and their content in the parent materials of soils, that is the natural background. Table 2 shows the classes of soil contamination with heavy metals that were prepared in the form of their geochemical load index. As the contamination of the City of Poznan soils is smaller than in other industrial regions of Poland, only six classes of geochemical load degree were differentiated. Class zero includes non-contaminated soils in which the content of metals is close to the natural background. The second class comprises soils containing from 1.5 to 3 times higher concentration of metals than in the natural background. The soils included in the second class of geochemical load degree contain from 3 to 6 times greater amounts of metals than the natural background. For the third class, the content of metals is from 6 to 12 times higher than in the background. The fourth class contains from 12 to 24 times higher values than the background, whereas the highly polluted soils (fifth class) contain 24 times more metals than the natural background.

Table 1. Descriptive statistics of basic soil properties in the surface horizon.

Soil properties		Statistics						
		Min.	Max.	$\bar{x} \pm t_{\alpha,Sx}$	S	K[1]	Sk[2]	V %
Pb	mg/kg	5.4	280	30.59 ± 2.74	26.06	26.6	2.80	85
Cd		0.01	9.95	0.755 ± 0.086	0.811	49.4	5.23	107
Zn		9.0	400	72.98 ± 5.92	56.31	8.65	2.45	77
Cu		3.1	120	16.41 ± 1.16	11.08	23.6	3.48	68
Clay	%	0	7	2.60 ± 0.34	3.04	-0.590	0.21	67
C. org.		0.73	19.13	4.34 ± 0.56	8.60	12.11	2.65	68
CEC-KPW	cmol$_{(+)}$/kg	4.86	30.11	14.04 ± 0.93	23.19	0.235	0.49	34
pH in CaCl$_2$ (1:2)		6.13	7.85	7.17 ± 0.056	0.081	1.34	-0.93	–

[1] Kurtosis; [2] Skeewness

Table 2. Parameters of geochemical load index.

GLI	CGLD[1]	Level of loading	Mean background metals concentration in soils mg/kg			
			Pb	Cd	Zn	Cu
			16.8	0.3	31.7	10
			Range of metals concentration for CGLD			
< 0	0	Depleted to non-polluted	≤ 25.2	≤ 0.45	≤ 52.0	≤ 15
0-1	1	Non-polluted to slightly polluted	25.2 – 50.4	0.45 – 0.9	52.0 – 104	15 – 30
1-2	2	slightly polluted to moderately polluted	50.4 – 100.8	0.9 – 1.8	104 – 208	30 - 60
2-3	3	Moderately polluted	100.8 – 201.6	1.8 – 3.6	208 – 416	60 – 120
3-4	4	Moderately to high polluted	201.6 – 403.2	3.6 – 7.2	416 – 832	120 – 240
4-5	5	High polluted	> 403.2	> 7.2	> 832	> 240

[1] class of geochemical load degree

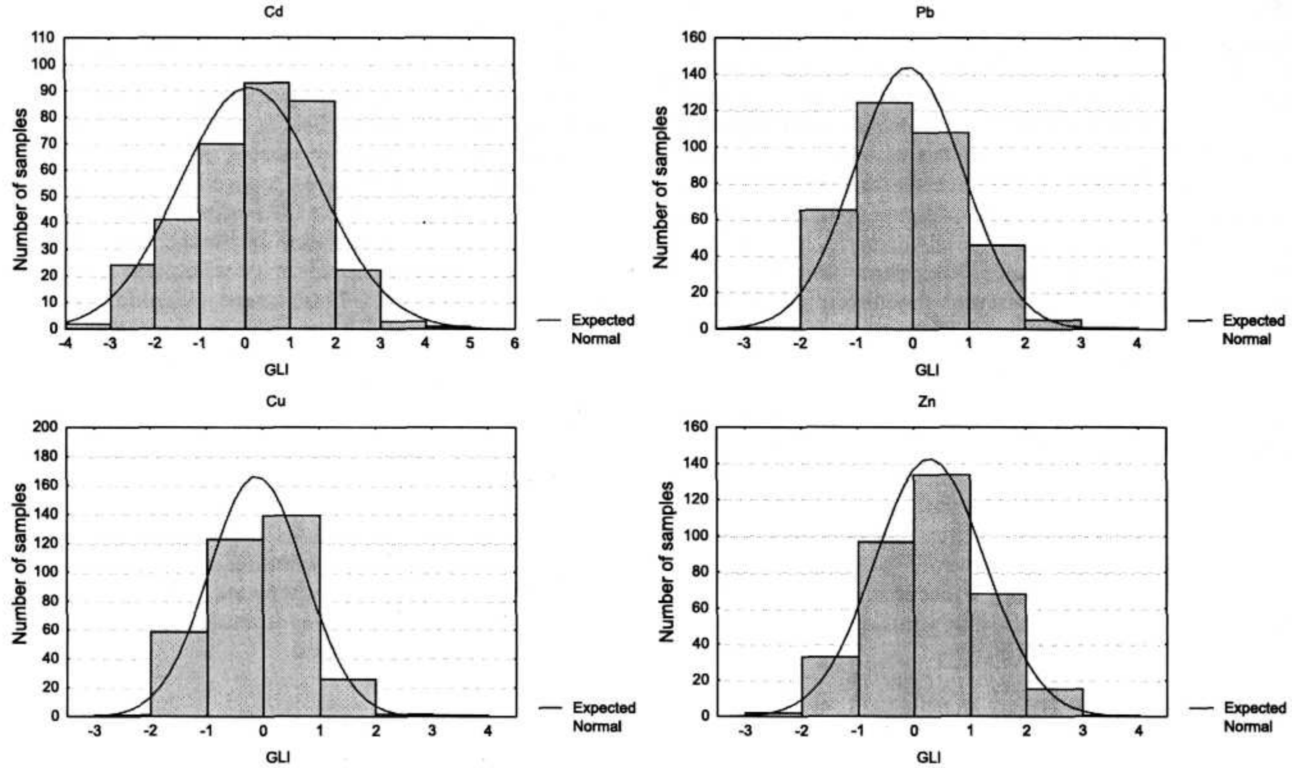


Fig. 2. Frequency distributions of heavy metals geochemical load index (GLI).

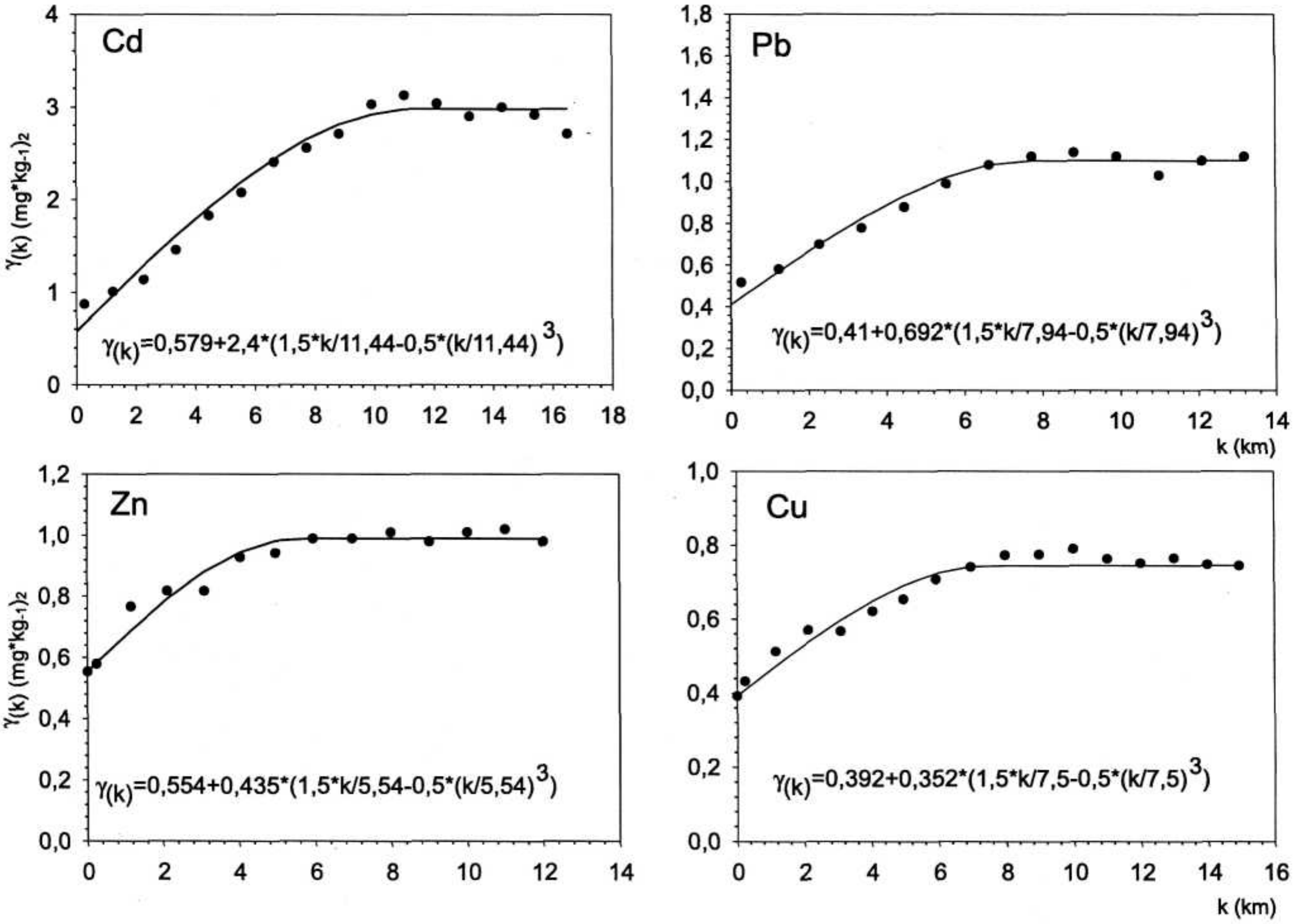


Fig. 3. Experimental (dots) and modeled (solid line) semivariograms of spatial variability of heavy metals geochemical load index in investigated soils.

Fig. 2 presents the histograms of the distribution of the geochemical load index in the soils of the City of Poznan. In 39% of the soil samples the content of cadmium was close to the natural background, 26% showed the first degree of pollution, and 32% of samples - from the second to fifth CGLI. In nearly 53% of samples, the content of lead is close to the values of the natural background, and those soils were classified as the zero CGLI. In 31% of soil samples the content of lead is slightly higher than background that gives first CGLI. Only 14% of samples show slightly to high lead contamination. Therefore, as regards contamination, they were included in the classes from the second to fifth. The content of copper in 51% of samples is close to background and the content of zinc in 63% of sample fits from the first to fourth CGLI.

Despite the large and seemingly chaotic variation in the content of heavy metals in the investigated soils it has been observed that the structure of their spatial variation (random and systematic) can be determined by means of the semi-variance function. The spatial variation of the geochemical load index in the soils of the City of Poznan is presented in Fig. 3. It results from the graphs that the

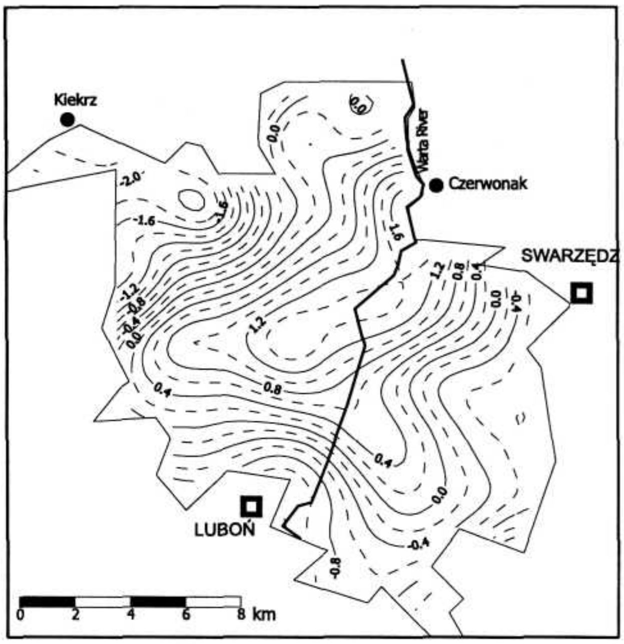
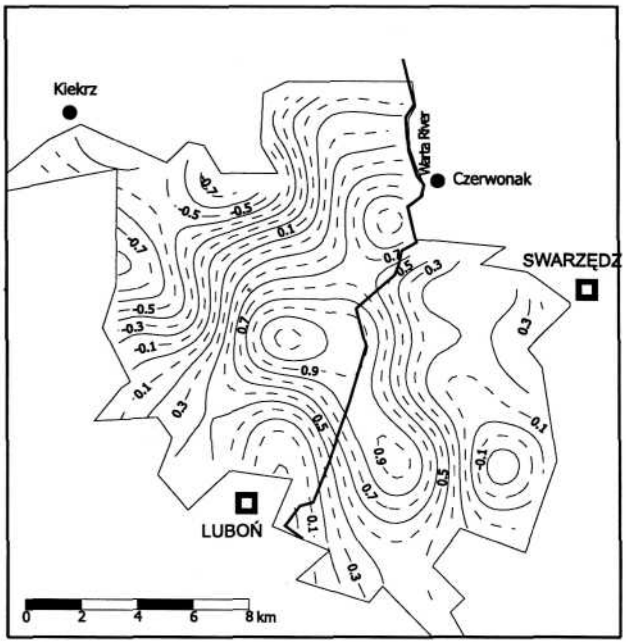
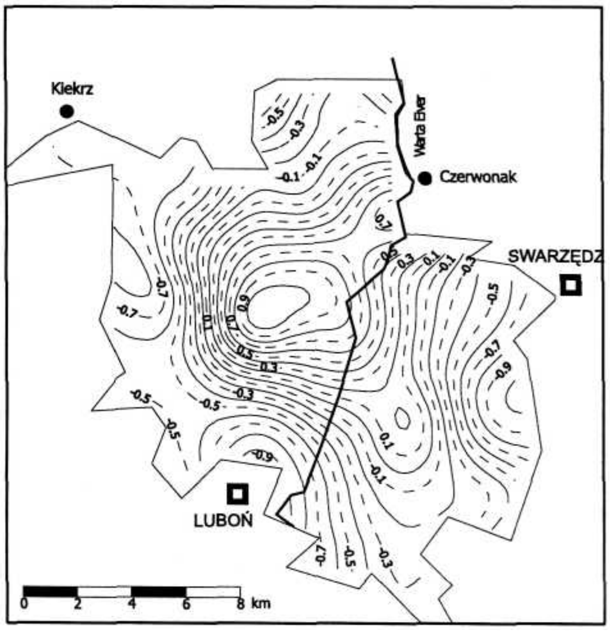


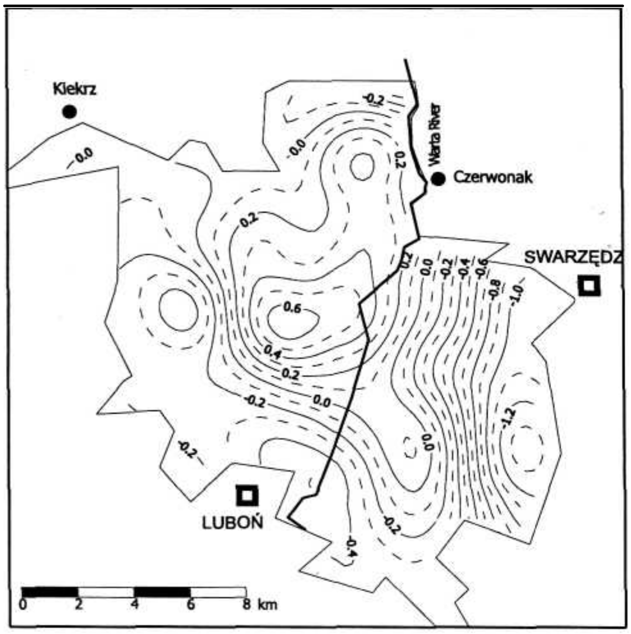
Fig. 4A. Contour map of spatial distribution of cadmium geochemical load index (GLI).



Fif. 4C. Contour map of spatial distribution of zinc geochemical load index (GLI).



Fif. 4B. Contour map of spatial distribution of lead geochemical load index (GLI).



Fif. 4D. Contour map of spatial distribution of copper geochemical load index (GLI).

GLI for lead shows spatial correlation (distinct gradual change) up to a distance of 7.94 km. The GLI for cadmium, in turn, is correlated with the distance of 11.4 km with a great share, however, of random variation in the general spatial variability structure. This demonstrates that an important change in the content of cadmium on the area smaller than the distance between the points of measurement may occur, and therefore a change in the value of GLI. This seems to be fully understandable, because city agglomerations are subject to intensive and local human interference. The GLI of zinc was correlated on the area of 5.54 km, and of copper up to a distance of 7.5 km. In the cases of both zinc and copper, a large share of random variation in the general spatial variation - it reached around 50%.

With the use of the spatial variation structure (semivariograms) of the investigated elements, maps of GLI isolines for the City of Poznan were drawn according to the Kriging method (Fig. 4). The highest values of the GLI for lead were present in the north-eastern part of the city at the Warta River, and in the center of the city. Increased GLI values were also present in the south-eastern part of the city. The spatial distribution of the GLI is strictly connected with the presence of industrial plants within the city, on one hand, and the intensity of vehicular traffic, especially in the center of the city and along highways, on the other. In the north-eastern part of the city there are chemical industrial plants, whereas in the south-eastern part - engineering industrial activity predominates. A similar GLI distribution can be observed for cadmium and zinc. The highest GLI for copper were reached in the center of the city.

When analyzing the issue of spatial variability of Cd, Cu, Pb, and Zn content in the soils of the City of Poznan, one has to state that the soil samples taken were characterized by a great deal of variation both in the content of the metals investigated and in basic physico-chemical properties. Although variability is a natural and unavoidable feature of soil materials, related to the spatial variability of factors and overlapping soil-forming processes [10] in city agglomerations this phenomenon is heightened by the anthropogenic factor. This problem affects to the greatest extent the surface layers and levels, and subsurface ones to a slightly smaller extent.

The results presented above indicate that around 50% of the soils of Poznan do not demonstrate any pollution with heavy metals (class 0), but there are also areas where the concentrations of heavy metals exceed the natural background and their permissible content published in the Regulation of the Ministry of Environmental Protection and Natural Resources (1986) by several times. It must be noted, however, that these soils show soil reaction close to neutral, which limits the mobility of these elements. For this reason, direct migration of these metals to groundwater should not take place, even from places where the GLI has the highest values (from class 3 to 5).

Therefore, in city agglomerations one should pay attention to the following factors [13]:

- identification of pollutants and pollution areas,
- definition of geographic area of impact,
- the monitoring of existing environmental quality,
- identification of receptors, and establishment of a monitoring system.

Conclusions

1. Despite a distinct disturbance of the natural structure of genetic horizons and layers of soils on the territory of Poznan, the heavy metals geochemical load index clearly indicates a spatial variation structure, which could be quantified by means of geostatistical methods.
2. As a result of the spatial variability analysis it was stated that the geochemical load indices of Lead, Cadmium, Copper and Zinc exhibited a systematic variation and were correlated on a distance of 7.94, 11.44, 7.5 and 5.54 km, respectively.
3. Assessment of environmental state of urban soils by means of geochemical load indices calculated for each metal showed that concentrations of heavy metals were higher than geochemical background in 61% of the samples for Cadmium, 47% of samples for Lead, 49% of samples for Copper, and 61% of samples for Zinc.
4. Areas contaminated by heavy metals are concentrated in industrial plants within the city and in the center of the city as well as along the highways.

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