ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 34 no.3 pp. 91 – 101 2008

PL ISSN 0324-8461

CONTAMINATION OF SOILS WITH HEAVY METALS IN REGION OF ŁÓDŹ

A. TUREK, J. KRYSTEK, W. WOLF, J. KUBICKI

Institute of General and Ecological Chemistry, Technical University of Łódź
90-924 Łódź, Żeromskiego 116 (Poland)
Corresponding author. Email :akturek@p.lodz.pl

Abstract: The aim of this work was to determine contents of cadmium, copper, lead, nickel and zinc in soils of 5 poviats in Łódzkie Voivodeship (Poviats: Łódź, Brzeziny, East Łódź, Pabianice and Zgierz). The objects of the investigation were over 500 samples of soils collected from cultivated fields, meadows, fallows and urban areas (lawns and city parks). The concentration of elements in all samples was analyzed by atomic absorption spectrometry after extraction with 1 mol/dm^3 HCl solution. The highest contents of heavy metals were detected in the City of Łódź area. The amounts of leachable metals in the samples under study were within the ranges: 0.3 – 48.4 ppm Cu, 1.7 – 162.9 ppm Pb; 0.9 – 357.6 ppm Zn; below 2.1 ppm Cd and below 7.6 ppm Ni.

Keywords: atomic absorption spectrometry, heavy metals, soil analysis

INTRODUCTION

Monitoring of chemical pollution of soils is one of the key method which helps to prevent soil degradation, displacement of harmful substances between different environmental components and keep these pollutants from entering the food chain. Anthropogenic contaminations influence majority of soils. Chemical degradation is based on excessive cumulation of ions or substances and finally reduces biological activity of soil, crop yield and plants quality. The sources of chemical contaminations are mainly industry, transport and agriculture. Anthropogenic impact causes unfavourable pH shift, toxic or harmful effects on plants, animals and people. Toxicity of substances depends on their amounts, physical and chemical properties and proportion between different soil components. Particular attention is paid to the heavy metal pollution of the soil. Their presence in mineral and organic fertilizers and sewage sludge used in agriculture, for wasteland reclamation or silviculture may be dangerous to soil-water environment. Therefore, the content of heavy metals is a good index of soil quality. However, it requires estimation of the natural concentration levels of individual components in different types of soil. The only method for evaluation of geochemical background of trace elements is determination of their total amounts (Kabata-Pendias, 1999). This approach does not take into consideration the differences in solubility of compounds, and consequently their bioavailability. In order to estimate the available form of elements extraction with diluted acids is recommended. On the other hand, these methods give incomparable results because of a great variety of solvents used in particular studies. One of the reagents applied for determination of available forms of metal cations is 10% solution of HNO_3. This extractant was introduced to soil analysis by the Warsaw Institute of Environmental Protection (Ostrowska, 1991). It is also often used to extract cations from standard soils (CRMs). In accordance with the Polish Standards, the amount of bioavailable forms of selected elements should be determined after soil extraction with 1 mol/dm^3 solution of hydrochloric acid. The latter method is recommended to assess nutritional requirements and currently is the only quantified method approved in Poland. Hydrochloric acid was also used to determine the heavy metal contents in the soil samples collected from allotment gardens (Jankiewicz, 2002, 2004; Turek, 2000) and to study changes of soil abundance in microelements (Kopeć, 2006). Pasieczna (2003) assessed urban soils enrichement by elements in relation to geochemical background in 334 Polish cities. The best extractant to release weakly bonded and easily leachable forms of metals was hot hydrochloric acid (1:4). The same method was used by Lis (1998) to draw geochemical maps of Łódź agglomeration. Treatment of soil with pure acids or their mixtures is often used in environmental studies. It enables a release mobile fraction of elements which participates in pollutant migration in the surface layer of land.

The majority of existing data are available for the urban and industrial sites. The surrounding agricultural areas have not been systematically investigated so far. The aim of the present work was to assess the soil acidity and the concentration of available forms of cadmium, lead, nickel (phytotoxic cations), copper and zinc (components of fertilizers) in soils in the region of Łódź. This work was carried out in cooperation with the Voivodeship Fund for Environmental Protection and Water Management in Łódź.

MATERIALS AND METHODS

Soil samples were collected in the City of Łódź and four surrounding poviats (Brzeziny, East Łódź, Pabianice and Zgierz) within the period of August-October 2005 and 2006. The 90% of samples were collected from agricultural land (cultivated fields, fallows, meadows) while the remaining covered urban areas (lawns and city parks in the case of Łódź and Zgierz). 531 sampling sites were selected at random, close to local or main roads with different intensity of traffic. All the samples are described in Table 1.

Table 1. Description of samples

Poviat	Number of samples	Cultivated fields	Fallows	Meadows	Lawns, city parks
Łódź	78	20	6	5	47
Brzeziny	114	110	2	2	-
East Łódź	94	73	5	16	-
Pabianice	82	69	1	12	-
Zgierz	163	151	3	6	3
Total	531	423	17	41	50

Soil samples of 0.5-1 kg mass were collected from an area of 0.2-0.25 ha (in the case of lawns and city parks it was ca. 0.1 ha), from the surface layer of soil 0-20 cm (Polish Standards, 1997a). Laboratory soil samples were prepared according to the same standard procedure. Prior to analysis, the samples were left for two weeks in a dry and airy place and thus brought to a state of "air dryness". Subsequently they were sieved to pass through a 2-mm stainless steel screen.

Soil pH was determined in 1:2.5 soil/KCl (1 mol/dm^3, pH=5.8-6.0) suspension (Polish Standards, 1997b; Branch Standards, 1975), using pH-meter Delta 350 (Mettler). The results are shown on Figure 1.

To determine the available forms of zinc and copper, about 10 g of soil was mixed with 50 cm^3 of 1 mol/dm^3 hydrochloric acid, left for 1h on a magnetic stirrer and passed through a filter, rejecting the first portion of filtrate (Polish Standards, 1992 a, 1992 b). The analyses of cadmium, nickel and lead were made by the same procedure. The concentrations of cadmium, copper, lead, nickel and zinc in the prepared solutions were determined by FAAS method, using AAS spectrometer GBC 932plus. The results are shown in Figures 2-6 and in Table 2.

Table 2. Metals contents in soil samples

Poviat		Amount of metal [mg/kg]				
		Zn	Cu	Pb	Cd*)	Ni*)
Łódź	range	2.5-357.6	0.8-48.4	4.1-162.9	< 2.1	< 7.6
	average	42.9	8.4	21.6	< 0.5	2.1
Brzeziny	range	0.9-23.4	0.3-7.0	1.7-17.6	< 0.5	< 3.0
	average	5.4	2.0	7.8	< 0.5	0.7
East Łódź	range	2.0-247.8	0.9-6.8	5.9-40.1	< 0.5	< 2.8
	average	11.9	2.5	11.0	< 0.5	0.8
Pabianice	range	2.4-159.3	1.0-21.7	5.1-38.6	< 0.8	< 2.9
	average	10.9	2.5	9.6	< 0.5	0.8
Zgierz	range	1.4-56.1	0.5-25.7	3.0-23.3	< 0.9	< 5.0
	average	7.1	1.4	7.9	< 0.5	1.0

*) limit of determination 0.5 mg/kg

RESULTS AND DISCUSSION

Acidity is an important index of soil degradation. Soil acidification strongly influence the physical and chemical properties of soil and subsequently its bioactivity. Acidification leads to higher mobility and bioavailability of metal ions. The results of pH determination show that the soils under study are degraded to a large extent. For all districts surrounding the City of Łódź 66-75% of samples were strongly acidic or acidic and only 7-14% of soils were neutral or basic. It is generally in agreement with the results of analyses of the agricultural fields carried out over the period of four years (1999-2003) and presented in Report (2004). It proves that environmental conditions are unfavourable for the plant growth. Only in Łódź Poviat neutral or slightly acidic soils predominate (70% of samples). However, for agricultural areas in Łódź pH < 5.5 is observed in 80% of samples. More acidified soils were found in the west, north and east suburbs of Łódź whereas samples collected in the city centre and south were basic or neutral. Higher pH values of soils in cities are probably caused by dust deposition from the municipal power plants and local industries. Average pH is 7.2 for the surface level of urban soils in Poland and 6.8 for urban and industrial areas of Łódź (Pasieczna, 2003; Lis, 1998).

Pasieczna (2003) reported that geochemical background level for zinc in a non-built-up areas of the Polish Lowlands in 0.0 – 20 cm surface layer of soils is usually below 50 mg/kg. An average enrichment coefficient of urban soils by Zn in Łódź was W = 3.1. As shown in Fig. 2, most soils do not require fertilization with zinc. In the whole area soils rich in zinc (above 3.3 mg/kg) predominate and about 20% of samples were classified as medium soil category (0.7 – 3.3 mg/kg). In Brzeziny Poviat Zn concentration did not exceed 23.4 mg/kg, in Pabianice Poviat < 25.2 mg/kg (with the exception of two samples containing about 60 mg/kg and one – 159.3 mg/kg), in Zgierz District < 31.2 mg/kg (56.1 mg/kg in one sample) and in East Łódź District < 35.4 mg/kg (in two samples approx. 124 and 248 mg/kg were found) – Table 2. The amount of Zn in Łódź Poviat ranged between 2.5 and 357.6 mg/kg (in 27% of samples it was higher than 50 mg/kg)

According to the Decree of the Polish Minister of Environment (2002), for agricultural, forest and urban soils as well as for fallows (group B) the total amount of zinc should not exceed 300 mg/kg. Since as much as about 80% of the total content of zinc in light, sandy soils could be in mobile forms (Kabata-Pendias, 1999), the permitted concentration of zinc was exceeded only in one sample in Łódź. In 96 - 100% of soils in Brzeziny, East Łódź, Pabianice and Zgierz Poviats the content of metal is at the geochemical background level (below 50 mg Zn in 1 kg of soil).

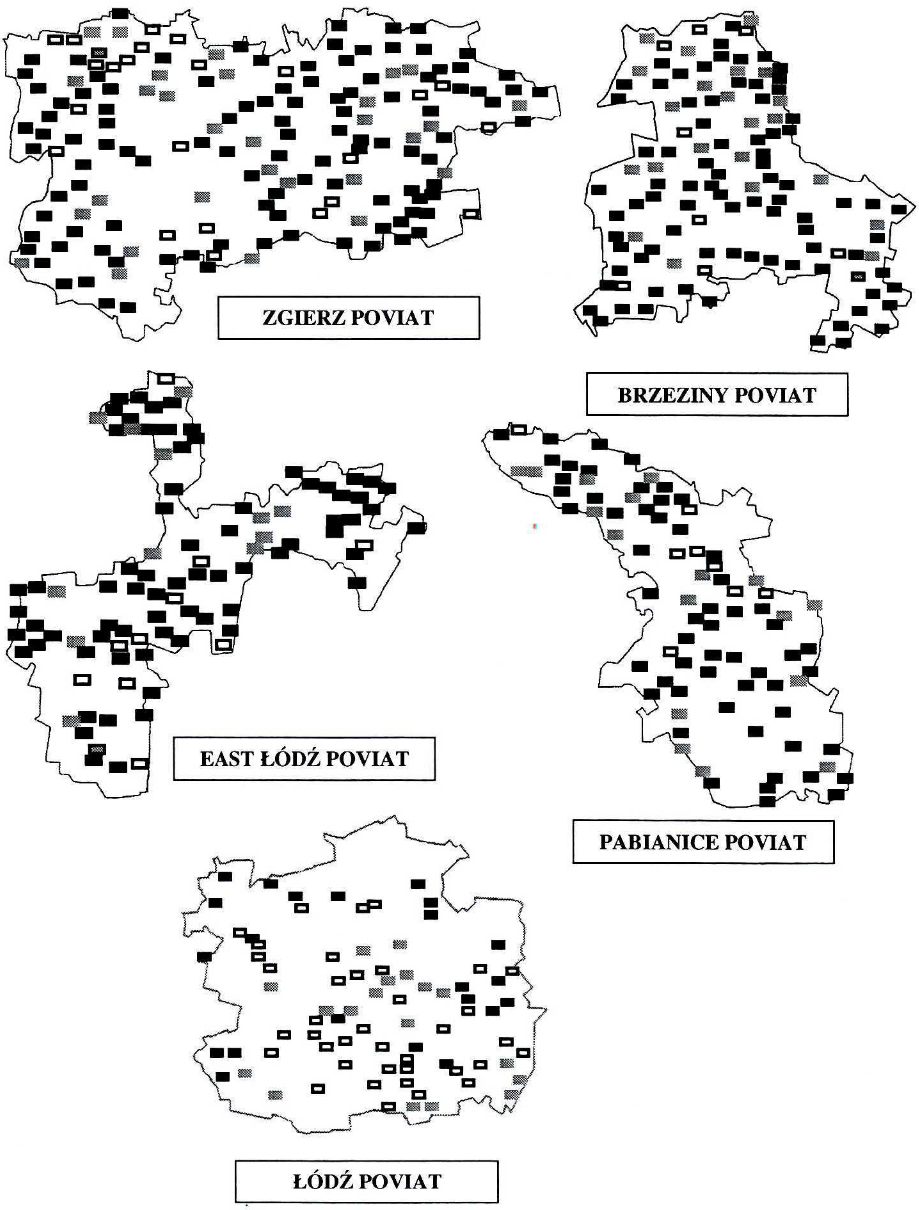

Fig.1. Soil acidity: ■ strong acidic and acidic; ▒ slightly acidic; □ neutral and basic

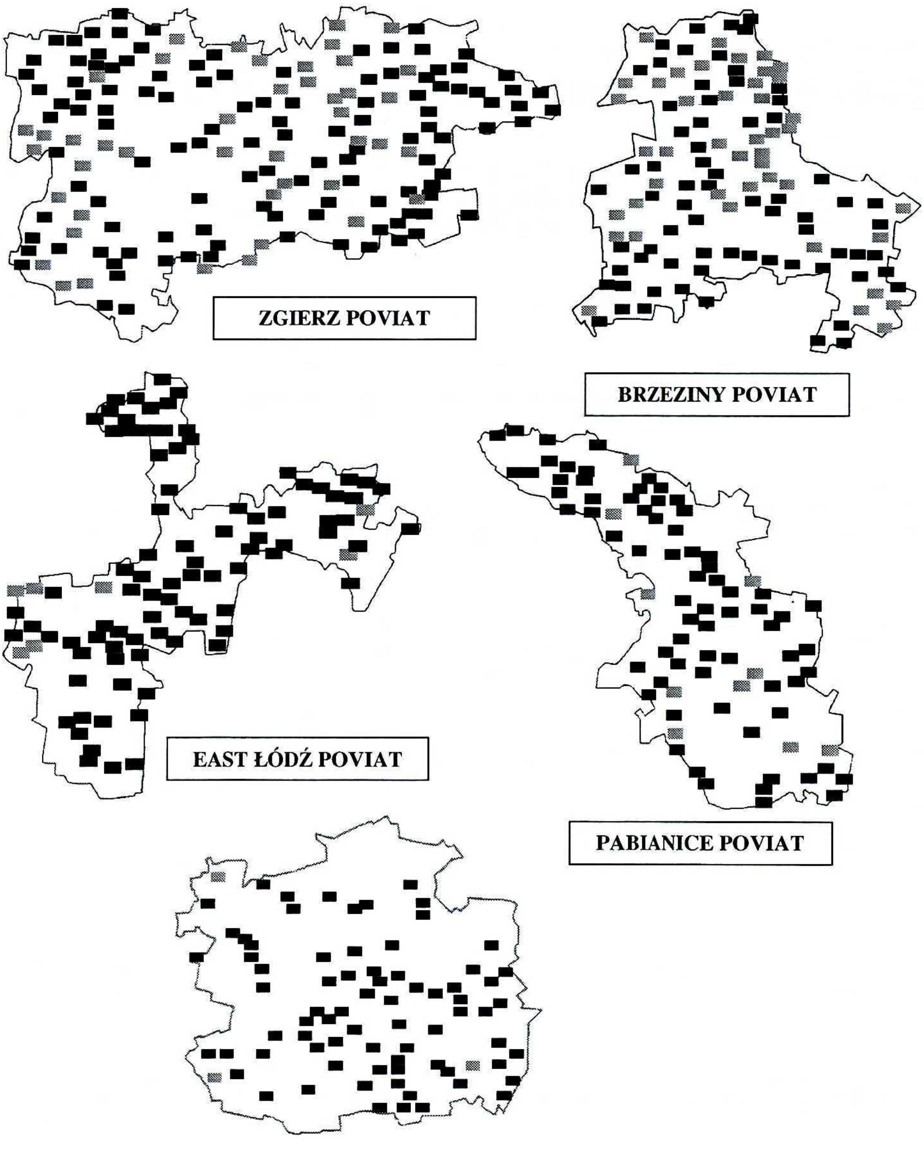

Fig. 2. Soil abundance in zinc: ■ high (> 3.3 mg/kg); ▒ medium (0.7 – 3.3 mg/kg)

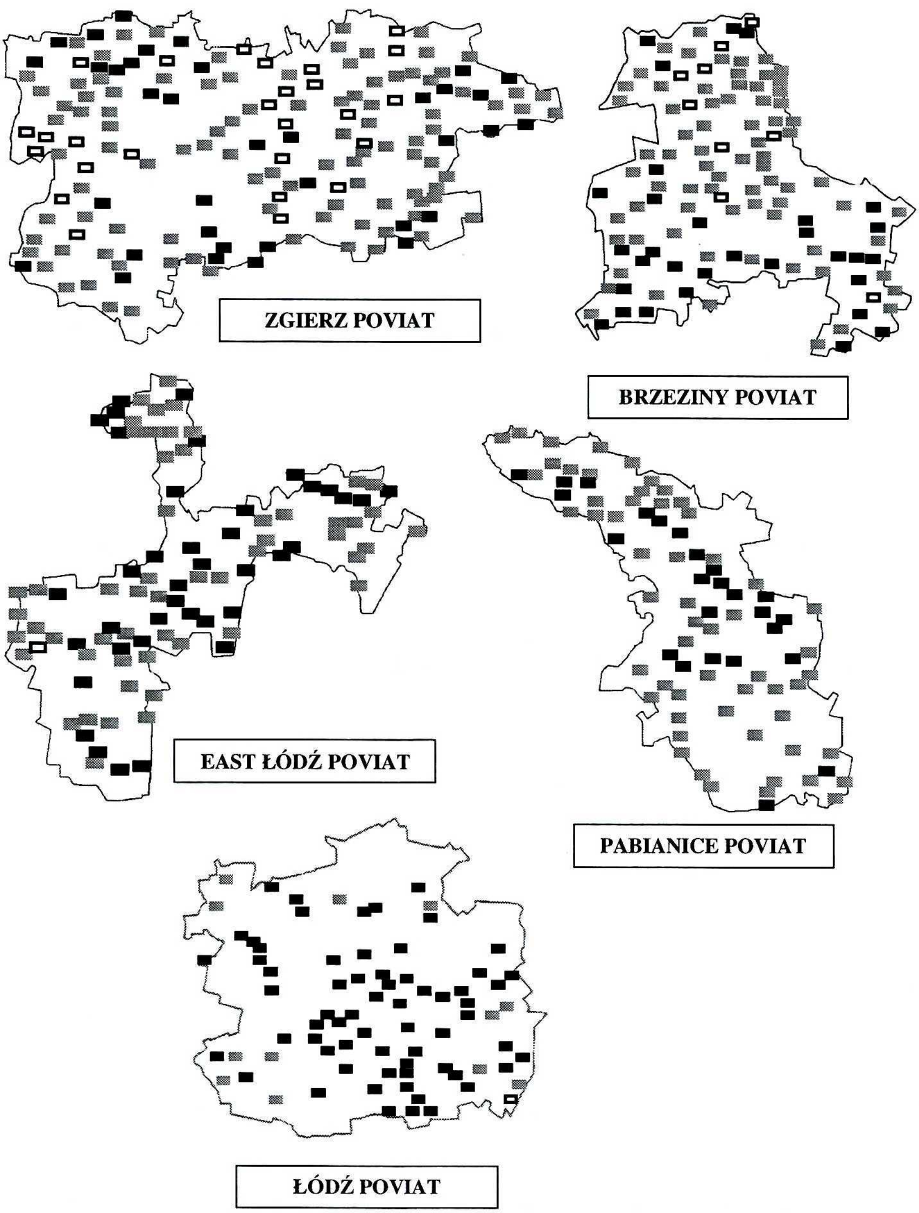

Fig. 3. Soil abundance in copper: high (> 2.5 mg/kg); medium (0.9 – 2.5 mg/kg) low (< 0.9 mg/kg)

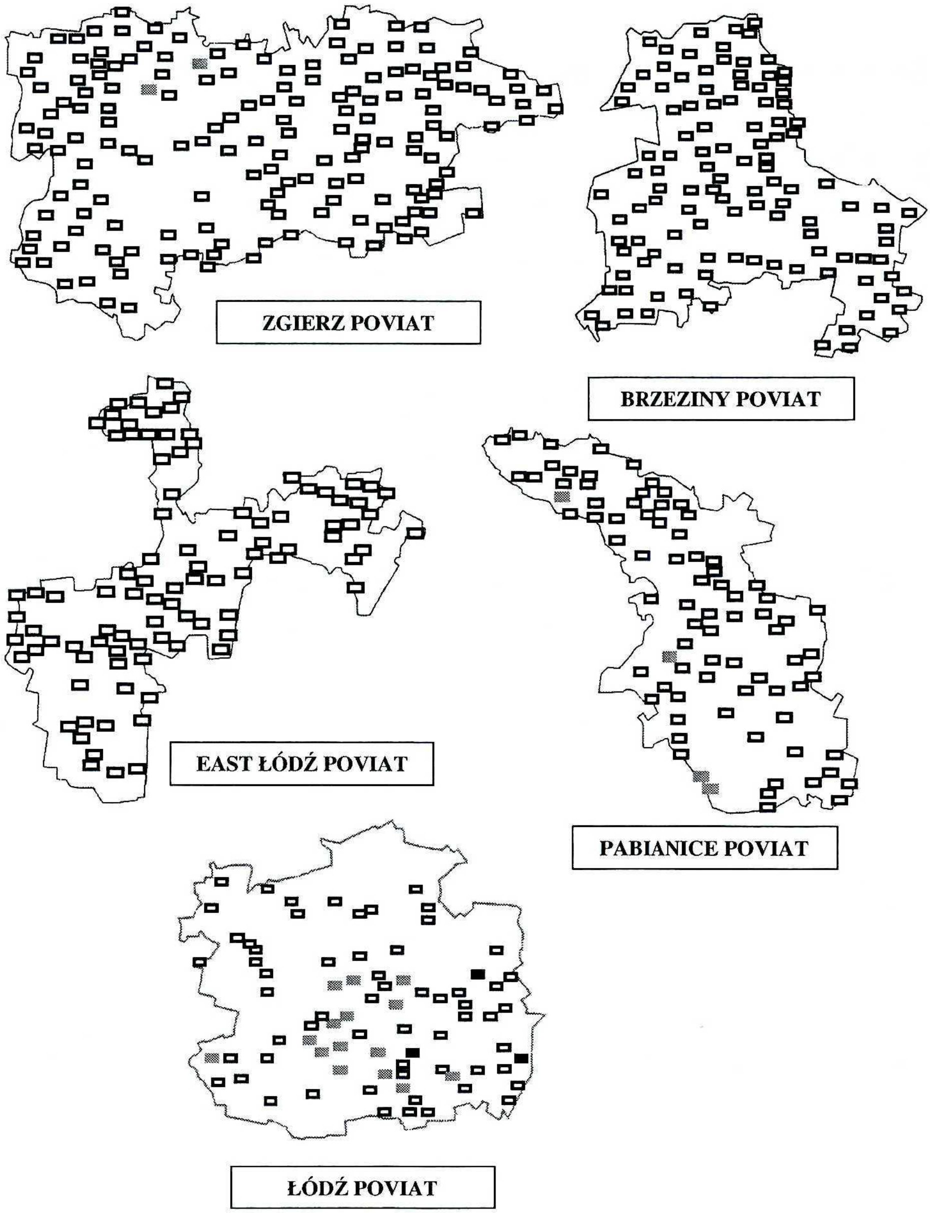

Fig. 4. Soil abundance in cadmium: > 1.0 mg/kg; 0.5 – 1.0 mg/kg; < 0.5 mg/kg

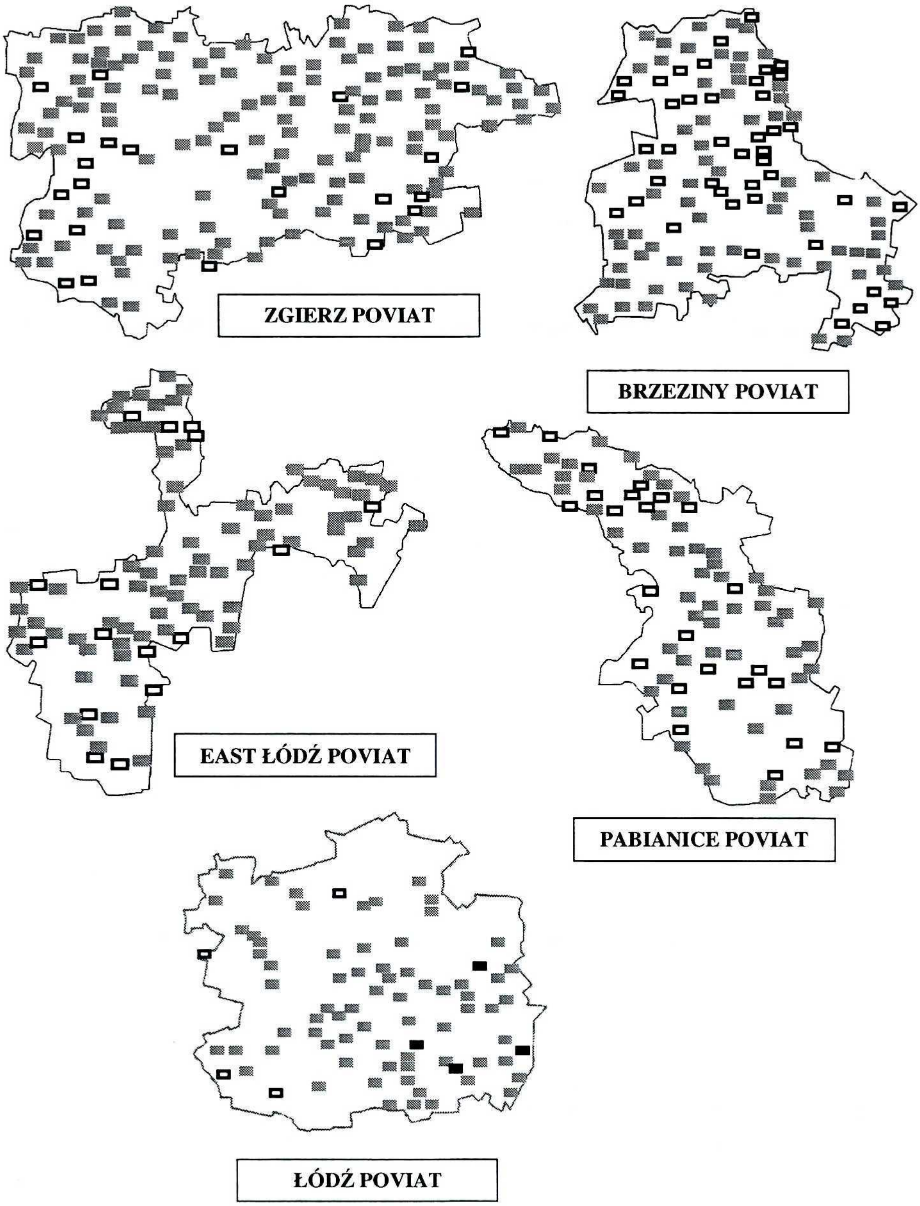

Fig. 5. Soil abundance in nickel: ■ > 6.0 mg/kg; ▒ 0.5 – 6.0 mg/kg; □ < 0.5 mg/kg

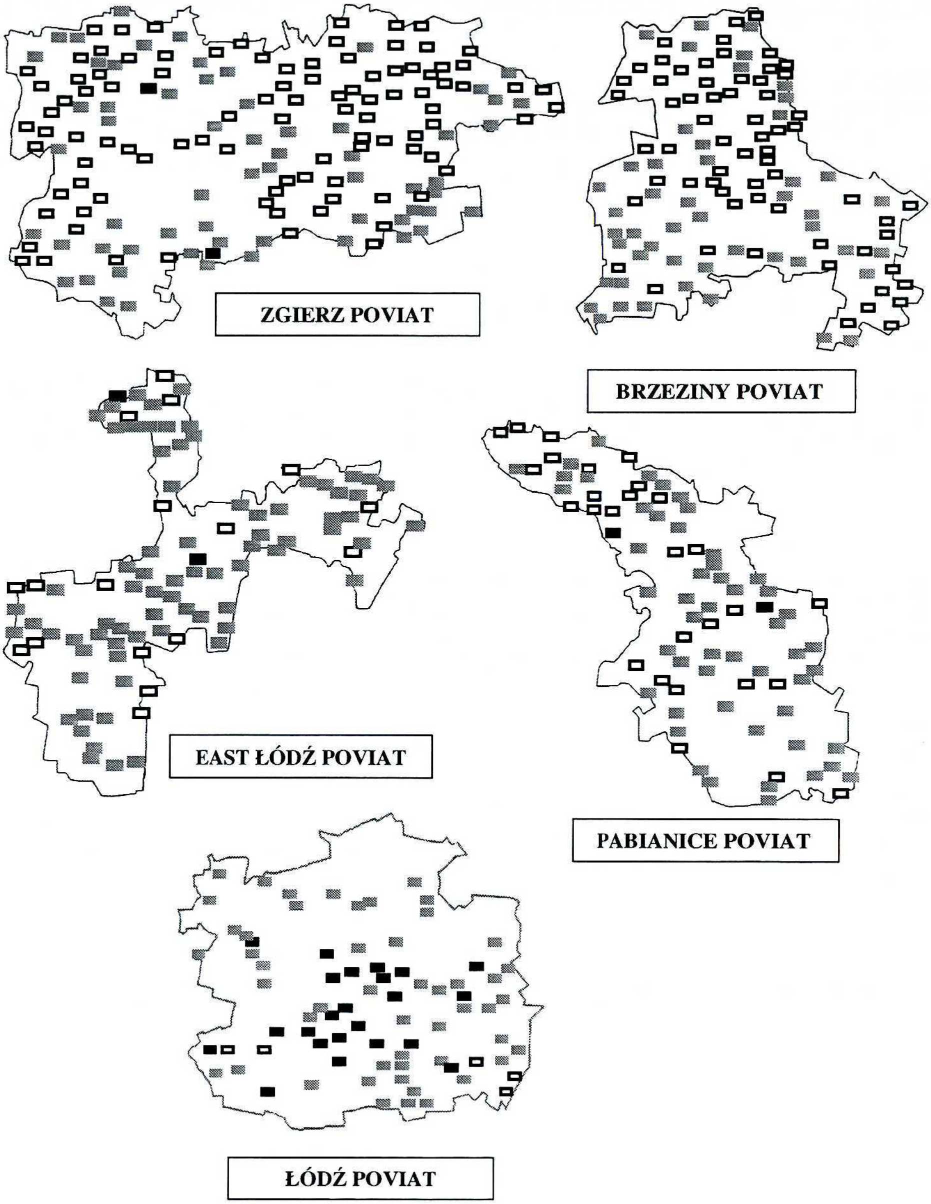

Fig. 6. Soil abundance in lead: ■ > 21.0 mg/kg; ▒ 8.0 – 21.0 mg/kg; □ < 8.0 mg/kg

Geochemical background level for copper in a non-built-up areas (for surface layer) is below 4 mg/kg, in urban areas the value of median is 12 mg/kg. The copper content in Łódź was 4 –18 mg/kg (except for the city centre, where it reached 39 mg/kg and in allotments – 160 mg/kg) and the coefficient of enrichment of urban soils with Cu in Łódź is 4.3 (Pasieczna, 2003). About 60 – 70% of soils in the Łódź region (19% in Łódź Poviat) were classified as soils with medium abundance of copper (0.9 – 2.5 mg/kg). In Brzeziny and Zgierz Poviats low amount of the metal (< 0.9 mg/kg) was observed in 7 and 12% of samples, respectively. Almost 80% of samples in Łódź Poviat shoved a high content of Cu (Fig. 3). The background level was exceeded in about 5 – 10% of soils in all poviats except Łódź (in that case above 50% of samples were contaminated with copper). For soils belonging to the "B" group (Decree, 2002) the total content of the metal should be below 150 mg/kg. As approximately 60% of copper in sandy soils may be bioavailable (Kabata-Pendias, 1999), it is very likely that in no sample the permitted Cu concentration was exceeded.

The geochemical background level for Cd is 0.5 mg/kg. The amount of cadmium in urban areas usually does not exceed this value but in the centre of Łódź up to 3 mg/kg of metal was found (Pasieczna, 2003). In Brzeziny and East Łódź Poviats cadmium content did not exceed the background level. In Zgierz and Pabianice Poviats higher amounts of Cd were observed in 1.2% and 3.7% of samples, respectively (Fig. 4). The most contaminated soils were in Łódź (approximately 15% of soils with Cd concentration above 0.5 mg/kg). The permitted limit of total Cd in soil of the "B" group is 4 mg/kg (Decree, 2002). The part of mobile forms of the metal was about 50% (Kabata-Pendias, 1999). This means that all samples under study follow the criterion and may be used for purposes as defined for soils of the "B" group.

The content of nickel in background in the area of the Polish Lowlands and in agricultural soils is almost the same, i.e. < 6 mg/kg. Nickel accumulation in urban soils is insignificant (for example 1.7 in Łódź) and the amount of the metal ranges between 3 and 12 mg/kg within the cities (Pasieczna, 2003). The data presented in Table 2 and Fig. 5 indicate that except for four samples in Łódź Poviat, the concentration of nickel in all soils was below the background level.

The background level of lead in a non-built-up areas of the Polish Lowlands is estimated at 8 – 21 mg/kg (average in Poland 12 mg/kg). For cultivated areas it is 14 mg/kg and the element tends to accumulate in soils. In Łódź its concentration was above 31 mg/kg (up to 105 mg/kg in the centre and 361 mg/kg in allotments) with enrichment coefficiant W = 2.1 (Pasieczna, 2003). Only in Brzeziny Poviat the lead concentration was found to be at the background level (Table 2). In the other poviats the proportion of non-polluted soils (i.e. < 21 mg of Pb in 1 kg of soil) was 98 – 99% in East Łódź, Pabianice and Zgierz Poviats and 70% in Łódź (Fig. 6). Taking into considaration that the amount of Pb for the "B" group of soils is to be below 100 mg/kg (Decree, 2002) and up to 45% of total Pb content can easly migrate (Kabata-Pendias, 1999), the limit value was exceeded only in five samples from Łódź Poviat.

CONCLUSIONS

In the Łódź region (the City of Łódź and four surrounding districts) the content of mobile forms of cadmium, copper, lead, nickel and zinc in majority of sampling sites were at the background level. Most samples with high metal concentrations were collected in the area of Łódź. The distribution of metals in Łódź agglomeration presented in this work differs from that previously reported in literature (Lis, 1998). The average amounts of metals in 1127 soil samples in Łódź reported by that author were: 36 mg Zn, 7 mg Cu, < 0.5 mg Cd, 3 mg Ni and 14 mg Pb in 1 kg of soil. It may result from different sampling sites, conditions of soil extraction, industrial and transportation changes. A very serious problem in the examined area is the high acidity of cultivated soils in all poviats surrounding Łódź.

Acknowledgement

This work was financed by the Voivodeship Fund for Environmental Protection and Water Management in Łódź (project No. 201/BN/D/2005).

REFERENCES

[1] Branch Standards. 1975. Chemical and agricultural analysis of soil. Determination of pH. BN-75/9180-03 (in Polish). Polish Committee for Standardization, Warszawa.

[2] Decree of Minister of Environment from 09 September 2002 referring to standards of soil quality and standards of ground quality. *Journal of Laws* (in Polish). **165**: 1359.

[3] Gondek, K. and Filipek-Mazur, B. 2006. Selected Soil Properties and Availability of Some Microelements from Soil with Compost Supplement. *Pol. J. Soil Sci.* **39**: 81-90.

[4] Jankiewicz, B., Ptaszyński, B. and Turek, A. 2002. Spectrophotometric Determination of Iron(II) in Soil of Selected Allotment Gardens in Łódź. *Pol. J. Environ. St.* **11**: 745-749.

[5] Jankiewicz, B., Kobyłecka, J., Ptaszyński, B. and Turek, A. 2004. Determination of Bioavailable Forms of Heavy Metals in the Soils from Selected Allotment Gardens in Łódź. *Chem. Inz. Ekol.*. **11**: 907-913.

[6] Kabata-Pendias, A. and Pendias, H. 1999. Biogeochemistry of trace elements (in Polish). PWN, Warszawa 398pp.

[7] Kopeć, M. and Przetaczek-Kaczmarczyk, M. 2006. Changes of Soil Abundance in Microelements in Long-Term Fertilizer Experiment (Czarny Potok). *Pol. J. Soil Sci.* **39**: 91-96.

[8] Lis, J. and Pasieczna, A. 1998. Geochemical Atlas of Łódź Agglomeration. Part I: Soils, Water Sediments, Surface Waters (in Polish). Polish Geological Institute, Warszawa 72pp.

[9] Ostrowska, A., Gawliński, S. and Szczubiałka, Z. 1991. Methods of analyses and estimation of soils and plants properties (in Polish). Institute of Environmental Protection, Warszawa 334pp.

[10] Pasieczna, A. 2003. Atlas of urban soils contamination in Poland (in Polish). Polish Geological Institute, Warszawa 83pp.

[11] Polish Standards (a). 1992. Chemical and agricultural analysis of soil - Determination of assimilated zinc content. PN-92/R-04016 (in Polish). Polish Committee for Standardization, Warszawa.

[12] Polish Standards (b). 1992. Chemical and agricultural analysis of soil - Determination of assimilated copper content. PN-92/R-04017 (in Polish). Polish Committee for Standardization, Warszawa.

[13] Polish Standards. 1997 (a). Agrochemical soil analyses - Sampling. PN-R-04031:1997 (in Polish). Polish Committee for Standardization, Warszawa.

[14] Polish Standards. 1997 (b). Soil quality - Determination of pH. PN-ISO 10390:1997 (in Polish). Polish Committee for Standardization, Warszawa.

[15] Report on the environmental state of the Łódź Province in 2003 (in Polish). 2004. Library of Environmental Monitoring, Łódź.

[16] Turek, A., Verpoucke, G., Ptaszyński, B. and Jankiewicz, B. 2000. Determination of Bioavailable Copper(II) in the Soil. *Chem. Inz. Ekol.* **7**: 857-863.

Received: September, 2007; accepted: June, 2008.