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# ASSESSMENT OF LEAD AND CADMIUM SOIL CONTAMINATION IN THE VICINITY OF A NON-FERROUS METAL SMELTER

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Keywords: Soil contamination, lead and cadmium in soil.

Abstract: The aim of this study was to assess soil contamination with toxic metals in the area of Piekary Śląskie (Silesian Voivodeship), taking into consideration various land use patterns. The scope of research covered the determination of lead and cadmium concentration in soil in the following areas: allotment gardens, fallow lands and kindergarten playgrounds. The lead and cadmium concentrations in soil samples were determined using a flame atomic absorption spectrometry technique, after the *aqua regia* extraction in a MDS 2000 microwave digestion system. The metal contents in the analyzed soil samples varied remarkably, depending on the sampling location and its distance from the main emitter of toxic metals in Piekary Śląskie, i.e. "Orzeł Biały" Non-Ferrous Metal Smelter. Metal concentrations determined in all soil samples significantly exceeded the concentration levels accepted in Poland for arable lands and residential areas. The lead and cadmium concentrations in soil should become the basis for stopping edible plants cultivation in the area of Piekary Śląskie. The contaminated soil in kindergarten playgrounds can be an important source of lead and cadmium contamination, posing hazard to the children's health. Contamination of playgrounds with toxic metals should stimulate undertaking actions aimed at modernization of playgrounds and reduction of the children's contact with soil. In the context of the applied result assessment criteria the soil concentrations of these metals observed in the region of Piekary Śląskie should arouse great concern among its users and local authorities.

## INTRODUCTION

In the recent years in Poland a significant reduction of particulate matter emission has been observed, although in industrial regions the environmental contamination, particularly soil contamination with heavy metals, is still quite high. From a toxicological point of view the most important metals are lead and cadmium emitted from industrial and communication sources. The above-mentioned metals deposited in soil, pose hazard to people for many years after stopping the emission.

In the Silesian Voivodeship the lead and cadmium emission comes mainly from non-ferrous metal ore treatment plants but the high natural concentration of metals in shallow-bedded deposits of zinc and lead ores also has a significant impact. Furthermore, a very disadvantageous feature of the Silesian Voivodeship – especially for its inhabitants – is an immediate surroundings of industrial plants, housing facilities and arable lands. One of the facilities posing the highest environmental nuisance in the region is "Orzeł Biały" Non-Ferrous Metal Smelter in Piekary Śląskie, which has emitted toxic metal compounds to the environment (in that lead and cadmium) for a dozen of years. In the 1990s production processes became modernized and the emission was reduced but the

metals accumulated in the soil still pose risk to the environment and human health. The lead and cadmium concentrations in soil surrounding the smelter exceed the permissible limits defined for arable soil and residential areas. The toxic metal contaminated soil in Piekary Śląskie is a secondary source of toxic metals, particularly dangerous for sensitive children's organisms. This situation is a source of great concern about the health of the inhabitants, and especially about the development of children, as the dusting surface layer of soil in the kindergarten and housing estate playgrounds contributes the most to the children's exposure to lead and cadmium [12, 17].

The aim of this study was to assess soil contamination with toxic metals in the area of Piekary Śląskie in the context of different land use patterns. The scope of research covered the determination of lead and cadmium concentration in soil samples collected from the following areas:

- allotment gardens,
- fallow lands,
- kindergarten playgrounds.

The research covered 11 allotment gardens, 20 lots representing fallow lands and 16 kindergarten playgrounds (Fig. 1).

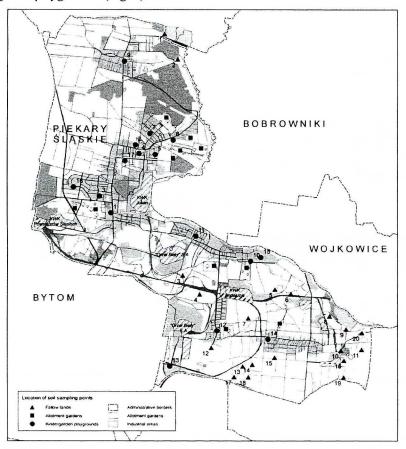


Fig. 1. Location of soil sampling points in Piekary Ślaskie

#### MATERIALS AND METHODS

Representative soil samples were collected in the period of 2000–2003. Samples from allotment gardens and fallow lands were collected at the depth of 0–20 cm and from kindergarten playgrounds – at the depth of 0–10 cm [1, 9]. After averaging and drying, analytical samples were prepared.

Metal content in soil was determined using the *aqua regia* extraction in MDS 2000 microwave digestion system and lead and cadmium concentrations were measured by the Flame Atomic Absorption Spectrometry (Varian model SpectrAA 300 [6].

#### RESULTS

The soil analysis results are presented in Tables 1–3 and illustrated in Figures 2 and 3.

Ta	Name of the allotment	Pb	Cd [mg/kg d.w.]	
Item	garden complex	[mg/kg d.w.]		
1	Pod Lipami	2035.0	58.60	
2	Azalia	2159.0	33.10	
3	Wieczorek	325.5	10.15	
4	Ustronie	201.0	5.52	
5	Zacisze	312.5	5.69	
6	Barbara	237.7	7.31	
7	Julianka	273.0	6.83	
8	Górnik	856.3	38.87	
9	Brzoza	477.3	20.87	
10	Róża	623.1	22.19	
11	Jedność	1383.0	56.24	
Range		201–2159	5.52-58.60	
Geometric mean		569.70	16.86	
Median		477.3	20.87	
Arithmeti	c mean	807.4	24.12	
Standard	deviation	725.7	19.99	

Table 1. Lead and cadmium concentrations in soil – allotment gardens

# Research result assessment criteria

The results obtained from the determination of lead and cadmium concentrations in soil samples in the area of Piekary Śląskie were interpreted based on the permissible soil concentration values defined in the Ordinance of the Minister of the Environment dated 9 September 2002 [18]. They were also compared with soil monitoring results obtained in Poland [13] and results of the Institute for Ecology of Industrial Areas own retrospective research carried out in this region [7, 8, 11, 15, 16].

In the Ordinance of the Minister of the Environment the permissible values for lead and cadmium concentrations in soil and ground were presented in the context of different land development and land use patterns as well as the depth of the contaminants. The following three groups of soil were distinguished:

Table 2 Lead	and cadmium	concentrations	in soil -	fallow lands

Lot number	Pb [mg/kg d.w.]	Cd [mg/kg d.w.] 2.46		
1	98.1	2.46		
2	323.7	6.60		
3	9301.0	507.3		
4	1592.0	71.88		
5	914.9	49.64		
6	401.5	15.16		
7	426.7	12.96		
8	165.4	5.68		
9	370,2	12.79		
10	353.4	13.97		
11	551.4	18.17		
12	611.6	20.84		
13	627.1	14.75		
14	286.5	10.02		
15	278.3	9.52		
16	436.5	17.33		
17	405.6	14.71		
18	92.7	3.17		
19	245.0	7.87		
20	415.5	18.40		
Range	92.7-9301.0	2.46-507.30		
Geometric mean	429.2	15.07		
Median	403.5	14.34		
Arithmetic mean	894.9	41.66		
Standard deviation	2005.8	110.79		

Group A – land property protected by law under the Water Act and nature protection regulations (parks, natural reserves).

Group B – agricultural land, forest land, tree-covered and shrub-covered land, fallow land, built-up and urbanized land (residential areas).

Group C – industrial, mining and transportation land.

In Polish legislation there are no standard concentration values which would define the permissible values for soil contamination with toxic metals in children's and school playgrounds. Therefore, in the interpretation of results obtained from the analyses of topsoil samples collected from the kindergarten playgrounds the permissible values defined in the Ordinance of the Minister of the Environment for soil from Group B were taken into consideration (Tab. 4).

The lead and cadmium contamination of kindergarten playgrounds in Piekary Śląskie was compared with soil contamination in the southern part of the Silesian Voivodeship in the recreational mountainous region, which was considered as a reference area [13].

Metal concentration values used for interpretation of the obtained results were presented in Table 4.

Table 3 Lead and	cadmium concentrati	ons in soil - kind	lergarten playgrounds

Kindergarten	Address	Pb	Cd	
number	Address	[mg/kg d.w.]	[mg/kg d.w.]	
1	1 ul. Bytomska 79		22.66	
2	ul. Cicha 38	92.4	2.00	
3	ul. Piłsudskiego 17	1269.0	48.49	
4	ul. Ofiar Katynia 13	132.7	3.66	
5	ul. Alojzjanów 5	264.3	7.78	
6	ul. Bytomska 20 A	_	-	
7	ul. J. Hallera 1	64.2	1.30	
8	ul. ks. Czempiela 5	74.4	1.61	
9	ul. Tarnogórska 40	538.4	21.99 45.06	
10	ul. M. Skłodowskiej 65	1546.0		
11	ul. K. Makowskiego 10	557.8	14.03	
12	ul. Bednorza 26	755.8	21.16	
13	ul. Kotuchy 32	582.2	12.72	
14	ul. Przyjaźni 48	251.6	13.57 10.49	
15	ul. M. Skłodowskiej 104	357.4		
16	ul. Lortza 88	176.5	7.06	
17	ul. Konstytucji, ul. 3 Maja	85.7	2.74	
Range		64.2-1546.0	1.30-48.49	
Geometric mean		293.1	8.82	
Median		310.8	11.60	
Arithmetic mean		455.8	14.77	
Standard deviation	1	433.5	14.44	

<sup>\*-</sup> liquidated kindergarten

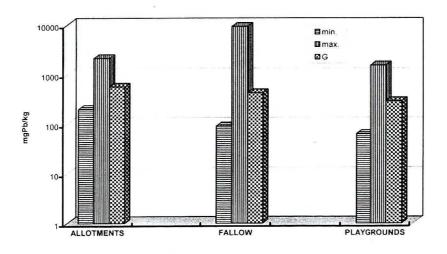


Fig. 2. Lead concentration in soil for the Piekary Śląskie area

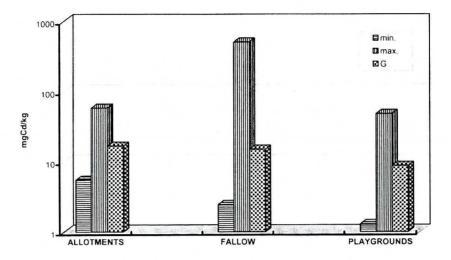


Fig. 3. Cadmium concentration in soil for the Piekary Śląskie area

#### DISCUSSION

#### Metals in allotment gardens

Lead in soil samples collected from allotment gardens was determined within the concentration range of 201–2159 mg/kg and the geometric mean for this range was 569.7 mg/kg (Tab. 1). The highest lead concentrations in soil, which exceeded even the permissible values for industrial areas (600 mg/kg), were determined in samples collected from allotment gardens in the vicinity of "Orzeł Biały" smelter (Jedność – 1383 mg Pb/kg, Górnik – 856 mg Pb/kg, Róża – 623 mg Pb/kg) and in the centre of the town: Azalia – 2159 mg Pb/kg, Pod Lipami – 2035 mg Pb/kg. In the soil of other allotment gardens the lead concentrations were much lower, although still exceeding the permissible value of 100 mg/kg, defined for soil from Group B [18] (Tab. 4).

Cadmium in soils collected from the allotment gardens was determined within the range of: 5.52–58.60 mg/kg (G = 16.86 mg/kg) (Tab. 1). The cadmium contents here were higher than the permissible values defined for soils from Group B, i.e. 4 mg Cd/kg (Tab. 4). Just like in the case of lead, the highest cadmium concentrations were determined in allotment gardens located in the vicinity of "Orzeł Biały" smelter and in the centre of the town, whereas the lowest – in gardens situated far away from the emitter, i.e. in the northern part of the town. The cadmium contents in most of the allotment gardens (54.5%) were even higher than the permissible concentration value for industrial areas, classified for Group C (15 mg/kg) (Tab. 4).

#### Metals in fallow lands

Lead in soil of fallow lands was observed in a very wide range of concentrations: 92.7-9301.0 mg/kg (G = 429.2 mg/kg) (Tab. 2). The lowest lead concentrations, not

Table 4. Lead and cadmium concentrations in soil used for interpretation of results

Comparative values				Literature			
Permissible soil concentration values [mg/kg d.w.]							
Group A	Group B				Group C		
	depth 0-0.3	depth 0-0.3 m			depth 0–2 m	[18]	
50	100		100–200 5–6		600		
1	4				15		
letal content	in agricultural l	and to	psoil in Pola	nd (0–2	20 cm) [mg/kg]		
Silesian Voivodesh	ip $n=2.18$	7	G range		39.8 3.6–5 000.0		
Poland	n = 48 59	n = 48 590 G range			13.6 0.1–5 000.0	[20]	
Silesian Voivodesh	ip n = 2 18	7	G range		0.87 0.08–49.73		
Poland	n = 48 59	90	G 0.21 range 0.01–49.73			1	
content in soi				ılts of I	ETU's own research		
		mg/kg					
	$X \pm SD$						
n = 35	range					[11]	
11 33	$X \pm SD$				(1984)		
	range						
	$X \pm SD$		NEW PLANSES NEW TOTAL OF	- 1		[15]	
n = 8	range		223.0–1017.	5	allotment gardens		
" 0	$X \pm SD$ 24.6 ± 13.2 (198		(1984)	[15]			
	range						
	$X \pm SD$						
n = 20	7(1)						
11 20	$X \pm SD$ range		$16.2 \pm 11.4$ $3.9-47.8$		(1996)	[16]	
	$X \pm SD$					[10]	
n = 8	range		232.0–1111.	8	allotment gardens		
11-6	$X \pm SD$ 22.4±14.2 (1996)		(1996)				
	range		4.6–47.8				
	X range		583.10 171.0–2118.			[8]	
n = 25	X						
Cd	range		4.3-52.3				
n = 28	range		128.9–1996.4 3.3–102.2		allotment gardens,	[7]	
11 20	range				(1991)		
Metal content in topsoil of kindergarten playgrounds – reference area [mg/kg d.w.]							
	G						
n = 28	rang	range		15.53–47.43		[13]	
n = 28		re		0	0.67 38–1.03		
	Group A  50 1  Itetal content in Silesian Voivodesh Poland Silesian Voivodesh Poland content in soi $n = 35$ $n = 8$ $n = 20$ $n = 8$ $n = 20$	$ \begin{array}{c c} & \text{Permissible soil} \\ \hline \text{Group A} & \text{Group B} \\ \text{depth } 0-0.3 \\ \hline 50 & 100 \\ 1 & 4 \\ \hline \\ \text{In etal content in agricultural listic Silesian Voivodeship} & n=2 18 \\ \hline \text{Poland} & n=48 59 \\ \hline \text{Silesian Voivodeship} & n=2 18 \\ \hline \text{Poland} & n=48 59 \\ \hline \text{Silesian Voivodeship} & n=2 18 \\ \hline \text{Poland} & n=48 59 \\ \hline Content in soil in Pickary Silestic Silesti$	Permissible soil concording Group A Group B depth 0-0.3 m  50 100 1 4  Idetal content in agricultural land to Silesian Voivodeship $n = 2 187$ Poland $n = 48 590$ Silesian Voivodeship $n = 2 187$ Poland $n = 48 590$ Content in soil in Piekary Śląskie - [mg/kg] $x \pm SD$ range $x \pm SD$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		

d.w. - dry weight

G – geometric mean

 $X \pm SD$  – arithmetic mean  $\pm$  standard deviation

IETU - Institute for Ecology of Industrial Areas

exceeding the permissible value of 100 mg/kg were observed only in lots number 1 and 18 (98.17mg/kg and 92.7 mg/kg, respectively), located along the northern and southern town boundaries. Lead concentrations determined in other soil samples were higher than the permissible concentration values for soils classified for Group C (Tab. 4). The highest lead concentrations were determined in fallow lands located in the southern districts of the town – near "Orzeł Biały" smelter.

Cadmium in the fallow lands was determined within the concentration range: 2.46-507.30~mg/kg (G = 15.07~mg/kg) (Tab. 2). Cadmium concentrations not exceeding the permissible value defined for soils from Group B – 4~mg/kg were recorded only in two lots situated in the northern part of the town, the most distant from the emitter and at the southern boundary of the town. The highest cadmium contents were recorded in soil samples collected from lots number 3 (507.30~mg/kg) and 4 (71.88~mg/kg), in the immediate neighborhood of the "Orzeł Biały" smelter and its landfills.

# Metals in kindergarten playgrounds

Lead in the topsoil samples from kindergarten playgrounds was determined in the concentration ranges: 64.2-1546.0~mg/kg (G=293.1~mg/kg) (Tab. 3). The lowest lead concentrations, not exceeding the permissible concentration of 100~mg/kg were determined in soil of four kindergarten playgrounds, situated in the northern part of the town (Kindergarten number 2, 7, 8 and 17). Extremely high lead concentrations were observed in the playground of Kindergarten No. 3 (1269~mg/kg) and Kindergarten No. 10 (1546~mg/kg), situated in the centre of the town and in the vicinity of the "Orzeł Biały" smelter.

Cadmium in topsoil collected from the kindergarten playgrounds was observed within the concentration range of 1.30–48.49 mg/kg (G = 8.82 mg/kg) (Tab. 3). In the case of 11 playgrounds the cadmium concentration in soil exceeded the permissible value of 4 mg Cd/kg, in 5 cases exceeding even the value acceptable for industrial areas, i.e. 15 mg/kg (Tab. 4).

The results obtained from determination of lead and cadmium in soil samples collected from allotment gardens, fallow lands and kindergarten playgrounds reflect great diversification of the toxic metal contamination in the area of Piekary Śląskie. Apart from the natural changeability of metal concentrations in soil, which is typical of this region, a relationship between contamination levels and land use patterns or distance of sampling points from the key emitter in Piekary Śląskie, i.e. "Orzeł Biały" smelter can be observed.

The lowest lead and cadmium contamination was observed in the northern part of the town and the extremely high – in all soil samples collected in the direct surroundings of the "Orzeł Biały" smelter. Lead and cadmium determined in allotment gardens and fallow lands were comparative to results of retrospective analyses carried out in Piekary Śląskie in the period of 1984–1996 [7, 8, 11, 15, 16]. In most of the soil samples metal concentrations exceeded the permissible values accepted in Poland [18]. They were much higher than the metal contents in the topsoil of fallow lands in other regions of the Silesian Voivodeship (39.8 mg Pb/kg, 0.87 mg Cd/kg) and higher than the average values calculated for Poland (13.6 mg Pb/kg, 0.21 mg/Cd/kg) [20] (Tab. 4).

No statistically important differences were noticed between soil concentrations of both metals in allotment gardens, fallow lands and playgrounds.

Slightly lower lead and cadmium concentrations determined in the topsoil of kindergarten playgrounds in Piekary Śląskie exceeded also the permissible concentration values defined for built-up and urbanized areas classified for Group B [18]. Metal concentrations in these samples were much higher than the concentrations determined in the kindergarten playgrounds situated in the southern part of the Silesian Voivodeship – in the recreational region of the Beskidy Mountains, which can be referred to as the reference area [13].

Metal contents in soil were compared with concentrations noted in reference and contaminated areas in Poland and abroad.

Mean concentrations of cadmium in soils of about 0.5 mg Cd/kg were published in a number of countries [22]. The median cadmium concentration in surface and subsurface soils was determined to be 0.20 mg/kg (n = 3067) and 0.10 mg/kg (n = 1717), respectively, in a survey of Swedish arable soils [4]. Cadmium in soil in the reference area in China was 0.12 mg/kg (geometric mean) [3]. Cadmium content in soil samples taken from Warsaw county was generally below 0.3 mg/kg. Lead content in these samples was below 12 mg/kg [14]. Cadmium content in surface soils of different countries varied from 0.01–2.7 mg Cd/kg for uncontaminated soil, reaching the value of about 100 mg/kg or more for contaminated soils, with very incidental values observed in heavily contaminated sites, e.g. 1781 mg Cd/kg. The same values for lead in uncontaminated and contaminated soils varied from 4 to 18500 mg Pb/kg [10]. The investigations carried out in the former mining area of northern France showed a wide range of concentrations which varied from 20-3711 mg/kg for lead and from 0.2 to 31.3 mg/kg for cadmium [19]. The range of cadmium in soil samples from eastern Turkey were 3.3-13.4 mg Cd/kg soil (mean 5.9 mg Cd/kg) [21]. Cadmium in soil near the smelter in southern China was 22.06 mg/kg (geometric mean) [3]. Concentrations of heavy metals in 50 soil samples (0-20 cm) taken from the vicinity of the smelter near Ploydiv in Bulgaria were: 0.33-87 mg/kg for cadmium and 46-4196 mg/kg for lead [2]. Studies conducted in 1995 in similar areas showed the following values: 1.2–22.5 mg/kg (cadmium) and 85–550 mg/kg (lead) [5].

The comparison presented above shows that metal contents abtained in our study are typical of very contaminated sites.

#### **CONCLUSIONS**

Based on the carried out assessment of lead and cadmium soil concentration in Piekary Śląskie, representing different development and land use patterns, the following conclusions can be drawn:

Soil from allotment gardens and fallow lands was heavily contaminated with lead and cadmium. Metal concentrations determined in all soil samples exceeded the values permissible in Poland.

In most kindergarten playgrounds the topsoil was contaminated with lead and cadmium. Concentrations of these metals exceeded the permissible values defined for recreational and built-up areas.

The highest concentrations of lead and cadmium were recorded in the vicinity of the main emitter—"Orzeł Biały" Non-Ferrous Metal Smelter (located in the southern part of the town) and in the centre, whereas the lowest ones were observed in the northern part.

The current results are similar to those obtained from the Institute for Ecology of Industrial Areas own retrospective research on lead and cadmium concentrations in allotment gardens and agricultural lands in the area of Piekary Śląskie.

## FINAL REMARKS

High concentrations of toxic metals – lead and cadmium – determined in soil, should contribute to stopping edible plants cultivation in the area of Piekary Śląskie. Accumulation of heavy metals in soil can result in their excessive uptake by plants and pose risk to plant consumers – people and animals. On the basis of observations made during the sampling campaign it was noted, however, that in most of the allotment gardens vegetable plants were not cultivated at all and in very few gardens they were cultivated only on a small area. The allotment gardens are mainly used for recreational purposes, as well developed green oases, covered with decorative plants, shrubs and trees. The ecological awareness of their users is quite high due to various information campaigns launched in this region on the allotment garden contamination and the health impact of the consumption of contaminated agricultural crops.

The obtained results also indicated that the contaminated soil in the kindergarten playgrounds might constitute an important environmental source of lead and cadmium contamination posing threat to the children's health. The observed health risk should become a stimulus for undertaking modernization actions at playgrounds aimed at reducing the children's contact with heavy metal contaminated soil.

Summing up, it can be concluded that in the context of the applied assessment criteria the soil concentrations of these metals in the Piekary Śląskie area should arouse great concern among its users and local authorities.

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# OCENA ZANIECZYSZCZENIA GLEB OŁOWIEM I KADMEM NA OBSZARZE ODDZIAŁYWANIA HUTY METALI NIEŻELAZNYCH

Celem pracy było dokonanie oceny stanu zanieczyszczenia metalami toksycznymi gleb na obszarze miasta Piekary Śląskie (województwo śląskie) z uwzględnieniem sposobu ich użytkowania. Zakres badań obejmował oznaczenie stężeń ołowiu i kadmu w glebach kompleksów ogrodów działkowych, nieużytków rolniczych i przedszkolnych placów zabaw. Stężenia ołowiu i kadmu w próbkach gleb oznaczano techniką płomieniowej spektrofotometrii atomowo-absorpcyjnej po ekstrakcji wodą królewską w mikrofalowym systemie MDS 2000. Zawartości metali w analizowanych próbkach gleb były bardzo zróżnicowane i zależały od lokalizacji miejsc ich poboru w stosunku do najważniejszego emitora metali toksycznych w Piekarach Śląskich – Huty Metali Nieżelaznych "Orzeł Biały" S.A. Stężenia metali oznaczone we wszystkich próbkach gleb przekraczały znacznie wartości stężeń dopuszczalnych w Polsce w glebach uprawnych i gruntach zabudowanych. Zawartości ołowiu i kadmu w glebach powinny być podstawą do zaprzestania upraw roślin jadalnych w badanych rejonach miasta Piekary Śląskie. Zanieczyszczona gleba na przedszkolnych placach zabaw może stanowić istotne środowiskowe źródło ołowiu i kadmu zagrażające zdrowiu dzieci. Stan zanieczyszczenia placów zabaw metalami toksycznymi powinien zobowiązywać do podejmowania działań modernizacyjnych ograniczających kontakt dzieci z glebą. W świetle zastosowanych kryteriów oceny wyników, zawartości metali występujące w glebach na obszarze Piekar Śląskich powinny budzić niepokój ich użytkowników i władz miasta.