

Geochemical and statistical approach to evaluate background concentrations of Cd, Cu, Pb and Zn (case study: Eastern Poland)

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Abstract An attempt was made to evaluate background concentrations of Cd, Cu, Pb and Zn by means of geochemical and statistical approach. As many as 753 samples taken from 51 profiles located in Eastern Poland were analysed. For the estimation of geochemical background values, direct geochemical methods and a statistical analysis for the whole population of samples were applied. Average values of heavy metal concentration in loess sediments (bedrock) as well as in profiles not affected by human activity were measured. The iterative 2σ technique and calculated distribution function were chosen as statistical methods. The resulting values (background concentrations range) were as follows: Cd 0.5–0.9 mg kg⁻¹, Cu 5–16 mg kg⁻¹, Pb 12–26 mg kg⁻¹ and Zn 31–47 mg kg⁻¹. All the methods applied gave similar results. The highest deviation of the background was noted for Cu and the lowest for Zn. The lowest values of background were obtained for loess sediments and the highest in the case of the multiple 2σ method.

Keywords Geochemical background · Heavy metals · Sediments · Eastern Poland

Introduction

Knowledge of the geochemical background (background concentrations) is the basic question when considering the

human impact on geochemical parameters of soils and sediments. It enables the qualification of the part of the elements or compounds that natural and one that is a result of human activity. The problem was considered in numerous geochemical investigations, such as Salminen and Tarvainen (1997), Tobias et al. (1997), Tarvainen and Kallio (2002), Horckmans et al. (2005), Wu et al. (2007), Zhang et al. (2007) and Appleton et al. (2008). The concept of the geochemical background is used universally, but it is often ambiguously defined. Reimann and Garrett (2005) quote 11 definitions for the term. Most often the geochemical background is understood as a concentration of the studied elements or chemical compounds in samples not affected by contamination of an anthropogenic character. Ambiguous definitions and measurements of the geochemical background produce many problems and equivocality (Matschullat et al. 2000; Reimann and Garrett 2005). For example, Gałuszka (2007) pointed out the fact that all chemical analyses in “natural” samples not only reflect natural processes, but also a diverse human impact.

The methods of valuation of the geochemical background are divided into two basic groups: direct (geochemical) and indirect (statistical). The following approaches are possible:

1. global or regional background usage,
2. analysis of samples not influenced by humans (basis rocks),
3. analysis of sediments from the period before intense human activity,
4. statistical methods.

The concept of a global standard of the background value is more often criticised because of considerable differences of a regional and even local character; many factors influence the natural concentration of elements

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whose spatial distribution is not equal (Reimann and Garrett 2005). The usage of geochemical parameters of basis rocks as natural values also faces some problems. They were formed in geochemical conditions different than the present ones and, therefore, the concentrations of elements natural for them are different than the present day ones. Sediments or the soils studied may also have different sedimentological or lithological (grain size composition, organic matter content) features from the basis rocks. In the case of determining the geochemical background by measuring the concentration in older (deeper) sediments, the idea of the lack of human influence before the Industrial Revolution is the basic concept. Such an assumption seems to be very risky in the light of the latest results (Küster and Rehfuess 1997; Matschullat et al. 1997; Weiss et al. 1997; Martinez Cortizas et al. 2002). The location of borders between natural formations (not affected by human impact) and contaminated layers becomes problematic.

Matschullat et al. (2000) presented a review of the statistical methods of geochemical background determination. Generally, these methods depend on the elimination of extreme samples to obtain a normal distribution for the analysed population. However, the fulfilment of several essential conditions is necessary: the use of suitable research methodology, homogeneity of collected samples, a sufficient number of samples and human impact limited to enrichment in contaminants only. Different statistical methods were used to quantify the geochemical background: the test of 4σ extreme values elimination, iterative 2σ technique, calculated distribution function and many

others (Tobias et al. 1997; Matschullat et al. 2000; Migażewski et al. 2004; Zhang et al. 2007). It should be underlined that the application of various statistical methods for the same population of samples does not give the same results (Matschullat et al. 2000; Gałuszka 2007).

The best solution seems to be use of geochemical and statistical methods simultaneously. Such an approach has been proposed in the present work to estimate the background concentrations for Cd, Cu, Pb and Zn in slope and river sediments in the western part of the Lublin Upland (Eastern Poland) (Fig. 1). For this area, number data concerning natural concentrations of these potentially toxic elements to humans and the environment are very limited. As the Lublin Upland is an area of intense agricultural production, knowledge of the intensity of geochemical human impact is extremely essential.

Area studied

The Lublin Upland has been under human impact for about 5,000 years, mainly through agricultural land use. At present, arable land covers nearly 60% of the area. The main crops are cereals (wheat and barley dominate), potatoes and sugar beets. Dry and wet fallout, fertilisers, municipal and industrial sewage and waste are the sources of deposited contaminants. Atmospheric deposits dominate in settlements and slope soils (Nicholson et al. 2003; Dach and Starmans 2005); however, the most important source in river valleys is contamination

Fig. 1 Location of the studied profiles in the context of terrain relief and important sources of pollutants in the western part of the Lublin Upland; 1 studied sites, 2 places of sewage discharge, 3 bigger dumping sites, 4 major cities. (relief—shaded relief map of Lublin Province, prepared by L. Gawrysiak)

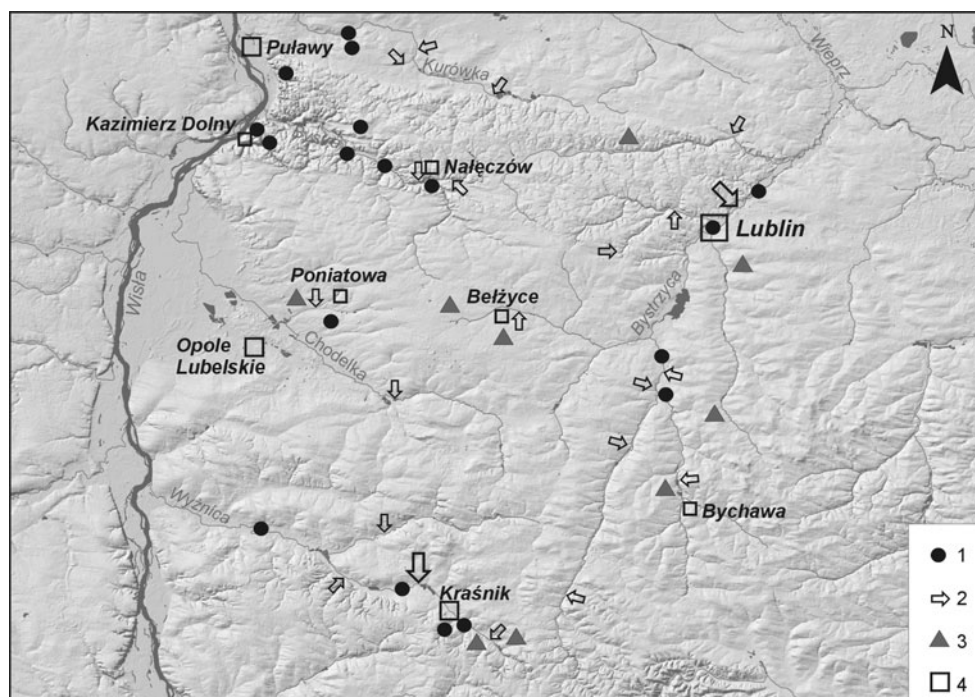


Table 1 Content of heavy metals in fluvial sediments of the Lublin province in 2004

River	Site	Cd (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)
Bug	Krzyszew	0.1 (<0.5)	2 (4)	<5 (<5)	16 (24)
Krzna	Neple	0.1 (<0.5)	1 (2)	<5 (<5)	16 (24)
Wieprz	Dęblin	3.0 (2.7)	6 (7)	7 (8)	38 (48)
Bug	Kryłów	0.2 (<0.5)	11 (8)	9 (6)	52 (43)
Bystrzyca	Spiczyn	65.5 (7.8)	46 (36)	63 (61)	305 (132)
Geochemical background		<0.5	7	15	<48

Data for 2002 in brackets (Raport o stanie środowiska województwa lubelskiego. WIOŚ, Lublin. 2006)

transported in the water. This is commonly proved by differentiation of their concentration in floodplains (Taylor 1996, Martin 2000). Lublin is the only larger city in this area, and the number of hazardous industrial plants is less than five.

According to the Atlas Geochemiczny Polski (1995), water sediments of the studied area are characterised by low concentrations of heavy metals: Cd < 1 mg kg⁻¹, Cu 10–20 mg kg⁻¹, Pb < 25 mg kg⁻¹, Zn < 100 mg kg⁻¹. Geochemical monitoring delivers similar data for the sediments of the Lublin province (Table 1). It should be emphasised that monitoring comprises only five location points. The geochemical background level of water sediments exceeded considerably only in one measuring point (the alluvia of the Bystrzyca River) for Cd, Cu, Pb and Zn. Particularly high concentrations of cadmium were observed and exceeded the geochemical background by 130 times.

High concentrations of heavy metals in the alluvia of the Bystrzyca river below the sewage dump point from the Lublin municipal sewage treatment plant were noticed by Bojakowska and Sokołowska (1996). The contamination of sewage by Cd, Co, Cu, Hg, Ni and Zn was observed along the whole section studied. The highest content of these elements was detected in samples taken in the closest neighbourhood of the river channel.

Materials and methods

In the work, 753 samples taken in 51 profiles located in the western part of the Lublin Upland were studied (Fig. 1; Table 2). The samples were collected with the Eijkelkamp sampler. Continuous cores were cut into 10 cm sections. At several points samples were obtained from characteristic levels of sediment exposures. The field work was conducted in the years 2006–2007. All samples were dried at 105°C, crumbled in a porcelain mortar and sieved with a <1 mm diameter steel sieve. Analyses of heavy metal concentration were executed in the <0.2 mm fraction according to the methodology applied in Poland for water sediments (Bojakowska and Sokołowska 1998).

Table 2 Types of analysed profiles

	Number of profiles	Number of samples
Natural profiles and Holocene soils	5	60
Slope sediments	11	176
Sediments of dry valleys	6	71
Sediments of river valleys (within agricultural areas)	6	122
Sediments of river valleys (within urban and industrial areas)	13	194
Archaeological sites	10	100
Loess samples	–	15
Other samples	–	15
Total	51	753

The acid decomposition of the samples was conducted with the aqua regia method (ISO 11466/2002). Cadmium, Cu, Pb and Zn concentrations were determined by ASA method (Spectr AA 880 Varian spectrometer, UMCS Analytical Laboratory). The spectrometric detection limits for the studied elements are as follows: Cd 0.006 mg kg⁻¹, Cu 0.03 mg kg⁻¹, Pb 0.1 mg kg⁻¹, Zn 0.008 mg kg⁻¹. The minimum measurable contents in the samples are: Cd 0.2 mg kg⁻¹, Cu 1.25 mg kg⁻¹, Pb 4.1 mg kg⁻¹, Zn 0.3 mg kg⁻¹.

The correctness of the applied methodology for heavy metal determination was checked with SAN JOAGUIN SOIL CRM 2709 reference material. The decomposition method used in this study permitted the separation of as much as 80–90% of the studied elements (see Table 3). Additionally, the digestion method enabled the detection of metals in unstable forms (Bojakowska and Sokołowska 1998).

The estimation of background concentrations of Cd, Cu, Pb and Zn was done based on their concentration in loess sediments (basis rock, tens of thousands of years old) and natural profiles (not influenced by human activity, except for the surface layers), as well as by statistical methods: the iterative 2σ technique and the calculated distribution function for 753 samples. Loess samples (in situ) were taken in 15 points. The sediment was collected in

Table 3 Certified and determined content of heavy metals in reference material SAN JOAGUIN SOIL CRM 2709

Element	Cd	Cu	Pb	Zn
Certified content (mg kg ⁻¹)	0.38 ± 0.11	34.6 ± 0.7	18.9 ± 0.5	106.0 ± 3.0
Measured content (mg kg ⁻¹)	0.32 ± 0.12	27.8 ± 0.9	17.3 ± 0.7	86.1 ± 4.0

Table 4 Basic statistical data of physical and chemical parameters of the studied samples (for mineral sediments)

	Content of fraction (%) ¹			pH ²	Organic matter content (%) ³
	Sandy	Silty	Clay		
Mean (mg kg ⁻¹)	37.7	53.2	9.1	–	3.3
Median (mg kg ⁻¹)	30.0	61.0	9.0	6.1	1.9
Standard deviation (mg kg ⁻¹)	22.7	19.5	4.3	–	3.8
1st quartile (25%)	22	45.2	6	5.0	1.0
3rd quartile (75%)	46	67.0	12	7.1	4.0

1 *n* = 599 samples (all mineral samples), *2* *n* = 630 samples (all samples, 4 profiles were not analysed), *3* *n* = 379 samples (samples from upper parts of profiles: 0–100 cm)

exposures with minimum 1 m depth under the surface, as well as about 30–40 cm depth from the surface of the loess walls. Additionally, samples from a nearly 14-m deep profile of loess sediments were analysed. Profiles referred to as “natural” consist of Holocene Luvisols and colluvial sediments deposited in the period of very limited geochemical human impact—samples were older than 1,000 years. Altogether 60 samples were analysed. The iterative 2σ technique is applied to obtain the normal distribution of the concentrations. At first one has to calculate the mean and standard deviation for the original data set. Next, all values beyond the mean $\pm 2\sigma$ are omitted. The procedure is repeated until all values lie within this range. The calculated distribution function method is based on the assumption that the lowest values of concentrations are not influenced by human impact. The data set from the minimal value to the median represents the natural background. Such an idea allows construction of the distribution function not affected by anthropogenic outliers. The second part of the function is created by “mirroring” every value against the median by adding the distance from the value to the median (Matschullat et al. 2000). The new data set represents the normal range of the natural background.

Results

The basic characteristics (% grain size, pH and organic matter content) of the studied sediments are listed in Table 4. The samples show a dominance of the silt fraction (loess and loess-like sediments); less frequently silty sands and loose sands appear. The median value of pH calculated for all samples equals 6.1 (range 2.1–8.1); 75% of the

studied samples show pH was greater than 5. This means that more than 50% of the studied samples have slightly acidic or neutral pH. Organic matter content in the studied profiles is fairly diversified: the standard deviation (3.8%) is larger from the mean value (1.9%). Most samples (80% of the studied population) reveal low and average content of organic matter.

Frequency distributions of heavy metal content in the studied samples show a high right-sided slant. It is related to less numerous occurrences of the extreme values (outliers), a feature characteristic of environmental contaminants. The most highly asymmetric graphs were obtained for Cu followed by Pb, Cd and Zn (Fig. 2). A significant number of samples with small concentrations as well as a small number of extremely high contents prove that basic statistical parameters calculated for the studied populations do not reflect their features well (Table 5). One of the results may be the overestimation of the mean value due to the presence of outlier values. It is particularly evident in the case of Cu: its mean value is three times as high as the median and twice as high as the third quartile. It seems that in such a case the median is the right parameter which adequately shows the relations between the absolute values of the elements studied (Table 5). Loess samples are characterised by similar mean and median values.

The medians of the concentrations of the individual elements calculated for all samples are as follows: Cd 0.5 mg kg⁻¹, Cu 7.0 mg kg⁻¹, Pb 16 mg kg⁻¹, Zn 32 mg kg⁻¹. The highest concentrations are: Cd 10.3 mg kg⁻¹, Cu 1073 mg kg⁻¹, Pb 223 mg kg⁻¹, Zn 79 mg kg⁻¹ (Table 5). In the case of copper, the maximum determined concentration is 153 times higher than the median, for Cd and Pb it is 19 and 14 times, respectively,

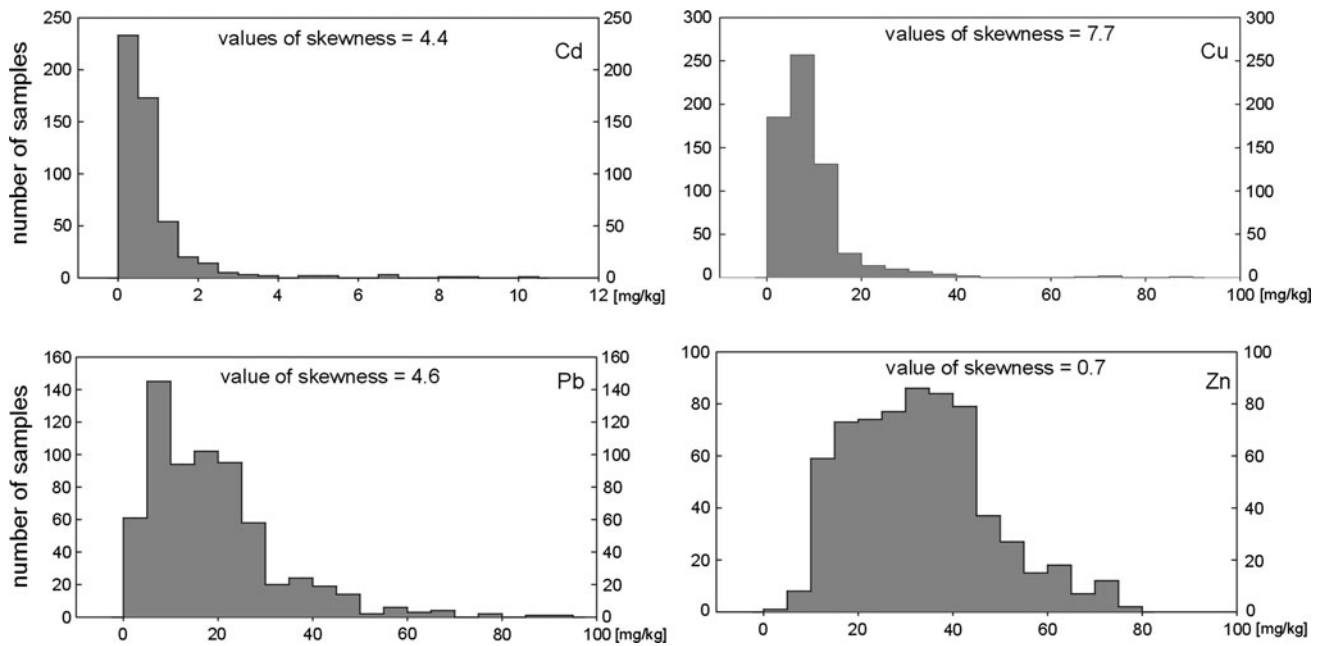


Fig. 2 Concentration histograms: Cd ($n = 401$), Cu ($n = 642$), Pb ($n = 650$) and Zn ($n = 659$) in the studied samples (extremely high values were discarded)

Table 5 Basic statistical coefficients of Cd, Cu, Pb and Zn concentrations

	Cd	Cu	Pb	Zn
Loess samples				
Mean (mg kg^{-1})	0.5	5.6	12.3	34.9
Median (mg kg^{-1})	0.5	5.5	12.2	34.6
Standard deviation (mg kg^{-1})	0.3	2.7	3.2	5.3
Highest value (mg kg^{-1})	0.8	9.1	22.5	37.6
Lowest value (mg kg^{-1})	0.0	1.9	5.7	17.9
All samples				
Mean (mg kg^{-1})	0.75	23.4	20.3	32.9
Median (mg kg^{-1})	0.53	7.0	16.3	32.0
Standard deviation (mg kg^{-1})	1.07	106.6	20.6	14.6
Highest value (mg kg^{-1})	10.3	1,073.0	223.0	79.7

whereas for zinc 2.5 times only. Such large variations in the concentration are proved by standard deviation values. For copper they are several times higher than the median and average values, for cadmium and lead they are approximately average and for zinc twice as low (Table 5). It should also be stated that for all analysed data, there are samples containing concentrations of Cd, Cu and Pb below the limit of detection. The average content in loess samples are (data for samples from deep loess profile in brackets): Cd 0.6 mg kg^{-1} (0.4 mg kg^{-1}), Cu 3.3 mg kg^{-1} (6.9 mg kg^{-1}), Pb 10.2 mg kg^{-1} (14.3 mg kg^{-1}) and Zn

35.4 mg kg^{-1} (35.2 mg kg^{-1}). These concentrations of heavy metals constitute the special reference level: loess sediments are not affected by geochemical human impact (Table 6).

Discussion

There are a number of data concerning “the natural level” of concentrations of various elements in the soils of Poland. For example, Czarnowska (1996) suggested the general content of heavy metals in bed-rocks as a geochemical background for soils produced from them. Slope sediments are less often studied than soils and alluvia. This causes lack of any information concerning background concentrations. Some data, based on a few measurements, may be found in a paper by Zgłobicki and Rodzik (2007). In the case of alluvia, a larger number of studies are available. Most frequently, the data proposed by Bojakowska and Sokołowska (1998) are accepted. These authors specify the geochemical background for water sediments in Poland by analysing the concentration of heavy metals in the alluvia of several Polish rivers. This is the only study presenting a complex classification of geochemical types of sediments for the whole country.

When comparing the data listed in Table 6 we note that the lowest and, simultaneously, very similar values of the geochemical background were obtained for loess by

Table 6 Geochemical background for slope and river sediments and soils

Data after other authors	Cd	Cu	Pb	Zn
Geochemical background for water sediments in Poland ^a	<0.5	6	10	48
Natural content in river sediments ^b	1	20	50	73
Content in surface levels of European soils (median) ^c	0.14	13.0	22.6	52
Content in water sediments of Europe (median) ^c	0.3	16	16	56
Geochemical background				
For loess ^d	0.0	4.6	6.8	17.8
Multiple 2 σ technique ^d	0.1	6.3	7.3	19.6
Geometric mean ^d	0.1	5.3	8.5	22.5
Geochemical background for loess soils ^e	0.23	6.0	7.6	22.0
Results of the study				
Mean content in loess ^f (A)	0.5	5	12	34
Mean content in natural profiles (B)	0.5	3	18	31
Multiple 2 σ technique ^g (C)	0.9	11	26	47
Distribution function method ^g (D)	0.8	16	21	31
Mean (results of the study)	0.7	9	19	35

Values are expressed as mg kg⁻¹

^a Bojakowska and Sokołowska (1998), ^bGeochemiczny Atlas Polski (1995), ^cGeochemical Atlas of Europe (2006), ^dZgłobicki and Rodzik (2007), ^eCzarnowska (1996), ^fanalysis of 35 loess samples, ^ganalysis of 753 samples taken from the western part of the Lublin Upland. Background concentrations obtained by various methods. A loess sediments, B natural profiles, C iterative 2 σ technique, D calculated distribution function method

Czarnowska (1996), as well as Zgłobicki and Rodzik (2007). In the case of Cd and Pb mean geochemical background reported in the paper is higher than mean content in water sediments of Europe (median), while for Cu and Zn is lower. Zgłobicki and Rodzik (2007) reported less diversified and lower values, especially in the case of Cd and Cu. However, the colluvial sediments studied in the above-mentioned paper come primarily from agricultural areas. Moreover, most of the samples represent old sediments (>1,000 years old). In general, the values calculated in this work for the Lublin Upland, especially for loess sediments, are similar to the geochemical background of water sediments in Poland proposed by Bojakowska and Sokołowska (1998). However, the mean values for Pb are almost twice as high. In the case of Cd and Cu, mean geochemical background is 40–50% higher. In general, background concentrations obtained in the study for loess and natural profiles are similar. The application of statistical methods for the analysed data set produces higher values, especially for copper, cadmium and lead (iterative 2 σ technique), see Table 6. Values obtained by means of statistical methods were 230% higher in comparison to geochemical methods for Cu, while in the case of Cd and Pb 60% higher. The lowest difference occurred in the case of Zn (20%). However, it should be mentioned that the first two methods (A and B) are based on the results obtained from colluvial sediments, much less contaminated than alluvial sediments, prevailing in the data set (Table 2). The

background, determined by concentration in loess, reflects the state of the geochemical environment before the start of human activity. As it was mentioned before the “loess background” is similar in absolute values to those obtained for natural profiles. Nevertheless, the latter reveal a generally higher content of organic matter, which favours binding heavy metals. We also note that even in the case of loess sediments not affected by human activity, the concentrations of the studied elements vary considerably (Fig. 3). The highest is for lead: 6–21 mg kg⁻¹ and lower for the remaining elements: Cd 0.0–0.8 mg kg⁻¹, Cu 4.5–10.0 mg kg⁻¹ and Zn 30.0–40.0 mg kg⁻¹.

Statistical methods are based on an analysis of the whole population of samples under smaller or larger human impact. Despite using suitable statistical processing, total elimination of anthropogenic influence is not possible. For this reason, the resulting values of background concentrations were clearly higher than those obtained by direct methods. We should also remember that the studied samples varied considerably (grain size distribution, pH, organic matter content), see Table 4.

Considering the data listed in Table 7, we may note that all methods applied reveal a similar degree of reliability of the results, measured as background deviation from the average values. The element which gave the most varied values of background concentrations is copper (52.5%), and one with the smallest values is zinc (14.5%) (Table 7; Fig. 4).

Fig. 3 Concentrations of Cd, Cu, Pb and Zn in the loess profile

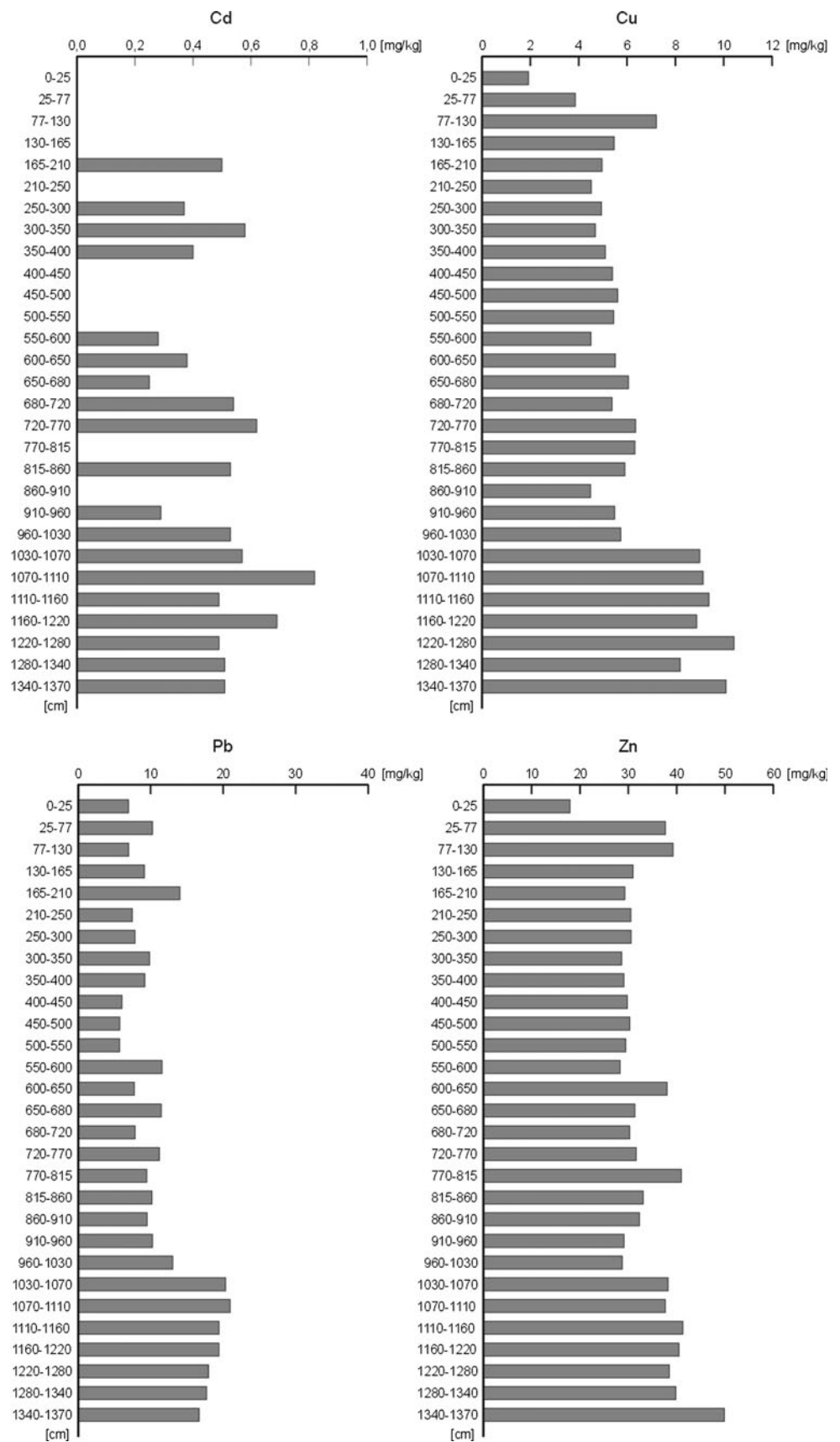


Table 7 Comparison of background concentration values obtained by four methods

	Cd	Cu	Pb	Zn	Sum
A	28	44	36	2	110
B	28	66	5	11	110
C	28	22	36	34	120
D	14	77	10	11	115
Sum	98	209	87	58	

Values are expressed as W (%)

$W_A = [(S-A)/S] \times 100\%$, where $S = (A + B + C + D)/4$; S mean background concentration (Table 6)

W_A index of background deviation (from the mean values); background concentrations obtained by various methods. *A* loess sediments, *B* natural profiles, *C* by the iterative 2σ technique, *D* by the calculated distribution function method

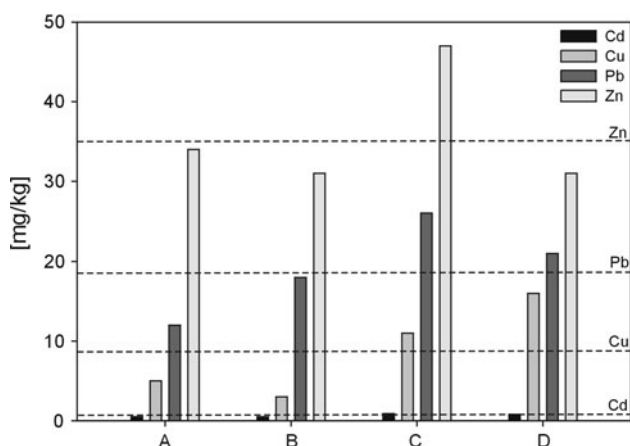


Fig. 4 Background concentrations obtained by various methods. *A* mean content in loess sediments, *B* mean content in natural profiles, *C* the iterative 2σ technique, *D* the calculated distribution function method. Broken lines mark the average value of the background

Conclusions

1. The clastic sediments analysed are characterised by a very large diversity of heavy metal concentration. Standard deviation in the case of copper was several times as high as the average value and median, similar in the case cadmium and twice as low in the case of zinc.
2. Values of background concentrations for Cd, Cu and Pb calculated by statistical methods, are considerably higher than those obtained by direct (geochemical) methods. This difference was smaller in the case of Zn.
3. All the methods applied gave similar results. The highest deviation of the background was noted for copper and the lowest for zinc.
4. The mean background concentration calculated for lead was considerably higher than published previously. It was also higher in the case of cadmium and copper (40–50%).

5. The mean geochemical background is exceeded in 36% of the samples in the case of copper and cadmium and 42% of the samples in the case of lead and zinc. This confirms the thesis of low contamination of sediments by heavy metals in the area studied.

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