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IMPACT OF PHYSICOCHEMICAL CHARACTERISTICS OF COLLUVIAL AND ALLUVIAL SOILS ON Cd, Cu, Pb AND Zn CONTENT (EAST POLAND)

Abstract. The physical and chemical parameters of soils play an important role in the binding and migration of trace elements in the environment. The study attempts to assess the correlation between the basic characteristics of colluvial and alluvial soils and the concentration of Cd, Cu, Pb and Zn. This will make it possible to indicate the key factors determining the binding of metals in soils. The studied soils were located in an agricultural region in Eastern Poland and subjected to generally low anthropogenic pollution. Sixteen profiles (160 samples) were analysed for total heavy metals content and selected soil properties: grain size distribution, soil organic matter (SOM) content, pH, Fe and Mn content. We used three statistical methods: principal component analysis, cluster analyses and Pearson`s correlations coefficient. Relations for colluvial and alluvial soils were different. SOM content was characteristic for the highest positive correlations with the heavy metals. The most distinct correlations with this parameter occur in the case of lead. No correlations with pH were found, the correlations with the particular fraction content were weak. Strong but diversified correlations occurred in the case of Fe and Mn. In general stronger correlations with soil characteristics were found for samples with the low heavy metals content; anthropogenic impact causing the disruption of natural correlations.

The content of heavy metals and other elements in soils is determined by the impact of numerous factors of natural and anthropogenic nature. The most important of those factors are: the type of parent rock, soil organic matter (SOM) content, pH, mechanical composition, content of other elements, location of the

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profile (geomorphological determinants), local hydrologic conditions, intensity and nature of anthropogenic supply [2, 7, 14, 20].

Numerous studies have dealt with the question of the correlation between heavy metals concentrations and selected sediment parameters, such as grain size distribution, pH, and organic matter content [e.g. 4, 9, 11, 15, 25 and many others]. The parameters above are the key factors responsible for the adsorption of metals by soils and their migration, i.e. the basic chemical processes causing the contamination of soils with heavy metals [6, 21]. However, the results obtained so far are not unequivocal.

The main objective of the study has been to assess the impact of the basic physicochemical parameters: SOM content, grain size distribution, pH and Fe, Mn content of two soil types on the total Cd, Cu, Pb, and Zn concentrations. The influence of the soil type and total heavy metals content on the intensity of studied relations has also been evaluated. Studied soils are located within the area of low heavy metals pollution, that is why relations between soil characteristics and heavy metals content should be more clear.

STUDY METHOD AND AREA

Study Area

The western part of the Lublin Upland has been subjected to anthropogenic pressure for 5 000 years; human influence has been manifested primarily in the agricultural use of land. The only large city is Lublin, and there are not more than five industrial plants with a very high environmental impact. The results of monitoring studies indicate the generally low degree of soil contamination with heavy metals [10, 22]. The same applies to the geochemical parameters of water sediments. The geochemical background is clearly exceeded in the case of only one measurement point (alluvial sediments deposited by the Bystrzyca River). It should also be mentioned that human activity modifies heavy metals content as well as sediment and soil parameters, such as grain size distribution, organic matter content and pH [18,22].

Methods

In the study, samples collected in 16 profiles in the western part of the Lublin Upland were analysed (Figure 1). The studied soils were divided into two groups: a) colluvial soils (Eutric Cambisols, A_p-B_{br}-C_{Ca}), b) alluvial soils (Eutric Fluvisols, A-AC-C). Studied colluvial soils were located in dry valley bottoms and cultivated. We took samples of alluvial soils from the bottoms of small river valleys (Bystra, Bystrzyca, Wyżnica). They are used as pastures. Samples were collected by means of an Eijkelkamp sampler. We applied continuous sampling instead of taking samples from the specific soil horizons. Vertical changes of soil horizons were represented by the diversity of characteristics like SOM, pH, grain size distribution, etc. The soils were sampled up to 100 cm and cores were divided into 10 cm sections. The collected material was air dried, ground in a porcelain mortar, and sieved through a steel 1 mm mesh sieve.

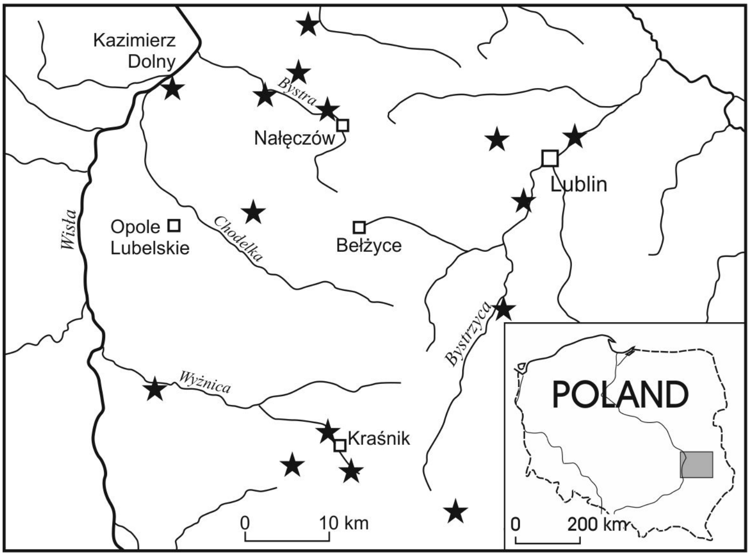

Figure 1. Location of studied soil profiles.

The samples were analysed in terms of the basic physical and chemical characteristics of soils: grain size distribution, pH, and soil organic matter (SOM) content. The pH was determined potentiometrically in KCl. The incandescence method (550°C) was used to assess the organic matter content. The grain size distribution was determined using the Malvern Mastersizer 2000 laser analyser. For the purposes of this study, the following particle diameters were adopted for the major fractions: sand (0.05–2.0 mm), silt (0.002–0.05 mm), clay (<0.002 mm).

The mineralisation of the samples was carried out with the use of aqua regia, according to the ISO 11466/2002 standard. Zinc, cadmium, copper, and lead were determined using the ASA method (Spectr AA 880 Varian spectrometer). The minimum detected content in a sample was as follows: Cd – 0.2 mg/kg, Cu – 1.25 mg/kg, Pb – 4.1 mg/kg, Zn – 0.3 mg/kg. SAN JOAQUIN SOIL CRM 2709 reference material was used to verify the applied method (Table 1). Fe and Mn content was also analysed by means of the ASA method.

TABLE 1. CERTIFIED AND DETERMINED CONTENT OF HEAVY METALS IN REFERENCE MATERIAL SAN JOAGUIN SOIL CRM 2709

	Cd	Cu	Pb	Zn
Certified content [mg/kg]	0.38 ± 0.11	34.6 ± 0.7	18.9 ± 0.5	106.0 ± 3.0
Measured content [mg/kg]	0.32 ± 0.12	27.8 ± 0.9	17.3 ± 0.7	86.1 ± 4.0

PCA is a multivariate statistical technique that reduces the original multidimensional space to a new lower dimensional space which is used to explain relationships among variables. This method was used to analyse all 11 variables (7 soil characteristics and 4 metal contents) separately for each depth range. A reduction of the number of dimensions and, consequently, the number of the analysed parameters in the collected samples would be justified if the same parameters were responsible for the strongest variation in each group analysed. When carrying out the PCA analysis, we were looking for parameters that could be regarded as key ones for analysing soil profiles.

The PCA also provides a visual representation of correlations between the principal components. Loading vectors with a positive mutual correlation are situated close to each other, vectors with a negative correlation are diagonal to each other, and when no correlation occurs, vectors are perpendicular to each other. The longer the vector the greater the impact of a particular factor on the principal component.

Pearson's coefficients were calculated to determine the degree of the linear correlation between the content of the heavy metals and the selected soil characteristics (SOM content, pH, and percentage share of three major fractions). For the analyses below, the significance level of 5% (α=0.05) was adopted. The computations were carried out for the entire population of samples divided into two groups of soils (colluvial and alluvial) as well as were calculated separately for sample subpopulations with varying metal content in relation to the geochemical background and with diverse origin of soil material.

The cluster analysis was carried out to find the characteristic features of certain profile groups. These would make it possible to concurrently distinguish groups of profiles with specific parameters as well as categorise profiles according to parameters other than profile origin. The cluster analysis is based on grouping data in separate classes with statistically homogeneous parameters. We conducted two three-dimensional analyses, separately for the metals and for the most important parameters of the samples (SOM, pH, and clay content). The obtained groups were analysed in terms of the other characteristics, which made it possible to identify the correlations between the components on which the grouping was based and the other components.

RESULTS

Soil Characteristics

The alluvial soils have a higher SOM content, a neutral pH, higher Fe, and lower Mn content, while the mean clay fraction content is similar in both types of soils (Table 2). A high variation of the SOM and clay fraction content were found within the entire population.

TABLE 2. THE BASIC STATISTICAL DATA FOR THE CHARACTERISTICS OF SOILS

	SOM [%]		pH		Clay [%]		Mn [mg/kg]		Fe [mg/kg]	
	C	A	C	A	C	A	C	A	C	A
Mean	1.5	4.4	6.0	6.9	9.9	11.0	390.2	283.8	8301	9447
Median	1.3	4.0	5.7	7.2	9.4	10.3	384.8	284.4	8494	10278
Minimum	0.3	0.1	4.0	4.3	2.4	2.8	113.8	142.0	5987	4012
Maximum	4.7	14.8	8.0	7.8	21.0	27.9	692.7	403.6	11131	13016

C – colluvial soils, A – alluvial soils.

Vertical diversity of the selected parameters is related to soil horizons. The SOM content decreases along with increasing depth; this process is particularly distinct in alluvial soils. The mean content is 9.5 % in the 0–10 cm layer and only 1.3 % in the 90–100 cm layer. In the case of colluvial soils, the values of the mean SOM content are clearly lower: 2.9-2.4% in the 0–20 cm layer (ploughing horizon), the content falling to about 1% at the depth of 50–60 cm and remaining at this level to the depth of 100 cm (Table 3).

TABLE 3. AVERAGED CHARACTERISTICS OF SOILS DEPENDING ON DEPTH

Depth [cm]	SOM [%]		pH		Sand [%]		Silt [%]		Clay [%]		Fe [mg/kg]		Mn [mg/kg]	
	C	A	C	A	C	A	C	A	C	A	C	A	C	A
0–10	2.9	9.4	5.9	6.5	30.0	27.8	53.2	55.2	9.8	10.2	10813.0	6046.0	325.8	327.3
10–20	2.4	6.8	5.6	6.2	29.7	15.9	53.9	71.6	9.9	10.1	7570.0	12185.8	342.9	340.6
20–30	1.8	6.1	5.6	6.5	30.9	18.2	52.2	65.4	9.4	10.0	7829.7	10494.8	349.3	343.4
30–40	1.4	5.4	5.7	6.6	33.5	18.2	49.7	64.7	8.8	11.0	7760.4	10534.5	388.4	348.0
40–50	1.2	4.0	5.8	6.8	33.8	15.3	47.8	70.2	8.7	10.6	7707.1	11121.0	300.8	290.5
50–60	0.9	3.7	5.8	6.8	35.8	15.2	42.9	69.6	8.2	9.4	7941.1	9691.9	407.4	281.3
60–70	0.9	3.1	5.8	6.8	36.3	16.2	44.9	68.8	8.5	8.8	8469.6	9043.5	462.2	252.1
70–80	0.9	2.9	5.8	6.8	36.6	17.4	41.6	68.1	8.3	9.3	8324.6	8791.7	441.6	253.5
80–90	0.9	2.5	5.8	6.9	33.7	18.2	42.9	67.6	8.7	9.8	8989.4	8896.6	436.7	257.0
90–100	0.8	1.3	5.8	6.9	33.5	19.7	43.2	67.2	8.9	7.2	6906.2	7611.3	281.9	202.1

C – colluvial soils, A – alluvial soils.

The mean pH value is the least changeable parameter. In the case of colluvial soils, the pH practically does not change with depth, staying within the range of 5.6–5.9, while in alluvial soils it rises in the deeper layers, from 6.2 (10–20 cm) to 6.9 (90–100 cm).

The mean content of the sands is clearly higher in colluvial soils (30–35%) than in alluvial (15–20%). In general, it increases with depth; the highest values in colluvial soils occur in the 60–70 and 70–80 cm layers. The mean silt fraction content in colluvial soils falls from 53% in the upper part of the profile to 41–42% in the lower part. In alluvial soils, silts constitute the fraction with the highest content, usually exceeding 65%. The lower content occurs in the upper part of the profiles. The mean clay fraction content in both types of profiles is similar and shows little variation related to depth. It is slightly higher in the case of alluvial soils. The lower layers of the analysed profiles have a slightly lower content of this fraction (Table 3).

The mean Fe content values are higher in the alluvial soils and decrease with increasing depth from 12,185 mg/kg in the 10–20 cm layer to 7600 mg/kg in the 90–100 cm layer. In colluvial soils, the highest Fe content, 10,800 mg/kg, occurs in the 0–10 cm layer. The pattern is slightly different in the case of Mn content: in colluvial soils, the highest values occur in the 60–70 cm layer (462 mg/kg) and decrease in the upper part of the profile to 325 mg/kg. In alluvial soils, Mn content values are slightly lower and decrease with increasing depth, from 340 to 202 mg/kg (Table 3).

Heavy Metals Content

The (mean) Cd, Pb and Zn content is slightly higher in the alluvial soils. The concentration of the studied elements shows strong variation within the analysed sample population. The highest differences were found for Cd, high for Cu and Pb, and the lowest for Zn (Table 4).

TABLE 4. VARIATION IN THE CONCENTRATION OF THE STUDIED TRACE METALS

	Cd [mg/kg]		Cu [mg/kg]		Pb [mg/kg]		Zn [mg/kg]	
	C	A	C	A	C	A	C	A
Mean	0.5	0.4	11.1	8.9	19.2	21.7	26.4	34.6
Median	0.5	0.1	6.6	6.9	19.5	16.2	22.6	33.3
Minimum	<0.1	0.0	<0.1	2.7	6.2	0.0	10.7	14.9
Maximum	1.6	2.1	86.8	35.5	41.8	67.2	63.0	64.2
Geochemical background[1]	0.7		9.0		19		35	

C – colluvial soils, A – alluvial soils; 1 – after Zgłobicki et al. [23].

The mean Cd concentrations are low, particularly in the alluvial soils, with the maximum level ranging from 0.1 to 0.2 mg/kg. Slightly higher concentrations occur in the colluvial soils (0.2–0.3 mg/kg) (Table 5). The mean Cu content is also low, 7–10 mg/kg in the alluvial soils and 2–10 mg/kg in the colluvial soils. In the alluvial soils, the Cu content clearly decreases with increasing depth. The mean Pb content in the studied profiles is generally low. The concentrations in the alluvial soils (27.1–9.9 mg/kg) are slightly higher than in the colluvial soils (21.4–15.4 mg/kg). In both cases, Pb content decreases with increasing depth; the decrease is much more distinct in the alluvial soils. The mean Zn concentrations are not high either: they range from 30 to 40 mg/kg in the alluvial soils and from 20 to 30 mg/kg in the colluvial soils.

TABLE 5. MEAN CONCENTRATIONS OF TRACE METALS IN THE PARTICULAR LAYERS

Depth [cm]	Cd [mg/kg]		Cu [mg/kg]		Pb [mg/kg]		Zn [mg/kg]	
	C	A	C	A	C	A	C	A
0–10	0.2	0.2	10.5	11.2	21.4	27.1	34.1	42.2
10–20	0.3	0.1	9.7	10.1	21.3	19.3	31.1	39.0
20–30	0.3	0.1	9.9	9.8	17.0	24.8	23.8	40.6
30–40	0.2	0.1	3.4	9.5	16.9	24.1	22.7	39.6
40–50	0.3	0.1	2.9	8.5	15.4	18.3	21.5	33.1
50–60	0.3	0.1	5.5	8.2	16.7	11.8	23.9	32.8
60–70	0.3	0.1	2.6	7.8	16.3	9.9	19.9	31.9
70–80	0.4	0.1	2.2	7.5	18.2	10.7	21.3	31.7
80–90	0.3	0.1	6.8	7.0	18.4	10.9	23.4	30.4
90–100	0.2	0.1	7.3	5.1	17.6	12.0	23.9	23.8

C – colluvial soils, A – alluvial soils.

Statistical Analyses

The PCA results show that the correlations between the studied characteristics in both soil types are different. In alluvial soils, positive correlations between metals and the SOM are visible but no correlations with silt and sand content occur. In colluvial soils, no strong correlations between metals have been found. Positive correlations of varying intensity occur between metals and Fe and the SOM. For both soil types there are no correlations with pH, sand and heavy metals, also with Mn for Pb and Zn, and with silt and clay for Cu and Cd.

In alluvial soils, the first two components account for 68% of the variation, while three components account for 82% of the variation. The other components have a negligible influence. The first component is primarily influenced by the highly mutually correlated metal contents as well as the SOM with which they are also highly correlated. The other parameters may be divided into two groups: those with the greatest influence on the second component, i.e. sand, silt, Fe and Mn, and those with the greatest influence on the third principal component, i.e. pH and clay.

The PCA results are entirely different for colluvial soils. Two principal components account for only 60% variation, three – for 74%. Only four principal components account for more than 83% of variation. The influence of the particular parameters on the principal components is also varied and less distinct than in alluvial soils. The first component depends on the SOM, sand, silt, clay, Pb and Fe. The second component is primarily influenced by Cu and Cd, the third – by pH and Zn, and the fourth by – Mn. It is thus evident that in colluvial soils it is impossible to statistically distinguish groups of parameters that would have similar characteristics.

The smallest number of Pearson`s correlations and the weakest correlations occur in the case of the analyses carried out for the entire sample population (Table 6). Heavy metals show more numerous correlations with soil characteristics in the case of colluvial soils but these correlations are usually weak, and negative correlations occur more often (pH, sand). The most numerous and most distinctly positive correlations have been found with the SOM content; they are the strongest in the case of Pb, while they practically do not occur in the case of Cu (Table 6). Correlations with pH are weak and occur slightly more often in colluvial soils; these correlations are often negative. This kind of correlations prevails in alluvial soils. Cd is the only element showing stronger positive correlations with sand content. Such a situation occurs in colluvial soils and alluvial soils. In the case of other metals, the correlations are weakly negative or do not occur at all. Cd exhibits moderate correlations with silt content: negative in colluvial soils, positive in alluvial soils. Pb in colluvial soils has moderate positive correlations with clay content. In the case of Zn and Cd, the correlations are weakly negative (Table 6). The studied metals have shown moderate and – in some places – strong correlations with Fe content (colluvial soils and alluvial soils) and slightly weaker correlations with Mn (alluvial soils).

The results for sample subpopulations with metal concentrations lower or higher than the geochemical background have been different for the particular elements and soil characteristics. In the case of soils with higher Cd concentrations, positive correlations with the SOM content, pH (alluvial soils) and sand content (colluvial soils) are stronger. A reversed situation occurs in the case of correlations with clay content (colluvial soils and alluvial soils).

For Cu, the correlations are similar for both subpopulations or do not occur at all. In the case of soils with higher Pb concentrations, positive correlations with the SOM, pH, and silt fraction content (colluvial soils) are more significant. A reversed relationship has been found for correlations with sand and clay content (colluvial soils) as well as the SOM, sand and silt content (alluvial soils). In the case of soils with higher Zn concentrations, positive correlations with silt

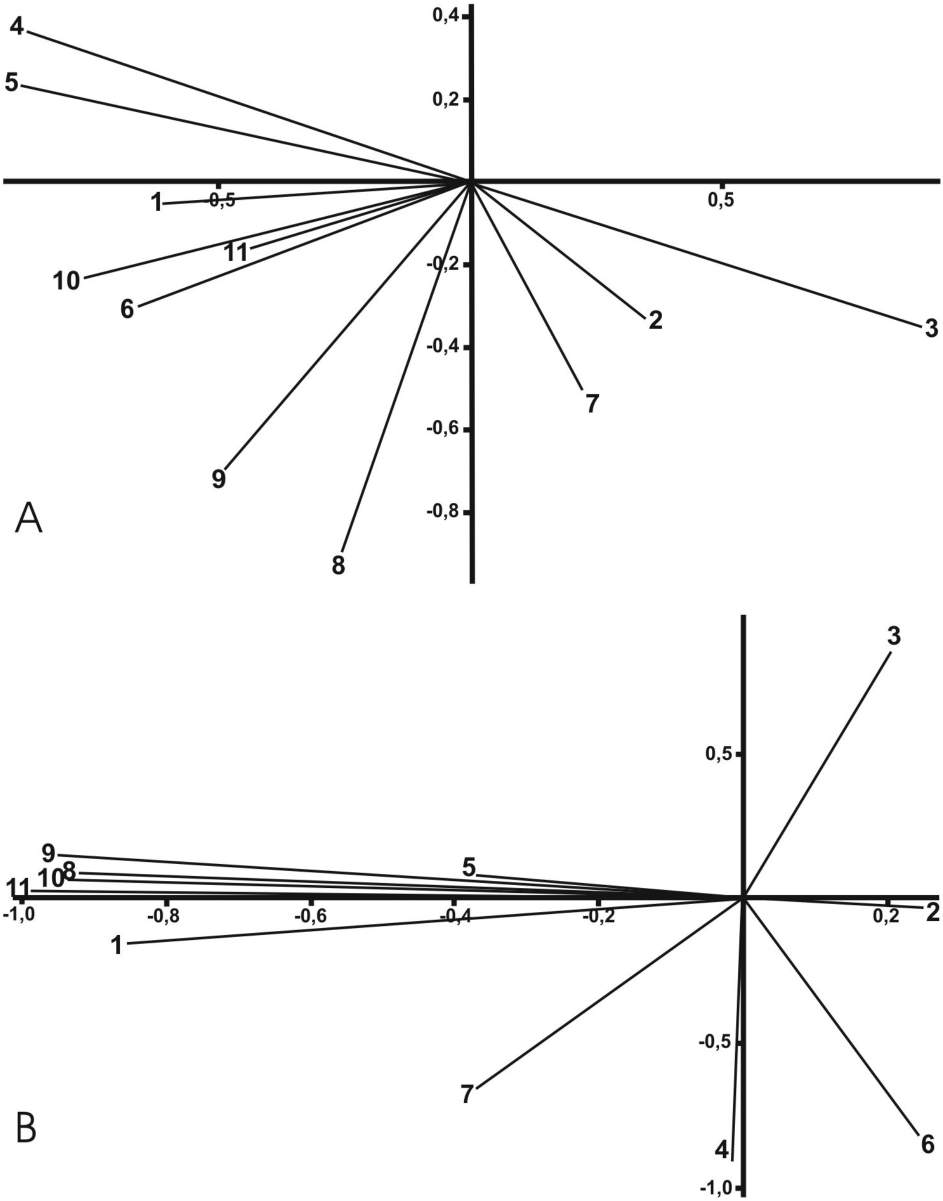

Figure 2. Principal Component Analysis. Location of loading vectors of soil characteristics against first two principal components. A – colluvial soils, B – alluvial soils. 1 – SOM, 2 – pH, 3 – sand, 4 – silt, 5 – clay, 6 – Fe, 7 – Mn, 8 – Cd, 9 – Cu, 10 – Pb, 11 – Zn.

content (colluvial soils) and pH (alluvial soils) are more significant. A different situation occurs for correlations with sand content (colluvial soils) as well as the SOM, sand and silt content (alluvial soils). In colluvial soils, stronger correlations with Fe have been found for samples with lower Cd and Cu content; those

TABLE 6. PEARSON`S CORRELATION COEFFICIENTS

Element	SOM			pH			Sand			Silt			Clay			Fe			Mn		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Colluvia																					
Cd	-	-0.27	-	0.26	-	0.27	-	0.53	-	-	-0.58	-	-	-0.29	-	0.31	-0.27	0.36	-	0.69	0.30
Cu	0.33	-	0.21	-	0.48	0.25	-0.21	-	-0.33	0.23	0.26	0.27	-	-	-	0.53	-	0.35	-	-	-
Pb	0.32	0.75	0.42	-0.36	0	-0.47	0.30	-0.31	-0.33	-0.31	0.29	0.28	0.53	0.39	0.54	0.30	0.53	0.50	-	-	-
Zn	-	-	0.25	-0.28	-0.42	-0.40	0.24	-0.28	-	-0.23	0.32	-	-0.25	-	-0.22	-0.42	-	0.21	-	0.23	-
Alluvia																					
Cd	0.28	0.86	0.53	-0.31	0.44	-	-	0.50	-	-	0.51	-	-	-0.34	0.23	0.44	-0.73	-0.29	0.30	-	0.27
Cu	-	-	-0.32	-0.36	-	-0.24	-0.23	0.25	-0.21	0.24	-0.34	-	-	-	0.23	0.21	-0.79	-0.41	0.28	-	0.29
Pb	0.58	0.28	0.64	-	-	-0.23	-0.48	-	-	0.42	-	-	-	-	0.25	0.75	-0.94	-0.30	0.38	-	0.29
Zn	0.56	0.40	0.66	-0.58	-	-0.35	-0.37	0.41	-	0.33	-0.44	-0.28	-	-0.23	-	0.36	-0.86	-0.23	0.68	-	0.32
Colluvia and alluvia																					
Cd	-	0.75	0.36	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.56	-	0.24	0.25	0.32
Cu	-	-	-	0.26	0.28	-	-0.25	-	-	0.26	0.28	-	-	-	-	-	-0.56	-	0.45	-	-
Pb	0.33	0.58	0.61	-0.23	0.27	-	-	-	-	-0.22	-	-	-	-	0.31	0.37	-0.42	-	0.64	-	0.20
Zn	0.46	0.43	0.63	-	-	-	-	-	-	-	-	-	-	-	0.21	-	0.59	-	-	-	-

A – only samples with content below geochemical background, B – only samples with content above geochemical background; C – all samples; „-„ lack of correlation.

correlations have been weaker for Pb and Zn. In alluvial soils, correlations have been positive (moderate) for all metals in samples with lower metal content and negative in samples with metal content higher than the geochemical background. In colluvial soils, correlations with Mn have practically not occurred, while in alluvial soils those correlations have been positive (weak) in samples with lower metal content.

When colluvial soils and alluvial soils were jointly analysed, more distinct positive correlations were found in the case of soils with higher Pb content (SOM and pH) and Cd content (SOM).

In the case of multiple correlations (two characteristics), the strongest correlations (moderate) with heavy metals content were found for Pb and Zn when the SOM content was one of the analysed characteristics. Correlation coefficients were usually above 0.6. This pattern did not occur for the other metals. For the other pairs of characteristics, correlations either did not occur at all or they were weak. It was found that in general, double correlation coefficients were higher for the SOM and pH and for the SOM and clay content than in the case of single correlations.

TABLE 7. RESULTS OF CLUSTER ANALYSIS*

A) BASED ON SOIL CHARACTERISTICS

Group	SOM [%]	pH	sand [%]	silt [%]	clay [%]	Fe [mg/kg]	Mn [mg/kg]	Cd [mg/kg]	Cu [mg/kg]	Pb [mg/kg]	Zn [mg/kg]
1	1.9	6.7	52.8	43.1	4.1	8800	364	0.3	6.4	14.5	26.0
2	1.7	6.8	32.4	58.4	9.2	8400	297	0.3	11.0	14.7	25.9
3	1.7	6.4	29.0	60.6	10.4	8486	332	0.3	10.2	16.7	26.8
4	2.0	6.2	26.5	61.9	11.6	8602	337	0.4	10.5	19.1	28.6
5	6.6	7.1	20.8	67.5	11.4	9515	301	0.7	12.2	32.5	42.9

B) BASED ON METAL CONTENT

Group	Cd [mg/kg]	Cu [mg/kg]	Pb [mg/kg]	Zn [mg/kg]	SOM [%]	pH	sand [%]	silt [%]	clay [%]	Fe [mg/kg]	Mn [mg/kg]
1	0.4	8.0	17.0	28.1	2.6	7.1	28.5	61.3	10.0	9907	312
2	0.4	7.1	17.5	27.3	2.1	6.4	33.2	57.0	9.7	9007	357
3	0.7	14.4	38.5	49.5	6.8	6.1	27.0	60.4	12.4	4864	268
4	0.7	23.1	34.5	45.4	6.1	6.3	26.4	61.4	12.0	4632	245
5	0.5	14.2	24.6	37.5	4.8	6.5	28.0	61.5	10.5	8078	301

* mean values for particular groups are presented

The cluster analysis conducted for the entire population of samples according to i) the SOM, clay Fe and Me content, and pH and ii) the content of the studied heavy metals, yielded similar results. Groups with the highest Cd, Cu, Pb and Zn concentrations had the highest SOM and clay content (Table 7). This pattern occurred for all metals. The group with the highest SOM and clay content had the highest concentration of heavy metals. This regularity was the most distinct for Pb and Zn, slightly less – for Cu and the least – for Cd. The pH was of no significance in this case. At the same time, respective samples with anomalous heavy metals content occurred at practically every depth within the designated groups. Metal concentrations were several times higher with very similar soils characteristics. The greatest number of anomalies occurred at the depth of 0–10 cm; they usually concerned one element.

DISCUSSION

A generally low, though varied, Cd, Cu, Pb and Zn content was found in the soils. Mean concentrations were only slightly higher than the geochemical background. The maximum values exceeding the geochemical background were found for Cu in the colluvial soils and Pb in the alluvial. With increasing depth, the content of the studied elements decreased. At the same time, the characteristics of the studied soils varied. This provided a good basis for the statistical analyses of correlations between these two groups of characteristics.

The correlation between heavy metals concentrations and parameters such as grain size distribution, pH, and organic matter content is an important and complex issue. Owing to the synergic effects of the respective factors and the influence of other factors not discussed here, it is sometimes difficult to identify the correlations for one specific factor [1]. An understanding of the impact of the characteristics discussed makes it possible to assess the environmental hazards associated with anthropogenic geochemical impact (intensity of contaminant accumulation, intensity of migration). Studies of the vertical migration of metals point to the fact that it depends on the clay fraction content, pH, SOM content, carbonate content, CEC as well as Fe and Al oxide content [5].

Results of the PCA analysis indicate that in alluvial soils there is a strong correlation between all studied heavy metals and the SOM. In colluvial soils such relations exist only in the case of Pb and Zn. It could be a result of a much higher SOM content in alluvial soils and its more intensive vertical changes.

Most of the correlations (Pearson`s) found between heavy metals concentration and the characteristics under study were not distinct; weak correlations prevailed. The SOM content was the soil characteristic that showed the most distinct correlations with the heavy metals. Strong positive correlations were found for: a) Pb and the SOM (colluvial soils), b) Cd and the SOM (alluvial soils). Moderate positive correlations occurred for Zn and the SOM in alluvial soils. In the case of a double correlation, the SOM content was also a significant factor impacting the strength of correlations. Basically, no impact of pH on metal concentrations was found. Moderate negative correlations occurred only for Zn. The impact of grain size distribution was insignificant. Cd was the element that showed different correlations: a moderate positive correlation with sand content occurred here. The impact of clay fraction content was observed only in the case of Pb (moderate positive correlations). All metals showed a generally positive correlation with Fe in colluvial soils as well as alluvial soils with low metal content. The relationships between Mn content and metal concentration were visible in alluvial soils with low metal content (weak positive correlations).

This study demonstrated that metal content, i.e. the relation to the geochemical background, influences the nature and intensity of correlations with soil characteristics. It was found that correlations were generally lower in samples with higher metal concentrations than in those with lower metal concentrations. The respective metals showed different patterns. The increase in Cd content in the samples caused the decrease in the correlation intensity. In the case of Cu, it was difficult to indicate distinct patterns: correlations did not occur at all in a considerable number of cases (30%). The patterns for Pb varied as well: higher concentrations resulted in its weaker correlations with sand and Fe in both types of soils, and with the SOM (colluvial soils), silt and Mn (alluvial soils). The most varied relationships were found for Zn: in alluvial soils, higher Zn concentrations resulted in its weaker correlations with sand, silt, Fe and Mn. In colluvial soils, the situation was reversed: in samples with greater Zn concentrations, its correlations with silt, clay and Fe were stronger.

After analysing the respective soil parameters, it should be noted that a distinct decrease in the intensity of the correlation between heavy metals in samples with higher heavy metals concentrations occurred in the case of sand fraction content and Fe concentration. In colluvial soils, this pattern was observed for the SOM content, while in alluvial soils – for silt and Mn. The pH of the samples was the only characteristic, for which the intensity of correlation increased in samples with a higher heavy metals content.

Assuming that in natural conditions, free of human geochemical impact, the correlations between heavy metals concentrations and soil characteristics are stronger, it is possible to estimate the anthropogenic impact on soils based on correlation coefficients. Alluvial soils are characterised by greater anthropogenic impact manifested in more frequent positive and stronger correlations in samples with lower metal content. Based on the analysis of correlation coefficients for the respective soil characteristics and types, it has been found that Cd is the metal with the largest anthropogenic input: here the number of cases when correlation intensity decreases in samples with higher metal content is the largest. Anthropogenic impact is distinctly lower for Pb and Cu; it is the lowest for Zn. In addition, anthropogenic pressure, along with metal input, causes changes in soil characteristics. Lower soil pH (high acidity) is the most distinct result of anthropogenic pressure. Certain influences may also be found for silt and Mn in colluvial soils, the SOM – in alluvial soils as well as for clay – in colluvial soils and alluvial soils. The other characteristics, particularly sand content and Fe, do not change.

Studying the impact of the parent rock on heavy metals content in soils in eastern Poland, Melke et al. [13] found the following patterns: a) increased accumulation occurred for nearly all metals in the A horizon; this correlation was particularly distinct in the case of Pb; b) there was a distinct positive correlation of the content of the studied metals with clay fraction content and colloidal clay fraction content (r^2=from 0.88 to 0.99). Analysing heavy metals content in Poland's arable soils (51 profiles, 220 samples), not subjected to a distinct impact of industrial pollution, Kabata-Pendias [6] found a correlation between heavy metals and clay fraction content (<0.02 mm). Czarnowska [3] also found a correlation between heavy metals and clay fraction content, although the value of the correlation coefficients was not high (r^2=0.50–0.67). A correlation with silt and organic carbon content did not occur (except for Pb).

In his study of alluvial sediments of the Lahn River, Martin [12] found the occurrence of very weak correlations of heavy metals content and the percentage share of the clay fraction and organic matter. On that basis, he inferred that those two factors had a small influence on the concentration of heavy metals in sediments. Based on studies conducted in the Rhine catchment, Thonon [19] found other correlations: concentrations of heavy metals in floodplain deposits rose with increasing soil organic matter and clay fraction content. The same correlations were found in harbour sediments by Chen et al. [4] who stressed the greater importance of the SOM content. The results of other studies have also indicated a significant correlation between the content of metals such as Pb, Zn and Cu in sediments and the clay fraction content [e.g. 17, 24].

CONCLUSIONS

1. Different regularities were found for heavy metals content and selected soil characteristics in colluvial soils and alluvial soils. In some cases the content of Cd, Cu, Pb and Zn in relation to geochemical background was also important.

2. In general, the correlations found between heavy metals content and the soil characteristics under study were not very distinct: weak and moderate correlations prevailed.

3. The SOM content is the characteristic with the strongest correlations with heavy metals content. Such relation was generally more clear in alluvial soils. The most distinct correlations occurred for Pb and Zn.

4. No clear impact of soil pH on metal concentrations was found. Negative correlations occurred quite frequently, especially in alluvial soils.

5. Correlations with the particular fraction content were usually weak or did not occur at all. More distinct correlations were found for Pb and clay content (alluvial soils) as well as Cd and sand content (alluvial and colluvial soils).

6. Distinct correlations were found between metal concentration and Fe content. These correlations were positive in colluvial soils and negative in alluvial soils with a higher content of heavy metals.

7. Samples with the highest SOM and clay content had the highest concentration of heavy metals. This regularity was the most distinct for Pb and Zn, slightly less for Cu and the least for Cd.

8. In general, stronger correlations occurred in samples with low metal content. Anthropogenic influences caused the disruption of natural relationships between soil characteristics and heavy metals concentration. These changes were the most intensive in the case of Cd, and the least intensive for Zn.

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WPŁYW FIZYKOCHEMICZNYCH PARAMETRAMI GLEB KOLUWIALNYCH I ALUWIALNYCH NA ZAWARTOŚĆ CD, CU, ZN I PB (E POLSKA)

Fizyczne i chemiczne parametry gleb odgrywają ważną rolę, jeśli chodzi o wiązanie i migrację metali śladowych w środowisku. W pracy podjęto próbę oceny korelacji pomiędzy podstawowymi cechami gleb koluwialnych i aluwialnych oraz koncentracji Cd, Cu, Pb i Zn. Pozwoli to na wskazanie najważniejszych czynników wiązania metali w glebach. Badane gleby położone są na obszarze rolniczym we wschodniej Polsce i poddane generalnie niskim antropogenicznym zanieczyszczeniom. Ogólną zawartość metali śladowych oraz wybranych cech glebowych: skład granulometryczny, zawartość substancji organicznej, pH oraz zawartość Fe i Mn analizowano w 16 profilach (160 próbek). Użyto trzech metod statystycznych: analizę głównych składowych, metoda grupowania oraz analizę wskaźników korelacji Pearsona. Zależności dla gleb koluwialnych i aluwialnych były odmienne. Zawartość substancji organicznej była parametrem o najwyższej pozytywnej korelacji z metalami śladowymi. Najbardziej wyraźne zależności stwierdzono w przypadku ołowiu. Nie stwierdzono korelacji z pH a związki z zawartością poszczególnych frakcji słabe. Związki z zawartością Fe i Mn były silne ale zróżnicowane. Generalnie silniejsze korelacje z cechami gleb stwierdzono w próbach o niższej zawartości metali śladowych, wpływ człowieka powoduje zaburzenie naturalnych relacji.