Contents of Potentially Risk Elements in Natural and Reclaimed Soils of the Sokolov Region

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Abstract: Anthropogenic soils are formed by human activities. The contents of potentially risk elements are one of the most important criteria of the exploitability of such soils for the agricultural production. The aim of this paper is to assess the contents of the selected potentially risk elements in 16 areas of the Sokolov region, including 5 reclaimed areas and 11 natural soils. 116 sampling locations were analysed in total. Another aim is to analyse the relationships between the elements, using multivariate statistical methods. The contents of the risk elements studied were in most cases under the limit values. In some cases, as with Pb, they were very low compared to the limit values. In the principal component analysis, four components explaining 74% of total variability were selected. The first component (30.2% of variability) showed strong correlations with Mn, V, Ni, and Cu contents. The second component (15.8% of variability) correlated with As and Be. The third component (14.3%) correlated with Pb and Cd. The fourth component (13.7%) correlated with Zn and Cr. The mean scores of each area were projected into the component plots, which enables the assessment of the relative importance of each group of elements in each particular area. The reclaimed and the natural soils are clearly distinguished. It can be concluded that the contents of the risk elements studied do not currently present any important problem in the reclaimed areas. Nevertheless, the situation should be further monitored.

Keywords: soil reclamation; potentially risk elements; principal component analysis

Anthropogenic soils are formed by human activities. Their areas still increase due to the mining, abandoned waste deposits, building construction, industry, etc. In the Czech soil classification, they are classified as a specific soil class Anthrosols (Němeček *et al.* 2001). In the World Reference Base for the soil resources, they were recently recognised as a separate reference soil group called Technosols (IUSS Working Group WRB 2006). The soils formed after open-cast brown coal mining are formed by different reclamation procedures, including layering of mineral materials, covering with natural topsoil, planting with agricultural crops or forests, and other methods (Haigh 2000). A reasonable reclamation can help to achieve the rehabilitation process much faster in comparison with the natural succession (Wali 1999).

In Northern Bohemia, large-scale strip mining (or open-cast mining) of brown coal has been going on for a long time. Permanent dumps of sterile rock account for a large area. In agreement with the Czech legislation, an effort is concentrated on the landscape reclamation and revitalisation. In order to make either agricultural or forest usage possible, it is necessary to reclaim the sterile rock by a natural topsoil cover, which is, however, limited, or by the addition of organic matter and other amendments. The reclamation methods used in

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Northern Bohemia were summarised and described by Dimitrovský (2000, 2001). The heterogeneity of those anthropogenic soils is usually high, as the deposited material is very heterogeneous, including sterile rock with variable composition and coming from different depths, remains of brown coal carbon, and possibly added materials rich in organic matter (Borůvka & Kozák 2001; Rohošková *et al.* 2006). This heterogeneity did not develop naturally as the result of pedogenetic processes and natural spatial distribution, as in the case of the natural soils, but is the result of human activities.

The reclaimed soils are studied from different points of view. Attention is paid to the development of the contents and forms of C, N, and other major elements (for example Rumpel *et al.* 1999; Delschen 1999; Šourková *et al.* 2005). Soil structure stability is often used as an indicator of the reclaimed soil quality (Valla *et al.* 2000; Rohošková & Valla 2004). Populating with soil organisms and microbial activity are also often used for the evaluation of the reclaimed soil development (Waschkies & Hüttl 1999; Topp *et al.* 2001; Wanner & Dunger 2001). One of the most important criteria of the exploitability of these soils for the agricultural production is the content of potentially risk elements. However, the studies dealing with the risk elements contents and behaviour in the reclaimed soils after coal mining are rather rare. The input of the potentially risk elements into the reclaimed soils can be potentially increased, as the related industry is often concentrated in the mining areas (Haigh 2000). On the other hand, as the soils have been just recently exposed on the surface, the effect of the atmospheric deposition should be low, except for the soils where the natural topsoil cover with the previous accumulation of deposited substances was used. Most of the elements present in these soils should therefore originate from the mineral materials. A higher content in the coal mining deposits is often reported for As (for example Ding *et al.* 2001). The lack of organic matter as a sorption medium can lead to a greater risk of the element release after weathering and their increased mobility and bioavailability. However, Dang *et al.* (2002) reported that only a small fraction of the metals released during the natural weathering of coal mine spoils is released to the environment. Nevertheless, the vulnerability of the reclaimed soils to the potential pollution can be strong. It is therefore necessary to assess the risk and potential threat.

The aim of this paper is to assess the contents of selected potentially risk elements in soils of 16

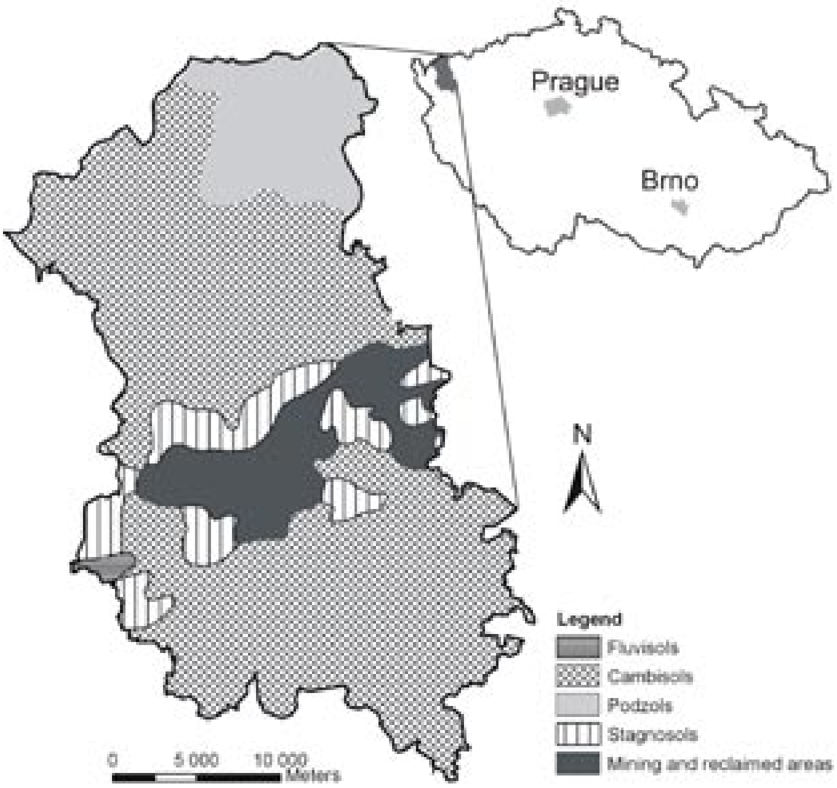

Figure 1. Location of the Sokolov district in the Czech Republic (top right) and a simplified soil map of the district

areas, including both natural and reclaimed soils, in a region strongly impacted by open-cast brown coal mining, and to analyse their relationships, using multivariate statistical methods. The contents of potentially risk elements in the natural and anthropogenic soils formed on the reclaimed dumpsites are compared.

MATERIALS AND METHODS

Sampling sites

Southern part of the Sokolov district in the West of the Czech Republic was studied (Figure 1). Anthropogenic soils formed on the reclaimed dumpsites after open-cast brown coal mining cover an important part of this region. The samples were collected on 11 natural localities adjacent to the mining areas, formed mainly by Cambisols, and 5 reclaimed areas, where the soils can be classified as Spolic Technosols (IUSS Working Group WRB 2006). The reclamation was done in three localities by covering the dumpsite surface with a 20 cm layer of natural topsoil; two areas have no topsoil cover. The age of reclamation varies from 15 to 30 years. In total, 82 sampling sites were selected on the natural soils and 34 sites were selected on the reclaimed ones (Table 1). All areas are used for the agricultural production.

Soil sampling and analysis

The samples of soils were collected from the depth of 0 to 20 cm. The samples were air dried and sieved to pass through a 2 mm mesh. They were further extracted with cold 2M HNO_3 at the ratio solution:soil 10:1 (v/w) (Němeček *et al.* 1995). The extracts were separated by centrifugation. The concentrations of 10 elements (As, Be, Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn) were determined in the extracts by means of atomic absorption spectrophotometry under standard conditions.

Statistical treatment

The summary statistics and statistical distributions for all variables were determined. Table 2 gives the descriptive statistics and the skewness. Most element concentrations did not show the normal distribution. Their values were therefore transformed to common logarithms for further analyses. The *t*-test was used for the comparison between the reclaimed and the natural soils, and between the reclaimed soils with and without the

Table 1. Characteristics of the localities studied (part 1)

Name	Number of samples	Type	Reclamation type and age
Dasnice	5	natural	–
Chodov	4	natural	–
Chranišov	8	natural	–
Dolní Chodov	5	natural	–
Gustav	4	reclaimed	topsoil cover (20 cm), 30 years
Lítov	6	reclaimed	topsoil cover (20 cm), 20 years
Loket	3	natural	–
Loketská výsypka	17	reclaimed	topsoil cover (20 cm), 20 years
Nové Sedlo	8	natural	–
Pochlovice	7	natural	–
Smolnice	2	reclaimed	no cover, 15 years
Sokolov	5	natural	–
Staré Sedlo	28	natural	–
Vintířov	5	reclaimed	no cover, 20 years
Vítkov	5	natural	–
Železný dvůr	4	natural	–

Table 2. Basic statistical parameters of the potentially risk elements contents (mg/kg). Maximum tolerable limits for non-sandy soils are given for comparison (MŽP, 1994)

Parameter	As	Be	Cd	Cr	Cu	Mn	Ni	Pb	V	Zn
Limit	4.5	2.0	1.0	40.0	50.0	–	25.0	70.0	50.0	100.0
Mean	1.98	0.30	0.08	1.35	1.67	85.1	1.25	16.70	4.65	29.06
Median	1.7	0.24	0.1	1.07	1.41	74.7	0.6	17.0	4.0	26.0
Variance	1.588	0.040	0.003	1.006	0.958	1133.2	2.883	48.73	7.745	184.0
Std. error	0.117	0.019	0.005	0.093	0.091	3.13	0.158	0.648	0.260	1.259
Minimum	0.4	0.08	0.0	0.23	0.37	35.2	0.2	1.6	0.9	1.6
Maximum	9.5	1.47	0.2	5.84	5.18	193.3	10.6	40.0	15.0	78.0
Skewness	3.222	2.609	0.029	1.896	1.429	1.004	3.541	0.493	1.378	1.033
CV(%)	63.6	67.4	75.0	74.6	58.6	39.6	136.0	41.8	59.9	46.7
Logarithmic transformation										
Mean	0.559	–1.378		0.062	0.365	4.372	–0.241		1.378	
Variance	0.219	0.327		0.477	0.291	0.139	0.752		0.316	
Standard error	0.043	0.053		0.064	0.050	0.035	0.081		0.052	
Skewness	0.781	0.197		0.043	0.220	0.303	0.883		0.155	

CV(%) – coefficient of variation

topsoil cover. Pearson correlation coefficients were calculated to examine the relationships between the variables. For the principal component analysis (PCA), the data were standardised to zero mean and unit variance, and the analysis was done on the correlation matrix. The first four principal components (PC) were retained and rotated using Varimax rotation (Kaiser 1958); the latter redistributes the variance in each variable so that each contributes strongly to one of the components and little to the others (Sharma 1996). The software Statgraphics Centurion XV (StaPoint, Inc., Virginia, U.S.A.) was used for the data analysis.

RESULTS AND DISCUSSION

The contents in the anthropogenic soils of the risk elements studied were in most cases under the limit values for agricultural soils (MŽP 1994; Table 2). In some cases, as with Cu and Cr, they were very low compared to the limit values. Arsenic is the only element that exceeded the limit value. This happened on three sites in Staré Sedlo, once in Nové Sedlo, and once in Loket; all these sites are natural soils. All reclaimed areas were in this respect under the limit. Very small concentrations of potentially risk elements in lignite

Table 3. Differences between natural and reclaimed soils assessed by *t*-test. Differences significant at $P < 0.05$ are in bold

Areas	As[a]	Be[a]	Cd	Cr[a]	Cu[a]	Mn[a]	Ni[a]	Pb	V[a]	Zn
Natural	0.65	–1.33	0.084	0.25	0.19	4.36	–0.340	19.2	1.34	28.5
Reclaimed	0.35	–1.50	0.056	–0.38	0.80	4.40	–0.003	10.8	1.48	30.5
t-value	**3.28**	1.51	**2.49**	**4.90**	**–7.48**	–0.53	–1.93	**7.00**	–1.18	–0.71
P	0.001	0.133	0.014	< 0.001	< 0.001	0.594	0.056	< 0.001	0.239	0.478

[a]values were logarithmically transformed

mine soils were found also by Vega *et al.* (2004). These authors attributed their origin to the parent material and fertilisers.

The comparison between the natural and the reclaimed soils (Table 3) showed that the natural soils have significantly higher concentrations of As, Cd, Cr, and Pb than the reclaimed soils. They can be influenced by atmospheric deposition, especially in the case of Cd and Pb. Although the region under study represents an area with a small to moderate level of deposition (Suchara & Sucharová 2002), a long-term exposure of the natural soil surface to deposition could increase the element contents in the topsoil as compared to deeper layers. In contrast, the concentration of Cu was significantly higher in the reclaimed soils in comparison to the natural ones. This suggests a low input of this element to soil from atmospheric deposition and the prevalence of lithogenic origin. The concentrations of Ni, V, Zn, and Mn in the reclaimed soils were also slightly higher than those in the natural ones; however, this difference was not significant.

The comparison of the reclaimed areas with different types of reclamation (Table 4) showed that the covering with topsoil led to a higher Ni content and a lower Be content as compared to those in soils without the topsoil cover; the other differences were not significant. It should be noted that the term "topsoil" as it is used in the reclamation practice means not only the very superficial soil layer, but the whole humic horizon that is excavated before mining. Therefore, the enrichment with potentially risk elements from the deposition in this material needs not be strong. The most important effect of this cover is the increase of

Table 4. Differences between reclaimed soils with and without topsoil cover assessed by *t*-test. Differences significant at $P < 0.05$ are in bold

Reclamation	As[a]	Be[a]	Cd	Cr[a]	Cu[a]	Mn[a]	Ni[a]	Pb	V[a]	Zn
With cover	0.31	–1.64	0.054	-0.39	0.89	4.37	0.19	9.9	1.45	32.7
Without cover	1.74	–1.05	0.063	–0.35	0.51	4.50	–0.62	13.6	1.57	23.3
t-value	–1.10	**–2.62**	–0.38	–0.14	1.73	–0.98	**2.66**	–1.77	–0.55	1.77
P	0.280	0.013	0.709	0.892	0.093	0.337	0.012	0.086	0.586	0.086

[a] values were logarithmically transformed

Table 5. Correlation matrix of the elements concentrations in the soils. Correlations significant at $P < 0.05$ are in bold

Element	As[a]	Be[a]	Cd	Cr[a]	Cu[a]	Mn[a]	Ni[a]	Pb	V[a]	Zn
As[a]	1.000									
Be[a]	**0.332**	1.000								
Cd	–0.098	**–0.211**	1.000							
Cr[a]	**0.234**	0.041	0.002	1.000						
Cu[a]	–0.167	0.046	–0.174	**–0.250**	1.000					
Mn[a]	**–0.251**	**0.491**	–0.059	–0.089	**0.414**	1.000				
Ni[a]	**–0.207**	0.105	–0.139	0.160	**0.748**	**0.479**	1.000			
Pb	**0.288**	0.059	**0.351**	0.145	**–0.299**	–0.116	**–0.224**	1.000		
V[a]	–0.032	**0.352**	–0.092	0.056	**0.716**	**0.622**	**0.725**	–0.060	1.000	
Zn	0.018	–0.047	0.030	**0.227**	**0.216**	–0.005	**0.252**	–0.137	0.182	1.000

[a] values were logarithmically transformed

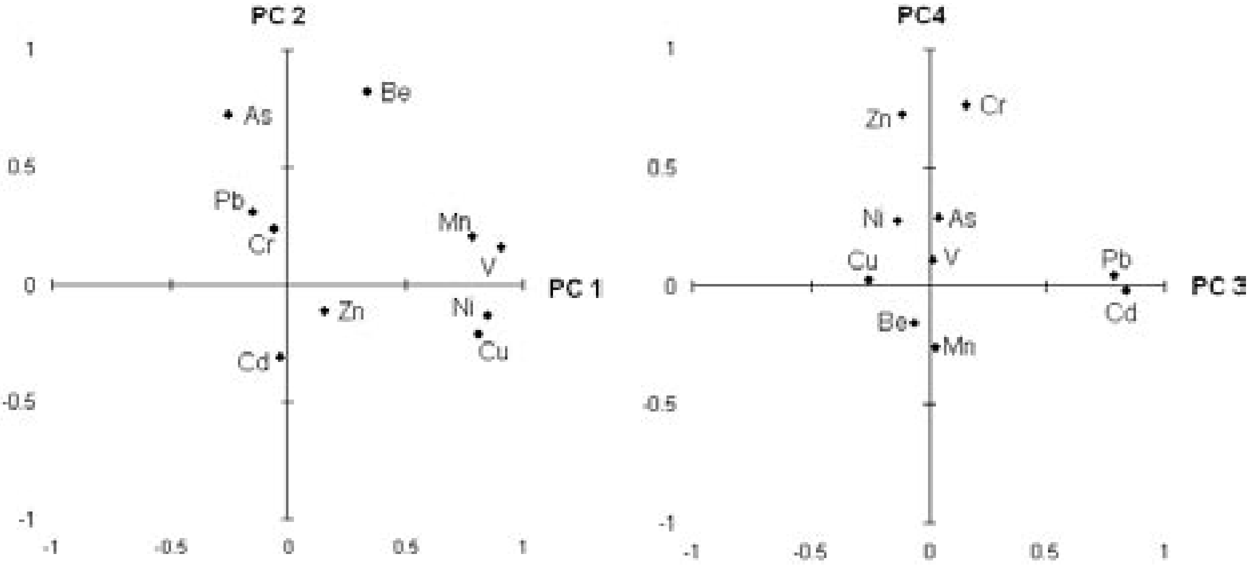

Figure 2. Projection of correlations between the elements concentrations and principal components

the organic matter content in soil and the consequent improvement of the conditions for the plant growing.

Correlation analysis showed in most cases a weak relationship between elements (Table 5). The exceptions are correlations of V with Cu (r = 0.716), Mn (0.622), and Ni (0.725), and between Cu and Ni (0.748). Medium is the correlation of Mn with Be (0.491) and Cu (0.414), and between Ni and Mn. The inverse relationship was found between Mn and As, Ni and As, Cd and Be, Cu and Cr, Pb and Cu, and Pb and Ni.

In principal component analysis, four PC explaining 74% of total variability were selected (Table 6). The first PC (30.2% of variability) showed high correlation with Mn, V, Ni, and Cu contents. These are the elements that showed the strongest correlation with each other. All these elements exhibited also higher contents in the reclaimed soils than in the natural ones; prevailing influence of lithogenic origin is supposed. The second PC (15.8% of variability) correlated with As and Be. These two elements, on the contrary, showed higher contents in the natural soils. The third PC (14.3%) correlated with Pb and Cd. The elements correlated with the second and third PC are supposed to be the main elements having a contribution from atmospheric deposition. Nevertheless, the

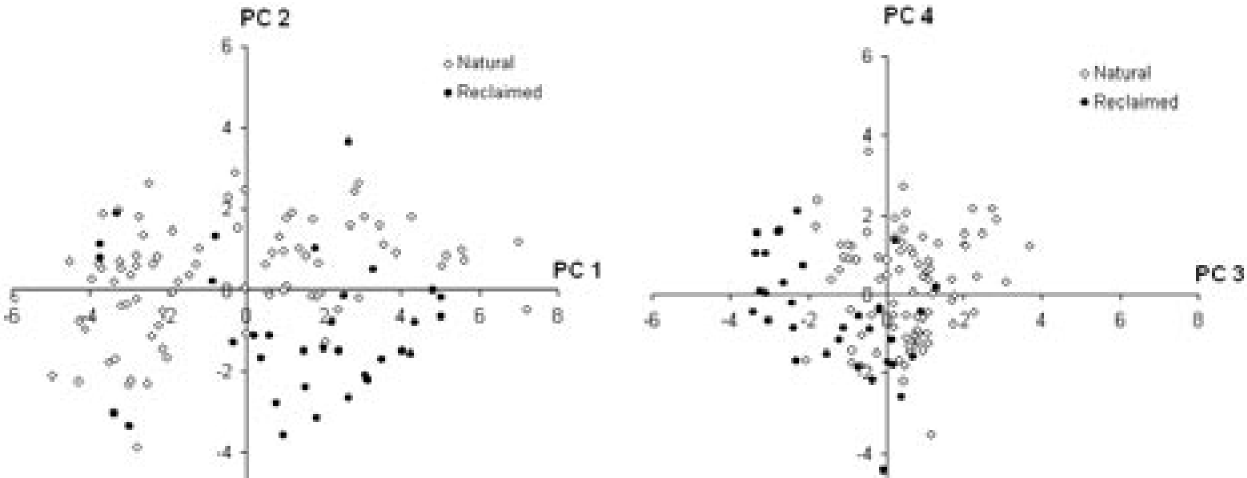

Figure 3. Projection of principal component scores for all individual sampling sites

proportion of variability explained by these two components (30.1% in total) shows rather a low importance of this way of input. The fourth PC (13.7%) correlated with Zn and Cr. The projection of PC weights (Figure 2) shows distinct clusters of the elements.

The projection of PC scores (Figure 3) distinguished the reclaimed and the natural soils very well. In the projection of the 1st and 2nd PC, most reclaimed soils are in the bottom right corner, which represents the soils with higher amounts of elements originating mainly from the parent material (Cu, Mn, Ni, V), and smaller amounts of As and Be. A smaller importance of atmospheric deposition is apparent also from the position on the left hand side in the projection of the 3rd and 4th PC.

The mean scores of each sampling area were also projected into the component plots (Figure 4). This enables to assess the relative importance of each group of elements in each particular area. The effect of atmospheric deposition on one side and of lithogenic origin of elements on the other side can be also assessed in each area based on this plot. Nevertheless, none of the areas showed a high mean score at the 2nd or 3rd PC, so that the anthropogenic pollution does not seem to be strong. The distinction between the reclaimed and the natural areas is also apparent in this projection, except the reclaimed dumpsite Vintířov.

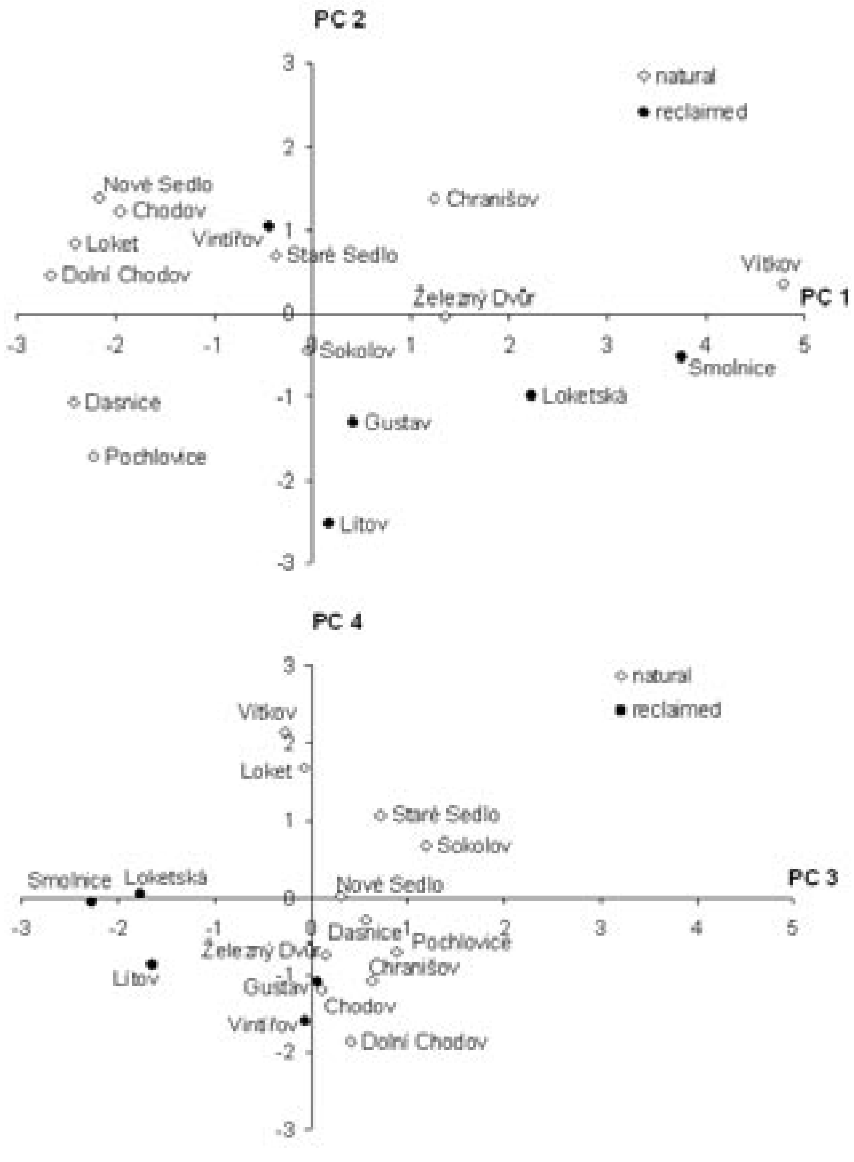

Figure 4. Projection of mean principal component scores for each separate area

Table 6. Correlations between elements concentrations and rotated principal components (PC), and estimated communalities of the variables

Element	PC 1	PC 2	PC 3	PC 4	Communality
As[a]	–0.251	0.725	0.045	0.286	0.672
Be[a]	0.338	0.817	–0.058	–0.157	0.810
Cd	–0.034	–0.310	0.834	–0.022	0.793
Cr[a]	–0.058	0.236	0.155	0.763	0.665
Cu[a]	0.809	–0.207	–0.256	0.023	0.764
Mn[a]	0.782	0.203	0.028	–0.256	0.720
Ni[a]	0.842	–0.135	–0.131	0.276	0.821
Pb	–0.151	0.309	0.779	0.043	0.727
V[a]	0.903	0.161	0.015	0.106	0.853
Zn	0.157	–0.113	–0.116	0.724	0.575
Eigenvalue	3.020	1.581	1.429	1.369	7.399
Cumulative % of variation	30.20	46.01	60.30	73.99	

[a]values were logarithmically transformed

While the reclaimed areas with the topsoil cover (Gustav, Lítov, and Loketská) are close to one another and do not exhibit any apparent differences, the reclaimed areas without the cover (Vintířov, Smolnice) differ much more. This suggests that the topsoil cover can eliminate the differences in the dumpsite materials and thus make the areas more homogenous.

CONCLUSIONS

It can be concluded that the contents of the selected risk elements in the reclaimed dumpsites under study do not currently present any important problem. The effect of atmospheric deposition is rather small and the contents of the potentially risk elements are conditioned mainly by the soil parent material. The contents of potentially risk elements in the reclaimed soils do not exceed the levels common in the natural soils, in some cases they are even smaller. A higher heterogeneity was found in the reclaimed soils without the topsoil cover than in the soils with this cover. Nevertheless, the effect of the topsoil covering did not strongly influence the potentially risk elements contents.

In conclusion, the potentially risk elements contents do not currently represent any limitation for the agricultural use of the reclaimed soils. Nevertheless, the situation should be further monitored to see the changes caused by weathering and other factors influencing the development of these soils.

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