

GEOCHEMICAL ASSOCIATIONS IN TECHNOGENIC SOILS (TECHNOSOLS) OF CONTRASTING HYDROLOGICAL CHARACTERISTICS FROM THE REGION OF MARITSA-IZTOK COAL MINE IN BULGARIA

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Abstract

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Studied were metal associations and contamination status of hydrophilic and hydrophobic technogenic soils from the area of Maritsa-Iztok coal mine region in Bulgaria. Four sites with contrasting hydrologic and acidic properties were chosen for investigation. At two of the sites following humus and non-humus reclamation under grass vegetation, soils were hydrophilic. At the other two sites (non-vegetated and pine-vegetated), soils were severely hydrophobic (water drop penetration time WDPT 10802s - 14440s). The Principle Component (PCA) and cluster analyses performed on the hydrophobic technogenic soils revealed that four principle components were distinguished explaining 80.5% of the total variance of the thirteen variables tested. The first component was loaded by Zn, Co, Ni, Mg and clay content, implying affiliation of the aforementioned metals to overburden clays, the second by WDPT, Cu, Cr, Fe, organic carbon (OC) and cation exchange capacity (CEC) implying affiliation of metals to the organic matrix of the coal and ash, the third, by Mn and Fe, and the fourth by Pb related to other anthropogenic sources. For the hydrophilic Technosols only two principle components were distinguished containing 91% of the total variance of the twelve original variables. Most of the heavy metals and Mg loaded the 1st component as well as the cation exchange capacity (CEC), % clay and OC. Manganese and lead loaded the 2nd component and were not related with rest of the metals, which indicates a different source. In some samples of the hydrophobic Technosols the measured contents of Cu and Pb exceeded the national guidelines for agricultural arable lands. The hydrophobicity of the Technosols seems to be related to the contents of Cu and Cr present in the soil organic matrix.

Key words: heavy metals, technogenic soil, hydrophobicity, Principal Component Analysis, geochemistry

Abbreviations: WDPT – Water Drop Penetration Time, OC – Organic Carbon, CEC – Cation Exchange Capacity, SOM – Soil Organic Matter, PCA – Principle Component Analysis

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Introduction

Mining activities cause land alteration and may lead to drastic changes in the ecological conditions. The waste piles often pose extreme threats to environmental restoration. Mining activities lead to disruption of the morphology of the soil profile, soil horizons, disturbance of soil microbial populations and the ecosystem in general Sheoran et al. (2010). The overburden dumps are often characterized by elevated bioavailability of metals, lack of enough moisture, increased compaction and relatively low organic matter content. They may be acidic, due to pyrite and metal sulphides and, which generate acid-mine drainage. A common practice in land reclamation is to apply surface soil humus layer, which assists in the prevention of further oxidation of the overburden layers of black clays consisting of a mix of sandstone, pyrites and waste coal, therefore facilitating the subsequent revegetation of the site (Barnhisel and Hower, 1997). Forestation, or biological reclamation initiates soil-forming processes in surface coal mine spoils (Krümmelbein et al., 2012).

Garbucheve et al. (1975) have conducted complex long-term studies of the Maritsa-Iztok Coal Basin for reclamation of lands for agricultural purposes. Pliocene sediments located above the coal layer are used as a main substrate for reclamation purposes. Hristov and Banov (1996) studied several profiles reclaimed without spreading of humus horizon on the surface, with different land use type and different period of development for establishment of changes that occur in substrates. Banov and Marinkina (2002) studied the conditions for biological restoration of reclaimed soils from Maritsa-Iztok Mines through spreading a humus layer of ~ 40 cm thickness. The authors found that the reclaimed soils were of heavy texture which determines unfavorable water physical properties. In spite of the low humus content (1.52 to 2.35%), the pH is slightly alkaline (pH H₂O 7.3 – 7.7) which prevents mobilization of heavy metals. The yellow and green clays could be a suitable substrate for development of vegetation, however the high acidity of the black clays may cause serious environmental consequences. Magnesium exhibits higher contents in primary and secondary minerals in the yellow clays comprising the uppermost layer of the stratigraphic profile, immediately underlying the soil layer and comprising a major component of the reclaimed soils (Garbucheve et al., 1975). A useful amendment and ameliorant of the overburden substrate is the coal ash (pH 7-7.3) a waste product from the nearby coal incineration thermal power plant. Heavy metals in coal may be classified according to their association with the organic fraction, the mineral fraction or with both.

The elements including As, Cd, Hg, Pb and Zn are mostly concentrated in the organic fraction of the coal, while Cr, Cu and Se were present in both the mineral and organic matter (Chadwick et al. 1987). Coal ash is characterized by higher concentration of metals (Schwab et al., 1991) with arsenic pollution being directly related to trace element production from the combustion of coal (Huggins et al. 1993). The trace elements may be enriched to 10 times during coal combustion (Fernandez-Turiel et al., 1994).

The objective of the present study was to evaluate the local geochemical and contamination associations of eight heavy metals i.e. Cu, Zn, Co, Cr, Ni, Mn, Fe and Pb ($\rho > 5 \text{ g/cm}^3$, Duffus, 2002), and the alkaline earth metal Mg ($\rho 1.7 \text{ g/cm}^3$) and relate these patterns with the hydrophobicity and/or hydrophilicity of the studied soils.

Materials and Methods

The study was carried out on four plots, two of them near Mednikarovo village, subject to humus and non-humus reclamation > 20 years ago, and the other two at Obruchishte village, between Troyanovo 1 and Troyanovo 3 mines of Maritsa-Iztok coal mine in Bulgaria. The experimental plots near Obruchishte were located in several hectares of large area, afforested with *P. nigra*. These spoils were created > 30 years ago and consisted of loam-textured Pliocene overburden sediments from the nearby open-cast lignite mines. The GPS coordinates (UTM-system) of the sites are: Obruchishte, Site 1: N 42.16434, E 25.94285, and N 42.16452, E 25.94318 and Mednikarovo, Site 2: N 42.11007, 42.11445 and E 26.03877, 26.02697. A lack of plant density and water repellency (hydrophobicity) was observed at spots of ~200 m² amongst a uniformly pine vegetated area at the Obruchishte site.

At the four sites, grids $\Delta 2 \text{ m}$, ~ 40 m² were constructed and sampling was at two depths where water repellency was demonstrated on the field 0-5 (10) cm and at 10-20 cm. At the non-vegetated site of Obruchishte, soils were of sandy loam texture mixed with degraded finely dispersed lignitic particles and coal ash, and of sandy clay (0-5 cm) and clay texture at 10-20 cm at the pine vegetated site. Layers of greyish-green and yellow clays intermixed with coal and ash were located at surface depths of 0-10 cm and prevailing black clays at depths > 20 cm. At the non-vegetated site, the substrate 0-50 cm was found to be water repellent since water drop penetration time (WDPT) which is an indicator of the persistence of potential water repellency was > than several minutes. Soil cores were taken to a depth of 0-10 and 10-20 cm and at two points to a depth of 0-50 cm using a 3 cm wide and 25 cm

long core sampler. Soil samples at the field were classified as non-repellent (WDPT < 5s), strongly (60 s < WDPT < 600 s) and severely > 600s water repellent according to the scale of De Bano (1981). The soil samples were equilibrated at the ambient air humidity for four days before measuring water drop penetration time (WDPT) in the laboratory at recorded humidity and temperature.

Soils at the Mednikarovo site were non-water repellent (hydrophilic), since WDPT was < 5s. At Mednikarovo site the investigated soils were: (i) humus layer-reclaimed soil of clay loam texture and non-humus reclaimed soil of sandy loam texture. The surface horizon with ~ 40 cm depth is a translocated humus horizon of natural Vertisol occupying the territory prior to mining. The sub-layers of ~ 2 m are composed of yellow and green clays comprising the overburden sediments of the stratigraphic profile and possessing suitable physico-chemical characteristics (pH ~ 7).

Total organic carbon (TOC) in the studied spoils was determined by oxidation with K₂Cr₂O₇/H₂SO₄ and organic carbon fractionation by the method of Kononova (1963), modified by Filcheva and Tsadilas, 2002), cation exchange capacity (CEC) was assessed as sum of titratable acidity (pH 8.2) and extractable Ca, by saturation with K malate at pH 8.2 (Ganev and Arsova, 1980). Soil water-repellency (soil hydrophobicity) was measured by the water drop penetration time (WDPT) method (Doerr et al. 2002). Three droplets of distilled water (80 µl) were placed on the soil surface and the time was recorded for droplet penetration. Total (pseudo-total) content of metals were assessed according to ISO 11466:1995 aqua-regia method.

Statistical analysis (principal component PCA and cluster CA) was performed by SPSS 22 for MS Windows.

Results and Discussion

General soil characteristics

The mobility of heavy metals in coal mine spoils-turned soils depends strongly on the properties of the technogenic soils. In the process of coal mine spoils-water interaction, sulfides release metals, which are then adsorbed and complexed by organic matter and iron (oxy)hydroxides resulting from pyrite oxidization (Dang et al., 2002). During the natural weathering of coal mine spoils in acid conditions, a considerable fraction of these metals becomes mobile and is released to the environment. Texture is another factor influencing heavy metal adsorption. The soils at Obruchishte under pine vegetation contain between 21% and 36% clay (< 0.001 mm) in the 0-5 cm layer and 30-70% in the 10-20 cm layer, and those at the

non-vegetated plot had a lighter texture, i.e. 14-28% clay at a depth of 0-20 cm. The Technosols under humus and non-humus reclamation at Mednikarovo site were heavier in texture ranging from 23-44% clay for the 0-10 cm layer and from 26-51% clay for 0-20 cm layer. The soil reaction was near neutral (Table 1) thus preventing most of the heavy metals from being mobilized to considerable amounts. At the Obruchishte site, however, soil samples were extremely acidic (Table 1), although having been mixed with coal ash (coal ash from the cinder embankment has a pH 7-7.3, Zheleva and Tsoleva, 2004). The high acidity of the non-vegetated site is a result of the weathering of black clays present in the overburden layers releasing amphoteric metals such as Fe and Al. The electrical conductivity of the hydrophobic technogenic soils was an order of magnitude higher than in the hydrophilic soils from Mednikarovo (Table 1), due the higher ionic strength (mostly sulfate) of overburden clays containing coal and ash impurities. Total organic carbon (TOC) of Mednikarovo soils was low ~ 1% and was higher for the humus reclaimed soils, than in the non-humus reclaimed ones. The higher TOC of the hydrophobic technogenic soils than in the hydrophilic ones was due to admixtures of coal and ash during the reclamation process (Table 1).

Total metal contents and geochemical associations

Total metal contents at the four sites of the reclaimed soils studied (Table 2) were below the maximum permissible loads designated by the national regulation standards (Regulation No 3, 2008). However, at the very acid pH values of the Obruchishte Technosols some contents of Cu and Pb for some samples (Table 2) exceeded the national regulation standards. In addition, the soluble metal concentrations e.g. Al, Fe, Cu, Zn and Co, provoked by the extremely acid pH ~ 3 were higher than maximum permissible levels for surface waters (Regulation No 12, 2002, unpublished data, Project DN 06/1 NSF, Ministry of Education and Science).

Statistical analysis

Hydrophobic Technosols (Obruchishte)

The Principal Component Analysis (PCA) for the water repellent Technosols at Obruchishte was used in the simultaneous study of thirteen factors and explained the data variability in the process of factor reduction to several unrelated components. Four factors with eigenvalue > 1 were extracted when analyzing data. The Principal component analysis was based on the thirteen variables: Cu, Cr, Co, Ni, Pb, Zn, Fe, Ni, Mn, Mg, % clay, % TOC and cation exchange capacity

Table 1. Main soil properties of the experimental soils. (From Atanassova et al., 2017, submitted to BJAS)

| Site | Depth cm | WDPT * (s) | pH | | EC (mS/cm) | | TOC % | | CEC _{8.2} (cmol.kg-1) | | Clay % | |
|--------------------------------------------|-------------|---------------|------|------|------------|-------|-------|------|-----------------------------------|------|--------|------|
| | | | Mean | ± SD | Mean | ± SD | Mean | ± SD | Mean | ± SD | Mean | ± SD |
| Mednikarovo hu- mus reclamation | 0-10 | 1 | 6.9 | 0.01 | 0.04 | 0.01 | 1.50 | 0.02 | 56.3 | 0.2 | 38.6 | 5.21 |
| | 10-20 | 2 | 6.9 | 0.02 | 0.05 | 0.01 | 1.53 | 0.03 | 56.3 | 0.1 | 45.4 | 4.48 |
| Mednikarovo, non-humus recla- mation | 0-10 | 2 | 7.2 | 0.01 | 0.04 | 0.005 | 1.04 | 0.02 | 29.6 | 0.2 | 24.4 | 1.25 |
| | 10-20 | 1 | 7.2 | 0.01 | 0.04 | 0.005 | 0.37 | 0.01 | 29.8 | 0.1 | 26.6 | 0.96 |
| Obruchishite, pine vegetation | 0-5 | 14-9589 | 4.6 | 0.20 | 0.19 | 0.14 | 5.09 | 0.42 | 41.27 | 3.89 | 28.0 | 7.21 |
| | 10-20 | 2-128 | 4.2 | 0.43 | 0.63 | 0.14 | 3.00 | 1.67 | 44.60 | 3.52 | 55.1 | 21.7 |
| Obruchishite, non-vegetated | 0-10 | 76-14440 | 3.2 | 0.11 | 1.72 | 0.76 | 6.43 | 3.98 | 67.77 | 6.16 | 17.8 | 3.86 |
| | 10-20 | 202-2470 | 3.1 | 0.10 | 1.61 | 0.69 | 6.11 | 0.96 | 69.90 | 8.70 | 17.0 | 2.37 |
| | | 614 | | | | | | | | | | |

* Range and median (underlined)

Table 2a. Total (pseudo-total) contents (aqua-regia) of metals, mg.kg⁻¹ in Technosols.

| Site | Depth, cm | Cu | | Zn | | Co | | Cr | | Ni | |
|--------------------------------------------|--------------|-------|------|------|------|------|------|------|------|------|------|
| | | Mean | ± SD | Mean | ± SD | Mean | ± SD | Mean | ± SD | Mean | ± SD |
| Mednikarovo humus reclama- tion | 0-10 | 22.83 | 1.26 | 36.3 | 0.76 | 12.8 | 0.58 | 26.7 | 1.44 | 26.5 | 0.87 |
| | 10-20 | 22.33 | 1.26 | 36.5 | 4.33 | 12.8 | 0.76 | 26.5 | 3.97 | 27.0 | 1.0 |
| Mednikarovo, non-humus rec- lamation | 0-10 | 7.83 | 0.58 | 18.8 | 3.18 | 4.3 | 0.76 | 4.5 | 1.32 | 5.8 | 1.61 |
| | 10-20 | 6.33 | 1.26 | 19.8 | 5.01 | 3.8 | 0.29 | 4.5 | 0.87 | 5.0 | 1.0 |
| Obruchishite, pine vegetation | 0-5 | 63.67 | 4.25 | 57.7 | 10.0 | 6.0 | 0.87 | 9.3 | 0.29 | 12.7 | 0.76 |
| | 10-20 | 62.83 | 7.15 | 54.0 | 9.85 | 6.2 | 2.25 | 9.0 | 2.29 | 15.5 | 4.27 |
| Obruchishite, non-vegetated | 0-10 | 73.83 | 9.29 | 39.8 | 3.75 | 4.8 | 0.29 | 11.5 | 2.5 | 10.8 | 0.58 |
| | 10-20 | 69.83 | 7.97 | 41.7 | 7.22 | 4.7 | 0.58 | 12.5 | 1.73 | 10.0 | 3.61 |

(CEC), as it has been proved that relationship exists between litho(geo)genic metals and some soil parameters, such as organic carbon and % clay contents (Micó et al., 2006). When analyzing data for the hydrophobic soils, four components have been identified with eigenvectors (eigenvalue) > 1, explaining 43,5%, 17,1%, 11,1% and 8,8 of the total variance 80,7%. The correlation matrix and the component matrix are presented in Table 3 and Table 4. The first three components explaining 70.5% of the variance (80.5%) were rotated in space and the respective distribution is presented in Figure 1. The 1st component was loaded by Zn, Co, Ni, Mg, % clay and Mn (by a lower coefficient). The 2nd component was loaded by WDPT, Cu, Cr, OC, CEC and Fe, the 3rd component, by Mn and Fe, therefore these metals are influenced by two components, and the 4th component was loaded by Pb. Manganese readily substitutes for Fe^{2+} and Mg^{2+} in minerals (Ure and Berrow, 1982). The negatively charged MnO_2 is responsible for the high degree of association of Mn oxides with some transition metals, in particular with Co, Ni, Cu, Zn, Pb, etc. The distribution of MnO_2 in soil has been found to be closely related to the contents of Fe_2O_3 and a close correlation exists between Mn and ferrous iron in igneous rocks, with Mn:Fe ratios in the range 0.015-0.02 (Mielke, 1979).

In our study a positive, although insignificant correlation existed between Mn and Fe ($R=0.408$) (Table 3). The dual origin of Mn, as observed by the statistical analysis may be due to the fact that Mn may in addition have a biogenic source, since it is involved in electron transport in photosynthesis and enzymatic reactions. This assumption is supported by the higher values observed for manganese in the vegetated Technosols (Table 2), than the non-vegetated site.

Cluster analysis for grouping variables in a cluster containing members of similar characteristics and/or origin was performed on the water repellent soils (Figure 2). Two main groups were distinguished in the dendrogram. The first main group was subdivided into two sub-groups: one consisted of the geogenic metals Co, Ni, Zn, Mg, related with the clay fraction and the other by Mn, Fe and Pb. The second main group consisted of the metals Cr and Cu closely related with TOC, WDPT and CEC. This branch of the cluster tree contains the metals related with organic matter causing water repellency, most probably present in the black clays, containing coal and ash having being added as an ameliorant to the substrates.

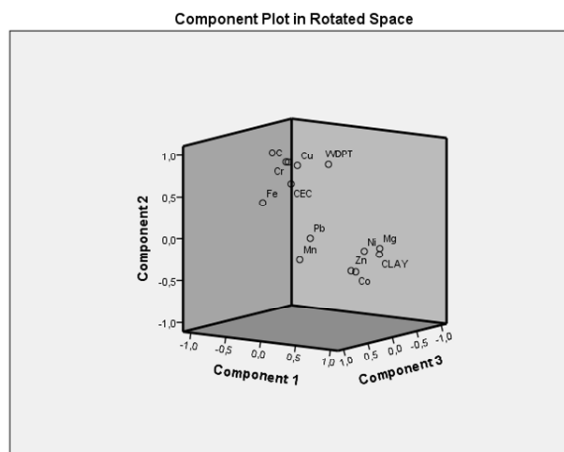


Fig. 1. Three components in rotated space (hydrophobic Technosols, Obruchishte site).

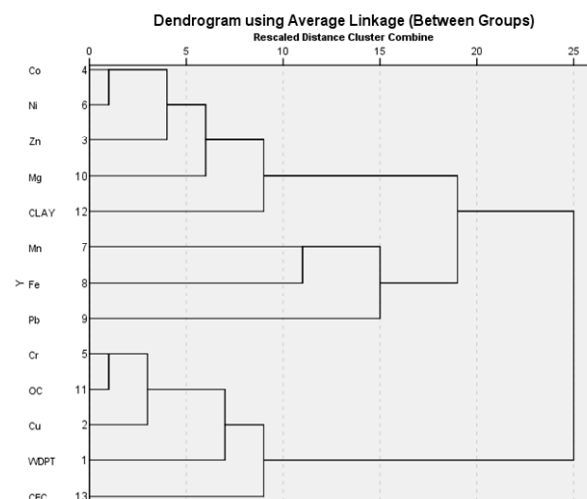


Fig. 2. Cluster analysis with dendrogram for the hydrophobic Technosols from Obruchishte site.

Table 2b (continued). Total (pseudo-total) contents (aqua-regia) of metals, mg.kg⁻¹ in Technosols (continued).

| Site | Depth, cm | Mn | | Fe | | Pb | | Mg | |
|------------------------------------|-----------|-------|--------|-------|-------|------|------|------|------|
| | | Mean | ± SD | Mean | ± SD | Mean | ± SD | Mean | ± SD |
| Mednikarovo humus reclamation | 0-10 | 950 | 229.13 | 21183 | 3286 | 17.3 | 4.3 | 68.8 | 0.76 |
| | 10-20 | 1000 | 229.13 | 24217 | 1767 | 40.6 | 35.4 | 68.3 | 0.76 |
| Mednikarovo, non-humus reclamation | 0-10 | 900 | 785.8 | 8500 | 6106 | 25.2 | 34.9 | 61.8 | 0.76 |
| | 10-20 | 566.7 | 275.4 | 5317 | 1955 | 24.7 | 23.7 | 61.7 | 0.76 |
| Obruchishite, pine vegetation | 0-5 | 800 | 217.95 | 9800 | 985 | 30.0 | 9.9 | 61.5 | 3.12 |
| | 10-20 | 833 | 711.22 | 13133 | 10069 | 43.7 | 16.2 | 62.2 | 1.76 |
| Obruchishite, non-vegetated | 0-10 | 400 | 50 | 12583 | 3761 | 27.0 | 13.3 | 59.5 | 0.87 |
| | 10-20 | 366.7 | 76.4 | 12917 | 5.07 | 38.0 | 5.1 | 60.0 | 1.80 |

Table 3. Correlation matrix for heavy metals and major soil properties of the hydrophobic technogenic soils at Obruchishite site (coal and coal ash treated).

| | WDPT | Cu | Zn | Co | Cr | Ni | Mn | Fe | Pb | Mg | TOC | CLAY | CEC |
|------|-------|--------|--------|--------|--------|-------|-------|-------|-------|--------|--------|--------|--------|
| WDPT | 1.000 | .487* | -.278 | -.177 | .549* | -.087 | -.135 | .247 | .203 | -.063 | .699* | -.116 | .408 |
| Cu | .487* | 1.000 | -.483* | -.659 | .706* | -.352 | -.261 | .354 | -.217 | -.303 | .757* | -.240 | .394 |
| Zn | -.278 | -.483* | 1.000 | .674* | -.365 | .690* | .623* | -.289 | -.126 | .648* | -.401 | .434 | -.533* |
| Co | -.177 | -.659* | .674* | 1.000 | -.378 | .852* | .465* | -.185 | .147 | .577* | -.491* | .398 | -.501* |
| Cr | .549* | .706* | -.483* | -.659 | 1.000 | -.161 | -.123 | .615 | -.002 | -.262 | .811* | -.462* | .623* |
| Ni | -.087 | -.352 | .690* | .852* | -.161 | 1.000 | .475* | -.016 | .041 | .691* | -.396 | .587* | -.446* |
| Mn | -.135 | -.261 | .623* | .465* | -.123 | .475* | 1.000 | .403 | .124 | .267 | -.116 | .146 | -.503 |
| Fe | .247 | .354 | -.289 | -.185 | .615 | -.016 | .403 | 1.000 | .307 | -.270 | .442* | -.359 | .222 |
| Pb | .203 | -.217 | -.126 | .147 | -.002 | .041 | .124 | .307 | 1.000 | .085 | -.124 | -.064 | -.050 |
| Mg | -.063 | -.303 | .648 | .577* | -.262 | .691* | .267 | -.270 | .085 | 1.000 | -.446* | .615* | -.402 |
| TOC | .699* | .757* | -.401 | -.491 | .811* | -.396 | -.116 | .442* | -.124 | -.446* | 1.000 | -.442* | .466* |
| CLAY | -.116 | -.240 | .434 | .398 | -.462* | .587* | .146 | -.359 | -.064 | .615* | -.442 | 1.000 | -.603* |
| CEC | .408 | .394 | -.533* | -.501* | .623* | -.446 | -.503 | .222 | -.050 | -.402 | .466* | -.603* | 1.000 |

Table 4. Rotated component matrix for the hydrophobic soils at Obruchishte: varimax with Kaiser normalization

| | Component | | | |
|------|-----------|-------|-------|-------|
| | 1 | 2 | 3 | 4 |
| WDPT | .080 | .825 | -.164 | .283 |
| Cu | -.288 | .792 | -.053 | -.301 |
| Zn | .742 | -.315 | .318 | -.213 |
| Co | .747 | -.339 | .230 | .219 |
| Cr | -.238 | .873 | .203 | .022 |
| Ni | .883 | -.074 | .248 | .072 |
| Mn | .383 | -.143 | .856 | .004 |
| Fe | -.256 | .458 | .701 | .289 |
| Pb | .006 | -.029 | .102 | .940 |
| Mg | .863 | -.093 | -.097 | .077 |
| OC | -.324 | .856 | .128 | -.142 |
| CLAY | .754 | -.199 | -.244 | -.121 |
| CEC | -.511 | .521 | -.244 | .120 |

Table 6. Rotated Component Matrix. Rotation Method: Varimax with Kaiser normalization for the hydrophilic soils from the Mednikarovo site.

| | Component | |
|------|-----------|-------|
| | 1 | 2 |
| Cu | .993 | .074 |
| Zn | .969 | -.040 |
| Co | .992 | .102 |
| Cr | .993 | .028 |
| Ni | .987 | .129 |
| Mn | .269 | .805 |
| Fe | .900 | .405 |
| Pb | -.068 | .846 |
| Mg | .983 | .110 |
| TOC | .852 | .281 |
| CLAY | .905 | .147 |
| CEC | .983 | .113 |

Table 5. Correlation matrix for heavy metals and major soil properties of the hydrophilic technogenic soils at Mednikarovo site (humus and non-humus reclamation).

| | WDPT | Cu | Zn | Co | Cr | Ni | Mn | Fe | Pb | Mg | TOC | CLAY | CEC |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| WDPT | 1.000 | .949* | .993* | .990* | .992* | .317 | .919* | .003 | .993* | .878* | .889* | .990* | 1.000 |
| Cu | .949* | 1.000 | .956* | .966* | .955* | .232 | .853* | -.084 | .946* | .777* | .860* | .943* | .949* |
| Zn | .993* | .956* | 1.000 | .992* | .998* | .335 | .935* | .035 | .984* | .861* | .906* | .992* | .993* |
| Co | .990* | .966* | .992* | 1.000 | .990* | .251 | .909* | -.003 | .983* | .829* | .889* | .987* | .990* |
| Cr | .992* | .955* | .998* | .990* | 1.000 | .339 | .939* | .075 | .984* | .860* | .904* | .996* | .992* |
| Ni | .317 | .232 | .335 | .251 | .339 | 1.000 | .585* | .391 | .363 | .504* | .342 | .299 | .317 |
| Mn | .919* | .853* | .935* | .909* | .939* | .585* | 1.000 | .259 | .924* | .869* | .881* | .918* | .919* |
| Fe | .003 | -.084 | .035 | -.003 | .075 | .391 | .259 | 1.000 | .023 | .092 | .080 | .088 | .003 |
| Pb | .993* | .946* | .984* | .983* | .984* | .363 | .924* | .023 | 1.000 | .856* | .881* | .982* | .993* |
| Mg | .878* | .777* | .861* | .829* | .860* | .504* | .869* | .092 | .856* | 1.000 | .740* | .848* | .878* |
| TOC | .889* | .860* | .906* | .889* | .904* | .342 | .881* | .080 | .881* | .740* | 1.000 | .907* | .889* |
| CLAY | .990* | .943* | .992* | .987* | .996* | .299 | .918* | .088 | .982* | .848* | .907* | 1.000 | .990* |
| CEC | 1.000 | .949* | .993* | .990* | .992* | .317 | .919* | .003 | .993* | .878* | .889* | .990* | 1.000 |

*Significant at $p < 0.05$

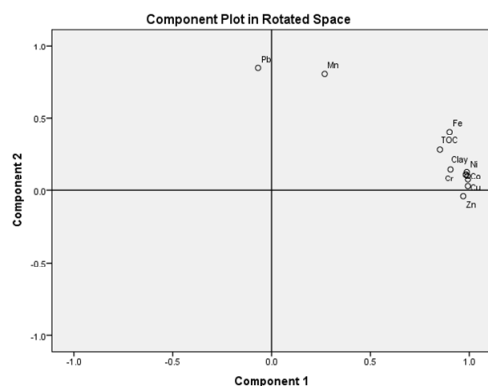


Fig. 3. Component plot in rotated space for the hydrophilic Technosols from the Mednikarovo site.

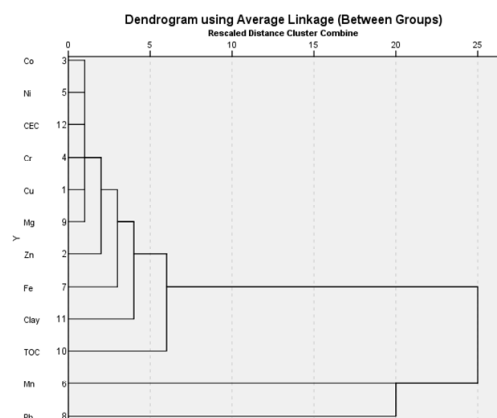


Fig. 4. Cluster analysis for the hydrophilic Technosols from the Mednikarovo site.

Hydrophilic Technosols (Mednikarovo)

A completely different pattern was obtained when performing the PCA and Cluster analyses for the hydrophilic soils from Mednikarovo. Only two principle components were identified explaining 79% and 12% of the total variance (91%, Table 6, Figure 3). The correlation matrix (Table 5) revealed strong statistically significant correlations between most of the heavy metals and their close association and strong correlation with the first component (Table 6). The second component was loaded by the elements Mn and Pb, implying a different source for these metals. The cluster analysis supports the PCA data (Figure 4). The dendrogram includes two main groups. All

the metals Co, Ni, Cr, Cu, Mg, Zn and Fe were related with the clay and organic carbon (OC) content from the first main group. The fact that for the water repellent Technosols only Cu and Cr were associated closely with OC implies more or less association with different type and/or source of organic carbon compared with the organic carbon of the hydrophilic soils. The second main group consists of Mn and Pb of different origin and/or source. Manganese may have biogenic sources and Pb predominantly anthropogenic, e.g. from vehicle emissions during transportation of overburden sediments.

Conclusions

Assessed weremetal associations of hydrophilic and hydrophobic Technosols possessing contrasting hydrologic and acidic characteristics from the region of Maritsa-Iztok coal mine region in Bulgaria. The PCA and cluster analyses performed on the water repellent Technosols revealed that four principle components were distinguished explaining 80.5% of the total variance of the thirteen variables tested. Zinc, Co, Ni, Mg contents were related with the % clay, implying affiliation of the aforementioned metals to overburden clays. Water repellency (WDPT), Cu, Cr, Fe, organic carbon (OC) and cation exchange capacity (CEC) were closely associated, indicating links of these metals to the organic matrix of the coal and ash. Manganese and Fe had a dual source, while Pb is related to different anthropogenic sources, e.g. motor vehicle emissions.

For the hydrophilic soils most of the heavy metals and Mg were present in organo-mineral associations with the clay fraction and organic carbon. Manganese and Pb were not related with rest of the metals, and therefore originate from a different source. The measured total contents of Cu and Pb for some hydrophobic soils exceeded the national guidelines for agricultural arable lands at the acid pH~3. The hydrophobicity of the soils seems to be related to the concentrations of Cu and Cr present in the soil organic matrix.

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