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Soil pollution

INFLUENCE OF SOIL WATER REPELLENCY ON HEAVY METAL MOBILITY IN COAL ASH RECLAIMED TECHNOSOLS

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Abstract. Soil water repellency has major implications for surface and subsurface water transport and organic and inorganic contaminant mobilisation. Heavy metal mobility and speciation in solutions from acidic coal ash reclaimed Technosols from a major coal mine region in Eastern Europe were studied with the aim to reveal relationships with soil water repellency and other soil characteristics. The non-vegetated and pine-vegetated Technosols studied exhibit small-scale spatial variability of water repellency with 'water drop penetration times' (WDPT) varying from 14–14440 s. Metal mobility (H_2O, 0.01 M $CaCl_2$ and 1 M NH_4NO_3) was closely related with the cation exchange capacity (CEC) and WDPT. Principal component analysis (PCA) and cluster analysis involving exchangeable and soluble forms of Co, Cu, Fe, Mn, Ni, Zn and Pb and other soil properties and characteristics revealed that soil water repellency and mobile Fe had the coal as a source. Most of the 0.01M $CaCl_2$ soluble and exchangeable heavy metals were positively and significantly correlated with the WDPT. The majority of metal species at the non-vegetated site were represented by free ions (M^{2+}) and sulphate complexes (MSO_4^0). Results suggest that coal and ash are sources for mobile fractions of heavy metals. The high share of free and neutral dissolved species may pose a risk for metal contamination in these water repellent Technosols.

Keywords: Technosols, soil water repellency, heavy metal mobility, speciation, sources.

AIMS AND BACKGROUND

The overburden dumps around coal mines are often characterised by elevated bioavailability of metals, lack of enough moisture, increased compaction and water repellency[1,2]. In addition, high acidity due to pyrite and metal sulphides may generate acid-mine drainage[3]. Pliocene sediments composed of yellowish-green and greyish-green clays located above the coal seams are used as a main substrate for reclamation purposes at Maritsa-Iztok coal mines, the biggest coal mine complex in Eastern Europe. A common practice in land reclamation is the application of surface soil humus layer, which prevents further oxidation of the overburden

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layers of black clays consisting of sandstone, pyrites and waste coal admixtures[4]. Forestation, i.e. biological reclamation, is considered a useful practice for initiating soil-forming processes in surface coal mine spoils[2]. In spite of the low humus content, the slightly alkaline pH of the overburden clays prevents mobilisation of heavy metals. In the beginning of the reclamation period (1970s), however the black 'greasy' clays situated just above the coal seams have been inadvertently mixed with the yellowish-green and greyish-green clays thus causing serious problems, due to extreme acidity. Coal ash (pH 7–7.3), a waste product from the nearby coal incineration thermal power plant was then applied as a potential amendment and ameliorant[5,6] found that the elements including As, Cd, Hg, Pb and Zn were mostly concentrated in the organic matrix of the coal, Cr, Cu and Se were present in both the mineral and organic fraction, while ash was enriched with trace elements[7].

It has been estimated that in acid sulphate drainage waters from mine waste tailings, sulphate may modify the aqueous geochemistry of Al, Fe and other heavy metals and the solubility of Al/Fe is controlled by Al/Fe oxides, oxyhydroxides and sulphates[8,9].

Based on the literature survey, this is the first study to investigate metal mobility and speciation in water repellent Technosols possessing coatings of hydrophobic (amphiphilic) compounds[10]. The transport of contaminants in these soils follows concentrated heterogeneous preferential flow path patterns of water in more wettable zones, hence enhancing preferential transport of contaminants to the subsurface and ground water[11].

The objective of the present study was to examine mobile (soluble and exchangeable) metals in Technosols reclaimed with coal ash and to investigate links with soil wettability (soil water repellency).

EXPERIMENTAL

A lack of plant cover and the occurrence of water repellency was observed at areas of ~ 200 m^2 amongst a uniformly pine vegetated area. At two sites, one non-vegetated and one uniformly vegetated area, grids Δ2 m, ~ 40 m^2 were constructed and sampling carried out at two depths where water repellency was evident in the field at 0–5 cm and at 10–20 cm. At the non-vegetated site, 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 (10–20 cm) at the pine vegetated site. Layers of greyish-green and yellow clays intermixed with black clays containing coal and ash were located at the surface and at depths of 0–10 cm.

Soil cores were taken to a depth of 0–5 (10) and 10–20 cm using a 3 cm wide and 25 cm long core sampler for laboratory analysis. 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.

Soil water-repellency (soil hydrophobicity) was measured by the water drop penetration time (WDPT) method[12].

Total organic carbon (TOC) in the samples taken was determined by oxidation with $K_2Cr_2O_7/H_2SO_4$ and fractionated TOC into humic-organic carbon (HOC) and fulvic-organic carbon (FOC) upon treatment with 0.1M $Na_4P_2O_7$ and 0.1M NaOH by the Kononova method, 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. Electrical conductivity (EC) was determined in soil:water (1:5) according to Ref. 13. Soil pH/Eh were measured in a soil:water slurry of 1:2.5. Texture was analysed by the Kachinski method. Statistical analysis (principal component PCA and cluster) was performed by SPSS 22 for MS Windows.

Heavy metals in soils (in three replications) were determined by the following methods: water soluble forms in soil:water ratio 1:5, shaking for 1 h, centrifuging and filtering through 0.45 μm acetate cellulose filter[14]; 0.01 M $CaCl_2$ extractable forms in soil:sollution ratio (1:5) and shaking for 2 h (Ref. 15); exchangeable metals were determined by extraction with 1M NH_4NO_3 (Ref. 16). Cationic composition of metals in 1M NH_4NO_3 and aqua regia extracts was determined by AAS (Perkin Elmer). Anions in the soil solution including dissolved organic carbon (DOC) were analysed with Spectroquant tests, Merck Millipore (PHARO 100). Heavy metal speciation was performed by using Visual Minteq V 3.1.

The analytical laboratory investigations of H_2O and 0.01M $CaCl_2$ extracts were performed with a high resolution radial viewing ICP – OES system – HORIBA JY ULTIMA 2 (Jobin Yvon, Longjumeau, France). Each element was determined by two most prominent lines, free from line interference level from the matrix elements (Al, Ca, Fe, Mg and Ti).

RESULTS AND DISCUSSION

Metal solubility and mobility. General soil properties are presented in Table 1*a*, *b*. It is evident that samples from the non-vegetated Technosol have higher contents of sand than the pine-vegetated, respectively lower clay contents, however, their CEC values, EC and TOC are higher than at the vegetated site. This is owing to the accumulation of coal particles in the sand fraction (unpublished data from soil aggregate analysis, Project DN 06/1 NSF) and the high proportion of humified organic matter in coal[18]. Total heavy metal contents did not exceed the national regulation standards for agricultural soils, except for Cu and Pb at $pH < 5$ (Refs 19 and 20). However, water soluble and readily available (0.01 M $CaCl_2$) concentrations of Fe, Mn, Ni, Cu and Zn (Table 2) associated with the extremely acid $pH \sim 3$ at the non-vegetated site were higher than maximum permissible levels for surface waters[21] and may become a source of contamination. Concentration levels at or below the detection limits for ICP-OES for Co, Fe, Cd and Pb were measured at the pine-vegetated Technosol due to the slightly higher pH, lower DOC and the role of vegetation. It is interesting to note, that metal concentrations in 0.01M $CaCl_2$ extracts were lower than those in H_2O, due to several obvious reasons: Ca^{2+} ions decrease the solubility of metal-organic complexes and help colloids aggregation as found for Cu (Ref. 22) and assessed for large sets of data[23].

Table 1*a*. Main soil properties of the experimental soils, PV pine vegetation, NV non-vegetated[17]

Site	Depth (cm)	WDPT (s)	Sand (%)		Silt (%)		Clay (%)		Hygroscopic moisture (%)		CEC (cmol/kg)	
		range median	mean ±	SD	mean ±	SD	mean ±	SD	mean ±	SD	mean ±	SD
PV	0–5	14–9589 1200	47.5	7.21	22.4	0.07	28.0	7.21	8.2	0.69	41.27	3.89
	10–20	2–128 10	25.5	20.45	22.04	0.03	55.1	21.72	8.4	0.54	44.60	3.52
NV	0–10	76–14440 1282	59.0	1.89	21.8	0.08	17.8	3.86	8.2	0.63	67.77	6.16
	10–20	202–2470 614	62.8	4.84	21.3	0.10	17.0	2.37	7.8	1.9	69.90	8.70

Table 1*b*. Main soil properties of the experimental soils (continued)[17]

Site	Depth (cm)	$pH_{(H_2O)}$		EC (mS cm^{-1})		TOC (%)	
		mean	SD	mean	SD	mean	SD
PN	0–5	4.58	0.20	0.19	0.14	5.09	0.42
	10–20	4.18	0.43	0.63	0.14	3.00	1.67
NV	0–10	3.18	0.11	1.72	0.76	6.43	3.98
	10–20	3.13	0.10	1.61	0.69	6.11	0.96

Table 2. Heavy metal concentrations in H_2O and 0.01 M $CaCl_2$ extracts in the soils studied

	Co	Cu	Fe	Mn	Ni	Zn	Al	Cr	Pb
H_2O									
Range	0.008–	0.089–	0.067–	0.415–	0.29	0.48 –	0.442–	–	–
(mg l^{-1})	0.380	0.278	10.02	26.53	–1.08	3.15	192.1		
Mean	0.23	0.15	2.90	9.13	0.62	1.62	75.67	–	–
± SD	0.08	0.06	2.68	7.83	0.27	0.98	51.51	–	–
0.01M $CaCl_2$									
Range	0.005–	0.007–	0.005–	0.04–	0.008–	0.25–	0.12–		
(mg l^{-1})	0.268	0.235	12.21	1.95	0.745	19.22	203.1	–	–
Mean	0.11	0.08	1.97	0.70	1.91	1.34	55.98	–	–
± SD	0.10	0.07	3.09	0.57	3.09	0.82	62.69	–	–
1M NH_4NO_3							from CEC		
Range	0.03–	0.20–	0.65–	4.95–	0.10–	0.20–	54–	0.05–	0.40–
(mg kg^{-1})	2.48	1.98	148	194.0	4.80	15.38	2358	0.48	1.43
Mean	1.13	0.69	25.45	77.75	2.67	5.12	1044	0.18	0.81
± SD	0.99	0.72	43.08	64.38	2.04	5.57	731	0.18	0.29

To obtain more information about the interrelation between the various forms of metals and major soil properties and characteristics we conducted Principal Component Analysis (PCA) and cluster analyses. For the 0.01 M $CaCl_2$–soluble forms three major components with eigen values > 1were distinguished explaining 80% of the total variance, for the H_2O – soluble forms, four components with eigen values > 1 containing 86% of the total variance and for the exchangeable 1M NH_4NO_3 forms three components containing 81% of the total variance (Table 3*a*, *b*, *c*). Mobility and solubility of metals (1 M NH_4NO_3, 0.01 M $CaCl_2$) were closely related with the cation exchange capacity (CEC) and WDPT. Lead solubility and mobility was less satisfactorily predicted from measured soil characteristics than solubility and mobility of the other heavy metals. Principal component analysis (PCA) and cluster analysis involving exchangeable and soluble forms of Co, Cu, Fe, Mn, Ni, Zn, Pb and other soil properties and characteristics (CEC, organic carbon (OC) content, % clay, % sand and WDPT) are presented in Tables 3*a*, *b*, *c*, Figs 1–3. All heavy metals (1M NH_4NO_3, 0.01M $CaCl_2$), except Pb were positively related with % sand.

Table 3*a*, *b*, *c*. Component matrix: WDPT, TOC, clay, sand and silt contents and H_2O (a) and 0.01M $CaCl_2$ (b) and exchangeable 1M NH_4NO_3 (c) metals

a

	Rotated component matrix			
	Component			
	1	2	3	4
WDPT	0.118	0.910	0.132	0.178
OC	0.033	0.889	0.201	–0.250
Clay	0.214	0.495	0.728	–0.292
CEC	0.691	0.279	0.121	0.206
Co_W	0.494	0.242	–0.561	0.514
Cu_W	0.870	0.261	–0.035	0.034
Fe_W	0.297	0.847	–0.214	0.219
Mn_W	0.649	0.053	–0.375	–0.042
Zn_W	0.358	0.061	0.068	0.898
Ni_W	0.932	0.052	0.021	0.252
Sand	–0.109	–0.263	–0.947	0.050
Silt	–0.074	–0.232	0.829	0.403
Al_W	0.893	–0.032	0.283	0.202

b

Rotated component matrix				
	Component			
	1	2	3	4
WDPT	0.215	0.012	*0.910*	0.010
OC	0.274	0.279	*0.798*	–0.065
Clay	–0.320	–0.899	–0.040	0.154
CEC	0.843	0.412	0.219	0.094
Co_S	0.833	0.334	0.373	0.144
Cu_S	0.850	0.137	0.375	0.032
Fe_S	0.439	0.138	*0.804*	0.110
Mn_S	–0.057	–0.608	–0.223	0.142
Zn_S	0.269	0.565	0.432	0.591
Ni_S	0.937	0.254	0.189	0.019
Sand	0.350	0.894	0.045	0.007
Silt	0.005	0.317	0.058	–0.918
AI_S	0.946	0.109	0.216	–0.074

c

Rotated component matrix			
	Component		
	1	2	3
WDPT	0.186	0.926	–0.100
OC	0.237	0.839	0.255
Clay	–0.545	–0.123	–0.756
CEC	0.908	0.268	0.169
Pb_Ex	–0.314	–0.338	0.527
Ni_Ex	0.896	0.301	0.141
Cr_Ex	0.781	–0.084	–0.370
Co_Ex	0.901	0.333	0.157
Fe_Ex	0.515	0.798	–0.095
Mn_Ex	0.789	0.478	0.121
Zn_Ex	0.792	0.346	0.018
Cu_Ex	0.830	0.428	0.071
Sand	0.591	0.140	0.671
Silt	–0.031	0.041	0.682

Water soluble fractions of Fe (Fe_W) only were highly correlated with WDPT (R_{H_2O} = 0.80, $p < 0.003$) and Fe_W, Fe_S and Fe_Ex, and WDPT and TOC loaded on one component (Table 3*a*, *b*, *c*). Soluble 0.01 M $CaCl_2$ Co (R = 0.51*), Cu (R = 0.49*), Fe (R = 0.77*), Zn (R = 0.50*) and Al (R = 0.43*), $p < 0.05$, as well as exchangeable Ni (R = 0.55*), Co (R = 0.47*), Fe (R = 0.82*), Mn (R = 0.55*), Zn (R = 0.53*) and Cu (R = 0.54*) $p < 0.05$ were significantly correlated with WDPT.

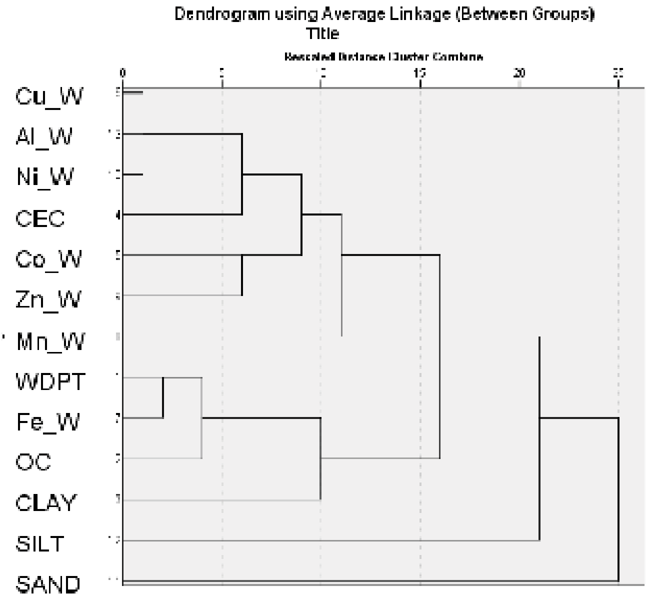

Fig. 1. Cluster analysis representing soluble (H_2O) metals, WDPT, organic carbon (OC=TOC), CEC, clay, silt and sand contents

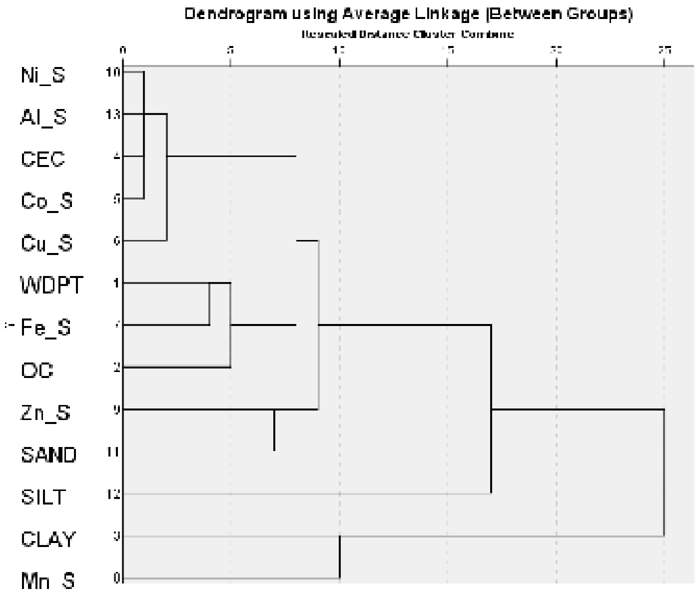

Fig. 2. Cluster analysis representing soluble (0.01 M $CaCl_2$) metals, WDPT, organic carbon (OC=TOC), CEC, clay, silt and sand contents

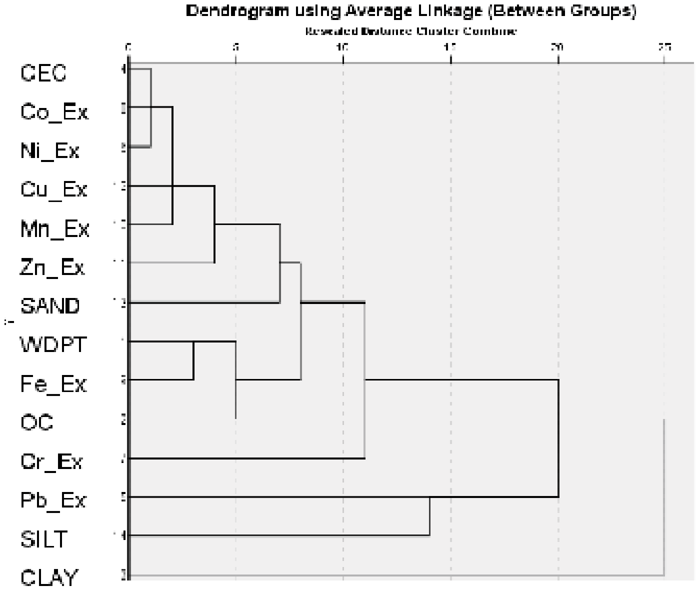

Fig. 3. Cluster analysis representing exchangeable (1M NH_4NO_3) metals, WDPT, organic carbon (OC=TOC), CEC, clay, silt and sand contents

Cluster analysis supported the data from the PCA (Figs 1–3). For the water soluble metals, the dendrogram was composed of four main groups, clustering WDPT, Fe_W and TOC into one sub-group. For the metal – 0.01M $CaCl_2$ (M_S) and metal – 1 M NH_4NO_3 (M_Ex) fractions the dendrogram was divided into three main groups. Soluble metals, CEC, % sand, WDPT and TOC comprise the 1st main group, silt the 2nd main group and % clay and soluble Mn (Mn_S) the 3rd main group. Similarly, the exchangeable metals M_Ex were linked in one main group with CEC, % sand and organic carbon (TOC), exchangeable Pb is linked with % silt into the 2nd main group and % clay is separately grouped in a 3rd group, implying association of exchangeable metals to particles in the sand fraction. The fact that mobile (M_W, M_S and M_Ex) fractions are positioned close to WDPT on the cluster tree and comprise one sub-group of one bigger cluster supports the hypothesis that soil water repellency and soluble and exchangeable fractions of most heavy metals have a similar source.

We suspect that the correlation between mobile fractions of metals, i.e. soluble Fe_W and M_S and soil water repellency (WDPT) might be due to the following: (i) the majority of complex-forming sites on soil colloids are covered by adsorbed organic (hydrophobic) compounds, and (ii) due to preferential flow paths in water repellent soils, water avoids water repellent areas, leaving a greater share of mobile (labile) metal fractions at these sites in contrast to hydrophilic areas, where water removes the labile fraction, leaving more 'specifically' sorbed metals on soil colloids.

Ion speciation in solution. The majority of heavy metal species in the studied Technosols were represented by free ions (M^{2+}) and neutral sulphate complexes (MSO_4^0). Generally, solutions were extremely acidic (pH 3–4) and possessed high electrical conductivity at the non-vegetated site (1.61–1.72 mS cm^{-1} (Table 1*b*) with large amounts of weathering products derived from pyrite oxidation (Fe^{2+}, SO_4^{2-}, H^+), as well as Al^{3+}, Ca^{2+}, Mg^{2+} and Mn^{2+} from mineral weathering. The metal speciation (Table 4) showed that: (i) in the more acidic non-vegetated plot (pH ~ 3.0) mono and disulphate complexes were the most dominant species for Al^{3+}, while M^{2+} were the most common for Cu, Fe, Mn, Ni and Zn; (ii) the distribution of Fe species is controlled by the SO_4^{2-} concentration in solution. In the non-vegetated soil with a pH ~ 3.0, Fe was present as free Fe^{2+} and $FeSO_4^0$ complexes. It was reported that fly ash may cause increase of saturated hydraulic conductivity and additional mobilisation of nutrients and contaminants in the course of acidification[24]. The hydrophobic interactions in the soil organic matrix help decrease the release of organic colloids. In addition, at the acid pH range (3–4) there is: (i) an increase of DOC sorption on soil sesquioxide surfaces and (ii) acidic functional groups on organic compounds are protonated, which leads to a weaker dissociation and charge reduction further lowering metal binding through electrostatic interaction. The range of DOC for the water repellent soils was 10–35.2 mg/l with higher values detected for the more water repellent non-vegetated Technosol. The positive relationships between DOC, WDPT and total organic carbon TOC are given in Fig. 4.

Table 4. Metal speciation in the water extracts

Metal ion	pM[a]	% of total dissolved ions in solution	Species[b]
1	2	3	4
Al^{3+}	3.95–4.65	3.86–11.12	Al^{3+}
		0.04–0.08	$AlOH^{2+}$
		57.65–70.69	$AlSO_4^+$
		17.37–27.78	$Al(SO_4)_2^-$
		0.01–6.36	$AlHPO_4^+$
		0.17–0.26	/FA-Al+3G(aq)
		1.49–4.70	/FA_2Al^+(aq)
Co^{2+}	6.12–7.10	53.6–68.4	Co^{2+}
		28.5–41.0	$CoSO_4$ (aq)
		1.36–2.54	/FA-Co+2G (aq)
		0.46–0.61	/$FACo^+$(aq)

to be continued

Continuation of Table 4

1	2	3	4
Cu^{2+}	6.04–6.90	34.2–63.0	Cu^{2+}
		0.01–0.06	$CuCl^+$
		19.5–43.3	$CuSO_4$ (aq)
		0.02–0.03	$CuHSO_4^+$
		0.38–1.59	/FA-Cu+2G (aq)
		0.77–8.20	/FA_2Cu(aq)
		6.73–30.3	/$FACu^+$ (aq)
Fe^{2+}	4.03–5.26	43.2–66.6	Fe^{2+}
		0.01–0.03	$FeCl^+$
		33.1–55.6	$FeSO_4$ (aq)
		0.22–17.4	$FeH_2PO_4^+$
		0.09–2.30	/FA-Fe+2G (aq)
		0.12–0.79	/FA-Fe(II)$^+$(aq)
Mn^{2+}	3.96–4.46	51.1–73.4	Mn^{2+}
		0.01–0.03	$MnCl^+$
		26.5–47.6	$MnSO_4$ (aq)
		0.49–1.20	/FA-Mn+2G (aq)
		0.03–0.34	/$FAMn^+$ (aq)
Ni^{2+}	5.39–5.89	47.1–69.8	Ni^{2+}
		0.09–1.10	/FA-Ni+2G (aq)
		28.2–49.3	$NiSO_4$ (aq)
		0.01–0.02	$Ni(SO_4)_2^{2-}$
		1.90–12.2	/$FANi^+$ (aq)
Zn^{2+}	4.95–5.78	40.3–64.6	Zn^{2+}
		0.36–0.94	/FA-Zn+2G (aq)
		0.01–0.06	$ZnCl^+$
		29.5–46.2	$ZnSO_4$ (aq)
		2.71–11.3	$Zn(SO_4)_2^{2-}$
		1.01–4.31	/$FAZn^+$(aq)

[a] Negative log activity of free metal ions; [b] bidentate (FA_2M) and M-FA gel fraction species (FA-M+2G; FA-Al+3G).

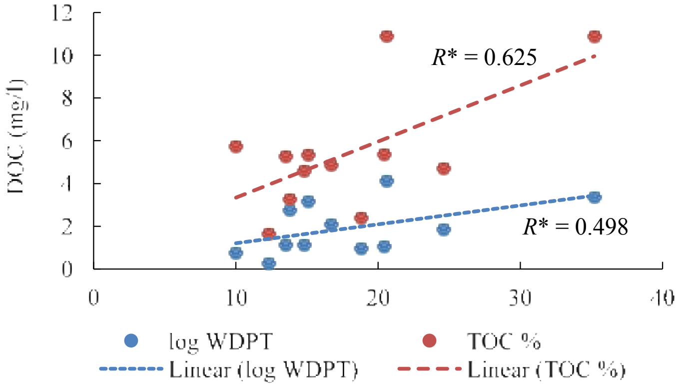

Fig. 4. Relationship between DOC/TOC (WDPT) in hydrophobic Technosols

These results confirm the outcomes from our previous study[25] that DOC contains hydrophobic compounds, including alkanes, associated with amphiphilic colloid micelles in water extracts of water repellent soils.

CONCLUSIONS

Our study attempted to investigate links of heavy metal mobility with soil water repellency in technogenic soils (Technosols) from the largest mine area in Eastern Europe, which have been transformed into 'hot spots' of metal release into the environment.

The key findings are the following: (1) There was a tendency of higher heavy metal mobility in the non-vegetated (pH 3.2 ± 0.1) than the pine-vegetated Technosols (pH 4.6 ± 0.2) as assessed by 1M NH_4NO_3, H_2O and 0.01 M $CaCl_2$ extraction; (2) Mobility of metals, except Pb was closely related with CEC and WDPT, especially strongly for Fe_W, Fe_S and Fe_Ex; (3) Principal component and cluster analysis demonstrate that lignitic coal and ash particles are the main sources for soluble and exchangeable fractions of heavy metals; (4) The high share of free (M^{2+}) and neutral (MSO_4^0) dissolved species may enhance heavy metal mobility and transport in the ash-reclaimed hydrophobic Technosols; (5) Dissolved organic carbon (DOC) was significantly correlated with TOC and WDPT.

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REFERENCES

1. H. H. GERKE, E. HANGEN, W. SCHAAF, R. F. HÜTTL: Spatial Variability of Potential Water Repellency in a Lignitic Mine Soil Afforested with *Pinus nigra*. Geoderma, **102** (3–4), 255 (2001).

2. J. KRÜMMELBEIN, O. BENS, T. RAAB, M. ANNE NAETH: A History of Lignite Coal Mining and Reclamation Practices in Lusatia, Eastern Germany. Can J Soil Sci, **92** (1), 53 (2012).
3. D. S. JONES, C. KOHL, C. GRETTENBERGER, L. N. LARSON, W. D. BURGOS, J. L. MACALADY: Geochemical Niches of Fe-oxidizing Acidophiles in an Acidic Coal Mine Drainage. Appl Environ Microbiol, **81** (4), 1242 (2015).
4. R. BARNHISEL, J. HOWER: Coal Surface Mine Reclamation in the Eastern United States: the Revegetation of Disturbed Lands to Hayland/Pasture or Cropland. Adv Agron, **61**, 233 (1997).
5. A. P. SCHWAB, M. B. TOMECEK, P. D. OHLENBUSCH: Plant Availability of Lead, Cadmium, and Boron in Amended Coal Ash. Water Air Soil Poll, **57** (1), 297 (1991).
6. M. CHADWICK, N. HIGHTON, N. LINDMAN: Environmental Impacts of Coal Mining and Utilization. Pergamon Press, Oxford, 1987, p. 332.
7. J. L. FERNANDEZ-TURIEL, W. de CARVALHO, M. CABANAS, X. QUEROL, A. LOPEZ-SOLER: Mobility of Heavy Metals from Coal Fly Ash. Environ Geol, **23** (4), 264 (1994).
8. M. SHUM, L. LAVKULICH: Speciation and Solubility Relationships of Al, Cu and Fe in Solutions Associated with Sulfuric Acid Leached Mine Waste Rock. Environ Geol, **38** (1), 59 (1999).
9. A. VITAKU, B. BARUTI, I. MALOLLARI, F. SHALA: Impact of Polluted Acidic Waters Discharged from Trepca Pb-Zn Mines, Kosovo, on the Pollution of Cross-Border Rivers in the Region. J Environ Prot Ecol. **14**, 29 (2013).
10. I. ATANASSOVA, S. DOERR: Organic Compounds of Different Extractability in Total Solvent Extracts from Soils of Contrasting Water Repellency. Eur J Soil Sci, **61** (2), 298 (2010).
11. C. J. RITSEMA, L.W. DEKKER, J. M. HENDRICKX, W. HAMMINGA: Preferential Flow Mechanism in a Water Repellent Sandy Soil. Water Resources Research, **29**, 2183 (1993).
12. S. H. DOERR, L.W. DEKKER, C. J. RITSEMA, R. A. SHAKESBY, R. BRYANT: Water Repellency of Soils: The Influence of Ambient Relative Humidity. Soil Sci Soc Am J, **66** (2), 401 (2002).
13. ISO 11265: Soil Quality – Determination of the Specific Electrical Conductivity. 1994.
14. M. KATOH, M. SATOSHI, T. SATO: Single-step Extraction to Determine Soluble Lead Levels in Soil. Int J GEOMATE, **3** (2), 375 (2012).
15. E. van RANST, M. VERLOO, A. DEMEYER, J. M. PAUWELS: Manual for the Soil Chemistry and Fertility Laboratory: Analytical Methods for Soils and Plants Equipment and Management of Consumables. Ghent University, Faculty of Agricultural and Applied Biological Sciences, Department of Applied Analytical and Physical Chemistry, 1999, p. 243 http://hdl.handle.net/1854/LU-113771.
16. H. ZEIEN, G. BRUMMER: Chemische Extraktionen zur Bestimmung von Schwermetallbindungsformen in Boden. Mitteilungen der Deutschen Bodenkundlichen Gesellschaft, **59**, 505 (1989).
17. I. ATANASSOVA, M. BANOV, T. SHISHKOV et al.: Relationships between Soil Water Repellency, Physical and Chemical Soil Properties in Hydrophobic Technogenic Soils from the Region of Maritsa-Iztok Coal Mine in Bulgaria. Bulg J Agric Sci, **24** (2), 10 (2018a).
18. A. PICCOLO, G. PIETRAMELLARA, J. S. MBAGWU: Effects of Coal Derived Humic Substances on Water Retention and Structural Stability of Mediterranean Soils. Soil Use and Management, **12** (4), 209 (1996).
19. DECREE No 3: For Standards of Acceptable Content of Harmful Substances in the Soil. State Gazette, **71**, 2008 (in Bulgarian).
20. I. ATANASSOVA, M. BENKOVA, M. BANOV, TS. SIMEONOVA, L. NENOVA, M. HARIZANOVA: Geochemical Associations in Technogenic Soils (Technosols) of Contrasting Hydrological Characteristics from the Region of Maritsa-Iztok Coal Mine in Bulgaria. Bulg J Agric Sci, **24** (2), 18 (2018b).
21. DECREE No 12: For the Quality Requirements for Surface Waters, Intended for Drinking and Domestic Water Supply. State Gazette, 2002, p. 63 (in Bulgarian).

22. P. F. RÖMKENS, J. DOLFING: Effect of Ca on the Solubility and Molecular Size Distribution of DOC and Cu Binding in Soil Solution Samples. Environmental Science and Technology, **32** (3), 363 (1998).
23. M. McBRIDE, S. SAUVE, W. HENDERSHOT: Solubility Control of Cu, Zn, Cd and Pb in Contaminated Soils. European Journal of Soil Science, **48** (2), 337 (1997).
24. P. HARTMANN, H. FLEIGE, R. HORN: Changes in Soil Physical Properties of Forest Floor Horizons Due to Long-term Deposition of Lignite Fly Ash. Journal of Soils and Sediments, **10** (2), 231 (2010).
25. I. D. ATANASSOVA, S. H. DOERR, G. L. MILLS: Hot-Water-soluble Organic Compounds Related to Hydrophobicity in Sandy Soils. In: Progress in Soil Science: Soil Carbon (Eds A. E. Hartemink, K. McSweeney). Springer International Publishing, Switzerland, 2014, 137- 146.

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