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Pedological characteristics of open-pit Cu wastes and post-flotation tailings (Bor, Serbia)

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Abstract

To gain a better knowledge of mining areas and potential remediation processes, some characteristics (morphological, physical, chemical and microbiological) of soils formed on open-pit Cu mine waste (OPW) and Cu post-flotation tailings (PFT) dumps were investigated. Soil profiles and surface samples were studied. In general, the investigated soils are characterized by large proportion of coarse soil particles, degraded structure, low humus content, low pH, high As and Cu concentrations, and low soil microbial activity. In all investigated profiles there is no recognizable topsoil layer containing *in situ* formed humus probably due to soil age, lack of plant cover and organic litter, as well as other unfavorable soil conditions. The specificity of investigated soils is an irregular distribution of some soil characteristics (porosity, humus content, microbiological activity) over depth, which is a result of their technogenic origin. By establishing correlations between the studied surface sample parameters, using principal component analysis (PCA), poorer aggregate properties of PFT than of OPW soils were found, resulting most likely from aggressive mining, i.e., flotation processes. Both OPW and PFT soils compared with control natural soils are characterized by lower clay and humus content, and poorer aggregate properties.

Keywords: Technosols, aggregates, humus, microbiological activity, PCA

1. Introduction

Agriculture, industry and urbanization induce soil degradation through dramatic physical, chemical and biological transformations but also create new soils characterized by the presence, in various proportions, of pedological, geological and technogenic materials. Soils developed on non-traditional substrates largely generated by intensive human activity are now referenced as Technosols in the World Reference Base for Soil Resources (WRB) 2007 (IUSS Working group WRB 2007). They are composed of various materials, some of which have no equivalent in nature such as technogenic materials, i.e., artefacts (Séré *et al*., 2010).

One of the technogenic materials is the mine waste dumped at or near the mine site turning the modern landscape into waste areas. The original surface soil is usually unevenly buried under mine tailings, so that natural processes of soil evolution are hindered. Similar to natural parent materials, technogenic materials evolve under the influence of pedogenetic contributing to their evolution. The pedogenesis of these soils has not been studied enough remaining therefore mostly unknown (Séré *et al*., 2010), and the processes and mechanisms taking place under such conditions are not easy to predict (Scholtus *et al*., 2009). Different reclamation technologies significantly affect the future technogenic soil development (Courtney, 2013). Recently increased interest in Technosols including better understanding of their functioning and evolution is a result of increasing number of sites affected by technogenic materials and their impact on the environment as growing media for plants or as sources of pollutants (Monserie *et al*., 2009). The recorded trend of soil evolution contributes to a better knowledge of areas affected by similar waste materials, and may be utilized in remediation of abandoned mine areas (Bini and Gaballo, 2006). Most frequently investigated soil processes and characteristics of Technosols are mineral transformations, aggregation, hydraulic properties, accumulation and/or transformation of organic matter, biological activity, etc. (Akala and Lal, 2001; Šourkova *et al*., 2005; Monserie *et al*., 2009; Séré *et al*., 2010).

So, mining activities are one of the causes of man's disruption of the natural land cover and a source of pollutants to the environment. One of the largest mines in Serbia is the Copper Mining and Smelting Basin – Bor, where the exploitation of copper ore started in 1903. In the period of over a hundred years, more than 1,820 million of tons of mine spoil were removed in open-pit mining operation and deposited forming large waste dumps. As a result of copper ore processing, post-flotation tailings dumps were also formed. In addition to degradation of large land areas, these mine wastes are sources of pollution to the surrounding environment (especially the nearby town). In order to restore the function of a portion of the mine waste area, reclamation measures (reconstruction of the top soil by natural, arable soil and/or by planting of trees and grasses) were implemented from the late 70s to the late 90s of the last century. The objective of this paper was to study morphological, physical, chemical and microbiological characteristics of soils formed on open-pit Cu mine waste and post flotation tailings dumps (aged at least 20-30 years). Pedological characteristics of studied soils were compared with natural soils around the mine and natural soils used for the reclamation of post-flotation tailings. Also, the differences between open-pit wastes and post-flotation tailing soil characteristics were discussed.

2. Material and Methods

2.1. Study area

The study area comprises copper mine waste and tailings dumps located in the immediate vicinity of the town of Bor, East Serbia, at about 400 m a.s.l. (440 05' N, 220 06' E). The climate in the region is of a temperate continental type characterized by short hot summers and long, cold winters. Average annual air temperature is 11 ºC, while the minimum and the maximum temperature are -14 C and 35 ºC, respectively. Average annual precipitation is 550 mm. The winds blowing from the northwest are the most frequent and strongest contrary to those from the east.

Two copper mine waste sites: (i) open-pit mine waste dump "Visoki planir" (OPW) and (ii) post-flotation tailing dump "Polje 2" (PFT) were investigated. (i) OPW was formed by disposal of spoils from the open-pit mine active until 1993 when it was definitively abandoned. The dump is of an irregular shape with horizontal terraces and very steep slopes, 32-38°, depth of about 100 m. The primary mineral found is pyrite, then follow coveline, chalcocite, enargite, chalcopyrite and bornite, as well as oxides and hydroxides: limonite, chalcanthite, cuprite, etc. The most common non-ore minerals present are: quartz, kaolin, gypsum and anhydrite (research carried out by Copper Mining and Smelting Basin – Bor, unpublished work). Some areas of the flat terraces were reclaimed from 1979 to 1998 with several species of deciduous trees (locust, wild pear, sycamore, linden, poplar, oak, ash, birch, willow, maple, black pine). Compost was added into the holes for planting trees. Our research covered the main terrace over which walking and therefore sampling was only possible. (ii) The PFT dump was definitively abandoned in 1987, tailings thickness of about 60 m. Pyrite is dominant among the minerals found in the tailings, and then follow chalcopyrite, coveline, enargite, chalcocite, pyrotine, molybdenite, electrum, magnetite, hematite, rutile, limonite, malachite, etc. Non-ore minerals present are silicates, quartz and rarely carbonates (research carried out by Copper Mining and Smelting Basin – Bor, unpublished work). An amount of tailings is in the liquid, the other in the slurry and finally the third (covering about 25 hectares) in the solid state, which as such was included in our investigation. In 1991, an area of about 16 ha was reclaimed by reconstructing the topsoil with natural arable soil, an average depth of 40 cm. The soil was taken from the southern part of the town where the residential area expanded (Novi gradski centar - New Town Center). One part of the reclaimed area was planted with grass and the other with trees. However, strong winds dispersed the tailings particles over the reclaimed area (as well as the town and its surroundings). There are no data on soil characteristics of these waste areas collected before and/or immediately after the remediation.

Today, both mine waste sites are almost bare, with no vegetation. On OPW, birch (*Betula pendula* L.), wild pear (*Pyrus pyraster* (L.) Burgsd.) and shrubs (*Rubus caesus* L. and *Rosa canina* L.) are only sporadically present. Among grasses, *Panicum* spp. and *Agropyrum repens* L. are dominant. Also, the presence of *Euphorbia* spp. and *Potentilla reptens* L. are evident. As for PFT, on reclaimed area only, birch (*Betula pendula* L.), shrubs (*Rosa canina* L. and *Rubus caesus* L.), and several grass species among which dominant *Nardus stricta* L. and *Agropyrum repens* L. are present but very sporadically. Here and there, *Verbascum phlomoides* L. and *Bryopsida* spp sedge appear too.

2.2. Soil survey

A. Soil study was carried out on soil profiles and surface soil samples (Figure 1).

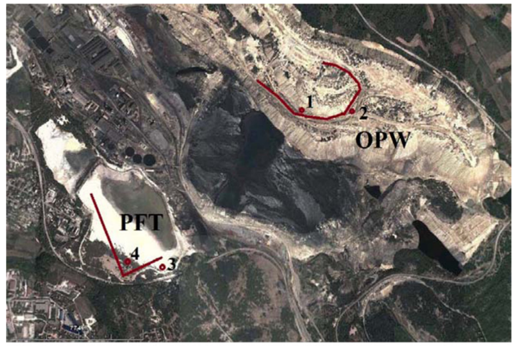

Figure 1. Aerial view of study area. Direction of taking surface samples on both areas is designated by a line, location of profile openings is designated by a point (OPW – open-pit mine wastes, profile 1: lat. 44º04´23.62´´N, long. 22º07´25.68´´E; profile 2: 44º04´21.34´´N, 22º07´43.50´´E; PFT - post-flotation tailings, profile 3: 44º03´52.29´´N, 22º06´51.43´´E, profile 4: 44º03´52.90´´N, 22º06´42.04´´E).

Field investigations were conducted in 2010. Two profiles at each studied mine waste site were opened and described (Table 1). Disturbed and undisturbed soil samples were collected from each soil layer. The soil color was identified according to the Munsell Soil Color Chart. As most of the traces left by soil reclamation and possible pedogenetical processes were expected to be found on the soil surface, 30 disturbed soil samples from each examined site were collected at a 0-25 cm depth. Samples were taken from reclaimed and non-reclaimed areas of both sites at approximately 30 m intervals. Sampling was very difficult; the only possible way to do it on OPW was through the center of the main terrace, and on PFT in the direction of the letter L. Five control disturbed surface soil samples (0-25 cm depth) were collected from each natural soil location; OPWc - natural soil conterminous with the mining area, and PFTc - arable soil originating from the location of the new residential area (Novi gradski centar - New Town Center) used for reclamation of PFT. Control samples were collected in a straight line at ca. 100 m intervals.

Table 1. Location and description of the soils investigated

Profile	Location and field setting	Vegetation	Soil description
1	Cu open pit wastes (OPW), surface of a dump terrace, level, southwest. Alt. 420 m a.s.l.	Sporadic shrubs	Very weakly developed two-layer (C1-C2) soil profile in the upper 100 cm from the soil surface; disposal of spoils from the open-pit mine; contains skeleton; characterized by mix soil colors.
2	Cu open pit wastes (OPW), surface of a dump terrace, gently sloping, southwest. Alt. 451 m a.s.l.	Sporadic locust, low grasses	Very weakly developed two-layer (C1-C2). Formed like C1 and C2 in soil profile 1, but with different skeleton content.
3	Cu post-flotation tailings (PFT), reclaimed part with surface tailings wind deposition, flat. Alt. 366 m a.s.l.	None	Three-layer soil profile (C1-A-C2) in the upper 100 cm from the soil surface. Horizon A, formed by reclamation process, represents a mixture of natural arable soils and tailings. C1 is a wind-transported layer of light yellow post-flotation tailings material from non-reclaimed area. C2 contains uniform color tailings resulting from flotation processes.
4	Cu post-flotation tailings (PFT), reclaimed part, flat. Alt. 368 m a.s.l.	Grasses	Two-layer soil profile (A-C). Horizon A and C formed like A and C2 in profile 3.

B. Coarse fragments, soil texture, bulk density, porosity, size distribution of water-stable aggregates, organic C and pH were determined using common methods (Carter, 1993), while humus content = C x 1.72 was calculated and the soil texture classified using the USDA triangle. Soil aggregate stability based on mean water diameter (MWD) was evaluated in accordance with Le Bissonais (1996); and the structural stability index (SI), proposed by Pieri (1992), to assess the risk of structural degradation was calculated.

Elemental composition of fine soil samples was determined by X-ray fluorescence spectrometry (EDXRF) using a milli-beam XRF spectrometer. The spectrometer (in-house developed at

Vinča Institute of Nuclear Sciences, Serbia) is based on an air-cooled X-ray tube (Oxford Instruments, Rh-anode, max 50 kV, 1 mA) with a pinhole collimator and a SiPIN X-ray detector (6 mm2/500 µm, Be window 12.5 µm thick), associated with a DSP (X123, Amptek, Inc.) for spectra acquisition. Two laser pointers were used for proper positioning of the analyzed sample in the cross-point of the exciting X-ray beam and the detector axis, respectively. ADMCA software was used for spectra analysis. Two experimental setups, 20 kV and 40 kV, 800 µA, no filter and 120 s measuring time were selected and kept constant during all measurements. The soil samples of 500 mg were pressed into pellets 25 mm in diameter. Calibration was carried out using certified reference material (NCS CRM DC 73301 - rock) and two reference materials (IAEA XRF-PT China ceramic and lake sediment) to cover the whole spectrum of elements that might be present in soil samples.

Total number of bacteria was estimated by determination of colony-forming units (CFUxg^{-1} soil) on 0.1xTSA (tryptic soy agar), fungi abundance on rose bengal streptomycin agar (Peper *et al*., 1995), and actinomycetes on starch-ammonia agar. The presence of *Azotobacter* sp. was detected on Fyodorov`s agar. Dehydrogenase activity (DHA) and the phosphomonoesterase activity (PME) were determined by the methods proposed by Casida *et al*. (1964) and Tabatabai (1994), respectively.

Based on the data obtained, the studied soils were classified according to the WRB 2007 classification (IUSS Working group WRB, 2007).

C. The correlation of soil profile data was made by StartSoft Statistica 7.0. The PCA of surface soil sample data, autoscaled prior to analysis, was performed using an IBM SPSS Statistics 19 software package.

3. Results

3.1. Soil profiles

Soil material of OPW was represented by two-layer soil profiles 1 and 2 (Table 2). Both soil layers are characterized by mix soil colors. In surface layers, C1, pale yellow, orange and bright brown are dominant, followed by dark red and reddish brown or gray and grayish white. Dominant colors in subsurface layers, C2, are light gray and grayish white, while bright yellowish brown and gray are less present. Soil structure of both profiles is similar, as well as boundary. The consistency of profile 2 is less hard, and less sticky. Few or very few abundance of roots is the only biological activity registered. The texture of both profiles is very skeletal, sandy loam over depth (Table 3). Also, the soil porosity decreases over depth. Extreme acidity exists in both profiles (except C2 layer of profile 2, which is very acidic). Humus content is very low in both layers of profile 1, and surface layer C1 of profile 2. There is no significant difference in humus content between C1 and C2 layers of profile 1, while it is higher in the subsurface layer of profile 2.

Soil material of PFT was represented by two- and three-layer soil profiles. The two-layer profile (profile 4) consists of the A surface horizon characterized by dominant dull yellowish brown and less by bright yellowish brown soil. The subsurface horizon, C, is characterized by uniform light gray soil color. The three-layer profile (profile 3) has also A and C (designated as C2) horizons, and above the A horizon about 20 cm thick wind transported layer of light yellow tailing material from non-reclaimed area (C1). Soil aggregates are present only in A horizons (formed by reclamation process) of both profiles, while C horizons are structureless (single grain). No biological activity was registered in profile 3 (no vegetation), while roots were found in profile 4. The soil is loamy sand in C1, loam in A and C2 (profile 3), and sandy clay loam in A, and loamy sand in C2 (profile 4).

Table 2. Morphological properties of soils on Cu open-pit mine wastes (OPW, profiles 1 and 2) and post-flotation tailings (PFT, profiles 3 and 4)

Profile	Depth	Horizon	Color (dry)		Color (moist)		Structure[a]	Consistence[b]	Roots[c]	Boundary[d]
	cm		dominant	less	dominant	less				
1	0-60	C1	5Y 8/4 2.5YR 7/6	10R 3/4 2.5YR 3/4	5Y 8/3 10YR 7/8	2.5YR 4/8	mo, gr, mc	shh, st, pl	f, v	c, w
	60-100	C2	10YR 8/2	10YR 7/6	5Y 8/3	10YR 4/6	mo, gr, mc	shh, st, pl	none	bottom
2	0-65	C1	7.5YR 6/8 5/8	7.5Y 6/1 N 8/0 7/0 6/0	7.5YR 7/8 5/6	2.5GY 2/1	mo, gr, mc	sha, sst, spl	m, fe	c, i
	65-100	C2	10YR 6/8, N 7/0	N 4/0	10YR 5/8	N 4/0	mo, gr, mc	sha, sss, pl	f, v	bottom
3	0-15	C1	2.5Y 7/4	-	2.5Y 6/3 6/4	-	single grain	lo, nst, npl	none	a, w
	15-60	A	7.5YR 5/3	-	7.5YR 4/3 4/4	-	st, gr, fm	vha, st, pl	none	a, w
	60-100	C2	5Y 8/1 2.5Y 8/1	-	2.5Y 8/1 8/2	-	single grain	so, st, pl	none	bottom
4	0-45	A	10YR 5/4	2.5Y 7/6	10YR 5/6	-	st, gr, fm	vha, st, pl	fm, v	a, s
	45-100	C	10YR 8/2	-	5Y 8/3, 7.5Y 8/3	-	single grain	so, nst, npl	m, v	bottom

[a] mo -moderate, st -strong; gr -granular; mc -medium to coarse, fm -fine to medium. [b] lo -loose, so -soft, sha -slightly hard, shh -slightly hard to hard, vha -very hard; nst -non-sticky, sst -slightly sticky, sss -slightly sticky to sticky, st -sticky; npl -non-plastic, spl -slightly plastic, pl -plastic. [c] f -fine, m -medium, fm -fine and medium; v -very few, fe -few. [d] a - abrupt, c -clear; s -smooth, w -wavy, i -irregular

Table 3. Some physical and chemical properties of soils on Cu open-pit mine wastes (OPW, profiles 1 and 2) and post-flotation tailings (PFT, profiles 3 and 4)

Profile	Depth	Coars. fragm. >2 mm	Sand 2-0.02 mm	Silt 0.02-0.002 mm	Clay < 0.002 mm	SI[a]	Bulk density	Porosity	C_{org}	pH H_2O
	cm	%	%	%	%	%	g cm^{-3}	cm^3 dm^{-3}	%	
1	0-60	60	55	28	17	0.8	1.3	529	0.2	3.6
	60-100	63	52	31	17	0.7	1.4	435	0.2	3.1
2	0-65	39	57	26	17	0.9	1.2	532	0.2	4.3
	65-100	65	62	23	15	3.6	1.2	516	0.8	5.5
3	0-15	0	82	5	13	1.5	1.1	558	0.2	3.5
	15-60	6	40	35	25	1.1	1.3	482	0.4	4.2
	60-100	0	45	36	18	0.5	1.3	502	0.1	3.8
4	0-45	11	53	21	26	1.7	1.2	514	0.6	4.2
	45-60	0	84	8	8	0.6	1.3	513	0.1	3.8

[a]SI-structural stability index

Soil porosity in the A horizon, profile 3, is lower than in the underneath C2 layer. All horizons of both profiles are extremely acidic. Humus content in all horizons of both profiles is very low, being slightly higher in A horizons compared with C horizons and especially in the wind deposited C1 surface layer, profile 3. PFT layers (C1 and C2) are not skeletal, low gravel contents are present in reclaimed A horizons of both profiles. In all layers of the profiles (OPW and PFT) studied, SI<5% confirming structurally degraded soils. According to Serbian national regulations (The Official Gazette of the RS, 1994), As concentrations in all profiles (all layers) are higher than the maximum permissible levels (Table 4). Also, Cu concentrations are higher in one of layers (surface or subsurface) in all profiles. The concentration of Cu in profile PFT3 (15-60 cm depth) exceeds even the limit values given in the EC Directive (EC C, 1986).

Table 4. Concentrations of elements in soils on Cu open-pit mine wastes (OPW, profiles 1 and 2) and post-flotation tailings (PFT, profiles 3 and 4)

Profile	Depth	Si	Fe	Ca	K	Ti	Mn	Cu	Rb	Sr	Zn	As
	cm					mg·kg^{-1}						
1	0-60	179000	49700	24500	10900	3420	173	122	<10	303	<20	67.2
	60-100	194000	67700	17900	12750	4820	67	73	40.1	363	<20	119.0
2	0-65	189000	41800	33300	16700	3520	324	84	32.8	52.6	126	46.3
	65-100	161000	38100	45700	14650	3780	1309	127	41.5	133	318	49.4
3	0-15	331000	16800	3300	6000	3540	257	68	18.2	1106	<20	110.0
	15-60	268000	35700	12700	15900	5470	1296	223	35.0	264	<20	60.9
	60-100	339000	7100	7400	4200	4460	225	42	<10	1705	161	36.7
4	0-45	295000	41000	11900	13120	4400	952	143	59.5	377	28	42.8
	45-100	377000	12200	9600	6000	2970	176	<10	<10	891	<20	110.0
MPL[a]		-	-	-	-	-	-	100	-	-	300	25

[a]Maximal permissible levels defined by national regulations (The Official Gazette of the RS, 1994).

The obtained results showed low microbial activity in examined mine spoil and tailings samples (Table 5). Total number of bacteria and sporogenous bacteria decrease with depth. The exception is the PFT3 profile where the total bacteria number in the C1 layer, made of wind deposited tailings material, is lower than in the subsurface of the reclaimed A horizon. *Azotobacter* sp. appear in three soil layers only and decrease with depth. Total number of bacteria showed positive correlation with clay and Cu ($r=0.72^{*}$ and 0.86^{**}, respectively). *Azotobacter* sp. also showed positive correlation with clay ($r=0.88^{**}$). The absence of actinomycetes and the low number of fungi in all samples were observed. Alkaline PME is highly correlated with clay as well as with *Azotobacter* sp. ($r=0.80^{**}$ and 0.76^{**}, respectively). Acidic PME is in positive correlation with Fe (r=0.81**). Also, DHA decreases with the increasing number of all examined microbial species, but this dependence is statistically insignificant.

According to WRB 2007 (IUSS Working group WRB, 2007), all examined soils belong to the RSG Technosols (Table 6) because they have 20% or more artefacts (mine spoil) in the upper 100 cm from the soil surface, which have substantially the same properties as when first excavated and modified. All examined profiles, also, satisfy the criterion for Spolic prefix qualifier having 20 percent or more artefacts (consisting of 35 percent or more of mine spoil) in the upper 100 cm from the soil surface. Explanation of suffix qualifiers for each single profile is given in Table 6. As can be seen, only the second suffix qualifier indicates the differences between the profiles.

Table 5. Microorganisms abundance and phosphomonoesterase (PME) and dehydrogenase (DHA) activity in soils on Cu open-pit mine wastes (OPW, profiles 1 and 2) and post-flotation tailings (PFT, profiles 3 and 4)

Profile	Depth	Total bacteria	Sporogenous bacteria	*Azotobacter* sp.	Actinomycetes	Fungi	PME		DHA
							acid	alkaline	
	(cm)	(CFU 10^3 g^{-1})					(µg p-nitrophenol g^{-1} h^{-1})		(µg TPF g^{-1} h^{-1})
1	0-60	15.12	8.25	0.00	0.00	0.00	6.60	0.62	3.98
	60-100	6.12	2.04	0.00	0.00	0.00	7.44	2.65	6.91
2	0-65	10.31	0.69	0.02	0.00	0.07	0.72	2.16	8.78
	65-100	4.81	0.00	0.00	0.00	0.48	2.06	0.20	2.78
3	0-15	6.67	4.00	0.00	0.00	0.67	5.00	0.50	9.43
	15-60	26.94	2.69	0.07	0.00	0.20	1.32	3.04	7.11
	60-100	6.80	0.00	0.00	0.00	0.00	0.61	0.92	9.24
4	0-45	12.24	4.76	0.12	0.00	0.41	2.24	3.18	6.04
	45-100	2.69	0.00	0.00	0.00	0.00	0.30	0.61	7.13

3.2. Surface samples

Figure 2 shows the PCA scores and loadings plots, respectively, of the chosen physical and chemical parameters of 30 OPW and 30 PFT surface samples. The first three principal components describe 67% of the total variance in the initial set in such a way that the first principal component (PC1) describes 34.5% and the second (PC2) 17.6% of the total variance. The scores plot shows that two groups of samples are separated along the PC2 axis, in terms of linear separability and classification. It can be concluded that there is good cohesion within the OPW group of samples, which is slightly undermined for the PFT group. The conclusion drawn from the figure is that coarse sand, total skeleton and water-stable PFT group. The conclusion drawn from the figure is that coarse sand, total skeleton and water-stable aggregates >3 mm (characteristic of the OPW group), and fine sand and water-stable aggregates 1-0.5 mm (characteristic of the PFT group of samples and also negatively correlated with coarse sand, total skeleton and water-stable aggregates >3 mm) are responsible for the separation of groups along the PC2 axis. The following parameters could cause the lowering within PFT group cohesion: water-stable aggregates >0.25 mm, MWD, and water-stable aggregates 2-1 mm, negatively correlated with water-unstable microaggregates <0.25 mm). In order to gain a deeper insight into pedological characteristics of the mine waste soils they were compared with natural soils in the maximum variance space by applying PCA onto the dataset formed of the same parameters as those used in the previous analysis. As found by PCA, the first three components describe 68% of the total variance in the dataset, where PC1 describes 38.7% and PC2 15.8% of the total variance. The group of control samples is clearly distinguished from those of the mine waste samples. The parameters that characterize the group of control sample are MWD, humus, >3 mm water-stable aggregates, and clay. On the other hand, mine waste samples are characterized by the variance of parameters <0.25 mm water-unstable microaggregates, coarse and fine sand and coarse fragments.

Table 6 . Classification of investigated soil according to WRB 2007

Profile	Soil classification	Criteria for suffix qualifiers
OPW 1	Spolic Technosol (Phytotoxic, Skeletic)	*Phytotoxic* - high concentrations of As and Cu.[a] *Skeletic* - 47.15% and 45.29% coarse fragments by volume over depth.
OPW 2	Spolic Technosol (Phytotoxic, Endoskeletic)	*Phytotoxic* - high concentrations of As.[a] *Endoskeletic* - 53.06% by volume coarse fragments over depth between 65 and 100 cm from the soil surface.
PFT 3	Spolic Technosol (Phytotoxic, Areninovic)	*Phytotoxic* - high concentrations of As and Cu.[a] *Areninovic* - above the soil there is a 15 cm tick layer with recent sediment, loamy sand (a new wind deposited flotation tailings material).
PFT 4	Spolic Technosol (Phytotoxic)	*Phytotoxic* - high concentrations of As and Cu.[a]

[a]Within 50 cm of the soil surface. Concentrations higher than maximal permissible levels - national regulations (The Official Gazette of the RS, 1994).

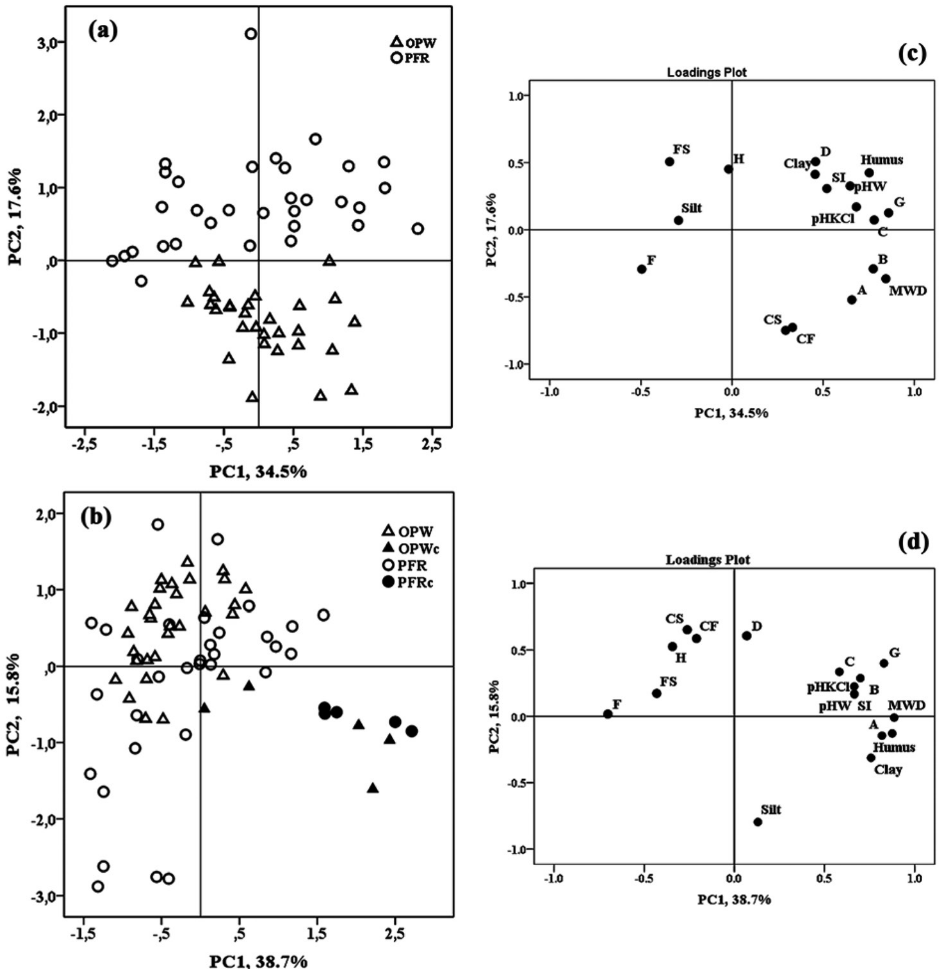

Figure 2. Results of PCA analysis of open-pit mine wastes (OPW), post-flotation tailings (PFT) and control (OPWc and PFTc) surface samples: Scores plot of (a) OPW and PFT, (b) OPW, PFT and control; Loadings plot of the physical and chemical parameters used to characterize (c) OPW and PFT, (d) OPW, PFT and control [CF - coarse fragments; CS - coarse sand; FS - fine sand; water-stable aggregates (mm): A >3, B 3-2, C 2-1, D 1-0.5, H 0.5-0.25; G - >0.25 total water-stable large aggregates; F - <0.25 water-unstable microaggregates; SI - structural stability index; MWD - mean water diameter; pHW - pH in water].

4. Discussion

The investigated soils represent very young technogenic soils developed on two types of Cu mine wastes some parts of which have been reclaimed. In general, the obtained results show that the characteristics of investigated soils are in agreement with those found in literature for soils formed on mine spoil sites, such as large proportion of coarse soil particles, low humus content, low soil pH (Simon, 2005), high metal concentrations (Asensio *et al.*, 2013), and low soil microbial activity (Akala and Lal, 2001).

Accumulation of organic C in surface layers of the spoil material is of crucial importance for the soil formation and one of the criteria for estimation of the influence of applied reclaiming methods (Bradshaw, 1997). But, the rate of organic C accumulation is not well understood, and available data are inconsistent and exhibit large differences (Šourkova *et al*., 2005). Generally, our investigated profiles are characterized by low humus content, which does not decrease in all profiles with depth. In all investigated profiles there is no recognizable topsoil layer, containing in situ formed humus probably due to soil age, lack of plant cover and organic litter, as well as other unfavorable soil conditions. In natural soils, total organic C contents strongly decrease with depth, but subsoil horizons in urban or technogenic areas may contain considerable amounts of soil organic matter due to soil mixing during construction of urban landscapes and translocation of organic compounds from natural soil and anthropogenic material to deeper soil layers (Lorenz and Lal, 2009). Higher humus content in the subsurface layer of profile OPW2 is a result of *in situ* accumulated humus but it is the top layer of the former natural soil deposited and buried in mining processes. Humus in OPW surface layers probably originates from natural soils disturbed and transferred in mining processes, too. Humus in A horizons of profiles PFT3 and PFT4 was probably brought onto the site during soil reclamation. It is difficult to find out whether some amounts were formed in situ, because no data on soil characteristics were collected immediately after reclamation. Unraveling the origin of humus in technogenic soils is the problem recognized by other authors as well (Šourkova *et al.*, 2005). PCA analysis showed significant differences in humus content between both investigated mine surface soil samples and control natural soil samples. Also, the humus content was higher in PFT compared with OPW soils, and the reason were reclamation measures, i.e., reconstruction of PFT topsoil with arable soil. As humus, the color of C layers in all profiles is probably a result of mixing of mine wastes of different characteristics, i.e., introduction of arable soil by reclamation and formation of A horizons in PFT3 and PFT4 profiles. Low pH of studied technosols is the following adverse factor, which restricts development of vegetation, accumulation of organic litter, as well as decrease in the number of microorganisms and their activities, all of which slow down the pedogenetic processes. The reclaimed area of PFT is mostly acidic (natural arable soil brought onto the site during reclamation is acidic according to control samples, PFTc). Organic C accumulation and formation of organic acids caused pH decrease over time in some non-reclaimed and reclaimed technogenic soils (Šourkova *et al*., 2005). Higher pH was found in investigated soil profiles and surface samples with higher humus content. Lower soil pH in C layers of both studied sites might be a result of higher content of sulfur compounds in which case the pH decrease is caused by weathering and oxidation of these sulfur compounds, as reported by some authors (Rumpel *et al.*, 1998). Soil aggregation plays a prominent role in physical, chemical and biological soil properties and represents a relevant indicator of the way the soil functions (Monserie *et al*., 2009). Poor characteristics of examined soil aggregates are confirmed by MWD values (Le Bissonnais, 1996), according to which 36% of OPW and even 69% of PFT surface samples have unstable or very unstable aggregates. Also, SI values (Pieri, 1992) indicate structurally degraded soils that cover more than 90 % of both OPW and PFT areas. According to PCA results, OPW surface samples have somewhat better soil aggregate characteristics than the PFT ones, probably because OPW compared with PFT underwent minor changes in mining processes.

PFT soils are less coherent due to variations in aggregate properties and humus content resulting from implemented reclamation measures to the portion of the PFT area, and wind transported post-flotation tailings over reclaimed area. Weak, unstable soil structure of the non-reclaimed PFT area led to wind erosion of loose material and its deposition on the reclaimed area (e.g., profile PFT3), conterminous natural soils as well as the town, the problem addressed in literature too (Courtney, 2013). PCA analysis indicated great heterogeneity of aggregate properties of OPWc and PFTc samples, but also their obvious separation from mine spoil and tailings samples. Both OPW and PFT soil surface samples exhibit less favorable aggregate properties than natural control soil samples, and the cause of it are dominant coarse fragments, sand, and low clay and humus content.

Concentrations of macroelements in soils from both waste sites are in agreement with those found for normal soils worldwide (Essington, 2004). High concentration of some microelements (As and Cu) in investigated mine and tailings soils is one of the limiting factors for better growing of vegetation on reclaimed areas and its expansion onto non-reclaimed ones. The content of Cu and Zn in the investigated topsoil is lower compared with the topsoil of Cu mine tailing soils from copper mine in Touro, Spain (Asensio *et al.*, 2013). However, the Cu content is markedly higher compared with the topsoil of urban soils of Szeged, Hungary, (Puskás and Farsang, 2009), as well as agricultural soils in urban area of Belgrade, Serbia (Marković *et al.*, 2010). The Zn content in the investigated topsoil is lower compared with the above mentioned urban and agricultural soils.

Low microbial activity of examined mine spoil and tailings samples arose from unfavorable physical (dominant coarse fragments and sand) and especially chemical soil properties (extreme and very acid soils with low humus content). Somewhat higher microbial activity took place in clayey layers, which can probably be explained by high reactivity of microorganisms with clay particle surfaces. Hafeez *et al*. (2012) found that bacteria abundance in Technosols decreased with increasing depth as previously observed in other soil systems. This is the case with the examined profiles, except PFT3 where the total bacteria number is higher in the subsurface horizon A than in the surface C1 layer. This can be linked with favorable conditions in the A horizon, which was formed by reclaimed measures (arable soil), while C1 is wind deposited tailings. The absence of actinomycetes is a consequence of extremely acidic soil conditions. Soil enzymes act as catalysts in some specific reactions controlled by different factors. Some enzymes, especially dehydrogenase, phosphatase and urease, also act as indicators of soil pollution by heavy metal. Our results for DHA (not correlated with the microbial activity) differ from those obtained by Skujins (1976), who suggest that DHA, used for determination of catabolic activity in soil, is correlated with microbial activity. Nevertheless, the use of DHA for estimation of microbial activity has already been criticized, primarily because of low efficiency of electron acceptors used in dehydrogenase assay (Benefield *et al*., 1977). The obtained positive correlation of PME with clay was confirmed in literature (Kandeler et al., 1999). Positive correlation between metals and microbiological activity can be explained by the tolerance of microflora to contaminating metals (Campbell *et al*., 1995). During the soil classification, according to WRB 2007 (IUSS Working group WRB, 2007), we faced two problems: one dealing with the criterion related to artefacts, to "have substantially the same properties as when first excavated and modified", which is very difficult to determine, and the other in determining the *Toxic* suffix qualifier. There are no quantitative criteria for the phrase "toxic concentrations", as well as for qualifiers such as Anthrotoxic, Ecotoxic, Phytotoxic, or Zootoxic. Therefore, in classification of examined soils, the qualifier "toxicity" was defined according to national regulations (The Official Gazette of the RS, 1994). These problems could be solved by determining appropriate classifier for artefacts, and quantitative criteria for the phrase "toxic concentrations", as well as for qualifiers such as Anthrotoxic, Ecotoxic, Phytotoxic, or Zootoxic (Rossiter, 2007).

5. Conclusions

In general, the characteristics of investigated soils formed on Cu mine waste sites OPW and PFT are large amount of coarse soil particles, degraded structure, low humus content, low pH, high As and Cu concentrations, and low soil microbial activity. In all investigated profiles there is no recognizable topsoil layer containing in situ formed humus probably due to soil age, lack of plant cover and organic litter, as well as other unfavorable soil conditions. The specificity of investigated soils is an irregular distribution of some soil characteristics (porosity, humus content, microbiological activity) over depth, which is a result of their technogenic origin.

Both OPW and PFT soils compared with control natural soils are characterized by lower clay and humus content, and poorer aggregate properties. Also, poorer aggregate properties of PFT than of OPW soils were found, resulting most likely from aggressive mining, i.e., flotation processes. Dimension reduction performed by PCA enabled better understanding of the dataset structure of soil samples, by determining clearly defined and separable groups of soils. In addition, the applied pattern recognition technique made possible examination of the influence of chosen physical and chemical parameters on the characteristics of individual groups through extraction of parameters.

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