

## Humus content and composition of soil from reclaimed Cu post-flotation tailings (Bor, Serbia)

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### Abstract

The aim of this work was to determine the content and composition of the humus in the Technosols from reclaimed post-flotation tailings of the Bor copper mine (Serbia). Part of the tailings was reclaimed about 20 years ago by restoring the topsoil with arable soil and planting trees and grasses. Humus parameters were used as indicators for the success of the reclamation. Samples of the natural soil, which served as a borrow pit for the reclamation of the tailing, were analyzed as a control. The humus composition was assessed on the basis of the ratio of humic acids to fulvic acids (Ch/Cf), the ratio of humic acids to total organic carbon (C) (Ch/C) and the ratio of fulvic acids to total organic C (Cf/C). Descriptive statistics, correlation and PCA were used to analyze the data. The decrease in humus content is due to the weak inflow of organic residues into the soil due to the weak development of the vegetation. A significant increase in Cf/C and a decrease in Ch/Cf values are probably the result of the degradation of humus substances under the conditions of a very acidic environment and a lower leaching of fulvic acids. The decrease and degradation of humus in the soil are the result of unfavorable soil quality and unfavorable re-vegetation as a result of inadequate reclamation measures.

*Key words:* humic acids, fulvic acids, humus degradation, Technosols

### Introduction

Mining and related activities cause drastic impacts on terrestrial ecosystems and lead to severe soil degradation (Akala and Lal, 2001). For example, the tailings resulting from the extraction and processing of copper ores damage native vegetation, resulting in large areas of wasteland, and are also source of metal contaminants in local water, air and soil, posing a major threat to biodiversity and human health (Wong, 2003). The Bor copper mining and smelting basin is one of the largest mines in Serbia. Over a period of more than a hundred years, the processing of copper ore has led to the degradation of large areas of land and the formation of tailings. These tailings are also a source of environmental pollution for the surrounding area. In order to restore the function of some of the tailings area, reclamation measures have been carried out on some of them. For example, in 1991, about 16 ha of the post-flotation tailings were reclaimed by restoring the topsoil with natural arable soil and by planting trees and grasses. Thereafter, there was no continuous monitoring or evaluation of the success of the reclamation carried out.

Mineral transformations, stoniness, aggregation and water resistance of structural aggregates, water permeability, accumulation and/or transformation of organic matter, biological activity, etc. are often used as indicators to evaluate and assess the quality of soils on tailings (Asensio et al., 2013). Humus plays an essential role in the functioning of ecosystems as it influences the chemical, but also the physical and biological properties of the soil (Dick et al., 2006). A detailed analysis of humus can provide information on the potential ability of the soil to mobilize or immobilize contaminating substances (such as heavy metals and organic pollutants) (Beyer et al., 2001; Cui et al., 2024; Čokeša et al., 2022; Viventsova et al., 2005), so knowledge of its composition in reclaimed soils is essential for planning follow-up and remediation procedures and for predicting the potential use of the soil (Dick et al., 2006; Viventsova et al., 2005).

The objective of this work was to assess quality of soils from reclaimed Cu post-flotation tailings from the Copper mine - Bor (PFT). According to the IUSS Working Group WRB (2007), the investigated soils were classified as Spolic Technosol (Phytotoxic) (Lilić et al., 2014). The aim of this study was to determine the content and composition of the humus as an indicator of the success of the reclamation measures carried out 20 years ago. As a control, the natural soil samples (CNS) from the southern part of the urban area of Bor, which served as a borrow pit for the reconstruction of the tailings, were also analyzed.

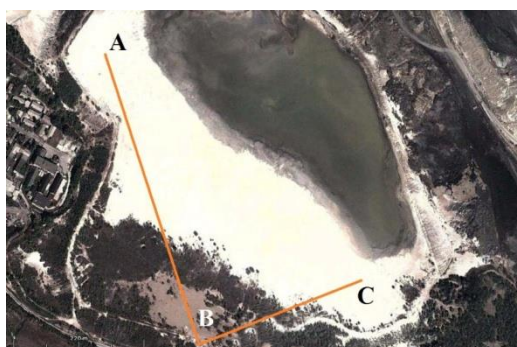
## Material and Methods

The study area of the PFT dumps of the copper mine is located in the immediate vicinity of the town of Bor in eastern Serbia. The climate in the region is temperate continental and characterized by short, hot summers and long, cold winters. The average annual air temperature is 11°C, while the minimum and maximum temperatures are -14°C and 35°C respectively. The average annual rainfall is 550 mm. Winds from the northwest are the most frequent and strongest, while winds from the east are very variable.

The PFT dump was finally abandoned in 1987. The thickness of the tailings is about 60 meters. Part of the tailings is in a liquid state, another in a muddy state and finally a third (about 25 ha) in a solid state, which was included as such in our investigation. In 1991, an area of about 16 ha was reclaimed by reconstructing the topsoil with arable soil at an average depth of 40 cm. The soil was taken from the southern part of the town, where the residential area has expanded (New Town Centre). Part of the reclaimed area was planted with grass and the other part with trees. Amendment and other measures before and after the reclamation were not carried out. Strong winds dispersed the tailings particles over the reclaimed area (and also over the town and its surroundings). This is one of the reasons for the decay of most of the plants. Today, the tailings site is almost bare, without any vegetation. Birches (*Betula pendula* L.), shrubs (*Rosa canina* L. and *Rubus caesius* L.) from the *Rosaceae* family, and several species from the *Poaceae* family among which *Nardus stricta* L. and *Agropyrum repens* L.

dominate, are only very sporadically present. *Verbascum phlomoides* L. and *Bryopsida spp.* also occur here and there.

As most traces of soil reclamation and possible pedogenetic processes were expected at the soil surface, 21 disturbed samples were taken at a depth of 0-25 cm at a distance of about 30 m in the direction of the letter L (Fig. 1). There is no data on the soil properties of these tailings collected before and/or immediately after remediation. Therefore, surface soil samples (0-25 cm) collected near an area that served as a borrow pit for the remediation of the PFT tailings 20 years ago were used as a control. Five samples were collected in a straight line approximately 100 m apart.



**Figure 1.** Aerial view of the study area. Direction of sampling: A 44°03'53.59"N, 22°06'51.04"E, 366 m a.s.l.; B 44°03'51.12"N, 22°06'40.12"E, 370 m a.s.l.; C 44°04'06.67"N, 22°06'31.76"E, 366 m a.s.l.

Selected soil properties were determined using the following laboratory methods: Texture by dry siving and pipette method with Na-pyrophosphate preparation, classification of soil texture according to the USDA triangle; total organic C by dichromate oxidation; humus content equals C x 1.72; soil pH in water (soil to water ratio: 1/2.5) by pH measurement; exchangeable acidity by KCl method; cation exchange capacity (CEC) by ammonium acetate method (Reeuwijk, 2002). In addition, the size distribution of water-stable aggregates was determined according to Angers and Mehuys (1993); the stability of soil aggregates based on mean weighted diameter (MWD) was evaluated according to Le Bissonais (1996) and the structural stability index (SI) proposed by Pieri (1992).

The analysis of the humus composition of the soil revealed three humic substances: humic acids (HA), fulvic acids (FA) and humins. HA are not soluble in water in an acidic environment, but become soluble at higher pH values. FA are the fraction that is soluble in aqueous media at all pH values. Humins represent the fraction that is not soluble in an aqueous medium at any pH (or cannot be extracted with an aqueous medium) (MacCarthy, 2001; Piccolo, 2002). The humus composition of the soil was determined according to the method of Kononova and Belchikova (Kononova, 1963). The humus condition was evaluated by the ratio of HA to FAs (Ch/Cf), the degree of humification (index) expressed as the ratio of HA to total organic C (Ch/C) or as the percentage of HA to total organic C

(Ch/Cx100), and as the ratio of FA to total organic C (Cf/C) or as the percentage of FA to total organic C (Cf/Cx100) (Orlov, 1985; Sellami et al., 2008).

Descriptive statistics, correlation analysis (StatSoft, Inc. STATISTICA for Windows, 8) and Principal Component Analysis (PCA) (IBM SPSS Statistics 19) were used to analyze the data.

## Results

Reclaimed PFT soil samples are dominantly sandy clay loam, and to a lesser part silt or clay loam (Table 1). Soil structure is characterized mostly by lower content of water-stable large aggregates (>0.25 mm), and, accordingly, high content of water-unstable micro-aggregates (<0.25 mm). MWD values also indicate mostly unstable (48% soil samples), less medium stable (38% soil samples) or stable (14% soil samples) soil structure. SI values, based on humus, silt and clay content, indicate structurally degraded soils (86% soil samples).

**Table 1.** Physical characteristics of the reclaimed Cu post-flotation tailings and the control soils

Soil properties	Post-flotation tailings				Control natural soils				
	<i>Mean</i>	<i>Min.</i>	<i>Max.</i>	<i>Std.dev.</i>	<i>Mean</i>	<i>Min.</i>	<i>Max.</i>	<i>Std.dev.</i>	
Coarse sand (%)	23.36	13.37	44.43	7.74	17.13	10.56	22.13	4.16	
Fine sand (%)	36.49	26.73	51.78	7.05	27.12	23.71	33.57	3.78	
Silt (%)	18.19	7.28	26.76	5.43	27.28	25.56	29.60	1.61	
Clay (%)	21.53	5.36	31.04	6.64	28.47	20.20	37.44	6.51	
Aggregates in mm (%)	>3	6.24	0.47	17.65	4.26	42.54	23.86	56.20	13.30
	3-2	5.73	0.25	17.28	4.11	9.32	7.41	10.69	1.38
	2-1	16.16	7.04	31.16	7.73	16.04	13.32	21.83	3.43
	1-0.5	18.98	1.83	38.73	7.12	8.03	4.76	11.48	2.68
	0.5-0.25	5.71	1.68	10.51	2.71	1.23	0.65	1.56	0.38
	>0.25	52.68	27.41	75.84	14.53	77.17	67.61	84.42	7.18
	<0.25	47.32	24.16	72.59	14.53	22.83	15.58	32.39	7.18
MWD	0.95	0.44	1.72	0.37	2.91	1.99	3.55	0.65	
SI	4.34	1.88	12.97	2.70	10.55	6.94	12.31	2.14	

MWD - mean weighted diameter; SI - structural stability index

The reclaimed PFT soil samples are predominantly acidic (slightly to extremely), predominantly very strongly acidic (Table 2). In general, the humus content in reclaimed PFT soils is low. The humus composition is characterized by a mostly low degree of humification (Ch/Cx100 <20% in 87% of the soil samples). The Ch/Cf value is mostly 0.5-1 (62% of the soil samples), less <0.5 (24% of the soil samples) and 1-2 (14% of the soil samples). On non-reclaimed PFT sites, the soil samples

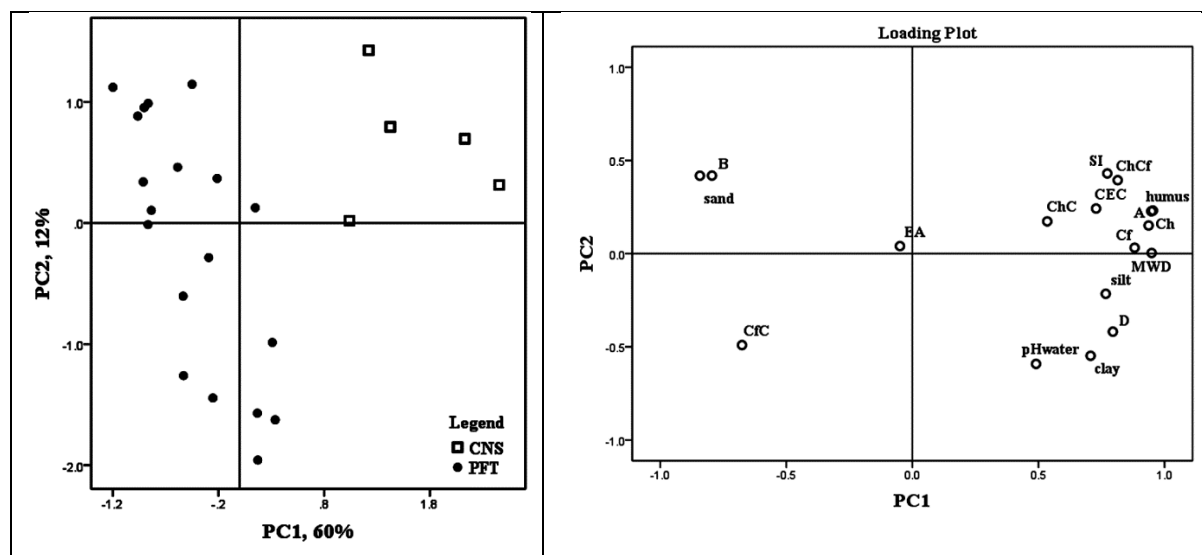
contain  $0.09 \pm 0.07\%$  organic C or  $0.16 \pm 0.11\%$  humus. The CNS samples generally have a medium humus content, a medium degree of humification and Ch/Cf 0.5-1 or 1-2.

**Table 2.** Chemical characteristics of the reclaimed Cu post-flotation tailings and the control soils

Soil properties	Post-flotation tailings				Control natural soils			
	<i>Mean</i>	<i>Min.</i>	<i>Max.</i>	<i>Std.dev.</i>	<i>Mean</i>	<i>Min.</i>	<i>Max.</i>	<i>Std.dev.</i>
pH in H <sub>2</sub> O	5.53	3.84	7.60	1.09	5.74	4.96	6.75	0.83
Exchangeable acidity (cmol <sub>c</sub> kg <sup>-1</sup> )	4.42	1.14	6.19	1.55	5.01	3.95	6.02	0.76
CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	26.05	10.75	40.00	7.23	43.90	34.00	56.50	9.51
C (%)	0.90	0.38	1.45	0.32	3.41	2.18	4.11	0.75
Humus (%)	1.55	0.65	2.50	0.55	5.88	3.76	7.08	1.28
Ch (%)	0.15	0.06	0.30	0.07	0.66	0.44	0.84	0.18
Ch/Cx100 (%)	16.39	12.00	21.28	2.85	19.42	14.16	22.74	3.17
Ch/C	0.164	0.120	0.213	0.028	0.194	0.142	0.227	0.032
Cf (%)	0.24	0.06	0.45	0.11	0.62	0.47	0.82	0.14
Cf/Cx100 (%)	26.79	11.58	34.74	6.13	18.69	13.58	23.91	4.69
Cf/C	0.268	0.116	0.347	0.061	0.187	0.136	0.239	0.047
Ch/Cf	0.674	0.360	1.820	0.321	1.062	0.860	1.310	0.175

C - total organic carbon; Ch - humic acids; Cf - fulvic acids

Figure 2 shows the results of the PCA obtained from the 19 PFT and 5 CNS surface samples (two samples from the PFT group were discarded as "outliers"). The first two components describe 72 % of the total variance in the dataset (PC1 thus describes 60 %, while PC2 describes 12 % of the total variance within the original dataset), which gives a good picture of the structure of the original dataset in the newly formed PC1-PC2 space. The two groups of samples can be separated along a PC1 axis, i.e. there is a linear segment that allows classification with the lowest possible error. The group cohesion in the PFT is slightly perturbed by the dimensional reduction process, which implies an influence of different parameters on the PFT group structure. Sand, water-unstable micro-aggregates <0.25 mm; Cf/C and exchangeable acidity are the parameters with the highest variance in the PFT sample group, while other parameters (especially the humus content, MWD, HA content and water-stable aggregates >3 mm) can be considered relatively stable. This does not relate to pH in water, clay content and total water-stable macro-aggregates >0.25 mm, as these parameters show greater variance in certain samples from this group than in the rest of the group (which has a direct impact on the cohesion of the group).



**Figure 2.** Scores plot (left) of reclaimed PFT (post-flotation tailings) from Copper mine Bor and CNS (control natural soils) samples and loadings plot (right) of humus properties and other chemical and physical parameters (aggregates (mm): water stable A >3, D >0.25; water unstable B <0.25; MWD - mean weighted diameter; SI - structural stability index; EA - exchangeable acidity; Ch - humic acids; Cf - fulvic acids; ChC - ratio of humic acids to total organic C; CfC - ratio of fulvic acids to total organic C; ChCf - ratio of humic acids to fulvic acids)

The humus content was significantly higher in samples that were more silty (Table 3), less sandy and less acidic. The humic acid content was significantly higher when the soil was less acidic and contained more humus. The Ch/C did not correlate significantly with any of the investigated parameters. FA content was higher in samples containing less sand, more clay and silt. The Cf/C was significantly higher in samples containing more clay, less sand and high exchangeable acidity. The soil structure (MWD and SI) is significantly more favorable in samples with more humus and FA.

## Discussion

The results of the data examination and analysis thus show clear differences in humus properties and some other soil properties between CNS and PFT, about 20 years after reclamation. In the PFT soils, the humus content is lower and its composition has deteriorated. It is well known that humus depletion is one of the most important processes caused by mechanical or chemical disturbances of the ecosystem (Akala and Lal, 2001; Viventsova et al., 2005). The reclamation of mining sites mitigates the negative environmental impacts associated with mining and leads, among other things, to an increase in the humus content of the soil. In reclaimed mining soils, humus build-up depends on time, climate, technogenic parent material, previous soil properties, vegetation and management before and after reclamation (Akala and Lal, 2001; Colombini et al., 2023; Ivanov and Banov, 2020; Kozłowski et al., 2022; Zhang and Zhang, 2022; Zhao et al., 2020). The authors exclude the influence of the productivity

of forests and pastures established on reclaimed mining land and the soil characteristics of the tailings (Akala and Lal, 2001) and the density of plant cover (Dick et al., 2006). More organic matter can be stored on tailings piles that have been reclaimed by restoring the topsoil than on non-rehabilitated tailings (Akala and Lal, 2001). Vegetation is only sporadically present on the reclaimed PFT soils investigated in this study. Remediation procedures included topsoil restoration and planting of trees and grasses, but amendments and other post-reclamation management were neglected, resulting in unsuccessful revegetation. The spontaneous establishment of vegetation is also very weak. The reasons for this are unfavorable general soil properties, which may be due, among other things, to the introduction of mulch by the wind from an unremediated part of the tailings pond. The content of heavy metals is most frequently cited in the literature as the reason for the failure of vegetation and the occurrence of other organisms (Néel et al., 2003; Vivotsova et al., 2005). There is also an increased concentration of the microelements As and Cu in PFT soils and very low microbiological activity in the surface layer (Lilić et al., 2014).

**Table 3.** Correlation coefficient between the humus and some physical and chemical characteristics of the reclaimed Cu post-flotation tailings (\*\*99% confidence level)

Soil properties	Humus	Ch	Ch/C·100	Cf	Cf/C·100	Ch/Cf
Sand	-0.58**	0.45	-0.04	-0.74**	-0.60**	0.54
Silt	0.56**	0.50	0.18	0.63**	0.41	-0.33
Clay	0.53	0.36	-0.10	0.76**	0.67**	-0.61**
MWD	0.60**	0.42	-0.11	0.65**	0.37	-0.31
SI	0.40	0.44	0.36	0.15	-0.35	0.59**
pH in water	0.70**	0.68**	0.38	0.47	-0.06	0.21
Exchangeable acidity	-0.23	-0.33	-0.36	0.18	0.59**	-0.54
CEC	-0.07	0.18	-0.32	0.06	0.32	-0.50
Humus	-	0.94**	0.42	0.86	0.12	0.08

MWD - mean weighted diameter; SI - structural stability index; C - total organic carbon; Ch - humic acids; Cf - fulvic acids

However, there are some contrary experiences, where reclaimed mine soils develop recognizable horizons in a relatively short periods of time and an increased humus content (Akala and Lal, 2001), which is a result of a different mullock quality or/and better reclamation technologies. For example, Ottenhof et al. (2007) reported that the addition of soil organic matter to mine wastes is similar to early stages of soil formation and with time, they expect the formation of well-developed Ah horizon on the surface of mine wastes. Tree vegetation and waste amendment both significantly increased the organic C in the copper mine soils (Spain), but amending with wastes was the only treatment that increased the humified soil organic C concentration to proper values (Asensio et al., 2014). Increase of

humified organic C was higher in the amended soils than in the vegetated soils, which led to a higher positive synergy between the organic C supply and microbial biomass development.

The HA and FA content decreased, but the Ch/C values decreased and the Cf/C values increased, so that the Ch/Cf value of the PFT soils decreased. The Ch/Cf value seems to be the most sensitive index for monitoring the humification process. The increase in the value of this humification index, also known as the “degree of polymerization”, reflects the formation of complex molecules (HA) from simpler molecules (FA) and a reduction in the non-humic components of the FA fraction (Shen et al., 2014; Sellami et al., 2008). In the reclaimed PFT soils studied, the reverse process probably took place, namely the degradation of complex HA to simpler FA, i.e. humus degradation. However, humic acids extracted from very strongly acidic PFT soils have a higher aromaticity index, degree of oxidation and aromatic condensation than humic acids from slightly acidic and neutral PFT and CNS soils (Radmanović et al., 2020).

Some authors have reported that FA content decreases in polluted soils, e.g. because metals can form soluble complexes with some soil organic substances, such as FA and low molecular weight substances and leach them (Viventsova et al., 2005). In the polluted soils surrounding the "Severonickel" mine, the Ch/Cf was often higher than in unpolluted soils although the humus content in the polluted soils was much lower (Lukina and Nikonov, 1998). Like humus content, its composition may also be related to vegetation, climate and the composition and properties of the soil in which it occurs (Ivanov and Banov, 2020; Swift, 2001).

Compared to the previously cited results, the FA content also decreased, but the Cf/C value increased in the PFT soils. The Cf/C increase can probably be related to some climatic, soil and vegetation factors. One of the reasons could be the lower FA leaching due to the different climatic conditions (less precipitation, 550 mm annual average). FA content and Cf/C as well as clay are significantly positively correlated, which also means that FA leaching is lower due to poor water permeability. In the PFT soils, the total number of bacteria and *Azotobacter* sp. as well as alkaline phosphomonoesterase (PME) activity showed a positive correlation with clay (Lilić et al., 2014), which can be explained by the high reactivity of microorganisms with the surfaces of clay particles. Thus, higher FA content and Cf/C ratio in clayey soils may be explained by higher microbiological activity. It is likely that FA originate from the decomposition of complex humus acids into simpler forms (Cf/C and clay are negatively correlated, not significant) than from the early stage of humification of organic compounds released from roots or organic litter (due to the very rare vegetation and low inflow of fresh organic residues).

The decrease in humus content followed the decrease in HA (there was a high correlation between Ch and C). Since HA is a nutrient component of humus and its concentration is directly related to the degree of soil fertility (Shen et al., 2014; Barančíková et al., 1997), the decrease in HA content indicated a significant decrease in the fertility level of PFT soils 20 years after reclamation. However, the degree of humification (Ch/Cx100 or Ch/C) is lower in the PFT soils compared to the CNS soils,



but not so significant. Compared to Ch/C, Ch/Cf better reflects humus degradation by reducing the degree of polymerization and humification.

It is well known that soil organic carbon is a crucial parameter that influences all aspects of physical soil quality (Asensio et al., 2013). A number of studies (e.g. Hayes and Valpp, 1991) have shown that long-term degradation of soil structure is associated with significant losses of soil organic matter. Our results also indicate a deterioration of soil structure; the content of larger water-stable aggregates decreases and MWD values in PFT soils are low compared to CNS. Correlation analyses showed that the humus composition also influences the soil structure. The SI value was higher in samples with a higher Ch/Cf value, which means favorable structural stability in soils with more HA. MWD values were higher in samples with a higher FA content, which is due to a positive correlation between FA and clay, with clay probably having the greatest influence on MWD values.

According to Shen et al. (2014), the rate of HA formation in wastelands composed of mineral copper wastes and tailings (China) was faster than that of FA, and the level of soil fertility gradually increased with vegetation succession in the process of natural restoration. However, the Ch/Cf value was  $<0.50$ , the Ch/C value was  $<0.015$  and the soil fertility was still very low even after 40 years of natural restoration. The organic carbon content in the soils of the non-reclaimed PFT areas was on average ten times lower than in the reclaimed area (Lilić et al., 2014). Although the humus of the PFT soils remediated for 20 years was degraded compared to the CNS, the humus properties are still very favorable compared to the above-mentioned 40-year-old mine soils from China. This is proof that these very poor habitats naturally regenerate very slowly and that reclamation is inevitable. The results of this study indicate that reclamation cannot only be partial, but that comprehensive reclamation of the entire area using pre- and post-reclamation measures is necessary.

## Conclusion

In PFT soils, about 20 years after reclamation, a decrease in the humus content and a deterioration in its composition can be observed, whereby the content of humic and fulvic acids decreases and the ratio of fulvic acids to humus and of humic to fulvic acids increases. Humus depletion has an effect on the deterioration of other soil properties such as soil structure. Humus degradation is the result of unfavorable soil quality and unfavorable re-vegetation as a result of inadequate reclamation measures. An increase in humus content and an improvement in humus composition would be possible through comprehensive reclamation and improved management before and after reclamation, which would help to avoid the negative effects of overburden from non-reclaimed areas, enable favorable re-vegetation and improve overall soil quality.

## Acknowledgements

This work was partially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant no. 451-03-65/2024-03/200116).

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## Садржај и састав хумуса у земљишту на рекултивисаним Си постфлотацијским јаловинама (Бор, Србија)

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### Извод

Циљ овог рада је био утврђивање садржаја и састава хумуса у техносолима на рекултивисаним постфлотацијским јаловинама Рудника бакра Бор (Србија). Део јаловине је рекултивисан пре око 20 година реконструкцијом површинског слоја обрадивим земљиштем и озелењавањем дрвећем и травама. Као контрола анализирани су узорци поприродног земљишта које је служило као позајмиште за рекултивацију јаловине. Параметри хумуса коришћени су као показатељи успешности рекултивације. Састав хумуса је процењен на основу односа хуминских и фулвокиселина (Ch/Cf), односа хуминских киселина према укупном органском угљенику (C) (Ch/C) и односа фулвокиселина према укупном органском C (Cf/C). За анализу података коришћена је дескриптивна статистика, корелациона анализа и РСА. До смањења садржаја хумуса долази услед слабог прилива органских остатака у земљиште услед слабог развоја вегетације. Значајно повећање Cf/C и смањење Ch/Cf вредности вероватно су последица разградње хумусних материја у условима веома киселе средине и мањег испирања фулвокиселина. Смањење садржаја и деградација хумуса су последица неповољних особина земљишта и неуспешне ревегетације, а што је резултат неадекватних мера рекултивације.

*Кључне речи*: хуминске киселине, фулвокиселине, деградација хумуса, техносоли

Received 11.10.2024

Revised 01.11.2024

Accepted 18.11.2024