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ACCUMULATON OF MICROELEMENTS IN TECHNOGENIC ECOSYSTEMS FROM THE VICINITY OF THE "MEDET" OPENCAST MINE

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Abstract

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Many studies have recently shown that phytocenosis in the reclaimed lands from the "Medet" mine region are poorly developed and do not provide a dense vegetation coverage.

The purpose of this study is assess the accumulation rate and toxicity of some microelements acting as chemical barriers for the vegetation growth in the reclaimed "Sever" dump built in the vicinity of the "Medet" opencast mine. The achieved results showed that Technosols from the "Sever" dump form a geochemical zone with a high total copper content (determined after soil mineralization with aqua regia), which in the upper part of catena (the ridge of the dump) reaches 668.0 mg/kg. Thus it exceeds the threshold of 500 mg/kg, defined as intervention (toxic) concentration in Bulgarian legislation with 1.3 times. In comparison to typical concentrations of the element in Bulgarian soils these concentrations are on average 16 fold higher. Mobile concentrations of copper extracted with 1 M NH_4NO_3 are also toxic and concentration into the birch leaves is comparable with the established in contaminated ecosystems (30.5 mg/kg). Lead, regardless of its high mobility in the studied soils slightly accumulates in plants.

The plant species used for reclamation have selective ability to accumulate copper, lead, zinc and manganese and might diversely influenced their cycle in studied ecosystem. Birch is a vigorous phyto-extractor of zinc and manganese, since Acacia preferentially accumulates only copper.

Fragmental rock texture of subsoil (below 25 cm) is both the physical and chemical barrier to plant development which restricts root penetration and retention of moisture and nutrients.

Key words: bioavailability; microelements; Medet; technosols

Introduction

Sulphide-containing materials occur in many coal and ore deposits in Europe, America, Australia and South Africa. These materials are transposing on the Earth surface by mining activity where they are intensively oxidizing, creating an aggressive phytotoxic environment and are quickly becoming uncultivated industrial deserts, devoid of any vegetation (Dudkin et al., 1987). For this reason, dumps containing sulphides are one of the most difficult for reclamation and use (Marinkina, 1999; Skousen et al., 2000).

The studies of Bulgarian sulphide-containing dumps revealed that the success of reclamation depends not only on the content of pyrite (the most common sulphide), but also by the method of technical and biological reclamation of the newly formed territories (Marinkina, 1999). Monitoring of the dumps located near the „Chukurovo" mine built of pyrite-containing materials shows that the biological reclamation lasts approximately 20 years when it is not applied selective method of dump construction or amelioration (Marinkina and Banov, 2001; Tsolova and Ilieva, 2005; Tsolova et al., 2014; Tsolova et al., 2014a).

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In the area of the „Medet" mine the vegetation monitoring made mostly with remote sensing showed that there has been no change associated with improving the density of the vegetation between 1996, when the dump restoration was started and 2000, when the monitoring took place (Nikolov et al., 2006; Borisova et al., 2015). The results of remote sensing sparked interest in conducting in-sito study to identify factors that limit the development of vegetation in this area.

The purpose of this study is assess the accumulation rate and toxicity of some microelements acting as chemical barriers for the vegetation growth in the reclaimed "Sever" dump built in the vicinity of the "Medet" opencast mine.

Materials and Methods

Geological materials with high content of pyrite and highly acidic character were discovered and dumped in the vicinity of "Medet" open cast mine as a result of the activities of mine-enrichment company "Medet". An object of the present study is the "Sever" dump which is formed about 20 years ago with these materials (Figure 1). The dump is chemically reclaimed with 150 kg/dka lime materials and manure in the rate of 6 t/dka in order to improve its chemical environment and nutritious status. Biological rehabilitation is carried out mainly with acacia (*Acacia Mill.*) but in the areas with a large slope birch (*Betula pendula Roth.*) is also planted.

Field study was conducted in accordance with modern pedological methods for study and morphogenetic diagnosis of soils (Koinov et al., 1968; Jolevski and Hadzhiyanakiev, 1976; FAO, 1990) and the catena concept (Young, 1972). Surface (AC) reclaimed horizon was sampled at the depth of 25 cm in accordance with the current standards for soil sampling (BDS ISO 10381-1, 2, 4). Stones and rocks of different sizes follow after this depth. One sample is taken from this layer located in the middle part of the catena, at a depth of 25-35 cm.

The following methods were used for analysis:

➢ Pretreatment of samples for physico-chemical analysis – BDS ISO11464 (2012).

➢ Determination of pH in H_2O by ISO 10390:2010.

➢ Determination of total content of trace metals – method of soil mineralization with aqua regia (ISO 11466:1995) and EAAS (ISO 11047:1998) using spectrometer Perkin-Elmer 2100.

➢ Determination of readily soluble trace element contents – extraction with 1 M NH_4NO_3 – ISO 19730 (2008).

➢ Determination of the total content of trace elements in plants – after a dry combustion and mineralization in 20% HCl at a ratio sample: solution 1:50 and subsequent direct element determination with EAAS (Miltcheva and Brashnarova, 1975).

In order to assess biomigration of trace elements in reclaimed ecosystems transfer coefficients or so called coefficients of biological uptake (Kbu) are calculated according to the general formula as a ratio between the total element content (µg/g) in plants and its average total /mobile content (µg/g) in soil samples.

Several concentration ratios that enable to assess the contents of the studied trace elements in soils are also calculated in the current study:

Fig. 1. General view of the research object and the catena location

• concentration coefficient (Kc^1), which reflects the enrichment of soils with the studied element compared to its local level (local geochemical background) – it is calculated as the quotient of the average content of each element in soils with its average content in the local rocks (Kamenov et al., 2007);

• concentration coefficient (Kc^2), which reflects the ratio between the content of elements in studied soils and the typical element concentration in Bulgarian soils (Atanasov et al., 2000) also expressed by their average values.

Descriptive statistical analysis is performed by the Microsoft Excel ™ statistical package.

Results and Discussion

The results obtained show that the "Sever" dump is characterized by strong spatial variations in the geochemical composition (Table 1). They are the most strongly expressed in terms of copper content which ranges from 228 to 668 mg/kg along the catena. The concentration coefficient of the element is very high – an average of 6.6 (Table 2), and its content exceeds maximum permissible concentration (MPC – concentration which, under certain conditions, leads to the disturbance of the soil functions and creates a danger to the environment and human health) with an average of 2.5 fold and intervention concentration (IC – toxic concentration which disturbs soil functions and poses a danger to the environment and human health) by up to 1.3 times (Regulation № 3). Studied soils are also 16 fold richer in copper than Bulgarian soils considering the background element content.

The data in Table 1 show that the reaction of the medium also greatly varies from moderately acid pH 5.6 (according to the classification of Ganev, 1990) to medium alkaline (pH 8.5), with no detectable interlink with the location of sampling points along the catena and slope. The lowest pH values are established in subsoil, wherein the copper content also exceed MPC over 2 times. In this layer the contents of the other elements is lower than the background, but manganese and lead content was higher than their average content in the surface layer.

Manganese also features with highly varying concentrations, but it is not accumulated in the studied soils according to the data on the average content of the element in the soil forming rocks (Table 2). Such a tendency is typical for lead as its concentration exceeds the background values in only two of the sampling points with an average of 1.2 times. The zinc content also exceeds the precautionary concentration of 110 mg/kg, but does not create a toxic environment. Indeed, the trend towards accumulation in the upper parts of microcatenas was found for all studied elements.

Lead is the most mobile element in studied soils, which easily soluble forms reach 80% of the total element content (Table 1). According to the critical level determined by Prüeß (1992) element is present in the toxic mobile concentration

Table 1
Absolute (mg/kg) and relative (%) content of trace elements in Technosols from the "Sever" dump

Para–meter	pH	Cu			Zn			Mn			Pb		
		Total	Extr.	%	Total	Extr.	%	Total	Extr.	%	Total	Extr.	%
In top soil (number of samples, n = 10)													
Max.	8.5	668.0	2.05	0.43	132.5	3.43	2.59	565.0	9.28	1.70	22.5	1.35	80.0
Min.	5.6	228.0	0.10	0.02	42.0	0.03	0.05	280.0	0.25	0.07	1.5	0.93	4.1
Mean	**7.0**	**380.0**	**0.46**	**0.11**	**62.5**	**0.59**	**0.64**	**431.7**	**4.04**	**0.84**	**9.3**	**1.13**	**23.6**
SD	1.04	163.9	0.62	0.12	26.9	1.04	0.81	90.2	3.64	0.68	7.2	0.14	23.5
In subsoil (25–35 cm)													
Mean	**4.7**	**178.0**	**8.4**	**4.7**	**30.0**	**0.75**	**2.5**	**485.0**	**8.25**	**1.7**	**11.5**	**1.2**	**10.4**
Maximum permissible concentrations (MPC)													
< 6.0		80	1.0	–	220	30.0	–	–	–	–	90	1.0	–
6.0–7.4		140	1.0	–	390	30.0	–	–	–	–	130	1.0	–

Table 2
Content (mg/kg) and concentration coefficients of studied elements in the surface horizon of Technosols from the "Sever" dump

Component	Cu		Zn		Mn		Pb	
	Mean content	***K*c**	Mean content	***K*c**	Mean content	***K*c**	Mean content	***K*c**
Local rocks	57.6	6.60[1]	47.6	1.31	1 000.0	0.43	18.8	0.49
Bulgarian soils	24.0	15.8[2]	69.0	0.91	740.0	0.58	18.0	0.51

[1] – concentration coefficient referring the mean element content in local rocks according to the data of Kamenov et al. (2007);
[2]– concentration coefficient referring the mean element content in Bulgarian soils (Atanasov et al., 2000)

Table 3
Total content (mean values in mg/kg) of elements in studied biogeosystem and coefficients of biological uptake

Plant species	Cu		Kbu	Zn		Kbu	Mn		Kbu	Pb		Kbu
	soil	leaves		soil	leaves		soil	leaves		soil	leaves	
Acacia*	361.6	30.5	0.08	59.6	14.5	0.24	436.6	52	0.12	9.5	< 1	–
Birch*	361.6	8.5	0.02	59.6	125.5	2.11	436.6	441	1.01	9.5	< 1	–
wild rose*	361.6	12	0.03	59.6	13	0.22	436.6	97	0.22	9.5	< 1	–

* n (number of samples) = 5

(> 1 mg/kg) in 22% of the sampled points. In plant species (Table 3) it however, remains below the limit of detection and the critical minimum, inducing toxic symptoms reported in the literature (> 30 mg/kg, Kamugi, 1990).

Copper is the most abundant element and its mobile concentrations are also toxic in the surface layers (> 1 mg/kg, Prüeß, 1992). It is known that the element is primarily concentrated in the roots of plants (Liao, 2000), but in the studied ecosystems acacia leaves contain up to 9 times more copper in comparison with species growing in contaminated areas (Pais and Jones, 1997).

Birch is already known for its ability to accumulate zinc from our previous studies (Tsolova et al., 2013). In studied dump it shows ability to accumulate manganese too, but its content cannot be assessed in phytoecological aspect yet (Table 3). This also concerns the wild rose leaves (*Rosa canina*), whose elemental composition has not been studied in contrast to the published literature of heavy metal content in plant fruits (Levent et al., 2010). The comparison between the obtained data and the literature shows that higher amounts of copper, lead, zinc and manganese were accumulated in leaves (in the fruits there are 6.01-9.29 mg/kg copper, 0.111-0.273 mg/kg lead, 35.29-66.7 mg/kg manganese, 7.98-13.32 mg kg zinc), than in fruits.

If the mobile concentrations of the elements in the soils have taken into consideration Kbu also decreases in the following order: Pb << Cu (37) < Mn (47) < Zn (86).

Conclusion

Technosols from the "Sever" dump form a geochemical zone with a high total copper content, which in the upper part of catena (the ridge of the dump) exceeds the threshold of 500 µg/g, defined as intervention concentration in Bulgarian legislation with 1.3 times. In comparison to typical concentrations of the element in Bulgarian soils these concentrations are on average 16 fold higher. Mobile concentrations of copper are also toxic and bioaccumulation into the birch leaves is comparable with the established in contaminated ecosystems (30.5 mg/kg). Lead, regardless of its high mobility in the studied soils slightly accumulates in plants.

The plant species used for reclamation have selective ability to accumulate copper, lead, zinc and manganese and diversely influenced their cycle (biomigration and subsequent re-accumulation with the plant litter) in studied ecosystem. Birch is a strong phyto-extractor of zinc and manganese since Acacia preferentially accumulates Cu.

Fragmental rock texture of subsoil (below 25 cm) is both the physical and chemical barrier to plant development which restricts root penetration and retention of moisture and nutrients.

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