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CHOSEN PROPERTIES OF CLAYEY SOILS ON AN AFFORESTED DUMPING GROUND OF A SULFUR MINE

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Summary. Research was located at the afforested outside dumping ground of a sulfur mine in Piaseczno, near Tarnobrzeg. Research on the contents of the selected trace metals (Cd, Cu, Pb, and Zn) and enzymatic activity of the clayey material was carried out: in the top layer, in the monoculture of verrucose birch (*Betula verrucosa*) and in the stand of verrucose birch and fine-leafed lime trees (*Tilia cordata*) in a group mixture; on the slope, in the one-species stand of aspen trees (*Populus tremula*).

The smallest content of Pb was stated in ground samples taken from the slope of the dumping ground. Contents of Cd, Cu, and Zn in the material taken from the slope of the dumping ground were significantly higher, as compared with the contents of those elements in ground samples taken from the top. The greatest activity from among the investigated soil enzymes was that of the clayey formations from the slope of the dumping ground.

Keywords: clayey soil, enzymatic activity, trace metals, dumping ground.

INTRODUCTION

Soil enzymes are very sensitive to environmental stresses [23], and therefore the enzymatic activity of the soil may be used for evaluating the degree of environment pollution [9]. According to Kiss et al. [11], the enzymatic activity reflects both the direction and the character of biogeochemical processes, as well

as the whole of basic transformations including the biology and physical-chemical properties of the soil. The mentioned authors indicated that the selected parameters of the enzymatic activity may be synthetic indexes of the evolution of the technogenic soils because they reflected both the previous biological state of the soil (thanks to the accumulation of the enzymes in the form of humus complexes), and the present one (due to the catalytic properties of the enzymes that are crucial for element circulation).

Contents of the selected trace metals and the enzymatic activity of the loamy formations of the dumping ground of the sulfur mine were investigated in this paper in order to evaluate the ecological situation of the examined ecosystem. Accumulation of toxic elements in the soil is dangerous from the ecological point of view because of the possibility of the delayed remobilization of those elements.

MATERIALS AND METHODS

The research was localized on the afforestated outer dumping ground of the sulfur mine in Piaseczno near Tarnobrzeg. The area is on the left bank of the Vistula river, on the wide inundation terrace (50^0 35' N; 21^0 47' E). The dumping ground was created in years 1959-1965 and afforestated in 1967-1969, after finishing the measurements concerning technical recultivation [26]. In relation to the geological composition of the overlay of the sulfur deposit, the Tertiary loamy formations with fraction contents of: >1 mm - 7.6 - 8.2%; 1 - 0.1 mm – 17 - 21%; 0.1 - 0.002 mm – 12 - 17%; 0.02 - 0.002 mm – 22 - 26%; <0.002 mm – 37 - 40%, dominate on the dumping ground. Preparation of the ground for afforestation on the top-soil was based on the one-year cultivation of Papilionaceous plants. About 0.4 m wide terraces were made on the slopes for rows of trees. Papilionaceous plants were sowed on the bands between the terraces. The entire area was fertilized with NPK. The species composition of the afforestation material included over a dozen species of trees and bushes using different forms of mixing. Black alder (*Alnus glutinosa*) was chosen to be the phytomelioration species and reduced along with the development of the destination species [26].

The following sites were selected for the investigation of the trace metal content and enzymatic activity of the loamy material:

1. on the top-soil in the monoculture of verrucose birch (*Betula verrucosa*) – 15 m high stand of trees, weakly developed brushwood - 20% of the cover, undergrowth with a great part of tree and bush seedlings - 70% of the cover, a highly developed moss layer - 70% of the cover, 0.5-1 cm thick litter layer.;

2. on the top-soil in the monoculture of verrucose birch and fine-leafed line (*Tilia cordata*) in a group mixture - two story stand of trees (1 story – 17 m high birch, 2 story – 10 m high line), brushwood - 10% of the cover, poor undergrowth - about 5% of the area, about 5 cm thick litter layer;
3. on the slope (northern exposure), in a one-specie stand of aspen trees (*Populus tremula*) with a brushwood of repent cornel (*Cornus stolonifera*), 12 m high stand of trees, brushwood - 70%, very poor undergrowth - 5%, moss layer - 20%, 0.5 cm thick litter.

Ground samples were taken for research from the mineral horizon, from two depths of 0 - 5 cm and 10 - 15 cm. They were taken in the second decade of October 1999. Contents of Cd, Cu, Pb, Zn were measured in the samples using the method of emission spectrometry ICP and the Leeman Labs PS 950 apparatus. The initial mineralization of the soil samples was carried out in microwave ovens Prolabo using the mixture of nitrogen acids and ultrachlorine acids (1:1, v/v). The total content of the investigated elements was measured.

The activity of the investigated enzymes was analyzed in the ground samples of natural humidity and the results were calculated into the ground dry mass. Determined was the activity of the following: dehydrogenase [22], phosphatase [21], urease [25], protease [14].

The physical-chemical propertied of the investigated ground were determined using the following methods [16]: texture soil using the Bouyoucose-Casagrande's method modified by Prószyński; soil pH in 1 M of KCl potentionmetrically; density of the still phase of the soil using the piknometric method; total organic carbon using the Tiurin's method; total nitrogen using the Kjeldahl's method; available phosphorus and potassium using the Egner-Riehm's method.

RESULTS

The content of the analyzed trace metals in the investigated material usually did not exceed the values considered as a natural background (Tab. 1). Only the loamy formations taken from the slope of the dumping ground from underneath the one-species stand of aspen (*Populus tremula*) with a brushwood of repent cornel (*Cornus stolonifera*) contained the higher content of Cd [10]. Within the samples taken from the top-soil, the content of Cd, Cu, Pb, and Zn in the ground under the monoculture of verrucose birch was not significantly different from the content of those elements in the ground under the stand of verrucose birch and

fine-leafed line trees in the group mixture. It was also twice as small (and the difference was significant) as compared to their content in the ground from the slope of the dumping ground. The content of the investigated trace metals in the surface horizon (0-5 cm) was higher than in the deeper horizon (5-10 cm).

Table 1. Content of selected trace metals of the investigated material [mg kg^{-1}]

Site*	Depth [cm]	Cd	Cu	Pb	Zn
1	0-5	0.62	12.80	10.20	41.5
	5-10	0.58	11.00	7.60	36.1
Means for site		0.60	11.90	8.90	38.8
2	0-5	0.71	14.70	12.00	45.7
	5-10	0.66	13.20	9.53	40.4
Means for site		0.69	13.95	10.77	43.3
3	0-5	1.42	27.20	6.68	70.7
	5-10	1.27	25.84	3.97	62.4
Means for site		1.34	26.52	5.32	66.6
Means for depth	0-5	0.91	18.23	9.62	52.6
	5-10	0.83	16.68	7.03	46.3
$LSD_{0.05}$ for	site	0.10	1.22	1.39	7.7
	depth	0.06	0.81	0.92	5.1

*1 – top in the monoculture of verrucose birch (*Betula verrucosa*)
2 – top in a stand of verrucose birch and small-leafed linden (*Tilia cordata*) in a group mixture
3 – slope, in a one-species stand of aspen-trees (*Populus tremula*) with a repent cornel brushwood (*Cornus stolonifera*)

The greatest content of TOC and TN was found in the loamy formations from the slope of the dumping ground, whereas the top-soil underneath the monoculture of verrucose birch contained the smallest amounts of those elements. The average content of TOC and TN in the ground samples taken from the slope was higher comparing to the content of those elements in the ground from the top-soil, by 30% and 40-50% respectively. Twice as high amounts of TOC and TN were found in the 0-5 cm layer, comparing to the 10-15 cm layer (Tab. 2). Values of the C:N ratios in the ground of the investigated sites were close - they remained within 12.3 - 12.8.

The investigated loamy material showed a natural reaction (pH_{KCl} 7.1).

The smallest bulk density of the loamy formations was stated in the ground from the slope of the dumping ground, while the greatest density was found in the ground from the top-soil underneath the monoculture of verrucose birch. Ground compaction in the 0-5 cm horizon was smaller that in the 10-15 cm horizon (Tab. 2).

Table 2. Properties of investigated material

Properties	Depth [cm]	Site*		
		1	2	3
TOC [%]	0-5	1.52	2.38	2.86
	5-10	0.90	1.27	1.60
TN [%]	0-5	0.12	0.19	0.23
	5-10	0.07	0.10	0.13
Bulk density [Mg· m^{-3}]	0-5	2.61	2.55	2.46
	5-10	2.58	2.43	2.40
Available P [mg· kg^{-1}]	0-5	41	95	79
	5-10	38	97	88
Available K [mg· /kg^{-1}]	0-5	204	124	618
	5-10	191	124	478

*see Table 1.

The content of the available phosphorus (which stayed at the level appropriate for rich soils) in the ground samples from the top-soil underneath the site and fine-leafed line site almost reached the content of that element in the dumping ground. It was also twice as high as in the ground from the top-soil underneath the monoculture of verrucose birch. In the case of phosphorus, which is not a very mobile component, there were no significant differences in its vertical distribution within the investigated horizons (Tab. 2).

The content of available potassium in the ground of the investigated sites was highly differentiated (from a low level up to the level that mean very high richness). In the ground from the top-soil, the average content of that form of potassium was 4 times lower that the content of that element in the material from the slope of the dumping ground. The differences in the vertical distribution of potassium were stated only in the ground samples from the slope of the dumping ground. The surface horizon (0-5 cm) showed a greater content of that element than the deeper horizon (5-10 cm), (Tab. 2).

Enzymatic activity of loamy formations was significantly differentiated depending on the object and depth (Tab. 3).

Table 3. Enzymatic activity of the investigated material

Site*	Depth [cm]	ADh	AF	AU	AP
1	0-5	6.67	74.50	892.0	32.47
	5-10	3.14	43.37	486.3	21.77
Means for site		4.90	58.93	689.2	27.12
2	0-5	7.32	134.23	997.3	49.73
	5-10	3.55	99.37	720.7	33.87
Means for site		5.43	116.80	859.0	41.80
3	0-5	7.62	137.17	1049.3	53.67
	5-10	4.33	111.57	752.4	36.30
Means for site		5.98	124.37	900.9	44.98
Means for depth	0-5	7.20	115.30	979.6	45.29
	5-10	3.67	84.77	653.1	30.64
$LSD_{0.05}$ for	site	0.09	0.26	2.1	0.55
	depth	0.06	0.18	1.4	0.37

ADh – Dehydrogenase activity in μg TPF/1 g ground/24 h
AF – Phosphatase activity in μg p-nitrophenol/1 g ground/1 h
AU – Urease activity in μg $N\text{-}NH_4^+$/1 g ground/24 h
AP – Protease activity in μg tyrosine/1 g ground/1 h
*see Table 1.

The greatest activity of the investigated enzymes (dehydrogenase, phosphatase, urease, and protease) was observed in the loamy formations from the slope of the dumping ground under the stand of aspen trees (*Populus tremula*) with a brushwood of repent cornel (*Cornus stolonifera*). Among the top-soil samples, higher enzymatic activity was stated in the soil from the stand of verrucose birch (*Betula verrucosa*) and fine-leafed line (*Tilia cordata*) in the group mix, comparing to the soil from the verrucose birch monoculture. In all the sites, the activity of the investigated enzymes in the 0-5 cm layer was 30-40% that that in the layer of 5-10 cm.

DISCUSSION

Changes in the enzymatic activity of the soil within the sites and the analyzed layers corresponded to the changes in the number of biogenic components in the investigated material, which means that higher activity of the enzymes was stated in the soil of greater amount of total C, total N, and available forms of P and K. The intensity of the biochemical processes depends most of all on the amount of the energetic material [5]. This also proves the introduction of nutrients into the biological circulation. Kobus [12], on the basis of the results of the recent research in biochemistry, ecology, and the role of microorganisms in soil environment, stated that the biological processes shaping the soil fertility in land ecosystems are mainly related to microorganisms and enzymes emitted by those microorganisms, as well as to the rate of the biogeochemical changes the element circulation carried out by them. According to Kiss et al. [11], enzymatic activity reflects both the direction and character of the biogeochemical processes and all of the basic changes with biology and physical-chemical properties of soils. That stimulation had lower density of the still phase of the ground, which favourable the development and activity of soil microorganisms because of the favorable impact on the state of water-air relations in the ground [8]. It is worth mentioning that in the loamy formations from the slope of the dumping ground that had the greatest activity of the investigated enzymes, the greatest content (except for Pb) of the trace metals (Cd, Cu, and Zn) was stated. Heavy metals are commonly considered to be inhibitors of the enzymatic and microbiological activity in soils [6, 15, 24]. While investigating the activity of the enzymes in the soils that were under a lot of pressure from industrial pollution, Olszowska [18] and Januszek [9] observed a slight influence of the heavy metals cumulated in the soil on the enzymatic activity of the investigated soils. The authors mentioned above justify the mitigation of the results of heavy metal activity in the investigated soils by the increased pH value in the soils with a greater content of heavy metals. Soil reaction is considered the main factor regulating the availability of heavy metals in soils [4, 7]. Sparks [20] emphasizes that loamy materials are capable of heavy metal adsorption, which limits the biocirculation. Quantities of specifically adsorbed heavy metals and the strength of the loamy formations binding them, clearly depend on the reaction [17]. Research carried out by Januszek [9] indicate that as the result of soil contamination with heavy metals, the activity of soil microorganisms is limited much stronger than the one of the extracellular soil enzymes. The registered significant activity of the extracellular enzymes (phosphatase; urease; and protease) in the investigated loamy formations

remaining at the level of the activity of those enzymes in the fertile forest soils of Southern Poland [9] could have been the result of their accumulation in the ground [11, 12]. Burns [3] claims that the loamy mineral are the main soil component that stabilizes the enzymes. Boyd and Mortland [1] proved that the activity of the loam-enzyme was often lower than that of the free enzymes in the homogenic solution, for example the reduction of the activity of phosphatase by the loamy minerals has the following pattern: smektyt > illit > kaolinit. Sundaram and Crook, however, [following 2] stated an increase in the activity of urease adsorbed on kaolinite. Dehydrogenase operating only in the live, undamaged cells are more sensitive to the natural and anthropogenic stress factors. Our own research and the quoted reference therefore indicate that the changes in the activity of the investigated enzymes could depend on both the individual properties of the enzyme and the properties of the investigated soil.

Another cause of the differentiation of the enzymatic activity of the ground of different objects could be found in the individual influence of particular tree species on the development of microorganisms and in different species composition of the bacterial inhabiting the roots of the spontaneously occurring herbs and forest trees [3]. Tissues of many plants emit allelosubstances. These compounds become toxic for soil microorganisms when being decomposed under the influence of plant enzymes [19]. Januszek [9] proved that the species of a tree significantly affected the enzymatic activity in forest soils. Koper and Piotrowska [13] also stated that the activity of the soil enzymes depended on the species composition of the plant cover, which influenced the accumulation of specific substrates for enzymatic reactions in the soil.

CONCLUSIONS

1. The content of Cu, Pb, and Zn in the investigated loamy material did not exceed the values considered as a natural background.
2. The loamy formations taken from the slope of the dumping ground from the one-specie stand of aspen trees (*Populus tremula*) with the brushwood of repent cornel (*Cornus stolonifera*) contained greater amounts of Cd.
3. The content of Cd, Cu, and Zn in the ground from the slope of the dumping ground was significantly higher than the content of those elements in the ground from the top-soil.
4. A greater content of Pb was stated in the loamy material from the top-soil than in the material from the slope of the dumping ground.

5. The greatest activity of the investigated soil enzymes was found in the loamy formations from the slope of the dumping ground.
6. In the top-soil, the enzymatic activity of the ground from under the stand of verrucose birch and fine-leafed linden trees in the group mixture was higher that that of the ground from under the monoculture of verrucose birch.
7. The enzymatic activity of the loamy material in the 0-5 cm horizon was higher than the activity of the same material in the 10-15 cm horizon.
8. Intensification of the investigated enzymatic processes corresponded to the growth of the content of biogenic components in the ground and with the decrease in the ground compaction.

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WYBRANE WŁAŚCIWOŚCI UTWORÓW ILASTYCH NA ZALESIONYM ZWAŁOWISKU KOPALNI SIARKI

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S t r e s z c z e n i e . Badania zlokalizowano na terenie zalesionego zwałowiska zewnętrznego kopalni siarki w Piasecznie koło Tarnobrzega (50^0 35' N; 21^0 47' E).

Do badań zawartości metali śladowych oraz aktywności enzymatycznej materiału ilastego wytypowano następujące obiekty:

1. na wierzchowinie w monokulturze brzozy brodawkowatej (*Betula verrucosa*),
2. na wierzchowinie w drzewostanie brzozy brodawkowatej i lipy drobnolistnej (*Tilia cordata*) w zmieszaniu grupowym,
3. na zboczu, w jednogatunkowym drzewostanie osiki (*Populus tremula*) z podszytem derenia rozłogowego (*Cornus stolonifera*).

Stwierdzono, że zawartość Cu, Pb i Zn w badanym materiale ilastym nie przekraczała wartości uznawanych za naturalne tło. Utwory ilaste pobrane ze zbocza zwałowiska spod jednogatunkowego drzewostanu osiki (*Populus tremula*) z podszytem derenia rozłogowego (*Cornus stolonifera*) zawierały podwyższoną zawartość Cd. Zawartość Cd, Cu i Zn w gruncie ze zbocza zwałowiska była istotnie większa, w porównaniu z zawartością tych pierwiastków w gruncie z wierzchowiny. Stwierdzono większą zawartość Pb w materiale ilastym z wierzchowiny niż w materiale ze zbocza zwałowiska. Największą aktywnością badanych enzymów glebowych (dehydrogenaz, fosfataz, ureazy i proteazy) cechowały się utwory ilaste ze zbocza zwałowiska. Na wierzchowinie aktywność enzymatyczna gruntu spod drzewostanu brzozy brodawkowatej i lipy drobnolistnej w zmieszaniu grupowym była większa niż aktywność enzymatyczna gruntu spod monokultury brzozy brodawkowatej. Nasilenie badanych procesów enzymatycznych korespondowało ze wzrostem zawartości składników biogennych w gruncie oraz ze zmniejszeniem zagęszczeniem gruntu.

S ł o w a k l u c z o w e : utwory ilaste, aktywność enzymatyczna, metale ciężkie, zwałowisko.