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SOIL ENZYMATIC ACTIVITY IN DETERIORATED FOREST ECOSYSTEMS IN THE OPERATION AREA OF THE PUŁAWY S.A. NITROGEN FACTORY

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A b s t r a c t. The present research (1998-1999) was carried out to evaluate soil enzymatic activity in the deteriorated forest ecosystems within the operation range of the Puławy S.A. Nitrogen Factory. Investigation covered podzolic soils from strong and medium forest pollution zones. Objects from the Puławy Forest Inspectorate were represented, i.e. samples from the Puławy district (Inspectorate Wronów) and Żyrzyn district (Inspectorate Zagórki). The obtained results indicate high degree of soil environment deterioration in the investigated forest habitats, in the form suppressed enzymatic activity and deformation of chemical properties. A significant increase in the enzymatic soil activity with the increasing distance from the nitrogen factory was observed. Changes in the activity of soil enzymes were related to the soil chemical properties.

K e y w o r d s: soil, enzymatic activity, forest ecosystems, nitrogen works.

INTRODUCTION

Biological and bio-chemical properties of soils are very sensitive in terms of reaction to stress factors affecting environment [23]. Research by Januszek [9] proved that enzymatic activity is an indicator of biological activity and fertility of forest soils. According to Kiss *et al.* [11], enzymatic activity of a soil is reflected by both its previous (resulting from enzyme accumulation in the form of humic complexes) and the present biological state (resulting from enzyme catalytic properties that play an essential role in the circulation of elements). The above authors stated also that there was a possibility of using enzymatic methods for evaluating evolution of technogenic soils (industrial and urban soils). Enzymatic activity is often used to evaluate the influence of anthropogenic stress factors, such

as excessive use of chemicals or industrial pollution, on the ecological status of soils [1,25].

The spatial structure of forest damage in the region of the Puławy S.A. Nitrogen Factory is of a zonal character. High rate of forest damage is most of all due to N-E winds, which dominate in this area [18].

The aim of this research was to investigate soil enzymatic activity on the background of deteriorated forest ecosystems under the pressure of Puławy S.A. Nitrogen Factory operations. The present authors concentrated also on the description of a possible relation between the activity of the investigated enzymes and the basic chemical properties of the soil.

MATERIALS AND METHODS

In the period 1998-1999, research on the soils of deteriorated forest habitats located in the Puławy Forest Inspectorate were carried out. The research included podzolic soils from strong (III) and medium (II) forest damaged zones. The following study sites were chosen in relation to the distance from the nitrogen factory (NF) (N-E direction):

- Puławy district, Forest Inspectorate Wronów: sector 199 d - 500 m; 120 f - 800 m; 136 a - 2000 m;
- Żyrzyn district, Forest Inspectorate Zagórki: sector 62 c - 8000 m.

Characteristics of the chosen objects are presented in Table 1.

Soil samples were taken from the soil mineral layer from two depths, i.e. 5-10 cm and 10-20 cm. Granulometric composition of the investigated soils is presented in Table 2. They were taken in the third decade of April in 1998 and 1999. The following properties were determined in the samples: activity of dehydrogenases [22], phosphatases [21], urease [26], and protease [13]; total carbon content using the Tiurin's method; total nitrogen by the Kjeldahl's method; ammonia nitrogen - colorimetrically,

Table 1. Characteristics of the investigated objects

Forest inspectorate	Sector	Damage zone	Bonitation	Forest type	Treestand
Wronów	119 d	III	IV	Bs	Brz, czm.
	120 f	III	IV	Bs	Brz, czm.
	136 a	III	II	BMśw	So, czm.
Zgórki	62 c	II	III	BMśw	So, Brz, Db, krusz.

Bs - dry forest, BMśw - mixed fresh forest; Brz - *Betula verrucosa* Ehrh.; So - *Pinus sylvestris* L.; Db - *Quercus robur* L.; czm. - *Padus seropina* Ehrh.; krusz. - *Frangula almus* Mill.

Table 2. Granulometric composition of the investigated soils

Sector	Distance from NF (m)	Depth (cm)	Fraction, mm (%)		
			1.0-0.1	0.1-0.02	<0.02
119 d	500	5-10	86.9	9.1	4.0
		10-20	86.7	11.3	2.0
120 f	800	5-10	83.0	12.0	5.0
		10-20	83.6	11.4	5.0
136 a	2000	5-10	90.6	7.4	2.0
		10-20	92.0	6.0	2.0
62 c	8000	5-10	71.6	21.4	7.0
		10-20	80.7	14.3	5.0

using the Nessler's method; nitrate nitrogen - colorimetrically; using the modified brucine method; pH in 1 M KCl - potentiometrically and granulometric composition by the Bouyoucos-Casagrande's method as modified by Prószyński.

RESULTS AND DISCUSSION

Data presented in Table 3 indicate that the enzymatic activity of the soil from the investigated objects increased significantly with the increasing distance from the Puławy NF. This relation, observed mainly in the 5-10 cm layer, had a linear character and corresponded to the degree of forest habitat damage (Table 1). Data received from the Puławy Forest Inspectorate (Puławy Forest Inspectorate is part of the Regional Management of National Forests in Lublin) indicate that the degree of forest ecosystem deterioration within the range of the Puławy NF decreases with the increasing distance from the source of emission [18]. An increase in the activity of the investigated enzymes was accompanied by a significant increase in the content of total carbon in the soil (Table 4). Research by other authors [3,5,16] proved importance of the correlation coefficient between the activity of soil enzymes and carbon content in organic compounds. Going further from the NF, an increase in the pH soil levels was also noted (Table 5). Frankenberger and Johanson [6] stated that soil enzymatic activity changed with changing concentration of hydrogen ions due to reversible reactions of ionisation or de-ionisation of prototropic groups in the active centre of enzymatic proteins and irreversible denaturation of the enzyme. According to the above mentioned authors, suppression in the enzymatic activity of a highly acidified soil could result from the damage to hydrophobic ions and hydrogen bindings which leads to an irreversible loss of the second-row structure of enzymatic proteins.

Table 3. Enzymatic activity of the investigated soils (average values for the years 1998-1999)

Sector	Distance from NF (m)	Depth (cm)	ADh	AF	AU	AP
119 d	500	5-10	5.71	11.43	151.61	13.60
		10-20	4.75	7.33	146.38	11.10
120 f	800	5-10	7.81	16.38	161.16	14.90
		10-20	4.68	9.05	128.93	11.34
136 a	2000	5-10	10.03	25.68	215.74	15.96
		10-20	4.67	11.27	151.37	12.12
62 c	8000	5-10	15.20	40.98	269.64	18.91
		10-20	4.38	17.02	157.46	16.02
$LSD_{0.01}$			0.09	0.71	2.32	2.02

ADh - dehydrogenase activity (μg TPF/g d.w. soil/24h); AF - phosphatase activity (μg p-nitrophenol/g d.w. soil/1 h); AU - urease activity (μg N–N H_4^+ /g d.w. soil/24 h); AP - protease activity (μg tyrosine/g d.w. soil/1 h).

Table 4. Content of total carbon, nitrogen and mineral forms of $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ in the investigated soil (average values for the years 1998-1999)

Sector	Distance from the NF (m)	Depth (cm)	Ct (%)	Nt (%)	N-N H_4^+ (mg/g d.w. soil)	$N\text{-}N_3^-$ (mg/g d.w. soil)
119 d	500	5-10	1.44	0.63	47.04	14.56
		10-20	0.76	0.22	49.89	8.81
120 f	800	5-10	1.51	0.55	62.78	9.68
		10-20	1.32	0.37	55.99	8.67
136 a	2000	5-10	1.56	0.53	59.18	8.47
		10-20	0.87	0.23	52.28	8.45
62 c	8000	5-10	2.52	0.78	62.16	8.71
		10-20	2.08	0.54	39.08	7.34
$LSD_{0.01}$			0.05	0.03	1.81	0.38

Soils of the deteriorated forest ecosystems usually had a very low level of enzymatic activity (Table 6). On the basis of research by other authors [2,7] and the present authors it can be concluded that disturbances in the intensity of enzymatic processes are related to changes in the soil chemical properties. Deformation of chemical properties was observed in the investigated soils. It was proved by very strong acidification (Table 5), and high total nitrogen content (Table 4) - several times higher than in an average podzolic soil [17]. It was also proved by a very narrow ratio of C:N (Table 5). Low content of mineral $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ forms

(Table 4) was noted in the soils of all objects. It could have been a result of component leaching. Research by Spychaj-Fabisiak *et al.* [20] proved that acid rainfall result in the increase in the amount of mineral nitrogen leached from the soil. The amount of the nitrogen ammonia form in the soil was several times higher than the amount of the nitrate form. This indicates predominance of ammonification processes and weak character of nitrification processes.

Soil enzyme activity level in the investigated soil depended on the distance from the NF, type of enzyme, and depth of the soil layer (Table 6).

Table 5. C:N ratio and pH_{KCl}

Sector	Distance from NF (m)	Depth (cm)	C : N		pH_{KCl}	
			Years			
			1998	1999	1998	1999
119 d	500	5-10	2.4	2.2	3.1	3.0
		10-20	3.4	3.5	3.4	3.3
120 f	800	5-10	2.8	2.7	3.1	3.3
		10-20	3.6	3.7	3.5	3.5
136 a	2000	5-10	3.0	2.9	3.5	3.6
		10-20	3.8	3.7	3.6	3.7
62 c	8000	5-10	3.2	3.3	3.7	3.7
		10-20	3.9	3.8	3.8	4.1

Table 6. Level of enzymatic activity in the investigated soils*

Enzymatic activity	Activity level	Depth (cm)	
		5-10	10-20
		Sectors	
ADh**	<15 - very low 15-30 - low 30-45 - medium	119 d; 120 f; 136 a 62 c	119 d; 120 f; 136 a; 62 c
AF	<20 - very low 20-40 - low 40-60 - medium	119 d; 120 f 136 a; 62 c	119 d; 120 f; 136 a; 62 c
AU	<100 - very low 100-200 - low 200-300 - medium	119 d; 120 f 136 a; 62 c	119 d; 120 f; 136 a; 62 c
AP	<10 - very low 30-40 - medium	119 d; 120 f; 136 a; 62 c	119 d; 120 f; 136 a; 62 c

*The activity level of a particular soil enzyme was evaluated (after considering methodical differences and calculations) according to Januszek [9]. **For explanation see Table 3.

In both investigated soil layers, hydrogenases activity remained at a very low level. Only at the distance of 8000 m from the NF (sector 62 c), in the 5-10 cm layer, activity of that enzyme was low. Similar results were noted in the case of phosphatase activity. The reason for such a low ADh level could be the fact that dehydrogenases are intracellular enzymes and are more sensitive to natural and anthropogenic stress factors than enzymes related to soil colloids [9,14]. Activity of dehydrogenase is a good eco-toxicological index [8,15]. Very low or low (sector 136 a and 62 c) level of AF was probably caused by high soil acidification. Phosphatases are the most sensitive enzymes that are highly dependent on pH. They are good indices of soil reaction [4,12]. Urease activity of the investigated soils remained at low or medium levels (Table 5). Urease is related mainly to soil humic substances. It is also related to clay content. It is very stable in these complexes [10]. AP remained at a low level in all the investigated objects and layers (Table 5). According to Watanabe and Hayano [22], low activity of that enzyme proves a small number of microorganisms active in protein decomposition (mainly *Bacillus* spp.).

CONCLUSIONS

1. Soil enzymatic activity in the deteriorated forest habitats within the range of the Puławy Nitrogen Factory increases significantly with an increasing distance from the factory.

2. Changes in the activity of the investigated soil enzymes (dehydrogenases, phosphatases, urease, and protease) were related to soil chemical properties. The investigated forest soils had very low and low level of enzymatic activity.

3. Deformation in the soil chemical properties was confirmed by high acidification and a very narrow ratio of C:N.

4. Content of the ammonia form of nitrogen in the investigated soils was several times higher than the content of the nitrate form of nitrogen.

5. The results indicate high intensity of soil environment deterioration in the region under the influence of the Puławy Nitrogen Factory.

6. Soil deterioration around the factory caused great transformations of the ecosystems, i.e. negative changes in the quantitative and qualitative composition of the forest tree species.

REFERENCES

1. **Bielińska E.J., Baran S., Domżał H.:** Katedra Biotechnologii Środowiskowej Politechnika Śląska Gliwice, 31, 1998.

2. **Chazijew F.C.:** Sistemno-ekologiczeskij analiz fiermientatiwnoj aktiwnosti poczw, Nauka, Moskwa, 130, 1982.
3. **Dick R.P.:** Agriculture, Ecosystems and Enviroment, 40, 1-4, 25, 1992.
4. **Dick W.A., Tabatabai M.A.:** Soil Sci., 173, 7, 1984.
5. **Frankenberger W.T. Jr., Dick W.A.:** Soil Sci. Soc. Am. J., 47, 945, 1983.
6. **Frankenberger W.T. Jr., Johanson J.B.:** Soil Biol., Biochem., 14, 433, 1982.
7. **Gostkowska K., Furczak J., Domżał H., Bielińska J.:** Polish J. Soil Sci., 31, 69, 1998.
8. **Januszek K., Kołodziejczyk P., Wolski P.:** Zesz. Probl. Post. Nauk Roln., 418, 779, 1995.
9. **Januszek K.:** Zesz. Nauk AR Kraków, 250, 1999.
10. **Kiss S., Dragan-Bularda M., Radulescu D.:** Adv. Agron., 27, 25, 1975.
11. **Kiss S., Dragan-Bularda M., Pasca D.:** Enzymology of Technogenic Soils. Casa Cartii de Stiinta, Cluj, 1993.
12. **Kobus J.:** Zesz. Probl. Post. N. Roln., 421, 209, 1995.
13. **Ladd J.N., Butler J.H.A.:** Soil Biol. Biochem., 4, 19, 1972.
14. **Ladd J.N., Foster R.C., Nannipieri P., Oades J.M.:** Soil Biochem., 5, 9, 1996.
15. **Malkomes H.P.:** Toxicol. Environ. Chem., 30, 167, 1991.
16. **Myśków W., Stachyra A., Zięba S., Masiak D.:** Roczn. Glebozn., 47, 89, 1996.
17. **Pondel H., Sadurski W., Wilkoś S.:** Pam. Puł. IUNG, 35.
18. Raport o stanie środowiska w rejonie oddziaływania ZA PUŁAWY, Lublin, 1982.
19. Raport o stanie środowiska w rejonie oddziaływania ZA PUŁAWY, Lublin, 1993.
20. **Spychaj-Fabisiak E., Murawska B., Cwojdziński W.:** Międz. Symp. Nauk "Przyrodnicze i antropogeniczne przyczyny oraz skutki zakwaszenia gleb". AR Lublin, 101, 1993.
21. **Tabatabai M.A., Bremner J.M.:** Biochem., 1, 301, 1969.
22. **Thalmann A.:** Landwirtsch. Forsch., 21, 249, 1968.
23. **Trasar-Cepeda C., Leiros C., Gil-Sotres F., Seoane S.:** Biol. Fertil. Soils, 26, 100, 1998.
24. **Watanabe K., Hayano K.:** Biol. Fertil. Soils, 18, 341, 1994.
25. **Will M.E., Graetz D.A., Roof B.S.:** J. Environ. Qual., 15, 4, 399, 1986.
26. **Zantua M.I., Bremner J.M.:** Soil Biol. Biochem., 7, 291, 1975.