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Dehydrogenase activity of technogenic soils of former sulphur mines (Yavoriv and Nemyriv, Ukraine)**

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A b s t r a c t. The dehydrogenase activity (an index of the total soil biological activity), sulphur content, pH and C_{org} were determined in technogenic soils of the former (1954-1994) sulphur mines in Ukraine (open pit and underground sulphur melting, Yavoriv and Nemyriv, respectively). The soils were neither managed nor reclaimed, and underwent natural self-restoration processes. Soils of former open pit sulphur mine showed C_{org} of 0.07-1.29%, pH of 7-7.9 and a high SO_4-S content (1.7-14.7 g kg^{-1}). Dehydrogenase activity was 2-3 fold lower than in the control forest podzolic soil. Sulphur mining by underground melting resulted in strong soil acidification (pH of 1.5-4.5) and a drastic lost of soil dehydrogenase activity, despite the relatively low S_{tot} content (0.02-0.2 g kg^{-1}). In upper horizons dehydrogenase activity decreased up to 28 fold as compared to the forest podzolic soil. In soil located 40 m from the boring well, with a high C_{org} of 8-9% (versus 0.07-1.11% in other soils that area) the decrease in the activity was not as heavy (11-fold) despite a low pH (1.5-1.8) and higher S_{tot} (2.1-3.3 g kg^{-1}).

K e y w o r d s: technogenic soil, former sulphur mine, soil dehydrogenase activity

INTRODUCTION

Technogenic soils (in Polish classification – anthropogenic industrial soils) are soils formed during reclamation of overburdens, tailings and other spoils and wastes resulting from mining and other industrial activities. The evolution of these soils is the process of transforming the wastes into agricultural or forest soils or into soils used for other purpose – parks, *etc*. (Paşca *et al*., 1998).

The largest sulphur mine in Ukraine is located in Yavoriv. In 1954-1994 the sulphur extraction in Yavoriv was conducted in the open pit and by underground melting (Frash method). The whole technogenic territory of sulphur mine in Yavoriv occupies about 7400 ha, including open-cast mine, technogenic dumps, territory of industrial wastes after sulphur flotation, territory of the underground sulphur melting, reservoir of industrial water and other industrial territories. The sulphur mining brought negative changes in the environment: technogenic transformation of the natural landscapes, destruction of fertile soils, pollution of the environment by sulphur compounds, chemical changes and pollution of the surface and underground waters, and changes of the natural vegetation. Now the trend of human activity is directed on restoration of disturbed territories left after the mining industry. In 2003 the project of the Yavoriv mine reclamation was accepted, which permits to form an artificial lake from the large hole left by sulphur excavation and to create a zone for recreation (Gaydin, 2000).

The processes of soil cover formation depend on the speed of plant colonization of technogenic territories and on the dynamics of primeval biological succession of plants and soil. The primary rock left after open cast sulphur mine is a potentially fertile substratum for soil cover formation and in the absence of human reclamation processes such technogenic territories are an interesting object for the investigation of natural self-restoration processes (Maryskevych *et al.,* 2000; 2005a).

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Development of such a field of biology as study of soil enzymes activity is very important because enzymes, as biological catalysts, play a large part in soil formation and soil fertility. Enzymes activity defines the level and direction of soil biochemical processes. Activity of enzymes is the diagnostic index of soils and it is very important in soil research of technogenic landscapes, for example technogenic territories of former sulphur mines.

The measurement of soil dehydrogenase activity (DHA) has been extensively used, as dehydrogenases are intracellular enzymes active in living cells, common through soil microbial species (Gliński and Stępniewski, 1985; Obbard, 2001; Brzezińska, 2002). Several studies have demonstrated that dehydrogenase activity of microorganisms is among the most sensitive parameters for evaluation of toxicity (Irha *et al*., 2003; Maliszewska-Kordybach and Smreczak, 2003).

The aim of the investigation presented herein was the determination of soil dehydrogenase activity, the main index of the total soil biological activity, of technogenic soils located on the territory of the former sulphur mines of Yavoriv enterprise 'Sulphur' in Ukraine.

MATERIAL AND METHODS

Soil samples were taken from 8 experimental plots located on different types of technogenic landscapes left after former sulphur mines (Table 1).

Open pit sulphur mine (Yavoriv):

- trans-accumulation part of the dump No. 3 (near the village Okilki), a natural meadow of *Calamagrostis epigeios* L. and *Carex sp.*;
- dam of tailing pit (near the village Cholgini), a natural meadow of *Calamagrostis epigeios* L.;
- tailing pit (near the village Cholgini), a natural meadow of *Artemisia absinthium* L. and *Calamagrostis epigeios* L.;
- podzolic soil in the neighbouring oak-pine forest.

Underground melting sulphur mine (Nemyriv):

- 5 m from the boring well, initial sandy soil without vegetation;
- 40 m from the boring well, sandy soil with isolated groupings of *Calamagrostis epigeios* L. and single *Pinus silvestris* L.);
- 120 m from the boring well, sandy soil with initial forest vegetation;
- 260 m from the boring well, podzolic soil in a spruce-oak-pine forest.

The investigated soils were neither managed nor reclaimed, and underwent natural self-restoration processes. The podzolic soil profiles in forests were not disturbed during sulphur excavation and were regarded as controls. The approximate locations of tested soil profiles on the territories of sulphur mines are shown in Figs 1-2.

T a b l e 1. Basic characteristics of tested soils

Location of soil profile	Soil horizon (cm)	C_{org} (%)	pH(H_2O)	Sulphur content (g kg^{-1})
Former sulphur mine in the open pit (Yavoriv)				
				SO_4-S
Trans-accumulation part of the dump (1)	0-20	1.29	7.70	3.2
	20-40	0.81	7.80	1.7
Transit part of the dam of tailing pit (2)	0-4	0.93	7.80	3.2
	4-10	0.28	7.90	12.3
	10-30	0.08	7.90	14.7
Tailing pit (3)	2-10	0.07	7.50	3.5
	10-20	0.46	7.80	14.2
	25-40	0.87	7.60	9.2
Forest podzolic soil (4)	0-17	1.16	7.03	n.t.
Former sulphur mine by underground sulphur melting (Nemyriv)				
Distance from the boring well (BW):				S_{tot}
20 m	0-10	0.59	3.13	0.190
	10-20	0.36	3.03	0.100
40 m	0-10	7.98	1.77	2.100
	10-20	8.88	1.48	3.280
120 m	0-10	0.15	3.23	0.020
	10-20	0.07	3.63	0.016
260 m (Forest podzolic soil)	0-10	1.11	4.26	0.025
	10-20	0.55	4.51	0.065

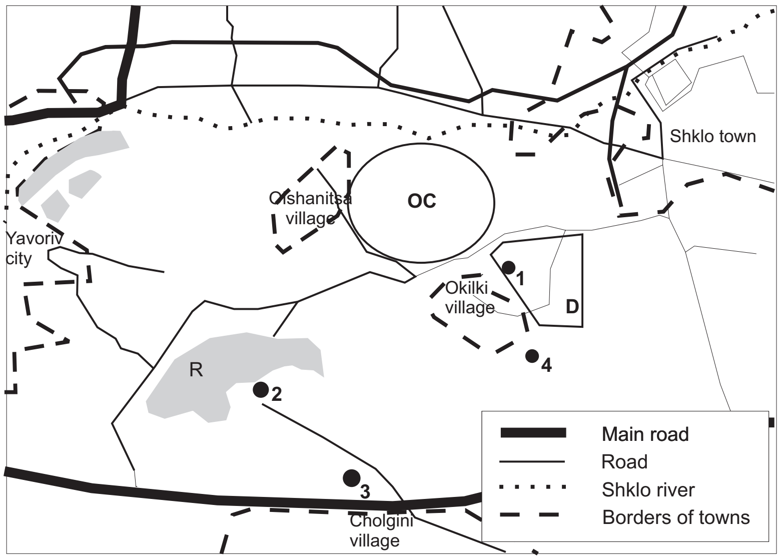

Fig. 1. Scheme of the open pit sulphur mine (Yavoriv, Ukraine). Tested soil profiles: 1 - on the trans-accumulation part of the dump No. 3 (near the village Okilki); 2 - on the transit part of the dam of tailing pit (near the village Cholgyni); 3 - on the tailing pit (near the village Cholgyni); 4 – podzolic soil profile in the oak-pine forest near former sulphur mine in Yavoriv. OC – open cast; D – dump; R – reservoir of industrial water.

Fig. 2. Scheme of the underground melting sulphur mine (Nemyriv, Ukraine). Tested soil profiles at the distance of: 20 m (1); 40 m (2); 120 m (3) and 260 m (4) from the boring well (BW).

All laboratory tests were conducted on air-dried sieved (2 mm) soils according to standard methods, in three replications: soil organic carbon (C_{org}) by the method of Turin (with Simakov modification); pH in H_2O by the potentiometric method in soil/water suspension (1:2.5 w/w); S_{tot} and SO_4-S – by the nephelometric method of Barsley- Lankaster; dehydrogenase activity (DHA) – according to Galstyan (1978).

RESULTS AND DISCUSSION

Soils located on the territories of the former sulphur mines in the open pit and by underground sulphur melting showed different characteristics (Table 1). Among the soils of the former open pit in Yavoriv, the lowest SO_4-S was measured on the trans-accumulation part of the dump – 3.2 g kg^{-1} and 1.7 g kg^{-1} at 0-20 and 20-40 depths, respectively. Similar SO_4-S content was recorded in the topsoil of the transit part of the dam of tailing pit and topsoil of the tailing pit (3.2-3.5 g kg^{-1}). Deeper soil horizons were more polluted with SO_4-S, reaching the values of 12.3-14.7 g kg^{-1}.

Sulphur processing by underground melting in Nemyriv resulted in lower sulphur accumulation. Soil located 20 m from the boring well showed S_{tot} of 0.1-0.2 g kg^{-1}. At the distances of 120 and 260 m from the well, S_{tot} of 0.016-0.065 g kg^{-1} was measured. Relatively high S_{tot} content was observed 40 m from the boring well (2.1-3.3 g kg^{-1}).

Depending on soil location on the technogenic landscape, and on the type and duration of soil reclamation, total sulphur content in the mining fields of former sulphur mines of Poland ranged from 0.04-15 g kg^{-1}, with SO_4-S amount of 0.007-12 g kg^{-1} (Martyn *et al*., 2002; Martyn and Jońca, 2006; Drożdż-Hara, 1978). However, Sołek-Podwika *et al.,* (2005) and Kołodziej (2005) observed S_{tot} up to 47 g kg^{-1} and 66 g kg^{-1} in soils of the 'Jeziórko' and 'Grzybów' sulphur mines, respectively.

Sulphur is one of the biogenic elements that are important for proper plant growth, playing a special role in the stabilization of biologically active structure of proteins. In unpolluted mineral soils, total sulphur content ranges from 0.05 to 0.4 g kg^{-1} (Kozłowska-Strawska and Kaczor, 2004). About 90-95% of soil S is present in organic forms, and only 5-10% in mineral forms that are available for microbes and plants. The process of S_{org} mineralization in soil is catalysed by arylosulphatase enzyme of microbial origin (Koper and Siwik-Ziomek, 2004). Excess of sulphur in soils of former sulphur mines gives rise to several transformations that are dangerous for soil microbes and plants. Strong soil acidification – in result of S oxidation to aggressive sulphuric acid – causes soil chemical degradation, heavy metals mobilization and secondary deficit of P and K (Wyłupek *et al.,* 2004; Martyn *et al.,* 2004; Sołek-Podwika *et al.,* 2005).

All soils of the former open pit in Yavoriv territory were slightly alkaline and showed pH (H_2O) in the range of 7.5-7.9, independently of the soil location and depth (Table 1). High pH values were measured also in soil horizons characterized by high SO_4-S content (9-14 g kg^{-1}) and resulted probably from the presence of minerals such as $CaSO_4$, $CaCO_3$ or $SrSO_4$, accompanying the sulphur deposits and remaining after the flotation process. Forest soil near Yavoriv showed pH neutral at 7.03.

Sulphur processing by underground melting in Nemyriv resulted in strong soil acidification. The values of soil pH were about 3-3.6, and in soil at 40 m from the boring well – as low as 1.48-1.77. Podzolic forest soil at the distance of 260 m out of the border of the sulphur mine area showed pH of 4.26-4.51. The S_{tot} content in Nemyriv soils was significantly negatively related to soil pH (y=-2.94 ln(x) +3.9, r=-0.93, P<0.001).

Strong acidification (pH (H_2O) of 2.6-3.6) was also observed in Polish soils of former underground sulphur melting mines (Kołodziej 2005; Dróżdż-Hara 1978; Martyn *et al.,* 2004). Wyłupek *et al.* (2004) observed soil pH as low as 1.0 in immediate vicinity of a sulphur mining hole in former 'Basznia' mine in Poland. This unnaturally low soil reaction indicates that the biological habitat of the soil was completely destroyed.

The content of organic carbon in soils depended on their location and depth. The oak-pine forest soil near Yavoriv showed C_{org} of 1.16%, and the soil situated on the trans-accumulation part of the dump showed C_{org} of 0.81-1.29%. Lower C_{org} was measured in profiles located on the dam of tailing pit (0.08-0.93%) and on the tailing pit 0.07-0.87% (Table 1).

The spruce-oak-pine forest soil near Nemyriv showed C_{org} of 0.55-1.11%. The C_{org} content was lower in soils located at the distances of 20 and 120 m from the boring well (0.59-0.36 and 0.15-0.07%, respectively). However, very high C_{org} content (up to about 8-9%) was measured in soil profile located 40 m from the boring well.

The organic carbon content in technogenic soils on territories of former sulphur mines in Poland depended *eg* on soil type, methods of reclamation and on plant cover (Kołodziej, 2005; Martyn *et al*., 2002 and 2004).

The forest topsoil near the sulphur mine in Yavoriv showed dehydrogenase activity of 0.289 mg TPF 10 g^{-1} 24 h^{-1} (Fig. 3). The open pit mining resulted in 2-3-fold decrease of the DHA down to the values of 0.123 mg TPF 10 g^{-1} 24 h^{-1} and 0.10 mg TPF 10 g^{-1} 24 h^{-1} in soils located on the dump and the tailing pit, respectively. Dehydrogenase activity of the upper horizon (0-4 cm) of profile located on the dam was relatively high (0.2 mg TPF 10 g^{-1} 24 h^{-1}), with a 30% decrease of the DHA as related to the forest soil. However, when considering a comparable, deeper soil layer, the calculated decrease in activity was more distinct, about 2-fold. All the soils showed a typical reduction of microbial activity with depth.

The dehydrogenase activity of the forest soil neighbouring the sulphur mine in Nemyriv was relatively high;

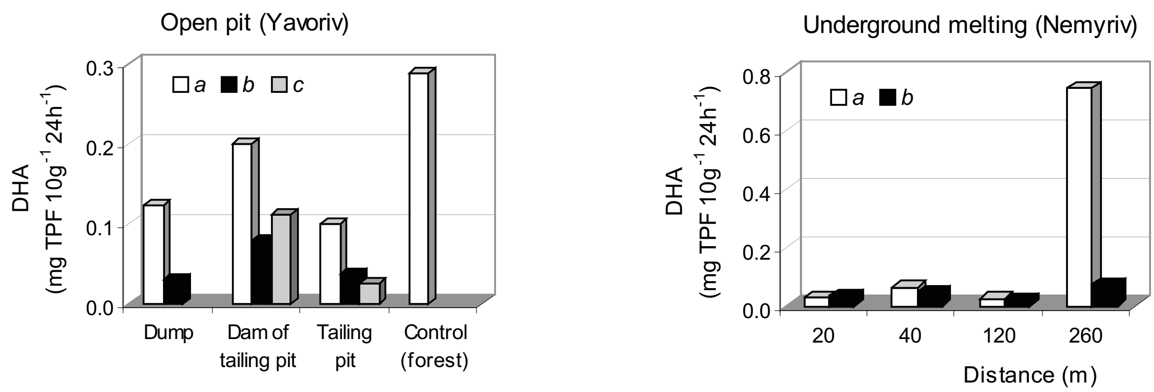

Fig. 3. Dehydrogenase activity in particular horizons of technogenic soils of former sulphur mines – in the open pit (Yavoriv) and by underground sulphur melting (Nemyriv). The soil horizons were denoted as: *a* (topsoil), *b,* and *c* (deeper horizons), explanation concerning the depths – in the text. The 20, 40, 120 and 260 m in Nemyriv sulphur mine – distances of the soil profiles from the boring well.

in the upper horizon it equalled 0.743 mg TPF 10 g^{-1} 24 h^{-1}. A drastic, 11-28-fold loss of the activity (in comparison to the forest soil) was observed in the upper horizons (0-10 cm) of soils located on the area closer to the boring well. Decrease of DHA was not as pronounced in the deeper horizons and was maximally 3-fold.

Results of this study suggest that the low dehydrogenase activity in the soils of the mining areas did result from damage of soil microflora due to the detrimental conditions of polluted soil ecosystem. Unfavourable habitats evidently developed in the strongly acid soils in Nemyriv. The dehydrogenase activity was not statistically related to sulphur content, but the tendency of the lower S, the higher DHA was observed.

The very high C_{org} content (about 8%) in both horizons of soil situated 40 m from the boring well is difficult to explain. Probably such a high organic matter content allowed soil microbes to express about 2-fold higher dehydrogenase activity in comparison to soils at 20 and 120 m from the boring well – despite their higher S_{tot} content (3.28 g kg^{-1}) and a very low pH <2.

In some opinions, natural succession can indeed eventually restore degraded mine land, but without human intervention it often takes 50-100 years. Self-sustaining systems can be developed from harsh environment by carefully applied ecological engineering approaches (Bradshaw, 1997; Panas, 1989). It has been shown for former Ukrainian sulphur mines that biological activity of soils on dumps was lower than biological activity of natural soils. However, enzyme activity of polluted soils was restored, and after 15-20 years it was quite similar to the enzymes activity of natural soils (Uzbek, 1991). Moreover, Maryskevych (1990) observed that enzyme activity on 15 year old dumps was 3-14-fold higher than on younger, 3 year old dumps. Determination of soil biological indices is widely used for investigation of natural soil restoration processes and for different kinds of forest and agricultural soil restoration processes. Long-term researches have shown that gradual restoration of disturbed technogenic territories is related with initial biological succession and the process of soil formation (Bilonoga, 1989; Levyk, 2006; Maryskevych *et al.,* 2000; 2005a; 2005b).

Technogenic soils of the territory of sulphur mining in open pit and by underground melting have been undergoing self-restoration processes for 13 years. Negative effects in soil environment remained over this period in both kinds of sulphur mining. The lack of plants on some areas proves strong deterioration of the soil system. At the distance of 20 m from the boring well on the underground sulphur melting area, an initial acid sandy soil (pH 3) without vegetation was noted. At the distance of 40 m, isolated groupings of *Calamagrostis epigeios* and single pines (*Pinus silvestris*) were observed, despite the very high S_{tot} content and low pH of sandy soil. The *Calamagrostis epigeios* grass, a pioneer plant of very low economic value, takes a considerable part in the grassland sward in strongly sulphated soils and can be found throughout the post-mining landscapes (Wyłupek *et al.,* 2004).

It has been commonly regarded that the method of underground sulphur melting is less detrimental than mining in the open pit. However, Martyn *et al.* (2002) pointed out that restoration of the territory of former sulphur mine by underground melting is difficult and must be complex because of soil acidification and hydrological problems. Our results indicate that soils of former sulphur mine in open pit created better habitats for soil microorganisms than the mine by underground melting. Indeed, the content of sulphate-S in soils of open pit area was very high. However, measured sulphates were not aggressive, as the soil reaction was slightly alkaline. Additionally, soil organic carbon content was relatively high (in upper horizons 0.07-1.29%). Finally, the loss of dehydrogenase activity, and index of total soil biological activity, was not as drastic as in strongly acid soils on the territory of mining by underground sulphur melting.

CONCLUSIONS

1. Dehydrogenase activity and basic properties of technogenic soil of the former sulphur mines varied among tested profiles and depended on the method of sulphur exploitation, location of soils profile, and soil depth.

2. Soils from the territory of open pit sulphur mine showed slightly alkaline reaction (pH 7.0-7.9), high SO_4-S content (1.7-14.7 g kg^{-1}) and C_{org} of 0.07-1.29%.

3. Sulphur mining by underground melting resulted in acid soil reaction (pH 1.5-4.5), relatively low S_{tot} content (0.02-3.3 g kg^{-1}) and C_{org} of 0.07-1.11% (plus one profile with a very high C_{org} of 8-9%).

4. The dehydrogenase activities reflected unfavourable changes of technogenic soils and were, as compared to control forest soils, about 2-3 fold lower in alkaline soils from the territory of the open pit sulphur mine and up to 28 fold lower in acid soils from the area of underground sulphur melting.

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