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# THE IMPACT OF PINE SELF-AFFORESTATION ON PODZOLIZATION PROCESS IN SEMI-NATURAL GRASSLAND AREAS OF VOLYN POLISSYA (UKRAINE)

***V. Kozlovskyy*** [1]****, N. Romanyuk*** [2]

[1] *Institute of Ecology of the Carpathians, NAS of Ukraine, 4 Kozelnytska St., Lviv 79026, Ukraine*

[2] *Ivan Franko National University of Lviv, 4 Hrushevskyi St., Lviv 79005, Ukraine*

**Corresponding author e-mail: vkozlovskyy@gmail.com*

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**Background.** Several theories have been proposed to explain the podzolization process. Currently, the role of organic matter in both weathering and immobilization in the illuvial horizon is clearly stated. The origin of soil organic matter and, accordingly, the various mechanisms of its influence on the soil material, create the basis of these theories. We assume that in the base-poor sandy soils under rich herbaceous vegetation with a well developed sod layer, the process of podzolization may also depend on $CO_2$ soil formation agent .

**Materials and Methods.** Four localities along a *Pinus sylvestris* L. self-afforestation chronosequence with pine stands of 10, 20, 40yrs and an adjacent semi-natural grassland area were investigated in order to determine the patterns of podzolization process on sandy glacial till deposits. Soil pH, exchangeable base, soil cation exchange capacity, total content of soil organic carbon, amorphous Fe, Si and Al and total contents of Al, Fe, Mn, Zn, Cd, Pb, Cu, Co, Ni, Na, K were determined. Statistical analysis of the results was performed using LibreOffice for Linux.

**Results.** During the pine succession, a previously well differentiated into horizons podzolic soil under the grassland vegetation community gradually degrades. Previously well-defined albic and spodic diagnostic horizons disappear, the soil profile becomes more acidic, the soil organic carbon, the base cation content and the base cation saturation decrease, the leaching rate of aluminium and iron increases. Secondary podzolization features in the soil profiles were detected 40 years after the onset of afforestation.

The podzolization has not been intensive enough to develop fully fledged albic and spodic diagnostic horizons over such a short period.

**Conclusions.** Based on the obtained soil morphological, physical and chemical properties, three most important agents of podzolization are proposed as principal for the studied area. The main gent under pine forest is fulvic acids that are produced during coniferous litter decomposition. Low molecular weight organic acids and carbon dioxide produced to the rhizosphere by roots and a root associated microbiota are mainly involved in the podzolization process under the grassland ecosystem.

***Keywords**:* podzols, reforestration, carbon dioxide soil formation agent

## INTRODUCTION

The transformation of agricultural land into forestland or grassland has been underway in many regions of Ukraine since early 1990s, when the contemporary agricultural land-use became economically unprofitable. The problem is not new worldwide. For instance, in Europe, 70 mln ha of land cover changed over the period 1950–2010 [13], including more than 21 mln hectares of new forest areas appearance recorded from 1990 to 2015 [9, 12]. The increase is believed to be due to large-scale afforestation programs in consequence of a worldwide strategy to mitigate $CO_2$ emissions (Kyoto Protocol) [7], as well as natural reverse of a low-productive agricultural land back to forests [10]. Thus, the study of the effects of afforestation on ecosystems at the local, regional and global scales has become a priority for researchers.

Despite the known effects of the afforestation on soils, little has been known about the mechanisms controlling these effects. Relatively few studies have dealt with the influence of vegetation on soil genesis and its morphology [4, 20, 24, 26, 27, 29] because soil transformation and soil evolution are slow processes. Therefore, the self-afforestation is a good opportunity for chronosequence (space-for-time substitution) studies as a natural way solving the problem of long-term observation of successive soil developments. Understanding the mechanisms by which afforestation alters podzols will aid in evaluating the true costs and benefits of afforestation in the long-term for big areas in the northern hemisphere.

Podzolization is the main process of soil development in the boreal zone, and it is a very important factor for soil formation in the temperate zone. Hovever, the podsolization process was not unanimously interpreted for years, several theories were proposed to explain its mechanism as reviewed by Buurman and Jongmans (2004) [5], Lundstrom *et al*. (2000) [19], Sauer *et al*. (2006) [28], Mokma and Buurman (1982) [22]. The difference in the concepts of podzolization was that the mobilization mechanisms of the organic matter and sesquioxides in the topsoil and their precipitation in spodic horizon were interpreted differently. With time, it became clear that podzolization is the process that can take place within the framework of all the previously stated concepts, which do not in fact contradict, but only complement each other.

The aim of the present study was to investigate changes in the podzolic soils genesis, morphology and properties of semi-natural grasslands on sandy glacial till deposits due to self-afforestation (secondary succession) with Scots pine (*P. sylvestris*).

## MATERIALS AND METHODS

**The Field Location**. Polissya belongs to the mixed forest subzone of the East European broad-leaved forest zone. In the past, the whole of Polissya was completely covered with forest and marshland. As a result of deforestation, mostly in the second half of the 19th century, forests now occupy scarcely one-third of the land area. Therefore, grasslands are common landscape in the Polissya part of Volyn Region and occupy about a quarter of its territory. The majority of these grasslands were developed by human activity, and are considered to be secondary vegetation replacing original forest vegetation. Most of the area is now plowed and grasslands do not form continuous fields, but are preserved in relatively small areas among arable land, on forest glades or margins, etc. Recently, due to economic reasons, the processes of natural overgrowing of abandoned agricultural land have begun to increase. Currently, self-afforestation of mesophilic grasslands with pine and birch trees, as well as hygromesophilic ones with various species of alder and willow is common for Ukrainian Polissya.

The study was performed in the southern part of Volyn Polissya, Ukraine (**Fig. 1**). Four localities along a 40-year long chronosequence with pine stands of 10, 20, 40yrs and adjacent semi-natural grassland area were investigated. Each locality was selected within a radius of 100 m so that the initial conditions would be similar. The first locality represented a mesophilic grassland area with the plant cover composed mainly of *Poa pratensis* L. The next two localities represented an area undergoing the process of natural afforestation with *Pinus sylvestris* L. of 10 and 20 year old stands. The soil of these locations was assumed to have had similar properties 0, 10 and 20 years ago and the only active variable of these localities is therefore the vegetation and the differences it provides. The fourth study site was a man-made pine forest with stand ages of 40yrs from which the overgrowing of the surrounding area began (most likely, the top soil layer was disturbed during the planting of trees 40 years ago). Soil sampling was very similar in all studies.

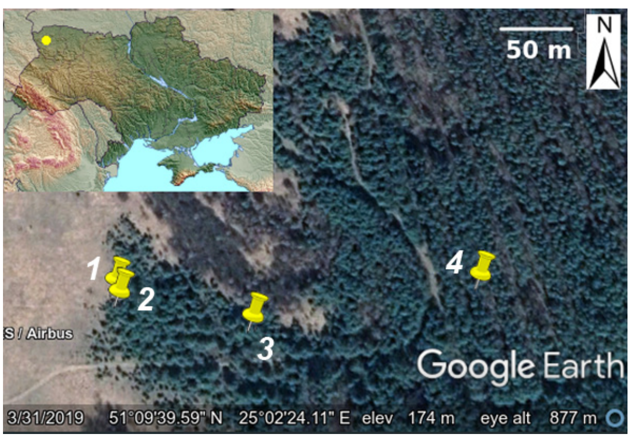


**Fig. 1.** Location of the research area: *1* – grassland (*Poa pratensis* L. seminatural herbaceous community); *2* – 10yrs pine stand (*Pinus sylvestris* L., natural overgrowth); *3* – 20yrs pine stand (*P. sylvestris*, natural overgrowth); *4* – 40yrs pine stand (*P. sylvestris*)

**Рис. 1.** Місцерозташування відбору зразків: ***1*** – лучна ділянка (*Poa pratensis* L., напівприродне трав'яне угруповання); *2* – 10-річне угруповання сосни (*Pinus sylvestris* L., природне заростання); *3* – 20-річне угруповання сосни (*P. sylvestris*, природне заростання); *4* – 40-річне угруповання сосни (*P. sylvestris*, штучне насадження)

Soil pits, approximately 80×50 cm, were excavated for soil description and sample collection [30]. The parent material was sandy, quartz-rich meltwater and alluvial deposits from middle and upper Quaternary. Soils were classified as Umbric Albeluvisol on each site [17, 33]. Samples from all sufficiently thick horizons were collected and analyzed.

**Soil Analysis.** Soil samples were air dried and passed through 2 mm sieves. In the prepared soil samples the soil properties were determined. Active and exchangeable soil acidity (pH $H_2O$ and pH KCl, respectively) were determined potentiometrically [16]. Hydrolytic acidity (HA) was determined by the Kappen's method (extraction with 1.0 M $CH_3COONa$, titration with 0.1M NaOH) [18, 30], exchangeable base cations (BC) were determined by the Kappen–Hilkovitz method (extraction by 0.1M HCl, titration with 0.1M NaOH) [21]. The soil cation exchange capacity (CEC) was calculated according to the standard formula: CEC = HA + BC. Base saturation (BS) was determined as the ratio of exchangeable base cations to CEC: BS = BC/CEC·100%.

The total content of soil organic carbon (SOC) was measured by the Tyurin photometric method (wet combustion method with kali bichromicum) [2].

The amorphous Fe fraction was obtained by the method of Chester and Hughes (1967) [6]; amorphous Si and Al – by 0.2 N NaOH extraction (w/v ratio – 1:400; extracting time – 24 h) [15].

For estimation of the total content of Al, Fe, Mn, Zn, Cd, Pb, Cu, Co, Ni, Na, K, the samples were mineralized using a dry combustion method (400–450 °C) followed by ash digesting with aqua regia and fluoric acid [21].

Mn, Fe, Zn, Cd, Pb, Cu, Co, Ni in extracts were measured by flame atomic absorption spectroscopy; Na, K – by flame emission spectroscopy; Si – colorimetrically using the molybdenum blue method [14]; Al – by colorimetry using the aluminon method [21].

**Statistical analysis.** Chemical analysis of the elements was carried out in triplicate. The soil chemical results are presented as arithmetic means and standard errors (±SE). The statistical analysis of the results was performed using software LibreOffice for Linux. The laboratory results were considered acceptable when the difference between the values obtained was less than 5 %.

## RESULTS

**Soil morphological characteristics.** Changes in the soil profiles and morphological properties were observed depending on the age of forest stands (**Fig. 2**). (**I**) The litter (O horizon) in the grassland *Poa pratensis* community was weak, poorly differentiated into layers, consisted mainly of 1–2yrs plant debris (L layer). In the pine chronosequence, the quantity of litter material, the percentage of needles and differentiation into layers gradually increased; litter layers of varying stages of decomposition were clearly visible under 40yrs pine forest (L, F, H layers). (**II**) The A horizon under *P. pratensis* community can be divided into two levels – the upper sod layer densely filled with grass roots and the lower one where the mass of roots decreased sharply. A less powerful sod layer was still present in 10yrs pine stand, but it was completely absent in the soil under 20 and 40yrs forests. (**III**) The bleached E horizon, which was clearly expressed under the *P. pratensis* community, was not observed so clearly under 10yrs pine, was absent under 20yrs forest, and once again, became slightly visible in a 40yrs pine soil profile. (**IV**) Among the profiles, the B horizon was much more distinct under grass vegetation, than under pine stands; its color indicated a significant enrichment with iron and the


**Fig. 2.** Soil profiles: *1* – grassland (*Poa pratensis* L. natural herbaceous community); *2* – 10yrs pine stand (*Pinus sylvestris* L., natural overgrowth); *3* – 20yrs pine stand (*P. sylvestris*, natural overgrowth); *4* – 40yrs pine stand (*P. sylvestris* L.)

**Рис. 2.** Ґрунтові профілі: *1* – лучна ділянка (природне трав'яне угруповання *Poa pratensis* L.); *2* – 10-річне угруповання сосни (*Pinus sylvestris* L., природне заростання); *3* – 20-річне угруповання сосни (*P. sylvestris,* природне заростання); *4* – 40-річне угруповання сосни (*P. sylvestris*, штучне насадження)

absence of obvious organic matter deposits signs. As in the case of the E horizon, the B soil horizons were significantly weakened under 10yrs pine, disappeared completely in 20yrs pine stand, and appeared again under 40yrs pine, but with organic matter deposits in the upper part (Bh) and $Fe^{3+}$ in the lower part of the horizon (Bs).

The texture of the studied soil profiles was loamy sand and overall similar for all sites.

**Chemical soil constituents and their changes.** The physico-chemical properties and distribution of elements in the grassland soil profile was clearly eluvial (podzolic). A breakdown or considerable translocation of all elements have taken place. The albic horizon was eluvial in relation to amorphous iron, aluminium, silicium and total iron (**Fig. 3**). As in the case of element distribution, soil acidity ($pH_{H_2O}$; HA), base saturation (BS), soil carbon content ($C_{total}$; $C_{H_2O}$), cation exchange capacity (CEC), loss on ignition (LOI) had their extremums in the podzolic horizon (see **Table**). A sharp increase in the total content of sodium, potassium, iron, amorphous iron, aluminium, silicium, organic carbon, as well as changes in physico-chemical properties indicate the development of the illuvial spodic horizon. The illuviation of elements in the profile had its special characteristics: (I) a high relative content of water-soluble organic carbon in the eluvial horizon and the lower part of the spodic horizon was noticeable; (II) a relatively high pH, a low hydrolytic acidity value and the degree of base saturation reaching its maximum in the albic horizon were not typical of podzolic soils; virgin podzols are characterized by a high acidity ($pH_{H_2O}$; HA) and a low base saturation. These conditions are markers of undersaturation and mobility of fulvic acids (main agents of soil formation according to the classical scheme), their potential to parent rock weathering and creation of albic horizon. So, high $pH_{H_2O}$, low HA and BS indicate low mobility of fulvic acids and their insignificant impact on the podzolization process in the grassland ecosystem.

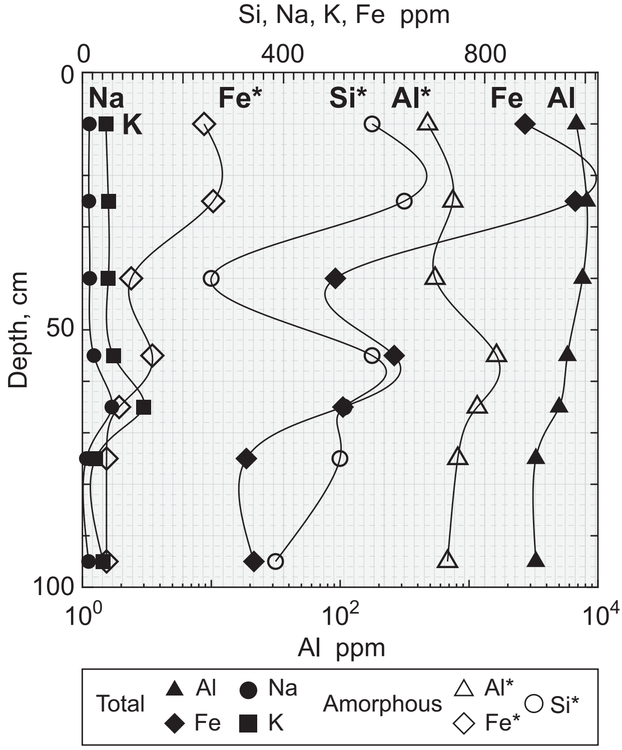


**Fig. 3.** Distribution of Na, K, Fe, Si, Al in the grassland soil profile (*Poa pratensis* L., herbaceous community)

**Рис. 3.** Розподіл Na, K, Fe, Si, Al у ґрунтовому профілі лучної ділянки (*Poa pratensis* L., трав'яне угруповання)

Next two pine stands of the chronosequence had no distinct eluvial-illuvial patterns of Al, Si, Fe and organic carbon translocation within the soil profile (**Table**; **Fig. 4, 5**). All studied parameters gradually changed with the increasing age of the pine forest. Total SOC, after its maximum in humic horizon of a 10yrs pine stand, decreased almost twice under 20yrs pine; actual ($pH_{H_2O}$) acidity that was even higher than the value in grassland, decreased again under 20yrs pine. In contrast to $pH_{H_2O}$, potential acidity (HA) sharply increased in the upper part of humic horizon (0–13 cm) of 10yrs pine and that value was much higher than in the adjacent plots of the chronosequence. Other constituents (CEC, BS, BC) having reached their maximum under grassland gradually decreased under 10–20yrs pine forest. Total contents and ratios $Al_{total}$ / $Al_{amorphous}$ and $Fe_{total}$ / $Fe_{amorphous}$ suggested that the leaching of aluminum and iron under pine stands was more intense compared to grassland.

**Soil physico-chemical properties along of studied 40yrs pine self-afforestation chronosequence (Polissya, Ukraine; 07.2020)**

**Фізико-хімічні властивості ґрунту в рамках 40-річної часово-просторової послідовності природного заростання сосною (Полісся, Україна; 07.2020)**

| Depth, cm | Horizon | Loss on ignition (LOI) | $pH_{H20}$ | Hydrolytic acidity (HA) | Exchangeable base cations (BC) | Cation exchange capacity (CEC) | Base saturation percentage (BS) | Soil organic carbon (SOC) total | Soil organic carbon (SOC) mobile ($H_2O$) | $Al_{total}$ / $Al_{amorphous}$ | $Fe_{total}$/$Fe_{amorphous}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | | meq/100 g of soil | | | % | % | % of total C | | |
| grassland soil profile | | | | | | | | | | | |
| 0–18 | A | 2.05 | 5.2 | 0.58 | 2.2 | 2.8 | 78.9 | 0.71 | 3.8 | 14.3 | 3.6 |
| 20–30 (35) | | 1.39 | 5.8 | 0.48 | 1.8 | 2.3 | 78.9 | 0.52 | 3.2 | 10.9 | 3.7 |
| 35–45 | E | 0.37 | 6.2 | 0.04 | 0.7 | 0.7 | 95.0 | 0.11 | 10.1 | 13.9 | 5.2 |
| 50–60 | Bsh | 0.73 | 5.9 | 0.29 | 0.3 | 0.9 | 50.8 | 0.18 | 0.9 | 3.5 | 4.5 |
| 60–70 | Bs | 0.52 | 5.9 | 0.19 | 0.3 | 0.5 | 60.8 | 0.11 | 1.7 | 4.3 | 6.9 |
| 70–75 | | 0.30 | 6.2 | 0.10 | 0.3 | 0.4 | 75.6 | 0.05 | 17.7 | 4.0 | 6.8 |
| 90> | BC | 0.25 | 6.3 | 0.05 | 0.3 | 0.3 | 86.1 | 0.03 | 4.0 | 4.8 | 7.1 |
| 10yrs pine stand soil profile | | | | | | | | | | | |
| 0–13 | A | 2.47 | 5.6 | 1.26 | 1.5 | 2.8 | 53.6 | 0.74 | 3.9 | 6.2 | 1.5 |
| 15–30 | | 2.21 | 5.9 | 0.40 | 1.5 | 1.9 | 78.4 | 0.62 | 1.3 | 6.6 | 1.7 |
| 35–45 | Bs | 0.96 | 5.9 | 0.19 | 0.3 | 0.5 | 60.8 | 0.21 | 0.8 | 4.1 | 3.2 |
| 45–55 | | 0.93 | 5.9 | 0.17 | 0.3 | 0.5 | 67.4 | 0.08 | 1.0 | 5.0 | 3.8 |
| 50–60 | | 0.51 | 5.9 | 0.15 | 0.3 | 0.5 | 67.4 | 0.07 | 1.8 | 4.8 | 4.0 |
| 60–70 | | 0.46 | 6.0 | 0.10 | 0.3 | 0.4 | 75.6 | 0.06 | 1.3 | 3.7 | 6.8 |
| 75> | BC | 0.34 | 6.3 | 0.10 | 0.3 | 0.4 | 75.6 | 0.03 | 1.7 | 7.0 | 9.8 |
| 20yrs pine stand soil profile | | | | | | | | | | | |
| 1–10 | A | 1.39 | 5.3 | 0.87 | 0.7 | 1.6 | 45.5 | 0.46 | 4.7 | 6.9 | 1.4 |
| 10–20 | | 0.88 | 5.5 | 0.39 | 0.7 | 1.1 | 65.2 | 0.32 | 0.8 | 9.3 | 1.4 |
| 20–30 | | 0.79 | 5.7 | 0.44 | 0.7 | 1.1 | 62.5 | 0.16 | 1.0 | 7.1 | 1.3 |
| 30–40 | Bsh | 0.72 | 5.7 | 0.34 | 0.3 | 0.6 | 47.0 | 0.19 | 0.9 | 5.8 | 1.5 |
| 40–50 | Bs | 0.47 | 5.8 | 0.19 | 0.3 | 0.5 | 60.8 | 0.11 | 1.0 | 6.1 | 4.3 |
| 60–70 | | 0.26 | 6.0 | 0.10 | 0.3 | 0.4 | 75.6 | 0.03 | 1.9 | 8.8 | 7.7 |
| 75> | BC | 0.21 | 6.5 | 0.07 | 0.3 | 0.4 | 80.5 | 0.03 | 2.4 | 9.3 | 6.1 |
| 40yrs pine stand soil profile | | | | | | | | | | | |
| 0–2 (3) | Ah | 3.24 | 4.1 | 3.00 | 0.4 | 3.4 | 10.8 | 1.23 | 1.3 | 13.1 | 2.6 |
| 2–7 | A | 1.19 | 4.9 | 1.02 | 0.4 | 1.8 | 26.3 | 0.33 | 3.1 | 7.1 | 2.5 |
| 10–18 | | 1.00 | 5.0 | 0.82 | 0.4 | 1.2 | 30.6 | 0.27 | 1.0 | 7.1 | 1.2 |
| 20–25 (30) | AE | 0.77 | 5.0 | 0.68 | 0.2 | 0.9 | 22.8 | 0.15 | 0.9 | 7.6 | 2.3 |
| 30–40 | EBh | 0.87 | 4.6 | 0.77 | 0.2 | 1.0 | 20.5 | 0.17 | 0.4 | 4.7 | 3.1 |
| 40–50 (55) | Bh | 0.72 | 4.8 | 0.53 | 0.2 | 0.7 | 27.3 | 0.12 | 0.4 | 6.2 | 5.2 |
| 50–65 | | 0.62 | 4.8 | 0.34 | 0.2 | 0.5 | 37.2 | 0.11 | 2.3 | 6.9 | 4.2 |
| 65–100 | Bs | 0.32 | 6.0 | 0.19 | 0.3 | 0.5 | 60.8 | 0.04 | 2.3 | 7.1 | 1.5 |
| 100> | BC | 0.22 | 5.9 | 0.07 | 0.3 | 0.4 | 80.5 | 0.03 | 2.8 | 6.7 | 5.6 |

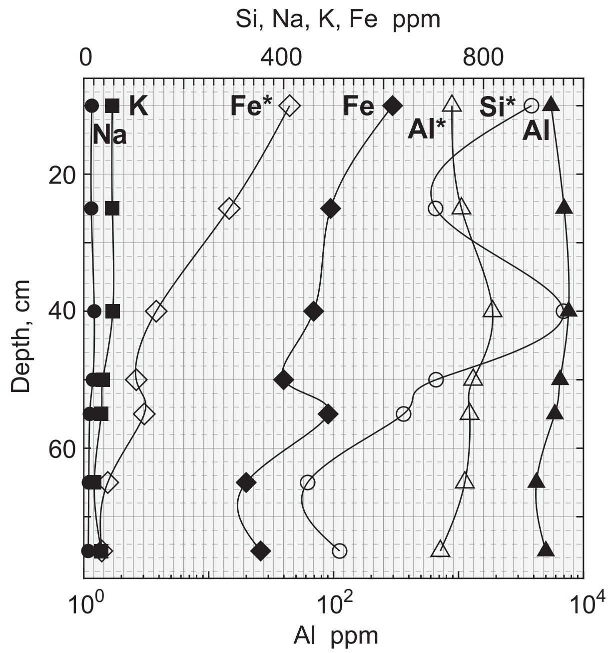


**Fig. 4.** Distribution of Na, K, Fe, Si, Al in the 10yrs pine stand soil profile (*P. sylvestris*, natural overgrowth)

**Рис. 4.** Na, K, Fe, Si, Al у ґрунтовому профілі 10-річного угруповання сосни (*P. sylvestris*, природне заростання)

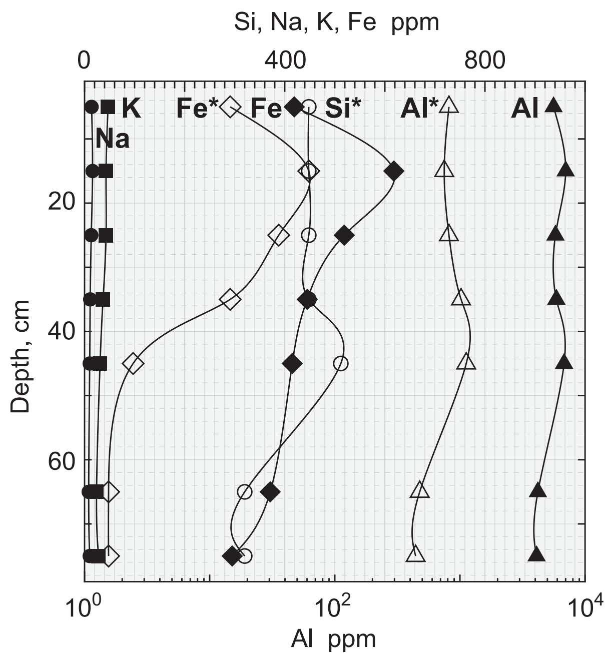


**Fig. 5.** Distribution of Na, K, Fe, Si, Al in the 20yrs pine stand soil profile (*P. sylvestris*, natural overgrowth)

**Рис. 5.** Na, K, Fe, Si, Al у ґрунтовому профілі 20-річного угруповання сосни (*P. sylvestris*, природне заростання)

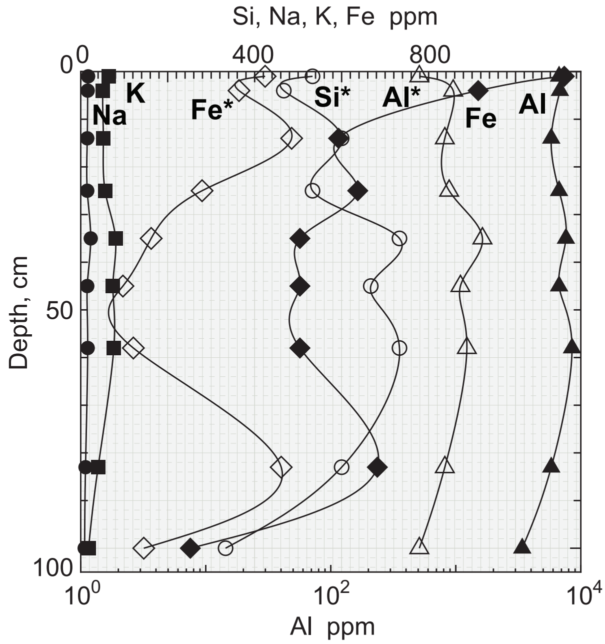


**Fig. 6.** Distribution of Na, K, Fe, Si, Al in the 40yrs pine stand soil profile (*P. sylvestris*)

**Рис. 6.** Na, K, Fe, Si, Al у ґрунтовому профілі 40-річного угруповання сосни (*P. sylvestris*, штучне насадження)

Unlike the previous two stands of the chronosequence, soil profile of the 40yrs pine had signs of podzol. As in the case of grassland, LOI, $pH_{H_2O}$, HA, BS, CEC (**Table**), K, Na, Si, Al, Fe had their extremums in the middle part of the soil profile (**Fig. 6**) indicating to some initial stage of podzolization.

## DISCUSSION

The podzolization process comprises reactions and processes involved in the formation of a podzol B or a spodic horizon and the removal of sesquioxides and organic carbon from overlying layers. It involves the translocation of organic compounds, aluminum and iron. The mechanisms of podzolization account for the release, mobilization, migration and immobilization of these materials.

Three major theories of podzolization are proposed: (I) the classic theory of podzolization [25], (II) the inorganic colloidal sol theory [1] and (III) the low molecular weight acids theory [21]. According to the classic theory, aluminium and iron move downward from the upper soil horizons as part of chelated organo-metallic complexes. Organic acids, which are mainly formed by means of decomposition of litter, produce chelate with Al and Fe ions released through weathering of the primary minerals to form soluble organo-metallic complexes. When moving, these complexes become saturated with metals to cause albic horizon creation; saturated Al and Fe organic complexes start to precipitate forming the spodic horizon.

According to the allophane theory, Al, Fe and Si, brought into solution by noncomplexing organic and inorganic acids, or by readily biodegradable small complexing organic acids, move downwards as inorganic positively charged colloidal sols, where they precipitate as amorphous iron oxides ($Fe_2O_3$), allophane ($(Al_2O_3)(SiO_2)_{1.3}\cdot 2.5(H_2O)$) and imogolite ($Al_2SiO_3(OH)_4$) due to an increase in pH (no precipitation in E horizon because of the low pH). After this, organic matter would precipitate on that imogolite-type-material leading to the appearance of a morphologically distinct Bh horizon.

The low molecular weight organic acid (LMW) theory postulates that LMW acids are responsible for the immobilization and transport of iron and aluminium to the subsoil. Precipitation of Fe and Al is caused by microbial breakdown of their complexes with LMW to induce a secondary enrichment in the B horizon.

None of these theories alone can satisfactorily explain the distribution of inorganic and organic components observed in the studied soil profiles. We suggest the existence of different mechanisms that lead to podzolization in the grassland ecosystem and the pine stands soil profiles.

The most noticeable morphological changes in the soil profile during pine succession are related to the degradation of the sod layer and a simultaneous gradual accumulation of acidic coniferous litter above mineral topsoil. The crucial role of litter in the podzolization process is well known. This is the basis of the mentioned classical theory. Well differentiated and powerful enough litter horizon of the fourth soil profile of the chronosequence (40yrs pine) produces a sufficient amount of fulvic acids necessary for the differentiation of the soil profile by the podzolic type. Mechanisms of mobilization, translocation and immobilization of sesquioxides and organic matter in the framework of classical theory are thoroughly described and there is no need to dwell on this in detail. We can only assume that the implementation of the scenario of podzolization according to the classical scheme in our case began not on the basis of pure sandy substrate, but on the soil relatively rich in organic and chemical elements. Therefore, soil profiles under 10- and 20yrs pine stands can be conditionally considered as preparatory stages, when the old soil formation matrix is destroyed and signs of a new one appear. The destruction of the previous stable state is evidenced by, at first glance illogically, an increase in organic matter content and hydrolytic acidity level of the humic horizon under the 10yrs pine, compared to grassland. The increase in these indicators is a consequence of the inflow of "fresh" organic matter due to the decomposition of roots in the sod layer and a deeper degradation level of the "old" organic matter accumulated at the previous stage of chronosequence. The intensity of destructive processes increases at the next stage of grassland transformation. The soil profile under 20yrs pine is more acidic, contains much less organic matter, has a lower base cations content and base saturation level than the previous one. And finally, the 40yrs pine soil profile has obvious signs of the soil profile that are typical of virgin podzols of boreal and temperate climatic zones. Morphologically, the soil profile under 40yrs pine stand, similarly to well developed virgin podzols, has the upper poorly decomposed stratified litter horizon (L), the underlying mineral horizon with dark colour due humus compounds (A), not yet formed, but with signs of formation bleached elluvial horizon (E) from which sesquioxides are being removed and the illuvial horizon (B) with already distinct deposits of secondary organic matter in the upper subhorizon (Bh) and iron in the lower one (Bs). In general, soil formation is a long process that takes hundreds and thousands of years, but there are examples when, as in our study, the soil age at which incipient podzolization becomes visible ranges from <43 years in extremely poor sands [31].

If the critical factor in the podzolic process under pine stands of the research area is coniferous acidic litter, then what is the causal factor in the grassland ecosystem? It is known that organic acids in soil solution contributing to mineral weathering and formation of the eluvial horizon, include humic acids (HA), fulvic acids (FA) and LMW aliphatic and aromatic acids [19]. In our case, the only factor that gradually disappears when pine self-afforestation occurs is the topsoil sod layer. Despite a partial presence of the sod layer in the next stage of chronosequence (less than 10 years of overgrowth), the previous soil system that was stable over the years began to collapse. This means that the existence and functional state of the sod layer, densely permeated with living roots of herbaceous plants, is an essential precondition for the podzolic process under the grassland ecosystem. Gradual dying of roots in the sod horizon did not lead to a decrease in the content of soil organic matter; its amount in the humus horizon of 10yrs pine even increased. Thus, the podzolic process under grassland is not associated with the influx of humic and/or fulvic acids, but with the functioning and impact on the soil system of living roots and their exudates, which include LMW organic acids. We suggest that the low value of acidity in the grassland sod layer is primarily a consequence of the action of acidic exudates secreted by living roots to their surrounding environment, and vice versa, the sod layer degradation under 10yrs pine is the reason for decline of acidity due to a decrease in living roots biomass and the amount of their exudates. Therefore, it is very likely that the soil formation process in the studied grassland ecosystem develops within the LMW theory of podzolization.

However, LMW organic acids might not just be a factor of immobilization and transport of iron and aluminium to the subsoil, as postulated by a LMW theory of podzolization. These small readily biodegradable complexing organic acids can also be an intermediate link in the chain of formation of imogolite/allophane precipitates in the B horizon, according to the allophane theory of podzolization. Allophane and imogolite can be formed only in the soils with pH ($H_2O$) > 4.9, irrespective of differences in soil groups and soil horizons [11]. Thus, high pH in the topsoil may be a precondition of podzolization under the researched grassland area according to the allophane theory.

In our opinion, in the case of grassland soil, the process may also depend on another agent of soil formation, namely $CO_2$, which is universal for all types of soil, but can be especially important for soil formation process in siliceous parent materials, that are low in weatherable minerals and have a low buffering capacity. The main source of carbon dioxide in the soil are roots and soil microbiota that continuously respire and liberate significant quantities of $CO_2$. The $CO_2$, when dissolved in soil water, produces carbonic acid that is a powerful weathering factor [8, 23]. Of course, the $CO_2$ factor is present in all studied ecosystems, but it should be taken into account that the concentration of carbon dioxide in the topsoil of the grassland ecosystem has to be significantly higher than in others due to a high concentration of living roots per relatively small volume of soil. The high density of roots in the topsoil causes a much higher concentration of carbon dioxide in the humic horizon under grass vegetation than in the rest of soil profiles of chronosequence, where the sod layer is absent and pine roots spread in a much bigger volume.

The chemical weathering involving carbon dioxide can be shown as follows:

1) carbonic acid dissociation to hydrogen ion and carbonate ion following soil $CO_2$ reacts with soil water to form dissolved inorganic carbonate (mixture of $H_2O$, $CO_2$ and $H_2CO_3$)

$$\text{Soil } CO_2 + H_2O \leftrightarrow H_2CO_3^* \leftrightarrow H^+ + HCO_3^-; \quad (1)$$

2) silicate minerals hydrolysis by $H^+$ (on the example of feldspar)

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+. \quad (2)$$

As can be seen, consumption of $H^+$ by mineral dissolution leads to the release of cations into the soil solution. As weathering progresses, the cation concentration will rise and the pH of the soil solution will rise too. In our case, unusual for typical podzols relatively high pH and BS of the albic horizon in the grassland ecosystem can be largely caused by chemical weathering with $CO_2$. Probably, the contribution of chemical weathering with carbon dioxide is at least comparable with the biological weathering caused by organic acids.

Carbon dioxide can affect the soil system not only directly due to the carbonic acid, but indirectly as well. Carbon dioxide is 1.5 times heavier than air, so due to the respiration of plant roots and associated microorganisms, the $CO_2$ accumulation in the soil can reach up to 100x excess of its open-air concentration level [3]. High organic matter content in topsoil of the grass vegetation ecosystem compared to pine stands may be the result of the preservative effect of high concentration of carbon dioxide. The preservative ability of $CO_2$ results in slowing down the decomposition rate of soil organic matter and consequently the low concentration of humic and fulvic acids, which are much more geochemically aggressive than $H_2CO_3$, in the soil solution.

## CONCLUSIONS

Self-afforestation of semi-natural grassland areas with *Pinus sylvestris* L. affects physical and chemical properties of the studied soil profiles. When overgrown, the soil becomes more acidic, the soil organic carbon, base cation content and base cation saturation decreases, the leaching rate of aluminium and iron increases. Podzolic features in morphology gradually disappear and become noticeable again 40 years after the beginning of pine succession.

The study of soil development on a base-poor sandy deposits has shown that in the temperate climate zone the process of podzolization can occur by at least two known mechanisms: (I) within the classic theory of podzolization due to the influence of organic acids that are produced during litter decomposition and (II) within the low molecular weight acids and allophane theories, where metabolites secreted to the rhizosphere by roots and roots associated microbiota are mainly involved in the podzolization process.

A third mechanism, that can be important for soil profiles with a well developed topsoil sod layer and consequently high concentration of $CO_2$ due to root and microbial respiration is proposed. $CO_2$ factor could be involved in two processes which occur simultaneously: a) in situ chemical weathering by a carbonic acid weathering process, and b) an elevated $CO_2$ pressure in rhizosphere strongly reduce soil organic matter decomposition activity in view of carbon dioxide ability to inhibit the growth of fungi and bacteria. As a result, the formation of humic and fulvic acids is suppressed, and roots exudates coupled with carbonic acid become the main factors in the process of soil formation.

## COMPLIANCE WITH ETHICAL STANDARDS

**Conflict of Interest**: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

**Human Rights**: This article does not contain any studies with human subjects performed by any of the authors.

**Animal Studies:** This article does not contain any studies with animal subjects performed by any of the authors.

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## ПІДЗОЛИСТИЙ ПРОЦЕС В УМОВАХ ПРИРОДНОГО ЗАРОСТАННЯ СОСНОЮ ЛУЧНИХ РОСЛИННИХ УГРУПОВАНЬ ВОЛИНСЬКОГО ПОЛІССЯ (УКРАЇНА)

***В. Козловський***[1]*, ***Н. Романюк***[2]

[1] *Інститут екології Карпат НАН України, вул. Козельницька, 4, Львів 79026, Україна*

[2] *Львівський національний університет імені Івана Франка*
*вул. Грушевського, 4, Львів 79005, Україна*

**Кореспондуючий автор e-mail: vkozlovskyy@gmail.com*

**Обґрунтування.** Є кілька теорій для пояснення механізмів підзолистого процесу. Роль органічної речовини ґрунту у процесах вивітрювання та іммобілізації речовин в ілювіальний горизонт встановлена. Походження органічної речовини ґрунту і, відповідно, механізми її взаємодії з компонентами ґрунту є основою цих теорій. На нашу думку, ґрунти під трав'яною рослинністю з добре розвинутим дерновим горизонтом зазнають, крім іншого, суттєвого впливу $CO_2$, який стає важливим чинником процесу ґрунтотворення.

**Матеріали та методи**. Чотири локалітети *Pinus sylvestris* L. в рамках часово-просторової послідовності з угрупованнями сосни 10, 20, 40 років та природного лучного угруповання з переважанням *Poa pratensis* L. було досліджено для встановлення закономірностей підзолистого процесу на піщаних відкладеннях льодовикового походження. Визначали pH ґрунту, основну та катіонообмінну здатність ґрунту, загальний вміст органічного карбону, аморфні Fe, Si, Al та загальний вміст Al, Fe, Mn, Zn, Cd, Pb, Cu, Co, Ni, Na, K. Статистичний аналіз отриманих даних здійснювали за допомогою програми LibreOffice for Linux.

**Результати.** Під час сукцесійних змін рослинного покриву початково добре диференційований за елювіально-ілювіальним типом ґрунтовий профіль лучного угруповання поступово деградує. Добре виражені ілювіальний та елювіальний горизонти зникають, ґрунт стає кислішим, вміст органічної речовини, ємність катіонного обміну, ступінь насичення основами знижується, інтенсивність вилуговування алюмінію та заліза зростає. Ознаки вторинного опідзолення в ґрунтовому профілі знову з'являються вже через 40 років після початку заліснення. Підзолис-

тий процес не є достатньо інтенсивним, щоб за такий короткий період розвинулись повноцінні підзолистий та ілювіальний діагностичні горизонти.

**Висновки**. Базуючись на отриманих морфологічних особливостях ґрунтових розрізів, фізико-хімічних властивостях досліджених ґрунтів, три чинники ґрунтотворення запропоновано як основні для досліджуваних екосистем. Головним чинником для ґрунтів соснових угруповань є фульвокислоти кислої хвойної підстилки. Низькомолекулярні органічні кислоти і вуглекислий газ, що продукуються у ризосферу коренями й асоційованою мікробіотою дернового горизонту, є основними чинниками підзолистого процесу в лучних рослинних угрупованнях.

***Ключові слова***: дерново-підзолисті ґрунти, сильватизація, вуглекислий газ

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