Humus stock degradation and its impact on phosphorus forms in arable soils – a case of the Ukrainian Forest-Steppe Zone

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ABSTRACT

Soil humus degradation strengthens nutrient mining, especially phosphorus. This study was carried out on the Ukrainian Forest-Steppe Zone (UFSZ). A total of 21 soil profiles have been investigated: 11 Phaeozems, 6 Luvisols, and 4 Chernozems. Soils were tested for particle size distribution, calcium carbonate (CC), pH, and organic carbon (C<sub>org</sub>). The evaluation of humus degradation as a reason of P depletion was performed based on indicators such as Humus Stock Gap (HSG), Humus Stability Index (S), and Yield Gap/Gain (YG/G). In order to evaluate the degree of P depletion, total phosphorus (P<sub>tot</sub>) and its five fractions: water soluble – P<sub>W</sub>, exchangeable – P<sub>EX</sub> and P<sub>H2O</sub>, bound to Fe and Al – P<sub>Fe/Al</sub>, bound to Ca – P<sub>Ca</sub>, and residual P – Pres, have been determined. Data revealed that in 14 of 21 investigated soils, S indices were below the threshold its value of nine, considered as the balanced content of humus with respect to soil texture. Next, in 11 of 21 cases, the negative humus balance indicates the yield gap in Phaeozems and Chernozems. The first three P pools (P<sub>W</sub>, P<sub>EX</sub> and P<sub>H2O</sub>) in Phaeozems were exhausted, constituting less than 10% of the P<sub>tot</sub>. In Phaeozems, P<sub>Fe/Al</sub> in Luvisols, P<sub>Ca</sub> and in Chernozems, P<sub>Fe/Al</sub> and P<sub>Ca</sub> fractions were basic indicators of available P status. Their pools were directly or indirectly controlled by PCA. Humus content in Phaeozems and Chernozems revealed as the key factor impacting both total P and/or its available resources. Amelioration of P depletion requires efforts oriented on restoration of soil humus stock, concomitant with P fertilization.

Introduction

The sustainable development of the Earth is a challenge of the overriding importance for the current world population. In general, this concept relies on a sound management of non-renewable resources to take into account food security and environment protection as the main objectives of the world economy. Agriculture, its sustainability and social viability of farms, and particularly the preservation of soil quality [1] occupies the leading role. Soil organic matter is the core of soil fertility, a factor decisive for water and nutrient supply to growing plants, including crops. It is well recognized, that any change in land use from natural to arable may lead to a drastic decrease in the humus content. Wander and Drinkwater [2] pointed out five reasons of soil degradation: (i) unbalanced input of fresh organic matter, (ii) input of plant residues poor in nitrogen, (iii) negative balance of nutrients, (iv) excessive tillage, (v) monoculture. The decline in humus content is concomitant with the disturbance in nutrient supply to plants, leading in turn to yield depression [3]. The causal relationship between humus degradation and phosphorus (P) depletion is a consequence of its multifunctional effects on soil/plant relationships. Negassa and Leinweber [4] clearly stated that even a medium period (10–25 years) of arable soil cultivation without P fertilizer leads to strong depletion of its available resources. Humus and nutrient losses were assessed as the major factors (43%) responsible for the degradation of soil fertility in Ukraine [5]. As reported by Wu et al. [6], the annual loss of organic carbon (OC) from a calcareous soil developed from loess (Calcic Kastanozems, FAO; the Loess Plateau, China) over 42 years of cultivation ranged from 0.96 to 1.06 t ha<sup>-1</sup>. According to these Authors, the native level of OC content can be restored provided the application of manure or straw in combination with nitrogen and phosphorus.

There are numerous indicators used for evaluating the quality and functions of arable soils. Irrespective of the soil group, the most important indicator of soil fertility is humus content, both in the topsoil and in...
the whole soil profile [7–9]. The concept of the humus critical level in arable soils is widely discussed with the impact of soil organic matter on physical stability of soil aggregates as the key issue. The critical organic carbon content for stability of soil structure has been fixed for soils in temperate regions of the World at the level of 2% [8]. In Ukraine, the OC of 3.5% is considered as the level required for the proper growth and yielding of crop plants [5]. It is well-recognized, that the amount and resistance of soil humus to degradation processes is a function of soil texture [10,11]. Pierri [12] developed an algorithm, relating soil aggregate’s stability to a relationship between the content of clay + silt and humus. The index, termed as the Humus Stability Index (S) is used to determine the current status of the soil structure [13].

Ukraine is worldwide recognized as a country of huge potential of food productivity. The reason for this optimistic statement is the soil cover. This is generally true, because the yield potential of wheat, as the dominant crop in this country is about 8.5 t ha⁻¹ [14]. The actual productivity of soils in Ukraine is much lower [15,16]. Two groups of factors are responsible for this state. The first group relates to the soil cover, assuming a high internal fertility strictly controlled by organic matter [5]. Chernozems cover about 72% of the country [17]. The second group of factors refers to the management of crop production. The yields of winter wheat in the Northern Forest-Steppe Zone of Ukraine, without any input of mineral fertilizers should reach the level of 3.4 t ha⁻¹ (range: 3.0–3.8) [5]. Under conditions of effective fertilization, the yield should increase up to 4.5 t ha⁻¹ (3.0–6.0). Within the period 2004–2013, the real yields reached on average, 3.0 t ha⁻¹. As a result of a deep economic shock at the end of the XX century, the consumption of fertilizers decreased 8-times (from 4.2 mln t in 1990 to 0.518 mln t in 2004). Consequently, yields of the main crops decreased by 50% [16]. The progress in the restoration of soil productivity is very slow. The reason is a low and imbalanced use of applied fertilizers, based mainly on N. The amount of consumed N, P₂O₅, and K₂O in 2006 were 14.0, 5.1, 4.5 kg ha⁻¹, but changed to 27.8, 5.8, 6.6 kg ha⁻¹, in 2012 respectively [15]. These data clearly indicate nutrient management oriented on mining of natural resources [18,19]. As a consequence, Ukraine is currently considered as a country seriously threatened with phosphorus depletion [20].

The current study outlines the impact of humus degradation initiating phosphorus depletion in the Ukrainian Forest-Steppe Zone. The specific aims rely on the evaluation of (i) organic matter resources, (ii) phosphorus distribution among its fractions in the upper soil horizons and (iii) potential phosphorus depletion.

Materials and methods

Study area

The studies on the impact of humus degradation inducing phosphorus depletion were carried out in September 2012 on typical soil groups of the Ukrainian Forest-Steppe Zone (UFSZ). The soil cover of this part of Ukraine originates from loess of loamy texture deposited on eluvium carbonate bedrock [21]. Soil sampling was performed in three counties of the Lviv Region. The first, Radekhiv (50°15′N, 24°32′E) is located 20 km north-east of Lviv. A total of 13 soil profiles have been investigated: Phaeozems (8), Luvisols (4), and Chernozems (1). The second study area, Brody (50°04′N, 25°09′E) is located 20 km north-east of Lviv, where five soil profiles, Phaeozems (3) and Luvisols (2) have been sampled. The third site, Sokal (50°29′N, 24°17′E) is situated 40 km north of Lviv. Three (3) soil profiles representing typical Chernozems were considered in this site.

The climate of the study area is defined as temperate cool with an average monthly temperature of 8.3 °C, varying from −2.5 °C (January) to + 19.4 °C (July) for the period 1990–2010 (station at Brody). The mean annual precipitation for the same period was 740 mm. Climatic conditions are suitable for intensive crop production, mainly with winter wheat, oilseed rape and sugar beets. Soil samples were collected in 2012 from fields sown with sugar beets. Wheat preceding sugar beets was fertilized only with nitrogen in the rate ranged from 68 to 85 kg ha⁻¹. For sugar beet, the following rates of basic fertilizer were applied in autumn 2011: 240 kg ha⁻¹ of K₂O as muriate of potash; 52 kg P₂O₅ as ammonium phosphate. Nitrogen was applied in spring 2012 in the rate of 79 kg ha⁻¹ of N as ammonium saltpeter (68 kg) and ammonium phosphate (11 kg).

Soil sampling and basic analysis

The collected soil samples were stored in dark-colored polythene bags and transported to the laboratory, where they were air-dried and passed through a 2 mm sieve. Particle-size distribution was determined by the hydrometer method. Soil groups and sub-units were evaluated according to the IUSS Working Group WRB [22]. The pH was determined in 1 mol KCl dm⁻³ and water at 1:5 (m/v) soil-to-solution ratio [23]. The analysis of organic carbon (C₉₀) and total nitrogen (N₉₀) was performed in Vario Max Elementar, after decalcination with phosphoric acid. Calcium carbonate (CC) content was measured by the Scheibler method. For total phosphorus (P₉₀), soil samples were first dry mineralized at 550 °C and next digested in concentrated HCl. Available phosphorus (P₉₋₅) was extracted by the calcium-acetate-lactate (CAL) solution of pH 4.1 according to the method suggested by Shüller [24]. Phosphorus concentration in extracts was
measured by the ammonium molybdate-ascorbic acid method [25].

**Sequential extraction of phosphorus**

Phosphorus fractions were determined in soil samples collected from the genetic layers of all soil profiles. The sequential fractionation procedure was performed according to the method by Hedley et al. [26], which differentiates five P fractions namely: (1) water soluble - $P_{H_2O}$, (2) exchangeable - $P_\mathrm{ex}$, (3) bound to Fe and Al - $P_{Al/Fe}$, (4) bound to Ca - $P_{Ca}$, and (5) residual - $P_{res}$. The extraction procedure involved the use of 2.0 grams of soil extracted for 16 h with respective chemical tests. In the first step for $P_{H_2O}$, the soil sample was weighted into a 100 mL centrifuge tube and 40 cm³ of deionised water was added. For the second step, the remaining soil residue was treated with 40 cm³ of 1.0 mol NaOH dm⁻³ for extracting P fixed by aluminum and/or iron. The $P_{Ca}$ was assessed in the fourth step, where the soil residue was treated with 40 cm³ of 1.0 mol HCl dm⁻³. The residue of this P fraction was first digested (5 cm³ H₂SO₄ and H₂O₂) and then extracted with 10 cm³ of concentrated HCl dm⁻³. The mixture was further made to 100 cm⁻³. At each step, the supernatant was recovered by centrifugation and P concentrations in all collected supernatants were measured by the colorimetric ascorbic acid method [25].

**Indices of soil degradation**

The index expressed as soil Humus Stability Index (S) has been calculated on the basis of the formula developed by Piéri [12]:

$$ S = \frac{H}{(Si + C)} \cdot 100 $$

where, $S$ – soil Humus Stability Index, $H$ – humus content (%), Si and C denote silt and clay content (%) respectively. The four classes of soil sensitivity to degradation with respect to the humus content are as follows:

1. $S < 5$ – structurally degraded soil;
2. $5 < S < 7$ – a great risk of soil structure degradation;
3. $7 < S < 9$ – a small risk of soil structure degradation;
4. $S > 9$ – no risk of soil structure degradation.

The last class informs that the humus content in a particular soil is at the optimal level to protect the stability of soil structure.

The Humus Stock Gap has been calculated by using data included in Table 1 according to Batjes [27]; Table 1: Phaeozems – 8.4 kg m⁻²; Luvisols – 5.0 kg m⁻²; Chernozems – 9.0 kg m⁻². The yield gap/gain (YG/G) has been calculated according to the equation:

$$ YG/G = HSG \cdot 15.6 $$

where, SHS$_{SD}$ – Standardized Humus Stock, t ha⁻¹; HS$_A$ – Actual Humus Stock, t ha⁻¹; HSG – Humus Stock Gap, t ha⁻¹; OC – mean value of organic carbon content, kg m⁻²; 1.7 – constant recalculating OC into humus; 10 – constant recalculating kg m⁻² into t ha⁻¹.

The OC data for SHS$_{SD}$ calculation were as reported by Batjes [27]; Table 1: Phaeozems – 8.4 kg m⁻²; Luvisols – 5.0 kg m⁻²; Chernozems – 9.0 kg m⁻².

**Statistical analysis**

Data on parameters of humus degradation as well as of phosphorus fractions and depletion were subjected to the conventional statistical analysis using STATISTICA program v. 10. The simple and stepwise regression was applied for defining the optimal set of variables for a soil characteristic. Best regression models were selected on the basis of the highest F-value for the entire model and significance of all independent variables.

**Results and discussion**

**General characteristics of main soil types**

The investigated soils showed a marked variability of physical as well as chemical characteristics, both between and within each group. Data reported in Table 1 implicitly underlined significant difference of soil properties, with CaCO₃ as the basic discriminator. Its content in Phaeozems, except the profile No. 5, increased progressively with depth. In 4 of 11 soil profiles of the Ap horizon, CaCO₃ mean values varied from 2 to 53%, but in the second genetic horizon, its content ranged from 11 to 72% (Table 1a). No free CaCO₃ was detected in three upper horizons of Luvisols, but the C horizons were very rich as recorded in three of six soil profiles (Table 1b). Chernozems were poor in carbonates, however, their content increased significantly in the C horizon, even above 10% (Table 1c). In spite of the observed differences, the CC distribution pattern in the studied soil profiles was very similar, indicating much stronger sensitivity of Luvisols and Chernozems bedrock to leaching.

It is important to stress, that the soil texture of all investigated profiles, except one, was dominated by silt. The first two soil groups coexist, irrespective of field location (Brody, Radekhiv). The typical attribute of Luvisols compared to Phaeozems was the wider sand to clay ratio and a frequent increase of CaCO₃ content in deeper soil horizons. As a rule, a distinct difference was observed between Ap and C horizons. This phenomenon is generally explained by the fact, that glacial and post-glacial
Table 1. Location, Soil Classification and physical and chemical properties of investigated soil profiles.

| No profile | Coordinates | Soil Horizon | Sampling Depth (cm) | Soil order (WRB, 2015) | Sand 2.0–0.05 | Silt 0.05–0.002 | Clay <0.002 | C_{org} | N_{tot} | HSG | YG/YG | pH_{H2O} | pH_{KCl} | CaCO3 % | Carbon and nitrogen t ha\(^{-1}\) kg ha\(^{-1}\) | Soil reaction and CaCO3 % |
|------------|-------------|--------------|---------------------|------------------------|---------------|----------------|-------------|---------|---------|------|-------|----------|----------|---------|-------------------------------------------------|--------------------------|
| 1          | 50° 19' 28.2" | Ap           | 0–32                | Chernic Rendzic Phaeozem (Epiloamtic, Katolalyc, Aric, Katoletic) | 19            | 48             | 33          | 2.05    | 0.169   | -3.57 ± 0.46 | -56 ± 7.1 | 8.21 | 7.61 | 43.03 |
|            | 24° 54' 5.90" | C             | <32                 |                        | 8             | 51             | 41          | <0.01   | <0.001  | 8.56 | 8.18  | 71.72 |
| 2          | 50° 19' 27.7" | Ap           | 0–30                | Chernic Rendzic Phaeozem (Epiloamtic, Katolalyc, Aric, Katoletic) | 21            | 45             | 34          | 3.92    | 0.278   | 89.3 ± 6.93 | 1392 ± 108 | 8.35 | 8.58 | 22.59 |
|            | 24° 54' 19.5" | C             | <30                 |                        | 6             | 53             | 41          | <0.01   | <0.001  | 8.62 | 8.08  | 66.34 |
| 5          | 50° 19' 28.3" | Ap           | 0–34                | Calcaric Someric Phaeozem (Episiltic, Katololamic, Aric) | 20            | 57             | 23          | 1.4     | 0.139   | -42.8 ± 3.28 | -668 ± 51  | 8.14 | 7.23 | 2.89  |
|            |              |               |                     |                        | 31            | 49             | 20          | <0.01   | <0.001  | 8.56 | 7.88  | 19.47 |
|            |              |               |                     |                        | 17            | 55             | 28          | <0.01   | <0.001  | 8.33 | 7.19  | 3.37  |

| 6          | 50° 19' 35.1" | Ap           | 0–32                | Simeric Rendzic Phaeozem (Pantoloamic, Aric, Katolalyc) | 22            | 49             | 29          | 2.11    | 0.19    | 7.85 ± 0.99 | 123 ± 15  | 8.28 | 7.59 | 33.35 |
|            |              |               | <32                 |                        | 21            | 50             | 29          | <0.01   | <0.001  | 8.5  | 7.96  | 50.71 |
| 7          | 50° 1' 29.7"  | Ap            | 0–31                | Calcaric Chernic Phaeozem (Pantoloamic, Aric, Tonguic) | 20            | 57             | 23          | 1.4     | 0.139   | -42.8 ± 3.28 | -668 ± 51  | 8.14 | 7.23 | 2.89  |
|            |              |               |                     |                        | 31            | 49             | 20          | <0.01   | <0.001  | 8.56 | 7.88  | 19.47 |
|            |              |               |                     |                        | 17            | 55             | 28          | <0.01   | <0.001  | 8.33 | 7.19  | 3.37  |

| 8          | 50° 1' 34.02" | Ap           | 0–35                | Calcaric Chernic Phaeozem (Pantoloamic, Aric, Tonguic) | 34            | 41             | 25          | 1.62    | 0.22    | -27.1 ± 3.71 | -423 ± 58  | 8.22 | 7.48 | 18.04 |
|            |              |               | <52                 |                        | 29            | 46             | 25          | 1.25    | 0.19    | 8.4  | 7.67  | 36.58 |
|            |              |               |                     |                        | 17            | 54             | 29          | <0.01   | <0.001  | 8.64 | 8.03  | 70.69 |

| 11         | 50° 2' 3.50"  | Ap            | 0–37                | Chernic Rendzic Phaeozem (Episiltic, Katolalyc, Aric, Pachic) | 23            | 59             | 18          | 1.715   | 0.161   | -20.4 ± 2.92 | -317 ± 46  | 8.16 | 7.4   | 1.51  |
|            |              |               | 37–52               |                        | 27            | 49             | 24          | 1.465   | 0.095   | 8.43 | 7.67  | 32.27 |
|            |              |               | <52                 |                        | 20            | 53             | 27          | <0.01   | <0.001  | 8.63 | 8.07  | 67.99 |

| 12         | 50° 2' 20.9"  | Ap            | 0–34                | Calcaric Chernic Phaeozem (Pantoloamic, Aric) | 53            | 32             | 15          | 2.595   | 0.25    | 42.5 ± 2.25 | 66 ± 35   | 8.19 | 7.52 | 6.64  |
|            | 24° 37' 57.2" | Ah            | 34–51               |                        | 41            | 37             | 22          | 1.895   | 0.111   | 8.41 | 7.88  | 34.83 |
|            |              |               | <51                 |                        | 20            | 51             | 29          | <0.01   | <0.001  | 8.65 | 8.15  | 59.38 |
| Coordinates | Soil order | Soil texture (fractions mm) | Carbon and nitrogen | HSG | YG/YG | Soil reaction and CaCO3 |
|-------------|------------|----------------------------|---------------------|-----|-------|------------------------|
| 0.05–0.002  | WGS 84, t ha−1 kg ha−1 | pH | pHKCl | H2O | ± | ± |
| 31–52       | 7.830 | 50.8 | 22 | 49 | 29 | 2.11 | 0.19 | 7.85 | ± | 0.99 | 123 | ± | 15 | 8.28 | 7.59 | 33.35 |
| 0–34 | Someric Rendzic phaeozem | pantosiltic, aric, pachic) | 10 | 58 | 32 | <0.01 | <0.001 | 7.62 | 7.51 | 56.7 |
| 40° 36′ | 24° 37′ 36.6″ | C | 19 | 7 | <0.01 | <0.001 | 5.90 | 8.50 | 66.34 |
| 24° 37′ 36.6″ | Chemical Rendzic phaeozem (Pantoloamic, Aric, Pachic) | 48 | 35 | 17 | 4.15 | 0.375 | 153.5 | ± | 29.4 | 2395 | ± | 458 | 8.1 | 7.47 | 4.41 |
| 24° 37′ 36.6″ | Chemic Rendzic phaeozem (Pantoloamic, Aric, Pachic) | 45 | 34 | 21 | 1.125 | 0.095 | 8.32 | 7.58 | 10.65 |
| 24° 37′ 56.4″ | C | <90 | 10 | 58 | 32 | <0.01 | <0.001 | 8.56 | 8.03 | 70.14 |
| 50° 22′ 31.6″ | Ap <35 | Skeletal Chernic Rendzic phaeozem (Pantoloamic, Aric, Endodemic) | 13 | 56 | 31 | 3.625 | 0.263 | 748 | ± | 193 | 1166 | ± | 30 | 8.21 | 7.62 | 53.79 |
| 24° 37′ 35.5″ | C | <35 | 13 | 56 | 31 | 3.625 | 0.263 | 748 | ± | 193 | 1166 | ± | 30 | 8.21 | 7.62 | 53.79 |
| 0–35 | Lamellic Abruptic Luvisol (Loamic, Aric, Ochric) | 60 | 37 | 3 | 0.922 | 0.089 | −19.2 | ± | 2.92 | −299 | ± | 46 | 6.8 | 6.4 | 2.8 |
| 24° 54′ 1.5″ | Bt | 31–42 | 70 | 23 | 7 | <0.01 | <0.001 | 7.24 | 6.03 | <1 |
| 0–30 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 23 | 63 | 14 | 1.296 | 0.129 | 7.46 | ± | 0.47 | 116 | ± | 7.4 | 7.77 | 7.13 | <1 |
| 24° 37′ 32.5″ | Bt | 26–80 | 25 | 50 | 25 | <0.01 | <0.001 | 7.81 | 6.53 | <1 |
| 24° 37′ 32.5″ | Ap | 0–25 | 31 | 54 | 15 | 1.52 | 0.138 | 23.5 | ± | 3.35 | 367 | ± | 52 | 7.87 | 7.13 | <1 |
| 0–27 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 36 | 46 | 18 | <0.01 | <0.001 | 7.81 | 6.75 | <1 |
| 24° 54′ 1.5″ | Bt | 48–70 | 23 | 51 | 26 | <0.01 | <0.001 | 7.88 | 6.73 | <1 |
| 24° 37′ 32.5″ | Ap | 0–25 | 33 | 50 | 17 | <0.01 | <0.001 | 8.58 | 7.73 | 10.57 |
| 0–31 | Haplic Chernozem (Aric, Cutanic, Ochric) | 24 | 57 | 19 | 0.965 | 0.107 | −16.1 | ± | 2.61 | −251 | ± | 41 | 6.97 | 6.13 | <1 |
| 0–35 | Haplic Chernozem (Aric, Cutanic, Ochric) | 13 | 59 | 28 | <0.01 | <0.001 | 6.7 | 5.32 | <1 |
| 24° 37′ 36.6″ | C | <50 | 12 | 72 | 16 | <0.01 | <0.001 | 7.63 | 6.87 | <1 |
| 50° 18′ 57.0″ | Ap | 0–31 | Lamellic Abruptic Luvisol (Loamic, Aric, Ochric) | 60 | 37 | 3 | 0.922 | 0.089 | −19.2 | ± | 2.92 | −299 | ± | 46 | 6.8 | 6.4 | 2.8 |
| 24° 54′ 1.5″ | Et | 31–42 | 70 | 23 | 7 | <0.01 | <0.001 | 7.24 | 6.03 | <1 |
| 24° 54′ 1.5″ | Bt | 31–42 | 70 | 23 | 7 | <0.01 | <0.001 | 7.24 | 6.03 | <1 |
| 24° 54′ 1.5″ | C | <64 | 27 | 51 | 22 | <0.01 | <0.001 | 6.24 | 4.26 | <1 |
| 30–60 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 23 | 63 | 14 | 1.296 | 0.129 | 7.46 | ± | 0.47 | 116 | ± | 7.4 | 7.77 | 7.13 | <1 |
| 0–30 | Lamellic Luvisol (Arenic, Aric, Ochric) | 81 | 14 | 9 | <0.01 | <0.001 | 5.13 | 4.34 | <1 |
| 0–30 | Lamellic Luvisol (Arenic, Aric, Ochric) | 81 | 14 | 9 | <0.01 | <0.001 | 5.13 | 4.34 | <1 |
| 30–60 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 23 | 63 | 14 | 1.296 | 0.129 | 7.46 | ± | 0.47 | 116 | ± | 7.4 | 7.77 | 7.13 | <1 |
| 24° 37′ 32.5″ | Bt | 26–80 | 22 | 50 | 28 | <0.01 | <0.001 | 7.73 | 6.55 | <1 |
| 0–25 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 36 | 46 | 18 | <0.01 | <0.001 | 7.81 | 6.75 | <1 |
| 24° 37′ 32.5″ | Bt | 48–70 | 23 | 51 | 26 | <0.01 | <0.001 | 7.88 | 6.73 | <1 |
| 0–25 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 33 | 50 | 17 | <0.01 | <0.001 | 8.58 | 7.73 | 10.57 |
| 0–25 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 33 | 50 | 17 | <0.01 | <0.001 | 8.58 | 7.73 | 10.57 |
| 0–25 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 33 | 50 | 17 | <0.01 | <0.001 | 8.58 | 7.73 | 10.57 |
| 0–25 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 33 | 50 | 17 | <0.01 | <0.001 | 8.58 | 7.73 | 10.57 |
| 0–25 | Endocalcaric Luvisol (Anosolitic, Endodemic, Aric, Ochric, Raptic) | 33 | 50 | 17 | <0.01 | <0.001 | 8.58 | 7.73 | 10.57 |

**Notes:** HSG – Humus Stock Gap; YG/YG – yield gap/yield gain.
air-transported particles, i.e. loess were deposited in the Eastern Europe on different Pre-Quaternary bedrocks such as Upper Jurassic black shale rich in calcium carbonate and Lower Cretaceous glauconite sandstone [28]. The bedrock of Phaeozems in the Western Ukraine is composed of weathering products of Upper Baden limestone, Cretaceous marl and marl [21]. In addition, variable climatic conditions during the Upper Pleistocene and Holocene resulted in a high heterogeneity of plant cover dominated by trees or grasses. The distinctive impact of interactions of soil bedrock with plants on the properties of soils resulted in a great variability of soil cover of the north zone of loess deposition in Eastern Europe [29,30].

This study indirectly supports the opinion by Kyrylchuk [21], who assumed a continuous loess cover in the permafrost zone during the Last Glacial Period. In the northern part of the European loess belt, its thin deposits on bedrocks of different mineralogical composition were subjected to a strong impact of leachates formed under forest and/or steppe plant cover during the Late-Pleistocene and Holocene [31]. This process was probably the key factor influencing the rate of CC dissolution and clay leaching, resulting in distinctive soil group formation in the Ukrainian Forest-Steppe Zone, such as Phaeozems and Luvisols. This hypothesis has been corroborated by the observed differences among the CC distribution patterns in the studied soil profiles.

**Indicators of soil degradation**

**Organic matter**

For the current study, two criteria for evaluating humus status in soils of the UFSZ have been applied. The first one relies on the Piéri [12] equation, describing the quantitative condition of humus status in soils based on silt and clay contents. Data reported in the Figure 1 showed, that most of the investigated soils were seriously degraded. Only six soils kept a good physical and geochemical status as indicated by the humus content. The values of stability indices were in these cases above the threshold S index of 9.0. This index value indicates that the humus content is well balanced with texture of a particular soil to protect the stability of soil structure [13]. In this group, four profiles represented Phaeozems and two Luvisols. The class of slight humus degradation (B class, for 7 < S < 9) has been represented by one soil belonging to Phaeozems. A high degree of soil degradation (C class for S < 5) was detected for six soil profiles, but soil physical degradation (D class for S < 5) was documented for Phaeozems (3), Luvisols (2), and Chernozems (3).

The second criterion used in the evaluation of soil’s horizon stability was Humus Stock Gap (HSG). It was calculated on the basis of actual (directly measured) and the Standardized Humus Stock (SHS_{soil}), which was assumed as the average humus content in the 0.30 m soil layer in a particular soil type. Based on Batjes [27], in Phaeozems the SHS_{soil} has been assessed at 142 800 kg ha⁻¹. The calculations showed that 4 of 11 soils were below this standard (Table 1a). In Luvisols, the SHS in the topsoil amounted to 85 000 kg ha⁻¹. Three of six soils were below the threshold level (Table 1b). In Chernozems, the SHS was 153 000 kg ha⁻¹. All studied soils were below this level (Table 1c). The HSG allows evaluating the extent in the loss of soil productivity and can be recalculated into the yield gap (YG) as proposed by Bauer and Black [3]. Following this concept, the data sets were reconverted into the equivalent of grain yield of spring wheat and next regressed against the values of S index.

The order of each soil group on the YG/G index was specific, as presented below:

\[
\text{Luvisols}(R^2 = 0.06) < \text{Rendzic Phaeozems}(R^2 = 0.82) < \text{Chernozems}(R^2 = 0.95)
\]

(5)

This order indicates a significant sensitivity of Chernozems and Phaeozems, but not Luvisols productivity to soil organic matter instability. The reliability of the S index as yield predicator increases significantly, when Luvisols are excluded from the model:

\[
\text{YG/G} = 0.39S + 4.97, \text{ for } n = 15, R^2 = 0.86 \text{ and } P \leq 0.001
\]

(6)

The reported facts clearly explain the reasons of the low productivity of main crops cultivated in the UFSZ. The real yields are at the level typical for non-fertilized soils [5,15]. In the investigated area, the HSG was at the level of 35% for Phaeozems and increased up to 64% in Luvisols and Chernozems. The presented set of data is much more pessimistic as compared with other studies concerning humus losses in typical Chernozems in Ukraine. As reported by Smith et al. [19], the average humus losses during the period 1881–2000 were in the range of 17–32%. The key agronomic way of soil fertility restoration is to plough down straw with mineral nitrogen and phosphorus fertilizers or to apply manure as documented by Wu et al. [6], who studied ways of optimizing organic matter management in soils of the Loess Plateau of China.

**Status of available P in soils**

The degree of available phosphorus (P_{CAL}) depletion was very high, irrespective of the soil type as compared to the required optimum of 170–200 mg P kg⁻¹ [5]. Phaeozems were extremely poor in P_{CAL} (Table 2a). On average, these soils showed the lowest P_{CAL} content within the studied profiles. In the majority of soil profiles, the available P content decreased along the soil profile. In the Ap horizon, it ranged from 9 to 63 mg kg⁻¹, whereas in the second genetic horizon from 5 to 35 mg kg⁻¹. The ratio between its content in the reported soil horizons was as...
variability in the P Cal content can be explained by soil group, taking into account only the Ap horizon. No significant impact of soil textural class on PCAL in Luvisols was observed. In the case of Phaeozems, the content of PCAL was significantly and negatively dependent on clay and calcium carbonate contents as well as pH. The applied stepwise regression revealed that soil pH exerted alone a significant impact on PCAL. However, the real control of phosphorus availability was due to the effect of factors such as clay (C), organic carbon (Corg), total nitrogen content (Ntot), and pH:

$$P_{Cal} = -121.2pH_{KCL} + 936.2, \text{ for } n = 11, R^2 = 0.55$$

3:1. The vertical pattern of P Cal content in Luvisols was typical for this soil type, i.e. decreasing with soil depth (Table 2b). The Ap layer of Luvisols was much richer in P, ranging from 41 to 96 mg kg\(^{-1}\). In the second horizon, it ranged from 26 to 63 mg kg\(^{-1}\). The ratio in the upper consecutive horizons of Luvisols was as 1:1.5. The P Cal content in Chernozems decreased with soil depth, with its content in the Ap layer being in the range from 23 to 100 mg kg\(^{-1}\), whereas in the second horizons from 11 to 39 mg kg\(^{-1}\). The ratio in these two layers was as 1:2.4.

In order to explain the current status of P Cal, its contents were regressed against basic soil properties, including total phosphorus. The study clearly showed, that the variability in the P Cal content can be explained by soil group, taking into account only the Ap horizon. No significant impact of soil textural class on P Cal in Luvisols was observed. In the case of Phaeozems, the content of P Cal was significantly and negatively dependent on clay and calcium carbonate contents as well as pH. The applied stepwise regression revealed that soil pH exerted alone a significant impact on P Cal. However, the real control of phosphorus availability was due to the effect of factors such as clay (C), organic carbon (Corg), total nitrogen content (Ntot), and pH:

$$P_{Cal} = -121.2pH_{KCL} + 936.2, \text{ for } n = 11, R^2 = 0.55$$

Figure 1. Diagram of soil humus degradation. Legend: A – area above the line H9 represents non-degraded soil profiles; B – area between lines H9 and H7 represents the class of low degradation; C area between line H7 and H5 represents the class of strong soil degradation; D area below the line H5 represents the class of soil physically degraded. Lines H9, H7 and H5 indicate the Humus Stability Indices with the threshold value of 9, 7 and 5, respectively.

Figure 2. Simulation of yield gap or gain of cereals as a result of humus degradation. Legend: Negative values are indicative of pronounced yield gap, whereas positive represent yield gain.
These two equations clearly indicate pH as the factor significantly impacting the current status of available phosphorus. In Chernozems, \( P_{\text{CAL}} \) responded positively to sand, but negatively to silt and clay content. In all soils, a negative impact of soil pH on \( P_{\text{CAL}} \) was observed. Its effect on P availability was significant only in Phaeozems. In these soils, pH is usually above 6.5 [32]. Consequently, free calcium carbonate particles react with phosphate ions in soil solution, resulting in the formation of:

\[
P_{\text{CAL}} = -1.79C + 28.2C_{\text{org}} - 326.2N_{\text{tot}} - 81.5pH_{\text{KCl}} + 687.8, \text{ for } n = 11, R^2 = 0.74
\]
be assumed that the elaborated two cross-line model reflects the status of total P depletion in Phaeozems. Its content on the plateau stage of 653 mg P kg\(^{-1}\) soil can consequently be considered as P\(_{\text{tot}}\) initial value. Calcium carbonate undergoes dissolution in neutral and acid pH soils, but reaching stability in alkaline soils with pH > 7.5 [32]. The pH\(_{\text{H2O}}\) of Phaeozems soils was 8.2 ± 0.1, i.e. within the typical range of calcareous soils (7.5–8.5). In the soil solution, under those conditions, dominate salts of HCO\(_3\)- and calcium carbonate [32]. The activity of phosphate ions in the soil solution depends on the activity of Ca\(^{2+}\) ions and solubility of calcium phosphate minerals. In calcareous soils, the soil solution pH is significantly correlated with Ca\(^{2+}\) activity [37]. In addition, calcium carbonate creates a surface on which calcium phosphates precipitate [38]. The analysis of Figure 4 indicates another reason of soil productivity degradation. This figure stresses on the importance of Soil Humus Stock (HSG) in the management of P\(_{\text{tot}}\) resources. A positive balance of HSG results in the progressive increase of P\(_{\text{tot}}\) content, but only for Phaeozems and Luvisols. This study implicitly corroborates the opinion expressed by Bauer and Black [3] and by Wu et al. [6], who indicated on organic matter management and P fertilizers as key factors of soil productivity maintenance, particularly P reserves.

**Status of total P in soils**

The total phosphorus (P\(_{\text{tot}}\)) content is another geochemical characteristic of phosphorus status in arable soils [20]. It showed a clearly defined stratification in most of the studied soil profiles (Table 2a). It has been found that the lower the P\(_{\text{tot}}\) content in the Ap layer, the smaller differences with depth and vice versa. This conclusion is corroborated by the P\(_{\text{tot}}\) patterns observed in the profile no. 1 and 7, for example. The vertical gradients of P\(_{\text{tot}}\) content in Luvisols were not as consistent as those recorded for Phaeozems (Table 2b). The drop of P content with depth has been observed in four of six profiles. In other two, the reverse pattern was found, indicating P exhaustion in the Ap horizon. The P\(_{\text{tot}}\) content in Chernozems was the most uniform, smoothly declining with soil depth (Table 2c). The observed differences between consecutive soil layers are less striking compared to Phaeozems.

A significant impact on the P\(_{\text{tot}}\) content was found only for calcium carbonate in Phaeozems. Its content below 8.8% resulted in an increase of P\(_{\text{tot}}\), but a further raise does not alter phosphorus accumulation (Figure 3). The level 8.8% represents the border line below which the soil P underwent degradation. Therefore, it can be assumed that the elaborated two cross-line model reflects the status of total P depletion in Phaeozems. Its content on the plateau stage of 653 mg P kg\(^{-1}\) soil can be, consequently, considered as P\(_{\text{tot}}\) initial value. Calcium carbonate undergoes dissolution in neutral and acid pH soils, but reaching stability in alkaline soils with pH > 7.5 [32]. The pH\(_{\text{H2O}}\) of Phaeozems soils was 8.2 ± 0.1, i.e. within the typical range of calcareous soils (7.5–8.5). In the soil solution, under those conditions, dominate salts of HCO\(_3\)- and calcium carbonate [32]. The activity of phosphate ions in the soil solution depends on the activity of Ca\(^{2+}\) ions and solubility of calcium phosphate minerals. In calcareous soils, the soil solution pH is significantly correlated with Ca\(^{2+}\) activity [37]. In addition, calcium carbonate creates a surface on which calcium phosphates precipitate [38]. The analysis of Figure 4 indicates another reason of soil productivity degradation. This figure stresses on the importance of Soil Humus Stock (HSG) in the management of P\(_{\text{tot}}\) resources. A positive balance of HSG results in the progressive increase of P\(_{\text{tot}}\) content, but only for Phaeozems and Luvisols. This study implicitly corroborates the opinion expressed by Bauer and Black [3] and by Wu et al. [6], who indicated on organic matter management and P fertilizers as key factors of soil productivity maintenance, particularly P reserves.

**Phosphorus pools and stratification in the soil profile**

**Phaeozems**

The distribution of P pools with soil depth was fraction-specific (Table 2a). The water-soluble P was almost equally distributed with depth in 5 of 11 studied profiles. The amounts of P\(_{\text{H2O}}\) in the Ap and Cca horizons averaged 3.4 and 3.0 mg P kg\(^{-1}\), respectively, ranging from 2.7 to 5.0 mg P kg\(^{-1}\) soil, with a share of this pool to the total P of about 1.0%. It is too low to cover crop...
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A series of soil characteristics, it should be considered as the key P pool responsible for the amount of the $P_{CAL}$. The content of total P was significantly dependent on the size of the $P_{Ca}$ as presented by the respective regression models:

$$P_{CAL} = 5.15 + 10.57P_{H2O} + 0.68P_{Al/Fe} - 0.12P_{Ca}, \quad n = 11, R^2 = 0.84$$ (9)

$$P_{Al/Fe} = 754.9 + 0.1P_{Ca} + 6.22C_{org} - 0.73C_{KCL} - 100.4pH_{KCL}, \quad n = 11, R^2 = 0.97$$ (10)

$$P_{tot} = 1.43P_{Ca} + 245, \quad n = 11, R^2 = 0.72$$ (11)

A special attention should be given to the $P_{Al/Fe}$ pool, which was significantly affected by the content of humus. There are numerous aspects of organic matter impact on P management in calcareous soils. The simplest one refers to the fact, that plant residues incorporated into soil contain phosphorus. Secondly, organic acids released during decomposition of plant residues or manure can compete with phosphate ions for free Ca$^{2+}$ ions [34,35]. Thirdly, the oxidation of organic matter is a factor leading to soil acidification. This process results in the decrease of the calcium carbonate pool [32]. Therefore, any enrichment of Phaeozems with organic matter may increase the amount of $P_{Fe/Al}$ as a crucial P source for crops during the vegetative season.

The second genetic horizon of Phaeozems is of interest with respect to a reliable assessment of phosphorus degradation in arable soils. The size of the first three fractions was negatively affected by carbon carbonate content (CC). The most important for the soil/plant systems balance is the $P_{Al/Fe}$ fraction. Its size was controlled by CC and sand (S) content.
Table 3. Correlation matrix of phosphorus fractions in Phaeozems, Ap/second horizons.

| P fractions | II | III | IV | V | \(P_{\text{cal}}\) | \(P_{\text{tot}}\) |
|-------------|----|-----|----|--|-----------------|-----------------|
| I**        | 0.35/0.81** | 0.18/0.71* | −0.09/0.32 | −0.08/0.32 | 0.61*/0.43 | −0.04/0.29 |
| II*        | 1.00 | 0.56/0.91*** | 0.57/−0.45 | 0.16/0.64* | 0.32/0.15 | 0.50/0.56 |
| III#       | 1.00 | 0.57/−0.64* | −0.27/0.47 | 0.04/0.37 | 0.70/0.32 |                |
| IV*        | 1.00 | 0.85/0.17 | −0.47/−0.25 | 0.85**/0.17 |                |                |
| V*         | 1.00 | −0.58/−0.29 | 0.78**/0.93*** |                |                |                |
| \(P_{\text{cal}}\) | 1.00 |                |                |                |                | −0.50/0.36 |

Notes: \(P_{\text{tot}}\), \(P_{\text{res}}\), \(P_{\text{Al/Fe}}\), \(P_{\text{Ca}}\), \(P_{\text{EX}}\) (more details see ‘Sequential extraction of phosphorus’).

* ** *** probability level and significance at 0.05, 0.01, 0.001.

\[
P_{\text{Al/Fe}} = −0.6CC + 43.9, \text{ for } n = 10, R^2 = 0.83, \text{ and } P ≤ 0.001
\]

\[
P_{\text{Al/Fe}} = −0.763S + 0.95, \text{ for } n = 10, R^2 = 0.67, \text{ and } P ≤ 0.001
\]

All soil characteristics, which showed a positive correlation with \(CC\), exerted a negative impact on \(P_{\text{Al/Fe}}\) pool. A negative correlation of carbon carbonate with sand content can be considered as an important characteristic of the trend of Phaeozems transformation. In calcareous soils, the activity of \(H_2SiO_3\) is both high and negatively correlated with \(pH\), in turn decreasing \(P\) fixation [37]. The exchangeable \(P\) pool (i.e. \(P_{\text{EX}}\)) is the first buffer in the sequence of processes responsible for phosphorus flows into soil solution. Data of this study showed, that \(P\) content in the \(P_{\text{EX}}\) fraction significantly depended on \(P_{\text{Al/Fe}}\) pool:

\[
P_{\text{EX}} = 0.57_{\text{Al/Fe}} + 6.63, \text{ for } n = 10, R^2 = 0.83, \text{ and } P ≤ 0.001
\]

The size of the \(P_{\text{Al/Fe}}\) pool as significantly controlled by the \(Ca\)-bound \(P\) is, therefore, decisive for covering crop plant requirements. Thereby, this \(P\) pool should be of great care by farmers.

**Luvisols**

The pattern of \(P\) content and distribution among its fractions in Luvisols was quite distinct as compared to Phaeozems (Table 2b). The distribution of \(P_{\text{H2O}}\) with depth did not show any regular pattern, but the fraction decreased with depth only in 3 of 6 profiles. The \(P_{\text{EX}}\) pool was several times larger as compared to the \(P_{\text{H2O}}\) one. The strong declining gradient was only recorded in two profiles. As a rule, the \(P_{\text{Fe/Ca}}\) fraction was larger with respect to the previous one. The majority of \(P\) on average, was recorded in the \(Ca\)-bound pool, which contributed to 50% of \(P\) total content in the Ap horizon. The difference in vertical gradients between \(P_{\text{Fe/Ca}}\) and \(P_{\text{Ca}}\) indicates the latter one as the pool critical for the \(P\) content maintenance in more labile forms. The most consistent pattern of the gradual \(P\) decrease with depth has been observed for \(P_{\text{res}}\).

The analysis of relationships between \(P\) fractions for the Ap layer decidedly showed, that the first and the second \(P\) fractions, representing its labile pools, significantly depended on the \(P_{\text{Ca}}\) (Table 4). At the same time, the \(P_{\text{Ca}}\) was influenced by the residual \(P\) pool, however, no correlations were found with the \(P_{\text{cal}}\). Total \(P\) content was influenced by each of the \(P\) pools, but significant relationships were recorded only for the Ap layer. The established relationships in the second soil horizon were much simpler compared to the Ap ones as reported for the dependence of both \(P_{\text{H2O}}\) and \(P_{\text{cal}}\) on exchangeable \(P_{\text{EX}}\):

\[
P_{\text{H2O}} = 0.37_{\text{EX}} − 4.14, \text{ for } n = 6, R^2 = 0.78, \text{ and } P ≤ 0.001
\]

\[
P_{\text{cal}} = 0.89_{\text{EX}} + 11.5, \text{ for } n = 6, R^2 = 0.70, \text{ and } P ≤ 0.01
\]

These two equations clearly inform that exchangeable \(P\) in the horizon beneath the Ap layer was the decisive pool for determining the amount of extractable \(P_{\text{cal}}\) in Luvisols.

**Chernozems**

The first three \(P\) pools and \(P_{\text{res}}\) showed an uniform pattern of vertical distribution compared to Phaeozems and Luvisols (Table 2c). All these pools showed a gradual \(P\) decline with depth (Table 5). The contribution of \(P\) in the first three \(P\) pools was 15% for the Ap and 10% for the second soil horizon. In the Ap layer, the dominant \(P\) pool was \(P_{\text{res}}\) whereas in the succeeding one \(Ca\)-bound. The differences between soil horizons were small and in two profiles, a strong depletion of \(P\) in the Ap horizon was recorded. This trend indicates again the \(P_{\text{cal}}\) pool as the crucial for maintaining its content in more labile \(P\) pools.

The content of water soluble \(P\) (\(P_{\text{H2O}}\)) in the Ap horizon was on average 5-times lower as compared to the \(P_{\text{EX}}\) and 7-times lower compared to the \(P_{\text{Al/Fe}}\) pools, respectively. At the same time, the \(P_{\text{Al/Fe}}\) pool was 5-times lower with respect to the \(P_{\text{Ca}}\) pool. Its size was significantly and positively correlated with \(pH_{\text{SCF}}\). However, only the \(P_{\text{res}}\) pool showed a significant correlation with soil characteristics responsible for organic matter transformation, such as the content of \(C_{\text{org}}\), total nitrogen, and C:N ratio. The size of the \(P_{\text{res}}\) fraction was fully dependent on \(C_{\text{org}}\):

\[
P_{\text{res}} = 0.60_{\text{Corg}} + 79.49, \text{ for } n = 4, R^2 = 0.99, \text{ and } P ≤ 0.01
\]

This equation clearly corroborates the importance of humus as the critical component for phosphorus content in the degraded Chernozems [5,6]. The content of the \(P_{\text{H2O}}\) depended closely on the \(P_{\text{EX}}\) but the latter one was...
Table 4. Correlation matrix of phosphorus fractions in Luvisols, Ap/second horizon.

| P fractions | II | III | IV | V | P_{CAL} | P_{tot} |
|-------------|----|-----|----|---|----------|---------|
| I^1         | 0.96*/*0.89* | 0.21/0.26 | 0.90/*0.30 | 0.58/−0.23 | −0.31/0.57 | 0.92*/0.61 |
| II^2        | 1.00 | 0.11/0.45 | 0.97**/0.13 | 0.75/0.14 | −0.41/0.84* | 0.98**/0.64 |
| III^3       | 1.00 | −0.06/−0.06 | −0.39/−0.29 | 0.67/*0.46 | 0.98**/0.61 |
| IV^4        | 1.00 | 0.84/*−0.81* | 0.67/−0.06 | 0.99**/*0.70 |
| V^5         | 1.00 | −0.73/0.52 | 0.81**/−0.34 |
| P_{CAL}     | 1.00 | 0.09/0.49 |

Notes: P_{CAL}, P_{H2O}, P_{EX}, P_{AlFe}, P_{Ca}, P_{Res} (more details see Sequential extraction of phosphorus). *, **, *** probability level and significance at 0.05, 0.01, 0.001.

Table 5. Correlation matrix of phosphorus fractions in Chernozems, Ap/second horizons.

| P fractions | II | III | IV | V | P_{CAL} | P_{tot} |
|-------------|----|-----|----|---|----------|---------|
| I^1         | 0.96*/0.98* | 0.61/*0.97* | 0.94*/−0.79 | 0.45/−0.69 | 0.99**/0.99 | 0.92/0.60 |
| II^2        | 1.00 | 0.81/0.99** | 0.99*/−0.69 | 0.19/−0.78 | 0.97*/0.99** | 0.85/0.58 |
| III^3       | 1.00 | 0.81/−0.66 | −0.39/−0.78 | 0.66/0.99* | 0.45/0.58 |
| IV^4        | 1.00 | 0.23/0.11 | 0.97*/−0.74 | 0.89/−0.81 |
| V^5         | 1.00 | 0.41/*−0.75 | 0.65/*0.05 |
| P_{CAL}     | 1.00 | 0.94/*0.56 |

Notes: P_{H2O}, P_{EX}, P_{AlFe}, P_{Ca}, P_{Res} (more details see Sequential extraction of phosphorus). *, **, *** probability level and significance at 0.05, 0.01, 0.001.

Conclusions

The basic attribute of soil cover of the Ukrainian Forest-Steppe Zone is the coexistence of different soil groups, which originated from loess and loess-like mineral material deposited on calcium carbonate bedrock. Humus content can be used as the essential index of soil degradation. The Humus Stability Index (S) was below the upper standard value in 14 of 21 investigated soil profiles. It indicates a saturation status of humus with respect to the content of silt and clay required for soil structure stability in a particular soil. Next, in 11 of 21 cases, the humus stock balance can be considered as the index decisive for the yield gap development, especially in Phaeozems and Chernozems. The content of available phosphorus is an important indicator of soil degradation in the Ukrainian Forest-Steppe Zone. In Phaeozems, its availability undergoes additional reduction due to high content of calcium carbonate and alkaline pH. The total phosphorus content is also a good indicator of soil degradation, being significantly affected by the PCa pool. The stepwise analysis clearly showed that the P_{CAL} was controlled by P_{H2O}: P_{CAL} = 8.08P_{H2O} − 11.46, for n = 4, R^2 = 0.99, and P ≤ 0.001 (18)

The P_{H2O} pool in the second horizon was 2 and 5-times lower as compared to its content in the Ap horizon, and in the P_{EX} pool, respectively. The latter one was in turn 2-times lower when referring to the P_{Ca} pool. It is necessary to indicate three facts, with respect to soil characteristics. First, the P_{H2O} content significantly depended on clay content (C), but negatively on soil pH. Consequently, the content of P_{CAL} showed a significant dependence on P_{H2O}: P_{H2O} = 0.79C + 12.64, for n = 4, R^2 = 0.92, and P ≤ 0.01 (19)

P_{H2O} = −3.99pH_{H2O} + 35.1, for n = 4, R^2 = 0.99, and P ≤ 0.001 (20)

P_{CAL} = −3.99P_{H2O} − 2.47, for n = 4, R^2 = 0.99, and P ≤ 0.001 (21)

It can be stated, that in Chernozems, the P_{CAL} depends in fact upon the size of the P_{H2O}. Its size in the second horizon is positively controlled by P_{EX} and P_{AlFe} pools. The levels of these three easily available P pools in this horizon are significantly reduced under conditions of high soil pH. Phosphorus resources in the Ap horizon depend on soil organic matter content. In the degraded Chernozems, P resources and its availability can be managed by simultaneous application of organic fertilizers with phosphorus [6].
interactions with both $P_{\text{H}_2\text{O}}$ and $P_{\text{CAL}}$, the $P_{\text{EX}}$ may be considered as indicator of P pool in this soil group. In the case of Chernozems, the $P_{\text{H}_2\text{O}}$ pool was significantly sensitive to soil pH, $P_{\text{CAL}}$, and clay content. Phosphorus depletion in the Ukrainian Forest-Steppe Zone can be alleviated only by decisive efforts oriented on slowing the degradation of soil humus. The basic way is to increase the amount of incorporated fresh organic matter (harvest residues, manure) concomitant with simultaneous P fertilizer application.

Disclosure statement

No potential conflict of interest was reported by the authors.

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