

Iron content and qualitative composition in a waterlogged agricultural soil under long-term agrogenic influence, Western Ukraine

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Abstract. Iron, a typomorphic element of hydromorphic and semi-hydromorphic soils, significantly influences soil formation processes. Despite being relatively well studied, there is a lack of data on the content of its mobile compounds in Albic Pantostagnic Luvisol. Therefore, the study's main objective is to determine the amount, profile distribution, and seasonal dynamics of Fe compounds in a waterlogged agricultural soil subjected to different levels of long-term anthropogenic influence. Research conducted in a long-term stationary experiment shows that the composition of mobile forms of iron in Albic Pantostagnic Luvisol is dominated by the oxide form Fe³⁺. The highest Fe³⁺ content (160.6 mg kg⁻¹) was found in the humus-eluvial layer of the control soil without fertilizer, while Fe²⁺ compounds reached 46.6 mg kg⁻¹ at pH_{KCl} 4.30. Long-term application of an organo-mineral fertilization system combined with liming by hydrolytic acidity reduced the content of mobile iron compounds to 128.0 mg kg⁻¹, of which Fe²⁺ accounted for 12.64 mg kg⁻¹ at pH_{KCl} 5.45. Under an identical fertilization system with liming by pH buffering capacity, the Fe²⁺ content was 28.0 mg kg⁻¹, with a total content of 118.0 mg kg⁻¹ and pH_{KCl} of 5.54. In the natural conditions of forest and fallow land, the highest contents of mobile iron were 231.7 and 383.1 mg kg⁻¹ in the 0–20 cm horizon with a significant predominance of Fe³⁺ compounds, 210.1 and 366.3 mg kg⁻¹, respectively.

Key words: acidity, fertilizer, iron, liming, Albic Pantostagnic Luvisol.

INTRODUCTION

An important indicator of soil's chemical state, properties, and genesis is its elemental composition. Iron is one of the soil's most abundant and important components, as it can significantly influence and actively participate in soil formation processes. At the same time, iron is a necessary element for plant life. Both an excess and a deficiency of iron lead to certain plant diseases. As an element with variable

valence, its mobility changes significantly with changes in redox conditions and acidity (Tripathi et al., 2018).

Iron ranks 4th among heavy metals and is an essential trace element for numerous physiological and biochemical processes and reactions that take place in all living organisms, in particular, DNA synthesis, respiration, and photosynthesis. However, most crops' requirement for a neutral or near-neutral soil reaction to ensure maximum productivity is confronted with the problem of the limited availability of iron ions under these conditions. It is estimated that approximately 30% of the world's cultivated soils, where liming is applied to neutralize excessive acidity as part of many crop cultivation techniques, are characterized by low availability of oxidized forms of iron (Römheld & Nikolic, 2006).

High soil pH, free calcium carbonate, and low organic matter often lead to iron deficiency in plants. Currently, about one-third of the world's soils are iron-deficient, limiting plant growth and development (Wei et al., 2010).

With the change in moisture regime and the prevalence of anaerobic conditions in the soil, ferric (Fe^{3+}) forms of iron are easily converted to the active soluble ferrous form (Fe^{2+}), leading to its excess in the soil solution and disruption of plant micronutrient nutrition (Truskavetsky & Palamar, 2020). Reducing ferrous (Fe^{2+}) compound concentration improves the trace element regime, especially Cu, Zn, and Mo as Fe^{2+} antagonists (Foy, 1977).

At the same time, it should be considered that climate change alters the stability of Fe-organic compounds, affecting the weathering of Fe-containing minerals and microbial activity, which contributes to the decomposition of organic matter and the release of CO_2 (Song et al., 2022). Rising temperatures and altered moisture regimes accelerate humus mineralization and stimulate biological processes, influencing soil structure, fertility, and carbon release.

Episodes of waterlogging under changing precipitation patterns may further lower redox potential, enhancing the reduction of Fe^{3+} to Fe^{2+} and mobilizing organic matter previously stabilized by Fe (Patrick & Jugsujinda, 1992; Fuss et al., 2011). The destabilizing effect of waterlogging on Fe–organic complexes is further supported by experimental evidence from paddy soils: Sun et al. (2019) showed that within only 5 days of flooding, up to 92% of Fe^{3+} was reduced to Fe^{2+} , which markedly enhanced the decomposition of soil organic carbon and increased dissolved organic carbon concentrations more than four-fold. This confirms that Fe reduction under anaerobic conditions plays a central role in mobilizing organic matter and accelerating C losses as CO_2 and CH_4 .

Iron oxides are widely recognized for preventing the degradation of organic matter and thus supporting soil carbon storage (Li et al., 2023). However, recent findings also emphasize their dual role: while stabilizing SOC under oxic conditions, reductive dissolution under anoxia may accelerate SOC mineralization and CO_2 release (Chen et al., 2020). Moreover, climate warming may alter soil organic matter dynamics by reshaping the formation and stability of mineral–organic associations (Nguyen et al., 2019), while Fe compounds continue to act as central drivers of redox processes and nutrient availability in soils worldwide.

Free iron compounds interact with soil solution phosphates and mobile organic matter to form organo-mineral complexes inaccessible to plants (Truskavetsky et al.,

2018). The presence of organic compounds (humus) in the soil also leads to the formation of various chelates of mainly trivalent iron (Boguta et al., 2019). These forms of iron are important for plants' uptake, as they cannot assimilate trivalent Fe (Briat et al., 2005).

Iron availability to plants depends primarily on the redox potential and pH of the soil. Increases in soil redox potential and pH (including during liming) result in the transition of iron to poorly soluble forms. On the contrary, in acidic soils, Fe compounds dissolve, making metal ions available for uptake by plant roots (Zaid et al., 2017). The amount of dissolved iron increases 1,000-fold when the pH decreases by one unit (Chorna & Vahner, 2016).

According to several researchers, the concentration of soluble Fe can increase by several orders of magnitude in waterlogged soils due to low redox potential. Under such conditions, iron can enter plants, but with negative consequences for them. The anthropogenic impact of soil acidification, resulting from the intensive use of fertilisers (mainly nitrogen), increases the mobility of iron (Jones, 2020).

Despite the relatively good study of the element, there is not enough data on the content of its mobile compounds in Albic Pantostagnic Luvisol. There is a limited number of studies on changes in the content of mobile iron compounds during the growing season. Therefore, the study's main objective is to determine the amount, profile, and seasonal dynamics of Fe compounds in Albic Pantostagnic Luvisol with different levels of anthropogenic load.

According to a number of researchers, the concentration of soluble Fe can increase by several orders of magnitude in waterlogged soils due to low redox potential. Under such conditions, plants can take up iron, often with negative physiological consequences. In addition, anthropogenic soil acidification, resulting from the intensive use of fertilizers (mainly nitrogen), increases the mobility of iron (Jones, 2020).

Although iron has been relatively well studied as a chemical element, there is still insufficient information on its mobile compounds' content and seasonal behavior in Albic Pantostagnic Luvisol. This soil type is of high regional importance: in Ukraine, about 2.3 million ha are represented by light gray (Albic Luvisol) and gray forest soils (Haplic Luvisol) (Polupan et al., 2005). Similar soils are widespread across Europe (Tóth et al., 2008). Given their wide distribution and intensive agricultural use, understanding Fe transformations in these soils is essential for improving management practices such as fertilization and liming. Therefore, the main objective of this study is to determine the content, vertical distribution, and seasonal dynamics of mobile Fe compounds in Albic Pantostagnic Luvisol under different levels of long-term anthropogenic influence. We hypothesize that long-term liming and organic fertilization systems induce more substantial modifications in the amount and profile distribution of mobile iron compounds than mineral fertilization alone, thereby contributing to a more balanced soil chemical environment and improved fertility.

MATERIALS AND METHODS

This research was carried out within a long-term stationary experiment framework at the Department of Agrochemistry and Soil Science, Institute of Agriculture of Carpathian Region NAAS (49°47'54.3" N, 23°52'26.9" E), established in 1965. The

experiment is located in the Western Forest-Steppe zone of Ukraine, characterized by a moderately continental climate with a mean annual temperature of about 7.5–8.0°C, annual precipitation of 650–700 mm, and a vegetation period of 160–180 days (Nazaruk, 2018). According to recent climatic studies, the warm period in Western Ukraine increased to 300–320 days in 1991–2010 compared with 1961–1990, reflecting a clear regional warming trend (Krakovska et al., 2023). Snow cover usually lasts about 85 days, and in early spring, the soil may become waterlogged due to snowmelt and rainfall. Depending on weather conditions, such waterlogging may persist for several days, and in wet years for several weeks.

During the study years (2022–2023), mean air temperatures were consistently above the long-term norm, with January (+2.2 °C vs –4.6 °C) and August (+21.2 °C vs +16.9 °C) showing the largest deviations. Precipitation was highly variable: exceptionally high in September 2022 (130.1 mm vs 55 mm) and July 2023 (134.0 mm vs 102 mm), but very low in May 2023 (20.3 mm vs 85 mm). These fluctuations created alternating periods of excess moisture and drought stress, influencing soil waterlogging, redox conditions, and the mobility of Fe compounds.

The stationary experiment consists of three plots, each with 18 treatments replicated three times, following a single-row sequential layout. The total plot area is 168 m² with an accounting area of 100 m². The site is situated on flat terrain, ensuring homogeneous conditions across the experimental plots.

The crop rotation follows a four-field cycle: corn for silage, spring barley sown with meadow clover, meadow clover, and winter wheat. Standard agronomic tillage and crop management practices are applied consistently across the rotation.

The soil of the experimental plot is classified as Albic Pantostagnic Luvisol (WRB, 2022). The arable layer (0–20 cm) has the following average initial fertility indicators: humus content (according to Tyurin) 1.42%, pH (KCl) 4.2, hydrolytic acidity (according to Kappen) 4.5, exchangeable acidity (according to Sokolov) - 0.6 mg eq 100 g⁻¹ soil, mobile aluminium content 60.0, mobile phosphorus (according to Kirsanov) and exchangeable potassium (according to Maslova) - 36.0 and 50.0 mg kg⁻¹ soil, respectively.

A combination of organic and mineral fertilisers was used in the study, including semi-decomposed cattle manure from straw bedding, ammonium nitrate (34.5%), granulated superphosphate (19.5%), potassium salt (40%), and nitroammophoska (NPK 16%) (with NPK levels balanced according to the application of simple fertilisers). Manure application ranged from 40 to 60 tonnes per hectare under corn. Phosphorus-potassium fertilisers were applied in the autumn, while nitrogen fertilisers were applied before sowing.

Liming treatments were carried out according to the experimental protocol before the start of the 10th rotation (2016) within the crop cycle, with fertiliser doses adjusted accordingly. Limestone powder (93.5% CaCO₃) was used as the liming material. Starting from the 8th rotation (2008), the second mowing of meadow clover was integrated as an organic fertiliser in all experimental treatments.

The changes in the levels of mobile iron compounds were studied within the embedded soil profiles under the forest canopy, within the fallow areas, and within the most representative treatments of the stationary experiment during the 11th rotation. These treatments included: a control with no fertilisation (C), an organo-mineral fertilisation system (10 tonnes per hectare of manure + N₆₅P₆₈K₆₈) together with periodic

liming with 1.0 n CaCO₃ per hectare (equivalent to 6.0 tonnes per hectare of limestone flour) (OM1), an identical fertilisation system with liming using a pH buffering capacity (2.5 tonnes per hectare) (OM2), mineral fertilisation systems (N₁₀₅P₁₀₁K₁₀₁) with liming using 1.5 n CaCO₃ based on hydrolytic acidity (equivalent to 9.0 tonnes per hectare of limestone flour) (M1), a lime dose calculated by pH buffering capacity (2.5 tonnes per hectare) (M2) and a mineral fertilisation system (N₆₅P₆₈K₆₈) (M) (Table 1).

Table 1. Scheme of the studied treatments of the stationary field experiment (11th rotation)

Fertilization system		Per 1 ha of crop rotation area			Corn for silage	Spring barley + meadow clover	Mea-dow clover	Winter wheat
		rate of lime	Manure, t	NPK, kg of active substance				
Without fertilizers (control)	C	0	0	0	0	0	0	0
Organo-mineral with liming	OM1	1.0 norm by hydrolytic acidity (6.0 t ha ⁻¹)	10	N ₆₅ P ₆₈ K ₆₈	Manure, 40 t ha ⁻¹ + N ₁₂₀ P ₉₀ K ₉₀	N ₇₀ P ₉₀ K ₉₀	0	N ₇₀ P ₉₀ K ₉₀
	OM2	Optimal by the acid-base buffering capacity (2.5 t ha ⁻¹)	10	N ₆₅ P ₆₈ K ₆₈	Manure, 40 t ha ⁻¹ + N ₁₂₀ P ₉₀ K ₉₀	N ₇₀ P ₉₀ K ₉₀	0	N ₇₀ P ₉₀ K ₉₀
Mineral	M	0	0	N ₆₅ P ₆₈ K ₆₈	N ₁₂₀ P ₉₀ K ₉₀	N ₇₀ P ₉₀ K ₉₀	0	N ₇₀ P ₉₀ K ₉₀
Mineral with liming	M1	1.5 norms by hydrolytic acidity (9.0 t ha ⁻¹)	0	N ₁₀₅ P ₁₀₁ K ₁₀₁	N ₁₈₀ P ₁₃₅ K ₁₃₅	N ₁₂₀ P ₁₃₅ K ₁₃₅	0	N ₁₂₀ P ₁₃₅ K ₁₃₅
	M2	Optimal by acid-base buffering capacity (2.5 t ha ⁻¹)	0	N ₁₀₅ P ₁₀₁ K ₁₀₁	N ₁₈₀ P ₁₃₅ K ₁₃₅	N ₁₂₀ P ₁₃₅ K ₁₃₅	0	N ₁₂₀ P ₁₃₅ K ₁₃₅

Soil samples were collected from Albic Pantostagnic Luvisol and prepared for analysis according to DSTU ISO 11464-2001. The soil profile at the experimental site is characterized by a sequence of gleyic horizons. In the control treatment (without fertilizers), the profile consisted of an arable AEG horizon (0–0.18 m) underlain by a sub-arable AEG horizon (0.18–0.31 m), followed by an eluvial horizon Ehg (0.31–0.64 m). Below, the illuvial horizons Beg (0.64–1.10 m) and Bg (1.10–1.31 m) were observed, gradually transitioning into BCg (1.31–1.80 m) and CBg (1.80–2.00 m). Under long-term fertilization and liming, the thickness of individual horizons varied slightly: for example, the AEG horizon extended to 0.20–0.22 m, while the boundaries of eluvial and illuvial horizons shifted by several centimeters, reflecting modifications in soil structure and redox status (Olifir, 2021). Representative photographs of soil profiles under natural forest, unfertilized control, and long-term organo-mineral fertilization (OM1) are presented in Fig. 1.

For analytical purposes, composite soil samples were collected from standard depth intervals of 0–20 cm, 20–35 cm, and 35–50 cm, corresponding to the arable layer, the sub-arable layer, and the upper part of the eluvial horizon. Sampling was conducted from

three replicate plots for each treatment, with two replicates per plot. Within each plot, five subsamples were taken diagonally across half of the accounting area (50 m²) and pooled to obtain one composite sample. In total, each treatment was represented by six composite samples. All laboratory determinations (pH, Fe²⁺, Fe³⁺, and mobile Fe) were duplicated to ensure analytical reliability.

Soil pH was determined potentiometrically in a 1:2.5 soil to 1.0 N KCl suspension using a 'pH-301' pH meter with glass electrodes, according to DSTU ISO 10390:2001.

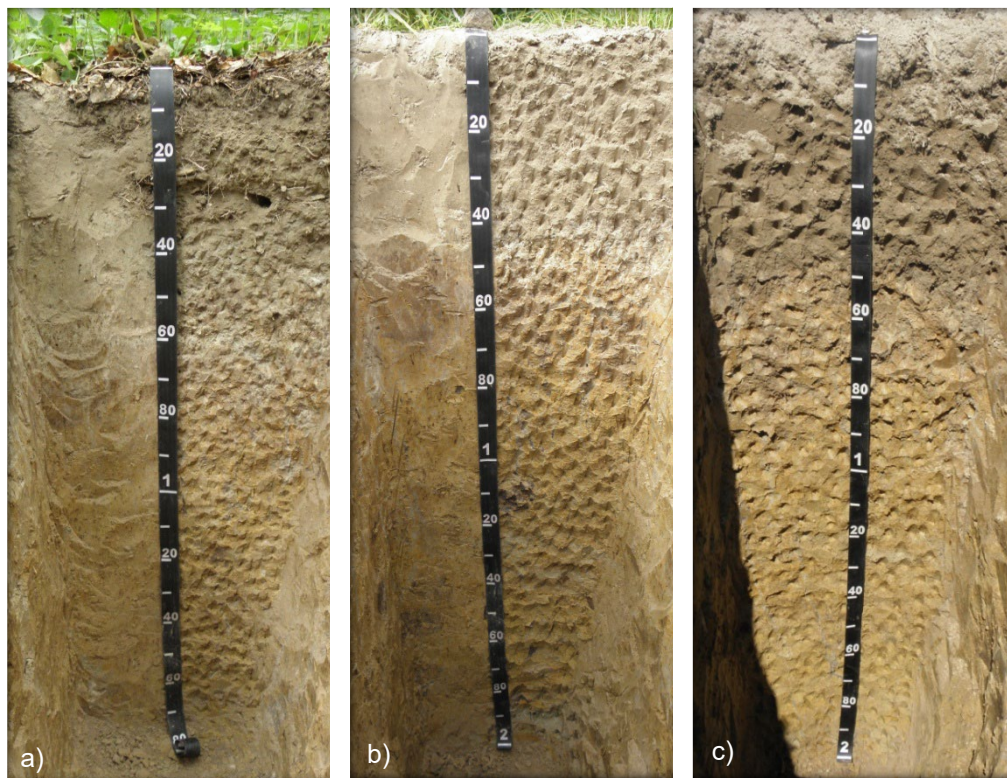


Figure 1. Soil profiles of Albic Pantostagnic Luvisol under different land use and management conditions: a) natural forest; b) control (no fertilization); c) organo-mineral fertilization system (OM1).

Mobile divalent and trivalent iron compounds were quantified according to DSTU 7913:2015, using an extract of 0.1 N sulphuric acid. The subsequent determination of divalent iron and total iron in the extracts (after the reduction of trivalent iron to divalent iron with hydroxylamine) was performed by photocolometric analysis using o-phenanthroline. The soil:extractant ratio was maintained at 1:10.

The obtained research data were analyzed using OriginPro 2019b software (OriginLab Corporation, USA, 2019). Data presented in tables as arithmetic means.

RESULTS AND DISCUSSIONS

Most soils contain sufficient amounts of iron to meet the requirements of plant growth and development, but chemical and environmental factors reduce its availability and lead to inhibited uptake or use by plants (Jones, 2020). Although the total Fe content of soils is usually high, the amount of available Fe is usually very low and is determined by the low solubility of Fe oxides (Colombo et al., 2014). Therefore, under a stationary experiment, we studied the changes in the content of mobile forms of iron during long-term periodic liming and fertilisation and compared them with similar indicators in a natural state on fallow land and under a forest.

The observations show that in the composition of mobile iron in the Albic Pantostagnic Luvisol, its oxidised form predominates, while divalent iron is much less abundant. This regularity is observed in all of the experimental treatments. Thus, the dynamics of changes in the content of mobile forms of iron according to the experiment in the spring period show that their highest amount of 207.2 mg kg⁻¹ of soil is observed in the humus-eluvial layer of the soil (0–20 cm) in the control without fertilisers. This includes Fe²⁺ compounds with 46.6 mg kg⁻¹ and Fe³⁺ with 160.6 mg kg⁻¹ of soil at a pH_{KCl} of 4.30. Subsequently, the content of Fe²⁺ compounds decreases to 8.2 mg kg⁻¹ in the subsoil layer (20–35 cm) and further to 7.00 mg kg⁻¹ in the eluvial-low humus horizon (Table 2).

Table 2. Dynamics of the content of mobile iron compounds in Albic Pantostagnic Luvisol in spring under different fertilisation systems, XI rotation, mg kg⁻¹ ($n = 6$)

	Soil layer, cm		OM1	OM2	M	M1	M2	Fallow	Forest
Fe ²⁺	0–20	46.6 ^a	12.6 ^b	12.8 ^b	18.1 ^{bc}	21.3 ^c	20.1 ^{bc}	16.8 ^{bc}	21.6 ^c
	20–35	8.2 ^a	11.4 ^{ad}	12.2 ^{ac}	18.3 ^b	19.2 ^b	17.7 ^{bc}	9.6 ^{ad}	14.3 ^{bcd}
	35–50	7.0 ^a	8.8 ^{ab}	11.7 ^{bc}	13.7 ^{cd}	15.8 ^d	14.9 ^{cd}	7.5 ^a	9.4 ^{ab}
Fe ³⁺	0–20	160.6 ^a	115.0 ^{bc}	104.9 ^b	128.1 ^c	105.1 ^b	99.0 ^b	366.3 ^d	210.1 ^c
	20–35	107.2 ^{ab}	104.6 ^{ab}	101.6 ^{ab}	123.9 ^a	114.7 ^{ab}	85.7 ^b	236.6 ^c	131.9 ^a
	35–50	106.9 ^a	93.9 ^{ac}	99.2 ^a	128.2 ^b	103.7 ^a	80.1 ^c	166.1 ^d	106.4 ^a
Total	0–20	207.2 ^a	127.6 ^b	117.7 ^b	146.2 ^c	126.4 ^b	119.1 ^b	383.1 ^d	231.7 ^c
	20–35	115.4 ^{ac}	116 ^{abc}	113.8 ^{abc}	142.2 ^{abc}	133.9 ^{bc}	103.4 ^c	246.2 ^d	146.2 ^c
	35–50	113.9 ^{ac}	102.7 ^{ad}	110.9 ^{ac}	141.9 ^b	119.5 ^c	95 ^d	173.6 ^e	115.8 ^{ac}
pH _{KCl}	0–20	4.30 ^a	5.45 ^b	5.54 ^b	4.35 ^a	5.23 ^{bc}	5.02 ^c	4.17 ^a	3.54 ^d
	20–35	4.21 ^a	5.35 ^b	5.57 ^c	4.15 ^a	5.52 ^{bc}	5.06 ^d	4.11 ^a	3.80 ^e
	35–50	4.20 ^a	5.60 ^b	5.43 ^c	4.28 ^a	5.42 ^c	5.32 ^c	4.03 ^d	3.85 ^e

Note: values labeled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test ($p < 0.05$) within the same soil layer.

According to Patra et al. (2021), the availability of Fe to plants is influenced by soil reaction, the amount of soil organic matter, soil aeration, and the presence or absence of other macro- and microelements.

In the long-term and systematic application of the mineral fertiliser system (M) with a pH_{KCl} of 4.35, the total concentration of mobile iron compounds in the fertile topsoil reaches 146.2 mg kg⁻¹ soil. Of this, 128.1 mg kg⁻¹ consists of mobile trivalent iron compounds. Previous studies conducted under similar conditions with Albic

Pantostagnic Luvisol have shown that this mineral fertiliser system significantly increases hard-to-reach iron phosphate. Compared to the unfertilised control, the concentration increases by 1.9–2.5 times, reaching 562.0 mg kg⁻¹ soil compared to 280.0 mg kg⁻¹ in the unfertilised control (Habryiel et al., 2006).

A significant content of mobile forms of iron, including Fe²⁺ in the control, is because under conditions of high acidity of the soil solution (in this treatment the pH of the solution was 4.2) and a lack of calcium and magnesium (Ca content 1.8–2.0 mg-eq 100 g⁻¹ soil and mg content 0.42–0.52 mg-eq 100 g⁻¹ soil) the mobility of iron increases. Under these conditions, the content of mobile iron can increase to 175.0 mg kg⁻¹ and more.

Finally, it is known that one of the important properties of iron is its ability to change its valence depending on the soil regime. Under aerobic conditions, it is a trivalent oxide (Fe₂O₃) - practically insoluble in water, and under anaerobic conditions, it is divalent (FeO) and is the most soluble and mobile (Pankiv et al., 2023).

It should also be considered that high availability of Fe in soils can lead to toxic effects when excessive iron uptake damages cellular structures, resulting in reduced plant growth and leaf damage (Ayeeni et al., 2014).

Studies have shown that the stability of Fe in soils is closely related to the presence of organic carbon (Lalonde et al., 2012). As an electron donor, organic matter facilitates microbial dissimilatory reduction of Fe, leading to the dissolution of soil Fe³⁺ hydroxides and possibly the release of Fe²⁺ ions (Tittel et al., 2022). Therefore, the higher organic matter content caused by the application of organic fertilisers increases the mobility and solubility of Fe through the reduction reaction. In fact, the reduced form of Fe (Fe²⁺) is more mobile than the oxidised form, which increases plant uptake and facilitates leaching (Fuss et al., 2011).

In the organo-mineral fertilisation system combined with liming with 1.0 n CaCO₃ based on hydrolytic acidity (OM1), the total concentration of mobile iron compounds decreases to 127.6 mg kg⁻¹ soil during the period indicated. Within this, the concentration of Fe²⁺ compounds is 12.6 mg kg⁻¹ soil at a pH_{KCl} of 5.45. Conversely, within an identical fertilisation and liming system using the pH buffering capacity (OM2), the concentration of Fe²⁺ compounds is slightly higher at 12.8 mg kg⁻¹ soil, while the total content of mobile iron compounds decreases to 117.7 mg kg⁻¹ soil at a pH_{KCl} of 5.54. In the scenario of liming with a dosage of CaCO₃ based on pH buffering capacity alongside a mineral fertilisation system (M2), the concentration of Fe²⁺ compounds is recorded at 20.1 mg kg⁻¹ soil at a pH_{KCl} of 5.02, compared to 21.3 mg kg⁻¹ soil within an identical fertilisation system supplemented with 1.5 n CaCO₃ based on hydrolytic acidity (M1) (pH_{KCl} 5.23).

It is known that liming increases the pH value of the soil, which accordingly affects its physical, chemical, and biological characteristics (Čop, 2015). Ghorashi et al. (2016) showed that lime application reduced iron concentration and iron uptake by plants compared to unamended soil by improving the response of acidic soils and increasing the calcium and magnesium content of the soil.

Under natural conditions of soil formation, in particular, under the forest, the content of mobile compounds Fe²⁺ is 21.6 mg kg⁻¹ of soil, decreasing in the horizon more than 35 cm to 9.4 mg kg⁻¹, with the total content of compounds Fe²⁺ + Fe³⁺ - 231.7 mg kg⁻¹ of soil and 115.8 in the horizon more than 35 cm. On the

fallow, the total content of mobile iron compounds is 383.1 mg kg⁻¹ of soil, including the content of mobile iron oxide compounds 6.8 mg kg⁻¹, decreasing to 7.5 mg kg⁻¹ of soil below 35 cm.

In all treatments of the experiment, there was a consistent tendency for higher accumulation of mobile iron compounds in the humus-eluvial layer (0–20 cm). This pattern can be explained by the higher content of soil organic matter and more intensive biological activity in the topsoil, which provides favourable conditions for forming and stabilizing organo-ferrous complexes. The enrichment of the surface horizon with mobile Fe is of particular importance, as it directly influences nutrient cycling, redox processes, and the availability of iron to plants. Therefore, maintaining and preserving the humus-eluvial layer is essential for sustaining soil fertility and preventing degradation under long-term agricultural use.

Our findings are consistent with well-established mechanisms of organo-metal interactions in soils. Organic matter in surface horizons is a key sorbent for Fe, facilitating the formation of stable Fe-organic complexes, as demonstrated in temperate soils (Wagai & Mayer, 2007). The elevated concentrations of mobile Fe observed in our humus-eluvial horizon indicate the presence of reactive Fe species capable of interacting with dissolved organic matter. Previous studies demonstrated that DOM is strongly and often irreversibly sorbed onto Fe and Al oxyhydroxides, especially through aromatic functional groups, thereby reducing degradability and promoting long-term SOM stabilization (Kaiser & Guggenberger, 2000). This suggests that mobile Fe in our soils serves as an important pool of reactive species contributing to the development of stable Fe–organic associations.

Such associations play a central role in SOC stabilization (Wagai & Mayer, 2007), and organo-mineral complexes with Fe and Al remain key retention forms of organic matter even under land-use change (Mikutta et al., 2009). Further mechanistic insights are provided by Wen et al. (2019), who showed that long-term organic amendments significantly increase poorly crystalline Fe concentrations, closely linked to enhanced SOC storage. The proposed mechanisms include co-precipitation of DOM with Fe, inhibition of Fe crystallization by aromatic constituents, and microbial shifts that favour the retention of reactive Fe. These processes reinforce a positive feedback loop in which organic inputs sustain reactive Fe, which in turn stabilizes SOC. Together, this evidence underscores the ecological importance of the humus-eluvial horizon as a critical soil compartment for both agricultural productivity and carbon sequestration under changing climate conditions.

Observations of the dynamics of changes in mobile iron compounds in Albic Pantostagnic Luvisol by seasons showed that the highest number of mobile iron compounds is precisely in the spring period at a humidity of 15.3–17.8% (Table 2–4). It is known that in the spring, regenerative processes start in the soil due to the melting of snow and an increase in its humidity. The highest content of mobile forms of Fe is in the spring period in the control without fertiliser. The lowest effect of fertiliser on the content of mobile iron compounds according to the experimental treatments was observed in autumn (Table 3).

In acidic unsaturated soils, the role of iron is compared to the role of calcium in chernozems, as it performs a number of important functions and serves as a basis for the diagnosis of soil formation processes (Pankiv et al., 2023).

The studies have shown that the Albic Pantostagnic Luvisols under the forest and on the fallow land have not lost their connection with other components of the landscape, all processes and properties correspond to the natural factors of soil formation. The highest amount of mobile iron compounds occurs in the humus-eluvial horizon of 0–20 cm, and the lowest in the eluvial low-humus horizon of 35–50 cm.

Table 3. Dynamics of the content of mobile iron compounds in Albic Pantostagnic Luvisol in summer under different fertilisation systems, 11th rotation, mg kg⁻¹ (*n* = 6)

	Soil layer, cm	C	OM1	OM2	M	M1	M2	Fallow	Forest
Fe ²⁺	0–20	13.1 ^a	14.5 ^a	18.6 ^b	5.2 ^c	4.1 ^c	5.3 ^c	19.8 ^b	34.9 ^d
	20–35	10.9 ^a	12.9 ^a	13.6 ^a	4.4 ^b	4.4 ^b	5.0 ^b	20.7 ^c	32.3 ^d
	35–50	9.7 ^{ab}	10.1 ^a	9.6 ^b	21.3 ^c	3.2 ^d	4.3 ^d	11.7 ^a	16.8 ^c
Fe ³⁺	0–20	67.5 ^{ac}	54.1 ^b	55.9 ^{bc}	57.3 ^{bc}	38.7 ^d	32.7 ^d	158.0 ^c	74.1 ^a
	20–35	55.7 ^a	46.0 ^b	56.6 ^a	40.4 ^{bc}	33.0 ^d	33.2 ^{cd}	100.0 ^c	46.0 ^b
	35–50	57.7 ^a	39.3 ^b	50.7 ^c	10.8 ^d	26.0 ^c	31.2 ^f	79.7 ^g	36.9 ^b
Total	0–20	80.6 ^a	68.6 ^{ab}	74.5 ^{ab}	62.5 ^b	42.8 ^c	38.0 ^c	177.8 ^d	109.0 ^c
	20–35	66.6 ^{ab}	58.9 ^a	70.2 ^{bc}	44.8 ^c	37.4 ^c	38.2 ^c	120.7 ^d	78.3 ^c
	35–50	67.4 ^a	49.4 ^b	60.3 ^c	32.1 ^{de}	29.2 ^d	35.5 ^e	91.4 ^f	53.7 ^g
pH _{KCl}	0–20	4.19 ^a	5.40 ^b	5.52 ^b	4.54 ^c	4.70 ^c	4.90 ^d	4.07 ^a	3.21 ^e
	20–35	4.01 ^a	5.17 ^b	5.23 ^b	4.20 ^a	4.90 ^c	5.06 ^{bc}	4.09 ^a	3.48 ^d
	35–50	3.94 ^a	5.22 ^b	5.10 ^b	4.00 ^a	4.71 ^c	5.10 ^b	4.00 ^a	3.53 ^d

Note: values labeled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test (*p* < 0.05) within the same soil layer.

The seasonal alternation of wet and dry cycles alters the redox conditions of soils and soil solutions, affecting the mobility of their components due to different solubilities, including Fe (Gangloff et al., 2016). In the summer months, the amount of mobile iron compounds in the soil under the forest is the lowest and amounts to 109.0 mg kg⁻¹ of soil with a predominance of Fe³⁺ content up to 74.1 mg kg⁻¹ against 34.9 mg kg⁻¹ of soil of Fe²⁺. Instead, in autumn, the amount of mobile compounds increases slightly to 120.0 mg kg⁻¹ of soil with a significant predominance of Fe³⁺ - 104.7 mg kg⁻¹ of soil and 15.4 mg kg⁻¹ of soil of Fe²⁺. In general, trivalent iron predominates in the composition of mobile iron compounds under the forest, on the fallow land, and in experimental treatments.

As in the case of the experimental treatments, the number of mobile iron compounds on the fallow land is highest in the 0–20 cm soil layer and gradually decreases up to the 35–50 cm horizon. On the fallow, the highest content of mobile iron compounds is 383.1 mg kg⁻¹ of soil in the humus-eluvial horizon 0–20 cm in spring, decreasing to 167.8 in summer and to 130.2 mg kg⁻¹ of soil in autumn with a strong predominance of Fe³⁺ compounds.

Research in a long-term stationary experiment has shown that the gross content of mobile iron compounds and their mobile forms in Albic Pantostagnic Luvisol is within the optimal level. However, in the case of long-term (more than 50 years) inclusion of Albic Pantostagnic Luvisol with an initial pH_{KCl} of 4.2 into the agricultural system without the addition of fertilisers and lime, the content of mobile iron in the humus-eluvial horizon increases to 207.2 mg kg⁻¹ (including the content of Fe²⁺

compounds 46.6 and Fe^{3+} 160.6 mg kg^{-1}). As a result, in such conditions, the nutrient iron can turn from a trace element into a toxic substance, which worsens the conditions of trace element nutrition and reduces the productivity of crops.

Table 4. Dynamics of the content of mobile iron compounds in Albic Pantostagnic Luvisol in autumn under different fertilisation systems, 11th rotation, mg kg^{-1} ($n = 6$)

	Soil layer, cm	C	OM1	OM2	M	M1	M2	Fallow	Forest
Fe ²⁺	0–20	1.5 ^a	5.9 ^b	10.5 ^c	8.7 ^d	3.1 ^c	3.8 ^c	6.6 ^b	15.4 ^f
	20–35	1.8 ^{ad}	7.3 ^{bc}	8.8 ^{be}	9.6 ^{be}	5.2 ^c	4.6 ^{cd}	7.6 ^{bc}	11.0 ^e
	35–50	1.7 ^a	6.6 ^{bc}	6.6 ^{bc}	9.4 ^b	4.1 ^{ac}	5.5 ^{cd}	5.9 ^{cd}	7.9 ^{bd}
Fe ³⁺	0–20	47.9 ^a	43.9 ^a	56.5 ^b	43.4 ^a	32.7 ^c	35.6 ^c	123.6 ^d	104.6 ^e
	20–35	50.2 ^a	34.3 ^{bd}	41.7 ^{bc}	45.8 ^{ac}	32.1 ^d	31.8 ^d	99.9 ^c	44.0 ^{ac}
	35–50	59.5 ^a	37.0 ^{bd}	39.3 ^{bd}	58.8 ^a	31.1 ^b	29.8 ^b	73.1 ^c	44.8 ^d
Total	0–20	49.4 ^a	49.8 ^a	67.0 ^b	52.1 ^a	35.8 ^c	39.4 ^c	130.2 ^d	120.0 ^e
	20–35	52.0 ^a	41.6 ^{bc}	50.5 ^{ab}	55.4 ^a	37.3 ^c	36.4 ^c	107.5 ^d	55.0 ^a
	35–50	61.2 ^{ac}	43.6 ^{bc}	45.9 ^b	68.2 ^a	35.2 ^c	35.3 ^c	79.0 ^d	52.7 ^{be}
pH _{KCl}	0–20	4.40 ^a	5.07 ^b	5.28 ^c	4.40 ^a	5.10 ^b	4.98 ^b	4.23 ^d	3.80 ^e
	20–35	4.30 ^a	5.10 ^{bc}	5.17 ^b	4.26 ^a	5.30 ^b	4.96 ^c	4.25 ^a	3.96 ^d
	35–50	4.39 ^a	4.98 ^b	5.27 ^c	4.29 ^d	5.46 ^c	5.10 ^f	4.28 ^d	3.91 ^g

Note: values labeled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test ($p < 0.05$) within the same soil layer.

With the long-term application of a mineral fertiliser system on Albic Pantostagnic Luvisol with a pH_{KCl} of 4.35, the content of mobile iron compounds in the humus-eluvial horizon in spring is 146.0 mg kg^{-1} soil, which is lower than the control without fertiliser. This is despite the additional application of 5,550 mg kg^{-1} of superphosphate and 454 mg kg^{-1} of iron with potassium chloride according to Shahid et al. (2016). The systematic use of mineral fertilisers increases the content of poorly soluble iron and aluminium phosphates that are inaccessible to plants. This led to a decrease in mobile iron compounds in this treatment.

In the summer months, the amount of mobile iron compounds in the soil under the forest is the lowest and amounts to 109.0 mg kg^{-1} of soil with a predominance of Fe^{3+} content up to 74.1 mg kg^{-1} against 34.9 mg kg^{-1} of soil of Fe^{2+} . Instead, in autumn, the amount of mobile compounds increases slightly to 120.0 mg kg^{-1} of soil with a significant predominance of Fe^{3+} – 104.7 mg kg^{-1} of soil and 15.4 mg kg^{-1} of soil of Fe^{2+} . In general, trivalent iron predominates in the composition of mobile iron compounds under the forest and on the fallow land as well as in the experimental treatments.

As in the case of the experimental treatments, the number of mobile iron compounds on the fallow land is highest in the 0–20 cm soil layer and gradually decreases up to the 35–50 cm horizon. On the fallow, the highest content of mobile iron compounds is 383.1 mg kg^{-1} of soil in the humus-eluvial horizon 0–20 cm in spring, decreasing to 167.8 in summer and to 130.2 mg kg^{-1} of soil in autumn with a strong predominance of Fe^{3+} compounds.

Research in a long-term stationary experiment has shown that the gross content of mobile iron compounds in Albic Pantostagnic Luvisol is within the optimal level. However, in the case of long-term inclusion of Albic Pantostagnic Luvisol with an initial

pH_{KCl} of 4.2 into the agricultural system without the addition of fertilisers and lime, the content of mobile iron in the humus-eluvial horizon increases to 207.2 mg kg⁻¹ (including the content of Fe²⁺ compounds 46.6 and Fe³⁺ 160.6 mg kg⁻¹). As a result, in such conditions, the nutrient iron can turn from a trace element into a toxic substance, which worsens the conditions of trace element nutrition and reduces the productivity of crops.

During the long-term application of the mineral fertiliser system at the pH_{KCl} of 4.35 on the Albic Pantostagnic Luvisol, the content of mobile iron compounds in the humus-eluvial horizon in spring is 146.0 mg kg⁻¹ of soil, of which Fe²⁺ compounds are 18.1 mg kg⁻¹. This is due to the fact that, according to Shahid et al. (2016), 5,550 mg kg⁻¹ of iron is applied with superphosphate and 454 mg kg⁻¹ of iron is applied with potassium chloride, which increases the content of this element in the soil.

Previous studies in a long-term stationary experiment indicate that it is the high toxicity of aluminium in the conditions of the Albic Pantostagnic Luvisol with a low concentration of magnesium and calcium ions that manifests the most harmful effect of soil acidity on the environment (Olifir et al., 2023). Research by experimental treatments and under natural conditions of soil formation under the forest and on the fallow land shows that the gross content of iron compounds and their mobile forms are within the optimal level in the Albic Pantostagnic Luvisol. Only in the long-term (50 years) use of this soil without fertilization (which is rare in production), iron, as a nutrient, can turn into a toxic substance that affects micronutrient nutrition. However, it is known that the limit values of iron content in soils are not legal norms and are not the main topic of discussion among scientists, since Fe is not a direct soil pollutant (Murtić et al., 2019).

CONCLUSIONS

The research under the conditions of a long-term stationary experiment demonstrated that in the composition of mobile iron in waterlogged Albic Pantostagnic Luvisol, the oxidized form (Fe³⁺) predominates. The maximum content of mobile Fe compounds was 207.2 mg kg⁻¹ in the unfertilized control, recorded in the humus-eluvial arable horizon (0–20 cm) at pH_{KCl} 4.30, of which mobile Fe²⁺ accounted for 46.6 mg kg⁻¹. Across all treatments, there was a consistent tendency for higher accumulation of mobile Fe in the humus–eluvial horizon, underlining the critical importance of this soil layer for nutrient cycling, redox processes, and soil fertility. Preserving and sustainably managing the organic-rich surface horizon is therefore essential for preventing degradation and maintaining productivity in acid soils under long-term agricultural use.

In the mineral fertiliser treatment, the content of mobile Fe compounds is significantly lower than in the no-fertiliser control, which is caused by a significant amount of iron supplied with mineral fertiliser. The greatest amount of mobile iron in the Albic Pantostagnic Luvisol is extracted in the spring, during the recovery of the winter wheat vegetation, at a moisture content of 15.3–17.8%.

In the treatments of organo-mineral and mineral fertilisation plus liming, both in terms of hydrolytic acidity and pH-buffering capacity, the total content of mobile Fe compounds, as well as Fe²⁺ compounds, does not differ significantly, which indicates

the economic feasibility and environmental safety of using a dose of lime on Albic Pantostagnic Luvisol, calculated by pH-buffering capacity.

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