The dynamics of mobile iron compounds and redox potential of Albic Pantostagnic Luvisol depending on long-term various fertilisation

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Abstract

Iron is one of the most important trace elements in plant nutrition. The content of ferric iron and ferrous oxide in the soil and their dynamics during the vegetation period can be used to assess not only the course of oxidation-reduction processes but also the supply of plants with this available trace element. Therefore, the main objective of the research was to find out the effect of long-term fertilisation and liming on the dynamics of the redox potential and mobile iron compounds in the Albic Pantostagnic Luvisol of the forest-steppe of Western Ukraine. The research was conducted under the conditions of a long-term experiment established in 1965 with different doses of mineral fertilisers, manure, and lime on the Albic Pantostagnic Luvisol. It was found that the gross content of iron compounds and the content of their mobile forms in the Albic Pantostagnic Luvisol are within the optimal range for the plant's growth and development. Only in the case of long-term use of this soil without fertilisation or in the conditions of long-term mineral fertilisation, which contributes to the increase of the acidity of the soil solution and to the creation of restoring conditions during the periods of overwetting, iron can turn into a toxic substance.

1. Introduction

Chemical composition of the soil is one of the most important fertility factors, as many chemical elements are not included in the composition of mineral fertilisers but are necessary for plant growth and development. Iron (Fe) is one of plant nutrition's most essential trace elements. Its role in oxidative and energy exchange and the formation of chlorophyll is crucial (Krohling et al., 2016).

Due to its ability to gain and lose electrons, iron is a cofactor for many enzymes involved in redox reactions (photosynthesis, respiration, hormone synthesis, DNA synthesis, etc.). This function makes iron an essential nutrient, and its deficiency causes iron chlorosis, severely inhibiting normal plant development (Rout and Sahoo, 2015).

Although Fe is abundant in well-aerated mineral soils, most of it is not available for plant uptake due to low biological activity and poor solubility of its major oxides/hydroxides, especially in neutral and alkaline soils (Rout and Sahoo, 2015; Colombo et al., 2018).

Low Fe bioavailability in arable soils can reduce crop yields and affect plant nutritional value (Briat et al., 2015; Bhatti et al., 2024). Iron is generally present in soils as Fe^{3+} (trivalent iron) and Fe^{2+} (divalent iron). Its availability depends mainly on the physical and chemical properties of the soil. Chemically, organisms have developed specific mechanisms for iron uptake from Fe oxides by protonation, chelation, and reduction reactions (Guerinot and Yi, 1994). The most crucial feature of iron from a chemical point of view is its ability to change valence. Its presence in the soil as Fe^{2+} or Fe^{3+} depends on the redox regime and pH of the soil (Tsapko and Sokolova, 2010; Slimani et al., 2023).

Therefore, the ratio of ferrous to ferric iron oxide in the soil can be used to assess not only the course of oxidation-reduction processes but also the supply of plants with the available trace element Fe^{2+}.

Studies of the ratio of oxidised and reduced iron forms under climate change conditions deserve special attention. Often, even short-term waterlogging leads to the activation of iron recovery processes, disturbing the ratio of oxidised and reduced

forms, which differ significantly in terms of their functional properties in soil (Sokolova, 2008).

The cyclic switching of iron in the soil between its reduced and oxidised states determines the availability of iron to plants as a trace element necessary for their growth (Calabrese and Porporato, 2019).

Reducing the concentration of iron oxide compounds improves the micronutrient regime, particularly Cu, Zn, and Mo, as Fe^{2+} antagonists (Foy, 1977). At the same time, the concentration of Fe^{2+} increases in over-watered soils. Under such conditions, plants can take up iron, but it has negative consequences.

Acidic conditions (pH<5.0) and low Eh values (<0.4 V) in soils tend to increase the concentration of ferrous ions (Fe^{2+}), while neutral and alkaline pH values at high Eh values (>0.6 V) lead to the predominance of iron hydroxides in the soil environment (Colombo et al., 2018). The solubility of Fe^{3+} (ferric iron oxide) decreases with increasing pH, while Fe^{2+} (ferrous iron oxide) is easily oxidised in aerated soils, which can lead to Fe deficiency in plants (Kaya et al., 2020).

Iron is known to be taken up by plants in its soluble form as divalent iron (Fe^{2+}) (Husson, 2013). However, Fe^{2+} can be toxic at high concentrations (Lapaz et al., 2022; Harish et al., 2023). Iron toxicity is a common problem, especially in areas prone to soil waterlogging, which can be caused by improper irrigation, high groundwater levels after heavy rainfall (mainly in compacted soils with poor natural drainage), and in low-lying soils, resulting in an exponential increase in iron availability, especially in acidic soils (Lapaz et al., 2020).

It is necessary to control the Fe balance strictly since both its deficiency and its excess affect the physiological processes of plants (Walker and Connolly, 2008), sometimes with negative consequences for their growth and development (Briat et al., 2010).

Among all the redox systems, the $Fe^{3+} \leftrightarrow Fe^{2+}$ system occupies a special place since the genesis of many soils of humid zones is related to the transformation of iron compounds and their migration in the soil profile. The oxidation and reduction reactions of iron occurring in the soil are reversible, and the decisive factor influencing these processes is soil acidity (Krohling et al., 2016; Colombo et al., 2018).

By influencing the degree of availability of certain nutrients, redox conditions provide plants with a more favourable ratio of these nutrients in soil solutions during the growing season of crops (Yevpak, 2010). In general, soils with low organic matter content, in the composition of which mobile components such as fulvic acids and low molecular weight organic compounds play an important role, have a low buffering capacity against redox potential decrease due to overwetting (Husson, 2013; Jiang et al., 2018).

Such soils include the Albic Pantostagnic Luvisol of the Western Forest Steppe, which occupies large areas of Ukraine and is characterised by low humus content with a predominance of fulvic acids in its composition (Olifir et al., 2020). For such soils, the redox potential is mainly determined by acidity and moisture (Kyrylchuk and Bonishko, 2011). Our previous studies showed that the amount of acidity (pH_{KCl} and hydrolytic acidity) under the conditions of the Albic Pantostagnic Luvisol is closely related to the content of mobile aluminium compounds, fertilisation systems, their aftereffects, and the crop rotation factor (Olifir et al., 2023). However, the processes of changes in the content of mobile iron compounds in these soils during the growing season have not been sufficiently investigated.

Therefore, the main objective of our research is to investigate the effect of long-term fertilisation and liming on the dynamics of redox potential and mobile iron compounds in the Albic Pantostagnic Luvisol of the forest-steppe of Western Ukraine.

2. Materials and methods

This study investigates the changes in the content of mobile iron compounds in a long-term field experiment carried out by the Department of Agrochemistry and Soil Science of the Institute of Agriculture of the Carpathian Region of the NAAS. Established in 1965 on Albic Pantostagnic Luvisol, the experiment is located at 49°47'54.3" N 23°52'26.9"E. The location of the long-term experiment (Google, Maxar Technologies) is given in our previous article (Havryshko et al., 2023).

It consists of three plots, each with 18 treatments in triplicate, arranged sequentially and single-tiered. The total plot area is 168 m², with an accounting area of 100 m². The crop rotation follows a four-field system: maise for silage, spring barley with meadow clover, meadow clover and winter wheat. Standard agricultural practices for planting, soil management and crop protection appropriate to the western forest-steppe zone are applied.

The soil of the experimental plot is classified as Albic Pantostagnic Luvisol (IUSS Working Group WRB, 2022), with the arable layer (0–20 cm) characterised by the following average initial fertility indicators: humus content (Tyurin method) of 1.42%, pH_{KCl} of 4.2, hydrolytic acidity (Kappen method) of 4.5, exchangeable acidity (Sokolov method) of 0.6 cmol(+) kg^{-1}, mobile aluminium content of 60.0 mg kg^{-1} and mobile phosphorus (Kirsanov method) and exchangeable potassium (Maslova method) contents of 36.0 mg kg^{-1} and 50.0 mg kg^{-1} respectively.

The experiment includes different doses and ratios of mineral fertiliser, manure, and lime. The fertilisers used are semi-rotted cattle manure on straw bedding, ammonium nitrate (34.5% N), granulated superphosphate (19.5% P_2O_5), potassium salt (40% K_2O) and nitro-ammophoska (NPK 16%). For nitro-ammophoska, the NPK content was balanced according to the fertilisation level with simple fertilisers. Manure (40–60 Mg ha^{-1}) was applied under maise, phosphorus-potassium fertiliser in autumn and nitrogen fertiliser before sowing. Liming was carried out according to the experimental scheme before the start of the crop rotation, with adjustments made to the fertiliser doses for the crops in the rotation. Limestone powder (93.5% $CaCO_3$) was used as the liming material. From the eighth rotation onwards, the second cut of meadow clover was ploughed in as an organic fertiliser in all experimental treatments.

The study of changes in the content of mobile iron compounds was carried out in the most representative treatments of the field experiment during the growing season of winter wheat

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of the last crop of the XI crop rotation: absolute control (no fertilisation) (C), organo-mineral fertilisation system (manure (10 Mg ha^{-1} of rotation area) + $N_{65}P_{68}K_{68}$) with the background of periodic liming with 1.0 dose of $CaCO_3$ calculated by hydrolytic acidity (6.0 Mg ha^{-1} of limestone flour) (OM1) and an identical fertilisation system with the background of liming with a dose based on pH buffering capacity (2.5 Mg ha^{-1}) (OM2), mineral fertilisation systems ($N_{105}P_{101}K_{101}$) with the background of liming with 1.5 dose of $CaCO_3$ (9.0 Mg ha^{-1} of limestone flour) calculated by hydrolytic acidity (M1) and the dose of lime calculated by pH buffering capacity (2.5 Mg ha^{-1}) (M2) and mineral fertilisation system ($N_{65}P_{68}K_{68}$) (M) (Table 1).

Soil samples for determining physicochemical properties were taken from the arable layer (0–20 cm) of Albic Pantostagnic Luvisol on the studied variants and prepared for analysis according to DSTU ISO 11464–2001. Soil samples were collected for analysis during three periods: May (spring), July (summer), and September (autumn).

Winter 2023 was characterised by above-average temperatures, with January being notably warmer than average. Precipitation levels were also elevated, particularly in December and January, leading to a wetter winter than usual. Spring witnessed fluctuating temperatures, with March experiencing a notable increase, averaging 4.9°C, well above the norm of 0.5°C. Precipitation in March reached 60.8 mm, surpassing the average of 44 mm. April saw further warming with an average temperature of 7.9°C, just above the norm of 7.4°C, and substantial precipitation of 84.2 mm, compared to the average of 51 mm. However, May shifted toward drier conditions, with precipitation dropping sharply to just 20.3 mm, compared to the much higher average of 85 mm. Summer was characterised by elevated temperatures, particularly in July, which had an average of 20.0°C, marking it the warmest month of the year. Precipitation in July peaked at 134.0 mm, exceeding the average of 102 mm. August continued the warmth with an average temperature of 21.2°C, higher than the norm of 16.9°C, but precipitation decreased to 74.7 mm, below the average of 82 mm. Autumn continued the trend of warmer-than-average temperatures. September saw an average temperature of 17.7°C, higher than the norm of 13.1°C, and precipitation of 68.2 mm, above the average of 55 mm. Precipitation remained significant, particularly in November, which recorded 86.0 mm, well above the average of 48 mm, contributing to a wetter environment as winter approached. This season displayed consistent warmth and increased rainfall, maintaining the moist conditions established during summer.

Laboratory and analytical studies were carried out in the Laboratory of Agrochemistry and Analytical Studies of the Institute of ACR of the NAAS. Determination of soil moisture was carried out by drying soil samples to constant mass at 105°C and using the difference in mass of an amount of soil before and after the drying procedure to calculate the dry matter and water contents on a mass basis (DSTU ISO 11465–2001). Determination of pH_{KCl} was carried out by the potentiometric method at the ratio of soil to a solution of 1.0 mol dm^{-3} KCl 1:2.5 using a pH meter "pH–301" and glass electrodes (DSTU ISO 10390:2007).

The content of mobile compounds of divalent and trivalent iron was determined according to DSTU 7913:2015 in an extract with a 0.1 N solution of sulphuric acid, followed by determination of the content of divalent iron and total iron in extracts (after reduction of trivalent iron to divalent iron with hydroxylamine) photocolorimetrically with o-phenanthroline. The soil: extractant ratio was 1:10.

Table 1
Scheme of the studied treatments of the field experiment (XI rotation)

Fertilisation system		Per 1 ha of crop rotation area			Corn for silage	Spring barley + + meadow clover	Meadow clover	Winter wheat
		rate of lime	Manure, Mg	NPK, kg				
Without fertilisers (control)	C	0	0	0	0	0	0	0
Organo-mineral with liming	OM1	1.0 dose by hydrolytic acidity (6.0 Mg ha^{-1})	10	$N_{65}P_{68}K_{68}$	Manure, 40 Mg ha^{-1}+ $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
	OM2	optimal by pH buffering capacity (2.5 Mg ha^{-1})	10	$N_{65}P_{68}K_{68}$	Manure, 40 Mg 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 dose by hydrolytic acidity (9.0 Mg 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 pH buffering capacity (2.5 Mg ha^{-1})	0	$N_{105}P_{101}K_{101}$	$N_{180}P_{135}K_{135}$	$N_{120}P_{135}K_{135}$	0	$N_{120}P_{135}K_{135}$

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The redox potential was measured potentiometrically during the growing season of winter wheat under field conditions using a platinum electrode and a silver chloride reference electrode according to DSTU ISO 11271:2004.

The obtained research results were processed using the software OriginPro 2019b (OriginLab Corporation, USA, 2019). Data were analysed using the Tukey test, with statistical significance set at $p < 0.05$. Results in the tables are presented as the arithmetic mean ± standard deviation (x ± SD).

3. Results and discussion

The dynamics of Fe in the rhizosphere are controlled by the combined effects of soil properties, uptake and activity of plants and microorganisms, and the interaction between them (Robin et al., 2008). Furthermore, plants' actual value of Fe uptake depends significantly on the fertiliser, the interaction between them and the fertiliser, and the harvest period (Ay et al., 2022).

The studies have shown that the composition of mobile iron in Albic Pantostagnic Luvisol is dominated by its oxidative form (Fe^{3+}), while the amount of ferrous iron (Fe^{2+}) is much lower. This pattern is observed in all experimental treatments during the growing season (Fig. 1a–b).

The highest average content of mobile iron compounds was observed during the spring season following months of elevated precipitation. It was the highest in the control treatment without fertilisers (C) – 207.2 mg kg^{-1} of soil, of which 160.6 mg kg^{-1} are Fe^{3+} compounds (Fig. 1a). This is due to the high acidity (pH_{KCl} was 4.30) of the soil solution, which, under conditions of calcium and magnesium deficiency (Ca content 1.8–2.0 cmol(+) kg^{-1} of soil and Mg 0.42–0.52 cmol(+) kg^{-1} of soil) (Olifir et al., 2017), contributes to increased iron mobility. It is known that soil pH is the most important parameter that affects the chemical composition of metal solutions and is the main variable that determines the adsorption of cations and anions (Bradl, 2004). In general, high acidity leads to increased mobility of many metals and their intensive uptake by plants (Jaguś and Skrzypiec, 2019).

On soils with high soil moisture, such as in early spring or during periods of significant rainfall, optimal conditions are created for anaerobic processes and the $Fe^{3+} \leftrightarrow Fe^{2+}$ cycle. Often, the resulting oxygen-free conditions stimulate the use of iron as an electron acceptor for carbon decomposition, and thus, an increase in the amount of Fe^{2+} as a reducing agent and decreasing Fe^{3+} (Calabrese and Porporato, 2019). These conditions, while beneficial for the formation of mobile Fe^{2+} compounds, are highly dependent on both soil moisture levels and the redox potential, which fluctuates seasonally.

With the mineral fertilisation system (M) at pH_{KCl} 4.35, the total mobile iron content is 146.2 mg kg^{-1} (Fig. 1a). Of these, 128.0 mg kg^{-1} are mobile trivalent iron compounds. In the mineral fertilisation system, the content of mobile iron compounds is lower than in control, despite the significant amount of iron supplied by mineral fertilisers. According to (Shahid et al., 2016), 5550 mg kg^{-1} of iron is additionally applied with superphosphate. However, consistent with previous findings from this experiment (Habryiel et al., 2006), the long-term and systematic

use of mineral fertilisers increases the content of inaccessible (insoluble) aluminium and iron phosphates for plants by 1.9 and 2.5, respectively, compared to the control treatment, where these values were 553 and 562 mg kg^{-1} of soil.

It is known that improving soil fertility and acidity management through a combination of organic and inorganic fertilisers can improve the efficient use of nutrients and increase agricultural productivity (Fekadu et al., 2018).

Studies (Daugherty et al., 2017) state that the bioavailability of iron depends on its solubility and oxidation, which are strongly influenced by complexation with natural organic matter. A study of the relationship between micronutrient availability and some soil properties showed that pH and organic matter are the most important properties that control micronutrient availability (Ammari and Mengel, 2006).

Long-term application of an organo-mineral fertilisation and liming system with 1.0 dose of $CaCO_3$ calculated by hydrolytic acidity (OM1) reduces the content of mobile Fe compounds in spring to 127.5 mg kg^{-1} (Fig. 1a). The content of Fe^{2+} compounds was 12.5 mg kg^{-1} at pH_{KCl} 5.45. An identical fertilisation system, but with liming by pH buffering capacity (OM2), gives a Fe^{2+} content of 12.8, with a total mobile Fe content of 117.7 mg kg^{-1} and a pH_{KCl} of 5.54.

With the introduction of 1.5 dose of NPK and 1.0 dose of $CaCO_3$ calculated by hydrolytic acidity (M1), the total content of Fe^{2+} and Fe^{3+} compounds was 126.4 mg kg^{-1} of soil (pH_{KCl} 5.23), of which mobile ferrous compounds are 21.3 mg kg^{-1} of soil. Under an identical fertilisation system and liming with a dose of lime according to the pH buffering capacity (M2), the content of mobile ferrous iron compounds is 20.1, with a total content of Fe^{2+} and Fe^{3+} of 119.1 mg kg^{-1} soil at pH_{KCl} 5.02.

It should be noted that in Ukraine when creating conditions for maximising yields, both in household plots and agricultural land, mineral fertilisers and a small amount of organic fertilisers are used mainly. Thus, these soil management practices may, to some extent, affect the accumulation of heavy metals and trace elements in soils, which should also be considered (Razanov et al., 2024).

During the summer, the content of mobile iron compounds showed a noticeable decrease compared to the spring, primarily due to reduced precipitation and higher temperatures, affecting soil moisture and iron mobility. In the control treatment without fertilisers (C), the total mobile iron content was 80.5 mg kg^{-1} of soil, consisting of 13.1 mg kg^{-1} Fe^{2+} and 67.4 mg kg^{-1} Fe^{3+} (Fig. 1b). The reduction in iron mobility can be attributed to lower soil moisture – 8.2% (Table 2), although the continued low soil pH (pH_{KCl} 4.19) still contributed to some degree of iron mobilisation.

In the mineral fertilisation system (M), the total mobile iron content in summer was 62.4 mg kg^{-1}. This decrease from spring levels is likely due to drier conditions (8.0%) and the ongoing transformation of iron into less mobile forms.

During the observation period, the content of Fe^{2+} in the organo-mineral fertilisation systems was highest in the summer, indicating a good supply of mobile iron compounds to the plants. This amount of Fe^{2+} (14.5 mg kg^{-1} and 18.6 mg kg^{-1} soil) and Fe^{3+} (54.1 mg kg^{-1} and 55.9 mg kg^{-1} soil) is within the optimal range for the plants' growth. The reduction of Fe^{3+} ions is largely
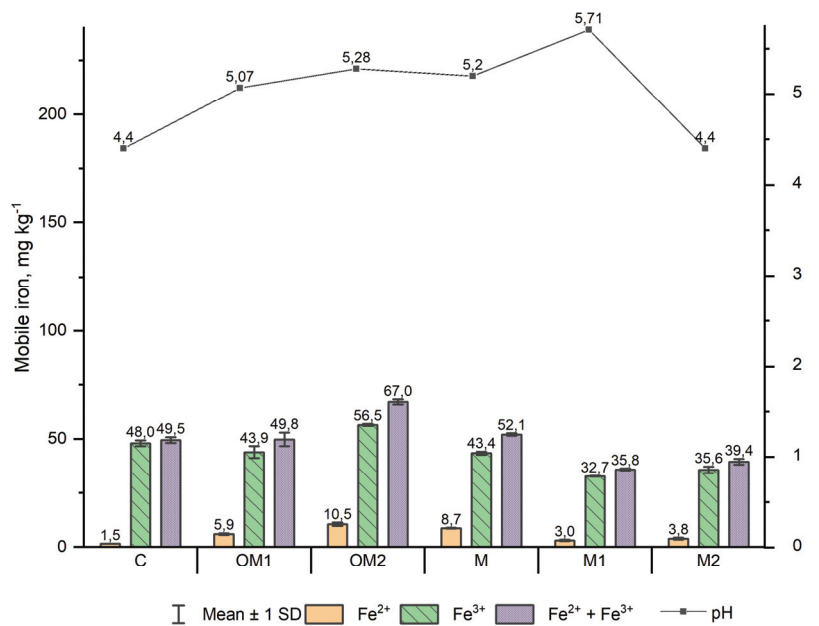
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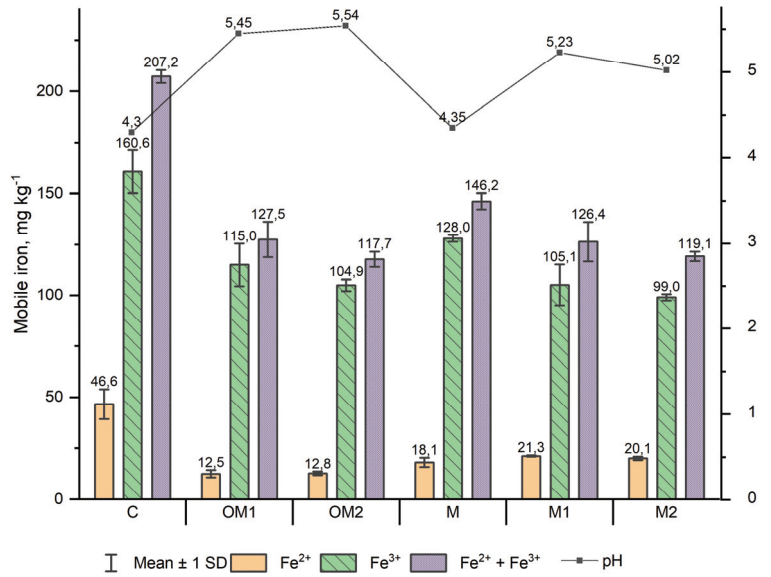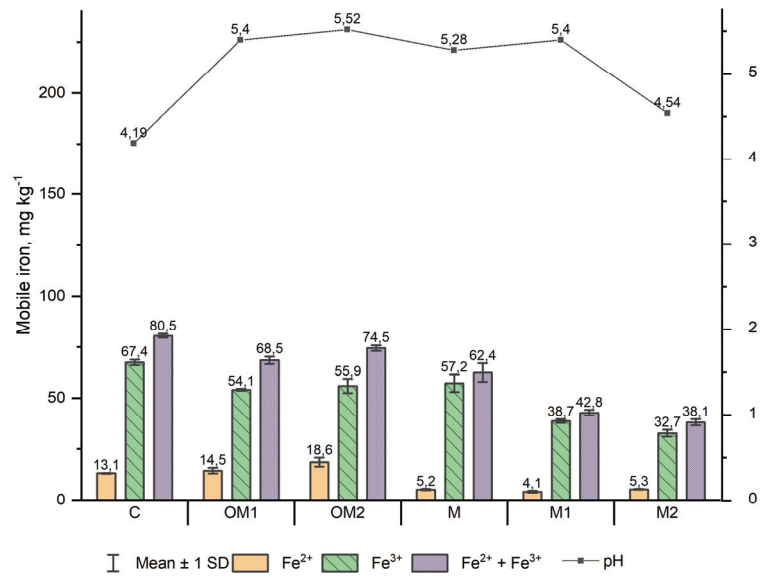
Fig. 1. Dynamics of mobile iron compounds of Albic Pantostagnic Luvisol depending on long-term anthropogenic influence in a) spring; b) summer; c) autumn

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Table 2

Dynamics of redox potential, pH_{KCl} and moisture in Albic Pantostagnic Luvisol by seasons of the year depending on different fertilisation systems (n = 6)

Treatment	Soil layer, cm	Spring			Summer			Autumn		
		redox potential, mV	pH_{KCl}	moisture, %	redox potential, mV	pH_{KCl}	moisture, %	redox potential, mV	pH_{KCl}	moisture, %
C	0–20	300±24[a]	4.30±0.02[a]	14.2±0.40[a]	341±23[a]	4.19±0.02[a]	8.2±0.53[a]	278±19[a]	4.40±0.08[a]	12.0±0.72[a]
	20–35	278±20[a]	4.20±0.04[a]	15.3±0.67[a]	335±16[a]	4.01±0.03[a]	8.8±0.74[a]	284±25[a]	4.30±0.02[a]	13.8±0.53[a]
OM1	0–20	405±18[b]	5.45±0.05[b]	11.3±0.31[b]	453±14[b]	5.40±0.09[b]	8.3±0.31[a]	331±22[ab]	5.07±0.03[b]	10.9±0.35[a]
	20–35	396±25[b]	5.35±0.02[b]	15.0±0.71[a]	439±15[b]	5.17±0.02[b]	8.6±0.40[a]	284±36[a]	5.10±0.09[bc]	12.8±0.30[a]
OM2	0–20	398±12[b]	5.54±0.01[c]	11.7±0.29[b]	489±13[b]	5.52±0.02[b]	8.2±0.31[a]	348±21[b]	5.28±0.02[c]	11.1±0.36[a]
	20–35	342±8[c]	5.57±0.07[c]	16.4±0.40[ab]	342±17[a]	5.23±0.02[b]	8.4±0.25[a]	320±15[a]	5.17±0.03[b]	12.8±0.87[a]
M	0–20	316±12[a]	4.35±0.01[a]	15.4±0.26[c]	387±20[a]	4.54±0.06[c]	8.0±0.50[a]	307±17[ab]	4.40±0.02[a]	12.0±0.55[a]
	20–35	289±27[a]	4.15±0.03[a]	16.5±0.56[ab]	339±16[a]	4.20±0.03[a]	8.2±0.25[a]	207±19[b]	4.26±0.01[a]	12.4±0.49[a]
M1	0–20	485±12[c]	5.23±0.01[d]	10.8±0.30[b]	453±30[b]	4.70±0.13[cd]	8.6±0.44[a]	360±22[b]	5.10±0.10[b]	11.8±0.47[a]
	20–35	391±12b[c]	5.52±0.02[c]	17.5±0.64[b]	403±15[b]	4.90±0.19[c]	8.8±0.38[a]	306±15[a]	5.30±0.15[b]	12.5±0.42[a]
M2	0–20	420±11[b]	5.02±0.01[e]	11.7±0.67[b]	458±29[b]	4.90±0.09[d]	8.4±0.55[a]	332±20[ab]	4.98±0.07[b]	11.0±0.50[a]
	20–35	396±15[b]	5.06±0.03[d]	17.8±0.61[b]	438±14[b]	5.06±0.09[bc]	8.8±0.56[a]	316±13[a]	4.96±0.02[c]	12.4±0.40[a]

Note. Values within a column for the same soil layer that share the same letter are not significantly different, as determined by the Tukey test (p < 0.05).

influenced by microbial activity and organic matter acting as electron donors (Annisa and Nursyamsi, 2017).

In the M1 treatment, which involved the application of 1.5 doses of NPK and a 1.0 dose of $CaCO_3$, the total mobile iron content was 42.8 mg kg^{-1}, with 4.1 mg kg^{-1} Fe^{2+} and 38.7 mg kg^{-1} Fe^{3+}. In the M2 system, the total mobile iron content was 38.0 mg kg^{-1}, with 5.3 mg kg^{-1} Fe^{2+} and 32.7 mg kg^{-1} Fe^{3+}.

Across all treatments, a general decrease in mobile iron content was observed from summer to autumn (Fig. 1c), with Fe^{2+} compounds showing the most significant reductions. The seasonal shifts in temperature, precipitation, and soil redox conditions likely played a significant role in reducing iron mobility, particularly the transformation of Fe^{2+} into Fe^{3+} as the soil environment changed.

In Albic Pantostagnic Luvisol, the content of mobile iron compounds is at the optimum level for crop growth. However, when reducing conditions prevail in the soil, which is created by high acidity and increased moisture, the amount of mobile iron compounds increases. This is especially evident in the control variant (no fertiliser) in the spring and, to a lesser extent, in summer. Under such conditions, iron as a nutrient can turn from a micronutrient into a toxicant, worsening the conditions of micronutrient nutrition and reducing crop productivity.

Iron toxicity depends on pH, organic carbon, groundwater level, nutrient status, and iron concentration. That is why iron toxicity occurs mainly in poorly drained inland valleys, often with lateral seepage and/or upward iron-containing water, coastal saline acidic soils, peat soils, acidic sulphate soils, and other hydromorphic soils (Suresh, 2005).

Engel et al. (2012) showed that excessive amounts of Fe^{2+} in the soil solution at low pH led to increased concentrations of Fe^{2+} in leaf cells, causing Fe toxicity. Therefore, to control iron toxicity, it is necessary first to regulate the pH and add organic matter, considering factors such as soil composition, iron forms and nutrient interactions.

According to Kome et al. (2019), adsorption reactions play a minor role in controlling the availability of Fe in soils. Instead, oxidation and precipitation reactions mainly control the concentration of Fe in soil solution.

That is why high pH, redox reactions, and saturation of the environment with phosphates and carbonates are the main factors that reduce the mobility of iron (Fernández and Ebert, 2005). In the study by Frohne et al. (2011), high concentrations of ferrous iron in soil solution are observed with a rapid decrease in Eh. If Eh value increases above +350 mV at pH 5, iron oxides and hydroxides are formed. That is why Fe solubility is mainly controlled by the formation of Fe (hydr)oxides under oxidising conditions and their dissolution under reducing conditions.

We tracked changes in the formation of the soil redox state of the experimental treatments. Redox processes are known to control the bioavailability, toxicity, concentration, and mobility of many major and trace elements, including Fe, in soil solutions (Borch, 2010; Mattila, 2024). Iron is the most abundant member of the redox-sensitive elements in soil. Redox reactions also change soil pH. For example, studies by (Nanzyo and Kanno, 2018) show that pH increases with the reduction of hydrated iron (III) oxide and decreases with the oxidation of ferrous iron (Fe^{2+}).

Studies (Annisa and Nursyamsi, 2017) have shown that the solubility and reactivity of iron oxides are affected by several factors, namely pH, soil redox potential (Eh) and environmental conditions. Changes in soil pH and Eh affect the stability and solubility of metal minerals. According to redox processes, organic carbon can reduce minerals directly or through biological reduction processes to form highly soluble Fe^{2+} (Xu and Tsang, 2024).

Changes in soil pH and redox conditions can alter the ability of the soil to retain or release organic matter and nutrients. For example, saturated conditions (anoxic environments) can favour the reductive dissolution of Fe(oxy)hydroxide minerals in the subsurface, whereas unsaturated conditions will create oxygenic conditions. This shift in redox conditions will either favour the dissolution or precipitation of Fe(oxy)hydroxide minerals, and in turn, the associated SOM and nutrients will be dissolved in the soil solution or sorbed to the surface (Franks et al., 2021).

It is known that a decrease in the redox potential leads to an excessive accumulation of Fe^{2+}, Mn^{2+}, and Al^{3+} compounds in the soil, which are toxic to plants and contribute to even more significant acidification of the soil, with adverse effects on plant nutrition and, ultimately, a sharp reduction in the yields of crops grown in crop rotation (Pozniak, 2010).

Studies have established that in a field of winter wheat, the lowest values of redox potential in the phase of spring tillering are in absolute control (C) and mineral fertiliser system (M). In the humus-eluvial horizon of 0–20 cm, Eh is 300 mV and 316 mV, characteristic of weakly-reductive processes (Table 2). Such values are closely related to these soils' water and thermal regimes, as hydrological fluctuations affect the soil's redox state. Soil moisture directly controls microbial respiration and the alternation of oxygen/anoxic conditions (Todd-Brown et al., 2012).

The highest average soil moisture in spring is observed in the mineral fertiliser system – 15.4% in the upper 0–20 cm horizon and 16.5% in the 20–35 cm horizon (Table 2), contributing to low (316 mV) Eh values. In the control treatment, the moisture content is slightly lower – 14.2% in the humus-eluvial arable horizon of 0–20 cm and 15.3% in the sub-arable horizon of 20–35 cm. However, it also led to the formation of weakly-reductive processes.

It is known that the reduction of Fe^{3+} compounds starts when the redox potential decreases to values of 300 mV and below. Particularly favourable conditions for forming soluble bivalent iron compounds are created at Eh values < 150–200 mV and an acidic reaction of the soil solution (Colombo et al., 2018). In our studies, the pH is 4.20 and 4.15, respectively, but the redox potential is higher than 200 mV. Therefore, moderately to weakly reducing conditions are created in 0–35 cm of soil.

In the organo-mineral fertilisation and liming system (OM1), the redox potential at the time of observation was 405 mV in the topsoil (0–20 cm) and 396 mV in subsoil (20–35 cm) humus-eluvial horizon, which is characteristic of weakly oxidative and weakly-reductive processes accordingly. When liming with a dose of $CaCO_3$ according to the pH buffering capacity (OM2), Eh in these horizons is 398 mV and 342 mV, which is evidence of weakly reductive processes according to the Khtryan scale

(Havryshko et al., 2020). In organo-mineral fertilisation systems with liming, the moisture content in OM1 is 11.3% in 0–20 cm and 15.0% in 20–35 cm soil layer and 11.7% and 16.4% in OM2, respectively.

In the mineral fertilisation system with liming (M1), the redox potential (Eh) in the topsoil (0–20 cm) was recorded at 485 mV. The moisture content in this horizon was 10.8%, which is lower than the control and organo-mineral systems. The Eh values indicate the presence of weakly oxidative conditions in the topsoil. Despite the slightly acidic pH values observed in the soil, the relatively high redox potential in the topsoil suggests that oxidative processes predominate in this fertilisation system, limiting the reduction of Fe^{3+} compounds and, thus, the formation of mobile Fe^{2+}.

In the M2 treatment, where liming was carried out based on pH buffering capacity, the redox potential in the topsoil (0–20 cm) was 420 mV. The moisture content in this system was slightly higher than in M1, at 11.7%, but did not differ significantly from M1. These Eh values indicate weak oxidising processes, where Eh values approach the threshold of reducing conditions. As a result, the M2 system creates more favourable conditions for the accumulation of mobile bivalent iron compounds compared to systems with more reducing environments.

The development of seasonal redox processes in the upper horizons of poorly structured soils is associated with seasonal surface excess moisture in spring or early summer, indicating a significant effect of soil moisture on redox potential. Preliminary studies of redox processes in Albic Pantostagnic Luvisol in the IX rotation of the control testify to the development of weakly oxidising processes in the soil profile. In the variant of systematic mineral fertilisation, there is a noticeable decrease in the redox potential in the direction of reduction processes (Havryshko et al., 2020).

In the dynamics of changes in the value of redox potential by the seasons and treatments, we observe some increases in the value of Eh in the summer months due to a decrease in humidity to 8.0–8.8% with preservation of regularities according to fertilisation and liming systems. This period coincides with the highest microbiological activity, intensive plant growth and development, and yield formation. Redox potentials are characterised as weakly reductive in the control (C) and mineral fertiliser system (M) in summer. Under the organo-mineral (OM1, OM2) and mineral fertilisation systems with liming (M1, M2), the intensity of oxidation-reduction processes increases to 453–489 mV and 453–458 mV in the topsoil, respectively, which makes it possible to classify them as weakly oxidative.

The decrease in redox potential in autumn and the absence of significant differences in Eh values between treatments are associated with both the attenuation of microbiological processes and the significant impact of torrential rains at the end of August, contributing to the increase in humidity in all treatments compared to the summer. At the same time, no significant differences in soil moisture were observed between the different fertilisation treatments. The moisture content remained relatively stable across all systems. In autumn, after harvesting winter wheat, the redox potential index decreases in all experimental treatments but to the greatest extent in the control and mineral

fertilisation system. The nature of redox processes in the experimental treatments is moderately and weakly reducing.

This consistency in moisture levels during summer and autumn contributed to the more uniform redox conditions across the treatments, influencing the mobility of iron and other micronutrients. Similar patterns are demonstrated by (Kyrylchuk and Bonishko, 2011), where abiotic factors (temperature, humidity, acidity) primarily determine the value of the redox potential for low-humus soils.

Therefore, understanding redox processes in soil dramatically improves the ability to characterise the related biogeochemical cycles and helps manage soil health. However, a key challenge in using redox as an indicator is that it changes rapidly depending on moisture and oxygen conditions (Zhang and Furman, 2021).

4. Conclusions

Oxidative processes generally predominate in Albic Pantostagnic Luvisol when used in agricultural systems. However, reduction processes can develop under waterlogged conditions, particularly when these soils are used without fertilisers or with continuous mineral fertilisation. The control treatment without fertilisers showed the highest mobile iron content, averaging 207.2 mg kg^{-1} in spring and 80.5 mg kg^{-1} in summer. Although continuous mineral fertilisation also led to weakly reducing conditions and a much smaller accumulation of mobile iron in the spring (146.2 mg kg^{-1}), the difference did not occur in summer and autumn.

The mobility and bioavailability of iron in Albic Pantostagnic Luvisol are significantly affected by soil properties such as pH, moisture, and redox potential, which fluctuate throughout the growing season.

During spring, the mobile iron content increased due to increased soil moisture, with Fe^{2+} (ferrous iron) ranging from 12.5 to 46.6 mg kg^{-1}. These conditions favour iron reduction and solubilisation in acidic and moist environments. However, soil moisture decreased to about 8.0–9.0% in summer, leading to a drop in mobile iron content as more oxidative processes dominated. The control treatment exhibited the highest mobile iron levels at 80.5 mg kg^{-1}, while organo-mineral systems with liming (OM1, OM2) promoted balanced redox conditions that optimised iron availability without excessive accumulation.

These seasonal fluctuations in iron mobility underscore the need for careful management of soil conditions to maintain stable iron availability for crops and prevent iron toxicity in acidic soils.

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