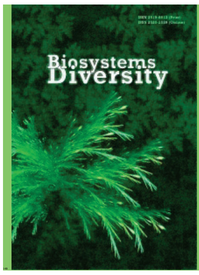

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Carbon dioxide emission and humus status of Albic Stagnic Luvisol under different fertilization regimes

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The increase in the carbon dioxide content in the atmosphere, which enhances the greenhouse effect and leads to climate change, is the fundamental scientific problem of nowadays. Modern approaches to fertility management technologies of acid soils based on the principles of resource conservation and environmental safety are presented. They are based on the results of the study of carbon dioxide emission intensity, humus status, and crop rotation productivity in a classic long-term agricultural experiment under the influence of long-term use of various fertilizer systems with the application of ameliorant doses calculated by pH buffering capacity and hydrolytic acidity. The organo-mineral fertilizer system with the addition of 10 t of manure per ha of crop rotation area + $N_{65}P_{68}K_{68}$, liming with a $CaCO_3$ dose calculated according to pH buffering capacity (2.5 t/ha) contributes most to the optimization of soil processes. At the same time, it ensures the rational use of fertilizers and ameliorants, preservation of fertility, optimizes the processes of humus formation and carbon dioxide release. A high level of productivity of Albic Stagnic Luvisols forms under these conditions – 7.38 t/ha of grain units. Application of 1.0 and 1.5 lime norms calculated according to soil hydrolytic acidity with organic-mineral and mineral fertilizer systems on Albic Stagnic Luvisols in a short four-field crop rotation is not only a high-cost measure. However, it causes significant carbon loss in the form of CO_2 due to additional mineralization. It is accompanied by calcium leaching and creates environmental problems in the conditions of the periodic washing-off water regime. Therefore, liming by $CaCO_3$ dose calculated according to acid-base buffering capacity should be carried out before each of the following rotations in order to harmonize the environmental and productive functions of Albic Stagnic Luvisols in the short crop rotation. The obtained research results will be used to improve the methodology for determining carbon dioxide emissions and predicting the effect of various fertilizer and liming systems on its balance in the soil.

Keywords: mineral fertilizers; liming; soil acidity; soil buffering capacity; CO_2; crop rotation productivity.

Introduction

Acid degradation of soils is one of the most acute problems of agriculture, today and in the future. The process of soil acidification is becoming global. It leads to the deterioration of the agroecological condition and loss of one of the main soil functions – fertility. Acidic soils account for approximately four billion hectares worldwide (30–40% of arable land) and are distributed mainly in tropical and subtropical regions (Martins et al., 2014). Acidic soils occupy approximately 5,500,000 ha of the arable land in Ukraine, including 636.1 thousand ha of strongly acidic soils (Tsapko et al., 2018).

The urgent need for early diagnosis of changes in transformed ecosystems and its components is forcing intensification of the search for new types of indicators that objectively reflect the agroecological state of the soil. The accumulation of carbon dioxide in the ground air and the intensity of its emission from the soil into the atmosphere is a sensitive indicator that responds instantly to the disturbances in the balanced natural cycles of substances, in particular carbon (Demydenko & Velychko, 2014; Gorban et al., 2020).

According to Houghton (2007), Silva-Olaya et al. (2013) and Oertel et al. (2016), the soil is the largest exchangeable natural reservoir and source of nutrient carbon in terrestrial ecosystems. It contains 2300 Gt of carbon, which exceeds the total stock of this chemical element in the atmosphere (800 Gt) and phytomass (550 Gt). The CO_2 flux from the soil surface is 60 Gt of carbon per year. As a result, atmospheric carbon dioxide in terrestrial ecosystems is about 25–40% of soil origin, according to (Bouwman & Germon, 1998), or even 80–90% according to (Dobrovolsky & Nikitin, 2012). In recent years, there has been an increase in the average global concentration of greenhouse gases in the atmosphere, including carbon dioxide,due to significant climate change (Bedernichek, 2017; Green et al., 2019).

CO_2 emission from soil to the atmosphere, or soil respiration, is an essential component of the carbon cycle in terrestrial ecosystems (Bradford & Ryan, 2008). However, carbon emission fluxes are one of the least known parts of the surface carbon cycle, depend on many factors and vary significantly in time and space (Mukhortova et al., 2015). Therefore, according to Smith (2016), an extremely relevant and essential point is an in-depth study of factors and processes that occur in the soil under the influence of anthropogenic factors and have a direct effect on the growth of CO_2 emission. Carbon dioxide emission is also closely related to the type of land use, depends on the hydrothermal conditions of the territory, types of vegetation and is an essential factor in the regulation of plant growth and development, soil biota, migration and accumulation of many chemical compounds (Miroshnychenko et al., 2011). The intensity of CO_2 emission is also affected by soil acidity. Therefore, changing the soil reaction by liming of acidic soils affects the emissions of carbon dioxide from the soil, and additional carbonate releasesas CO_2 (Snyder et al., 2009).

Data on CO_2 emissions from soils during the crop growing season is an integral component of assessing their fertility level. Moreover, the values of CO_2 emission by soils, together with their ability to sequester organic carbon in the context of climate change, can form a criterion base for sustainable land use (Trofimenko & Trofimenko, 2018).

Crop residues are valuable sources of soil carbon that have a significant impact on CO_2 sequestration and emission (Wang et al., 2020). The return of crop residues is a promising option for increasing soil organic carbon, which causes an increase in crop yield under environmentally sustainable agriculture and helps to mitigate the negative factors in climate change (Wang et al., 2020).

Labile organic matter is the primary source of carbon dioxide. It can be used to estimate the intensity of soil organic matter mineralization. Labile organic carbon is a more sensitive indicator of CO_2 emissions and changes in organic matter compared to other carbon fractions (Ibrahim et al., 2015). Labile organic matter can be easily lost depending on technologies, thereby increasing the concentration of CO_2 in the atmosphere (Segnini et al., 2019).

Indeed, changes in soil organic carbon are primarily associated with labile forms (He et al., 2016). The carbon of the labile soil organic matter itself is a critical component of the cycle due to its dynamism. However, how the processes of organic matter mineralization and CO_2 emission transform in response to climate change needs further research (Dmytruk & Demyd, 2019).

Continuous long-term application of manure effectively increases the content of organic carbon and its active fractions in the soil, contributing to soil fertility and carbon sequestration in farming systems (Zhao et al., 2017). Human intervention should seek to achieve a balance between carbon dioxide emissions and their absorption by both reducing anthropogenic emissions and increasing biotic runoff and replenishing soil organic carbon, which is considered a principal direction in the strategy to minimize climate disturbances (Minasny et al., 2017).

Therefore, the study of the ecosystem's functional state, which determines a particular level of carbon dioxide production, is very relevant. The survey of losses or accumulation of organic matter will primarily contribute to the application of practical measures aimed at the carbon sequestration in the soil and environmental stability.

Objective information about the state and changes of agroecosystems, its components under the influence of various anthropogenic loads, can be obtained only in long-term agricultural experiments. In this regard, the results of studying carbon dioxide emissions depending on different fertilizer and liming systems in long-term agricultural experimenton Albic Stagnic Luvisol are noteworthy.

Our research aimed to investigate in a long-term agricultural experiment the effect of prolonged use of various fertilizer systems and periodic liming on the intensity of carbon dioxide emissions from Albic Stagnic Luvisol during the growing season of winter wheat and corn for silage.

Materials and methods

A research study was performed in the classical long-term agricultural experiment of the Laboratory of Agricultural Chemistry of the Institute of Agriculture of the Carpathian Region of NAAS, established in 1965 and registered as a long-term agricultural field experiment of NAAS (NAAS registration certificate No. 29).

The agricultural experiment was located in three fields, each of which had 18 variants in triplicate. The arrangement of variants was single-tier, sequential. The total area of the plot was 168 m^2, accounting – 100 m^2. Crop rotation is four-field with the following crops: corn for silage – spring barley with the sowing of meadow clover – meadow clover – winter wheat. Agricultural cultivation techniques, tillage, and crop care are generally acceptable for the conditions of the Western Forest-Steppe zone.

Agrochemical characteristics of the arable layer of the soil before the establishment of the experiment were as follows: humus content (by Tyurin) – 1.42%, pH_{KCl} – 4.2, hydrolytic acidity (by Kappen) – 4.5 mg-eq./100 g of soil, exchangeable acidity (by Sokolov) – 0.6 mg-eq./100 g of soil, mobile aluminum (by Sokolov) – 60.0 mg/kg, mobile phosphorus (by Kirsanov) – 36.0 mg/kg, exchangeable potassium (by Maslova) – 50.0 mg/kg.

The experiment used semi-overripe cattle manure with straw bedding, ammonium nitrate (34.5%), granular superphosphate (19.5%), potassium salt (40%), nitroammophos (NPK 16%) (when using nitroammophos NPK content was balanced with simple fertilizers). Manure (40–60 t/ha) was applied before corn. Phosphorus-potassium fertilizers were applied in autumn, and nitrogen – before pre-sowing cultivation. Liming, according to the scheme, was carried out before the start of the ninth rotation. The dose of fertilizer application was also adjusted before the start of the IX rotation. Limestone flour (93.5% $CaCO_3$) was used as limestone material. Starting with the VIII rotation, the second mowing of meadow clover was plowed as fertilizer in all variants of the experiment.

Carbon dioxide emissions by Albic Stagnic Luvisol (light grey forest surface-gleyed soil) depending on long-term fertilization and periodic liming were studied during winter wheat vegetation (during 2017–2018 on II and III fields in the phase of spring tillering (BBCH26), stem elongation (BBCH31-33), full ripeness (BBCH89)) and corn for silage (during 2016–2018 on I, II and III field is in the phase of sprouting (BBCH09), 5–6 leaves (BBCH25-26), milk ripeness (BBCH75-77)). CO_2 was measured in the following variants: absolute control (without fertilizing), an organo-mineral fertilizer system (10 t manure per ha of crop rotation area + $N_{65}P_{68}K_{68}$) with periodic liming by 1.0 norm of $CaCO_3$ according to hydrolytic acidity (6.0 t/ha of limestone flour) and similar fertilizer systems with application of the optimal dose of lime, calculated according to the acid-base buffering capacity (2.5 t/ha); mineral fertilizer system ($N_{105}P_{101}K_{101}$) with liming by 1.5 norms $CaCO_3$ according to hydrolytic acidity (9.0 t/ha) and with an application of $CaCO_3$ according to acid-base buffering capacity (2.5 t/ha) and mineral ($N_{65}P_{68}K_{68}$) fertilizer system (Table 1).

The intensity of carbon dioxide emission from the soil surface was determined in the field using a two-channel infrared gas analyzer CO_2-meter K-30 Probe and corresponding software (DAS 100). Measurements were performed by the chamber-static method (Pumpanen et al., 2004) during the growing season of winter wheat and corn for silage in the indicated phases of vegetation. Gas analyzer measured the intensity of CO_2 emission from the soil surface (0.023 m^2) in a closed, isolated chamber (volume 4.5 L), immersed in the soil for 0.05 m for a fixed time (30 minutes) followed by calculation of carbon dioxide emissions. Due to the significant dynamics of the gas regime, we present the average data of CO_2 emission measurements obtained in the morning, day, and evening in the field of corn for silage in three fields of the long-term agricultural experiment in IX crop rotation. Measurements were performed 3–5 times a day, followed by determination of the average value.

Results of CO_2 concentration in ppm we translated in mL/m^2 with the subsequent calculation of the mass concentration in mg/m^2 using Avogadro's law to obtain comparable values characterizing the amount of carbon dioxide emitted from the soil depending on the fertilizer and liming systems. It makes it possible to account for carbon fluxes from the soil and use the results in future balance calculations of the carbon cycle.

Table 1
Characteristic of experimental variants (IX, X crop rotation)

Fertilizer system		Applied to 1 hectare of crop rotation area: rate of lime	rate of lime	NPK, kg of the active substance	Corn for silage	Spring barley + meadow clover	Red clover	Winter wheat
Without fertilizers (control)	C	0	0	0	0	0	0	0
Organo-mineral with liming	OM1	1.0 norm according to hydrolytic acidity (6.0 t/ha)	10	$N_{65}P_{68}K_{68}$	Manure, 40 t/ha + $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	0	$N_{70}P_{90}K_{90}$
	OM2	optimal according to acid-base buffering capacity (2.5 t/ha)	10	$N_{65}P_{68}K_{68}$	Manure, 40 t/ha + $N_{120}P_{90}K_{90}$	$N_{70}P_{90}K_{90}$	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 norm according to hydrolytic acidity (9.0 t/ha)	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 according to acid-base buffering capacity (2.5 t/ha)	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 taken from the arable layer (0–25 cm) of Albic Stagnic Luvisol (light grey forest surface-gleyed soil) and prepared for analysis according to DSTU ISO 11464-2001. Exchangeable acidity and total organic matter content were studied after harvesting cultivated crops. The pH_{KCl} was measured by the potentiometric method according to DSTU ISO 10390-2001, the amount of total organic matter – by the Turin method (DSTU 4289:2004). The content of labile organic compounds was determined during vegetation of winter wheat and corn for silage by the Egorov method, followed by their oxidation by the Turin method in the modification by Nikitin (DSTU 4732-2007).

Climatic conditions for the years of research 2016–2018 had their characteristics. There were temperature changes and sharp changes in precipitation, especially in the autumn–winter periods. During the growing season of winter wheat and corn for silage, the temperature was higher in all months compared to the average long-term norm. The deviation of the average monthly air temperature was +1.4…+2.2 °C in spring and +1.9…+2.8 °C in summer. The amount of precipitation during the years of research was insufficient throughout the growing season. Thus, compared to the average long-term data at the beginning of plant growth and development in April–May, there was a decrease in rainfall by 11.7–4.2 mm, and an even more significant shortage characterized the subsequent period of intensive growth and crop formation in summer (June–August) – 13.6–34.5 mm. 2016–2018 there were temperature differences and sharp changes in precipitation, especially in the autumn-winter periods. During the growing season of winter wheat and corn for silage the temperature was higher compared to the average long-term norm in all months. The average monthly air temperature deviated by +1.4…+2.2 °C in spring and by +1.9…+2.8 °C in summer. The amount of precipitation during the years of research was insufficient throughout the growing season. At the beginning of plant growth and development in April–May, there was a decrease in rainfall by 11.7–4.2 mm compared to the average long-term data. The subsequent period of intensive growth and crop formation was characterized by an even more significant shortage of precipitation (–13.6–34.5 mm) in summer (June–August).

The data were compared using Tukey's test. Differences between the samples were considered statistically significant at $P < 0.05$. The data was analyzed in OriginPro2019b (OriginLab Corporation, USA, 2019). The data in the tables are presented as an arithmetic mean with standard deviation (x ± SD).

Results

The intensity of CO_2 emission in the field of winter wheat during spring was not high, slightly varied between variants, and was 7.3–13.5 ppm/min in control without fertilizers. In the variant of the organo-mineral fertilizer system with liming by 1.0 dose of $CaCO_3$ according to hydrolytic acidity, it was 10.5–14.7 ppm/min and slightly exceeded the similar fertilizer system with the lime application by acid-base buffering capacity (9.8–13.7 ppm/min). Under the mineral fertilizer system, the carbon dioxide emission rate was up to 8.7–13.0 ppm/min (Fig. 1).

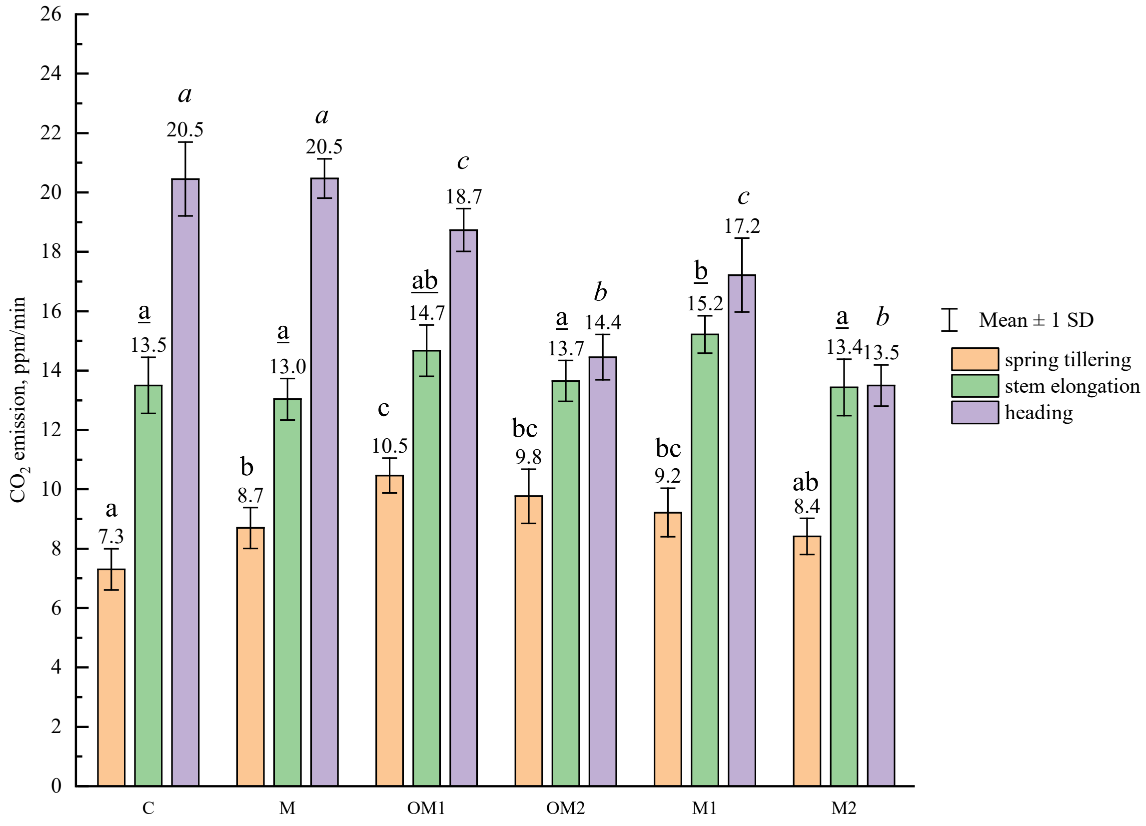

Fig. 1. CO_2 emission under winter wheat in the period of intensive growth and development, the end of the IX rotation (average for 2016–2017, n = 6): means labeled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test ($P < 0.05$); different lowercase letters indicate statistical significance between variants in the phase of spring tillering; underlined letters – in the phase of stem elongation; italic letters – in the heading phase; fertilizer systems: C – control without fertilizers; M – mineral without liming; OM1 – organo-mineral with liming by 6.0 t/ha; OM2 – organo-mineral liming by 2.5 t/ha; M1 – mineral with liming by 9.0 t/ha; M2 – mineral with liming by 2.5 t/ha

The intensity of CO_2 emissions in the summer increased in all variants. In the control variant and mineral fertilizer system, it was the highest and reached 20.5 ppm/min. It indicates increased mineralization of organic matter of Albic Stagnic Luvisol at high acidity of the soil solution both without fertilizers and with a mineral fertilizer system. In the variants of the organo-mineral fertilizer system with liming by 1.0 dose of $CaCO_3$ according to hydrolytic acidity, the intensity of CO_2 emission was 18.7 compared to 14.4 ppm/min in the similar fertilizer system with liming by $CaCO_3$ dose, calculated according to acid-base buffering capacity. Under the mineral fertilizer system with liming by 1.5 norms of $CaCO_3$ according to hydrolytic acidity, the intensity of CO_2 emission also exceeded the variant of the similar fertilizer system with application of lime according to acid-base buffering capacity. It was 17.2 compared to 13.5 ppm/min accordingly. With a sharp decrease in air temperature from 19 °C to 5 °C for two days in autumn after plowing the intensity of carbon dioxide in the variant of the organo-mineral fertilizer system with liming more than halved from 14.9 to 6.7 ppm/min.

The dynamics of carbon dioxide emission in the field of corn for silage, which begins X crop rotation, had its characteristics, which are caused not only by the influence of various fertilizer systems but also by the duration of the lime application aftereffect. In particular, a gradual decrease of the application efficiency of 2.5 t of $CaCO_3$ calculated according to acid-base buffering capacity compared to 6.0 and 9.0 t/ha of $CaCO_3$ calculated by hydrolytic acidity was observed over the four years of IX rotation. Therefore, there is a direct correlation between the acidity (pH_{KCl}) and the intensity of CO_2 emission in the studied variants.

Early spring tillage and sowing in the field of corn for silage is also a vital factor, which causes additional mineralization and more intensive carbon dioxide emission, especially in the early stages of growth and development of corn plants compared to the field of winter wheat. During germination and in the phase of 5–6 leaves the intensity of CO_2 emission was the highest in control (13.3–6.0 ppm/min) and the variant of the mineral fertilizer system (9.7–5.6 ppm/min) with pH_{KCl} 4.22 and 4.03 respectively (Fig. 2). In the variants of organo-mineral and mineral fertilizer systems with liming by 1.0 dose of $CaCO_3$ by hydrolytic acidity,the intensity of CO_2 emission was 4.7–6.5 compared to 6.5–7.7 ppm/min in a similar fertilizer system with liming with a dose of $CaCO_3$ calculated by the acid-base buffering capacity. This dependence persisted throughout the vegetation period. It somewhat smoothened before harvesting and reached 11.9–9.3 ppm/min with pH_{KCl} 5.18 and 5.53 in the variants of organo-mineral and mineral fertilizer systems with application of 1.0 and 1.5 doses of $CaCO_3$ according to hydrolytic acidity compared to 15.0–9.7 ppm/min with pH_{KCl} 5.00 and 4.82 with liming with the optimal dose of $CaCO_3$ according to the acid-base buffering capacity. It indicates the advisability of re-liming (after four years of IX rotation) with the optimal dose of $CaCO_3$, calculated by the acid-base buffering capacity. Thus, an increase in the acidity of the soil solution increases the level of soil production of carbon dioxide and its additional losses. Previous studies of the humus state of light grey forest surface gleyed soil have shown that the content of mobile fulvic acids in humus increases to 22.54–22.64% with increasing acidity.

It indicates the advisability of re-liming (after four years of their rotation) with an optimal dose of $CaCO_3$ calculated by acid-base buffering. Thus, an increase in the acidity of the soil solution increases the level of carbon dioxide production by the soil and its additional losses. The content of mobile fulvic acids in the humus increased by 22.54–22.64% with an increase in acidity, as shown in previous studies of the humus state of Albic Stagnic Luvisol.

Although Ukraine participates in measures to counter global climate change, today, as in most countries of the world, we do not have reliable data on the share of the total carbon balance by agroecosystems under various anthropogenic impacts. These issues are fundamental because, in the new climatic conditions, the requirements and tasks for agricultural science are changing. Early diagnosis of changes that occur in transformed ecosystems is one of the main ones. Since anthropogenic impact leads to an imbalance of the carbon cycle in agrocenoses, it is crucial to establish the CO_2 production levels depending on the characteristics of soil use and the intensity of anthropogenic impact.

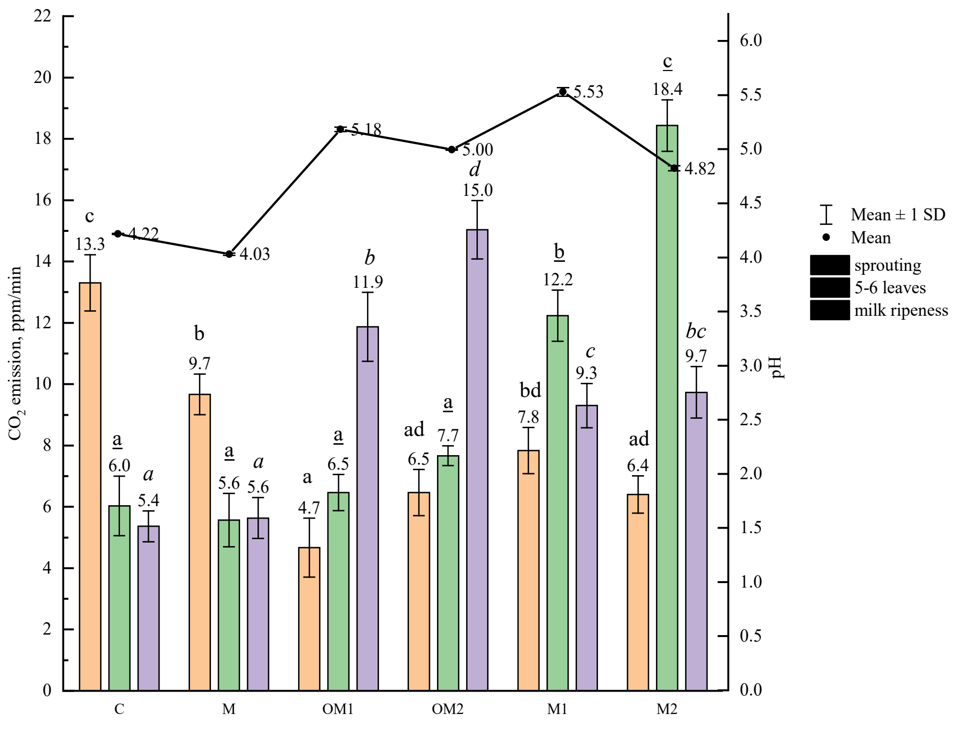

Fig. 2. CO_2 emission under corn for silage depending on acidity in X rotation (average for 2016–2018, n = 9): means labeled with the same letter are not significantly different from each other according to the results of comparison using the Tukey test ($P < 0.05$); different lowercase letters indicate statistical significance between variants in the phase of spring tillering; underlined letters – in the phase of stem elongation; italic letters – in the heading phase; fertilizer systems: C – control without fertilizers; M – mineral without liming; OM1 – organo-mineral with liming by 6.0 t/ha; OM2 – organo-mineral with liming by 2.5 t/ha; M1 – mineral with liming by 9.0 t/ha; M2 – mineral with liming by 2.5 t/ha

Studies have shown that in the field of corn for silage, the emission of CO_2 to the surface layer of the atmosphere changes up to three times during the day. It depends on the level of fertilizer, doses of lime, and the phase of development. In the germination phase, the losses of carbon dioxide during all hours of observations are highest in the control variant without fertilizers due to the influence of the cultivation and sowing, which cause additional mineralization of the soil organic matter. As a result, there is higher CO_2 emission in variants with high acidity of the soil solution (pH_{KCl} is 4.22). The highest losses of carbon dioxide were recorded at 14.00.

This time dependence is in all variants of the experiment during the entire growing season (Table 2). In the germination phase in control without fertilizers, the loss of carbon in the form of CO_2 reached 0.40 g/m^2 at 14.00 and gradually reduced to 0.16 g/m^2 before harvesting. In the variants of organo-mineral and mineral fertilizer systems with liming by 1.0 and 1.5 $CaCO_3$ norms according to hydrolytic acidity, carbon dioxide emission from the soil in the germination phase was 0.28 and 0.27 g/m^2 compared to 0.17 and 0.16 g/m^2 in similar fertilization systems with liming by $CaCO_3$ dose, calculated according to the acid-base buffering capacity.

Table 2
CO_2 emission (g/m^2) from Albic Stagnic Luvisol under corn for silage depending on long-term fertilization and periodic liming (x ± SD, n = 9)

Plant	Growth stage	Hours	Fertilization 1 ha of crop rotation area: without fertilizers (control)	manure, 10 t/ha + $N_{65}P_{68}K_{68}$ + $CaCO_3$, 1.0 norm according to hydrolytic acidity	manure, 10 t/ha + $N_{65}P_{68}K_{68}$ + $CaCO_3$, optimal according to the acid-base buffering capacity	$N_{105}P_{101}K_{101}$ + $CaCO_3$, 1.5 norm according to hydrolytic acidity	$N_{105}P_{101}K_{101}$ + $CaCO_3$ optimal according to the acid-base buffering capacity
Corn for silage	sprouting	6.00	0.247 ± 0.018^a	0.105 ± 0.011^b	0.091 ± 0.017^b	0.221 ± 0.024^a	0.109 ± 0.016^b
		14.00	0.398 ± 0.019^a	0.283 ± 0.026^b	0.171 ± 0.025^c	0.276 ± 0.007^b	0.163 ± 0.009^c
		22.00	0.228 ± 0.018^a	0.171 ± 0.021^b	0.084 ± 0.021^c	0.176 ± 0.010^b	0.103 ± 0.025^c
	5-6 leaves	6.00	0.129 ± 0.017^a	0.245 ± 0.012^b	0.111 ± 0.013^a	0.217 ± 0.021^c	0.171 ± 0.008^d
		14.00	0.171 ± 0.034^a	0.516 ± 0.024^b	0.329 ± 0.018^c	0.338 ± 0.026^c	0.217 ± 0.017^d
		22.00	0.106 ± 0.011^a	0.401 ± 0.039^b	0.244 ± 0.011^c	0.305 ± 0.034^d	0.185 ± 0.026^e
	milk ripeness	6.00	0.113 ± 0.009^a	0.274 ± 0.017^b	0.164 ± 0.029^c	0.249 ± 0.040^b	0.165 ± 0.011^c
		14.00	0.163 ± 0.010^a	0.327 ± 0.025^b	0.167 ± 0.020^a	0.286 ± 0.027^c	0.176 ± 0.024^a
		22.00	0.101 ± 0.012^a	0.254 ± 0.017^b	0.139 ± 0.010^c	0.234 ± 0.018^b	0.139 ± 0.024^c

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

As plants grew and developed, the losses of carbon dioxide increased significantly and amounted to 0.51–0.35 g/m^2 in the phase of 5–6 leaves in the indicated variants compared to 0.33–0.21 g/m^2 in fertilizer systems with liming with the optimal dose of $CaCO_3$. Before harvesting, they reduced to 0.32–0.29 compared to 0.17–0.18 g/m^2 of the studied agroecosystems with the application of the optimal dose of $CaCO_3$ calculated by the acid-base buffering capacity. The losses were lower in all variants of the experiment in the morning and evening. However, when applying high doses of lime, calculated according to hydrolytic acidity, losses significantly prevailed over similar fertilizer systems with liming with the optimal dose calculated on acid-base buffering capacity and reached up to 0.27–0.25 against 0.16 g/m^2 before harvesting.

We studied the dynamics of labile organic compounds, which are the starting points for the creation of stable humic substances in the fields of winter wheat and corn for silage. At the same time, due to enzymatic and oxidative processes, they are quickly mineralized and serve as a source of energy for microorganisms and as the most available nutrients for plants. Long-term use of the mineral fertilizer system on Albic Stagnic Luvisol and the use of this soil without fertilizers reduced pH_{KCl} to 4.03 and 4.22 respectively. It mostly contributed to the growth of the labile humus compounds' content to 0.58–0.66% in the field of winter wheat and to 0.54–0.61% under corn for silage. At the same time, the accumulation in these variants primarily of mobile fulvic acids of the 1 + 1"a" fraction is observed, which is capable of rapid mineralization and migration along with the profile. The indicated dependence, together with a decrease in the pH_{KCl}, indicates the negative consequences of this anthropogenic impact and leads to increased soil degradation (Table 3). The content of labile humus did not change significantly with the application of the same doses of manure and mineral fertilizers, both with liming with a dose of $CaCO_3$ calculated by hydrolytic acidity and acid-base buffering capacity under winter wheat. It reaches 0.56–0.55–0.46% and 0.58–0.57–0.48% during wheat growing. In the field of corn for silage, these numbers are 0.52–0.52–0.50% and 0.52–0.47–0.44% accordingly. The use in Albic Stagnic Luvisol of much lower rates of lime calculated by pH buffering capacity is not only cost-effective but also contributes to maintaining the environmental stability of the agroecosystem (Table 3).

Table 3
Change of humus state of Albic Stagnic Luvisol depending on fertilizer levels (x ± SD, n = 9)

Fertilization 1 ha of crop rotation area	Labile organic matter, %: winter wheat: spring tillering	winter wheat: stem elongation	winter wheat: milk ripeness	corn for silage: 3–5 leaves	corn for silage: inflorescence emergence	corn for silage: milk ripeness	Total humus, %	Humus, stocks, t/ha
Without fertilizers (control)	0.582 ± 0.043^a	0.606 ± 0.030^a	0.580 ± 0.019^a	0.605 ± 0.010^a	0.562 ± 0.015^a	0.540 ± 0.006^a	1.484 ± 0.014^a	40.674 ± 0.390^a
Manure, 10 t/ha + $N_{65}P_{68}K_{68}$ + $CaCO_3$, 1.0 norm according to hydrolytic acidity	0.556 ± 0.015^a	0.554 ± 0.013^b	0.461 ± 0.036^{bc}	0.527 ± 0.024^b	0.522 ± 0.019^a	0.505 ± 0.037^{ac}	1.927 ± 0.047^b	52.791 ± 1.292^b
Manure, 10 t/ha + $N_{65}P_{68}K_{68}$ + $CaCO_3$, optimal according to the acid-base buffering capacity	0.576 ± 0.022^a	0.568 ± 0.021^b	0.480 ± 0.017^{bd}	0.523 ± 0.021^b	0.468 ± 0.019^b	0.440 ± 0.009^b	1.754 ± 0.040^c	48.072 ± 1.105^c
$N_{65}P_{68}K_{68}$	0.631 ± 0.015^b	0.660 ± 0.018^c	0.574 ± 0.013^a	0.557 ± 0.008^b	0.575 ± 0.033^a	0.542 ± 0.017^a	1.576 ± 0.015^d	43.170 ± 0.436^d
$N_{105}P_{101}K_{101}$ + $CaCO_3$, 1.5 norm according to hydrolytic acidity	0.474 ± 0.035^c	0.437 ± 0.026^d	0.442 ± 0.027^c	0.447 ± 0.026^c	0.448 ± 0.021^b	0.432 ± 0.019^b	1.699 ± 0.067^c	46.550 ± 1.840^c
$N_{105}P_{101}K_{101}$ + $CaCO_3$ optimal according to the acid-base buffering capacity	0.517 ± 0.026^d	0.501 ± 0.012^e	0.498 ± 0.021^d	0.537 ± 0.019^b	0.550 ± 0.029^a	0.500 ± 0.025^c	1.620 ± 0.027^d	44.388 ± 0.750^d

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

The content of labile organic matter in both winter wheat and corn fields was higher and close to the control values without fertilizers under the mineral fertilizer system. With a low level of crop rotation productivity, this indicates additional losses of mobile humus compounds at high acidity of the soil solution. The mineral fertilizer system with liming with both according to hydrolytic acidity and acid-base buffering capacity reduced the content of labile humus compounds in the soil in the field of winter wheat to 0.44–0.50% and the field of corn for silage to 0.43–0.50 before harvest.

Mathematical models based on correlation-regression analysis were created according to the results of the research. They show the relationship between the intensity of CO_2 emission depending on the content of labile humus and acidity under winter wheat and corn for silage during intensive growth under different fertilizer systems (Table 4). The given multiple correlation coefficient ($R = 0.820–0.882$) confirms the close relationship between the indicators included in the equations, and the determination coefficient ($R^2 = 0.672–0.778$) indicates a significant influence of labile humus (argument – x) and pH_{KCl} (argument – x_1) on the intensity of CO_2 emission (function – Y).

The results indicate that the nature and speed of humus formation are strictly related to the system of fertilization and liming of crops on low nutrient content Albic Stagnic Luvisol. At the end of the ninth rotation, the highest humus content of 1.93 ± 0.05% was in the organo-mineral fertilizer system with liming with the joint application of the full dose of mineral fertilizers $N_{65}P_{68}K_{68}$, 10 t/ha of manure and 1.0 norm of lime according to hydrolytic acidity. Humus stocks increased to 52.88 ± 1.37 t/ha simultaneously. The use of a similar fertilizer system but with liming according to acid-base buffering capacity increased the humus level to 1.76 ± 0.04% and stocks to 48.22 ± 1.10 t/ha (Table 3).

The decrease in the total humus content and its stocks in the variant of organo-mineral fertilizer system with liming by the $CaCO_3$ dose calculated according to acid-base buffering capacity compared to the dose of lime according to hydrolytic acidity after four years of IX rotation was primarily due to the systematical application of limestone and sulfur waste of Rozdil Mining and Chemical Plant during the previous eight rotations. At the end of the eigthth rotation, humus content was 1.72%.

Co-application in the crop rotation of the increased dose of mineral fertilizers $N_{105}P_{101}K_{101}$ and 1.5 norms of lime according to hydrolytic acidity did not show proper efficiency on influence on the content of humus and its stocks. The humus content was only 1.69 ± 0.06%, and the stock was 46.30 ± 1.64 t/ha and inferior to the efficiency of organo-mineral fertilizer systems. This fertilizer system,with liming according to the acid-base buffering capacity, contributed compared with the control variant to an even smaller increase up to 1.62 ± 0.02% in the humus content. It indicates that the effectiveness of the combined use of organo-mineral fertilizers and lime in terms of the impact on humification processes in acidic Albic Stagnic Luvisol prevails over mineral fertilizer systems with liming. Long-term systematic application (more than 50 years) of mineral fertilizers increased the humus content at the end of the ninth rotation up to only 1.58 ± 0.01% compared to 1.48 ± 0.01% in control. Its stocks increased to 43.29 ± 0.27 compared to 40.55 ± 0.27 t/ha on the variant without fertilizers (Table 3).

Increasing the yield and productivity of crop rotations remains the main task of agricultural production, and every year becomes more and more relevant. The influence of fertilizing and liming systems, and as a result, soil acidity affects the content of total humus and crop rotation productivity in general. Systematic fertilization and periodic liming improve nutrient regime, chemical, and physical properties is primarily due to the reduction of soil acidity. At the same time, these agricultural measures make it possible to obtain in Albic Stagnic Luvisols relatively high and stable crop yields and crop rotation productivity in general.

Studies have shown that the organo-mineral fertilizer system provided the highest yield of winter wheat grain (5.53 ± 0.58 t/ha) and green mass of corn (61.7 ± 6.2 t/ha) with periodic liming with one norm of lime. Compared to the control without fertilizers, where the yield of cultivated crops was 1.97 ± 0.29 and 22.5 ± 1.7 t/ha, the increase was 3.56 and 39.2 t/ha, respectively. The use of a similar fertilizer system, but with the optimal dose of lime according to the acid-base buffering capacity, increased winter wheat yield up to 5.05 ± 0.32 t/ha and corn for silage up to 58.6 ± 3.3 t/ha (Table 5).

Table 4
Dependence equation of the CO_2 amount on the content of labile organic matter and soil acidity under crop rotation cereals

Crop	Growth stage	Equation	Determination coefficient, R^2
Winter wheat	intensive growth	$Y = 77.3307 – 215.6082x + 177.7595x^2$	0.672
Winter wheat	earing	$Y = 18.8348 + 2017.1811x – 1817.4979x^2 – 234.5839x_1 + 24.6709x_1^2$	0.702
Corn for silage	milk ripeness	$Y = –258.1196 + 443.5629x – 417.8595x^2 + 58.2087x_1 – 5.5283x_1^2$	0.778

Note: Y is the amount of CO_2, ppm/min; x is the content of labile organic matter, %; x_1 is pH_{KCl}.

Table 5
Influence of different fertilizer systems and periodic liming on the yield of cultivated crops and crop rotation productivity (x ± SD, n = 9)

Fertilization 1 ha of crop rotation area	The yield of cultivated crops, t/ha				Crop rotation productivity, t/ha of grain units
	winter wheat		corn for silage		
	yield	increase to control	yield	increase to control	
Without fertilizers (control)	1.97 ± 0.29[a]	0	22.5 ± 1.7[a]	0	2.81 ± 0.13[a]
Manure, 10 t/ha + $N_{65}P_{68}K_{68}$ + $CaCO_3$, 1.0 norm according to hydrolytic acidity	5.53 ± 0.58[b]	3.56	61.7 ± 6.2[b]	39.2	7.68 ± 0.45[b]
Manure, 10 t/ha + $N_{65}P_{68}K_{68}$ + $CaCO_3$, optimal according to the acid-base buffering capacity	5.05 ± 0.32[b]	3.08	58.6 ± 3.3[b]	36.1	7.38 ± 0.34[bc]
$N_{65}P_{68}K_{68}$	2.58 ± 0.12[a]	0.61	39.5 ± 2.2[c]	17.0	3.68 ± 0.45[a]
$N_{105}P_{101}K_{101}$ + $CaCO_3$, 1.5 norm according to hydrolytic acidity	5.09 ± 0.31[b]	3.12	54.8 ± 5.7[b]	32.3	6.67 ± 0.39[cd]
$N_{105}P_{101}K_{101}$ + $CaCO_3$ optimal according to the acid-base buffering capacity	4.08 ± 0.20[c]	2.11	49.7 ± 5.5[bc]	27.2	6.24 ± 0.25[d]

Note: values labeled with the same letter within one column of the table are not significantly different from each other according to the results of comparison using the Tukey test (P < 0.05).

The intensive mineral fertilizer system with application in crop rotation of only mineral fertilizers for more than 50 years formed 2.58 ± 0.12 t/ha of winter wheat and 39.5 ± 2.2 t/ha of green mass of corn, which is only by 0.61 and 17.0 t/ha higher than in control variant. The joint application of 1.5 norms of mineral fertilizers and 1.5 norms of $CaCO_3$ according to hydrolytic acidity ensured sufficiently high grain yield of winter wheat (5.09 ± 0.31 t/ha) and corn's green mass (54.8 ± 5.7 t/ha) in crop rotation. This fertilizer system, with application $CaCO_3$ according to the acid-base buffering capacity, formed a lower yield of cultivated crops – 4.08 ± 0.20 and 49.7 ± 5.5 t/ha, respectively.

The highest productivity for the ninth rotation of crop rotation in general (7.68 ± 0.45 t/ha of grain units) was obtained by the organo-mineral fertilizer system with application 10 tons of manure per hectare of crop rotation area and mineral fertilizers $N_{65}P_{68}K_{68}$ dose with liming by 1.0 $CaCO_3$ norm according to hydrolytic acidity. It is 4.87 t/ha higher than the variant without fertilizers. This fertilizer system, with liming with the optimal dose of lime according to the acid-base buffering capacity, increased productivity of hectare of crop rotation area to 7.38 ± 0.34 tons of grain units. Natural fertility provided 2.81 ± 0.13 t/ha of grain units at 4.22 pH_{KCl}. The productivity per hectare of crop rotation area was very low with unilateral long-term application of solely mineral fertilizers, which caused an increase in soil acidity to 4.03 pH units. Yield was 3.68 ± 0.45 t/ha of grain units or only 0.87 t/ha higher than the control variant.

The use of mineral fertilizers solely is valid only in the case of liming. Thus, the use of a mineral fertilizer system with an application of 1.5 $CaCO_3$ norms according to hydrolytic acidity and acid-base buffering capacity provides high productivity per hectare of crop rotation area – 6.67 ± 0.39 and 6.24 ± 0.25 tons of grain units, respectively. A mathematical model was developed based on the obtained experimental data. It reproduces the dependence of crop rotation productivity on acidity and the amount of humus under different fertilizer systems and periodic liming. The relationship between these indicators is described by the regression equation, in which crop rotation productivity has a reasonably close (R = 0.898) relationship with soil acidity and humus content. In this case, the coefficient of determination (R^2 = 0.806) indicates a significant effect of total humus and pH_{KCl} on crop rotation productivity (Table 6).

Table 6
Dependence equation of crop rotation productivity on the content of total humus and soil acidity

Equation	Determination coefficient, R^2
$Y = -46.0867 + 57.2637x - 13.4691x^2 - 3.2082x_1 + 0.3966x_1^2$	0.806

Note: Y – crop rotation productivity, t/ha of grain units; x – total humus, %; x_1 – pH_{KCl}.

Table 7
Relationship between intensity of CO_2 emission and crop rotation productivity

Crop	Growth stage	Equation	Determination coefficient, R^2
Winter wheat	Earing	$Y = 47.9986 - 13.7453x + 1.331x^2$	0.895
Corn for silage	Milk ripeness	$Y = -14.0363 + 10.6546x - 1.0354x^2$	0.487

Note: Y – CO_2 emission, ppm/min; x – crop rotation productivity, t/ha of grain units.

The relationship between the intensity of CO_2 emission and crop rotation productivity based on the calculations of the correlation dependence under winter wheat indicates the presence of a close relationship (determination coefficient is 0.895). However, under corn silage, a less close relationship is traced, approaching the average bond and determination coefficient is 0.487 respectively (Table 7).

The research results and mathematical correlation models indicate that the most critical factor influencing the optimization of carbon dioxide emission, humus state, and crop rotation productivity on Albic Stagnic Luvisol of the Western Forest-Steppe is a primary decrease in soil acidity.

Discussion

Today, due to significant climate change, the problem of efficient and environmentally safe use of acid soils has become much more acute. The solution to this issue lies in the development and application of innovative agricultural measures that will contribute to the balanced use of acidic soils.

The primary sources of CO_2 in the atmosphere are soil organic matter; dead plant remains in the soil and on its surface; organic substances produced by vegetative roots of plants (Kuzyakov & Larionova, 2006). The constant supply of plant residues and the synthesis of microbial biomass provides a continuous replenishment of the organic carbon content in the soil profile. The rate and growth limits in the soil depend not only on the quantity and quality of incoming organic material but also on the speed and strength of the stabilization of organic components in the soil (Paul, 2016).

The regulation of carbon regime in the context of maintaining natural soil fertility at high potential and the mechanism of humus-accumulative soil formation is still poorly understood and not adequately reflected in the scientific literature despite the full range of approaches to the study of the biogeochemical transformation of carbon in nature (Halytska et al., 2018).

The magnitude of the gas concentration in the above-ground air layer, in addition to the global patterns of their formation, depends on the local conditions of soil use within agricultural landscapes and the peculiarities of their functioning during crop cultivation. Production of CO_2 caused by organic matter decomposition predominates over the processes of rhizosphere respiration during the plant's growth period in the structure of the soil gas carbon pool. Intensive emission of carbon dioxide by soils in the warm period changes to its sluggish production in the cold due to the natural slowdown of biological processes. In this case, the soil seems to "rest", passing into a state that we call the recreational period (Trofimenko et al., 2019).

Studies by (Siabruk & Tsyhichko, 2016) conducted on podzolic chernozem found that the intensity of carbon dioxide production depended more on hydrothermal conditions than on the levels of biologization of agriculture. The difference between traditional and organic farming in terms of CO_2 emissions is insignificant and directly depends on the microbiological activity of the soil.

Tillage also significantly influences the intensity of carbon dioxide emission along with fertilizer systems, hydrothermal conditions. The effect of tillage is also noted in studies by (Wang et al., 2020). In particular, the lack of tillage reduced CO_2 flow by 14.5% compared to plowing.

Studies by Demydenko & Velychko (2019) on heavily degraded low-humus podzolized chernozem have found that for the organic fertilizer system the C:N ratio in short-rotational crop rotation agrocenoses is the most optimal and most favourable for humification and sequestration of carbon and a decrease in mineralization intensity, and carbon dioxide emission accordingly.

According to Volkohon et al. (2019), the use of mineral fertilizers without providing the soil with fresh organic matter in a field agricultural experiment on leached chernozem leads to an imbalance of mineralization ↔ synthesis processes and causes dominance of organic matter mineralization. Organo-mineral fertilizer system provides a balance of these processes in the soil. Cuhel et al. (2010) found that carbon dioxide emissions were highest at neutral pH values. Other studies show that agroecosystems on soils with a high content of organic matter act as a runoff of carbon, and with a low – as its source (Liu et al., 2011).

The obtained results in a long-term experiment provide an opportunity not only to study the systematic impact of various agricultural technologies on soil fertility, biological processes, ecological status, but also to determine the cycle of substances and the direction of energy flows under changing climate conditions.

The dynamics of CO_2 emission during the growing season under winter wheat and corn for silage in Albic Stagnic Luvisol depended on the fertilizer systems and the duration of the liming aftereffect. The application of high doses of lime, calculated according to the hydrolytic acidity is accompanied not only by significant material costs but also environmental problems, increasing the concentration of carbon dioxide in agroecosystems.

In our previous studies conducted in the ninth rotation of crop rotation of a long-term agricultural experiment on acidic Albic Stagnic Luvisol with low humus content we showed that the intensity of carbon dioxide emissions undergoes significant seasonal and daily fluctuations, depending on temperature, soil moisture, fertilizer system, doses of ameliorant application and the phase of crop growth. The emission of carbon dioxide is the highest for organo-mineral and mineral fertilizer systems with liming by 1.0–1.5 $CaCO_3$ norm according to hydrolytic acidity both in the field of corn for silage with direct application of fertilizers and lime, and in the aftereffects under spring barley. It significantly outperforms a similar fertilizer system with liming according to the optimal dose of $CaCO_3$ according to the pH buffering capacity (Habriel et al., 2016).

The inclusion of cover crops in crop rotations is a promising element of carbon sequestration in agroecosystems. Cover crops, compared to other management methods,increase soil organic carbon without causing a reduction in yield and carbon stock (Poeplau & Don, 2015).

The traditional system of cultivation of acid soils by applying high doses of lime, calculated according to hydrolytic acidity, does not provide progressive development of soil formation processes on an environmentally friendly basis. It is due to significant calcium leaching into groundwater in the conditions of the washing-off water regime, excessive mineralization, and emission of carbon dioxide. It is expedient to apply lime fertilizers in a short-rotation crop rotation at a dose calculated according to pH-buffering capacity with repeated liming before each of the following rotations. That measure will provide a gradual shift of acid-base balance, environmentally friendly, and balanced use of acid soils.

Conclusions

Seasonal dynamics of carbon dioxide production in fields of winter wheat and corn for silage depending on different fertilizer systems and periodic liming were studied in the conditions of a long-term agricultural experiment. The organo-mineral fertilizer system with application of 10 tons of manure per hectare of crop rotation area, $N_{65}P_{68}K_{68}$ with 2.5 t/ha of $CaCO_3$, calculated according to the acid-base buffering capacity, in the field of winter wheat – the last crop of ninth crop rotation, optimized the seasonal dynamics of CO_2 emissions. Under these conditions, the application of lime in Albic Stagnic Luvisol in the short four-field crop rotation 1.0 and 1.5 lime norms, according to hydrolytic acidity, is not only a highly costly measure. However, it causes significant losses of carbon in the form of CO_2 due to additional mineralization, significant leaching of calcium, and environmental problems.

In the field of corn for silage, which begins the X rotation of crop rotation, variants of organo-mineral and mineral fertilizer systems with application of the optimal $CaCO_3$ dose (2.5 t/ha) along with increasing pH_{KCl} to 5.00 and 4.82 units increased the intensity of carbon dioxide emission compared to the similar fertilizer systems with application of 6.0 and 9.0 t/ha of $CaCO_3$ according to hydrolytic acidity (pH_{KCl} 5.14–5.53). It indicates the feasibility of re-liming before the next rotation with a dose of $CaCO_3$ calculated by acid-base buffering capacity due to an increase in carbon dioxide emission. An intensification in mineralization processes due to increased soil acidity causes these losses.

CO_2 emission from the soil surface in the field of corn was greatest at 14.00 h during the seedling phase in control without fertilizers and is 0.40 mg/m^2. During the period of milk ripeness in the variants with high doses of lime, calculated according to the hydrolytic acidity, carbon losses significantly prevail over similar fertilizer systems with application of the optimal dose of $CaCO_3$ according to the acid-base buffering capacity. They are 0.29–0.32 compared to 0.17–0.18 g/m^2, respectively.

Systematic long-term application for more than 50 years of the mineral fertilizer system at the end of the ninth crop rotation does not provide a significant increase in total humus content in Albic Stagnic Luvisol. The content of labile humus compounds in winter wheat and corn is higher. It reaches the control variant without fertilizers, which at a low level of crop rotation productivity, indicates additional losses of mobile humus compounds at high acidity (pH 4.03) of the soil solution.

The organo-mineral fertilizer system provides the highest humus content of 1.76–1.93% and crop rotation productivity of 7.38–7.68 t/ha of grain units at the end of the ninth rotation with an application of 10 t/ha of manure, $N_{65}P_{68}K_{68}$, periodic liming with 1.0 norm according to hydrolytic acidity and pH buffering capacity (2.5 t/ha). However, we recommend an organo-mineral fertilizer system with the introduction of 10 t of manure on ha of crop rotation area + $N_{65}P_{68}K_{68}$, liming by $CaCO_3$ dose, calculated by pH buffering capacity (2.5 t/ha), which most optimizes the release of carbon dioxide, humus formation processes, provides a significant reduction in material and energy costs, harmonization of the environmentally friendly and productive functions of Albic Stagnic Luvisol.

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