Results of the changes in the physicochemical properties and fractional group composition of the humus-leached chernozem under the influence of fertilizers and ameliorant

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Abstract. Currently, in the Russian Federation there is a tendency towards a decrease in the content of organic substance in the soil and its acidification. It is impossible to stop these processes without applying organic fertilizers and calcium containing ameliorants. Their effect on the soil properties depends on the edaphoclimatic conditions. In order to study the effect of fertilizers and ameliorants on the fertility of leached chernozem in the forest-steppe zone of the Central Black Earth zone of the Voronezh region in 2018 – field experiments were conducted. The results showed that prolonged application of mineral fertilizers led to the acidification of the soil both against the background of exposure to organic substances and liming. Reliming calcification of the leached chernozem contributed to a noticeable decrease in soil acidity (pH$_{KCl}$ increased by 0.7-1.0, Hr decreased by 2.1-2.9 mg-Eq/100 g of soil, the content of exchange forms of calcium and magnesium increased to 26.2-26.9 mg-Eq/100 g of soil). Some optimization of the acidity of the soil was also observed even with the reapplication of manure. The calcification of the soil led to the optimization of its fractional-group composition of humus.

1. Introduction

In modern conditions, one of the main factors limiting soil fertility and obtaining high crop yields is the increased acidity of the soil. The influence of the acid reaction of the environment on plants is very versatile: the growth and the process of branching of the roots deteriorate, which negatively affects the physicochemical state of the plasma of the root cells, their permeability, therefore, the usage of nutrients from the soil and fertilizers by the plant decreases and, as a result, their productivity. In addition, various soil organisms do not relate equally to soil acidity. Mold fungi tolerate an acid reaction of the environment, among which there are many parasites and pathogens of various diseases. At the same time, the activity of nitrogen-fixing and nitrifying organisms in such conditions is being suppressed [1].

2. Statement of the problem

The area of acid soils in the Russian Federation is 32% of the surveyed area of arable land, in the Central Federal District – 53.7%. By 01.01.2017 – acid soils in the Voronezh region occupied 699 thousand ha or 27.9% of arable land. Moreover, their area, in compare with the previous cycle of agrochemical inspection (for five years), has increased by 71.2 thousand hectares [2, 3].
The main reason for the increase of soil acidity is the removal of the absorbed calcium, magnesium and their salts from the soil. The decalcification of soils is a kind of "trigger" of their degradation. This process develops under the influence of physiologically acidic mineral fertilizers and due to the uncompensated removal of calcium and magnesium with harvest. As a result, in addition to acidifying of the soil fluid, the loss of organic substance in the soil increases, its structure and other agrophysical parameters deteriorate, the microbiological activity decreases, the efficiency of fertilizers decreases (up to 40%), and ultimately the yield and quality of the crop. [1]. It is possible to stop the process of removing absorbed calcium from the soil by introducing calcium-containing ameliorants into the soil (calcification).

In the Voronezh region, despite a clear tendency to soil acidification, liming is carried out on an insufficient scale. For example, in 2016 only 4.4 thousand hectares of arable land were subjected to chemical reclamation [3]. Small volumes of liming are associated with additional costs for this agronomic technique. It is possible to reduce the cost of liming when using waste products, for example, defecate, which is formed in the factories for the production of sugar from sugar beets. At the same time, sugar producers are ready to give it away free.

In this regard, the aim of the research was to establish the effect of many years of fertilizer and defecate component application on the physicochemical properties and fractional group composition of the leached chernozem humus.

3. Materials and methods

The studies were carried out during a field experiment, superimposed on leached chernozem, of heavy loamy granulometric composition with medium thickness, low humus content on cover loams in the forest-steppe zone of the Central Black Earth Zone of the Voronezh Region. Before the experiment (1986), the soil had the following agrochemical characteristics: exchange acidity (pH_{KCl}) – 5.5, hydrolytic acidity – 6.0 mg-Eq/100 g of soil, the number of exchange bases – 27.3 mg-Eq./100 g of soil, the degree of saturation of the soil with bases – 84.4%, the content of humus – 3.96%. In the experiment, crop rotation was developed with the following crop rotation: pure steam – winter wheat – sugar beets – vetch-oats for green fodder – winter wheat – barley. The experimental design includes 15 options. Only 7 were taken for the research (table 1). The recurrence of the experiment is fourfold, the placement of the repetitions is two-tier, the arrangement replications is systematic staggered. The total area of the experimental plot is 191.7 m² (35.5m x 4m).

Mineral fertilizers were applied annually according to the experimental design. The NPK fertilizer dose was accepted as the optimal one, recommended for the application on the leached chernozem of the central chernozem zone according to the results of field experiments. Organic fertilizers were applied to black steam under a winter wheat. The liming was carried out with a decrease in acidity to pH_{KCl} <6.0, Hr > 1.8 mg-Eq/100 g of soil. The dose of the defecate component was calculated by the total hydrolytic acidity and was introduced into the field of pure steam in the first, second, fourth and sixth rotation of the crop rotation. In terms of acidity, the soil in the third and fifth rotations did not need liming.

Soil samples were taken from the field of pure steam in two terms: before applying the manure and the defecate (04.18.2018) and after four months of their operation (09.11.2018). Soil samples were taken in five replicates from two non-adjacent repetitions. Agrochemical properties were determined according to generally accepted methods [4]. The fractional group composition of humus was determined according to the scheme of I.V. Tyurin (as modified by V.V. Ponomareva and T.A. Plotnikova) .This technique allows dividing the humus of the soil into three fractions of humic acids (HA), four fractions of fulvic acids (FA) and humine – an insoluble part of the humus of the soil. The HA fractions were studied: fraction 1 – free and associated with mobile one and a half oxides; fraction 2 - associated with calcium; fraction 3 – associated with clay minerals and fixed sesquioxides. The following PC fractions were distinguished: fraction 1a – free and bound to mobile sesquioxides ("aggressive fraction"); fraction 1 – associated with fraction 1 HA; fraction 2 – associated with fraction 2 of the civil code; fraction 3 – associated with fraction 3 of HA [4].
4. Discussion of the results

The results of our studies on the change in the physicochemical properties of a leached chernozem under the influence of fertilizers and defecate are presented in table 1.

Table 1. Effect of fertilizers and ameliorant on the physicochemical properties of leached chernozem, layer 0-40 cm, 2018

| Variant | $pH_{H_2O}$ | $pH_{KCl}$ | $H_r$, mg-Eq/100 g. soil | $Ca^{2+}+Mg^{2+}$, mg-Eq/100 g. soil |
|---------|-------------|------------|--------------------------|-------------------------------------|
|         | 1           | 2          | 1                        | 2                                  |
| 1. Control | 5.9     | 5.7       | 4.9                      | 4.8                                |
| 2. 40 t/ha manure (aftereffect-background) | 6.4 | 6.8 | 5.0 | 5.2 | 4.8 | 4.0 | 24.3 | 24.6 |
| 3. background + NPK | 6.2 | 6.5 | 4.9 | 5.2 | 6.0 | 4.3 | 23.6 | 23.8 |
| 5. background + 2NPK | 5.9 | 6.7 | 4.7 | 5.1 | 6.4 | 5.2 | 23.4 | 23.5 |
| 12. background + defecate (background) + NPK | 6.6 | 7.3 | 5.5 | 6.5 | 4.2 | 1.3 | 24.8 | 26.9 |
| 13. background + defecate (background) | 6.6 | 7.3 | 5.6 | 6.4 | 3.7 | 0.9 | 25.2 | 26.9 |
| 15. NPK + defecate (background) | 6.5 | 7.1 | 5.4 | 6.1 | 4.2 | 1.9 | 24.9 | 26.2 |

* Before applying the manure and the defecate (end of the fifth rotation of the crop rotation, 18.04.2018)
* four months later since the moment of their influence (11.09.2018)

It can be seen from the presented data that when mineral fertilizers had been applied against the background of manure aftereffect (options 3 and 5), the soil from the slightly acidic class (before the experiment) passed into the medium acid class (by the time the fifth rotation of the crop rotation was completed). The use of only manure (option 2), although improved the physicochemical properties of the soil, but did not lead to a significant decrease in soil acidity, and, accordingly, the creation of any favorable conditions for the growth and development of crops. The introduction of mineral fertilizers against the background of the aftereffect of manure (options 3 and 5) led to an increase in soil acidity compared with the period before the laying of the experiment. This was manifested to the greatest extent on the option with a double dose of mineral fertilizers. Options with periodic liming provided the best indicators of soil acidity. The repeated applying of the manure and the defecate component in the sixth rotation of the crop rotation led to a noticeable change in all the physical and chemical properties of the soil. Therefore, if the control showed a slight acidification of the soil in the second term for sampling soil with a simultaneous decrease in the content of exchangeable bases, then in the case of using only manure, the acidity of the soil decreased, and the content of exchangeable bases increased. When mineral fertilizers were applied against the background of the manure, even in a double dose, the optimization of the physicochemical properties of the soil took place.

These indicators have undergone the greatest change when reintroducing lime into leached chernozem. The condition of the exchange bases increased to 6.1-6.5, the active acidity of the soil – to 7.1-7.3, the hydrolytic decreased to 0.9-1.9 mg-Eq / 100 g of soil. The soil from weakly acidic and almost neutral classes passed into the neutral class, significantly enriched with bases.

The content of exchangeable calcium in the soil (table 2) had the same regularities of distribution according to the experimental variants as the content of the total amount of exchange bases. When reintroducing the defect, it increased by 1.1-2.5 mg-Eq / 100 g of soil. The greatest increase in the content of exchangeable calcium was observed in the variant with the combined introduction of mineral, organic fertilizers and defecate (option 12).
The content of the water-soluble form of calcium was significantly lower than the exchange – on average, 22-23 times. Its minimum value at all time intervals for soil sampling was observed in the control variant. Repeated application of manure increased it in comparison with the control, and when mineral fertilizers were added to the manure, the content of water-soluble calcium decreased again, but it was still higher than in the control variant.

**Table 2.** Change in the content of calcium and the activity of its ions in leached chernozem, layer 0-40 cm, 2018

| Variant | $\text{Ca}_{\text{chan}}$, Eq/100 g. soil | $\text{Ca}_{\text{H}2\text{O}}$, mg-Eq./100 g. soil | pCa | K liming |
|---------|-------------------------------------|---------------------------------|-----|----------|
| 1. Control | 19.5 | 0.65 | 3.1 | 4.4 | 4.1 |
| 2.40 t/ha manure (aftereffect-background) | 20.6 | 0.85 | 2.9 | 4.9 | 5.5 |
| 3. background + NPK | 19.9 | 0.75 | 2.9 | 4.7 | 5.1 |
| 5. background + 2NPK | 19.4 | 0.65 | 3.0 | 4.4 | 5.2 |
| 12. background + defecate (aftereffect) + NPK | 20.0 | 1.50 | 2.9 | 5.2 | 5.9 |
| 13. background + defecate (aftereffect) | 22.8 | 1.65 | 3.0 | 5.1 | 5.9 |
| 15. NPK + defecate (aftereffect) | 21.9 | 1.55 | 3.0 | 5.0 | 5.7 |

a Before applying the manure and the defecate (end of the fifth rotation of the crop rotation, 18.04.2018)
b four months later since the moment of their influence (11.09.2018)

According to the gradation of soils by calcium deficiency [5], at the end of five rotations of crop rotation, the soil of all experiment variants experienced an average need for calcium. In cases where lime was added, the soil need for calcium was assessed as weak, approaching the lower boundary of this class.

**Table 3.** Content of the humus in the analyzed options

| Soil layer, cm | 1 var | 2 var | 3 var | 5 var | 12 var | 13 var | 15 var |
|---------------|-------|-------|-------|-------|--------|--------|--------|
| 0-20          | 4.15  | 4.31  | 4.60  | 4.90  | 4.79   | 5.19   | 4.90   | 4.98   | 6.00   | 6.05   | 5.64   | 5.91   | 5.52   | 5.57   |
| 20-40         | 3.95  | 4.07  | 3.97  | 4.14  | 4.48   | 4.67   | 4.33   | 4.53   | 5.28   | 5.34   | 4.47   | 4.62   | 4.57   | 4.64   |
| The average for the layer 0-40 cm | 4.05 | 4.19 | 4.28 | 4.52 | 4.64 | 4.93 | 4.62 | 4.76 | 5.64 | 5.70 | 5.05 | 5.27 | 5.05 | 5.10 |

a Before applying the manure and the defecate (end of the fifth rotation of the crop rotation, 18.04.2018)
b four months later since the moment of their influence (11.09.2018)

The reintroduction of lime into the soil led to a decrease in soil calcium requirements. In addition, although the calcareous potential still corresponded to the class of low soil calcium needs, now its
value was approaching the upper limit of the class. The positive effect of organic fertilizers on the calcareous potential of the soil was also observed. The introduction of both manure and the addition of mineral fertilizers to it led to an increase in the calcareous potential by 0.4-0.8, and the need for soil in calcium decreased to weak, as in the case of reclaimed options.

In the studied soil samples of different sampling periods, the humus content was determined. The results of the analysis are presented in table 3. From the data of the table, it can be seen that the minimum humus content in the root-inhabited layer of 0-40 cm is noted in the control variant. The maximum is typical for the variant with the joint application of mineral fertilizers against the background of manure and defecate. After the April sampling of soil samples, the recommended dose of manure was introduced. It was established that after this there was an increase in the humus content in the upper layers of all the studied variants.

Figure 1 shows the distribution curves of the profile of the content of the sum of all fractions of HA and FA in% of the total carbon content (spring and autumn sampling periods). It was established that in the spring the maximum content of humic acids is observed on options 12 and 15 with the combined introduction of defecate and mineral fertilizers. In autumn, a high content of HA is characteristic for the control and background variants, as well as for the variants with lime addition. For options with the introduction of different doses of mineral fertilizers against the background of manure, HA is relatively small.

The profile distribution curves of the profile profile of the sum of HA fractions are S-shaped with 2 maxima in the layer 0-20 and 40-60 cm. This feature is especially clearly visible in the variants without adding lime. Perhaps this is due to an increase in the mobility of HAs, a partial blurring of their boundaries of the upper horizon and fixing in the middle of the profile.

The nature of the distribution of FK over the soil profile of the analyzed variants is complex, which can be explained by their high mobility. The maximum number of FC fractions in the spring is noted on the background option, in the fall - on options with the introduction of mineral fertilizers (options 3 and 5). In the samples of the autumn sampling period, the HA content is somewhat higher than in the spring ones. Possibly, the formation of high molecular weight HA requires more time than low molecular weight FA. In addition, it was found that the application of mineral fertilizers contributes to the destruction of HA molecules, and their fragments can enter the FA fractions during analysis [6].

In samples of spring and autumn selection periods, similar patterns are noted. This indicates that the fractional and group composition of humus is a stable indicator. However, the absolute values of the carbon content of HA and FA have changed.

It is also of interest to compare the content HA 2 fractions at different sampling dates as the most significant characteristic of the state of humus (table 4). GK 2 plays a crucial role in the formation of soil fertility [7]. They contribute to the fixation of humus in the soil profile and participate in the formation of the soil structure [8]. From the data of the table, it can be seen that high HA 2 values are noted on the ameliorative options in accordance with the background of manure (options 12 and 13).

Accordingly, it was revealed that during the period from April to September, the basic laws of the fractional-group composition of humus are preserved, due to the typical features of the studied soils. The absolute values of the content of individual fractions of humic acids vary. It was noted that the content of FA in the samples of the autumn selection period is somewhat higher than in the spring ones. Perhaps this is due to their formation due to the introduction of manure. Apparently, the formation of highly condensed HA requires more time, and low molecular weight FAs form faster.
Figure 1. Profile distribution of the sum of all fractions of HA and FA in % of total carbon:
(a, b– selection term 04.18.2018; c, d - selection period 09.11.2018)

Table 5 presents some characteristics of the humus state of the analyzed soil sample of different selection dates. It was established that the maximum supply of humus is noted in the variant with the joint introduction of defecate, manure and mineral fertilizers. The minimum indicator is characteristic for the control variant, which may be associated with the smallest intake of organic matter.
Table 4. HA 2 content fractions (spring and autumn samples)

| Layer, cm | Var. 1 | Var. 2 | Var. 3 | Var. 5 | Var. 12 | Var.13 | Var.15 |
|-----------|--------|--------|--------|--------|--------|--------|--------|
|           | 1a     | 2b     | 1      | 2      | 1      | 2      | 1      | 2      |
| 0-20      | 48.9   | 40.4   | 45.5   | 45.8   | 33.8   | 40.2   | 34.2   | 38.1   | 42.8   | 48.4   | 43.7   | 47.2   | 27.8   | 34.4   |
| 20-40     | 44.1   | 38.6   | 45.0   | 43.0   | 28.1   | 43.5   | 37.9   | 41.4   | 44.1   | 42.6   | 34.4   | 54.1   | 24.5   | 26.8   |
| 0-40      | 46.5   | 78.9   | 45.3   | 44.3   | 30.9   | 83.7   | 36.0   | 39.7   | 43.5   | 45.5   | 39.0   | 50.7   | 26.2   | 30.6   |

a Before applying the manure and the defecate (end of the fifth rotation of the crop rotation, 18.04.2018)
b four months later since the moment of their influence (11.09.2018)

Table 5. Parameters of the humus state of leached chernozem

| Variant | The stock of humus in the m layer, t/ha | Cha: Cfa | Degree of humification, % | Sum of mobile fractions, % C | The coefficient of humus mobility |
|---------|----------------------------------------|----------|---------------------------|-------------------------------|---------------------------------|
|         | 1a         | 2b       | 1   | 2   | 1   | 2   | 1   | 2   | 1   | 2   | 1   | 2   |
| 1. Control | 332    | 333   | 3.03 | 3.71 | 54  | 59  | 81.0 | 76.2 | 0.47 | 0.40 |
| 2. 40 t/ha manure | 385    | 387   | 1.77 | 2.96 | 50  | 62  | 77.5 | 83.4 | 0.45 | 0.44 |
| 3. background+ NPK | 466    | 468   | 1.54 | 2.39 | 42  | 51  | 68.4 | 72.7 | 0.31 | 0.42 |
| 5. background + 2NPK | 518    | 521   | 1.67 | 2.49 | 49  | 53  | 78.8 | 74.6 | 0.36 | 0.40 |
| 12. background + defecate +NPK | 584    | 587   | 4.07 | 4.43 | 57  | 68  | 70.4 | 83.0 | 0.43 | 0.53 |
| 13. background + defecate | 529    | 532   | 2.36 | 5.14 | 55  | 67  | 76.6 | 80.5 | 0.40 | 0.50 |
| 15. NPK + defecate | 488    | 490   | 2.37 | 2.63 | 41  | 49  | 58.3 | 66.3 | 0.26 | 0.31 |

The degree of the humification of an organic substance in all variants of the experiment is very high. The amount of mobile fractions (recoverable organic substances) has high rates for all options. This can be explained by the prolonged usage of the irrepealable soils in intensive agricultural production, as a result of which - stable molecules of humic acids start to gradually decompose up to the condition of less mobile high molecular weight compounds, which have greater mobility and can migrate to lower horizons or beyond soil profile.

The maximum values of the coefficient of mobility of humus are noted on the control variant in the spring, as well as on the variant with combined fertilizer and defecate in the fall. The higher the mobility coefficient, the more stable the molecules of humic substances. Therefore, it can be assumed that the application of mineral fertilizers increases the mobility of humic substances, due to which, when washed out, their content decreases.

5. Conclusion
1. A long-term application of mineral fertilizers against the background of organic aftereffect contributed to a decrease in $\text{pH}_{\text{KCl}}$ by 0.6-0.8 and depletion of the soil with bases. The usage of fertilizers against the background of the aftereffect of defecate optimized these indicators. However, by the end of the fifth crop rotation, the soil in the described experimental variants began to feel the need for liming. The reliming of the leached chernozem led to a marked decrease in soil acidity. So, the $\text{pH}_{\text{KCl}}$ value increased by 0.7-1.0, Hg decreased by 2.1-2.9 mg-Eq/100 g of soil, the content of exchange forms of calcium and magnesium increased to 26.2-26.9 mg-Eq/100 g of soil. The reapplication of manure has also contributed to some optimization of soil acidity.

2. The introduction of lime at the beginning of the sixth rotation of the crop rotation led to an increase in the content of both exchange and water-soluble forms of calcium – by 1.1-2.5 and 0.14-0.33 mg-Eq/100 g of soil, respectively. However, the calcareous potential still corresponded to the class of weak soil needs for calcium, but its value was approaching the upper boundary of the class. The positive effect of organic fertilizers on the calcareous potential of the soil was also observed. The introduction of both manure and the addition of mineral fertilizers into it led to an increase in the calcium potential by 0.4-0.8, and the need for soil in calcium decreased to weak, as in the case of reclamation options.

3. It was revealed that all the studied agricultural techniques lead to a change in the fractional group composition of humus. Under the influence of mineral fertilizers, the proportion of FA increases. The usage of the defecate component promotes the accumulation in the soil of HAs associated with calcium cations. It was established that the combined introduction of the defecate component and organic fertilizers leads to a decrease in the mobility of humus.

It is worth noting that the observed changes have occurred quite quickly. A number of scientists believe that calcium-containing ameliorants, gradually dissolving in the soil, have a maximum effect on its properties in the second year of their application. Therefore, it is logical to expect further optimization of the acidity of leached chernozem in the variants of the experiment with defecate.

The introduction of the ameliorant in the form of calcium promotes the accumulation of stable humus in the soil, which is firmly held by the mineral matrix. A sharp decrease in the content of humus does not occur, and its supply increases slightly.

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