Effect of liming and fertilisation systems on the physico-chemical properties of leached chernozem (black soil)

E V Zheryakov, Y I Zheryakova and E S Breducheva
Penza State Agrarian University, 30 Botanicheskaya St., Penza, 440014, Russia

E-mail: zheryakov.e.v@pgau.ru

Abstract. Long-term agricultural use of chernozems (black soils) leads to a decline in their effective fertility. The depletion of the arable and subsoil horizons in calcium can occur under the influence of natural and anthropogenic factors. The strongest anthropogenic impact on physico-chemical properties is caused by varying levels of fertilizer application. Average annual rate of pH\textsubscript{kcl} decrease on unfertilized variant was 0.008-0.01 units per year. At the same time in the grain-fallow crop rotation the decrease of pH\textsubscript{kcl} is more intensive than in the grain-grass crop rotation. Under the influence of mineral fertilizers the growth rate of acidity increased by 1.8-2.1 times. After 12 years after application of organic fertilizers the value of acidity increased by 0.13-0.15 units after carrying out the experiment with pH\textsubscript{kcl} in comparison with initial values. The application of dolomite flour contributed to the increase of pH\textsubscript{kcl} by 0.41-0.53 units as early as one year after application of the ameliorant, the maximum shift was observed on the 4th-5th years. The application of organic and mineral fertilizers contributed to the trend of increasing the content of available phosphorus in the soil, compared with the unfertilized variant in both crop rotations. The content of mobile forms of phosphorus increased in the variants where green manure crops were sown. The application of manure and mineral fertilizers had no significant effect on the content of potassium in the soil. When using organo-mineral fertilizer system, as well as its combination with crop-sideration, there was a tendency of some increase in potassium content in the arable layer. The minimum additional yield was obtained for all crops with the application of 8 tonnes of manure per hectare of crop rotation land, and the maximum was obtained with the organo-mineral fertilisation system and its combination with crop-sideration. Liming increased the productivity of all crops.

1. Introduction
The long-term agricultural use of chernozems leads to a decline in their effective fertility. The depletion of the arable and subsoil horizons of calcium as a result of its leaching, removal with agricultural products and consumption for neutralisation of physiologically acidic mineral fertilizers can lead to an increase in acidity. The most important cause of soil acidification is the development of leaching processes, when a significant part of alkaline and alkaline-earth elements previously located in the highly dispersed organic-mineral colloids and mud particles, turn into water-soluble form, which causes their strong migration under partially leaching regime.

One of the decisive factors for plant growth and development is the neutralization of the soil environment. Simultaneously with increase of pH value at liming, hydrolytic acidity decreases, the sum of absorbed bases, the capacity of cation exchange, the degree of saturation of soil with bases increase. Until now the influence of organic fertilizers on soil acidity remains controversial. In some
researches the application of organic fertilizers does not influence soil acidity, while in others a positive influence of them especially of manure on physicochemical properties of acidic soils is noted. In this connection study of dynamics of physico-chemical properties of chernozem soils under different intensity of their use in conditions of long-term application of fertilizers is of particular relevance.

2. Materials and Methods
The research was conducted in a stationary field experiment under the scheme (2x2x5)x4 with the following factors and gradations: A - crop rotations: 1 - grain-fallow (clean fallow, winter wheat, maize, spring wheat, millet); 2 - grain-grass fallow (barley with undersowing clover, first year clover, second year clover, winter wheat, maize); B - liming: 1 - without lime; 2 - liming by 1.0 H; C - fertilization systems: 1. biological zero (control); 2. organic - 8 t manure per 1 ha of crop rotation; 3. mineral (N\textsubscript{26-32}P\textsubscript{26-32}K\textsubscript{26-32}); 4. organo-mineral (8 t/ha manure + N\textsubscript{26-32}P\textsubscript{26-32}K\textsubscript{26-32}); 5. organo-mineral with crop sideration. The crop siderate (oilseed radish) was sown after winter wheat. The soil - medium-deep heavy-loamy leached chernozem, before starting the experiment, the 0-30 cm layer was characterized by the following data: рН\textsubscript{salt} = 4.70-4.75, H\textsubscript{g} = 7.60-7.90; S = 28.7-29.5 mg-eq. per 100 g of soil; V = 78.0-79.5 %, humus content 6.50-6.68 %, N\textsubscript{hydrol.} = 7.05-9.40 mg/100 g soil (according to Tyurin-Kononova); P\textsubscript{2}O\textsubscript{5} = 8.03-9.46; K\textsubscript{2}O = 10.2-12.3 mg/100 g soil. The repetition of experiments was 4 fold, the location of variants was randomized in two tiers, the total area of plots - 53 m\textsuperscript{2}, the accounting area - 50 m\textsuperscript{2}.

3. Results and Discussion
Observations of the рН\textsubscript{KCl} value for 12 years showed that its average annual decrease rate on an unfertilized variant was 0.008-0.01 units per year. At the same time, in the grain-fallow crop rotation decrease of рН\textsubscript{KCl} is more intensive than in the grain-grass crop rotation. The main reason for this, on the one hand, is greater leaching of carbonates in a clean fallow and, on the other hand, the ameliorating effect of clover, which deeply penetrating root system is able to use calcium carbonates from deep soil horizons. The fertilizer systems studied had unequal effects on soil acidity. Under the influence of mineral fertilizers in doses of N\textsubscript{32}P\textsubscript{26}K\textsubscript{26} the annual growth rate of acidity increased by 1.8-2.1 times and рН\textsubscript{KCl} decreased by 0.015-0.02 units. Organic fertilizers had ameliorating effect on value of acidity: after 12 years after setting the experiment рН\textsubscript{KCl} increased by 0.13-0.15 units in comparison with the initial values. Combined application of organic and mineral fertilizers levelled ameliorating effect of manure, and рН\textsubscript{KCl} values remained practically at the initial level. Duration and depth of influence on acid soils of chemical ameliorants depends on many factors: chemical properties and granulometric composition of initial soil, dosage, composition and degree of crushing of ameliorant applied, hydrothermal conditions of region, level of crop yields.

The use of dolomite flour had a dramatic effect on the exchange acidity of leached chernozem. Already in a year after application of the ameliorant the value of рН\textsubscript{KCl} increased by 0.41-0.53 units. The maximum shift of acidity was observed on all variants of fertilizer systems in the 4-5th year of the ameliorant application, after which рН\textsubscript{KCl} values started to decrease gradually. However, even in 12 years after liming, the exchange acidity was 0.57-0.77 units lower in comparison with unlimed variants.

Numerous observations of рН\textsubscript{KCl} values allowed to describe their changes by means of appropriate regression equations (Table 1). Their use will allow, on the one hand to predict the values of рН\textsubscript{KCl} when using appropriate fertilizer systems in field crop rotations, and on the other hand - to determine the duration of ameliorating effect of lime and the timing of the next liming.

Mid-saturated chernozems of the Volga upland forest-steppe even under virgin herbaceous vegetation are characterized by significant hydrolytic acidity reaching 3-6 mg-eq/100 g of soil. In the process of use of these chernozems there is an increase of hydrolytic acidity caused by a decrease of exchangeable bases in the soil absorbing complex and their replacement by hydrogen ion.
Table 1. Dependence equations of pH$_{KCl}$ dynamics under liming and the use of different fertilizer systems.

| Variant                     | Background | Equation                                      | R$^2$ |
|-----------------------------|------------|-----------------------------------------------|-------|
| Grain-fallow crop rotation  |            |                                               |       |
| Control                     | Ca$_{0}$   | $y = -5E-05x^3 + 0.0006x^2 - 0.012x + 4.71$ | 0.987 |
|                            | Ca$_{1.0}$ | $y = 0.003x^3 - 0.068x^2 + 0.463x + 4.791$  | 0.967 |
| Manure                     | Ca$_{0}$   | $y = -3E-05x^3 + 6E-05x^2 + 0.012x + 4.74$ | 0.983 |
|                            | Ca$_{1.0}$ | $y = 0.003x^3 - 0.066x^2 + 0.454x + 4.86$  | 0.947 |
| NPK                        | Ca$_{0}$   | $y = -6E-05x^3 + 0.001x^2 - 0.02x + 4.66$  | 0.988 |
|                            | Ca$_{1.0}$ | $y = 0.003x^3 - 0.06x^2 + 0.396x + 4.784$ | 0.959 |
| Manure + NPK               | Ca$_{0}$   | $y = -6E-05x^3 + 0.0011x^2 - 0.003x + 4.702$ | 0.819 |
|                            | Ca$_{1.0}$ | $y = 0.0024x^3 - 0.061x^2 + 0.435x + 4.82$ | 0.962 |
| Manure + NPK + green manure crop | Ca$_{0}$ | $y = -4E-05x^3 + 0.0022x^2 - 0.012x + 4.736$ | 0.819 |
|                            | Ca$_{1.0}$ | $y = 0.0022x^3 - 0.0572x^2 + 0.42 + 4.85$ | 0.958 |
| Grain-grass crop rotation  |            |                                               |       |
| Control                     | Ca$_{0}$   | $y = -4E-05x^3 + 0.0001x^2 - 0.0001x + 4.75$ | 0.968 |
|                            | Ca$_{1.0}$ | $y = 0.0025x^3 - 0.072x^2 + 0.55x + 4.279$ | 0.957 |
| Manure                     | Ca$_{0}$   | $y = -0.0002x^3 + 0.003x^2 + 0.004x + 4.78$ | 0.832 |
|                            | Ca$_{1.0}$ | $y = 0.0013x^3 - 0.034x^2 + 0.244x + 5.27$ | 0.985 |
| NPK                        | Ca$_{0}$   | $y = 0.0001x^3 - 0.004x^2 + 0.009x + 4.689$ | 0.982 |
|                            | Ca$_{1.0}$ | $y = 0.003x^3 - 0.062x^2 + 0.42x + 4.75$   | 0.926 |
| Manure + NPK               | Ca$_{0}$   | $y = -0.0002x^3 + 0.0042x^2 - 0.007x + 4.68$ | 0.992 |
|                            | Ca$_{1.0}$ | $y = 0.0013x^3 - 0.036x^2 + 0.298x + 4.99$  | 0.976 |
| Manure + NPK + green manure crop | Ca$_{0}$ | $y = 0.0002x^3 - 0.005x^2 + 0.033x + 4.59$ | 0.978 |
|                            | Ca$_{1.0}$ | $y = 0.0014x^3 - 0.036x^2 + 0.25x + 5.281$ | 0.983 |

The studies showed that in the first 3-4 years on the unfertilized variant there was a tendency of growth of this type of acidity. The use of mineral fertilizers without liming contributed to an increase in hydrolytic acidity to 8.00 mg-eq/100 g of soil. The use of organic fertilizers decreased hydrolytic acidity to 7.55-7.57 mg-eq/100 g of soil. The organic-mineral fertilizer system as well as its combination with crop sideration had no significant effect on hydrolytic acidity.

The application of dolomite flour resulted in a significant reduction of hydrolytic acidity - by 2.06-2.36 mg-eq/100 g of soil already in the first year after application of the ameliorant. In the 3rd-4th years acidity values decreased by 30-40% till the initial value, and in the 5th-6th years after the application of all the systems studied a gradual increase of acidity began. At the same time, 12 years after liming, the greatest ameliorating effect was seen in the organic fertilizer system, the least in the mineral one. The $H_p$ shift was 1.41 and 0.91 mg-eq/100 g of soil, respectively.

In the process of agricultural use of soils, the arable and the root layer as a whole are depleted due to removal with the alienated crop products and migration with the filtered precipitation. The greatest alienation of carbonate, up to several metric centners, was observed in perennial legumes, root crops and vegetable crops with high yields and in clean fallows. Calcium losses increase significantly with the use of physiologically-acidic mineral fertilizers, especially in higher doses.

Our studies showed that the use of unfertilized leached chernozem for 12 years of use in a grain-fallow crop rotation showed a tendency to reduce the content of the amount of exchangeable bases. The application of manure ensured the preservation of the content of the sum of exchangeable bases at the initial level. The application of mineral fertilizers led to an increase in losses of calcium and magnesium. The application of manure and green manure ensured the maintenance of this indicator at the initial level. Liming of medium-acid chernozem was accompanied by profound changes in the composition of the soil-absorbing complex and had a positive effect on the content of exchangeable calcium and magnesium cations. A positive effect of liming was observed during the whole period of observations. The largest increase of exchangeable cations was noted in the 3rd-4th years after application of dolomitic flour: the content of the sum of exchangeable bases was increased by 13-15%
depending on the applied fertilizer system. The trend of changes in the physico-chemical properties of
leached chernozem was also manifested in the grain-grass crop rotation.

At the present stage of farming development the natural sources of nutrients in the soil (root and
crop residues, fallen and root excretions, residues of microbial and animal origin) do not compensate
the alienation of nutrients with crop yields.

All nutrients needed by plants, with the exception of nitrogen, are naturally derived from parent
rocks. The accumulation of nitrogen in soils takes place in organic form as a result of the activity of
symbiotic, free-living and associative nitrogen fixers from the molecular nitrogen of the atmosphere,
as the parent rocks can only retain a small amount of the non-exchange-absorbed elements of
ammonium ions in their crystalline lattices. Phosphorus, potassium, calcium and all other macro - and
microelements originally are available only in mineral forms, but in the process of soil formation this
or that part of some of these elements in soils can be contained in organic forms.

As studies have shown, the use of organic and mineral fertilizers contributed to the trend of
increasing the content of available phosphorus in the soil, compared with the unfertilized variant in
both crop rotations. The content of mobile forms of phosphorus has increased in the variants with
green manure crops because green manure has the ability to use phosphorus from difficult-to-reach
compounds.

Activation of microbiological activity with the application of organic fertilizers also contributed to
an increase in the content of phosphorus. The use of mineral and organic fertilizers indirectly affected
the accumulation of phosphorus in the soil by increasing the total number of roots, through which in
the process of breathing the plants emit carbon dioxide, which dissolves in water to form carbonic
acid. The anions of carbonic acid then displace the adsorbed phosphorus into the solution.

Soil pH determines the solubility of calcium, magnesium and iron salts, which interact with water-
soluble salts and phosphate ions and convert them to hard-soluble compounds. Soil acidity affects the
plant uptake of phosphorus by influencing the physiological permeability of root cell walls, the
behaviour of soil phosphorus, the competition of phosphorus with other ions. Calcium can lower the
phosphorus availability of apatite, especially for plants with poor phosphorus uptake. Conversely, the
addition of lime with iron and aluminium phosphate seems to increase the availability of phosphorus
through the formation of more soluble calcium phosphates.

When lime is applied, the lowest phosphate binding and the highest phosphate activity is observed.
The effectiveness of mineral fertilizers increases when applied in combination with lime, manure and
green manure. This has also been noted by a number of other scientists. Joint application of manure
and mineral fertilizers was the most effective.

In calcareous soils phosphorus is predominantly in mineral form, even if it does not reach the final
stable form of apatite. Previously, it was thought that when phosphorus fertilizer was applied to
calcareous soils, phosphorus was very quickly converted to an insoluble form, possibly Ca₃(PO₄)₂. It
has repeatedly been shown that phosphate in aqueous solutions is fixed by the soil instantly when
applied to calcareous soils. However, phosphorus remains available to plants.

In addition to phosphorus and nitrogen, potassium is one of the main nutrients for plants. It is
essential for all plants and microorganisms. When applied to the soil, potassium fertilizers are
dissolved in the soil solution and then interact with the soil absorption complex through exchange and
partly non-exchange absorption. As a result of transition of potassium to the exchange-absorbed state,
its mobility in the soil is limited and it is prevented from leaching outside the arable layer. The
exchangeable potassium of the fertilizer is well available to the plants. Normally, the level of available
soil potassium is equated with the level of exchangeable potassium. However, it is clear that plants do
not only use this form of potassium, because in the absence of other sources they would quickly
deplete all of the exchangeable potassium in the soil. Consequently, potassium is released from the
insoluble form and, by changing to an exchangeable form, it replenishes the available potassium.

The amount of fixed potassium in the soil depends on several factors. Liming increases potassium
fixation and the addition of soil improvers decreases it. Acidic soils fix less potassium due to the
presence of aluminium in the interlayer spaces. As our researches showed, in grain-fallow and grain-
grass crop rotations, the application of manure, mineral fertilizers did not give a reliable increase of potassium content in soil after 10-year application of different systems of fertilizers.

When using an organo-mineral system of fertilizers, as well as its combination with green manure application showed a tendency to some increase in potassium content in the arable layer. Considering the change in potassium content under different fertilizer systems it can be noted that the studied fertilizer systems in the grain-grass crop rotation contributed to a greater increase in potassium content than in the grain-fallow crop rotation. This can be explained by the increase of clover crop residues, which contain 0.86-1.78% potassium, as well as by the increase of winter wheat stubble and root residues due to the additional nutritional elements accumulated by clover.

In specific conditions it is necessary to determine the balance of nutrients, as it is this indicator that reflects the information about the relationship of fertilizers with the soil, the plant and the environment. The balance characterizes not only the share of participation of fertilizer in the small biological cycle, the provision of crops with nutrients, but also determines changes in their content in the soil, allows quantitative prediction of trends in soil fertility.

The studies established that the systematic application of fertilizers has significantly changed the balance of phosphorus and potassium. In the grain-fallow crop rotation on the variants with the joint application of organic and mineral fertilizers the balance of phosphorus is positive. When using organic and mineral fertilizers separately the phosphorus balance was negative (Table 2).

### Table 2. Phosphorus and potassium balance in field crop rotations.

| Fertilization systems | Applied with fertilizers, kg/ha | Removed by crops, kg/ha | Balance intensity, % |
|----------------------|-------------------------------|-------------------------|----------------------|
|                      | P\(_2\)O\(_5\) | K\(_2\)O | P\(_2\)O\(_5\) | K\(_2\)O | P\(_2\)O\(_5\) | K\(_2\)O |
| **Grain-fallow**     |                              |                         |                      |
| Zero                 | C\(_0\)         | -               | 227                  | 572       | 0             | 0        |
|                      | C\(_1\)         | -               | 249                  | 635       | 0             | 0        |
| Organic              | C\(_0\)         | 45              | 107                  | 268       | 689           | 16.8     | 15.5     |
|                      | C\(_1\)         | 45              | 107                  | 294       | 756           | 15.3     | 14.1     |
| Mineral              | C\(_0\)         | 260             | 260                  | 285       | 736           | 91.2     | 35.3     |
|                      | C\(_1\)         | 260             | 260                  | 318       | 819           | 81.7     | 31.7     |
| Organo-mineral       | C\(_0\)         | 305             | 367                  | 303       | 776           | 100.6    | 47.3     |
|                      | C\(_1\)         | 305             | 367                  | 339       | 881           | 89.9     | 41.6     |
| Organo-mineral with crop sideration | C\(_0\)         | 348             | 519                  | 313       | 805           | 111.2    | 64.5     |
|                      | C\(_1\)         | 348             | 519                  | 354       | 921           | 98.3     | 56.4     |
| **Grain-grass**      |                              |                         |                      |
| Zero                 | C\(_0\)         | -               | 218                  | 611       | 0             | 0        |
|                      | C\(_1\)         | -               | 232                  | 633       | 0             | 0        |
| Organic              | C\(_0\)         | 45              | 107                  | 243       | 620           | 18.5     | 17.3     |
|                      | C\(_1\)         | 45              | 107                  | 252       | 655           | 17.8     | 16.3     |
| Mineral              | C\(_0\)         | 320             | 320                  | 271       | 693           | 118.0    | 46.2     |
|                      | C\(_1\)         | 320             | 320                  | 278       | 719           | 131.0    | 59.4     |
| Organo-mineral       | C\(_0\)         | 365             | 427                  | 291       | 747           | 125.4    | 57.2     |
|                      | C\(_1\)         | 365             | 427                  | 299       | 773           | 139.1    | 80.4     |
| Organo-mineral with crop sideration | C\(_0\)         | 391             | 579                  | 281       | 720           | 130.8    | 74.9     |
|                      | C\(_1\)         | 391             | 579                  | 299       | 773           | 130.8    | 74.9     |

Crop removal of K\(_2\)O in all the studied fertilizer systems exceeded its annual input to the soil with fertilizer.

In the grain-grass crop rotation, different results were obtained: a negative P\(_2\)O\(_5\) balance was detected only when using an organic fertilizer system. In all other systems of fertilization the balance is positive. Using liming did not change the identified pattern. When liming was applied, the
expenditure item of phosphorus and potassium balance increased due to increase of crop productivity from application of chemical ameliorant. The intensity of the phosphorus balance reached 111% in the grain-fallow crop rotation and 125-139% in the grain-grass crop rotation depending on lime treatment.

Consequently, the fertilizer systems used provide expanded reproduction of phosphorus. This serves as a basis to preserve both effective and potential soil fertility, and allows, firstly, to increase soil productivity by increasing the content of nutrients, secondly, to return more than removed during harvesting, thirdly, to increase the integral tolerance of soils to anthropogenic influences.

Comparing the data of phosphorus and potassium balance with the actual change of their content in the soil, it should be noted that the actual changes in phosphorus are close to the calculated: on unfertilized variants a decrease in its content was revealed, while when using organo-mineral - there was an increase in all crop rotations. As for potassium content, it was found that its content slightly decreased without the use of fertilizers. The application of mineral fertilizers promoted the growth of K2O content in the arable layer of leached chernozem.

The fertilizer systems studied had different effects on crop yields. The minimum additional yield was obtained for all crops with the application of 8 tons of manure per hectare of crop rotation, and the maximum was obtained with the organic-mineral fertilizer system and its combination with crop-sideration.

The differences between the organo-mineral fertilization system and its combination with crop sideration were largely insignificant. Liming increased the productivity of all crops. In the second rotation of the grain-fallow crop rotation the increase of the productivity was 0.12-0.24 t/ha of grain units, in the grain-grass crop rotation - 0.14-0.29 t/ha of grain units. Organic system of fertilization provided additional annual harvest of 0.42-0.46 t/ha of grain units, mineral - 0.60-0.66 t/ha. The greatest increase in productivity in the second rotation was obtained using the organic-mineral fertilizer system and its combination with sideration: 0.85-0.91 0.96-1.10 t/ha of grain units, respectively.

4. Conclusion

Extensive use of leached chernozem and the use of mineral fertilizers worsen the physical and chemical properties: pHKCl and S decreases, Hg increases. Full hydrolytic acidity liming has a meliorative effect on the soil, which reaches a maximum on the 3rd-4th years and has an effect within 12 years. The shift of pHKCl reaches 5.82, Hg - 4.6 mg equivalent/100 g soil and S - 34.6 mg equivalent/100 g soil.

To reduce acidity and to improve physical, chemical properties of leached chernozem in conditions of the Volga forest-steppe it is necessary to apply liming of soils on full hydrolytic acidity. The results obtained on the dynamics of physical and chemical properties of the soil can be used for agro-ecological monitoring, as well as determining the sequence of liming medium acid soils.

References

[1]  Arefiev A N, Kuzina E E and Kuzin E N 2017 Niva Povolzhya 1 (42) 9–15
[2]  Safonov A V, Kuzin E N, Arefiev A N and Kuzina E E 2020 Niva Povolzhya 2 (55) 10–15
[3]  Kuzina E E, Arefiev A N and Kuzin E N 2019 Sursky Vestnik 3 (7) 29–33
[4]  Arefiev A N, Kuzina E E and Kuzin E N 2015 Niva Povolzhya 3 (36) 18–26
[5]  Lebedeva T B, Arefieva M V and Arefiev A N 2010 Plodorodie 2 (53) P 39–41
[6]  Knyazhneva E V, Nadezhkin S M, Frid A S 2006 Eurasian Soil Science V 39 1011–20
[7]  Zheryakov E 2020 Scientific Papers-Series A-Agronomy V 63 P 642–646
[8]  Bogomazov S V et al 2018 Agrotechnological Bases of Crop Cultivation Technologies (Penza: PSAU) p 257