Assessment of the potassium state of leached chernozem with long-term application of fertilizers and ameliorant

A N Kozhokina, N G Myazin, P T Brehov and P I Podrezov

Voronezh State Agrarian University, 1, Michurina Street, Voronezh, 394087, Russian Federation

Email: annakozh27@yandex.ru

Abstract. An objective assessment of the ability of the soil to supply plants with potassium is possible only when determining a set of indicators - the content of various forms of potassium in the soil and the degree of their mobility. In this regard, we conducted studies to study the effect of long-term fertilizer and ameliorant application on the content of various forms of potassium and potassium buffer capacity of the soil. The studies were carried out in a field experiment laid down in 1986. A six-field crop rotation was mastered in the experiment. We studied 7 options for experience. Soil samples were taken after the fifth rotation of the crop rotation. The results showed that long-term fertilizer application creates quite high reserves of various forms of potassium in the soil. The most intensive accumulation of forms available for plant nutrition (mobile and metabolic) was facilitated by the introduction of mineral fertilizers against the background of organic aftereffects. The use of ameliorant leads to the increase in non-exchange fixation of potassium. The study of the potential buffering capacity of leached chernozem with respect to potassium showed that even with a sufficiently high content of its mobile and metabolic forms, the soil can be characterized by a deterioration of the potash state.

1. Introduction
Potassium is one of the most important biophile elements. Plants consume significantly more potassium per unit of formed yield than other elements of mineral nutrition. This is especially true for crops that form a large number of sugars, starch, fat, etc.

Organic compounds whose structure would include potassium are unknown in plants. It is referred to as functional elements. Potassium is involved in the most important physiological processes: it increases the intensity of photosynthesis; activates the activity of over 60 enzymes; increases the rate of assimilation of nitrogen, the formation of protein and reduces the content of nitrates; optimizes the acid-base balance of cells and performs many other functions. The presence of potassium in plant nutrition is a prerequisite for their growth and development. In this regard, the ability of the soil to provide optimal conditions for potash nutrition of crops plays an important role [1].

2. Formulation of the problem
Currently, the agrochemical service is evaluating the potash state of soils, determining the content of only the mobile form of potassium. Depending on the properties of the soil, three methods are adopted: for non-carbonate soils, the method Chirikova (0.5 n CH₃COOH), acid soil method Kirsanova (0.2 n HCl), carbonate soils – method Machigina (1% (NH₄)₂CO₃). However, scientists note the imperfection of the existing assessment system [2].
So, according to the data of the SCAS “Voronezhsky” as of 01.01.2017, the weighted average potassium content in the soils of the Voronezh region was 124 mg / kg of soil. This corresponds to the class of high soil availability with potassium. Moreover, it increased by 9 mg / kg of soil compared to the first round of the agrochemical survey (1964–1970). At the same time, if for the period 1964-1970 the potassium input into the soil with mineral and organic fertilizers was 35 kg a.v. / ha, as of 01.01.2017, 18.5 kg a.v. potassium per hectare [3, 4]. Thus, it becomes unclear, due to which the increased potassium content in the soils of the region.

Meanwhile, studies have established that potassium in the soil is contained in several forms. That is why the determination of the content of only one form of potassium does not characterize its potassium state as a whole [5]. In addition, one of the reasons for the deterioration in the supply of plants with potassium may be not an absolute decrease in its quantity, but a weakening of the ability of the soil to maintain its initial state and to restore the necessary potassium content in an accessible form (potential buffering ability of the soil with respect to potassium is PBA\textsuperscript{K}) [6].

In this regard, the aim of our research was to assess the effect of long-term fertilizer and ameliorant application on the potassium state of leached chernozem using extensive (content of various forms of potassium) and intensive (PBC\textsuperscript{K}) indicators.

3. Materials and methods
The studies were conducted on the territory of the ESTC "Agrotechnology" in a stationary field experiment of the Department of Agrochemistry and Soil Science of the Voronezh State Agrarian University, founded in 1986. The soil of the experimental plot is represented by leached chernozem of low-humus medium-power heavy loamy on integumentary loams. Agrochemical characteristics of the soil of the experimental plot before laying the experiment are presented in table 1.

| Table 1. Agrochemical characteristics of leached chernozem before the experiment, (layer 0-40 cm) |
| --- | --- | --- | --- | --- |
| Humus content, % | pH\textsubscript{KCl} | Hg \textsuperscript{mg-eq./100 g of soil} | S \textsuperscript{%,} | V, % | Content of mobile forms, \textsuperscript{mg/kg of soil} |
| 3.96 | 5.5 | 5.2 | 27.3 | 84.4 | 122.0 | 99.0 |

In the experiment, a six-field crop rotation was developed with the following crop rotation: black steam - winter wheat - sugar beet - vetch-oat mixture for green fodder - winter wheat - barley. By the time of the present research, the fifth rotation of the crop rotation had ended.

The experience design includes 15 options. Our research was conducted on seven (table 1). The repetition of the experiment is fourfold, the placement of the repetitions is two-tier, the arrangement of the plots is systematic staggered. The total area of the experimental plot is 191.7 m\textsuperscript{2} (35.5 m * 5.4 m).

The NPK fertilizer dose was accepted as the optimal one, recommended for spreading under crops on leached chernozem of the central chemistry center according to the results of field experiments. Fertilizers and ameliorant were introduced into the field of pure steam in the autumn for plowing. In the fifth rotation of the crop rotation, liming of the soil was not carried out.

To carry out the research, after completing the fifth rotation of the crop rotation (after harvesting the barley), soil samples were taken to a depth of 100 cm, layer by layer every 20 cm from two non-adjacent repetitions in five repetitions. The determination of the basic agrochemical properties of the soil was carried out according to generally accepted methods [7]. The determination of potassium status indicators was carried out using the following methods: readily available form according to the Golubeva method, mobile form according to the Chirikov method (GOST 26204–91), exchange form according to the Maslova method (GOST 26210–91), easily hydrolyzed non-exchangeable form - according to the Pchelkin method (copyright certificate № 1220684 30–15), hard-hydrolyzed non-exchangeable form - according to the Gedroits method, potential potassium buffering (PBA\textsuperscript{K}) - according to Becket [7].
4. The discussion of the results

The results of a study of the basic physicochemical properties of leached chernozem (table 2) showed that soil acidification was observed both on an unfertilized version of the experiment and when various combinations of mineral and organic fertilizers were used (options 2, 3, and 5). The pH\textsubscript{KCl} value decreased by 0.5–0.8 compared with the period before the start of the experiment.

Table 2. Effect of fertilizers and ameliorant on the physicochemical properties of leached chernozem, layer 0-40 cm, 2018

| Experience Options                             | pH\textsubscript{H2O} | pH\textsubscript{KCl} | Hg, mg\textsubscript{eq}/100 g of the soil | Ca+Mg, mg\textsubscript{eq}/100 g of the soil |
|-----------------------------------------------|-----------------------|-----------------------|------------------------------------------|---------------------------------------------|
| 1. Control                                    | 5.9                   | 4.9                   | 5.1                                      | 23.7                                       |
| 2. Background - 40 t/ha of manure (residual effect) | 6.4                   | 5.0                   | 4.8                                      | 24.3                                       |
| 3. Background + NPK                           | 6.2                   | 4.9                   | 6.0                                      | 23.6                                       |
| 5. Background + NPK                           | 5.9                   | 4.7                   | 6.4                                      | 23.4                                       |
| 12. Background + NPK + lime (aftereffect)     | 6.6                   | 5.5                   | 4.2                                      | 24.8                                       |
| 13. Background + lime (aftereffect)           | 6.6                   | 5.6                   | 3.7                                      | 25.2                                       |
| 15. Defecate (aftereffect) + NPK              | 6.5                   | 5.4                   | 4.2                                      | 24.9                                       |
| SSD\textsubscript{0.95}                       | 0.20                  | 0.07                  | 0.32                                     | 0.35                                       |
| Sx, %                                         | 2.28                  | 2.21                  | 2.96                                     | 3.02                                       |

In variants with liming aftereffect (options 12, 13 and 15), soil acidity indicators stabilized almost at the initial level. It is worth noting that in 2018 was the twelfth year of the aftermath of the defect.

According to their accessibility to plants, scientists in the following series arrange all forms of soil potassium compounds: water-soluble potassium> exchange potassium> non-exchange potassium, and consider that there is a dynamic equilibrium between these forms [8, 9]. Sychev V.G. distinguishes two forms of non-exchanged potassium, which are the closest reserve of replenishment of exchange potassium. The first (easily hydrolyzable) is diagnosed using an extract of 2 n HCl (Pchelkin's method), the second (difficultly hydrolyzed) - 10% HCl (Gedroits method) [10]. The participation of non-exchange potassium in plant nutrition has been confirmed in the works of many scientists [11, 12, 13].

The results of our studies to determine the content of mobile potassium in leached chernozem (table 3) showed that, upon completion of the fifth rotation of the crop rotation, on the option without fertilizing it not only did not decrease, but also even increased by 18 mg / kg of soil compared to the period before laying experience (1986). Less than the control content of this form of potassium was provided by variants with aftereffect of only manure, application of mineral fertilizers in a single dose against this background, and reclaimed experimental options (options 2, 3, 12, 13 and 15).

The highest content of mobile potassium in the soil was observed with long-term application of fertilizers in a double dose (option 5), where it was 7 mg / kg of soil above the control and 21 mg / kg of soil with a single dose of mineral fertilizers.

The content of easily exchanged and hardly exchanged forms of potassium was subject to other laws. So, if, with the aftereffect of 40 t / ha of manure, the content of the easily exchanged form was at the control level, and the hardly exchanged form was slightly lower, then the application of mineral fertilizers against this background led to a noticeable increase in it, the higher the higher the dose. The reclaimed variants of the experiment were characterized by a lower content of the easily exchanged form of potassium, while the hardly exchanged potassium was 32-91 mg / kg more soil than on the variants without defecate.
Table 3. Content of various forms of potassium in leached chernozem, mg/kg of soil, 2018

| Experience Options | Mobile potassium (Chirikov) | Easy exchange (Golubeva) | Hard exchange (Maslova) | Easy hydrolyzable (Pchelkin) | Hard hydrolyzable (Gedroits) |
|--------------------|-----------------------------|-------------------------|------------------------|-----------------------------|----------------------------|
| 1. Control         | 117                         | 2.7                     | 332                    | 273                         | 3540                       |
| 2. Background - 40 t/ha of manure (residual effect) | 97                          | 2.7                     | 312                    | 294                         | 3849                       |
| 3. Background + NPK | 103                         | 3.6                     | 384                    | 249                         | 3785                       |
| 5. Background + NPK | 124                         | 4.1                     | 448                    | 251                         | 3650                       |
| 12. Background + NPK + lime (aftereffect) | 99                          | 3.3                     | 416                    | 305                         | 3966                       |
| 13. Background + lime (aftereffect) | 107                         | 2.6                     | 403                    | 304                         | 3664                       |
| 15. Defecate (aftereffect) + NPK | 104                         | 3.2                     | 401                    | 309                         | 3740                       |
| SSD_{0.95}         |                             |                         |                        | 3.61                        | 3.82                       |
| Sx. %              | 3.69                        | 2.97                    | 3.61                   | 3.82                        | 5.06                       |

The content of the easily hydrolyzable non-exchangeable form of potassium was greatest in the calcined variants of the experiment (variants 12, 13, 15). Moreover, among themselves, these options for this indicator practically did not differ. The aftereffect of 40 t/ha of manure (option 2) provided 21 mg/kg of soil with a higher content of easily hydrolyzable non-exchange potassium in relation to the control. In addition, the introduction of mineral fertilizers in single and double doses against this background reduced it by 55 and 43 mg/kg of soil, respectively, to option 2.

The value of hard-hydrolyzable non-exchange potassium took the smallest values in the control variant. The aftereffect of organic fertilizers increased this indicator by 309 mg/kg of soil. When mineral fertilizers were added against the background of manure, the content of hard-hydrolyzable non-exchange potassium in relation to the background variant decreased by 64 mg/kg of soil in the case of a single dose and by almost 200 mg/kg of soil when using a double dose of mineral fertilizers.

The use of a single dose of mineral fertilizers in various combinations with manure and defecate (options 12 and 15) ensured the content of hard-hydrolyzable non-exchange potassium at the level of option 3, and the combined introduction of manure and defecate without mineral fertilizers at the level of the option with a double dose of mineral fertilizers.
Considering the distribution of potassium reserves according to the experimental options (Figure 1), it should be noted that the application of mineral fertilizers against the background of organic aftereffects (options 3 and 5) created conditions for the accumulation of potassium mainly in the exchange and hardly hydrolyzed non-exchange state. This is probably due to the fact that freshly introduced potassium of mineral fertilizers was absorbed metabolically, but since not all of it was consumed by plants, conditions were created for its non-exchange fixation. In the variants with liming aftereffect, the reserves of both exchange and mobile potassium were slightly less than in the variants without ameliorant. At the same time, the stocks of its non-exchange forms increased.

The sorption isotherms of the potential potassium buffering of leached chernozem are presented in Figure 2. Most of the experimental points on the curves lie above the abscissa axis, which indicates the ability of the soil to take potassium from the solution to a greater extent than to give it away. Moreover, even with the option of long-term double-dose application of mineral fertilizers against the background of manure aftereffect (option 5), despite the fairly high reserves of all the studied forms of potassium, the soil gave out potassium only if it was not in the displacing solution (0.002 n CaCl$_2$).
In the soil absorption complex, two groups of adsorption sites are distinguished. These are energetically homogeneous sites with a lower binding energy, corresponding to exchange cations at non-specific positions in the soil absorbing complex located on the upper surfaces of crystals - p-sites and places with a larger, but not the same bond energy - e-sites per rib, corners, surface protrusions, “specific” exchange positions [7]. Potassium adsorbed at p-sites to be directly accessible to plants (\(-\Delta K_0\)). Occupying e-potassium is classified as inaccessible mobile potassium (\(K_X\)). In total, these two parameters give the total amount of mobile (labile) potassium reserves in a given soil (\(K_L\)).

Our studies (table 4) showed that in the fertilized versions of the experiment, the maximum value of \(-\Delta K_0\) was observed in the upper part of the profile and gradually decreased with depth. This is probably due to the introduction of fertilizers, which contribute to the accumulation of potassium in a more mobile state. In the calcined variants of the experiment, a tendency to a lower content of mobile potassium was observed in comparison with the non-reclaimed variants of the experiment. Changes in the content along the profile of labile (\(-K_L\)) and inaccessible mobile (\(-K_X\)) potassium are also subject to the same laws.

The value of \(AR_0\), which characterizes the ratio of the activities of potassium and calcium ions in an equilibrium solution, is called the intensity factor. The higher it is, the more energy must be expended in order to displace potassium from the exchange-absorbed state by a calcium cation. Studies have shown that the value of \(AR_0\) decreased with depth. In addition, on options with the introduction of mineral fertilizers against the background of organic aftereffects (options 3 and 5), it
was slightly lower than on the reclaimed options for the experiment. This suggests that when liming potassium in the soil absorbing complex becomes less mobile, moving from p-sites (non-specific exchange positions) to e-places (specific positions).

Table 4. Buffering capacity of leached chernozem (PBC$^K$)

| Options | Layer, cm | PBC$^K$ | AR$_0$$\times 10^3$ (mol/l) | $-\Delta K_0$ (mg-eq./100 g of soil) | $-K_L$ | $-K_X$ |
|---------|-----------|---------|----------------------------|------------------------------------|--------|--------|
| 0-20    | 11.1      | 1.80    | 0.02                       | 0.30                               | 0.28   |
| 20-40   | 15.0      | 2.00    | 0.03                       | 0.90                               | 0.87   |
| 40-60   | 50.0      | 1.40    | 0.07                       | 0.55                               | 0.48   |
| 1       | 60-80     | 41.7    | 1.20                       | 0.05                               | 0.50   | 0.45   |
| 80-100  | 33.7      | 0.89    | 0.03                       | 0.47                               | 0.44   |
| 0-20    | 43.3      | 1.50    | 0.08                       | 0.47                               | 0.39   |
| 20-40   | 30.0      | 1.50    | 0.06                       | 0.42                               | 0.36   |
| 40-60   | 16.7      | 1.20    | 0.02                       | 0.41                               | 0.39   |
| 1       | 60-80     | 9.1     | 1.10                       | 0.01                               | 0.37   | 0.36   |
| 80-100  | 33.3      | 0.90    | 0.03                       | 0.31                               | 0.28   |
| 0-20    | 52.4      | 2.10    | 0.11                       | 0.81                               | 0.70   |
| 20-40   | 45.0      | 2.00    | 0.09                       | 0.51                               | 0.42   |
| 40-60   | 31.3      | 1.60    | 0.05                       | 0.41                               | 0.36   |
| 3       | 60-80     | 53.8    | 1.30                       | 0.07                               | 0.36   | 0.29   |
| 80-100  | 30.0      | 1.00    | 0.09                       | 0.33                               | 0.24   |
| 0-20    | 86.6      | 1.27    | 0.11                       | 0.87                               | 0.76   |
| 20-40   | 55.0      | 2.00    | 0.11                       | 0.80                               | 0.69   |
| 5       | 40-60     | 58.3    | 1.20                       | 0.07                               | 0.60   | 0.53   |
| 60-80   | 51.7      | 1.16    | 0.06                       | 0.41                               | 0.35   |
| 80-100  | 33.7      | 0.89    | 0.03                       | 0.32                               | 0.29   |
| 0-20    | 41.7      | 2.40    | 0.10                       | 0.65                               | 0.55   |
| 20-40   | 41.2      | 1.70    | 0.07                       | 0.61                               | 0.54   |
| 12      | 40-60     | 50.0    | 1.20                       | 0.06                               | 0.59   | 0.53   |
| 60-80   | 26.7      | 1.50    | 0.04                       | 0.44                               | 0.40   |
| 80-100  | 20.7      | 1.45    | 0.03                       | 0.36                               | 0.33   |
| 0-20    | 38.3      | 2.40    | 0.07                       | 0.57                               | 0.50   |
| 20-40   | 31.6      | 1.55    | 0.05                       | 0.54                               | 0.49   |
| 13      | 40-60     | 21.4    | 1.40                       | 0.03                               | 0.45   | 0.42   |
| 60-80   | 23.4      | 1.28    | 0.03                       | 0.37                               | 0.34   |
| 80-100  | 15.4      | 1.30    | 0.02                       | 0.30                               | 0.28   |
| 0-20    | 48.8      | 1.70    | 0.10                       | 0.55                               | 0.45   |
| 20-40   | 42.2      | 1.34    | 0.07                       | 0.47                               | 0.40   |
| 15      | 40-60     | 58.1    | 0.86                       | 0.05                               | 0.40   | 0.35   |
| 60-80   | 41.7      | 1.20    | 0.05                       | 0.38                               | 0.33   |
| 80-100  | 27.3      | 1.10    | 0.03                       | 0.32                               | 0.29   |

Soil buffering capacity for potassium (PBC$^K$) was the lowest in the control. The introduction of manure increased the PBC$^h$ value by almost four times, and the use of mineral fertilizers against its background, depending on the dose, by 5-8 times in relation to the control. The buffer capacity of the soil with respect to potassium increased also on the reclaimed variants of the experiment. However, this increase was to a lesser extent.
Moreover, according to Beckett’s classification, in the variants with single and double doses of mineral fertilizers (variants 3 and 5) in the upper soil layers, PBA was assessed as medium, in variants 2, 12, 13 and 15 - low, and in the control version - very low.

5. Conclusion
The conducted studies allow concluding that, long-term application of fertilizers creates quite high reserves of various forms of potassium in the soil. The most intensive accumulation of forms available for plant nutrition (mobile and metabolic) is facilitated by the introduction of mineral fertilizers against the background of organic aftereffects. The use of ameliorant leads to the increase in non-exchange fixation of potassium. However, only a quantitative determination of the content of various forms of potassium did not fully reflect the potassium state of leached chernozem. The study of the potential buffering capacity of leached chernozem with respect to potassium showed that even with a sufficiently high content of its mobile and metabolic forms, the soil can be characterized by a deterioration of the potash state.

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