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Potassium Status and Clay Mineralogy in Ordinary Chernozems Treated with Different Rates of Potassium Fertilizers

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Abstract—The effect of a single instance of potassium fertilization at rates of 0, 70, 140, and 280 kg/ha on the potassium status and clay mineralogy was studied in a field experiment on ordinary chernozems. The content of exchangeable potassium determined by the Maslova method and the potassium potential vary with greatest reliability in response to increasing fertilizer rates. The content of easily exchangeable potassium and the potassium-buffering capacity are insignificantly affected by the application rate of potassium fertilizers. The chernozems under study without fertilization are characterized by a low supply of available potassium. When potassium fertilizers are applied at rates of 70 and 140 kg/ha, the soils pass into the category of unstable or high supply according to different gradation systems. The lower limit of the high or optimal supply category is reached only at the application of 280 kg/ha of potassium fertilizer. However, even in this case, chernozems are characterized by a low potassium supply according to the value of potassium potential and the content of nonexchangeable potassium. A single application of potassium fertilizers does not cause significant changes in the contents of illites in the clay fraction.

Keywords: potassium, fertilizers, chernozem, mineralogy
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INTRODUCTION

The role of potassium in plant nutrition is well known: it significantly improves the quality of crops, favors the formation of ATP, increases the resistance of plants to different stresses, activates the fixation of nitrogen by legumes, and reduces the input of radionuclides into agricultural crops [12]. The element also favors the increase in the swelling capacity of colloids, the hydrophilicity of protoplasm, and the conductivity of cell walls [2].

Plants obtain the majority of their potassium from the soil, where this element exists in the form of compounds of different availability. The most available potassium occurs in the soil solution, to which it arrives from weathered potassium-containing minerals, decomposed plant residues, and applied potassium fertilizers. When the concentration of potassium in the solution decreases, some amount of the element can come from the soil exchange complex. When the reserve of exchangeable potassium is exhausted, is can be replenished from nonexchangeable compounds mainly composed of less stable illites inherited from the rock and secondary illites formed during the fixation of the element by labile clay minerals. These well-known ideas are reflected in the model of soil potassium status [26], in accordance with which the commonly used set of parameters was developed, which involves the determination of exchangeable, easily exchangeable, and nonexchangeable potassium [15, 26]. The assessment of the binding strength of potassium to the solid phase and, hence, its availability to plants also includes the following thermodynamic parameters: potassium potential and potential buffering capacity of soils for potassium [7, 21–23, 28].

It has been found that the Maslova method is more suitable for the determination of exchangeable potassium in soddy-podzolic soils and chernozems than the Kirsanov and Chirikov methods, because the amount of potassium extracted by the 0.1 M CH_3COONH_4 solution more adequately reflects the changes in the potassium status of soils with different particle-size distributions caused by the application of potassium fertilizers [8].

It has been shown in some works that the long-term application of potassium fertilizers at high rates results in the accumulation of illites in the fine fractions because of the fixation of potassium by labile clay minerals. The potassium exhaustion of soils gives an opposite result: the transformation of illites to labile structures [9, 20, 24, 27]. Thus, the behavior of potassium in the *soil solid phase* ↔ *solution* ↔ *plant* system represents a rather dynamic buffer structure. In its different links, equilibriums shift depending on the input

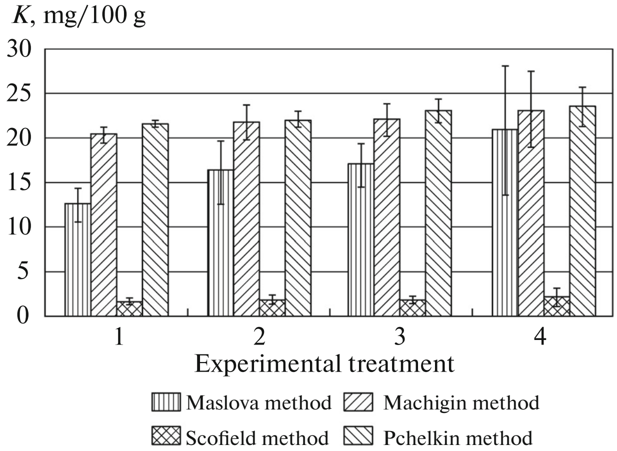

Fig. 1. Content of potassium determined by different methods (means ± confidence interval at $P = 0.8$, $n = 3$).

of potassium and its consumption by plants in different seasons [20].

This paper presents the results of studying the potassium status and clay mineralogy of ordinary chernozems after a single application of potassium fertilizers at different rates. The work was performed within the framework of the Project of the Russian Branch of International Plant Nutrition Institute "Improvement of recommendations on potash fertilizer use and adjustment of currently used soil K test interpretation classes in intensive cropping systems." The implementation of the project is related to the insufficient attention that has been paid to the optimization of the potassium status of arable soils, especially chernozems, in Russia.

Although chernozems are considered to be soils with increased content of available potassium [13], the analysis of mass data on this element in soils of the Central Chernozemic Zone showed that the stabilization of their potassium status and the ensuring of balanced mineral nutrition of agricultural crop require increasing the input of potassium into agrolandscapes [18]. The first results of work on the Project showed that the application of potassium fertilizers to chernozems in Voronezh oblast increased the yield of sugar beet and its sugar content [6].

MATERIALS AND METHODS

Samples of ordinary chernozems were taken from four plots of the field experiment established in the Anna district of Voronezh oblast with the application of mineral fertilizers at different rates. The experimental design included the following treatments: (1) $N_{58}P_{104}$ (background), (2) NP + 70 kg K_2O/ha, (3) NP + 140 kg K_2O/ha, and (4) NP + 280 kg K_2O/ha. Experiments were performed in triplicate. Fertilizers were applied in fall of 2012; during the 2013 vegetation period, the plots were occupied by sugar beet. Samples were taken after harvest in fall of 2013.

For general chemical characterization of soils, the following parameters were determined: humus (by the Tyurin method), exchangeable Ca and Mg (by the Pfeffer method); pH (by potentiometry [3]), exchangeable K in a 1 M CH_3COONH_4 solution (by the Maslova method) and in a 0.1 M $(NH_4)_2CO_3$ solution (by the Machigin method), easily exchangeable K in a 0.01 M $CaCl_2$ solution (by the Scofield method), nonexchangeable K in a 2 M HCl solution (by the Pchelkin method [10]), and potassium-buffering capacity and potassium potential (according to Beckett [22] and Woodruff [28], respectively). The determination of potassium in extracts was performed by flame photometry on a Jenway PFP7 instrument. The mineralogy of the clay fraction separated according to Aidinyan [1] was studied using X-ray diffractometry [16]; the content of illites was estimated from the content of K_2O in the clay fraction under the assumption that its content in illites is 7.5% [14].

The obtained results were processed by both parametric and nonparametric statistic methods using Excel and Statistica software [11]. Nonparametric methods were used, because the distributions of some parameters in separate experimental treatments strongly differed from the normal law.

RESULTS AND DISCUSSION

Chernozems have a weakly alkaline reaction in all of the experimental treatments, which indicates the presence of carbonates, and a high content of C_{org}. Calcium and magnesium are the dominant exchangeable cations. No regular differences in these parameters are observed among the experimental treatments.

Exchangeable potassium determined by the Maslova method. The mean and median values of exchangeable potassium content regularly increase with increasing rate of potassium fertilizers (Figs. 1 and 2). The significance of differences is confirmed by the *t*-test at $P =$ 0.99 in the comparison between the control and experimental treatment 3 (140 kg K_2O/ha) and $P = 0.81$ in the comparison between the control and treatment 4 (280 kg K_2O/ha). The use of the nonparametric Wilcoxon test reveals differences between the control and experimental treatments 3 and 4 at $P = 0.89$.

Exchangeable potassium determined by the Machigin method. The solution extracts significantly more potassium than the Maslova solution (Figs. 1 and 3), although appreciably less concentrated reagent is used. The same displacing cation (NH_4^+) is used in both methods; therefore, the revealed differences can be attributed to the higher pH values in the Machigin solution (9.0 [4]) than in the Maslova solution (6.8–7.0 [5]). The mean and median contents of exchangeable potassium determined by the Machigin method

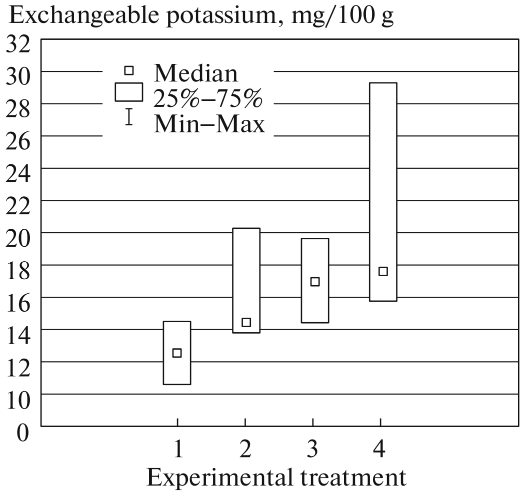

Fig. 2. Content of exchangeable potassium in the Maslova solution.

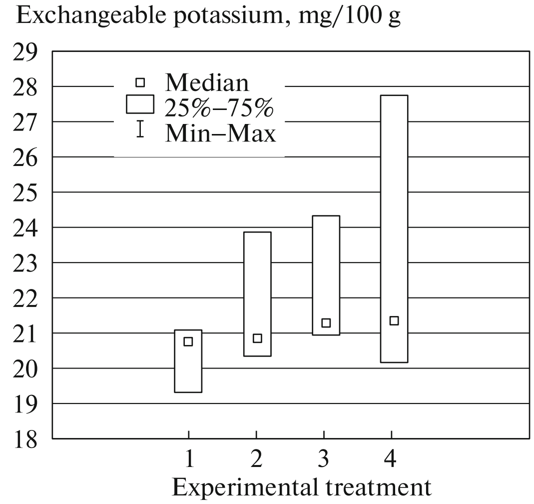

Fig. 3. Content of exchangeable potassium in the Machigin solution.

also regularly increase at an increasing rate of potassium fertilizers.

The nonparametric sign test does not reveal differences between the experimental treatments at $P > 0.8$. The weaker Wilcoxon test reveals differences between the control and treatments 1, 2, and 3 at $P = 0.9$.

The comparison of the median potassium contents in the Maslova and Machigin solutions (Fig. 2 and 3, respectively) allows it to be concluded that the differences between the experimental treatments with different rates of potassium fertilizers are better traced in the former solution. In these terms, the former extract can be considered as more informative.

Easily exchangeable potassium determined by the Scofield method. This weak salt solution (Figs. 1 and 4) extracts an order of magnitude less potassium than the Maslova and Machigin solutions. This is related to the lower reagent concentration and the use of calcium as the displacing cation, the potassium-displacing ability of which is lower than that of ammonium.

No differences between the experimental treatments are observed at the use of the nonparametric sign test. The Wilcoxon test reveals differences between the control and the other experimental treatments significant at $P = 0.90$. The absence of clear differences in the content of the element in the weak salt extract between the experimental treatments can be related to the sampling in fall, when the major reserve of easily exchangeable potassium is already exhausted.

Nonexchangeable potassium determined by the Pchelkin method. It can be seen (Fig. 1) that the mean contents of nonexchangeable potassium in this solution exceed those for exchangeable potassium in the Maslova solution, as should be expected, and are very similar to the contents in the Machigin solution. These results can be explained as being a result of the combined effect of several factors. First, the studied chernozems contain some amount of carbonates and have a significant acid-buffering capacity due to their presence and the high contents of organic matter and exchangeable bases, which should reduce the concentration of protons in the equilibrated liquid phase and, hence, decrease the acid impact on the soil. Second, the higher pH value in the Machigin solution can result in the partial dissolution of humic films on the surface of particles and aggregates so that an additional amount of potassium becomes available for extraction by the reagent. Therefore, the content of potassium in the Machigin solution is close to that of nonexchangeable potassium.

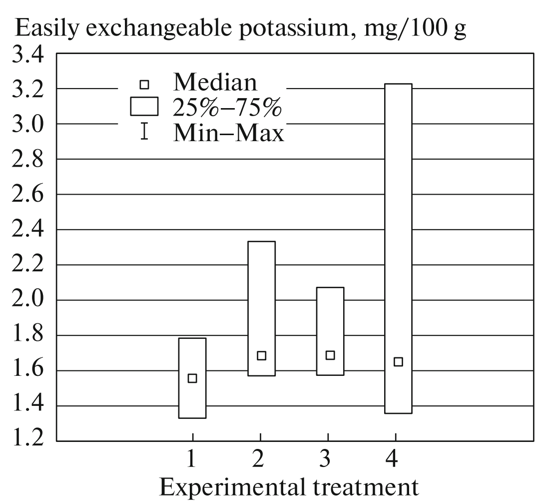

Fig. 4. Content of easily exchangeable potassium in the Scofield solution.

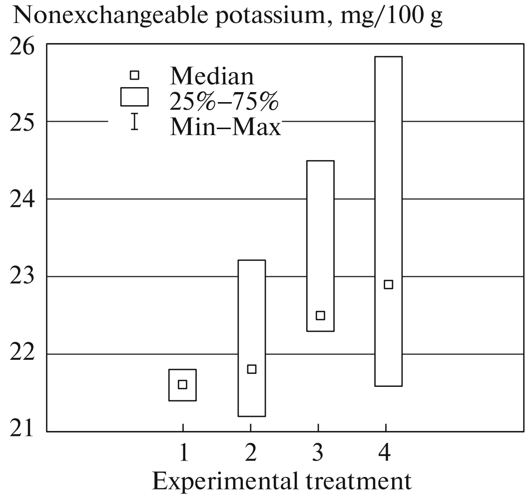

Fig. 5. Content of nonexchangeable potassium in the Pchelkin solution.

The mean (Fig. 1) and median (Fig. 5) contents of nonexchangeable potassium regularly increase with increasing rates of potassium fertilizers. Significant differences between treatments 1 and 3 at $P = 0.87$, between treatments 2 and 3 at $P = 0.94$, and between treatments 2 and 4 at $P = 0.83$ are revealed using the t-test. The significance of differences at $P = 0.9$ between these treatments is confirmed by the nonparametric Wilcoxon test.

A direct correlation is observed between all of the considered parameters of chernozem potassium status; the Spearman correlation coefficients are significant at $P > 0.95$. The closest correlation exists between the content of potassium in the Machigin solution and in the Pchelkin and Scofield solutions (Table 1).

Potential potassium-buffering capacity and potassium potential of soils. It can be seen (Table 2) that the application of fertilizers regularly affects the potassium potential, which decreases with increasing rates of potassium fertilizers from 3.92 in the control to 2.74 in treatment 4 with the maximum fertilizer rate (280 kg/ha).

Table 1. Speakman coefficients of pair correlation between the potassium status parameters

	Potassium by Maslova	Potassium by Machigin	Potassium by Scofield
Potassium by Maslova	1.00		
Potassium by Machigin	0.70	1.00	
Potassium by Scofield	0.62	0.85	1.00
Potassium by Pchelkin	0.79	0.96	0.80

The values of potential potassium-buffering capacity (PBC^K) of soils are more stable; they vary in the range 101–104 (mmeq/100 g)/(mol/L)$^{-0.5}$ in the first three experimental treatments and slightly increase only in the treatment with the application of the highest fertilizer rates. Beckett and Nafady [23] also noted the relative constancy of the PBC^K value and its slight change upon the application of potassium fertilizers.

It follows from the data considered that a single application of potassium fertilizers at different rates in combination with similar amounts of nitrogen and phosphorus has the highest effect on the content of exchangeable potassium determined by the Maslova method and the potassium potential of soils.

Evaluation of soil supply with mobile potassium using the existing gradations. According to the Russian gradation of soils depending on their supply with mobile potassium, its content in the Maslova solution equal to 5–10, 10–15, 15–20, and 20–30 mg/100 g corresponds to low, medium, increased, and high supply, respectively. The above categories correspond to the element contents of 10–20, 20–30, 30–40, and 40–60 mg/100 g, respectively, in the Machigin solution and to 10–20, 20–50, 50–100, and 100–150 mg/100 g, respectively, in the Pchelkin solution [13, 17]. Yakimenko [19] developed a gradation of soils by their supply with mobile potassium for loamy chernozems and gray forest soils of Western Siberia. For the former soils, the categories of low, unsteady, optimal, and increased supply correspond to the potassium content in the Maslova solution equal to <15, 15–20, 20–25, and >25 mg/100 g, respectively. The latter three categories are characterized by a content of nonexchangeable potassium of <60, 60–100, and >110 mg/100 g, respectively.

Woodruff [28] proposed to estimate the potassium supply of soils from the value of potassium potential and developed the corresponding gradation for this parameter: the insufficient, optimal, and increased supply with this element correspond to potassium potential ranges of 2.2–2.9, 1.8–2.2, and <1.5, respectively.

Thus, according to the conventional gradation system [13, 17], the soils in the control treatment without application of potassium fertilizers can be considered as low-supplied with all potassium compounds determined by the Maslova, Machigin, and Pchelkin methods. In treatments 2 and 3 (70 and 140 kg K_2O/ha, respectively), the soils pass to the category of increased supply with exchangeable potassium by Maslova and medium supply with exchangeable potassium by Machigin and nonexchangeable potassium by Pchelkin. In treatment 4 with the maximum rate of potassium fertilizers (280 kg/ha), the soils remain in the category of increased supply according to the median values in the Maslova solution and correspond to the lower boundary of high supply according to the mean values. The soils also remain in the category of

Table 2. The values of pH, contents of C_{org} and exchangeable Ca and Mg, potassium-buffering capacity, and potassium potential in the experimental treatments (means ± standard deviation, $n = 3$)

Experimental treatment	pH_{water}*	C_{org}, %	Exchangeable bases, ceq/kg		Potassium-buffering capacity, $(mmeq/100\ g)/(mol/L)^{-0.5}$	Potassium potential
			Ca	Mg		
1, NP	7.1	4.38 ± 0.50	15.33 ± 0.60	3.67 ± 0.58	101.7***	3.92***
2, NP + K_{70}	7.1	3.18 ± 0.27	14.67 ± 2.50	3.33 ± 2.31	104.8*	3.89*
3, NP + K_{140}	7.4	3.07 ± 0.44	15.00 ± 1.00	5.33 ± 2.31	101.3**	3.44**
4, NP + K_{280}	7.2	4.43 ± 1.40	18.00 ± 2.00	3.00 ± 2.00	115.9**	2.74**

* single replicate, ** average of two replicates, *** average of three replicates.

medium supply according to the content of potassium in the Machigin and Pchelkin solutions.

The use of the gradation developed by Yakimenko [19] gives slightly different results. The soil of the control treatment can be considered as low-supplied with all of the determined potassium forms. At the application of 70, 140, and even 280 kg K_2O/ha, the soils pass to the category of unsteady supplied with potassium according to the median values of the Maslova method. At the estimation from the mean values, the soils remain at the lower boundary of optimal supply. From the content of nonexchangeable potassium (both mean and median values), the soils of the all four experimental treatments belong to the category of unsteady supplied.

Thus, without the application of potassium fertilizers, the chernozems are characterized by the low supply with exchangeable potassium. At the application of fertilizers at 70 and 140 kg/ha, they pass to the category of unsteady or increased supply according to different gradations. Only at the application of potassium fertilizers at a rate of 280 kg/ha, the lower boundary of the high or optimal supply category is reached. However, even in this case, the soils are characterized as low supplied from the content of nonexchangeable potassium and the values of potassium potential.

The study of clay mineralogy in the studied soils showed that the set of clay minerals common for chernozems on loess-like loams prevails in clay: illite–smectite interstratifications with smectite layers, illites, kaolinite, and chlorite.

The content of illites (minerals most closely related to the potassium status of soils) slightly and irregularly varies among the experimental treatments from 28 to 31%. No significant differences between the control and any experimental treatment are revealed at $P =$ 0.9. The increase in the content of illites caused by the application of potassium fertilizers that has been revealed by some authors [9, 20, 24, 27] is apparently manifested only after the long-term application of potassium at sufficiently high rates ensuring the development of illitization.

CONCLUSIONS

• A single application of potassium fertilizers at rates of 0, 70, 140, and 280 kg/ha to soils (ordinary chernozem) in field experiments results in a regular increase in the content of exchangeable potassium (determined by the Maslova and Machigin methods) and nonexchangeable potassium (determined by the Pchelkin method) and a decrease in potassium potential. The increase in the rate of fertilizers most probably affects the content of exchangeable potassium by Maslova and the potassium potential. The content of easily exchangeable potassium and the potassium-buffering capacity vary insignificantly.

• A high direct correlation exists between the content of exchangeable potassium determined by the Maslova and Machigin methods and the content of nonexchangeable potassium: the coefficients of correlation between all pairs of parameters are significant at $P > 0.95$.

• Without the application of potassium fertilizers, chernozems are characterized by low supply with exchangeable potassium. At the application of potassium fertilizers at rates of 70 and 140 kg/ha, they pass to the category of unsteady or increased supply according to different gradations. At the application of potassium fertilizers at 280 kg/ha, the lower boundary of the high or optimal supply category is reached. However, even in this case, the soils are characterized as low supplied according to their content of nonexchangeable potassium and the potassium potential.

• A single application of potassium fertilizers causes no reliable change in the content of illites in the clay fraction.

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