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SOIL CHEMISTRY

Potential Potassium Buffer Capacity
4 # of Kamchatka Volcanic Soils

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4 **Abstract**—The volcanic soils of Kamchatka are characterized by low and very low values of their potential potassium buffer capacity. The largest amount of readily exchangeable potassium ($-\Delta K_0$) is observed in the surface layers of the natural soils and is due to the active biogenic accumulation. The soddy horizons have a high content of strongly fixed potassium (K_X). The main factors determining the content of the labile potassium and its mobility are the contents of physical clay, humus, and exchangeable potassium. The extremely nonuniform distribution of all the potassium status parameters throughout the soil profile reflects the discrete character of the volcanic pedogenesis. The low values of the potential buffer capacity for the potassium (PBC_K) at the high values of the equilibrium potassium potential (AR_0) and the medium content of the labile potassium in the light-textured synlithogenic soils simultaneously indicate both the good potassium supply of the plants and the incapability of the soils to resist potassium exhaustion under agricultural production conditions for a long time.

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INTRODUCTION

1 The set of conventional extensive agrochemical parameters (water-soluble, exchangeable, and unexchangeable potassium) cannot completely characterize the potassium nutrition of plants, because it provides no information on the capacity of the exchangeably adsorbed potassium ions to pass into the soil solution and on the resistance of the soil system to potassium exhaustion. Therefore, it is advisable to extend it with parameters based on the theoretical concepts of the mechanisms of the chemical reactions in soils in terms of the thermodynamic principles. These are the potential buffer capacity of soils for potassium (PBC^K); the equilibrium potassium potential (AR_0) and the related potassium potential (PP = $\log AR_0$); and the contents of readily exchangeable potassium ($-\Delta K_0$) occupying the nonspecific exchange sites, low available potassium occupying the specific sorption sites ($-K_X$), and labile potassium (total mobile potassium) ($-K_L$) [14]. All these parameters can be determined by the Beckett method [1]
1 rather than by several agrochemical procedures.

Until recently, most studies of the thermodynamic parameters of the potassium status have dealt with the European soils of the former Soviet Union [3, 4, 8, 9, 15, 16]; very few works were devoted to the soils of Siberia and the Far East [2, 5, 6, 11], and no data are available on the potential potassium buffer capacity of synlithogenic Russian soils. Therefore, this work deals with the estimation of the potential potassium buffer
capacity in the natural and agrogenic soils of Kam- 4
chatka and the revelation of the controlling factors.

OBJECTS AND METHODS OF STUDY

Agrogenic volcanic soils and their analogues were used as the objects of the study. Samples of light ochreous and stratified ochreous podzolized soils were taken
in the Central Kamchatka Depression (Kamchatka 4 4
River valley, Ust'–Kamchatsk district, between the settlements of Kozyrevsk and Esso). Alluvial gray-humus, stratified ochreous, and stratified light ochreous soils developed on different deposits were sampled
on the eastern coast of Kamchatka (Avacha River val- 4
ley, Elizovsk district); alluvial gray-humus and ochreous podzolized soils of different textures were samples
in the Western Kamchatka Lowland (Bystraya River 4
valley, Ust'–Bol'sheretskii district). Samples were taken from the entire soil profile of the natural soils and from the plow (0- to 20-cm) and subsurface (30- to 35-cm) horizons of the agrogenic soils.

The physicochemical properties of the soils and the contents of the mobile potassium forms were reported earlier [7]. The tangent potential potassium buffer capacity (PBC^K) was determined by the Beckett method [1]. For this purpose, the value of $\pm\Delta K$, which represents the amount of mobile potassium released ($-\Delta K$) or adsorbed ($+\Delta K$) by the soil up to the moment of the equilibrium between the soil potassium and the solution potassium, and the AR value equal to the activity ratio between the potassium and calcium ions were determined in equilibrated solutions obtained after the interaction of the soil with a series of six calcium chloride solutions of the same concentrations containing different amounts of potassium (from 0 to 1.0 meq/l) at a soil : solution ratio of 1 : 10. The concentration of potassium was determined by flame photometry, and the sum of the calcium and magnesium was determined by complexometry. The sorption isotherm, a characteristic line straight in the upper part and curved in the lower part, was plotted in the ΔK and AR coordinates.

The line's intersection with the abscissa gives the AR_0 value corresponding to the $aK^{+}\sqrt{aCa^{2+}}$ activity ratio in the $CaCl_2$—KCl solution at which the soil neither adsorbs nor releases potassium, i.e., the activity ratio typical for water. The potassium potential is an essential chemical parameter of soil. From the sorption curve, the directly available (readily exchangeable) potassium $-\Delta K_0$ and the total mobile (labile) potassium $-K_L$ were calculated. The – $-\Delta K_0/AR_0$ ratio expresses the potential potassium buffer capacity of soils, which is considered very low at the ratio <20, low at the ratio between 20 and 50, medium at the ratio between 50 and 100, and elevated at the ratio >200. Sorption isotherms of traditional shape were obtained for all of the studied soil samples: a gently sloping straight line (adsorption) in the upper part and a curved line (desorption) in the lower part. The slope was low, which indicated low values of the buffer capacity. The thermodynamic parameters were calculated using the described procedure [4].

RESULTS AND DISCUSSION

4 *The Western Kamchatka Lowland.* The highest values of the potential potassium buffer capacity are typical for the upper horizon of the alluvial gray-humus typical sandy loamy soils on alluvial deposits; they decrease with the depth to very low values (Table 1). The maximum amount of highly mobile potassium ($-\Delta K_0$) and low available mobile potassium ($-K_X$) is found in the humus horizon; in the deeper horizons, it is negligible. The value of the potassium potential is unsatisfactory only in the middle part of the profile. A decrease in the buffer capacity is noted in the plowed soil analogues because of the significant decrease in the content of mobile potassium (both $-\Delta K_0$ and $-K_X$). The equilibrium activity of the potassium ions AR_0 also decreases abruptly.

The ochreous podzolized soils have low values of PBC^K throughout their profiles (very low in the EL horizon), although, in the illuvial horizons, they are slightly higher than in the upper horizons. The values of the potassium potentials are optimum in the upper part of the profile and unsatisfactory in the middle and lower parts of the profile. The highest content of available potassium is recorded in the soddy horizon; its content in deeper layers is low and uniformly distributed. The highest content of low available mobile potassium ($-K_X$) is also observed in the humus horizon; in the rest of the profile, it is low, although slightly higher than in the alluvial gray-humus soils. The values of the potassium potential are unsatisfactory in the middle part of the profile.

The different ratios between the highly and low available potassium in the ochreous podzolized soils of different textures are noteworthy. The content of low available mobile potassium ($-K_X$) varies from 14 to 31% of the content of the mobile potassium ($-K_L$) in the sandy loamy soils and from 36 to 50% in the medium loamy soils; the differences in the content of the highly mobile potassium ($-\Delta K_0$) are insignificant.

A slight increase in the values of the PBC^K was noted in the plow horizons of the agro-ochreous podzolized soils compared to the virgin analogues because of the appreciable decrease in the content of readily exchangeable potassium ($-\Delta K_0$) at the insignificant decrease in the equilibrium potassium potential (AR_0). A decrease in the content of low available potassium ($-K_X$) was also observed, which was more pronounced in the sandy loamy soils.

The Central Kamchatka Depression. Very low values 4
of the buffer capacity in the profile of the lstratified ochreous podzolized soils are observed in the upper layers: the raw-humus horizon and the subsurface layers of ashy material. Slightly higher values are typical for the deeper humus-illuvial and ochreous horizons (Table 2). The maximum content of labile potassium ($-K_L$) is also observed in the deep horizons; the content of low available mobile potassium ($-K_X$) is low throughout the profile; its total absence in the surface layer consisting of raw organic material is typical. The values of the potassium potential are optimum throughout the profile.

This distribution can be related to the low content of adsorption sites in the surface horizons because of the low weathering of the relatively fresh ash material and the higher weathering of the mineral component in the deeper horizons, as was noted by Sokolov [12]. Thus, the extremely nonuniform distribution of all the potassium status parameters in the different soil horizons reflects the discrete character of the volcanic pedogenesis.

The light ochreous sandy loamy soils on pebbly alluvium are characterized by low PBC^K values in the upper horizons and medium and elevated values in the underlying horizons. The content of labile potassium ($-K_L$) is relatively high throughout the profile of the natural soils. The availability of potassium is high in

4 **Table 1.** Parameters of the potential potassium buffer capacity of the soils of the Western Kamchatka Lowland

Horizon	Depth, cm	PBC^K	$AR_0 \times 10^{-3}$ mol/l$^{0.5}$	$-\Delta K_0$	$-K_L$	$-K_X$	pK-0.5pCa
				meq/100 g of soil			
Profile 15, alluvial gray-humus typical sandy loamy soil on alluvial deposits							
@АУ	0–20	34.37	20.15	0.46	0.66	0.20	1.70
BHi	20–36	24.05	3.38	0.08	0.09	0.01	2.47
BChi	36–60	14.98	4.04	0.06	0.07	0.01	2.39
BAN	60–85	14.39	8.05	0.12	0.14	0.02	2.09
C~~	85–110	7.02	5.65	0.04	0.04	0.00	2.25
Profile 16, agrohumus alluvial sandy loamy soil;							
P	0–20	29.22	12.32	0.36	0.48	0.12	1.91
BHi	20–35	22.55	5.32	0.12	0.13	0.01	2.24
Profile 19, ochreous podzolized sandy loamy soil on volcanic deposits							
@АУ	0–9	26.76	11.58	0.31	0.45	0.14	1.94
EL	9–14	19.01	9.84	0.19	0.26	0.07	2.01
1BH	14–30	33.74	5.61	0.19	0.24	0.05	2.25
2BH	30–47	42.51	4.10	0.17	0.21	0.04	2.39
BAN	47–65	38.15	3.72	0.14	0.17	0.03	2.43
BC	65–95	31.62	4.25	0.13	0.16	0.03	2.37
C~~	95–150	41.81	4.45	0.19	0.22	0.03	2.35
Profile 20, agro-ochreous podzolized sandy loamy soil							
P	0–20	28.08	9.11	0.26	0.36	0.10	2.04
BH	20–35	15.75	10.16	0.16	0.23	0.07	1.85
Profile 21, ochreous podzolized medium loamy soil on alluvial deposits							
@АУ	0–10	27.83	15.19	0.42	0.67	0.25	1.82
EL	10–15	17.29	7.15	0.12	0.21	0.09	2.15
1BH	15–25	30.38	4.82	0.15	0.24	0.09	2.32
2BH	25–40	18.44	5.56	0.10	0.18	0.08	2.25
BC	40–60	21.41	5.08	0.11	0.17	0.08	2.29
C~~	60–75	19.23	3.40	0.06	0.12	0.06	2.47
2C~~	75–130	19.87	5.02	0.09	0.14	0.05	2.30
Profile 22, agroochreous podzolized medium loamy soil							
P	0–20	29.21	11.39	0.33	0.45	0.12	1.94

the upper part of the profile and abruptly decreases with the depth.

The appreciable increase in the potential buffer capacity and the decrease in the potassium potential observed in the agrogenic analogues of the stratified ochreous podzolized and light ochreous soils are related to the significant increase in the content of labile potassium (both highly and low available) in the upper horizons, which is apparently due to the application of mineral fertilizers. It should be noted that the proportion of low available mobile potassium ($-K_X$) significantly increases in this case; i.e., the potassium of the mineral fertilizers is partly fixed in the reserve.

The Eastern Kamchatka coast. The stratified ochre- 4
ous sandy loamy soils of the Eastern Kamchatka coast 4
are characterized by very low and low values of their buffer capacity almost throughout the profile; the minimum values are observed in the layers of slightly weathered ash material, and the minimum values are revealed in the soil-forming rock (Table 3). The highest content of labile ($-K_L$) and low available mobile potassium ($-K_X$) is typical for the humus horizon; in the deeper layers, it is very low. The values of the potas-

4 **Table 2.** Parameters of the potential potassium buffer capacity of soils of the Central Kamchatka Depression

Horizon	Depth, cm	PBC^K	$AR_0 \times 10^{-3}$ mol/l$^{0.5}$	$-\Delta K_0$	$-K_L$	$-K_X$	pK-0.5pCa
				meq/100 g of soil			
Profile 7, stratified ochreous podzolized sandy loamy soil on volcanic deposits							
AOe	0–10	5.72	16.27	0.09	0.09	0.00	1.79
C''	10–12	8.56	8.82	0.07	0.12	0.05	2.05
BH	12–25	13.74	11.56	0.16	0.22	0.06	1.94
2C''	25–28	7.76	8.61	0.07	0.08	0.01	2.07
BAN	28–37	22.46	7.61	0.17	0.21	0.04	2.12
3C''	37–47	11.38	10.03	0.11	0.12	0.01	2.00
2BH	47–67	44.21	4.05	0.18	0.20	0.02	2.39
Profile 8, agro-stratified ochreous podzolized sandy loamy soil							
P	0–26	13.28	24.85	0.33	0.43	0.10	1.49
B1	26–40	19.06	8.39	0.16	0.22	0.06	2.08
Profile 10, light ochreous sandy loamy soil on pebbly alluvium							
AO	0–18	22.99	14.24	0.33	0.33	0.00	1.85
BH	18–35	64.52	4.89	0.32	0.38	0.06	2.31
BAN	35–60	109.93	3.65	0.40	0.43	0.03	2.44
C~~	60–80	70.66	5.42	0.38	0.44	0.06	2.27
Profile 9, agro-light ochreous sandy loamy soil							
P	0–20	29.33	15.68	0.46	0.56	0.10	1.56
BH	20–35	47.52	6.73	0.32	0.38	0.06	1.91

sium potential indicate the high availability of potassium in the upper profile and are unsatisfactory in the middle and lower profile.

The buffer capacity in the stratified light ochreous soils is low throughout the profile, except for the deep ochreous horizon, where it is medium. The minimum value is observed in the layer of slightly weathered ash material. The PBC^K value gradually increases with the depth. The content of labile potassium ($-K_L$) is maximum in the upper horizons; the content of low available mobile potassium in the soddy layer ($-K_X$) is comparable to that of the highly mobile potassium (($-\Delta K_0$)). The potassium potential is optimum only in the upper part of the profile.

The alluvial gray-humus typical sandy loamy soils on volcanic deposits also have a low buffer capacity throughout their profiles with the maximum value in the soddy horizon. These soils are the most enriched in potassium, the highest content of labile potassium is observed in the upper horizons, and the soddy horizon is also characterized by a relatively high content of low available mobile potassium ($-K_X$). The mobility of the potassium ions is high only in the upper part of the profile.

A decrease in the buffer capacity in the plow layer is noted for all the agrogenic soil analogues of the East-
4 ern Kamchatka coast because of the significant decrease in the content of all the mobile potassium forms and the equilibrium potential.

On the whole, the highest values of the PBC^K in the root-inhabited layer were revealed in the alluvial gray-humus typical soils; the lowest values were found in the stratified ochreous podzolized soils. The analysis of the data obtained in the paired profiles of the virgin and arable soils shows that the buffer capacity in the upper soil layers is variable. Its values in the agrogenic alluvial gray-humus, stratified ochreous, and stratified light ochreous soils are higher than in the virgin analogues, and those in the ochreous podzolized, stratified ochreous podzolized, and light ochreous soils are lower than in the virgin analogues. A possible reason is the formation of the plow horizon by the addition of material from the lower layer to the thin surface layer; its buffer capacity increases or decreases depending on its change with depth in the natural soils.

In most virgin soils of Kamchatka, the highest con- 4
tent of readily exchangeable and low available potassium is typical for the upper humus horizons, which is related to the active biological uptake of potassium by plants in the root-inhabited layer, as was repeatedly noted [10, 13]. At the same time, the high intensity of the biogenic and chemical decomposition of the primary minerals in the deep layers of the soil profile results in the low accumulation of fine silt particles [6];

4 **Table 3.** Parameters of the potential potassium buffer capacity of soils of the Eastern Kamchatka coast

Horizon	Depth, cm	PBC^K	$AR_0 \times 10^{-3}$ mol/l$^{0.5}$	$-\Delta K_0$	$-K_L$	$-K_X$	pK-0.5pCa
				meq/100 g of soil			
Profile 35, stratified ochreous sandy loamy soil on volcanic deposits							
@AУ	0–9	19.36	12.40	0.24	0.36	0.12	1.91
BH	9–18	9.63	6.34	0.06	0.07	0.01	2.20
C''	18–31	7.16	9.78	0.07	0.12	0.03	2.03
2BH	31–41	15.81	1.48	0.02	0.02	0.00	2.83
2BAN	41–65	16.42	2.65	0.04	0.05	0.01	2.58
BC	65–85	25.16	1.69	0.04	0.04	0.00	2.77
Profile 36, agro-stratified ochreous sandy loamy soil							
P	0–20	13.28	9.04	0.12	0.15	0.03	2.04
BH	20–35	11.94	8.38	0.10	0.12	0.02	2.08
Profile 24, stratified light ochreous sandy loamy soil on volcanic deposits underlain by alluvial sandy-pebbly sediments							
@AУ	0–9	27.58	17.70	0.21	0.38	0.17	1.75
BH	9–21	23.92	5.72	0.14	0.21	0.07	2.39
C''	21–32	16.76	9.49	0.16	0.20	0.04	2.02
BH	32–43	32.07	3.09	0.09	0.11	0.02	2.51
2BH	43–53	33.79	2.37	0.08	0.12	0.04	2.56
BAN	53–75	64.36	1.14	0.07	0.07	0.00	2.94
Profile 25, agro-stratified light ochreous sandy loamy soil							
P	0–20	22.27	8.08	0.18	0.25	0.07	2.09
B1	20–35	19.72	5.07	0.10	0.14	0.04	2.29
Profile 31, alluvial gray-humus typical sandy loamy soil on volcanic deposits underlain by alluvial sandy-pebbly sediments							
@AУ	0–12	30.54	13.38	0.41	0.56	0.15	1.87
BHi	12–26	25.82	5.71	0.15	0.16	0.01	2.24
BChi	26–35	17.12	2.92	0.05	0.06	0.01	2.53
C~~	35–60	14.13	4.12	0.06	0.06	0.00	2.39
Profile 32, agro-humus alluvial sandy loamy soil							
P	0–20	29.64	10.13	0.30	0.35	0.05	1.99
BH	20–35	17.39	11.51	0.25	0.28	0.03	1.94

some increase in the amount of exchangeable positions; and, hence, an increase in the potential buffer capacity of the soils. The percolative conditions and acid reaction favor the active removal of all the alkaline and alkaline-earth cations from the profile. Therefore, the mobility of the potassium ions is high, and the values of the potassium potential are optimum only in the upper part of the soil profile. In the deeper layers, the potassium mobility is lower and the potassium potential is unsatisfactory in almost all of the soils studied.

Positive correlations were revealed between the readily exchangeable ($-\Delta K_0$) and mobile ($-K_L$) potassium and the contents of physical clay ($r = 0.53$–0.61), clay ($r = 0.42$), humus ($r = 0.53$), and exchangeable potassium ($r = 0.57$–0.70) throughout the profile of the soils studied (the degree of certainty was 0.99) (Fig. 1). The closer correlation between the mobile potassium and the physical clay can be due to the active role of silty particles in the sorption of potassium ions. It was supposed earlier [12] that intensive biochemical weathering in the soils of Kamchatka 4
occurs not only at the periphery of the fine particles but also in pores within particles, which strongly enlarges the contact surface between the solid phase and the solution.

The value of the equilibrium potassium potential AR_0 is determined by the content of humus ($r = 0.37$) and the exchangeable potassium ($r = 0.49$) (the degree of certainty 0.99), as well as by the proportion of potassium in the soil exchange complex (SEC) ($r = 0.30$) (the degree of certainty 0.95) (Fig. 2). A similar effect of

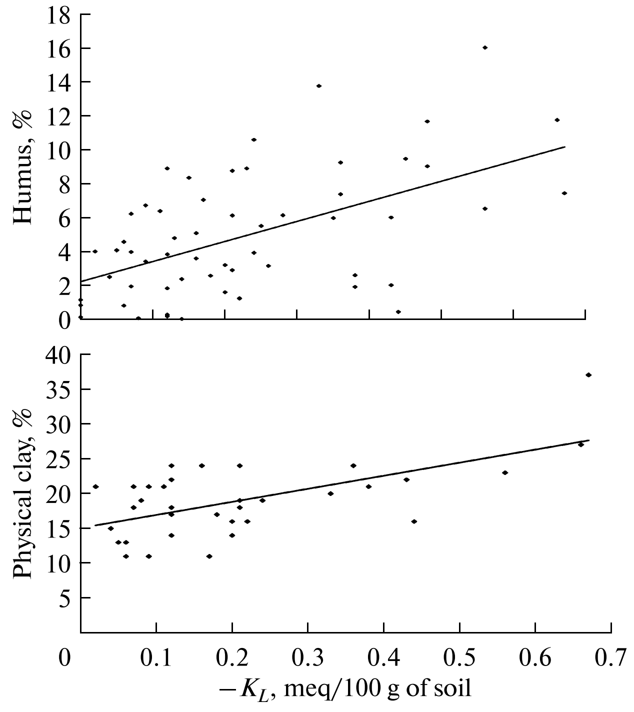

Fig. 1. Relationships between the content of mobile potassium and the contents of physical clay and humus.

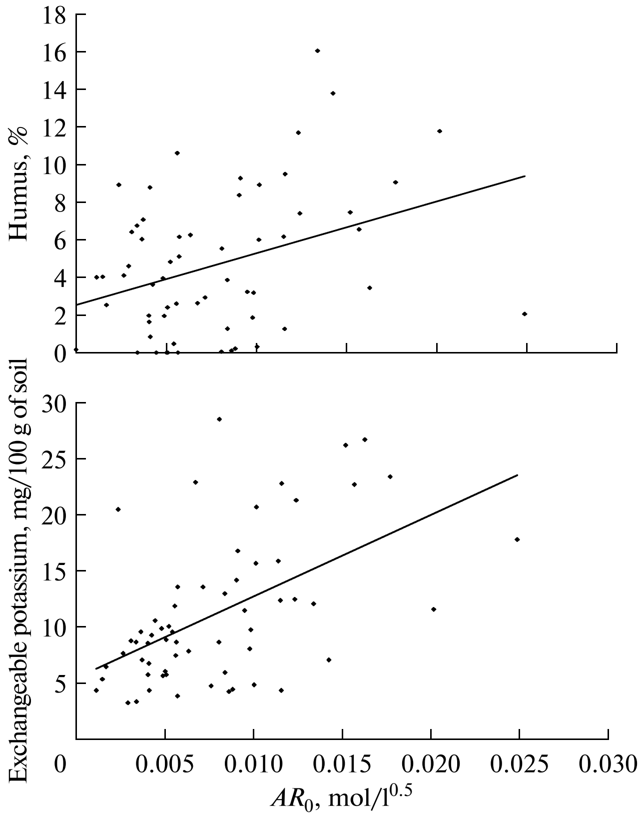

Fig. 2. Relationships between the equilibrium potassium potential AR_0 and the contents of humus and exchangeable potassium.

the texture, humus content, and SEC composition on the parameters of the potential buffer capacity of the soils was previously noted for gray forest soils [15], chernozems, chestnut soils [2], and different soils in the southern regions of the Far East [5, 6].

CONCLUSIONS

(1) Most of the soils studied are characterized by very low or low values of the potential potassium buffer capacity in the upper humus horizons. The highest values of the PBC^K are typical for the upper horizons of the alluvial gray-humus soils; the lowest values are noted in the stratified ochreous podzolized soils.

(2) The maximum content of readily exchangeable potassium ($-\Delta K_0$) is typical for the surface horizons of most of the soils and is due to the active biogenic accumulation. The soddy horizons contain a larger amount of strongly fixed potassium ($-K_X$) than the agrogenic horizons.

(3) The content of labile potassium ($-K_L$) in the plow horizons is lower compared to the virgin soils
4 (except for the soils of the Central Kamchatka Depression); i.e., the active removal of potassium (especially of strongly fixed ions ($-K_X$)) by agricultural crops takes place.

(4) The content of readily exchangeable ($-\Delta K_0$) and mobile ($-K_L$) potassium is controlled by the contents of physical clay, clay, humus, and exchangeable potassium throughout the profile of the soils studied.

(5) The values of the potassium potential in the upper horizons are optimum; the potassium ions are loosely bound to the SEC. Therefore, the availability of potassium to plants is high. The value of the equilibrium potassium potential (AR_0) is affected by the contents of the humus and exchangeable potassium and the proportion of potassium in the SEC.

(6) The extremely nonuniform distribution of all the potassium status parameters in the genetic horizons of the soils reflects the discrete character of the volcanic pedogenesis.

(7) The low and medium values of the potential potassium buffer capacity of the soils (PBC^K) at the high values of the equilibrium potassium potential (AR_0), which indicate the capacity to intensively release exchangeably adsorbed potassium ions into the solution, and the medium content of the labile potassium with the light texture simultaneously indicate both the good potassium supply in the root-inhabited zone and the incapacity of the soils to resist potassium exhaustion under agricultural production conditions without the application of additional potassium and organic fertilizers for a long time.

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