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EVALUATION OF POTASSIUM QUANTITY-INTENSITY PARAMETERS OF SELECTED POLISH AGRICULTURAL SOILS

Jean Bernard Diatta, Zdzisław Wacław Kociałkowski, Witold Grzebisz
Department of Agricultural Chemistry, Poznań Agricultural University, Poland

ABSTRACT

Potassium exchange-equilibrium parameters were outcome from quantity-intensity (Q/I) isotherms, i.e. K equilibrium activity ratio (AR^K_O), equilibrium potential buffering capacity for K (PBC^K_o), K labile (K_{Lab}), free energy of K replenishment ($-\Delta G^K_{equ}$); non-specific (K_x) and specific (ΔK_{equ}) potassium, preferential factor ($PF^{K_{ex}}_{(Ca+Mg)_{ex}}$) and the Gapon selectivity coefficient (k_G). It was found that soils did not generally differ in their exchangeable potassium (K_{ex}) but did for % K saturation as an estimate of K lability. Potassium was differently controlled by soil properties of which organic carbon (C_{org}) exhibited weak relationships with most of Q/I parameters. Potassium activity (AR^K_O) was controlled more by silt ($r = 0.97^{****}$ $P < 0.001$), Fe (DCB and Ox, $r = 0.81^{***}$ and $r = 0.71^{***}$, $P < 0.005$, respectively) and Mn (DCB and Ox, $r = 0.70^{***}$ and $r = 0.71^{***}$, $P < 0.005$, respectively) than by the cation exchange capacity (CEC) and exchangeable cations ($r = 0.50^{*}$, $P < 0.05$, on average). Of mineral soil constituents, it was found that Fe and Mn oxides also significantly influenced the free energy of changes ($-\Delta G^K_{equ}$ with $0.75^{***} \leq r \geq 0.63^{**}$). This implies that studies on potassium dynamics of soils should additionally consider the level of Fe and Mn, as well. Most of the Gapon selectivity coefficients (k_G) (i.e. 80%) fluctuated within the range 3.87-4.96 $(dm^3 \cdot mol^{-1})^{1/2}$, suggesting that the relative affinity for K was quite similar, irrespective of the degree of K saturation. The latter one along with the pool of labile K (K_{Lab}) indicated that soils will sufficiently support plant cropping without any threat of K shortage, as stated by the $-\Delta G^K_{equ}$ values.

Key words: potassium, quantity-intensity, activity ratio, potential buffering capacity, free energy of change, Gapon selectivity coefficient, preferential factor

INTRODUCTION

The quantity-intensity (Q/I) concept has been widely promulgated in the scientific literature to investigate the potassium (K) of soils. In this approach immediate availability of K is related to intensity factor, reserveness of nonexchangeable K to the quantity factor and replenishment capacity to the buffering capacity [2,14,24,31,33,36]. The activity ratio $AR_{equ}^{K} = \gamma K_{equ} / \gamma Ca_{equ}$ in the equilibrium soil solution [23] or its logarithm [37] has been proposed as a measure of the difference between the chemical potentials of K and Ca, which are frequently the predominant cations in the soil solution of most agricultural soils. In any particular soil the activity ratio value is a simple function of the relative amounts of labile K and (Ca + Mg) present.

Various attempts have been made to characterize the relationship between intensity and capacity of soil K or soil K buffering characteristics [7,26]. It was reported that higher values of labile K indicated a greater K release into soil solution resulting from a larger pool of soil K. A higher potential buffering capacity for potassium (PBC_{o}^{K}) value is indicative of a good K availability while a low PBC_{o}^{K} soil would suggest a need for fertilization. Potassium, calcium and magnesium equilibrium in the soil solution and solid phase may be described also by using the modified Gapon equation [11] as a graph of $K_{ex} / Ca_{ex} + Mg_{ex}$ (the ratio of exchangeable ions) against $\gamma K_{ex} / \gamma Ca_{equ} + \gamma Mg_{equ}$. However in most field soils $K_{ex} << Ca_{ex} + Mg_{ex}$. If so, small changes in K_{ex} may be accompanied by only insignificant changes in $Ca_{ex} + Mg_{ex}$ and the isotherm may be represented as a graph of K_{ex} *versus* $\gamma K_{ex} / \gamma Ca_{equ} + \gamma Mg_{equ}$. Therefore in this form, the isotherm directly relates the quantity factor to the intensity factor of soil K.

Some agricultural practices such as potassium fertilization and liming were found to induce changes in the magnitude of the potassium activity ratio at equilibrium (AR_{O}^{K}), labile K_{Lab} and PBC_{equ}^{K} values [34,36]. If, however, a Q/I is to be of any value in indicating the amount of soil K available for uptake during the growing season, its form must be unaffected by the amount of K fixation or release that is likely to occur during one growing season. Fergus et al. [9] have reported that potassium uptake by growing plants generally affect the pool of readily available potassium forms and moreover these changes, if considerable, might be expected to alter the form of the Q/I of a soil.

In Poland one of the most profitable cash crops are sugar beets, which in turn are extremely sensitive to soil K fertility. In addition the deficit of precipitation in the Wielkopolska region (Western part of Poland) is an essential factor which restricts agricultural production and decreases yields of sugar beet by up to 30-40%. However, successful soil K fertility management may significantly decrease the limitation due to water shortages [13]. The last decade of intensive sugar beet cropping without proper replacement of nutrients offtake, especially of K led to a marked depletion of soil K resources, which in turn were observed to become yield-limiting factors in some areas of Poland [12]. According to Fotyma and Gosek [10], in most areas of the country (from 30% to more than 50%) sugar beets are grown on soils generally considered as insufficiently rich in potassium. On the other hand, the recorded yield of roots does not fully confirm the assumption that K seems to be the principal yield-limiting factor. Since plant growth is not directly limited by the amounts of exchangeable soil K, therefore it should be necessary to elucidate this phenomenon on the basis of equilibrium studies in order to test the immediate power of soils to supply K to plants. This approach needs the use of equilibrium (Q/I) concept which should be a good tool, whose application may provide sufficient data about K dynamics in Polish soils under sugar beet cropping. Such comprehensive studies are intended to outline some specific information which should clearly determine the capacity of soils for K supply and replenishment.

The aim of the present study was to evaluate potassium dynamics of selected Polish agricultural soils under sugar beet cropping, by applying the quantity-intensity (Q/I) concept. The specific purpose was to point out the potential capacity of these soils for K supplying to sugar beets.

MATERIAL AND METHODS

Soil properties

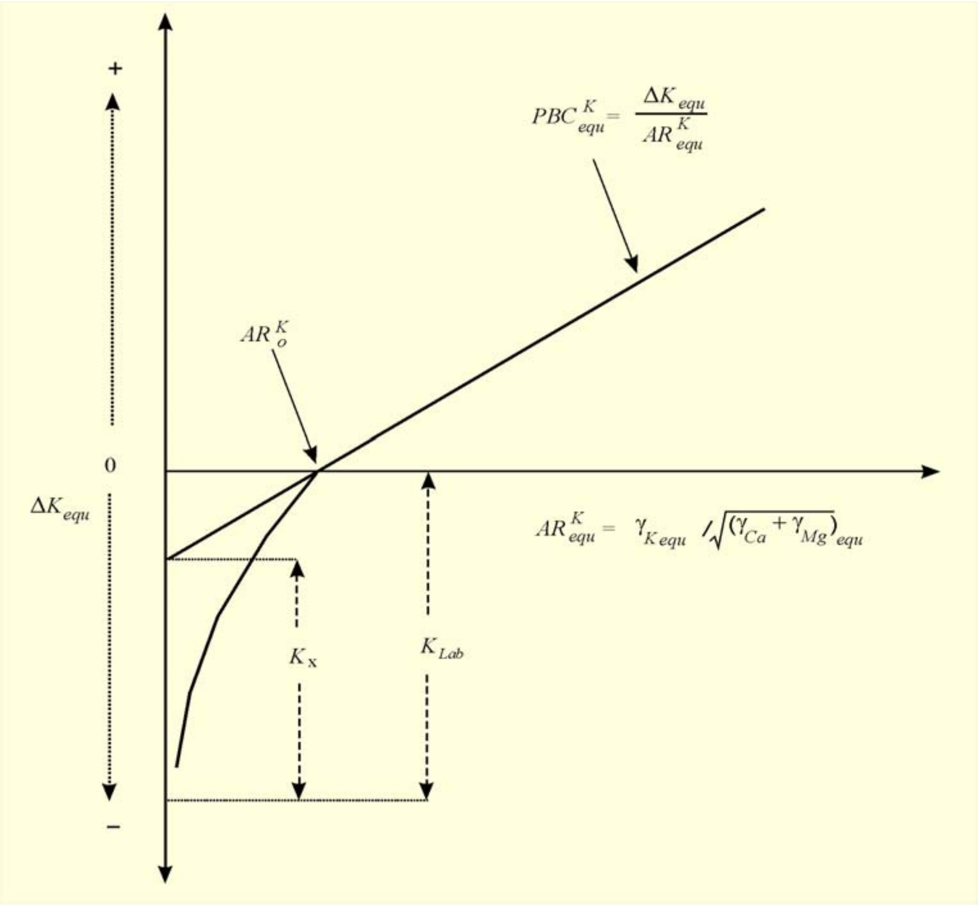
Ten soil samples under sugar beet cropping were collected at 0-20 cm depth from agricultural lands of the Wielkopolska Region (52°31’N, 17°16’E, Poland). Prior to basic analyses, soil samples were air-dried and crushed to pass through a 1 mm mesh sieve. Granulometric composition was determined according to Casagrande-

Prószynski areometric method [19,22]. Organic carbon was determined by the dichromate wet oxidative method of Tiurin, in which organic matter of soil is oxidized with potassium dichromate in the presence of sulphuric acid. The unreacted potassium dichromate was back titrated with ferrous sulphate. Soil pH was potentiometrically measured in water and 1 M KCl extracts at soil to solution ratio of 1:2.5, according to the Polish Standard [28] and ΔpH (= $pH_{KCl} - pH_{H2O}$) was calculated as reported by Arnold [1]. The cation exchange capacity (CEC) of the soils was obtained by the summation of exchangeable Ca_{ex}, K_{ex}, Mg_{ex} and Na_{ex}, which were extracted by 0.10M $BaCl_2$ according to Hendershot and Duquette [15]. The 0.10 M $BaCl_2$ solution prepared from the reagent showed pH = 5.50. Iron (Fe) and manganese (Mn) were extracted by using both the citrate-bicarbonate-dithionite (DCB) and ammonium oxalate methods as reported by Mehra and Jackson [21] and McKeague and Day [20], respectively. The specific surface area (SSA) was estimated by the ethylene glycol monoethyl ether (EGME) method as suggested by Carter et al. [6] and the surface charge density (*SCD*) was calculated from the relationship $^{CEC}/_{SSA}$ [29].

Quantity-Intensity (Q/I) graphical analysis

The linear portion of the curve (Fig. 1) has been ascribed to non-specific sites for K [2], which is attributed to planar surfaces, while the curved portion has been attributed to specific sites with high K affinity [18]. The AR_O^K value is a measure of availability or intensity of labile K in soil, whereas the PBC_o^K expresses the ability of the soil to maintain the intensity of K in the soil solution and is proportional to the cation exchange capacity.

Fig. 1. Typical quantity-intensity plot for labile soil K estimation



ΔK_{equ}	–	quantity by which the soil gains or loses K in reaching equilibrium or the quantity factor (Q)
AR^K_{equ}	–	activity ratio for K or the intensity factor (I)
AR^K_O	–	equilibrium activity ratio for K or the intensity factor (I)
K_{Lab}	–	labile K (amount of labile K able to exchange with 0.01 M Ca)
K_x	–	specific K sites (a measure of edge sites)
PBC^K_o	–	equilibrium potential buffering capacity for potassium at AR^K_O
PBC^K_{equ}	–	potential buffering capacity for potassium (gradient of the linear part of the Q/I, the part customarily described by the Gapon equation)

Batch analysis and model description

Potassium quantity-intensity (Q/I) study was performed according to the procedure described by Beckett [2], Hamdan et al. [14] and Wang and Alva [35]. Soil samples were weighted in duplicate (2.0 g) into a series of 50 cm^3 polypropylene centrifuge test-tubes. The samples were added with 20 cm^3 of 0.01 mol of $CaCl_2$ in dm^3 and from 0 to 84 or 125 mg $K \cdot dm^{-3}$ as potassium chloride (KCl). This form of K was used for equilibrium studies since it prevails in potassium fertilization in Poland. The test-tubes were stoppered, shaken in a rotative shaker for two hours at $20^{o}C$ after which they were equilibrated for 24 hours. The supernatants were filtered and analysed for Ca, Mg and K by flame atomic absorption spectrometry (FAAS), (Varian Spectra 250 plus).

The potassium quantity factor (ΔK_{equ}) was obtained by computing the differences in K concentration between the initial and equilibrium solutions. The intensity factor (AR_{O}^{K}) was calculated from the relationship of ΔK_{equ} *versus* $AR_{equ}^{K} = \gamma K_{equ} / \sqrt{(\gamma Ca + \gamma Mg)_{equ}}$, where γ represents the activity coefficient. All concentrations were expressed in $mol \cdot dm^{-3}$ in the equilibrium solution.

Intercept of the Q/I curve on the AR_{equ}^{K} axis, where K = 0, gave the soil K activity ratio at equilibrium (AR_{O}^{K}). Specific K (K_x) value was obtained by the extrapolation of the linear part of the Q/I curve to the ordinate and additionally from the difference $K_{Lab} - \Delta K_{equ}$. The equilibrium potential buffering capacity for potassium (PBC_{o}^{K}) was calculated as the slope of the linear section of the Q/I curve. The free energy of the K replenishment ($-\Delta G_{equ}^{K}$) was computed from the following equation as reported by Beckett [3]:

$$-\Delta G_{equ}^{K} = 2.303\, R\, T \log AR_{O}^{K} \tag{1}$$

where R and T are gas constant and absolute temperature, respectively.

Exchangeable potassium (K_{ex}), calcium (Ca_{ex}) and magnesium (Mg_{ex}) in the soil solid phase are considered to settle a dynamic equilibrium state with the concentration of the same cations in the soil solution. This state was outlined by Gapon [11], who suggested an equilibrium coefficient k_G relating K_{ex}, Ca_{ex} and Mg_{ex} with their solution concentrations, in terms of activity. Therefore the comparison of soils on the basis of the Gapon selectivity coefficient (k_G) should provide good comprehensive and indicative information of potassium replenishment capacity of the soils. The k_G as reported by [4] and Feigenbaum et al. [8] may be rearranged and calculated as follows:

$$K_{ex} \Big/ (Ca + Mg)_{ex} = k_G \cdot \gamma K_{equ} \Big/ \sqrt{(\gamma Ca + \gamma Mg)}_{equ} \tag{2}$$

By rearranging this equation to the quantity-intensity form, the following is obtained:

$$k_G = K_{ex} \Big/ (Ca + Mg)_{ex} \cdot \sqrt{(\gamma Ca + \gamma Mg)_{equ}} \Big/ \gamma K_{equ} \tag{3}$$

Assuming $Ca_{ex} + Mg_{ex} \approx$ CEC on exchange material, therefore the ratio $K_{ex} \big/ (Ca + Mg)_{ex}$ should describe the relative specificity of non-Coulombic forces on colloid surfaces for K and is intended to express the preference factor $PF_{(Ca + Mg)_{ex}}^{K_{ex}}$. For the soils studied, higher values should be indicative of increased preference for K over Ca and Mg, whereas lower values of the opposite process.

Potassium equilibrium parameters were computed with Ion Exchange-Equilibrium Softwares [16] and Excel sheet facilities. Statistical analyses were performed by the application of statistical software packages [17].

RESULTS AND DISCUSSION

Soil properties

The physical and chemical properties, as listed in Tables 1a and 1b, show that soils used for this study differed notably. For simplification, soils were given proper numbers (i.e. from 1 to 10) which will be used as soil references throughout the paper. Soil particles, especially silt and clay and organic carbon, varied significantly, with coefficients of variation (CV) of 59 and 60% and 51%, respectively. The soil pH in water (pH_{H2O}) was mostly neutral to slightly alkaline and the difference $pH_{KCl} - pH_{H2O}$ was negative for all soils, suggesting the predominance of negative charges. Soils were characterized by cation exchange capacity (CEC) values of which most were in the range from 13.37 to 21.41 $cmol(+)\cdot kg^{-1}$, except for soils no 3 and no 9 with respective CEC equaling to 32.97 and 94.60 $cmol(+)\cdot kg^{-1}$, as a basis of significant variability *ca* 93%. The occurrence of carbonates, typically encountered for calcareous soils, in the case of soils no 3 and no 9 should be considered as an "artifact" originating from the application of liming materials for controlling acidity of these soils. The exchangeable potassium (K_{ex}) content fluctuated from 1.14 to 1.74 $cmol(+)\cdot kg^{-1}$ soil, except for soil no. 9 characterized by $K_{ex} = 5.49$ $cmol(+)\cdot kg^{-1}$. Since soils did not greatly differ in their exchangeable potassium, it could be assumed that potassium exchangeability and lability as well as other K equilibrium characteristics to be indirectly dependent on the negative charge status (ΔpH) of soil mineral constituents than the organic matter content. This was confirmed by the correlation coefficients established for the pairs ΔpH *vs*: silt (r = -0.57**); clay (r = -0.49*); Fe_{DCB} (r = -0.62**); Fe_{Ox} (r = -0.55*); Mn_{DCB} (r = -0.62**); Mn_{Ox} (r = -0.72***). As it could be observed, Fe and Mn oxides promoted more the distribution of most of the negative charges of the soils studied. This finding in K dynamics was not expected and calls for more investigations of geochemical changes of potassium in agricultural soils. Some studies [25,31] have focused on the role of silt and clay content being responsible for retention of K on the exchange surface. The percent K saturation (%K) has been considered as the estimate of mobility parameters. The values of percent K saturation varied from 4.79 to 10.14, which is indicative of a good potassium status of these soils.

Potassium Quantity-Intensity (Q/I) Parameters

Soils reported in Fig. 2 were selected on the basis of the percent of K saturation (Table 1a), which in increasing order was as follows: 4.79% (no. 3) > 5.79% (no. 10) > 5.81 (no. 9) > 6.98% (no. 5) > 8.88% (no. 7) > 10.14% (no. 1). The first three soils exhibited steeper Q/I isotherm shapes, indicative of higher buffering capacity for potassium, as compared to the remaining soils, i.e. no. 1, no. 5 and no. 7. These Q/I relations are characteristic and confirmed that generally reported in the literature for agricultural soils and other soils constituents [14]. The Q/I derived-parameters are reported in Table 2 and additional relationships are depicted in Figs. 3, 4, 5. In each soil so far studied there is a linear or even curvilinear upper part and curved lower part. This indicates how AR_{O}^{K} in the soil solution depends on the exchangeable K content of soils. In field soils nearly all the labile K is exchangeable and available, basically, so Figure 2 is a very close approximation to the relation between the amount of labile K in a field soil (the quantity factor) and AR_{equ}^{K} (the intensity factor). The higher the potassium activity in the soil solution, the relatively lower the soil buffering capacity and inversely.

Table 1a. Selected physical and chemical properties of investigated soils

Soil no.	Granulometric composition %			pH			*CEC* $cmol(+)\cdot kg^{-1}$	Exchangeable cations $cmol(+)\cdot kg^{-1}$				
	Sand	Silt	Clay	pH_{H2O}	pH_{KCl}	ΔpH^a		Ca_{ex}	Mg_{ex}	K_{ex}	Na_{ex}	$\% K^b$
1	74	20	6	6.98	6.74	-0.24	14.95	11.39	0.66	1.52	1.39	10.14
2	66	17	17	7.03	6.05	-0.98	21.42	17.14	1.38	1.48	1.41	6.91
3	78	16	6	7.94	7.48	-0.46	32.97	28.37	1.60	1.58	1.42	4.79
4	66	21	7	7.09	6.31	-0.78	13.76	10.85	0.39	1.33	1.19	9.69
5	75	17	8	7.30	6.59	-0.71	19.11	15.59	0.88	1.33	1.30	6.98
6	78	19	3	6.90	6.06	-0.84	13.37	10.54	0.40	1.21	1.23	9.03
7	70	20	10	7.14	6.54	-0.60	19.54	15.86	0.58	1.74	1.36	8.88
8	77	17	6	7.57	7.23	-0.34	15.03	12.22	0.34	1.30	1.18	8.63
9	25	54	21	8.06	7.15	-0.91	94.60	73.68	11.26	5.49	4.17	5.81
10	38	53	9	5.99	4.90	-1.09	19.76	16.21	1.10	1.14	1.31	5.79

[a] according to Arnold [1], [b] (K saturation): $\% K = \frac{K_{ex}}{CEC} \cdot 100$, where: *CEC* – Cation exchange capacity

Table 1b. Selected physical and chemical properties of the soils investigated

Soil no.	Organic carbon C_{org}, %	Carbonate %	Surface area *SSA*, $m^2 \cdot g^{-1}$	SCD^b x 10^{-3} mmol(+)·m^{-2}	Fe $mg \cdot kg^{-1}$		Mn $mg \cdot kg^{-1}$	
					DCB	Ox	DCB	Ox
1	0.60	–[a]	9.90	15.10	2681	606	331	31
2	0.53	–	64.72	3.31	2960	1492	460	72
3	1.04	2.0	103.36	3.19	1566	1332	210	54
4	0.35	–	11.26	12.22	2608	788	207	62
5	0.77	–	38.44	4.97	1507	757	247	55
6	0.30	–	7.66	17.45	1596	588	300	59
7	0.77	–	16.59	11.78	1846	854	152	31
8	0.15	–	6.53	23.02	1232	553	152	33
9	0.27	4.8	142.82	6.62	3680	3228	653	139
10	0.65	–	32.72	6.04	4239	1893	480	94

[a] traces, [b] $SCD = \frac{CEC}{SSA}$ where, *SCD* – Surface charge density, mmol(+)·m^{-2}, *CEC* – Cation exchange capacity, cmol(+)·kg^{-1}

Fig. 2. Quantity-Intensity (Q/I) isotherms established for selected soils

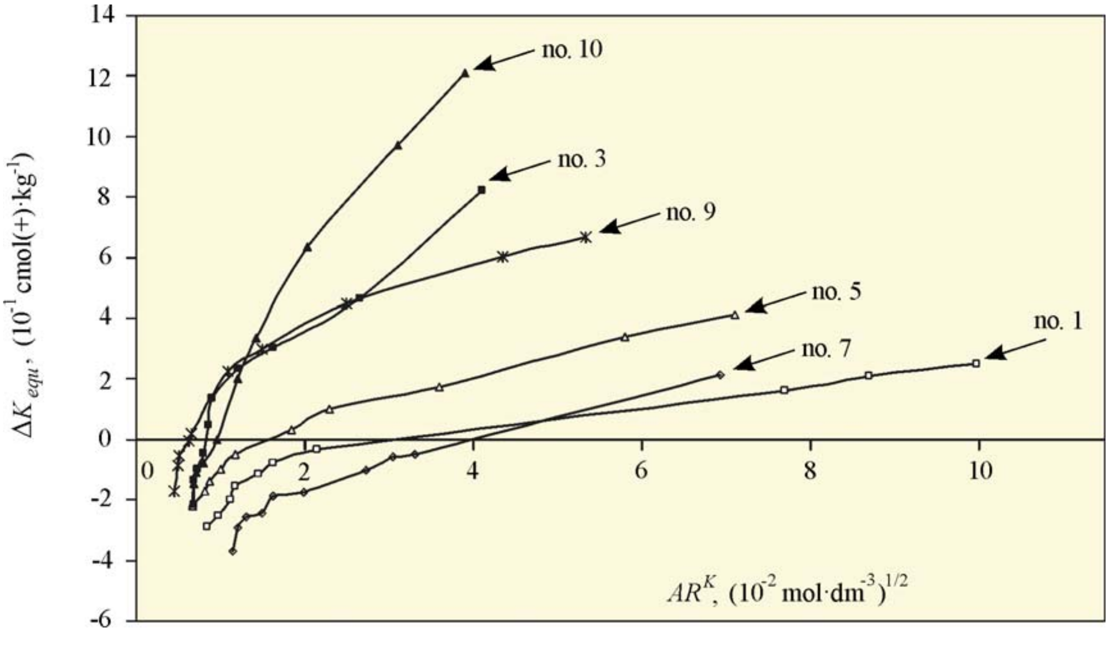


Table 2. Quantity-intensity (Q/I) parameters of the soils investigated

Soil no.	AR_O^K	$-K_{Lab}$	ΔK_{equ}	$-K_x$	PBC_O^K	$-\Delta G_{equ}^K$	k_G	Preferential Factor $PF_{(Ca+Mg)_{ex}}^{K_{ex}}$
	$(mol\cdot dm^{-3})^{1/2}$	$cmol(+)\cdot kg^{-1}$			$cmol(+)\cdot kg^{-1}$ $(mol\cdot dm^{-3})^{-1/2}$	$kcal\cdot mol^{-1}$	$(dm^3\cdot mol^{-1})^{1/2}$	
1	0.0221	0.417	0.140	0.277	18.87	-2.21	4.03	0.126
2	0.0110	1.110	0.076	1.034	100.83	-2.61	4.96	0.080
3	0.0082	1.100	0.100	1.000	134.62	-2.80	6.51	0.053
4	0.0149	0.503	0.155	0.348	33.71	-2.44	3.92	0.119
5	0.0130	0.444	0.090	0.354	34.07	-2.52	4.71	0.081
6	0.0182	0.295	0.060	0.235	16.15	-2.32	3.87	0.110
7	0.0218	0.710	0.310	0.400	32.63	-2.22	4.74	0.106
8	0.0189	0.426	0.055	0.371	22.51	-2.30	4.16	0.103
9	0.0694	0.345	0.004	0.341	49.66	-1.55	11.57	0.065
10	0.0917	0.597	0.350	0.247	65.11	-1.38	4.81	0.066

Fig. 3. Relationships of exchangeable potassium (*K_{ex}*) *versus* equilibrium potential buffering capacity (PBC_o^K) and surface charge density (*SCD*)

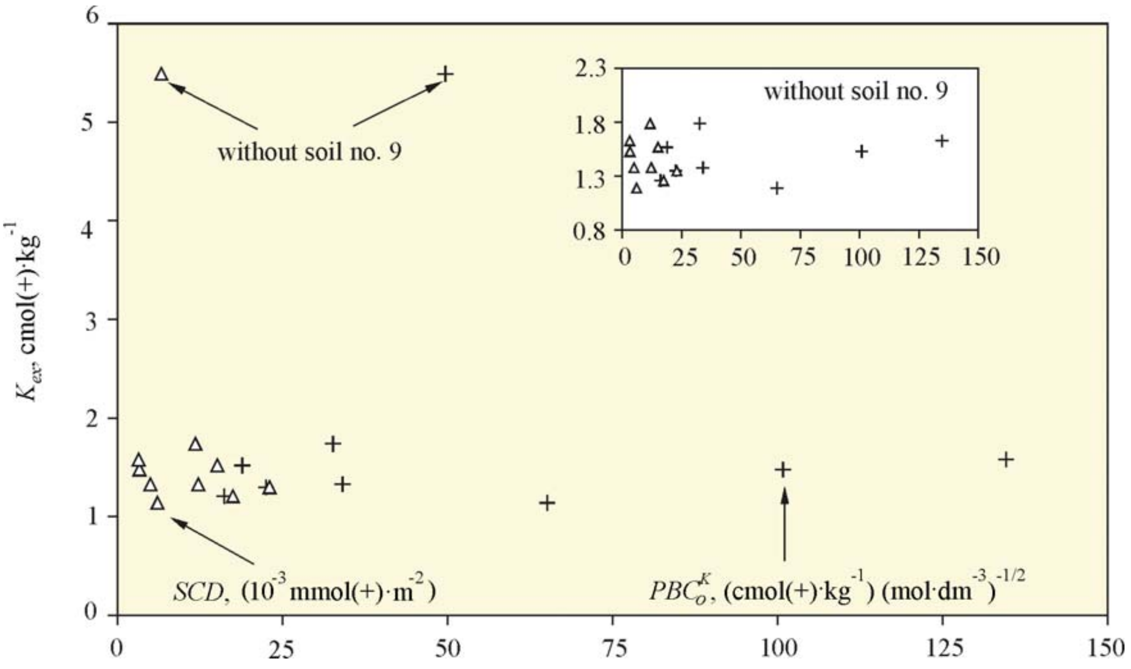


Fig. 4. Relationships of exchangeable potassium (K_{ex}) *versus* free energy of potassium replenishment ($-\Delta G_{equ}^{K}$) at equilibrium

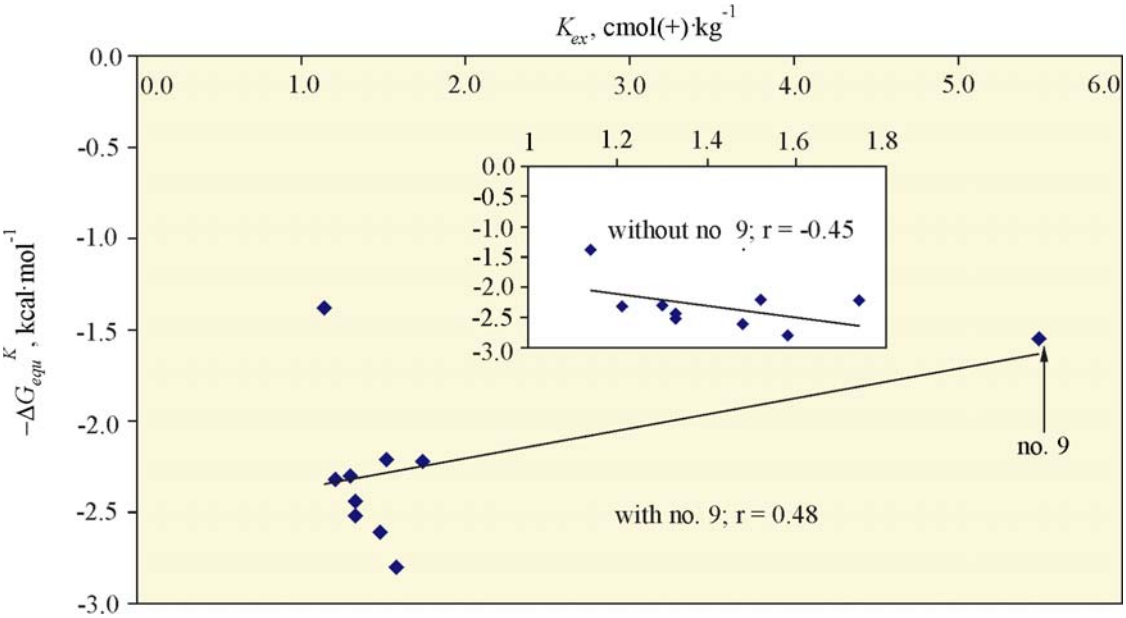
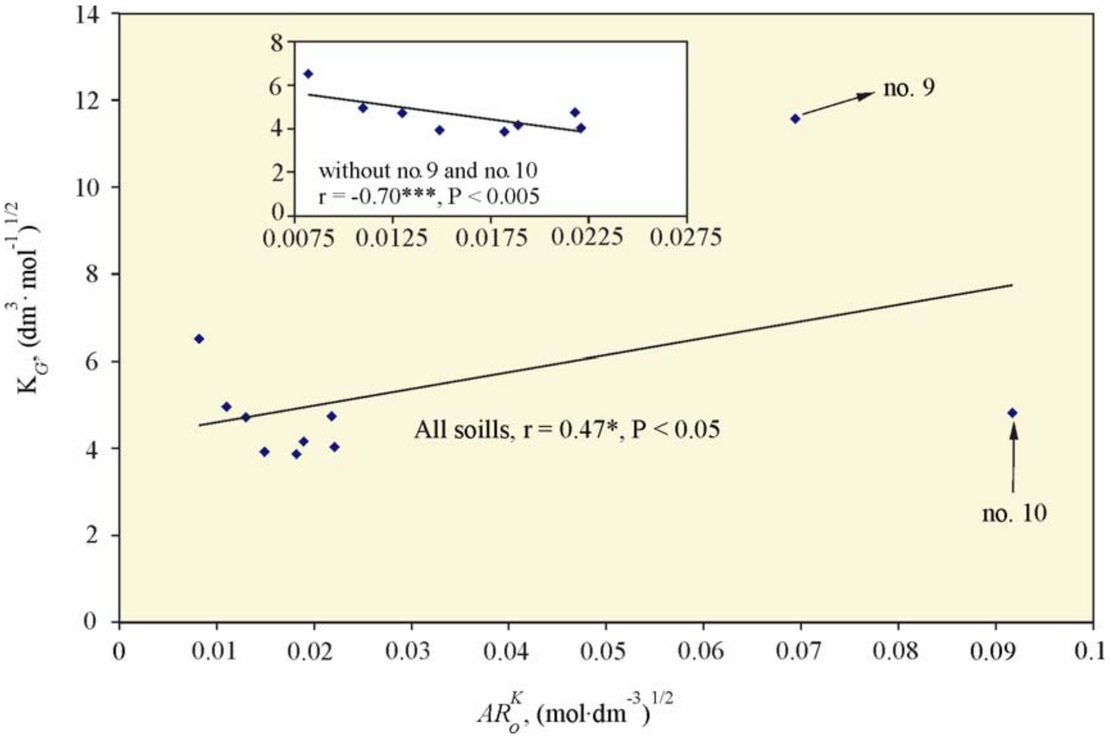


Fig. 5. Relationships of the Gapon selectivity coefficient (k_G) *versus* potassium activity ratio (AR_o^K) at equilibrium



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1. Labile Potassium (K_{Lab})

This form of potassium (Table 2) represents the amounts of K which is readily available (water soluble) and is capable of ion exchange during period of equilibration between soil colloids and soil solution. Soils differed significantly in the amount of K_{Lab} which varied between 0.295 and 1.110 cmol(+)·kg^{-1}. The K_{Lab} values reported by Hamdan [14] and Wang et al. [36] were comprised in the ranges 0.2098-0.3642 and 0.10-0.23 cmol(+)·kg^{-1}. This implies that soils currently investigated are characterized by high capacity for K supplying to plants, however this feature was not exhibited by the sole level of K_{ex} values, which fluctuated in the same range for quite all soils. The K_{Lab} values were lower than the exchangeable K (K_{ex}) indicating thereby that potassium of these soils should be released basically *via* exchange than solubility or diffusion processes. The labile potassium pool (K_{Lab}) represented 6.3 to 75.0% of exchangeable potassium (K_{ex}). Lower percentage share (70% of soils) should be indicative of strengthened K attraction by soil colloids, whereas higher share (30% of soils) – of the opposite case. Such soil reaction with K was unexpected, since soils were characterized by relatively high potassium saturation. This implies that most soil retention sites were predominantly occupied and any additional K (from fertilization practices) input in these soils could result in a significant partition of K to the soil solution, i.e. a strengthened K availability for growing plants.

2. Specific (K_x) and Non-Specific (ΔK_{equ}) Potassium

The quantity of potassium held on specific sites was obtained by extrapolation of quantity-intensity (Q/I) curves to the ordinates. The K_x values fluctuated widely from 0.235 to 1.034 cmol(+)·kg^{-1} (Table 2). This indicates that soils were characterized by differentiated selective exchange surface for potassium, as earlier shown for the level of the K_{Lab} values. Specific potassium constituted from 56.3 up to 98.8% of the labile pool of potassium, and confirms the assumption that K dynamics of these soils is rather a matter of exchange reactions, governed by the distribution of negative charges (ΔpH). A similar approach was reported by Poonia and Niederbudde [29] who stated that K-preference for soil colloids over Ca could be a resultant of an increase/decrease in surface charge density (*SCD*) and low/high K-specific adsorption sites. Potassium retained on non-specific sites (ΔK_{equ}) varied from 0.004 to 0.155 cmol(+)·kg^{-1} constituting 1.2 to 58.6% of labile pool (K_{Lab}) of potassium. More potassium was non-specifically retained by soils no. 1, no. 4, no. 7, and no. 10, properly 33.6, 30.8, 43.7 and 58.6% of K_{Lab}. If the amounts of K retained by non-specific sites are considered to be the immediately available K pool [7,9] for plant uptake, therefore any changes in the amount of K_{ex} should induce significant changes in the non-specific K pool. This is unlikely to occur since these soils are significantly low in organic matter content on the one hand and the pool of specific charges is developed enough, on the other hand.

3. Equilibrium Potassium Activity Ratio (AR_{O}^{K})

The overall values of AR_{O}^{K} listed in Table 2 ranged from 0.0082 to 0.0917 (mol·dm^{-3})$^{1/2}$, of which the highest ones represented soils no. 9 and no. 10, characterized by the lowest percent K saturation and the highest silt content. According to Schneider [32], the release of K increases and the fixation of K decreases when Ca concentrations in the surrounding solution increase. In the present study, potassium dynamics in soil solution should be related both to Ca_{ex} and Mg_{ex}, which directly influenced the overall potassium activity ratios of the soils. The significantly high share of both Ca_{ex} and Mg_{ex} (more than 88% of the CEC) was probably responsible for the relatively low AR_{O}^{K} values obtained in this study. This implies that apparently low concentration of K (except for soils no. 9 and no. 10 characterized by notably higher values of AR_{O}^{K}) would be available in the solution at equilibrium. This seems to be not convincing due to the relatively high level of the K labile pool (K_{Lab}) as well as the degree of K saturation. Equilibrium activity ratio values obtained by Wang et al. [36] from soils low in exchangeable potassium ranged from 0.001 to 0.010 (mol·dm^{-3})$^{1/2}$ and were decidedly lower than those reported for the current soils. Therefore in soil characterized by low exchangeable K pool there should be expected a direct influence of the latter one on the magnitude of AR_{O}^{K} values. This was recently confirmed by Fergus et al. [9] who reported that the intensity of soil potassium was reduced in soils by the exhaustive cropping and the calculated mean AR_{O}^{K} values amounted to 0.00047 (mol·dm^{-3})$^{1/2}$, under conditions of marked K depletion.

4. Equilibrium Potential Buffering Capacity (PBC_o^K)

Potassium dynamics in the soil system may also be controlled by exchange (and diffusion) process, in which the potential buffering capacity at equilibrium (PBC_o^K) plays one of the key roles. The PBC_o^K values are indicative of soil capacity for maintaining a given K activity (concentration) at equilibrium conditions in case of K uptake by plants or leaching [36]. The soils studied were characterized by notably different buffering capacities (Table 2), which varied from 16.15 to 134.62 cmol(+)·kg^{-1} (mol·dm^{-3})$^{-1/2}$ within the following ranges:

< 25 cmol(+)·kg^{-1} (mol·dm^{-3})$^{-1/2}$, for soils no. 1, no. 6, and no. 8,
25 < PBC_o^K < 50 cmol(+)·kg^{-1} (mol·dm^{-3})$^{-1/2}$, for soils no. 4, no. 5, no. 7 and no. 9,
> 50 cmol(+)·kg^{-1} (mol·dm^{-3})$^{-1/2}$ for soils no. 2, no. 3 and no. 10.

Soils with the highest PBC_o^K values were characterized by the lowest percent K saturation, indicative of higher potential to replenish K concentration in soil solution [1]. According to Le Roux and Summer [18], high PBC_o^K values are a measure of constant availability of K in the soil solution over a long period, whereas low PBC_o^K would suggest the need for frequent K supply throughout fertilization practices. Relationships of exchangeable potassium (K_{ex}) *versus* PBC_o^K and surface charge density (*SCD*) depicted in Fig. 3 showed that potassium exchangeability of the soils under study could not be predicted by these two parameters. The relationship *SCD versus* PBC_o^K (Tables 3a and 3b) yielded a negative coefficient of correlation ($r = -0.74^{***}$, $P < 0.005$), implying that the supplying power of soils is significant contrary to the number of accessible surface charges. This is in close agreement with the high level of K saturation, which limited the amount of net free K retention sites. Most of these charges could originate from Fe and Mn oxides, which under equilibrium state may generate additional low energetic charges responsible for K retention in these soils. In conditions similar to those reported here, the influence of the low organic matter content and its share in the generation of negative charges is practically marginal. Such relationships indicate that K dynamics in soils is basically subjected to interactions of several factors, of which PBC_o^K is a resultant.

5. Free Energy of Potassium Replenishment at Equilibrium ($-ÄG_{equ}^K$)

Potassium potential of the soils expressed as free energy of K replenishment ranged from -1.38 to -2.80 kcal·mol^{-1} (Table 2). According to the standard for $-\Delta G_{equ}^K$ reported by Woodruff [37], the K supply for all soils is relatively high (i.e. $-\Delta G_{equ}^K$ less than -3.0 kcal·mol^{-1}, basically). As stated by Roy et al., [31], soils with higher exchangeable K (%K saturation) were generally characterized by low $-\Delta G_{equ}^K$ values. As shown in Fig. 4 (imbedded illustration where soil no. 9 was rejected), the correlation between exchangeable potassium (K_{ex}) and $-\Delta G_{equ}^K$ for most soils was negative and significant ($r = -0.45^{*}$, $P < 0.05$), indicative that soils richer in exchangeable potassium may need less energy for K replenishment, as detailed by Evangelou et al. [7]. This was somewhat confirmed by data of the current study, where 70% of all the soils exhibited $-\Delta G_{equ}^K$ below -2.5 kcal·mol^{-1}.

6. Gapon Selectivity Coefficient (k_G) and Equilibrium Potassium Activity Ratio (AR_o^K)

The Gapon selectivity coefficient for potassium expresses the relative affinity soils may develop towards K in the presence of Ca and Mg both in the soil solid phase and soil solution under equilibrium conditions. Most of the k_G values (i.e. 80%) fluctuated within the range 3.87-4.96 (dm^3·mol^{-1})$^{1/2}$, suggesting that the relative affinity for K was quite similar (Table 2). Of all the soils studied, no. 3 and no. 9 deserve more attention since their k_G were higher, and amounted to 6.51 and 11.57 (dm^3·mol^{-1})$^{1/2}$, respectively. These two soils contain carbonates (Table 1b) and were characterized by the highest CEC (i.e. highest Ca_{ex} + Mg_{ex}) (Table 1a), highest SSA, factors which could account for the magnitude of k_G values observed for soils no 3 and no 9, decidedly. Gapon selectivity coefficients, reported by Feigenbaum et al. [8] varied between 2.3 and 5.3 (dm^3·mol^{-1})$^{1/2}$ for a ClO_4 background and between 2.3 and 6.3 (dm^3·mol^{-1})$^{1/2}$ for the Cl background used. Their data fluctuated within the range obtained in the current study, which implies that changes of k_G values are basically attributable to the levels of exchangeable Ca and Mg. The relationship of pairs k_G *versus* AR_O^K , as depicted in Fig. 5, shows an upward linear trend (exception for the imbedded illustration where soils no. 9, and no. 10 were rejected) with higher AR_O^K values. Best prediction of k_G changes can be made from the pairs AR_O^K *versus* k_G (imbedded illustration) since the coefficient of correlation is high, negative and significant ($r = -0.70^{***}$, $P < 0.005$). The inclusion of soils no. 9 and no. 10 gave weaker, positive and significant relationship, with $r = 0.47^{*}$, $P < 0.05$. It is noteworthy from equation 3 that any notable increase of exchangeable K (K_{ex}) will result in a narrowing of the ratio $K_{ex}/(Ca + Mg)_{ex}$ and simultaneously may lead to an increase in K concentration (activity) in the soil solution, as generally it takes place after K fertilizers application. There should be expected a lower affinity of soils for K as shown by the negative correlation coefficient, $r = -0.70^{***}$, $P < 0.005$.

Such soils selective behaviour for K in comparison with dominant Ca and Mg may also be attributed to preferential attraction of K ions over Ca and Mg [29] at some planar sites of soil colloids, if $Ca_{ex} + Mg_{ex} \approx CEC$ is assumed [5]. The preferential factor $PF_{(Ca+Mg)_{ex}}^{K_{ex}}$ values (Table 2) varied between 0.065 and 126, indicating that soils have generally exhibited quite similar preference for potassium. On the basis of these data soils may be divided into two groups of which the first one is expressed by $PF_{(Ca+Mg)_{ex}}^{K_{ex}} < 0.100$ (soils no. 2, no. 3, no. 5, no. 9, and no. 10) characterized by higher soils preference for Ca and Mg over K in contrast to soils of the second group (no. 1, no. 4, no. 6, no. 7, and no. 8) with $PF_{(Ca+Mg)_{ex}}^{K_{ex}} > 0.100$, where K seems to be more preferentially attracted.

Relationships of Quantity-Intensity parameters and Soil Properties

The coefficients of correlation for pairs Q/I parameters *versus* selected soil physical and chemical properties are detailed in Tables 3a and 3b. Potassium was differently controlled by soil properties of which organic carbon (C_{org}) was significantly and positively correlated with K_{lab} ($r = 0.62^{**}$), K_x ($r = 0.45^{*}$) and PBC_o^K ($r = 0.58^{**}$) only. This could be expected since the C_{org} level of soils was overall notably low. In such cases potassium dynamics of soils should be basically controlled by mineral soil constituents. Potassium equilibrium parameters i.e. AR_O^K, and $-\Delta G_{equ}^K$ were both significantly and positively ($r \geq 0.93^{****}$, $P < 0.001$) correlated with the silt content. Unexpectedly it was found that AR_O^K was significantly controlled more by oxide forms of Fe and Mn ($r = 0.72^{***}$, $P < 0.005$, on average) than by the cation exchange capacity (CEC) and exchangeable cations, but Fe and Mn oxides did not affect the level of labile potassium (K_{Lab}). These data point out at the specific role of Fe and Mn oxides jointly with CEC on K activities in soils, as supported evidently by $-\Delta G_{equ}^K$ values. The positive and significant correlations obtained for the pairs k_G *versus* soil properties may be attributed to the fact that this parameter links both the solid and solution soil phases and potassium changes depend fundamentally on Ca and Mg which predominate more in the solid than solution soil phases.

Table 3a. Linear coefficients of correlation between selected physical and chemical properties of soil and potassium quantity-intensity parameters (n = 10)

	Silt	Clay	pH_{H2O}	*CEC*	Ca_{ex}	Mg_{ex}	K_{ex}
AR_O^K	0.97^{****}	0.40	-0.35	0.48^{*}	0.47^{*}	0.51^{*}	0.51^{*}
K_{lab}	-0.27	0.20	0.08	-0.11	-0.08	-0.20	-0.06
$-\Delta K_{equ}$	0.23	-0.20	-0.70^{***}	-0.39	-0.38	-0.40	-0.38
K_x	-0.36	0.27	0.34	0.04	0.07	-0.04	0.08
PBC_o^K	0.02	0.03	0.21	0.20	0.23	0.11	0.25
$-\Delta G_{equ}^K$	0.93^{****}	0.37	-0.34	0.46^{*}	0.44	0.51^{*}	0.47^{*}
k_G	0.63^{**}	0.75^{***}	0.60^{**}	0.99^{****}	0.99^{****}	0.97^{****}	0.98^{****}

* significant at $P < 0.05$; ** at $P < 0.01$; *** at $P < 0.005$; **** at $P < 0.001$, at least

Table 3b. Linear coefficients of correlation between selected physical and chemical properties of soil and potassium quantity-intensity parameters (n = 10)

	$C_{org.}$	SSA	*SCD*	Fe (DCB)	Fe (Ox)	Mn (DCB)	Mn (Ox)
AR_O^K	-0.15	0.29	-0.20	0.81^{***}	0.71^{***}	0.70^{***}	0.71^{***}
K_{lab}	0.62^{**}	0.32	-0.60^{**}	-0.003	0.08	-0.07	-0.11
$-\Delta K_{equ}$	0.42	-0.39	-0.11	0.32	-0.11	-0.16	-0.19
K_x	0.45^{*}	0.47^{*}	-0.55^{*}	-0.12	0.12	-0.01	-0.03
PBC_o^K	0.58^{**}	0.63^{**}	-0.74^{***}	0.16	0.38	0.20	0.24
$-\Delta G_{equ}^K$	-0.31	0.16	0.01	0.75^{***}	0.62^{**}	0.65^{**}	0.63^{**}
k_G	-0.07	0.91^{****}	-0.42	0.41	0.90^{****}	0.68^{**}	0.79^{***}

* significant at P < 0.05; ** at P < 0.01; *** at P < 0.005; **** at P < 0.001, at least

CONCLUSIONS

1. The application of quantity-intensity (Q/I) approach for evaluating potassium dynamics of selected Polish agricultural soils have provided with parameters: labile K (K_{Lab}), equilibrium activity ratio for K (AR_O^K), equilibrium potential buffering capacity for K (PBC_o^K), free energy of the K replenishment ($-\Delta G_{equ}^K$), Gapon selectivity coefficient *(k_G)*, which helped assessing the degree of potassium lability.
2. The soils did not generally differ in their exchangeable potassium (K_{ex}) but did for the %K saturation as an estimate of potential K lability. Potassium was differently controlled by soil properties of which organic carbon (C_{org}) exhibited weak relationships with most of Q/I parameters.
3. Potassium activity ratio (AR_O^K) was controlled more by silt ($r = 0.97^{****}$, $P < 0.001$) and Fe and Mn ($r = 0.72^{***}$, $P < 0.005$, on average) than by the cation exchange capacity (CEC) and exchangeable cations ($r = 0.50^{*}$, $P < 0.05$, on average). Interestingly, of mineral soil constituents, it was found that Fe and Mn oxides also significantly affected the free energy of changes ($-\Delta G_{equ}^K$). This implies that studies on potassium dynamics in soils should additionally consider these two elements.
4. Most of the Gapon selectivity coefficients (k_G) (i.e. 80%) fluctuated within the range 3.87-4.96 $(dm^3 \cdot mol^{-1})^{1/2}$, suggesting that the relative affinity for K was quite similar, irrespective of the degree of K saturation. The latter one along with the pool of labile K (K_{Lab}) indicate that soils will sufficiently support plant cropping without any threat of K shortage, as stated by the $-\Delta G_{equ}^K$ values.

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Jean Bernard Diatta, Zdzisław Wacław Kociałkowski
Poznań Agricultural University, Department of Agricultural Chemistry
Wojska Polskiego 71F, 60-625 Poznań, Poland
e-mail: Jeandiatta@yahoo.com

Witold Grzebisz
Poznań Agricultural University, Department of Agricultural Chemistry
Wojska Polskiego 71F, 60-625 Poznań, Poland
e-mail: witegr@au.poznan.pl

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