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Cation Exchange Resins for Predicting Available K on K-Deficient Soils: Extraction Capacity among Different Soil K Pools and First Insights on the Contribution of K Solubilized by Rhizosphere Microbes

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Abstract: The contribution of non-exchangeable soil K in the total K availability may be essential to K deficient soils; however, less attention has been paid so far for proposing soil tests that assess the bioavailable structural K that is solubilized by soil microbes during a growing season. The objectives of this study were to evaluate cation exchange resins for their performance in predicting K uptake by plants; to investigate the relationships between rhizosphere soil microbes, different soil K pools, and soil parameters; and to assess their exchange capacity with respect to K derived by feldspars. A pot experiment with winter wheat was conducted on K deficient soils, several soil tests were examined, and rhizosphere K solubilizing microbial population was assessed. Single and multiple regressions showed that cation resins performed better in predicting total plant K uptake than the other chemical extractants (r^2 = 0.64, r^2 = 0.85, respectively, $p \leq 0.001$), whereas the PCA analysis and Pearson correlation tests revealed a positive correlation between K derived by feldspars, K uptake, and the K solubilizing rhizosphere microbial population. The above was further confirmed by the mapping of cation resins of extraction capacity, which showed a significant contribution of K derived by feldspars (15.6%).

Keywords: structural K; potassium availability; K solubilizing microbes; K soil testing

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1. Introduction

Potassium (K) is an essential macronutrient for plants, it highly impacts both crop yield and the quality of agricultural products, while it is required in large amounts, much greater than any other soil-supplied nutrient except nitrogen, to ensure adequate plant growth [1]. The amounts of total K in agricultural soils are in abundance, and as referred in literature, they may reach up to 62 Mg ha^{-1} in the upper 15 cm [2]. However, the amounts of soil K that are readily or even potentially available to plants during a growing season are often proven to be inadequate. The latter raises the potential danger of insufficient plant K uptake, and thus crop yield loses, or soil degradation phenomena due to the exhaustion of soil K pools.

To date, and notably for the case of Greek soils, despite the fact that for years a misconception had prevailed that "our soils are sufficiently supplied with K due to the presence of K bearing minerals", K exhaustion is also not an unusual phenomenon. The latter has particularly been evidenced by extensive research recently conducted on K-dynamics in soils of northern Greece [3–5]. In addition, the fact that K use as fertilizer in Greece is among the lowest in the European Union and remains low, as reported by FAO (2017) [6], further supports the hypothesis that K mining under intensive cropping conditions may be an additional soil degradation factor for Greek agricultural soils.

In cases like the above, fixation phenomena are not unusual and might occur when the presence of K-fixing clay minerals, such as illite or vermiculite, is dominant and/or intensive cropping practices are adopted in conjunction with drought conditions and low levels of water content of the soil. Under such conditions, crops might not respond to K fertilization applications. On the other hand, non-exchangeable K (diffusion-derived, or solubilized by rhizosphere microbes) might participate essentially in the total amount of plant-available K, which may also negate responses to K fertilization [7].

The inadequacy of conventional soil tests that are based on the assessment of exchangeable or readily available K to precisely predict bioavailable K has been extensively and well discussed in previous research works, and it often raises controversies stemming from different perspectives on K management in soils. The latter, aptly referred to in the literature as "the potassium paradox", poses the need for a more comprehensive context in the use of any soil test that is to be adopted for predicting soil-available K, at least as regards the complexity of K dynamics in soil [8].

However, while in the case of exchangeable K, the particular pool is considered as the surface-adsorbed K onto negatively charged soil constituents, there are two main non-exchangeable pools, corresponding to either K^+ contained in the interlayers of micas, such as illite, or in the structure of other K-bearing silicates, such as feldspars. These have been referred to as interlayer K and structural K, respectively, and although much work has been conducted in the past on the contribution of diffusion-derived interlayer K on total K availability [9,10], less attention has been paid so far to the bioavailable structural K that is solubilized during a growing season.

It is well known that a wide range of bacteria, fungi, or actinobacteria promote the solubilization of soil K-bearing minerals through various direct and indirect mechanisms. These mechanisms mainly include the release of organic and inorganic acids that can directly dissolve mineral K and K storage in their biomass, which potentially could be indirectly available to plants, or the chelation of cations bound to K, such as Si or Al [11–13].

The standard soil testing practice adopted by the majority of soil testing laboratories worldwide (and also for Greece) for predicting available K is the ammonium acetate extraction method (1 M NH_4OAc, pH 7, 1:10 w/v ratio), which, although proven reliable for many soil types [14], appears to be insufficient for soils containing significant amounts of 2:1 clay minerals [8,15], or for soils under intensive cultivation [16,17]. In soils such as the above, the contribution of non-exchangeable K can be significant [9] and, in this case, the use of a soil test that can simulate the K-release mechanisms in the soil solution might also contribute to a better understanding of K behavior in soil [18].

Among several extractants that are used to assess K from different soil K pools, sodium tetraphenylboron ($NaBPh_4$) has the ability to remove non-exchangeable K from the interlayer sites of 2:1 clay minerals, such as illite [19]. Thus, it has been suggested by previous works as a superior predictor of wheat K uptake over NH_4OAc [20], while additionally its use has been studied extensively in Greek soil conditions [3,4]. However, as reported by Núñez and Morón (2017), the adoption of a chemical soil test such as $NaBPh_4$ does not avoid limitations regarding its inability to accurately predict the exact amounts of diffusion-derived non-exchangeable K that are to be taken up by plants [21]. Moreover, its prediction weakness has also been observed in short-term cropping conditions, in which pot experimentation is usually conducted [22].

On the other hand, ion exchange resins, due to their high cation exchange capacity (CEC), when coming into contact between soil and solution phase, can act as a sink, keeping the levels of solution K low, and pushing out at the same time amounts of exchangeable and non-exchangeable soil K, released for plant uptake [23]. Thus, they have been tested in the past for their efficiency in simulating the plant K uptake process [24–26], and, moreover, they have given promising results for Greek agricultural soils, as well [22]. However, the contribution of each soil K pool (exchangeable, diffusion derived, non-exchangeable K solubilized by rhizosphere microbes) in the rate of solution K replenishment has not been studied so far. We consider that this alone constitutes a research gap that needs to be investigated due to the special importance that the selection of an appropriate extraction method acquires in understanding the K-dynamics in K-depleted soils.

We hypothesized that when conditions of soil K deficiency are present and conventional extraction methods fail, the soil test that can more precisely predict bioavailable K should also reflect the contribution of the other dynamically connected soil K pools (except those of soil solution K or exchangeable K) in the overall K availability during a growing season. In addition, we also speculated that if in such conditions the solubilization of K derived from primary minerals, such as feldspars, is triggered, the above could be related to a respective increase in the activity of the rhizosphere soil microbiota.

In this line, three objectives were investigated: (i) the evaluation of cation resins performance to successfully predict K uptake by plants on K-deficient soils, as compared with other chemical extraction methods of exchangeable and non-exchangeable K (NH_4OAc, $NaBPh_4$); (ii) the investigation of the relationships between K-solubilizing rhizosphere soil microbes, different soil K pools, and soil parameters, in order to evaluate their impact in the overall soil K availability; and (iii) the assessment of the resins cation exchange capacity with respect to the contribution of different soil K pools and the rhizosphere microbial population.

2. Materials and Methods

2.1. Soil Selection and Greenhouse Pot Experiment

Ten surface soil samples (0–30 cm), low in exchangeable K, representing typical soil types of northern Greece cultivated with wheat, sunflower, or maize were selected (Table 1). Before the establishment of the pot experiment, soils were analyzed for texture with the hydrometer method [27], pH (1:1 *w*/*v* suspension in water), organic carbon (OC) by the Walkley-Black procedure [28]. Total calcium carbonate ($CaCO_3$) was determined using a digital calcimeter (FOG L, bd INVENTIONS, Greece), and cation exchange capacity (CEC) was assessed by the $[Co(NH_3)_6]Cl_3$ method (ISO 23470). Total K content in soils was determined after digestion with aqua regia (ISO 11466), illite-K was determined by $NaBPh_4$ extraction at a 7-day incubation period [20], while the difference between total K and illite K was attributed to K derived from prime minerals (K-feldspars).

Table 1. Basic soil properties of the studied soils.

Soil Location		Classification	pH	Clay	$CaCO_3$	OM [1]	CEC [2]	NH_4OAc-K [3]
					%		$cmol_c\ kg^{-1}$	$mg\ kg^{-1}$
1	Kerasia	Luvisol	7.3	20.9	-	2.0	19.3	92.0
2	Assiros	Cambisol	6.2	33.7	-	2.6	30.1	121.0
3	Pente Vrises	Luvisol	6.3	38.2	-	2.6	24.8	93.0
4	Univ. Farm	Fluvisol	7.7	25.4	3.2	2.2	22.7	56.0
5	Sindos	Fluvisol	7.3	28.2	4.3	2.5	22.3	82.0
6	Kristoni	Cambisol	5.6	32.9	-	2.4	21.5	85.0
7	Pedino	Luvisol	5.0	28.4	-	2.2	21.1	81.0
8	Sirako	Vertisol	7.4	42.1	-	2.6	29.0	111.0
9	Gynekokastro	Fluvisol	7.3	26.3	-	2.5	14.9	87.0
10	Mouries	Entisol	6.3	12.0	-	2.0	12.3	60.0

[1] OM: organic matter; [2] CEC: cation exchange capacity; [3] NH_4OAc-K: exchangeable K.

Each one of these samples was chosen either from a former soil K availability study [3] after K depletion through successive wheat cultivation in pots (experiment conducted in 2011), from samples used as control treatments in a former K addition pot experiment [5] (experiment conducted in 2014), or from field sampling sites known for their low adequacy in soil exchangeable K (soil samples were collected in 2019). After collection, soils were air-dried, then they were sieved through a 1 cm sieve, while the obtained material was stored in polyethylene bags until they were used in a glasshouse pot experiment, cultivated with winter wheat.

The acquired soil samples after the above preparation (<1 cm) were blended with a minus K nutrient mixture [29], and part of this quantity was divided into 0.75 kg portions and placed in 1 L pots, so three replicates were created for each soil. A subsample of this material was ground, passed through a 2 mm sieve, and used for soil analyses.

Deionized water (EC < 0.001 dS m^{-1}) was used to moisten soils in the pots until they reached their field capacity, a condition which was maintained by weighing every second day in order to replenish water losses. The experiment began in January 2022 in a glasshouse with a mean temperature of 20 ± 5 °C under natural light conditions. The experimental setup was a completely randomized design (CRD), with repeated randomization every 7 days.

According to the cultivation history of selected soils, winter wheat was one of the most representative species, and so it was chosen as the experimental plant (*Triticum aestivum* L. var. 'Yecora'). Two cropping cycles were carried out in total, with one harvest of biomass of each cropping cycle. For each soil in the pots, 10 seeds of winter wheat were used, and thereafter were thinned to 5 plants after emergence. Harvest was carried out on the 28th day after the emergence of seeds, approximately at 2.5 cm above the soil surface. Then, after emptying the pots, soils were sieved moist (<1 cm) and a soil sample (50 g air dry basis) was taken for analysis. Pots were then refilled, and the same procedure was also carried out for the second cropping cycle.

Soil K analysis was conducted on initial soil samples and included soil solution K from the saturation extract (K-soluble), extraction with NH_4OAc (1 M, pH 7, 1:10 w/v ratio), $NaBPh_4$ at 1, 5, and 30-min extraction period [20], and the resins extraction method, which is detailed in the below section. Potassium adsorption ratio (PAR), representing an intensity factor of K in the soil solution, relative to Ca and Mg was calculated as follows:

$$\mathrm{PAR} = \frac{\mathrm{K}^{+}}{\sqrt{\frac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}{2}}} \tag{1}$$

where each chemical element symbol indicates a concentration in millimoles of charge per liter ($\mathrm{mmol_c\ L^{-1}}$)

Flame photometry was used for determining soil K, while all soil analyses were performed in triplicate. The sensitivity of the flame photometer was evaluated by calculating the limit of detection (LOD = 0.19 mg L^{-1}) and the limit of quantification (LOQ = 0.64 mg L^{-1}). Determination of dry matter (DM) yield was conducted after drying the aboveground biomass of each cropping cycle at 75 °C for 48 h. The wet digestion method with HNO_3 [30] was then used to determine the K concentration of plant tissue by flame photometry. Potassium uptake was calculated by the product of each yield times K concentration.

2.2. Resins Experiment with Soil Pots and Their Use as Soil Extractants

Cationic resins provided by Membranes International INC were functionalised with sulfonic acid, Na saturated, and their cation exchange capacity was 160 $\mathrm{cmol_c\ kg^{-1}}$, according to technical specifications provided by the manufacturer. From single membrane sheets of 1 × 0.5 m dimensions, membrane strips of 2 × 6 cm dimensions were cut as described by Ziadi et al. (1999) [31]. Resins were H^+ saturated with HCl (1M), while successive washings were applied with deionized water in order to remove the excess of HCl, until the negative test with $AgNO_3$.

H^+-saturated resins were then stored in bottles with deionized water, and soil K extraction was carried out on initial soil samples before the beginning of the pot experiment. Three different soil-water ratios and extraction times were applied (1:5, 1:10, 1:200 s/w ratios, and extraction times of 30-min and 60-min, respectively). One strip was used for the 1:5 and 1:10 s/w ratio, whereas a bunch of 3 strips was used for the 1:200 s/w ratio, respectively.

2.3. Determination of K Solubilizing Rhizosphere Microbial Population

At the end of the 2nd cropping cycle, the plant roots were shaken and roots with the remaining soil were placed in a plastic bag, where soil clumps adhering to the roots were broken. The rhizosphere soil (5 g) was added in 45 mL of sterile water, shaken for

5 min, and a 10-fold dilution series followed. A 0.1 mL aliquot was spread on a modified Aleksandrov medium Petri dish [32] in duplicates, incubated at 28 °C, and the microbial colonies were counted on the plates up to 18 d.

2.4. Statistical Analysis

The data of each variable were checked for homogeneity, and when values of these statistics were outside the expected range, appropriate transformations were applied to make them more normal. Principal Component Analysis (PCA) was applied to identify the variation of studied parameters, and interrelationships between K uptake, soil parameters, and respective patterns of K amounts derived from different soil K pools were checked with Pearson correlation tests. Single and multiple regression analyses using the backward stepwise selection method were applied to evaluate each extraction method's ability to predict plant K uptake. Relative weight analysis was applied to access the percentage among multiple predictor variables from respective multiple regression models [33]. For all statistical analyses, Statgraphics software was used (STATGRAPHICS, Centurion XVI, version 16.1.11, StatPoint Technologies, Inc., Warrenton, VI, USA).

3. Results

3.1. Soil Characteristics, Distribution of Soil K Pools, and Amounts of Soil K Extracted by Different Extraction Methods

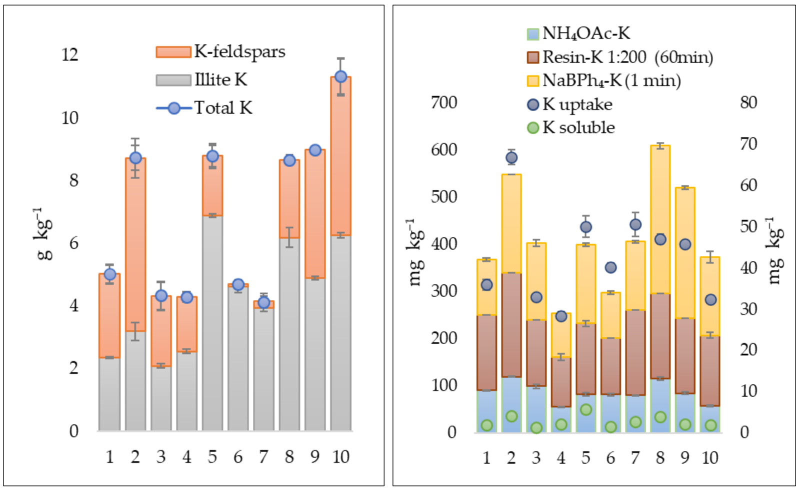
Selected physicochemical properties and classification (IUSS 2015) [34] of the soils are presented in Table 1. Clay content ranged from 12% in the medium texture loamy soil of Mouries to 42.1% in the case of the fine texture clayey soil of Siraco. The values of organic matter (OM) ranged from 2.0% to 2.6%, while CEC values varied between 12.3 and 30.1 $\text{cmol}_c\ \text{kg}^{-1}$. In addition, pH ranged from 5.0 to 7.7, while 2 of the 10 soils contained small amounts of $CaCO_3$ up to 4.3%. As far as the exchangeable amounts of K (extracted with NH_4OAc) are concerned, their values ranged between 56.0 and 121.0 mg kg^{-1}. For these soils, the above range is below the critical level of exchangeable K (135 mg kg^{-1}) as assessed by applying the Cate-Nelson calibration technique in a previous K-depletion experiment [3].

The distribution of K amounts from different soil K pools as extracted by the respective extraction procedures, alongside with K uptake patterns by wheat among the 10 soils, are presented in Figure 1. More specifically, illite K content ranged from 2.1 to 6.9 g kg^{-1}, K derived from feldspars ranged from 0.07 to 5.5 g kg^{-1}, and, in addition, total K content showed the lowest value in the soil of Pedino (4.1 g kg^{-1}) and the highest value in the soil of Mouries (11.3 g kg^{-1}), respectively (Figure 1a).

As regards the more dynamically connected with K uptake by plants soil K pools, the distribution of readily available K (soil solution K) and exchangeable K (NH_4OAc-K), together with amounts of K reflecting the rate of solution K replenishment by the non-exchangeable forms of K ($NaBPh_4$-K, resin-K), are shown in Figure 1b. Correlation trends between K uptake and the aforementioned soil K pools can be observed, a fact that will be discussed in detail below, where their performance in predicting K uptake will be further evaluated.

3.2. Distribution of Population of K Solubilizing Rhizosphere Microbes among Soils

Plate counts ranged 2.3–28.0 × 10^6 cfu g^{-1} soil d.w. and were higher for Assiros (2) soil and lower for Kristoni (6) and Syrako (8), while most soils did not differ in cfu (Figure 2).



(**a**) (**b**)

Figure 1. Distribution of K amounts from different soil K pools as extracted by respective extraction procedures: (a) total K; illite K; K derived from feldspars, and (b) readily available K (soil solution K); exchangeable K (NH_4OAc-K); amounts of K reflecting the rate of solution K replenishment ($NaBPh_4$-K, resin-K); K uptake by plants (For Figure 1b, bars are referenced in the left vertical axe, markers at the right); The error bars represent the standard error of the mean at the 95% confidence level ($p \leq 0.05$); 1–10: soil samples numbering.

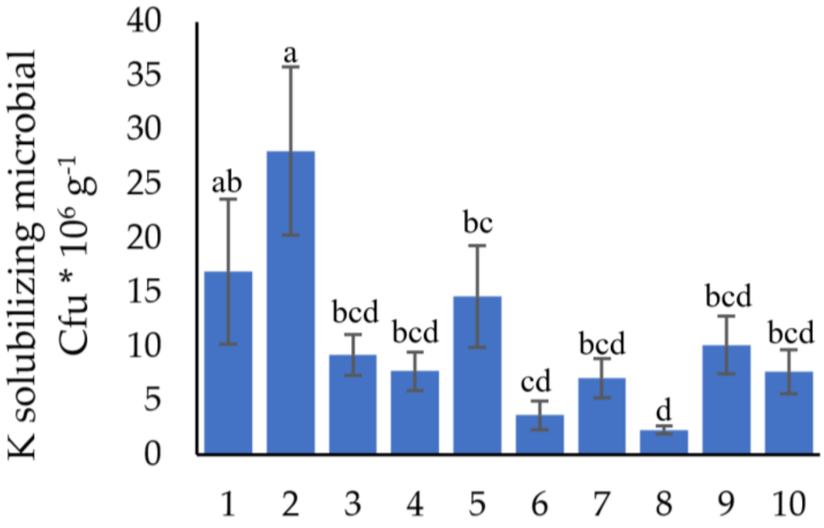


Figure 2. Rhizosphere K-solubilizing bacterial abundance. The error bars represent the standard error of the mean at the 95% confidence level ($p \leq 0.05$, $n = 3$). Comparisons were performed by LSD test ($p \leq 0.05$) and are demonstrated with lowercase letters. The presence of a common letter between each column implies no significant difference; 1–10: soil samples numbering.

3.3. Interrelationships between K Utake, Basic Soil Properties, and Soil K Pools

The PCA analysis revealed that the major portion of the total variance (85.6%) of the studied variables (plant K-uptake, soil K pools, and selected soil properties) was grouped between four components, and two of them explained almost 63% of it (Figure 3). According to these results, K uptake by plants, NH_4OAc-K, resin extracted K, alongside with the OM% parameter, were the variables recording the higher weights of the first component, whereas the rhizosphere K solubilizing microbial population, K derived by feldspars, and clay content determined the variability of the second. In addition, the convergence of the vectors that represent both the microbial population and K-derived by feldspars, as well as K uptake and resin-extracted K, denote respective positive correlations.

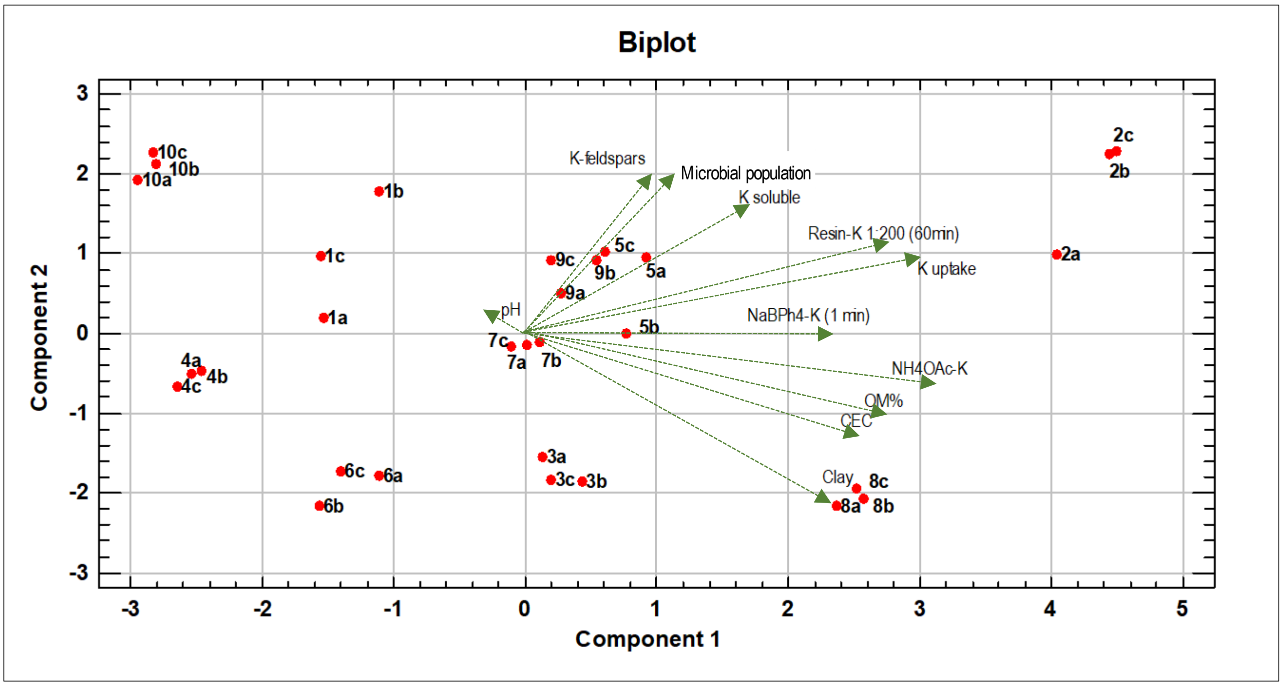


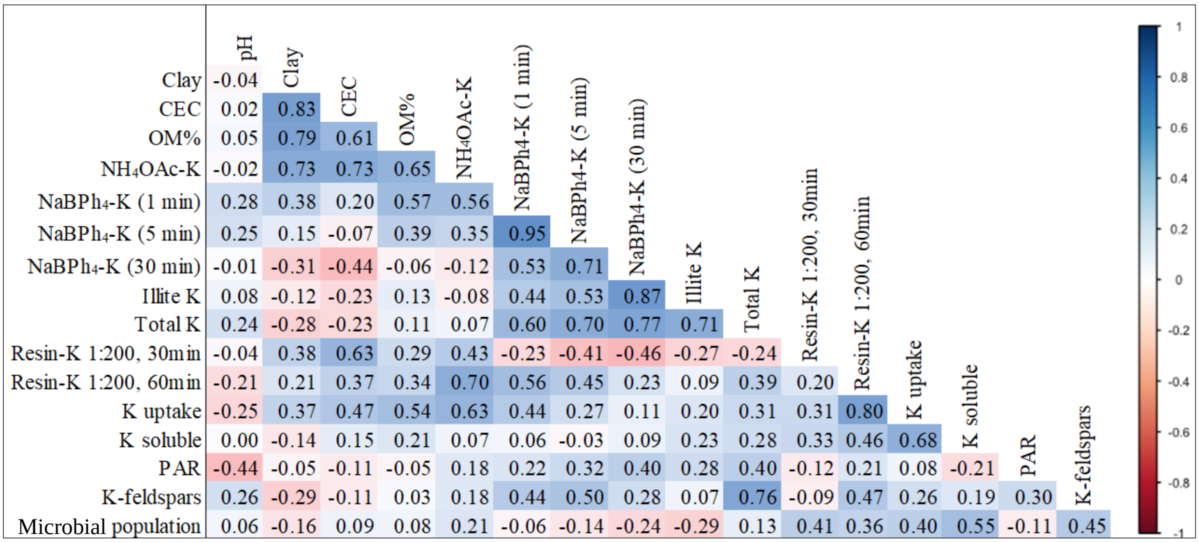
Figure 3. Biplot of the first two principal components of the studied variables (plant K-uptake, soil K pools, and selected soil properties) among different soils (1–10: soil samples numbering; a, b, c: their experimental replications). CEC is the cation exchange capacity; OM is the organic matter content; NH$_4$OAc is the ammonium acetate extracted K; NaBPh$_4$ is the sodium tetraphenylboron-extracted K.

Moreover, Pearson correlation tests confirmed the above findings and further showed positive correlations between plant K uptake and soil parameters, such as clay content, CEC, or OM%, while interestingly, the above positive correlation as regards the K uptake parameter was also observed in the case of the rhizosphere K-solubilizing microbial population (r = 0.4, $p \leq 0.05$). In addition, also noteworthy is the fact that the K-solubilizing microbial population gave statistically positive correlations with K derived from feldspars (r = 0.45, $p \leq 0.01$), with the readily available form of soluble K (r = 0.45, $p \leq 0.01$), as well as with the resin extracted K (r value up to 0.41, $p \leq 0.05$).

Furthermore, and as expected, different extraction procedures targeting different soil K pools gave positive correlations with a scaled correlation coefficient strength (r value from 0.44 in the case of NaBPh$_4$-K up to 0.80 as regards the resin-extracted K) with K uptake by plants. However, extracted amounts of K with the NaBPh$_4$ method gave contradicting correlations (positive or negative) with the respective amounts of resin-extracted K, while the extraction period at both extractants was the key factor that controlled the nature of the above relationships (Figure 4).

3.4. Performance of Cation Exchange Resins to Predict K Uptake by Plants

Single regression models were applied between total K uptake by plants and the respective amounts of K extracted by different extractants and several extraction periods. As regards the resin and the NaBPh$_4$ extracted K, the r^2 evaluation criterion was used to select the specific extraction period that gives the best fit in the prediction models, and additionally as far as the resin procedure is concerned, the same evaluation criterion was also used to find the most appropriate soil and water ratio.



	pH	Clay	CEC	OM%	NH_4OAc-K	$NaBPh_4$-K (1 min)	$NaBPh_4$-K (5 min)	$NaBPh_4$-K (30 min)	Illite K	Total K	Resin-K 1:200, 30min	Resin-K 1:200, 60min	K uptake	K soluble	PAR	K-feldspars
Clay	-0.04															
CEC	0.02	0.83														
OM%	0.05	0.79	0.61													
NH_4OAc-K	-0.02	0.73	0.73	0.65												
$NaBPh_4$-K (1 min)	0.28	0.38	0.20	0.57	0.56											
$NaBPh_4$-K (5 min)	0.25	0.15	-0.07	0.39	0.35	0.95										
$NaBPh_4$-K (30 min)	-0.01	-0.31	-0.44	-0.06	-0.12	0.53	0.71									
Illite K	0.08	-0.12	-0.23	0.13	-0.08	0.44	0.53	0.87								
Total K	0.24	-0.28	-0.23	0.11	0.07	0.60	0.70	0.77	0.71							
Resin-K 1:200, 30min	-0.04	0.38	0.63	0.29	0.43	-0.23	-0.41	-0.46	-0.27	-0.24						
Resin-K 1:200, 60min	-0.21	0.21	0.37	0.34	0.70	0.56	0.45	0.23	0.09	0.39	0.20					
K uptake	-0.25	0.37	0.47	0.54	0.63	0.44	0.27	0.11	0.20	0.31	0.31	0.80				
K soluble	0.00	-0.14	0.15	0.21	0.07	0.06	-0.03	0.09	0.23	0.28	0.33	0.46	0.68			
PAR	-0.44	-0.05	-0.11	-0.05	0.18	0.22	0.32	0.40	0.28	0.40	-0.12	0.21	0.08	-0.21		
K-feldspars	0.26	-0.29	-0.11	0.03	0.18	0.44	0.50	0.28	0.07	0.76	-0.09	0.47	0.26	0.19	0.30	
Microbial population	0.06	-0.16	0.09	0.08	0.21	-0.06	-0.14	-0.24	-0.29	0.13	0.41	0.36	0.40	0.55	-0.11	0.45

Figure 4. Pearson correlation matrix between K uptake, microbial population, soil parameters, and respective patterns of K amounts derived from different soil K pools. PAR is the potassium adsorption ratio; CEC is the cation exchange capacity, OM is the organic matter content; NH_4OAc is the ammonium acetate extracted K; $NaBPh_4$ is the sodium tetraphenylboron-extracted K. Blue color indicate positive correlations; red color indicate negative correlations.

Results showed that the application of cation resins performed better in predicting total plant K uptake than the other chemical extractants that were used as reference, giving the highest r^2 value and managing to explain 64% of the overall K uptake variability (Table 2). Among the other extractants, K-soluble by saturation extracts gave the second best performance ($r^2 = 0.50$, $p \leq 0.001$), followed by the NH_4OAc-K ($r^2 = 0.39$, $p \leq 0.001$), and the $NaBPh_4$-K with 1 min extraction period ($r^2 = 0.20$, $p \leq 0.05$).

Table 2. Single (**a**) and multiple (**b**) regression models of total K uptake prediction by soluble K from saturation extracts, soil K extracted with ammonium acetate (NH_4OAc), sodium tetraphenylboron ($NaBPh_4$, 1 min incubation period), and resin-extracted K (soil to water ratio, 1:200, 60 min extraction period). Soil parameters used in the multiple regression models (pH, clay content), were chosen by the backward stepwise selection method.

(a) $n = 30$ [1]	r^2
Total K uptake (mg kg^{-1}) = 3.60 K soluble (mg L^{-1}) + 24.20	0.50 ***
Total K uptake (mg kg^{-1}) = 0.34 NH_4OAc-K (mg kg^{-1}) + 13.52	0.39 ***
Total K uptake (mg kg^{-1}) = 0.07 $NaBPh_4$-K, 1 min (mg kg^{-1}) + 30.73	0.20 *
Total K uptake (mg kg^{-1}) = 0.29 Resin-K 1:200, 60 min (mg kg^{-1}) − 1.54	0.64 ***
(b) $n = 30$	r^2
Total K uptake (mg kg^{-1}) = 0.39 Clay (%) + 2.47 K soluble (mg L^{-1}) + 0.18 Resin-K 1:200, 60 min (mg kg^{-1}) − 12.99	0.85 ***
Total K uptake (mg kg^{-1}) = 0.32 Clay (%) − 4.35 pH + 3.50 K soluble (mg L^{-1}) + 0.06 $NaBPh_4$-K, 1 min (mg kg^{-1}) + 30.11	0.84 ***
Total K uptake (mg kg^{-1}) = −2.92 pH + 3.17 K soluble (mg L^{-1}) + 0.29 NH_4OAc-K (mg kg^{-1}) + 20.97	0.83 ***

[1] n value corresponds to the total amount of soil samples used in the pot experiment (10 initial soil samples, 3 replicates). *, *** Significant r^2 values at $p < 0.05$ and 0.001, respectively.

Multiple regression models were generated by including respective soil extractants studied (NH_4OAc, $NaBPh_4$, cation resins method) alongside the K soluble parameter along with other soil parameters selected by using the backward stepwise selection method. As seen in Table 2b, the above parameters significantly improved the prediction capacity of the total uptake, managing to express up to 85% of its total variability. Nevertheless, in the case of resins or the NH_4OAc method, only the clay content or the pH parameter alone was sufficient to give a good fit to the models, respectively; in the case of the $NaBPh_4$ method, it was necessary to add both parameters in order to give an acceptable prediction of total K uptake.

3.5. Participation of Soil K Pools on the Extraction Capacity of Cation Exchange Resins: First Insights on the Contribution of K Solubilized by Rhizosphere Microbes

The backward stepwise selection method was used to indicate which of the soil K pools or soil parameters significantly contributed to the overall variability of the cation resins method. The multiple regression model produced is presented in the following equation:

$$\text{Resin-K, 1:200, 60 min (mg kg}^{-1}\text{)} = 0.11 \text{ non exch.K(mg kg}^{-1}\text{)} + 0.004 \text{ K-feldspars (mg kg}^{-1}\text{)} - 55.7 \text{ OM\%} + 1.11 \text{ NH}_4\text{OAc-K (mg kg}^{-1}\text{)} - 12.6 \text{ pH} + 6.1 \text{ K soluble (mg L}^{-1}\text{)} + 212.6, \quad r^2 = 0.89, p \leq 0.001 \tag{2}$$

where non exch. K represents the difference between $NaBPh_4$-extracted K (1 min, extraction period) and the NH_4OAc-K, corresponding to the diffusion-derived amounts of the interlayer K that is non-exchangeable.

By applying a relative weight analysis, the percentage among multiple predictor variables was assessed, and the results are presented in Table 3. More specifically, almost 40% of the resins' total variability is attributed to the soil pool of exchangeable K, whereas the intensity parameter of soluble K represents 19.1%. Interesting is the fact that among the two sources of non-exchangeable K, K derived by feldspars occupies 15.6 of the total percentage, followed by the diffusion-derived K (the difference between $NaBPh_4$ extracted K and the NH_4OAc-K) which represents the 10%.

Table 3. Raw relative weight values (epsilons), and rescaled weights (scaled as a percentage of predictable variance) for every predictor in the multiple regression model of Equation (2).

Variables	Raw Relative Weight	Rescaled Relative Weight %
K-feldspars	0.140	15.6
OM% [1]	0.055	6.14
NH_4OAc-K	0.356	39.8
pH	0.082	9.17
Non exch. K	0.091	10.2
K soluble	0.171	19.1

[1] OM: organic matter.

4. Discussion

As previously noted in the Introduction section, the conventional soil test of K availability, based on the NH_4OAc extraction method, often fails to give accurate results, especially in K-deficient soils, or in cases where the presence of K-fixing clay minerals, such as illite or vermiculite, is dominant. The above considerations are well discussed in older and more resent literature and have been comprehensively highlighted by Murrell et al. (2021) in their latest book, which outlines a road map for improving potassium recommendations for agricultural crops [35]. As pointed out by the above authors (and references therein), alternative approaches which can manage more efficiently in accounting for the amounts of non-exchangeable K (diffusion-derived, or solubilized from primary minerals like feldspars) might be found more appropriate. Among them, methods of estimating the rate of K replenishment in the soil solutions seem to be the best option for elucidating soil K dynamics.

Nevertheless, it is common place that multiple temporal assays to measure the rate of K release (mainly caused by variations in extraction time), as well as different ratios between soil and extraction solution, are probably not feasible in a commercial laboratory setting. Thus, grouping of soils unified by a basic common characteristic (low levels of available K), as well as calibrating these methods in order to select the most efficient extraction procedure, was a necessary step that we adopted (using the r^2 evaluation criterion) in order to choose the most appropriate extraction procedures (1 min extraction period for the $NaBPh_4$ method, and 1:200 soil-water ratio, 60 min extraction period for the cation resins method).

Soils selected for the present study were low in exchangeable K, as determined with the NH_4OAc-extraction method, with a wide range of clay content from 12 to 42%. It is well discussed from previews studies that in these conditions, a possible explanation of the NH_4OAc weakness is that K extracted with such extraction solutions might not correspond to the actual amounts of available K derived from clay planar sites, but might also represent some amounts of K ions fixed on some clay interlayer sites [16,36].

Corroborating the above assumption, our study showed that the NH_4OAc method indeed gave weaker relationships with the actual amounts of K that were taken up by plants as compared with the intensity factor of water soluble K, or the application of cation resins, which performed better, giving the highest r^2 value, and after all, they managed to explain 64% of the overall K uptake variability (Table 2). However, the fact that out of all the extraction methods tested, $NaBPh_4$ extraction (which also is considered, along with the resins method, as an index of solution K replenishment) gave the weakest results is an indication that for the given soils and for the given short-term pot experimentation conditions, the large amounts of diffusion-derived K (originating from illite interlayer sites), might not reflect the major pool of K replenishment in the solution phase.

The above weakness of the $NaBPh_4$ method is also reported by other researchers [14,21], and although this method seems superior (at least when compared with the conventional NH_4OAc method) in cases where the exchangeable soil K is recorded at adequate levels, or the presence of clay minerals such as illite are dominant [20], our results show that on K-deficient soils, it cannot perform well, and other sources of K, except those that are diffusion-derived, should be examined also. In addition, the negative correlations that were observed between the CEC parameter and the $NaBPh_4$ extracted K, at the long incubation period of 30 min, could also be an indication that the variation of CEC values might be dominantly attributed to the presence of smectites. Thus, it could not follow similar patterns with the respective variation of K extracted with $NaBPh_4$, which primarily targets the interlayer illite K [19].

In this line, it could be argued that the effectiveness of cation resins to better reflect soil K dynamics that provide K to plants might also be attributed to K sources, such as those found in primary minerals like K-feldspars. However, these K amounts should first be subjected to a solubilization process, first to be released in the soil solution, and then to be up taken by the plants from their root system.

PCA analysis, Pearson correlation tests, as well as the multiple regression model that assessed the resins cation exchange capacity with respect to the contribution of different soil K pools and the rhizosphere microbial population, gave further evidence of the above hypothesis. The interconnection between microbial activity and K derived by feldspars is evidenced in Figure 3 by the respective convergence of the vectors observed, while the positive correlation that was revealed between the microbial population and the total K uptake is also an indication of the contribution of the solubilization process offered by rhizosphere microbes to K released to soil solution. In addition, the fact that the variation of microbial population among soils is better correlated with the cations resin method in contrast with the other soil tests studied, in conjunction with the better performance of this method in explaining the total K uptake, suggests that cation resins have the ability to account for some amounts of K solubilized by soil microbes.

In older and recent literature it is well documented that K derived from feldspars might essentially contribute to the overall soil K availability, as well as that a major solubilization process could be offered by the activity of the rhizosphere soil microbes. In a general agreement with our results, Rehm and Sorensen (1985) attributed the lack of maize response to the added K to the presence of bioavailable K in feldspars [37], while Sadusky et al. (1987), also using a cation resins extraction method in soils that had high quantities of feldspars in the sand fraction, reported high potassium release rates after a period of 30 days [38]. In addition, Niebes et al. (1993), in a short term experiment of 8 days of rape growth (*Brassica napus* cv Drakkar), found that a substantial portion of K had been extracted by the roots, and 80–100% of the bioavailable K was not originating in the ammonium-exchangeable pool [39]. Recently, Ali et al. (2021) found that soil available K increased when K-felspars inoculated with potassium solubilizing bacteria were added in a sandy clay loam soil, suggesting that this increase was attributed to their solubilizing properties [40].

Nevertheless, while the role of the solubilizing rhizosphere microbes on the enhancement of the overall K availability is well documented and has been extensively discussed [11], there is a lack of documentation concerning which particular extraction procedure could assess and predict the respective amounts of K that are to be released from primary minerals like K-feldspars during a growing season. Our study thus provides some first insights on the suitability of the cation resins extraction method to account for the contribution of K released by K feldspars, a fact that can be further observed by the multiple regression model that was used to predict the specific amounts of K extracted by the resin method Equation (2), from different soil K pools and relative soil parameters.

The above equation could be considered as a contribution map of each K form in the extractability potential of the resin method, denoting the weight that each K form delivers on its overall variability. In this line, although exchangeable K (extracted by the NH_4OAc method) represents the major K source of the resin method extraction capacity, K derived by feldspars occupies a significant portion of the total percentage (15.6%). Interestingly, the diffusion-derived interlayer K (non exch. K), while it would be expected to be the primary supplier of non-exchangeable K, as dynamically connected to the K pool of exchangeable K, records a lower contribution (10.2%). We therefore suggest that the particular distribution of weights of each soil K pool in the overall resins extraction capacity reflects more closely the buffering process that determines the rate of replenishment of solution K, and thus renders this extraction method most suitable in predicting the actual amounts of total K uptake.

5. Conclusions

Our study showed that cation resins performed better in predicting total plant K uptake on K-deficient soils than the other chemical extractants tested, as recorded by single and multiple regression models applied ($r^2 = 0.64$, $r^2 = 0.85$, respectively, $p \leq 0.001$). In addition, PCA analysis and Pearson correlation tests revealed a positive correlation between K derived by feldspars, K uptake, and the K-solubilizing rhizosphere microbial population, suggesting that under conditions of K deficiency, structural K solubilized by rhizosphere microbes contributes significantly to the overall K bioavailability. The above was further confirmed by the assessment of the cation resins extraction capacity, which showed a significant contribution of K derived by feldspars (15.6%), higher than the respective amounts of diffusion derived by interlayer K. We therefore suggest that the particular distribution of weights of each soil K pool in the overall resins extraction capacity reflects more closely the buffering process that determines the rate of replenishment of solution K, and thus renders this extraction method most suitable in predicting the actual amounts of total K uptake. Thus, we suggest that cation resins could be considered a useful tool for predicting soil K availability of K-deficient soils, a fact which should be further evaluated under field conditions.

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