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Potassium dynamics in agricultural soils in Córdoba (Argentina)

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Abstract
The Argentine Pampas region is one of the most productive agricultural areas in the world. Its soils, originally well supplied with potassium (K), are considered among the richest in this nutrient. Equilibrium reactions between K forms in soils are not commonly addressed in Argentina. Therefore, a study was initiated to determine the magnitude of solution K (Ks) and exchangeable K (Ke) and to analyze the effect of Ks depletion by successive extractions as an index of Ke lability in soils in the central region of Córdoba. Fifteen surface subsamples were collected from each site representing each previously identified soil types (Entic and Typic Hplustolls). A composite sample was taken in triplicate, and the Ke content and K depletion kinetics were determined by successive extractions with 0.1 M $CaCl_2$*. The native Ks stock size, calculated as the sum of Ks values from successive extractions, was 75 % higher in the Typic Haplustoll than in the Entic Haplustoll. The power function equation was the best model to successfully describe the* K^+ *released from all experimental soils. Finally, the determination of the adsorption capacity and K release kinetics at the site-specific level will help to understand the relative potential of soils to supply K and to plan an effective K fertilization strategy.*
Keywords: *Haplustoll; exchangeable potassium; K depletion kinetics.*

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I. Introduction

The need to apply N and P to the different soils in the central region of Córdoba (Argentina) is well documented. It has also been repeatedly expressed that measures that conserve and enrich soil organic matter help improve N-P status, especially when supported by sustainable agricultural tools such as increased crop diversity and livestock manure that can be effectively used to maintain soil quality and nutrition (Dionisi et al., 2020).

The annual use of nitrogen and phosphorus fertilizers is high. The K situation differs considerably from that of N and P. Potassium is only found in soil in inorganic form and it is not a significative part of soil organic matter. The application of potassium fertilizers in the province of Cordoba is very low. The amount of K extracted with the increase in crop yields during the last decade exceeded almost 30 times the K additionally applied with fertilizers (Delbuono, 2019).

The original sediments that form the province's soils contain various potassium-rich components (e.g. illite), which is why they do not present K deficiencies.

The analysis of the exchangeable potassium content in the representative soil series of the province of Cordoba yields average results above the critical levels (> 1,5 cmol kg^{-1}). These are, in comparison with the values prevailing in different parts of the world, and with those predominating, for example, in the United States, definitely high amounts.

The continuous cropping without K inputs through fertilizers or manure caused a decline in nonexchangeable K reserves and release rate while application (Larrea et al., 2023). It is estimated that in future years systematic fertilization with potassium will be necessary.

Based on the differences in its bioavailability, K soil is divided into four fractions: soluble (Ks), exchangeable (Ke), nonexchangeable but potentially available for plants (Kno), and that present in the mineral or structural matrix (Shil et al., 2021).

The Ke is considered the primary source of K for plants as it rapidly replaces the Ks absorbed by plants from the soil solution. The analytical procedures used to estimate the needs of potassium fertilizer are based on extractants, solutions that replace a significant amount of Ke, which is analyzed. The equilibrium between Ke and Ks occurs almost instantaneously; therefore, the capacity of a soil to replenish Ks from Ke is an index of Ke lability and of the equilibrium between Ks and Ke (Aguado-Lara et al., 2002)

Taking these points into account, the objectives of this study were: to measure the pool size of Ks and Ke and to analyze the effect of Ks depletion by successive extractions as an index of Ke lability.

II. Material and methods

The size of the K reserves (Ks and Ke) as well as the dynamics of Ks and Ke were measured in two soils: Typic Haplustoll and Entic Haplustoll. Composite samples were used, consisting of 15 subsamples from two sites and soils of the experimental field of the Faculty of Agricultural Sciences, National University of Cordoba, Argentina.

The particle size distribution was determined by the pipette method. The organic matter content was determined by the Walkley and Black method, the contents of exchangeable K, Ca, Mg and Na were extracted with 1N NH_4 acetate at pH 7.0 and the cation exchange capacity (CEC) was determined by the method described by Nelson and Sommers (1996).

The size of the Ks reserves was measured by extracting it with 0.1 M $CaCl_2$ and that of Ke by exchanging it with NH_4^+ by the methodology used, as described by Aguado-Lara et al. (2002) for a similar study.

To determinate the Ks release a soil:solution ratio of 1:10 was used; each of which was carried out in triplicate. Successive extractions were carried out up to obtain a constant value for the amount of Ks. The accumulated values of potassium extracted (mg kg^{-1}) were plotted against the number of extractions and a theoretical mathematical model was fitted to each soil.

The results were analyzed using ANOVA to assess differences between means. The correlation between soil parameters and K levels of both reservoirs (Ks and Ke) was also examined. A significance level of $p \leq 0.05$ was used to determine statistical significance. The statistical analyses were performed using InfoStat (Di Rienzo et al., 2020).

III. Results

Table 1 shows the values, pH, total OM, CEC and exchangeable cations for each type of soil. In Table 2 the percentages of sand, silt and clay are listed for each soil. Total Ks (sum of several successive extractions) and Ke are shown in Table 3. The dynamics of the successive extractions of native Ks from the soils can be seen in Figure 1.

Table 1: Soil granulometric composition for each soil.

Soil:	Typic Haplustoll	Entic Haplustoll
Horizont	Ap	Ap
Clay, < 2 µm (%)	20,96	16,81
Silt, 2-50 µm (%)	60,1	66,46
Very fine sand, 50-100 µm (%)	9,82	13,36
Fine sand, 100-250 µm (%)	4,15	2,49
Medium sand, 250-500 µm (%)	3,49	0,67
Coarse sand, 500-100 µm (%)	1,74	0,14
Very coarse sand, 1-2 mm	0,03	0,07

Table 2: Soils chemical properties: soil pH, organic matter (OM), exchangeable cations and cation exchange capacity (CEC)

Soil	pH (1:1)	OM %	Soil exchange complex composition ($cmol_c\ kg^{-1}$)				
			Ca	Mg	K	Na	CEC
Typic Haplustoll	7,2	3,1	14	3,1	2,6	1,06	21
Entic Haplustoll	7,3	2,0	11,2	2,2	2,5	0,74	19,3

Table 3. Potassium soluble (Ks) totals (sum of various successive extractions) and potassium exchangeable (Ke).

Soil	Ks	Ke
	µg g^{-1}	
Typic Haplustoll	1240 a	1014 A
Entic Haplustoll	705 b	975 A

Equal lowercase letters do not differ significantly between Ks (Tukey α=0.05), equal uppercase letters do not differ significantly between Ke (α=0.05).

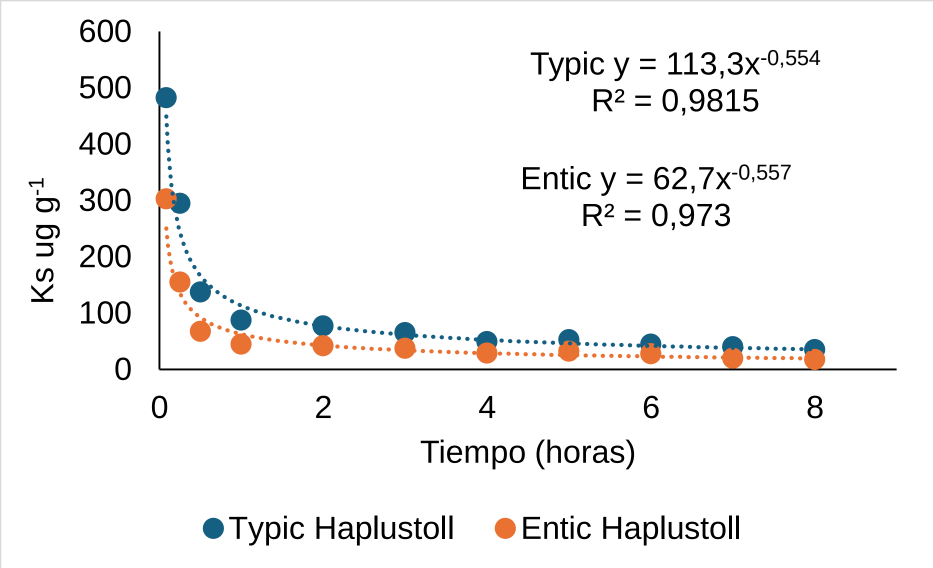

Figure 1. Dynamics of the successive extractions of native potassium (Ks).

IV. Discussion

The soils under study presented different granulometric composition but the same textural class (silty loam) which coincided with those observed by Cordoba et al. (2022) in relation to the Haplustolls of the central area of Cordoba (Argentina).

The contrasting clay percentage and high exchangeable potassium level are related to their genesis as a result of the greater horizon differentiation of the Typic Haplustoll (Moscatelli et al., 2001).

In practical terms, the Ke is the most commonly used indicator of soil potassium supply for crops and pastures hence the importance of its quantification. This can be conducted through the study of the relationship that exists between changes in the concentration of adsorbed K to changes in the concentration of solution K. (Al-H Amandi et al., 2019).

The size of the native Ke pool did not differ significantly among the soils studied (Table 3). The quantified values are within the high to very high range above the critical ranges described in the literature for Barbagelata and Mallarino (2013) and are like those reported for (Correndo et al., 2012) for Mollisols of the Argentine northern Pampas region.

The size of the native Ks stock, calculated as the sum of the Ks values of successive extractions, was 75 % higher in the Typic Haplustoll than in the Entic Haplustoll. The contents were 1240 and 705 ug g^{-1} respectively (Table 3). These figures show that these agricultural soils have a high level of soluble potassium, which would be related to their genesis (Moscatelli, Luters, Gómez, 2001).

The Ks release kinetics were characterized by a rapid desorption during the first hours. Among the tested models, the power function was the best to describe the cumulative Ks data of the experimental soils (R^2 of 0.98 and 0.97 for Typic and Entic Haplustoll, respectively) this fit agrees with that achieved by Haymanot, Sheleme, Alemayehu (2024).

The evaluation of this pool raises the question of whether the measurement of Ks by a single extraction (in this case with 0.01 M $CaCl_2$) is sufficient to solubilize all the Ks present in the soil. The results of this experiment indicate that a single extraction is not sufficient to remove the entire fraction, and it was necessary to

perform at least eight successive washes to reach a constant Ks value (Figure 1). These last values (35 and 20 ug g^{-1} in Typic Haplustoll and Entic Haplustoll, respectively) would be the result of the contribution of the exchangeable pool (Ke) to the Ks fraction. Therefore, as pointed out by Aguado-Lara et al. (2002) the value of the first extraction of Ks should be considered more as an index of the soluble fraction than its total value.

In the Typic Haplustoll, the total amount of K desorbed (Ks) by successive extractions corresponded to 1.2 times the Ke, suggesting that a certain proportion of the Kne associated with minerals concentrated in the two finest fractions (clay and silt) was also desorbed, indicating that these minerals continue delivering K beyond the levels indicated by Ke.

There is experimental evidence that fine silts are an important source of Kne that, when passed into solution, can be used by crops (Andrist Rangel et al., 2013). Peinemann et al. (2000) found that the silt of these soils has a CEC of between 6.5 and 7.1 $cmol_c$ kg^{-1} for the Haplustolls and Hapludolls of the Semi-Arid Pampa region of Argentina. The origin of the electrostatic properties of the silts of these soils seems to be related to their mineralogy, dominated not only by illites but also by variable amounts of pyroclastic materials (Bachmeier, 2011).

Debarup Das et al. (2019), while studying the potassium supply capacity of the soil, observed that transformation induced by crops and low K fertilization led to a decrease in the illite content with a concomitant increase in interstratified minerals with the consequent loss of K reserves in the soil. This coincides with what was observed by Correndo et al. (2012), whose results show a clear decrease in soil Ke levels due to the introduction of agriculture.

V. Conclusions

In the agricultural soils of this study, no reduction in Ke content was observed, and the Kne fixed in the clay fraction constitutes an important K reservoir and act as a regulator of the dynamics between Ks and Ke.
The development of predictive models of decreased K availability based on nutrient balance would be a fundamental tool, through which forecasts could be made on depletion rates and potassium fertilization needs.

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