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Changes in soil phosphorus fractions caused by cropping without nutrient reposition. A case study

Cambios en las fracciones de fósforo del suelo causado por la agricultura sin reposición de nutrientes. Un caso de estudio

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Abstract. Previous studies in soils of the Pampas region indicate the prevalence of calcium phosphates within the very complex mix of phosphorus (P) compounds in the soils. We studied the changes in P fractions in a punctual situation in the Pampas region. The sampling was carried out in a farm located near the city of Junín (-34.585; -60.9589) and the soil was Junín series Typic Hapludoll. The farm was devoted to grazing and sporadic crops, but from the last 30 years changed to continuous agriculture. At no time fertilization matched nutrients removal by crops. The soil P fractions were determined using an improved version of the classical Chang and Jackson method. Phosphorus linked to calcium decreased in absolute and relative terms (49.1%) and P linked to aluminum and iron increased (144.8 and 100.4%, respectively). However, the proportion of latter fractions was affected by the changes in organic and residual P fractions. If present punctual finding could be generalized, it would indicate a change in the composition of P fractions in the most cropped soils of the region.

Keywords: Phosphorus fractionation; Calcium linked to phosphorus; Mollisols; Effect of agriculture.

Resumen. Estudios previos en suelos de la región pampeana indicaron que los fosfatos de calcio prevalecen dentro de la compleja mezcla de compuestos de fósforo (P) del suelo. En el presente trabajo, estudiamos las diferentes fracciones de P del suelo en una situación puntual de la región Pampeana. El muestreo fue llevado a cabo en un establecimiento localizado cerca de la ciudad de Junín (-34,585; -60,9589), en un suelo Hapludoll típico, serie Junín. El establecimiento se dedicó al pastoreo y cultivos esporádicos, pero desde hace 30 años cambió a agricultura continua. En ningún momento la fertilización igualó la pérdida de nutrientes causado por los cultivos. Las fracciones de P del suelo fueron determinadas utilizando una versión modificada del método clásico de extracción de Chang y Jackson. El P ligado al calcio disminuyó en términos absolutos y relativos (49,1%) y el fósforo ligado al aluminio y al hierro aumentaron (144,8 y 100,4%, respectivamente). Sin embargo, la proporción de estas últimas fracciones fue afectada por cambios en las fracciones de P orgánico y residual. Si el presente hallazgo puede ser generalizado, indicaría un cambio en la composición de las fracciones de P para los suelos más agriculturizados de la región.

Palabras clave: Fraccionamiento del fósforo; Fósforo ligado al calcio; Molisoles; Efecto de la agricultura.

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INTRODUCTION

Since the beginning of soil science, it was recognized that soil phosphorus (P) forms part of a very complex mix of compounds. Inorganic soil P represents a mix of amorphous and crystalline forms of calcium (Ca), aluminum (Al) and iron (Fe) phosphates, including adsorbed and surface-precipitated phosphates. Organic P comprises primarily inositol phosphates, phospholipids, nucleic acids, phytates and other compounds (Pierzinki et al., 2005).

The knowledge of the proportion of different P compounds has several applications when studying the P chemistry and cycling. That is why the fractionation of the soil inorganic P was investigated at the beginning of the 20th century. By the mid-1950s decade, a pioneering sequentially extracting P with selective solvents method was published (Chang & Jackson, 1957), which provided the first comprehensive description of inorganic soil P and its relationship between P and soil components. This sequential method extracts the so call readily labile P, P linked to Ca, Al, Fe and residual P. However, because of its several limitations, modifications and improvements were made by different authors (Sparks et al., 1996). By the 1980s decade, the view of P fraction changed, focusing more on lability than chemical composition (Hedley et al., 1982; Sharpley & Smith, 1985; Pierzinki et al., 2005). Using those methodologies, it was established that P extraction by crops without proper nutrient replenishment causes not only decreases in the concentration of soil P but also the relative increasing of less available forms in the remaining P. Conversely, P fertilization exceeding crop requirements increase bioavailable fractions, which in time replenish more insoluble fractions (Tiessen et al., 1983; Sharpley & Smith, 1985) and causes changes in the proportion of P fractions (Verma et al., 2004). The first process is uncommon in cash crops agriculture, and most of the time it was studied on experimental conditions.

One of the regions which field crop production was carried out relying basically only on natural soil fertility was the Pampas region. Agriculture started in the last quarter of the 19th century, and slowly cropping spread across the region to be, finally, the dominant activity. Cropping was supported on the high fertility of the predominant soils, mainly Argiudolls and Hapludolls (Lavado & Taboada, 2009; Rubio et al., 2018). This soil management lead to P depletion (Urricariet & Lavado, 2001; Lavado & Taboada, 2009) and by early 1990s fertilization belatedly started in the region. Nutrient application is now a common practice, but the rate of fertilizers application is still low, and the nutrients exported by crop harvest exceeds fertilization inputs. Fertilization restored around the 39% of phosphorus removed by the main crops of the region (Cruzate & Casas, 2017).

Soil P fractionation in the Pampas has been studied several years ago using the criterion of Chang and Jackson (Barreira & López Domínguez, 1970; Culot & Bolaño, 1970; Conti et al., 1976). They found, as expected, according the parent material (loess-like sediments) and pedogenetic processes (Pierzynski et al., 2005), predominance of P linked to Ca. Phosphorus linked to Al and Fe tend to increase towards the north where more acidic soils predominate (Fernández López et al., 2006). Afterwards, P was studied using the Hedley et al. methodology (Vazquez et al., 1991). It was found, also as expected, that the more soil P labile forms decreased in cropped soils, increasing proportionally the non-labile forms.

Based on previous results we hypothesized that soil P depletion in the area lead to a decline on P related to Ca, and the consequent proportional increase of P related to Al and Fe. This work was performed to test such hypothesis.

MATERIALS AND METHODS

The sampling was carried out in a farm located near the city of Junín (-34.585; -60.9589) in the Province of Buenos Aires, Argentina. The soil is, according USDA Soil Taxonomy 2006 version, Junín series, coarse silt, mixed, thermic Typic Hapludoll (INTA, 2018). The main characteristics of the soil profile are shown in the Supplementary Table 1. For more than 100 years, livestock industry was the main activity in the farm. Cattle was fed with the remaining original grassland

Table S1. Characteristics of the representative profile of the Junín series, coarse silt, mixed, thermic Typic Hapludoll.
Tabla S1. Características del perfil representativo de la serie Junín, limo grueso, mezclado, Hapludoll típico.

Horizons	Ap	A	Bw	BC	C
Depth (cm)	0-16	16-30	30-70	70-126	126-150
Total carbon (%)	1.15	1.03	0.91	0.16	0.10
Nitrogen (%)	0.113	0.103	0.092	NA	NA
C/N relationship	10	10	10	NA	NA
Clay < 2 μ (%)	15.2	16.3	16.3	11.8	11.3
Silt 2-50 μ (%)	26.3	25.0	24.4	21.6	21.5
Sand 50-2000 μ (%)	58.5	58.7	59.3	66.6	67.2
Lime (%)	0.0	0.0	0.0	0.0	0.0
pH in paste	5.6	5.9	6.2	6.5	6.8
pH H_2O 1:2.5	6.1	6.4	7.3	7.5	7.9
Exch Ca meq/100 g	9.2	9.9	9.0	8.4	6.6
Exch Mg meq/100 g	1.7	1.5	2.2	2.5	3.6
Exch Na meq/100 g	0.4	0.5	0.5	0.5	0.5
Exch K meq/100 g	1.2	1.3	0.6	0.6	0.8
Exch H meq/100 g	4.5	4.7	2.7	1.9	1.6
CEC meq/100 g	14.2	14.8	12.6	11.7	10.8

Taken from INTA (2018).

and some alfalfa seeding, and subjected to periodical cropping, mostly maize. Since the 1990s-decade soybean, maize and barley were grown continuously in the farm plots. Maize was fertilized with urea, soybean with simple superphosphate, and barley did not receive any fertilization.

Samples coming from several subsamples were taken in the depth of the Ap horizon in two areas: Six within cropped plots (representing the soil subjected to agriculture, the cropped soil) and six in a not cultivated area rounded by planted trees and other vegetation as well as under a nearby wire fence installed several years ago (representing the pristine soil).

A modified technique of sequential extractions of Chang and Jackson (Sparks et al., 1996) was used. Fractionation schemes used NH_4F (0.5 M, pH 8.2) to separate Al-P from Fe-P, followed by the removal of Fe-P with NaOH 0.1 M and the reductant-soluble P with sodium citrate 0.3M-sodium dithionite-sodium bicarbonate 1M extractions. The remaining calcium phosphate, was extracted with H_2SO_4 0.25 M. The soluble and loosely bound P was extracted at the beginning of the procedure with NH_4Cl 1M. For organic P a modified ignition method of Saunders and Williams (Sparks et al., 1996) was used. Phosphorus was determined by ascorbic acid blue color method of Murphy and Riley (Sparks et al., 1996). Soil organic carbon was determined in the same samples, using the Walkley and Black method (Sparks et al., 1996).

We estimated the P fractions only in one plot per treatment and that is why the present study was not truly replicated for statistical evaluation. However, the experimental site was selected on the basis that the area has very homogeneous soils (INTA, 2018). This knowledge allowed us to assume that the soils for both treatments were initially similar, and differences were therefore judged subjectively. As a consequence, the level of statistical inference does not go beyond the soil we studied. With these limitations we applied ANOVA test to distinguish the significant differences among measured parameters. Means were compared using the Least Significant Differences test (LSD; $P<0.05$).

RESULTS

The organic carbon content for the pristine soil was 3.09 ± 0.15% and in the cropped soil was 1.72 ± 0.11%, a 44.4% significant decrease. Total P was 956.3 mg/kg in the pristine soil and 697.0 mg/kg in the cropped soil, a 27.12% significant reduction. Also, there were changes in the P fractions proportion. Supplementary Table 2 and Figure 1 show decreases in the absolute and relative proportion (respectively) of organic P, P-Ca, and residual P, in the cropped soil, related to the pristine one. The significant decreasing of those fractions were in percentage 55.9, 49.1 and 44.1%, respectively. Conversely, there were significant increases in P-Al and P-Fe (144.8 and 100.4%, respectively).

Table S2. Different fractions of soil P, in mg/kg.
Tabla S2. Diferentes fracciones de P del suelo, en mg/kg.

Fraction	Pristine soil	Cropped soil
Ca - P	95.7 ± 6.8	48.8 ± 2.5
Al - P	73.2 ± 8.3	179.2 ± 5.6
Fe - P	47.7 ± 0.8	95.6 ± 3.1
Res. P	229.2 ± 2.2	128.2 ± 0.5
Org. P	474.3 ± 3.4	209.2 ± 7.2
Available P	36.2 ± 0.8	36 ± 2

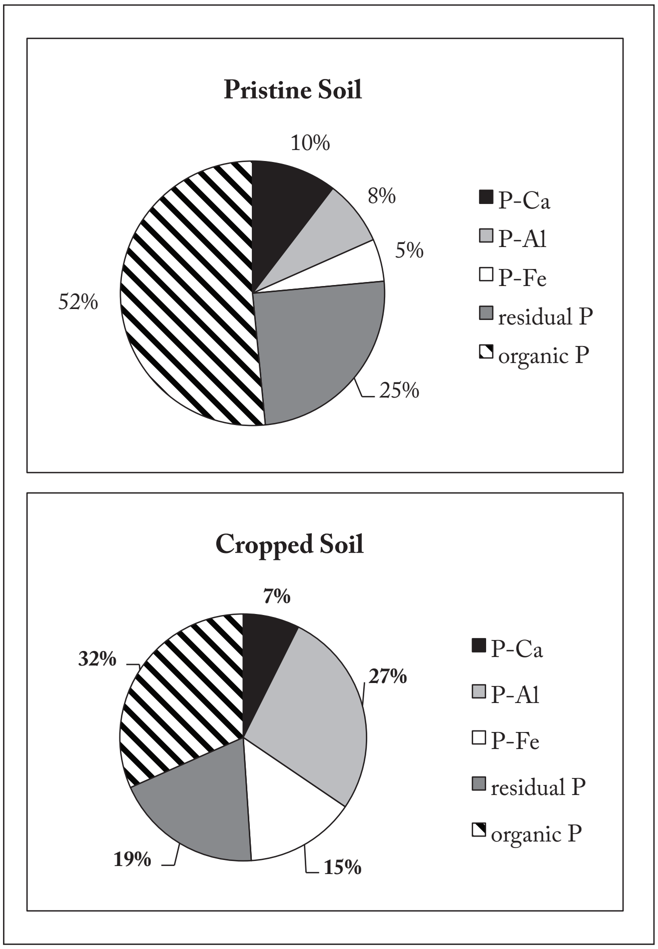

Fig. 1. Proportion of soil P fractions in pristine soil and cropped soil.
Fig. 1. Proporción de las fracciones de P en los suelos prístino y cultivado.

DISCUSSION

The decrease of soil organic carbon in tilled soils when it is compared to the amount found in pristine soils is a known fact (Follet et al., 1987; Urricariet & Lavado, 1999). Organic P followed the same tendency as found locally by Vazquez et al. (1991) and elsewhere (Hedley et al., 1982; Sharpley &

Smith, 1985). In the present case, organic C and organic P decrease in a similar degree. Phosphorus removal by crops harvest is considered the cause of the general changes in inorganic soil fractions. The decrease in P-Ca could be attributed to the relatively higher solubility of calcium phosphate compared to aluminum and iron phosphate (McLean, 1976). The residual P decreases in cropped soil could be related to the finding of Guo et al. (2000) that in some soils this complex P fraction was available to roots. The proportion of P linked to Al and Fe increased not only in relative terms but also in absolute ones. This increase could not be caused only by the removal of P-Ca by cropping. As found in other situations (Guo et al., 2000), part of residual P and organic P could transform into other fractions, mainly to Al and Fe linked P, but this was not verifiable in the present study.

CONCLUSION

Results partially agree with the proposed hypothesis. Due to the removal of P by cropping, P linked to Ca decreased in absolute and relative terms. However, P linked to Al and Fe increased in higher proportions, in both terms, which shows that organic and residual P fractions contributed to these increases. Considering the low P application rate, if the finding in this farm is generalized it would mean a virtual permanent change in the proportion of soil P fractions in the most cropped soils of this region.

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