



Long-term phosphorus fertilization of wheat, soybean and maize on Mollisols: Soil test trends, critical levels and balances

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ABSTRACT

Few reports have compared the P critical level between different crops under equivalent growing conditions and the impact of P balance and P fertilization practices on the long term dynamics of soil available P. The objectives of this study were: i) to determine and compare, under similar field conditions, the P critical values for soybean, maize and wheat; and ii) to evaluate the effect of long-term application of P fertilizer on P balance and soil-test P. Results from a long-term experiment (2000/01 and 2013/14) involving soybean, maize and wheat crops in five experimental sites located at the Pampean Region (Argentina) were analyzed. Phosphorus levels included a -P treatment without P application and a +P treatment with continuous P fertilization (annual average 37 kg P ha⁻¹).

The critical Bray-P thresholds were 14.3, 12.5 and 19 mg kg⁻¹ for soybean, maize and wheat, respectively. The rate of decline of the Bray-P pool in the -P treatments was described by an exponential decay function common to the five study sites. Obtained results indicated that a net extraction of 327 kg P per hectare is needed to reduce their initial Bray-P values by half, regardless of the initial soil Bray-P value. The soils fertilized with P showed a significant and linear increase in Bray-P. It was possible to fit a single function after pooling the data of the five sites. This combined function indicated that 3.2 kg P ha⁻¹ were necessary to increase Bray-P in 1 mg kg⁻¹. Obtained data on crop P critical levels and rates at which soil-test P declines or increases according to the P balance constitutes a useful tool for sustainable use of P resources in Mollisols and related soil units. They can help to monitor future changes of soil P levels and to estimate the P demand of croplands.

1. Introduction

In order to achieve optimum crop yields, soil phosphorus (P) availability should be above the critical level, defined as the value of soil P test above which no fertilizer response can be expected (Fixen and Grove, 1990). If the soil P test value is below the critical level, P is assumed to be a constraint to crop yield and positive responses to P fertilization are expected. Critical P values vary greatly according to the soil-test, the soil sampling depth, and the statistical model employed (Mallarino and Blackmer, 1992; Dodd and Mallarino, 2005; Gutiérrez Boem et al., 2011; Jordan-Meille et al., 2012). Among the several soil P tests that have been proposed, Bray-P is widely used in soils with acidic to neutral pH (Dodd and Mallarino, 2005; Rubio et al., 2008; Jordan-Meille et al., 2012).

The definition of accurate P critical levels is essential when planning P fertilization programs by providing a safe target soil P test level so

that yields are not constrained by soil P and environmentally harmful excesses are minimized (Dodds et al., 2008). Phosphorus critical levels are generally obtained from on-farm experiments that relate soil P tests to relative yields (RY), defined as the crop yield in the control treatment as percentage of crop yield in the fertilized treatment. In rotated cropping systems, it is particularly relevant to know the P critical level of the different crops to identify the convenient P level to be used as the target for the whole rotation (usually the highest P critical level). It is generally accepted that P critical levels vary among crops. This assumption comes mainly from data sets involving different areas and soils. However, the fact that critical levels are affected by soil properties and other environmental and management factors (Bray, 1954; Bell et al., 2013), suggests that accurate interspecific comparisons can be best evaluated through specific trials performed at the same experimental sites and growing conditions. However, only few reports meeting these conditions have been published so far (e.g. Dodd and

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Table 1

Soil classification, location and properties (0–20-cm depth) at the beginning of the experimental period (September 2000) for the five experimental sites. Balducchi and San Alfredo followed a bi-annual rotation: maize (first year) and double cropping wheat/soybean (second year). La Blanca, La Hansa and Lambare followed a tri-annual rotation: maize (first year), full season soybean (second year), and double cropping wheat/soybean (third year). In all cases the rootable depth exceeded 2 m.

Experimental site	Balducchi	San Alfredo	La Blanca	La Hansa	Lambare
Soil classification	Typic Hapludoll	Typic Argiudoll	Typic Hapludoll	Aquic Argiudoll	Typic Argiudoll
Location	34°09.461'S; 61°36.465'W	33°51'35.57"S; 61°28'7.84"W	33°29.923 S; 62°37.958'W	32°38.405'S; 61°19.967'W	32° 10.236'S; 61° 48.674'W
Agricultural history (years)	+60	8	6	+20	12
Soil series	Santa Isabel	Hughes	La Belgica	Bustinza	Los Cardos
Bray-P (mg kg ⁻¹)	10.8	11.5	16.2	17.7	67.7
Total organic C (g kg ⁻¹)	13.5	19.8	13.3	12.2	18.7
C: N ratio	11.6	11.1	10.3	11.6	10.9
pH	5.9	6.0	6.6	5.5	5.6
Ca (cmol kg ⁻¹)	8.1	11.0	7.2	7.6	9.9
Mg (cmol kg ⁻¹)	2.0	2.1	2.0	1.6	3.0
K (cmol kg ⁻¹)	1.4	1.7	1.9	1.7	2.6
Clay (g kg ⁻¹)	118	180	155	180	205
Silt (g kg ⁻¹)	531	620	564	789	765
Sand (kg ⁻¹)	351	200	281	31	30
Textural class	silt loam	silt loam	silt loam	silt loam	silt loam
Rotation	Bi-annual: maize-wheat/soybean		Tri-annual: maize-soybean-wheat/soybean		

Mallarino, 2005; Poulton et al., 2013).

Soybean, wheat and maize are three of the most important grain crops all over the world. In Argentina, they represent more than two thirds of the cropped area, mainly covered by highly fertile although P-deficient Mollisols (Rubio et al., 2008; Sainz Rozas et al., 2012). It has been reported that soybean is less responsive to P fertilization than maize and wheat (i.e. Colomb et al., 2007; Mallarino et al., 2013). In many cropping regions around the world, new farming systems have been progressively adopted in the last two decades (Pacini et al., 2003; Wezel et al., 2014). In Argentina, changes include the consolidation of soybean as the prevalent crop, the generalized adoption of no-tillage and the greater cropping intensity (Wingeyer et al., 2015; Andrade et al., 2017). Given these changes, there is a need to verify or fine-tune the currently accepted critical soil P levels. A long history of P exports without replenishment caused a widespread P depletion in most Argentinean agricultural soils (Sainz Rozas et al., 2012). This country does not have significant P reserves and must import almost all P fertilizers. At the international level, the depletion of P reserves makes uncertain the future of P fertilizer markets and an increase in extraction and manufacturing costs is expected (Gilbert, 2009). Therefore, P deficiency is a significant challenge for agricultural productivity and it is necessary to optimize the efficiency in the use of P by crops.

Besides accurate P critical levels, another key component for planning P management strategies is the rate at which soil P test declines or increases following the P balance of the system. Statistical functions or models are required to predict rates of change of soil P test driven by accumulated P balances over time. These functions help predict the rate of soil P test decline once P applications are ceased and also help at identifying limits to P rates to avoid risks of environmental pollution. Only a minor fraction of the P applied to the soil is absorbed by the target crop (about 5–25%, Morel and Fardeau, 1989; Benbi and Biswas, 1999). The remaining fertilizer P is retained by the soil matrix, and may eventually be available for subsequent crops. Residual effects of P fertilization mainly depend on the P balance and soil P sorption characteristics (Blake et al., 2003). In its simplest version, the P balance is calculated by subtracting the main output (P removed in harvested products: grain, forage) from the main input (fertilizer P or manure P). A positive or negative balance suggests an accumulation or a decline, respectively, of total soil P. However, because of the strong interaction of phosphates with the soil matrix, the relationship between P balance and available soil P is not directly predictable (Ciampitti et al., 2011). Whereas many field experiments reveal linear relationships between P balance and soil extractable P (Blake et al., 2000, 2003; Messiga et al., 2010; Ciampitti et al., 2011; Cao et al., 2012; Shen et al., 2014; Díaz and Torrent, 2016), Johnston et al. (2016) found exponential decay functions between time and soil available P. Some reports highlight that

the net balance of P in the system is the preeminent factor regulating the dynamics of soil P test (e.g. Blake et al., 2003; Messiga et al., 2015). In such sense, using the accumulated P balance as the independent variable instead of time, the rate at which available soil P decreases or increases could be estimated independently of the factor time. The identification of the function that fit the soil P test decline is relevant to define the timescale over which the decline is produced. Very short periods of analysis are more likely to describe linear paths and may mask the presence of curvilinear tendencies. In this sense, long-term field experiments arise as the best tool for quantifying the impact of P balance and P fertilization practices on the dynamics of available soil P.

The objectives of this study were: i) to determine and compare, under similar field conditions, the P critical values for soybean, wheat and maize; and ii) to evaluate the effect of long-term application of P fertilizer on P balance and soil P test. To this end, we performed a study from 2000/01 to 2013/14 in five experimental sites located at the Pampean Region (Argentina) involving soybean/maize/wheat rotations.

2. Materials and methods

2.1. Long term P fertilization experiment

A long term network was established in private farms of the Regional Consortium for Agricultural Experimentation (CREA) to evaluate the long term effects of different fertilization regimes on crop yields and soil fertility. The network started in 2000 and at present comprises five sites managed under no-tillage whose soils show a range of variability in initial Bray-P and other characteristics (Table 1). Each site followed one of the following two crop rotations: 1) bi-annual rotation (C-W/S): maize (first year) and double cropping wheat/soybean (second year); 2) tri-annual rotation (C-S-W/S): maize (first year); full season soybean (second year), and double cropping wheat/soybean (third year). The bi-annual rotation was employed in two sites (Balducchi and San Alfredo) and the tri-annual rotation in three sites (La Blanca, La Hansa and Lambare). In the present study, we evaluated the period between the 2000/01 and 2013/14 growing seasons (Fig. 1).

A similar experimental protocol was performed in all sites. The experimental design was a randomized complete block design with three replicates (except San Alfredo: two replicates). The plots were 25–30 m wide and 65–70 m long. Two treatments were compared: a) –P treatment, without P fertilization; and b) +P treatment, with continuous annual P fertilization. P rate was determined every year according to the anticipated P removals plus a 5–10%. The anticipated P removals were estimated by multiplying the expected crop yield by the grain P concentration. The goal of adding a 5–10% to the

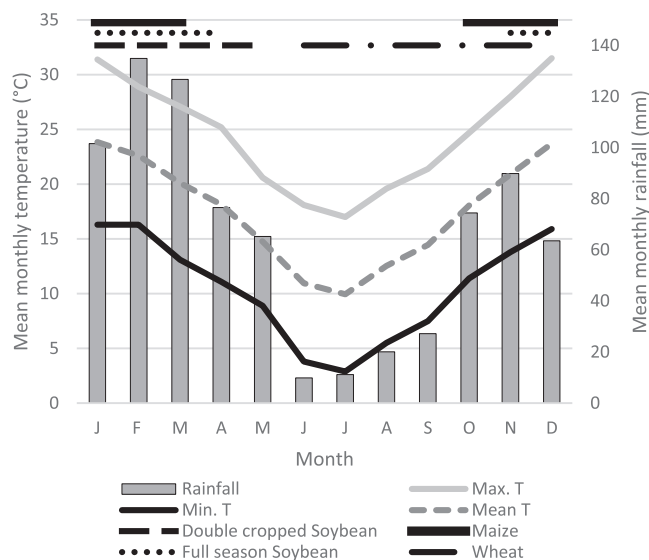


Fig. 1. Total monthly rainfall (bars) and average monthly maximum, minimum and mean temperatures (lines) during the evaluated period. Crop growth periods are indicated by horizontal intervals.

anticipated P removals was to obtain a positive P balance and gradually build-up soil P levels. On average, the annual P rate was 37 kg P ha^{-1} . Mono-ammonium phosphate was the P source and was banded and incorporated at 5 cm depth at sowing. Both P treatments received additional S and N fertilization. The doses of S for the three crops were determined with the same criteria as P and ranged $17\text{--}25 \text{ kg S year}^{-1}$. The doses of N for wheat and corn were determined annually according to the models employed by local farmers to obtain high yields. Applied nitrogen, which varied between 90 and $175 \text{ kg N year}^{-1}$, were within the range for maximum yields reported in the region by Pagani et al. (2008) for corn, and by Barbieri et al. (2009) for wheat. Soybean crops were not fertilized with N. The other nutrients do not usually limit yields in these soils.

Soil samples (0–20 cm) were collected every cropping season before P fertilization and seeding of wheat, maize or full-season soybean. One composite sample, composed by 20 subsamples extracted with a 2 cm diameter soil probe, was taken at each plot. Phosphorus was analyzed according to Bray-1 (Bray and Kurtz, 1945), and the P in the extract was determined colorimetrically (Murphy and Riley, 1962).

2.2. Relative yields and phosphorus critical levels for maize, soybean and wheat

The RY was calculated as the ratio between crop yields obtained in the $-P$ and $+P$ treatments. Crop yields were recorded annually for the whole sequence of years (2000–2014) and related with the values of Bray-P measured the same year at the $-P$ treatment. For the three crops, the Mitscherlich model with the maximum RY fixed as 100% was selected as the best fit model. One observation from the wheat data set was identified as an outlier and further not considered in the analysis.

The level of Bray-P corresponding to 90% RY was considered the critical P level for each crop. The functions adjusted to each crop were compared by an *F* test (Mead et al., 1993).

2.3. Relationship between P balance and Bray-P

Soil P balances were calculated along the experimental period as the difference between P inputs and outputs, as defined by Oenema et al. (2003). P inputs were annually estimated from the fertilizer P dose. P outputs were calculated from crop yields and grain P content (kg grain ha^{-1} , grain P concentration g P kg grain^{-1}). Grain P concentration for

the $-P$ and $+P$ treatments was measured in 35–45% of the years, depending on each experimental site. These measurements were performed in 45, 42 and 31% of the soybean, maize and wheat crops, respectively. In those years in which no grain P measurements were done, the average P content for each P treatment at each site was considered. Averaged across sites, these values for soybean were $5.44 (\pm 0.21)$ and $6.04 (\pm 0.09) \text{ mg P g}^{-1}$; for maize $3.09 (\pm 0.15)$ and $3.37 (\pm 0.18) \text{ mg P g}^{-1}$ and for wheat $3.68 (\pm 0.06)$ and $3.87 (\pm 0.10) \text{ mg P g}^{-1}$ (in all cases average \pm standard error for the $-P$ and $+P$ treatments, respectively).

For the $-P$ treatment (i.e. with no P addition and negative P balance), the relationships between Bray-P and P balances were described using an exponential decay function for each site:

$$y = a \exp(kx) \quad (1)$$

Where ‘y’ was the Bray-P, ‘a’ the initial Bray-P value, ‘k’ the relative rate of decay, and ‘x’ the cumulated P balance. The relative rates of decay (k) for the 5 sites were compared with a *F*-test. As these five ‘k’ were not significantly different ($p > 0.05$), a global fit were performed resulting in a model with five different ‘a’ (one for each site), but only one rate (a common ‘k’ for the five sites).

To be able to represent in a single curve this relationship for the five sites, the common ‘k’ was used to calculate the horizontal shifts needed to bring the individual curves into coincidence and placed on an extended x axis, representing the P balance. The horizontal shift for each site was calculated with the equation:

$$C_i = (\ln a_i - \ln a_{\max})/k \quad (2)$$

Where C_i was the constant (negative P balance) that was added to each observed x value at site i, ‘ a_i ’ was the initial Bray-P value at site i, a_{\max} was the ‘a’ parameter at the site with the greatest initial Bray-P, and ‘k’ was the relative rate of decay, common for the five sites.

A combined curve of Bray-P as a function of the modified x axis (i.e. an extended negative P balance) was fitted using Eq. (1). The obtained combined curve greatly extended and summarized the information on the negative P balance required for Bray-P to decline.

Additionally, the “half-life” of the initial Bray-P was estimated as:

$$P_{1/2} = \ln 2 / -k \quad (3)$$

Where $P_{1/2}$ was the amount of P to be exported (negative balance) so that the value of Bray-P was reduced by half.

The absolute rate of decay of Bray-P as a function of P balance could be calculated for any given value of Bray-P as:

$$dy/dx = -k \text{ Bray-P} \quad (4)$$

For the $+P$ treatment (which generally had positive P balance), the relationships between Bray-P and P balance were described using a linear function for each site:

$$y = a + b x \quad (5)$$

Where ‘y’ was the Bray-P, ‘a’ the initial Bray-P value, ‘b’ the slope, and ‘x’ the cumulated P balance. The slopes (b) for the 5 sites were compared with a *F*-test. As these five ‘b’ were not significantly different ($p > 0.05$), a global fit were performed resulting in a model with 5 different ‘a’ (one for each site), but only one slope (a common ‘b’ for the five sites).

The common ‘b’ was used to calculate the horizontal shifts needed in order to bring the individual lines into coincidence and placed on an extended x axis (P balance).

The horizontal shift for each site was calculated with the equation:

$$C_i = (a_i - a_{\min})/b \quad (6)$$

Where C_i was the constant (positive P balance) that was added to each observed x value at site i, ‘ a_i ’ was the initial Bray-P value at site i, a_{\min} was the ‘a’ parameter at the site with the less initial Bray-P, and ‘b’ was

Table 2

Crop yield for non-fertilized (–P) and fertilized (+P) treatments for each during the 14 years of evaluation. Asterisks (*) mean significant ($p < 0.05$) yield difference between –P and +P treatments.

Yield (Mg ha ⁻¹)										
Crop	Balducchi		San Alfredo		La Blanca		La Hansa		Lambare	
	–P	+P	–P	+P	–P	+P	–P	+P	–P	+P
Maize										
2000/01	7.97	9.03	9.90	11.46	9.06	8.97	–	–	11.76	11.97
2002/03	10.86	11.92	9.57	10.06	–	–	–	–	–	–
2003/04	–	–	–	–	10.86	11.72	9.03	11.92 *	9.37	8.64
2004/05	9.05	9.89 *	8.73	10.39 *	–	–	–	–	–	–
2006/07	7.61	14.20 *	13.31	14.74	14.08	16.09 *	11.16	11.42	11.31	11.19
2008/09	7.72	11.08 *	11.87	12.36 *	–	–	–	–	–	–
2009/10	–	–	–	–	8.61	10.27 *	11.72	13.94 *	15.89	15.94
2010/11	7.31	8.51 *	13.04	14.21 *	–	–	–	–	–	–
2012/13	8.83	9.36	11.61	11.91	13.64	14.31	10.16	11.31	11.57	11.31
average	8.47	10.56*	11.14	12.16	11.16	12.16	10.51	12.14*	11.8	11.97
Full season Soybean	–P	+P	–P	+P	–P	+P	–P	+P	–P	+P
2001/02	–	–	–	–	3.88	3.95	4.09	4.19	3.80	3.77
2004/05	–	–	–	–	4.96	5.60	3.62	3.95	4.38	4.41
2007/08	–	–	–	–	3.91	5.03 *	3.86	4.25 *	5.11	5.09
2010/11	–	–	–	–	3.88	4.87 *	3.64	4.14 *	5.17	5.29 *
2013/14	–	–	–	–	3.10	3.76 *	4.11	3.95	6.01	5.98
average	–	–	–	–	4.01	4.68*	3.85	4.10*	4.96	4.92
Wheat	–P	+P	–P	+P	–P	+P	–P	+P	–P	+P
2001/02	3.09	3.65 *	2.96	3.23	–	–	–	–	–	–
2002/03	–	–	–	–	2.62	2.91	1.48	1.74 *	3.63	3.67
2003/04	4.13	5.16 *	5.05	5.33	–	–	–	–	–	–
2005/06	4.09	5.48	3.48	4.36 *	3.03	3.76	2.85	4.05 *	4.39	4.26
2007/08	3.50	5.62 *	3.89	5.64	–	–	–	–	–	–
2008/09	–	–	–	–	2.06	3.68 *	2.39	1.83	1.79	1.93
2009/10	1.90	2.27 *	2.94	4.38 *	–	–	–	–	–	–
2011/12	1.86	3.87 *	3.50	5.83 *	3.15	3.88 *	3.81	4.54 *	4.23	5.14 *
2013/14	2.77	5.15 *	2.51	5.31 *	–	–	–	–	–	–
2014/15	–	–	–	–	4.41	4.93	4.02	4.01	5.12	5.24
average	3.04	4.45*	3.44	4.75*	3.05	3.83*	2.91	3.23	3.83	4.04
Double cropped Soybean	–P	+P	–P	+P	–P	+P	–P	+P	–P	+P
2001/02	3.21	3.28	3.33	3.45	–	–	–	–	–	–
2002/03	–	–	–	–	4.14	4.05	3.63	4.04 *	4.35	4.35
2003/04	3.03	3.35	3.30	3.57 *	–	–	–	–	–	–
2005/06	2.53	2.95 *	3.22	4.05 *	2.30	2.65 *	3.13	3.17	2.36	2.45
2007/08	1.74	3.13 *	2.39	3.90	–	–	–	–	–	–
2008/09	–	–	–	–	2.18	2.42	2.57	2.63	3.89	3.65
2009/10	2.22	3.08 *	2.70	3.72 *	–	–	–	–	–	–
2011/12	2.25	2.69	1.77	1.72	2.28	2.37	2.36	2.7 *	2.74	3.03 *
2013/14	3.26	4.09 *	3.33	3.56	–	–	–	–	–	–
2014/15	–	–	–	–	4.51	4.98	3.99	3.95	5.21	5.35
average	2.60	3.22*	2.89	3.42*	2.86	3.03	3.04	3.19	3.47	3.52

the slope, common for the five sites.

A combined line of Bray-P as a function of the modified x axis (i.e. an extended positive P balance) was fitted using Eq. (5).

The combined line greatly extended the information on the positive P balance required for Bray-P to increase.

Additionally, the “change rate” of the initial Bray-P was estimated as:

$$CR = 1/b \quad (7)$$

Where ‘CR’ indicates the amount of P that is needed (in excess of P removal by harvest) to increase Bray-P in 1 mg kg⁻¹.

For the –P treatment, the proportion of P exports accounted for by the changes in Bray-P was calculated as the ratio between the change in Bray-P and the total P removal (for each plot of the –P treatment). The change of Bray-P was calculated as the difference between the Bray-P at the beginning and at the end of the experiment. This value (in mg kg⁻¹) was converted into kg ha⁻¹ using a soil bulk density of 1.25 Mg m⁻³ and a depth of 0.2 m, which is the standard depth for available soil P diagnosis according to the local protocols. On the other hand, the total P removal in kg ha⁻¹ was calculated at the end of the experiment for each plot of the –P treatment, based on grain yield and P content.

3. Results

3.1. Crop yield

Observed yields ranged from adequate to high compared to local standards (Table 2). Yield for non-fertilized crops ranged between 7.3–15.9, 3.1–6, 1.7–5.2 and 1.5–5.1 Mg ha⁻¹ for maize, full season soybean, double-cropped soybean and wheat, respectively. Yields of fertilized crops ranged between 8.5–16, 3.8–6, 1.7–5.3 and 1.7–5.8 Mg ha⁻¹ for the four crops, respectively. Wheat was the crop most responsive to P, whereas P responses of maize and soybean were lower and somewhat equivalent. As expected, the site with the lowest initial Bray-P (Balducchi) had the highest responses to P whereas the site with the highest initial value (Lambare) had the lowest. The mean annual responses for maize were 1.6 Mg ha⁻¹ at La Hansa, there was no response at Lambare, 1.2 Mg ha⁻¹ at La Blanca, 1.0 Mg ha⁻¹ at San Alfredo and 2.0 Mg ha⁻¹ at Balducchi. For wheat, the responses were 0.3, 0.2, 0.7, 1.3 and 1.4 Mg ha⁻¹, respectively. For the double cropped soybean 0.2, 0.06, 0.2, 0.5 and 0.6 Mg ha⁻¹, respectively. Finally, the full season soybean had responses of 0.3 Mg ha⁻¹ at La Hansa, 0.015 Mg ha⁻¹ at Lambare and 0.6 Mg ha⁻¹ at La Blanca.

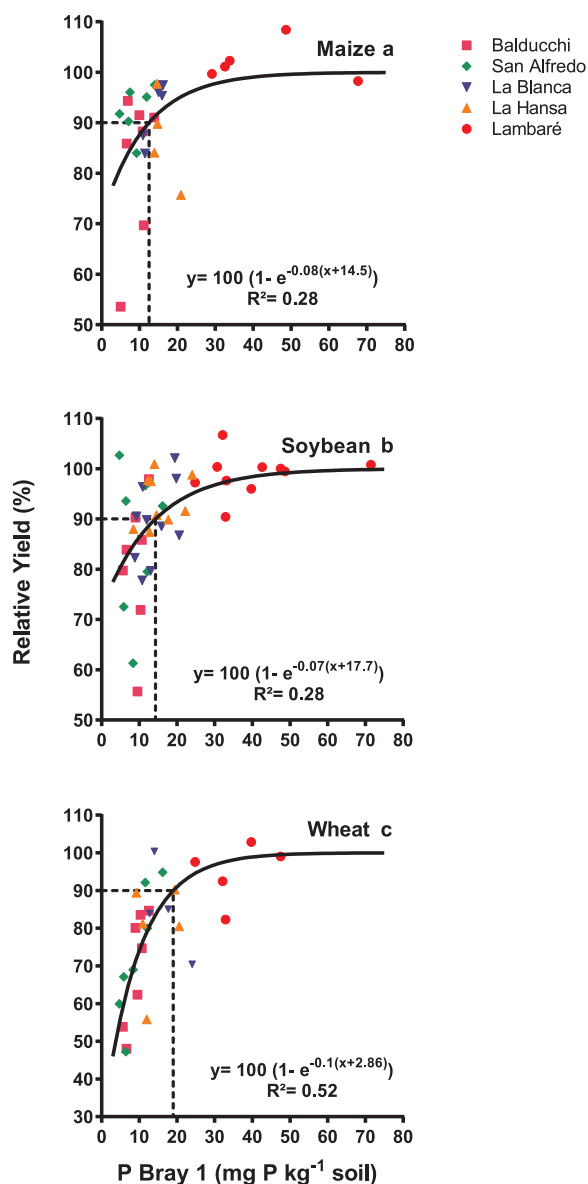


Fig. 2. Relationship between Bray-P (0–20 cm) and relative yield of maize, soybean and wheat at five locations of the Northern Pampean Region along the 14 years of the experimental period. The number of points was 27, 43 and 29 for maize, soybean and wheat, respectively. The relative yields were calculated as the crop yield in the control treatment expressed as percentage of crop yield in the fertilized treatment.

3.2. Critical P levels

The Mitscherlich model was selected to describe the relationship between RY and soil Bray-P (Fig. 2) because it showed better fit than the linear plateau model (data not shown) for wheat and corn, and similar fit for soybean. No statistical difference was found between models for full-season and double-cropped soybean, whereas wheat differed from soybean and maize ($p < 0.05$). For a 90% RY, wheat showed the highest P critical level (19 mg P kg^{-1}) followed by soybean ($14.3 \text{ mg P kg}^{-1}$) and maize ($12.5 \text{ mg P kg}^{-1}$). As the functions for maize and soybean did not differ from each other, a common critical value of $13.6 \text{ mg P kg}^{-1}$ could be estimated.

In the $-P$ treatments and at the end of the evaluated 14 years, Balducchi, La Blanca and San Alfredo were below the P critical level for the three crops: 5.6 , 9.2 y 6.4 mg P kg^{-1} , respectively. La Hansa reached Bray-P values of $14.0 \text{ mg P kg}^{-1}$, close to the critical P level

found for soybean and maize, but below that for wheat. Lambare remained at Bray-P values higher than the critical P levels for the three crops ($24.7 \text{ mg P kg}^{-1}$). In the $+P$ treatments, at the end of the evaluated 14 years the five sites reached Bray-P values higher than the critical levels.

3.3. Relationship between P Balance and Bray-P: $-P$ treatment

The P-rich site Lambare showed the most negative P balance ($-453 \text{ kg P ha}^{-1}$ along the experimental period), followed by San Alfredo ($-369 \text{ kg P ha}^{-1}$), La Blanca ($-338 \text{ kg P ha}^{-1}$), La Hansa ($-332 \text{ kg P ha}^{-1}$) and Balducchi ($-278 \text{ kg P ha}^{-1}$) (Fig. 3). A progressive decline in Bray-P, accompanying the increasing negative P balances, was observed in the five sites. This decline could be appropriately described ($p < 0.05$) by asymptotic decay models (Fig. 3; Table 3). The fitted models were defined by two parameters: the relative decay rate ‘k’ and the constant ‘a’, which is directly related to the initial Bray-P content. Interestingly, no significant differences ($p < 0.05$) between the k values of the five sites were found. The models fitted for each site only differed in the value of ‘a’. These results allowed us to fit a single decay function over an extended x axis after pooling the data from the 5 sites (Fig. 4). The average Bray-P half-life for these soils was 327, which indicates that a net extraction of 327 kg P per hectare is needed to reduce their initial Bray-P values by half regardless of the initial Bray-P value of the soil. The ratio of change in Bray-P to P removed by crop increased as initial Bray-P values increased, which indicate that soil P pools other than Bray-P would have exerted a greater contribution to crop P nutrition in the P-poor soils (Fig. 5). For the $-P$ treatments, the P-rich Lambare site showed the greatest decrease in Bray-P along the studied period (from 67.7 to $24.8 \text{ mg P kg}^{-1}$; about $42.9 \text{ mg P kg}^{-1}$). The other four sites, with low to moderate initial Bray-P ($< 20 \text{ mg P kg}^{-1}$), decreased less than 7 mg P kg^{-1} along the experimental period.

3.4. Relationship between P Balance and Bray-P: $+P$ treatment

Fertilized treatments showed positive P balances in the five sites (Fig. 3). At the end of the experimental period, Lambare and San Alfredo showed the lowest positive balances (50 and 47 kg P ha^{-1} , respectively), whereas Balducchi, La Blanca and La Hansa showed higher values 79 , 108 and 117 kg P ha^{-1} , respectively. The relationship between Bray-P and P balance could be described by linear regression model ($y = a + b x$) (Fig. 3; Table 3). The individual models for each site differed in the value of ‘a’ but there were no significant differences ($p < 0.05$) between slopes ‘b’ (Table 3). This indicates that the rates of Bray-P increase were similar between sites but each site departed from different initial Bray-P values (reflected by ‘a’ values). Therefore, it was possible to fit a single model after pooling the data of the five sites. This combined function was plotted on an extended x axis (Fig. 6) and indicated that the addition of 3.2 kg P ha^{-1} in excess of P removal by harvest were necessary to increase Bray-P in 1 mg kg^{-1} for this type of soils.

The sites with low to moderate initial Bray-P ($< 18 \text{ mg kg}^{-1}$) showed a somewhat similar increase in Bray-P after 14 years of continuous fertilization. Observed relative increases over the initial values were 258, 249, 241 and 249% for Balducchi, San Alfredo, La Blanca and La Hansa, respectively. Conversely, the site with the highest initial Bray-P content ($67.7 \text{ mg P kg}^{-1}$, Lambare) had only a 0.5% increase over the initial Bray-P value at the end of the experimental period.

4. Discussion

4.1. P critical levels

Our long-term P experiment on Pampean Mollisols allowed the identification and comparison of the P critical values of soybean, maize

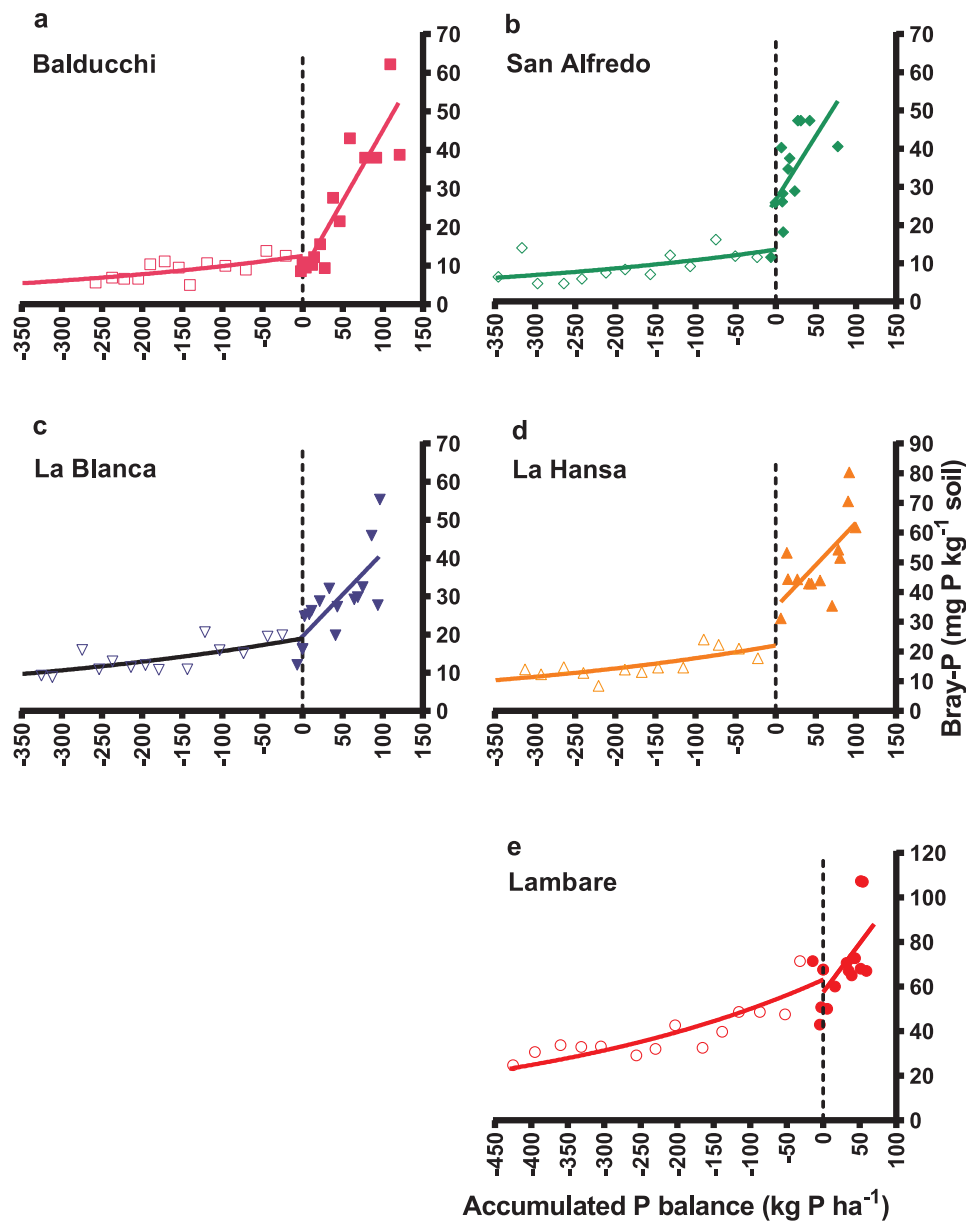


Fig. 3. Relationship between Bray-P and accumulated P balance during the experiment (14 yr) at five locations of the Northern Pampean Region. Open symbols represent the treatment with no P added (-P) and filled symbols the treatment with P addition as fertilizer (+P). All fitted functions were statistically significant ($p < 0.05$). Parameters for the fitted functions are shown in Table 3.

Table 3

Fitted equations for the relationship between Bray-P and accumulated P balance at five locations of the Northern Pampean Region. Individual (as in Fig. 3) and combined (global) functions (as in Figs. 4 and 6) are shown for the -P and +P treatments. The p-value for the comparison of the five relative rates of decay (k) in the -P treatments was 0.98, and of the five slopes (b) in the +P treatments was 0.49. All individual and global functions were statistically significant at $p < 0.05$ and $p < 0.001$, respectively.

Balance Equation Fit Site	-P treatments			+P treatments			+P treatments			+P treatments		
	y = a exp (k x)			y = a + bx			y = a + bx			y = a + bx		
	individual site fit			global fit			individual site fit			global fit		
	a	k ($\times 10^{-3}$)	R ²	a	k ($\times 10^{-3}$)	R ²	a	b	R ²	a	b	R ²
Balducchi	12.5	2.38	0.49	12.4	2.29	0.93	8.4	0.36	0.80	10.6	0.31	0.79
San Alfredo	13.5	2.24	0.32	13.6			26.6	0.33	0.40	26.9		
La Blanca	18.9	1.93	0.53	19.8			19.4	0.21	0.55	15.3		
La Hansa	22.0	2.16	0.51	22.3			34.8	0.28	0.45	33.0		
Lambare	63.1	2.33	0.78	62.7			57.5	0.43	0.37	60.8		

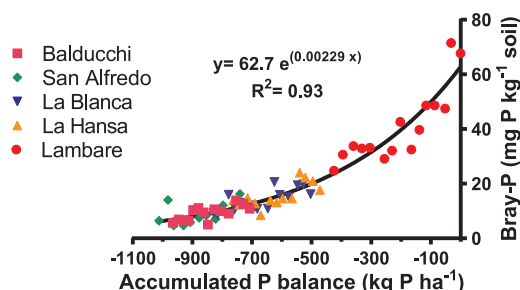


Fig. 4. Relationship between Bray-P and accumulated P balance for the treatment without P fertilization ($-P$ treatment) at five locations of the Northern Pampean Region. Data shown in Fig. 3 indicated that the five sites had a common relative rate of decay (k). In this figure each site was horizontally shifted in order to bring the individual curves into coincidence in a combined curve of Bray-P as a function of a modified x axis (i.e. an extended negative P balance). Fitted function was statistically significant ($p < 0.001$). Parameters of the global fit model are shown in Table 3.

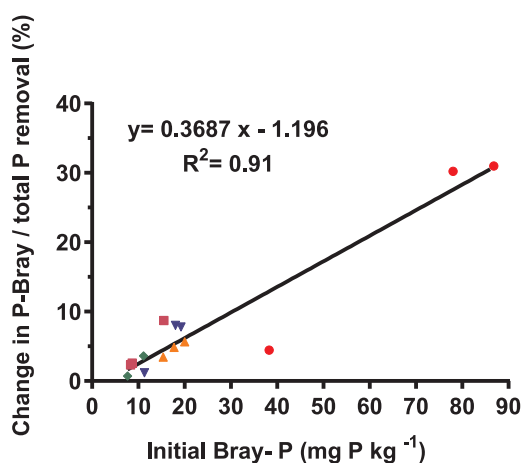


Fig. 5. Ratio of change in Bray-P to P removed by crop as function of Bray-P values at the beginning of the experiment. Each point represents a replicate for a period of 14 years. All experimental sites included. The regression without data from the site Lambare (red circles) was significant ($p < 0.01$), and the slope was not different ($p = 0.39$) from that of the regression with all the observations shown in the figure. Symbols as in Fig. 4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

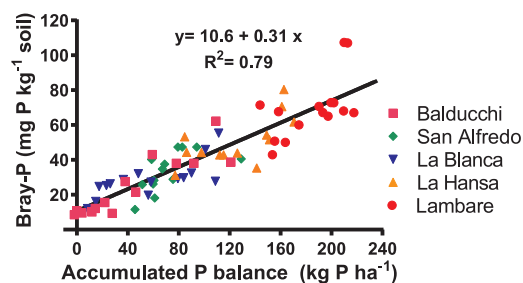


Fig. 6. Relationship between Bray-P and accumulated P balance for the fertilized treatments at five locations of the Northern Pampean Region. Data shown in Fig. 3 indicated that the five sites had a common slope. Each site was horizontally shifted in order to bring the individual lines into coincidence in a combined line of Bray-P as a function of the modified x axis (i.e. an extended positive P balance). Fitted function was statistically significant ($p < 0.001$). Parameters of the global fit model are shown in Table 3.

and wheat crops under equivalent growing conditions, including the same experimental sites and management practices (Fig. 2). In all cases, the best fit between RY and soil P test was obtained with Mitscherlich-

type functions, which showed curvilinear decreases of relative yield with decreasing Bray-P values. Using this model, wheat showed a higher R^2 (0.52) than soybean and maize (0.28 in both cases), which means that P nutrition was less relevant explaining yields in these last two crops. Although full season soybean yielded, on average, 20% more than double-cropped soybean, the P critical level did not differ between them, reaching a value of 14.3 mg kg^{-1} Bray-P for a 90% RY. This is consistent with the general assumption that, for immobile nutrients, the critical levels of any specific crop is relatively independent of crop yield (Bray, 1954; Bell et al., 2013). The model fitted for maize identified a critical level of $12.5 \text{ mg Bray-P kg}^{-1}$ (90% RY) and did not differ from the model adjusted for soybean. The equation obtained for wheat indicated a critical value of 19 mg kg^{-1} Bray-P, which was significantly different from that for soybean and maize.

The comparison between P critical values for different crops reported in the literature is complex because of the different statistical approaches, extractants and soil sampling methods used, among other factors. Correlations and conversion factors between different extractants and sampling depths are available for local and other soils (Gutiérrez Boem et al., 2011; Jordan-Meille et al., 2012). However, they are not recommended for generalized conversions between different soil-tests due to the intricate interactions between soils and chemical extractants (Jordan-Meille et al., 2012). On the positive side, the relative differences between P critical levels would be a sound approach for comparing crops, even when different soil P test or sampling depths are used. Colomb et al. (2007) found a decreasing order of critical thresholds following the rank wheat > soybean > maize (using Mitscherlich-type functions and Olsen-P as soil-test). Tang et al. (2009) also observed that maize had a lower Olsen-P critical level than wheat (-6%) and Dodd and Mallarino (2005) found that the critical level for soybean was lower than maize, using Bray-P as soil-test. Our ranking was wheat > maize = soybean, being the critical level of the combined function soybean/maize 28% lower than wheat. This ranking approximately coincides with the current soil-test interpretation in the US Midwest, where the critical value for soybean and maize is 24% lower than wheat (Mallarino et al., 2013).

After 14 years of study, all fertilized treatments exceeded the critical value of the crop with higher requirements (Fig. 2). The implication of our results for farmers that use a high proportion of wheat in their rotations (as the wheat/soybean/maize rotations analyzed here) is to maintain soil at about or slightly higher than 19 mg kg^{-1} Bray-P, which is the P critical level of the crop with highest requirements. This safe target level benefits the farmer so that yields are not constrained by lack of available P and no fertilizers are bought in excess. This strategy also benefits the environment by reducing the risk of detrimental P losses (Sharpley et al., 2013).

4.2. Residual decline of P with negative P balances

Recent long term studies have found linear relationships between Bray-P decline and P balance (Selles et al., 2011; Cao et al., 2012; Shen et al., 2014; Messiga et al., 2015). In the same line, other studies determined that the relationship between P balance and Bray-P variations were mainly regulated by the initial P-Bray (Ciampitti et al., 2011; Johnston et al., 2016). For example, in soils of USA, Dodd and Mallarino (2005) found that the Bray-P decline was curvilinear or linear over a three-decade period. Phosphorus-rich soils showed steep P declines that tended to stabilize as the soil becomes impoverished in P, whereas P poor soils had slower and somewhat steady declines. In the $-P$ plots of our five sites, the rate of P decline from the Bray-P pool was best described by exponential decay functions (Fig. 3) rather than by linear functions. The range of P balance found in our study was larger (up to -450 kg P) than most of the previous reports, which would have facilitated the identification of curvilinear functions. Interestingly, the curvatures of the five functions were similar so that a common curvilinear decay function could be fitted (Fig. 4). The y-intercept differed

between sites, indicating that each site departed from different initial Bray-P values (from 10.8 to 67.7 mg kg⁻¹) (Fig. 4, Table 3). The obtained equation is appropriate to predict the decline in available soil P after ceasing the P fertilization practices. The Bray-P half-life estimated from the obtained combined function indicates that a net extraction of 327 kg P per hectare is needed to reduce their initial Bray-P values by half regardless of the initial soil Bray-P. The relationship between the net P balance and the decline in soil P test is regulated by soil physico-chemical properties, climate, and availability of other major nutrients (Blake et al., 2000). In Pampean soils, clay content, initial P Bray, extractable aluminum and extractable iron have been identified as the key components defining P retention (Rubio et al., 2008; Cabello et al., 2016). Major differences were found between soils located South and North of the Region. Soils from this last sector (where the five sites compared here are located) showed less P retention capacity than their Southern counterparts. Results obtained in our experiments suggest that the differences between soil properties (Table 1) were not great enough to affect the dynamics of Bray-P in the -P treatments. The exponential decay of soil P test along the axis of P balance could be explained through the ratio of change in Bray P to P removed by crop at different initial Bray-P values, as in Johnston et al. (2016) (Fig. 5). The ratio of change in Bray P to P removed by crop increased as initial Bray-P increased. This means that a greater proportion of the P taken by the crop came from the soil P not recovered by the Bray extractant at low P levels than at high P levels. Then, the decline in Bray-P was steeper in P-rich soils because it was supported by the more labile P fractions and slower in poor-P soils because it depended more on P fractions which are not extractable with the Bray method. The curvilinear decline of extractable P may be then associated to the different reactions between Bray extractable and not extractable forms in soil as the Bray P in soil diminishes (McCullum, 1991). Overall, our results are consistent with Johnston et al. (2016), highlighting the effects of soil available P on the transfers between labile and less labile P fractions and how this affect crop P nutrition. In our experiments, the soil P not extracted by the Bray-P method accounted for 70–98% of the P taken by the crops, which indicates the central role of these fractions for plant P nutrition.

4.3. Build-up of P with positive P balances

After 14 years of continuous P fertilization, the progressive accumulation of positive P balances increased Bray-P following straight line functions in all sites (Figs. 3 and 6). No significant differences were found between the fitted slopes for each site, suggesting that the increase in Bray-P did not depend on initial Bray-P but on the magnitude of the accumulated positive P balance. The combined function was plotted on an extended x axis ranging from 0 to 240 kg of positive P balance and indicated that 3.2 kg P ha⁻¹ was necessary to increase Bray-P in 1 mg kg⁻¹ (Fig. 6). Some previous reports (Blake et al., 2003; Selles et al., 2011; Cao et al., 2012; Messiga et al., 2014, 2015; Shen et al., 2014; Díaz and Torrent, 2016) also found linear increases in available P in response to positive budgets, although McCullum (1991) found that rich-P soils needed more P to maintain soil P test than poor-P soils. In our study the accumulated positive balance range was small (+120 kg P ha⁻¹), which is in good agreement with Allen and Mallarino (2006), who proposed that the relationships can be curvilinear or linear depending on the degree of P accumulation.

Regardless the initial Bray-P value, at the end of the experimental period the +P treatments of the five sites reached Bray-P values above the critical values. This means that fertilization is no longer required to increase profitable yields on these plots. However, even in these cases, farmers should not abandon soil testing because it provides key information for P nutrition and environmental management.

In the originally P-richest soil (Lambare), Bray-P increased slightly, probably because the accumulated positive balance was much lower than in the other sites. This suggests that in this site actual yields were higher than the expected yields used to calculate the annual P doses

(anticipated P removals + 5–10%).

5. Conclusions

Our long-term field experiment indicated that the critical Bray-P levels did not differ between soybean and maize, but wheat showed a significantly higher value (13.6 mg kg⁻¹ and 19 mg kg⁻¹, respectively). The practical implication of these results for Pampean Mollisols is to maintain soil Bray-P at values about or slightly higher than 19 mg kg⁻¹ for rotations including a relevant proportion of wheat.

In our five sites, the rate of P disappearance from the Bray-P pool after ceasing P fertilization was described by exponential decay functions. The curvatures of the five functions fitted a common curvilinear decay model describing the relationship between Bray-P and P balance, which is appropriate to predict the decline in available soil P after discontinuing the P fertilization practice. The soils fertilized with P showed a significant and linear relationship between Bray-P and the accumulated P balance. In the same way as for the non-fertilized plots, it was possible to fit a single model after pooling the data of the five sites.

The obtained data on crop P critical levels and rates at which soil P test declines or increases according to the P balance constitute a useful tool to monitor future changes of soil P levels and to estimate the P demand of croplands in Mollisols and related soil units. It would also help at planning strategies that ensure that yields are not constrained by lack of available P and the risk of detrimental P losses to the environment is minimized.

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