

Fertilisation with Compost: Effects on Soil Phosphorus Sorption and on Phosphorus Availability in Acid Soils

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Abstract

Phosphate mineral fertilisers are manufactured from non-renewable resources. Soil fertilisation with composts is considered a good source of reuse nutrients such as phosphorus (P). The aim of this work was to evaluate the effect of compost fertilisation on soil P sorption and consequently on P availability. It was done an incubation experiment followed by a sorption experiment in a low-P acid soil fertilised with compost (CP) or single superphosphate (SSP). The P application rates were: 0, 6.5, 13, 26 and 52 ($\text{kg}\cdot\text{P}\cdot\text{ha}^{-1}$). In CP treatments, the rates 26 and 52 $\text{kg}\cdot\text{P}\cdot\text{ha}^{-1}$ were achieved by adding SSP to CP since it was not allowed to incorporate into soil more than 170 $\text{kg}\cdot\text{N}\cdot\text{ha}^{-1}$ from organic amendments. Although SSP has a higher proportion of easily available P than CP (86% vs 50%), the results showed that after 140 days of soil incubation, the available P was higher in CP treatments compared with SSP at the same rate of P application. The sorption experiment showed that after incubation of the fertilised soils, the P sorption maximum had lower values in treatments with CP in combination with SSP compared with only SSP fertilisation and the bonding energy had a deeper decrease in the same treatments. Also, the Standard Phosphate Requirement decreased in the CP in combination with SSP treatments. The reduction of soil P sorption capacity after compost addition to soil highlights the need of reducing P fertilisation rates to achieve similar levels of available P compared with only SSP fertilisation.

Keywords

Ammonium Lactate Method, Olsen Method, Sustainability of P Fertilization, Standard Phosphate Requirement

1. Introduction

The phosphorus (P) availability depends on the P sorption/desorption processes between the solid and the liquid phases of the soil. Phosphate sorption occurs onto sites of variable-charged soil constituents. The main phosphate-sorbing surfaces in soils are those of Al and Fe oxides, hydroxides, and oxyhydroxides, which are collectively referred to as oxides [1] [2] [3] [4], organic complexes of Al and Fe [5], edges of silicate clays, and calcite [6]. In acid soils of the temperate region [7], it showed that the main surfaces that sorbed P are the poor crystalline Al and Fe hydroxides and organo-complexes of Al and Fe. In turn, the desorbed P comes mainly from those soil constituents, being the degree of P saturation well correlated with the desorbed P indicating that the larger the amount of P sorbed, the less firmly it was held to soil solid phase. In order to improve the sustainability of soil P fertilisation and the objectives of the circular economy, the use of P mineral fertilisers must decrease and the use of other P sources has to increase. Some of these sources of P include the use of composts which contains organic matter (OM) in addition to P. However, within the factors that affect soil P sorption, capacity is the organic matter of the soil. The role of the organic matter addition to soils on P sorption/desorption and consequently on soil P availability is addressed in several works, but sometimes with contradictory conclusions as summarized by the works of Gérard, 2016 [8] and Guppy *et al.*, 2005 [9]. Some of those works [8] and [9] referred that the mineralisation of the OM added to soil releases several organic carbon compounds which has the potential to increase P concentration in the soil solution and thus increase P availability. The main processes to explain this conclusion include: 1) Competitive sorption between humic and fluvic acids [10] [11] [12] or low molecular weight aliphatic acids (LOA) and P for soil sorption sites resulting in increased P concentration in the soil solution [13] [14] [15]; 2) Metal complexation with OM compounds (LOA) or dissolution reactions affecting mainly Fe and Al oxides decreasing P sorption sites [14] [16] and 3) Sorption of OM compounds that could increase the negative charge on the soil surface, or decrease the point of zero charge (PCZ) increasing the resistance to P sorption. Unlike these effects, OM added to soil could increase the formation of metal bridges leading to increased P sorption sites [17] or in turn the P content of the added OM could also be a source of available P to soil solution [18] [19]. To assess P phytoavailability, some soil tests P (STP), like the Olsen (Olsen-P, [20]) and the Ammonium Lactate (AL-P, [21]) are commonly used. The Olsen method is used worldwide mainly in neutral and alkaline soils, but it could also be used in moderately acid soils as demonstrated by [22]. The Egnér *et al.* method is a routine soil test in some countries in Europe like in Belgium (Flandres), Norway, Portugal and Sweden [23]. These methods should provide accurate agronomic meaning in order to achieve a sustainable P fertilisation. Olsen method extracts P linked mainly from clay-humic complexes whereas Egnér method extracts P mainly adsorbed or precipitated on Fe and Al oxyhydroxides [23]. However, the proper-

ties of composts, namely the organic matter content together with the P-chemical forms in the fertilisers, could influence soil P sorption surfaces after fertilisation and consequently change the amount of P extracted by the STP. Using the same rate of P fertilisation applied through organic or mineral fertilisers (e.g. compost (CP) or single superphosphate (SSP)), we hypothesised that the OM of the CP will influence the P sorption processes enhancing the amount of P released to the soil solution compared to the mineral fertiliser. So, the main objective of this work was to evaluate the effects of compost fertilisation on P sorption and consequently on P availability. P availability was assessed by two soil tests commonly used in Europe, the Olsen and AL-P methods after application of compost or single superphosphate to a low-P acid soil.

2. Material and Methods

In order to assess changes in soil P availability caused by P fertilisation using CP or SSP fertilisers it was done an incubation experiment followed by a sorption experiment. This work was conducted in the Polytechnic Institute of Castelo Branco, Portugal, in 2017-2018.

2.1. Incubation Experiment

The soil used in the incubation experiment was a dystric Regosol [24], derived from granitic rock. A composite soil sample, taken from the layer 0 - 0.20 m, was air dried and sieved in a < 2 mm-mesh sieve. The soil used was acidic ($\text{pH}_{(\text{H}_2\text{O})} = 5.1$), of sandy loam texture (8% clay, 18% silt and 74% sand), low cation exchange capacity ($8.3 \text{ cmol}_{(+)}\cdot\text{kg}^{-1}$), medium level of organic matter ($20 \text{ g}\cdot\text{kg}^{-1}$), low level of available P (Olsen P of $10 \text{ mg}\cdot\text{kg}^{-1}$ and AL-P of $21 \text{ mg}\cdot\text{kg}^{-1}$) and low degree of P saturation (16%, $\text{DPS} = \frac{\text{Pox}}{0.5(\text{Feox} + \text{Alox})}$).

In the degree of P saturation equation (DPS) Pox, Feox and Alox are the amount of acid oxalate-extractable P, Fe and Al expressed in $\text{mmol}\cdot\text{kg}^{-1}$. The incubation experiment was performed during 140 days. The fertilisers used were a commercial compost obtained through aerobic composting of sewage sludge mixed with sawdust during 5 months (CP) and the single superphosphate (SSP). The experimental design was a completely randomized design with two fertilizers (compost and single superphosphate), four P application rates and four replications of each treatment, and a control without fertilisation generating a total of 36 incubation boxes. The P application rates ($\text{kg}\cdot\text{P}\cdot\text{ha}^{-1}$) were: 6.5, 13, 26 and 52. The SSP treatments were as follows: SSP6.5, SSP13, SSP26 and SSP52. Concerning CP treatments and according to the Portuguese guidelines the amount of compost used was constrained by the level of N for a sustainable fertilisation with a maximum application rate of $170 \text{ kg}\cdot\text{N}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ from organic amendments [25]. Therefore, P application rates of 26 and $52 \text{ kg}\cdot\text{ha}^{-1}$ of the CP treatments were achieved through the addition of SSP to the compost (CP + SSP): the rate of $26 \text{ kg}\cdot\text{P}\cdot\text{ha}^{-1}$ was set by adding $19.5 \text{ kg}\cdot\text{P}\cdot\text{ha}^{-1}$ in the form of SSP and use a

compost amount corresponding to the half-amount of maximum N input (CP6.5 + SSP19.5), and the 52 kg·P·ha⁻¹ rate by adding 39 kg·P·ha⁻¹ in the form of SSP and use a compost amount corresponding to the maximum N input (CP13 + SSP39). The treatment CP6.5 was achieved with a compost amount corresponding to the half-amount of maximum N input and the CP13 with a compost amount corresponding to the maximum N input. The compost and the SSP were finely grounded to 0.5 mm and sieved before applying to the soil, and maintained in the dark at 25°C and at 70% of field capacity. After 15 and 140 days of incubation (S15 and S140), a composite soil sample was taken of each treatment and repetition and analysed for Olsen-P and AL-P. These sampling dates were chosen to simulate the level of soil available P at sowing (usually after 15 days from the date of the fertilisation) and at the end of a crop cycle (≈ 140 days).

2.2. P Sorption Experiment

After the incubation period the P sorption capacity of the soil of all the treatments was evaluated.

The method of Fox & Kamprath, 1970 [26] was used to construct the P sorption (*i.e.* Q/I) curve; however, we used 0.002 M CaCl₂ as the supporting electrolyte to better match the ionic strength of the soil solution. The P rates (μg·P·g⁻¹·soil) applied to the soil were: 0, 10, 25, 50, 70, 100 and 150. Sorption data (seven points) were fitted to the following Freundlich curve

$$Q_s = AC^b \quad (1)$$

where A and b are constants typical of each soil, namely b is a constant that relates to the affinity of the sorbent for P . C (mmol·L⁻¹ or mg·L⁻¹) is the concentration of P in the soil solution, and Q_s (mmol·kg⁻¹ or mg·kg⁻¹) the total amount of P sorbed by the soil.

Sorption data were fitted also to the Langmuir isotherm:

$$Q_s = \frac{(KQ_{\max}C)}{(1 + KC)} \quad (2)$$

where Q_{\max} (mmol·kg⁻¹ or mg·kg⁻¹) is the P sorption maxima, and K (L·mg⁻¹) is a constant that relates to the bonding energy of phosphate to the soil solid phase.

2.3. Methods Used in the Chemical Characterisation of the Fertilisers and of the Soil

The compost was assessed for its moisture content through the gravimetric method; acidity (pH), with a glass electrode in a suspension of compost and water (1:5, wt/vol); electrical conductivity, in a suspension of compost and water (1:10, wt/vol); organic matter, through the loss of weight after drying at 550°C for 16 h; and total N, by the Kjeldahl procedure (N_k).

The compost was digested with *aqua regia* solution (HNO₃ + HCl) according to the CEN EN 13346:2000 [27] and quantified for its amount of P, by molecular

absorption spectrophotometry; total cations (Fe, Mn, Cu, Pb, Cd, Ni and Cr), by atomic absorption spectrophotometry. Total K, Ca, Mg and Na, were extracted from the hydrochloric acid solution of the ashes. K and Na were quantified by flame emission spectrophotometry and Ca and Mg by atomic absorption spectrophotometry. The class of stability/maturity of the compost was evaluated by the Dewar self-heating method ([28]).

P forms in the CP and in the SSP were evaluated by the sequential fractionation scheme of Traoré *et al.*, 1999 [29], using a compost to solution ratio of 1:200 (wt/vol). The first extraction was performed with H₂O (H₂O-P), the second with 0.5 M NaHCO₃ (pH 8.5; NaHCO₃-P), the third with 0.1 M NaOH (NaOH-P) and fourth with 1 M HCl (HCl-P). The inorganic P forms (Pi) in water or in the bicarbonate extracts are considered easily available to crops; the Pi extracted in NaOH solution is mainly bound to Fe and Al oxides or metal-organic complexes, and thus considered moderately labile; the Pi extracted in HCl is bound mainly to Ca in low-solubility precipitates, such as apatite or octacalcium phosphate, and thus considered as stable P forms [29] [30]. In the compost the total dissolved P in the extracts of the first three fractions was analysed after acid potassium persulphate digestion [31] and the dissolved organic P (Po) was calculated as the difference between the total dissolved P and inorganic P quantified in each fraction.

Olsen P and AL-P were evaluated by the [20] and by the [21] methods. Olsen P was extracted by an 0.5 M NaHCO₃ solution buffered at pH 8.5 at a soil to solution ratio of 1:20 and shaken during 30 min. AL-P was extracted by a 3.5 M ammonium lactate + acetic acid solution buffered at pH 3.75 at a soil to solution ratio of 1:20 and shaken during 120 min.

In all the cases, orthophosphate P in solution was determined by the molybdate blue method of [32].

2.4. Statistical Analysis

Statistical analysis of the data (Al-P and Olsen P, sorption constants and sorption indexes) were performed by one-way ANOVA with nine treatments using SPSS 26 software (<http://www.spss.com>). Tukey's test was used to identify differences between means at $p < \alpha = 0.05$ probability level.

For nonlinear curve fitting (e.g. Freundlich and Langmuir isotherms) Curve-Expert software (<http://curveexpert.findmysoft.com/>) was used.

3. Results and Discussion

3.1. Compost Properties and P forms in the Fertilisers

The compost used in this work had a dry matter content of 610 g·kg⁻¹, an organic matter content of 862 g·kg⁻¹ DM with a C:P ratio of 29, and a N:P ratio of 13 (Table 1). The compost has a high organic matter content. The Dewar self-heating method [28] indicates for this compost a class of stability of IV corresponding to a finished compost. The compost had a low C:P ratio indicating

Table 1. Selected characteristics of the compost (CP) used in the experiment.

Properties ^a	Dry Matter (DM)	Organic Matter (OM)	pH	Electrical Conductivity (EC)	N _k	P	K	Ca	C:P	N:P
	g·kg ⁻¹			dS·m ⁻¹		g·kg ⁻¹				
CP	610	862	5.7	0.68	22.1	1.7	150	121	29	13
Properties ¹	Mg	Na	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr
	g·kg ⁻¹					mg·kg ⁻¹				
CP	9.5	2.6	2.9	98.2	490	105	12	<0.04	14	22

a. All data referred to dry matter excluding dry matter, pH and EC.

that the mineralisation of the organic carbon could be rapid after addition to soil [33], and had a slightly high N:P ratio for use as fertiliser since the adequate ratio to meet crop needs ranges between 7 - 11 [34].

The chemical properties of CP (e.g. OM, nutrients, EC, pH) and the low levels of the phytotoxic elements (e.g. Cd, Cr, Pb, Ni, Cu and Zn), allow for its use as fertiliser of agricultural crops according to the Portuguese guidelines [35].

Concerning the P (Table 1) content CP had 1.7 g·P·kg⁻¹ DM with 80% of this total amount of P in inorganic forms (Pi). SSP had 94 g·kg⁻¹ of Pi. CP had almost 50% of the total amount of Pi in forms easily available to crops (H₂O plus NaHCO₃-Pi) and 37% in forms considered moderate labile (NaOH-Pi), mainly bound to Fe and Al oxides or metal-organic complexes (Figure 1). Contrary to this, in SSP the forms of Pi considered easily available to crops represent almost 86% of the total amount of P, with a trace amount of NaOH-Pi fraction. In addition, The HCl-Pi fraction was similar between CP (15%) and SSP (13%).

3.2. P availability after Fertilisation

Overall the fertilisation increased significantly ($p < 0.001$) P availability assessed by STP (Figure 2). We can also observe that irrespective to the STP used the variation between the treatments were similar at each sampling date (after 15 days or at 140 days of incubation). The addition of CP in combination with SSP at the higher P application rate (CP13 + SSP39) exhibited the higher STP at each sampling date, ranged between 28 mg·kg⁻¹ of Olsen P and 50 mg·kg⁻¹ of AL-P, S140. These levels of STP classify the soil in the high fertility class for P [36]. Irrespective to the sampling date, treatments with CP showed significant higher content of available P compared with SSP at the same rate of P application.

Nziguheba *et al.* 1998 [37] also concluded that the addition to soil of a high-quality organic material, in the case of this study the leaves of *Tithonia diversifolia* (Hemsley) A. Gray, applied either alone or in combination with TSP increased labile and moderately labile P in the soil. The same effect on increasing P availability was also observed by [38] with soil amendment with farmyard manure. However, Pi forms of the fertilisers used in our work (Figure 1) could in principle justify higher amounts of available P (AL-P or Olsen P) in SSP treatments since it had a higher amount of P in easily available forms to crops

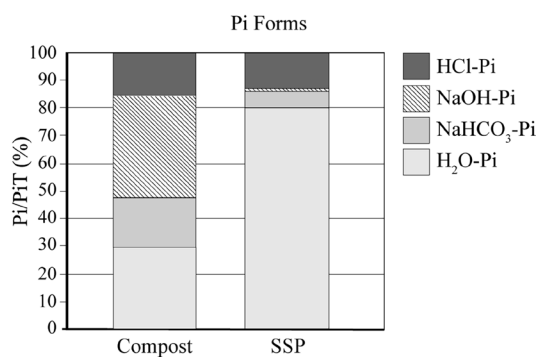


Figure 1. Pi forms ($\frac{Pi}{PiT}$, %) in the compost (CP) and in the single superphosphate (SSP).

(86% in H₂O-Pi) than CP (30% in H₂O-Pi or 50% in H₂O plus NaHCO₃-Pi). So, we tried to explain the behaviour of the CP treatments on the increase in available P evaluating the effect of each treatment on soil P sorption at the end of the incubation time.

3.3. Soil P Sorption at the End of the Incubation Experiment

The adjustment of the sorption data to the Langmuir isotherm showed higher R^2 values between 0.992 and 0.943 than to the Freundlich isotherm with R^2 values ranged between 0.985 and 0.882. Overall, fertilised treatments had significant lower Q_{max} and A values ($p < 0.001$, **Table 2**). The control treatment showed the highest values of Q_{max} and A , 145 and 51 mg P·kg⁻¹ respectively. The sorption data showed also that in general, CP treatments had lower Q_{max} and A values compared with only SSP at the same rates of P application (e.g. CP13 + SSP39 had 89 and 24 mg·kg⁻¹ and SSP52 had 110 and 32 mg·kg⁻¹ of Q_{max} and A values respectively).

The K constant is related with the bonding energy of phosphate to the soil solid phase. Thus, the decrease of the affinity constant (K value) with the increase of P application rate suggest a reduction in the affinity of the soil solid phase for P sorption. This trend is more evident in the CP13 + SSP39 and in the SSP52 treatments with K values decreasing from 0.71 in the Control treatment to 0.23 and 0.45 L·mg⁻¹, respectively. The increase in soil P availability after addition of organic fertilisers also observed in other works [37] [38] [39] was accompanied also by a significant decrease of the P sorption capacity of the soil. The authors explained this decrease by the competition with the phosphate anion for adsorption sites by the organic anions of the organic material produced during its decomposition into the soil. In addition, in our work the sorption of the fulvic or humic acids of the compost we used may also increase the negative charge on the soil solid surface, or decrease the point of zero charge (PZC) thus making it more difficult for P sorption to occur ([9] and references herein). Indeed, the compost used in our work was a mature compost having therefore a high level of humification. Pedra *et al.*, 2007 [40] after the addition to

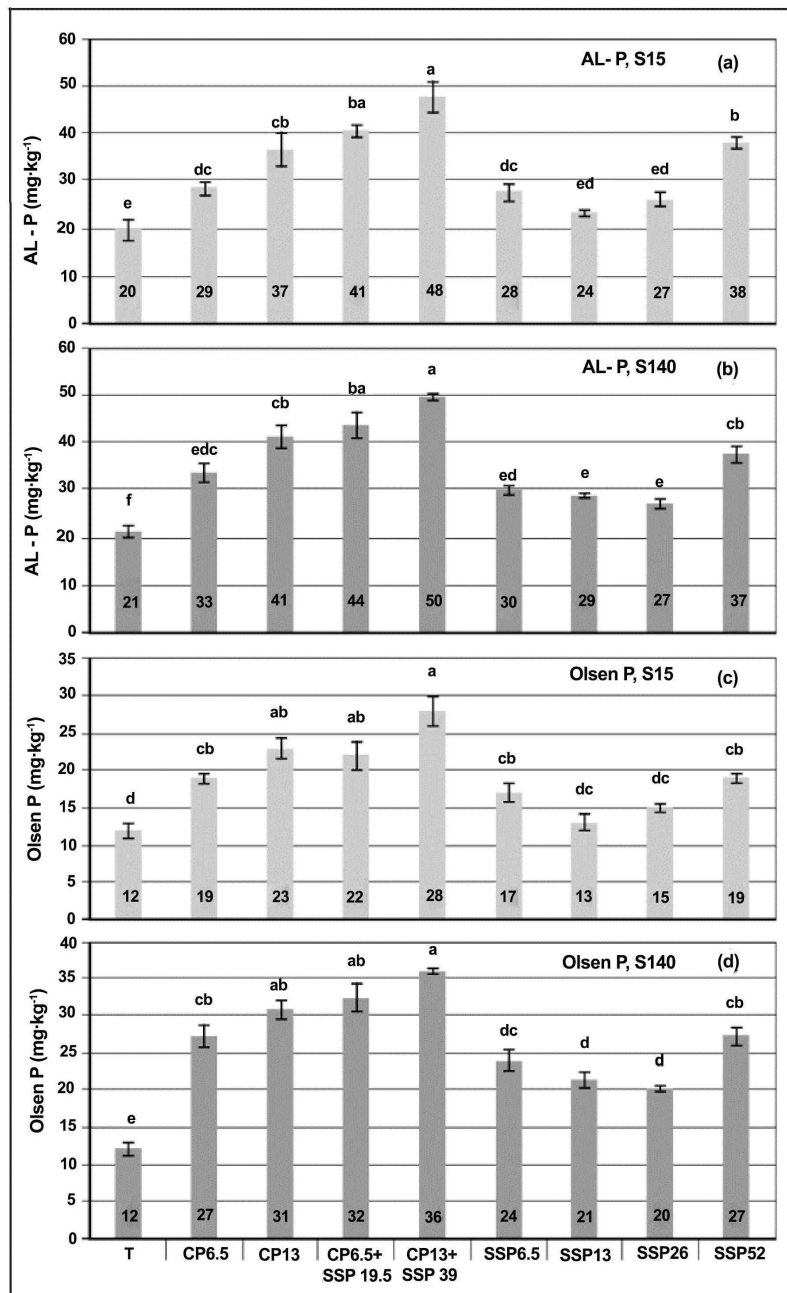


Figure 2. P quantified by the soil P tests (a) ammonium lactate method (AL-P) after 15 days (S15) of soil incubation (b) ammonium lactate method (AL-P) after 140 days (S140) of soil incubation, (c) Olsen method (Olsen-P) after 15 days (S15) of soil incubation and (d) Olsen method (Olsen-P) after 140 days (S140) of soil incubation with compost (CP) and with single superphosphate (SSP). Different letters over the bars indicate for each treatment significant differences at the $p < 0.05$ level.

soil of two amendments (urban sewage sludge-USS and compost of municipal solid waste-MSWC) observed an increased in their mineralisation capacity although USS having a lower C:N ratio showed a higher mineralisation rate than MSWC emphasizing the role of amendment maturation on the increase of the OM levels in the soil. In our work, the OM matter content of the soil after CP

Table 2. Sorption constants obtained at the end of the incubation experiment (after 140 days of soil incubation). Different letters indicate for each treatment significant differences at the $p < 0.05$ level.

Treatments/Sorption constants	Langmuir		Freundlich	
	Q_{\max}	K	A	b
	mg·kg ⁻¹	L·mg ⁻¹	mg·kg ⁻¹	
T	145a	0.71abc	51a	0.54ab
CP6.5	122ab	0.78abc	45bc	0.51bc
CP13	114bc	0.52cd	35ef	0.53b
CP6.5SSP19.5	88c	0.80ab	37def	0.41c
CP13SSP39	89c	0.23d	24g	0.65a
SSP6.5	122ab	0.94ab	50ab	0.50bc
SSP13	121ab	0.61abc	41cd	0.53b
SSP26	117b	0.55bcd	38de	0.52bc
SSP52	110bc	0.45cd	32f	0.54b
Significance Level	$p < 0.001$	$p < 0.001$	$p < 0.001$	$p < 0.001$

addition (on average 46 g·kg⁻¹) was significantly higher ($p < 0.001$) than in SSP treatments (39 g·kg⁻¹). So, the decrease in P sorption capacity observed in CP treatments could partially be explained by the mechanisms referred above. Nevertheless, in the works we cited above the treatments with TSP addition did not exhibit a reduction in P sorption capacity as we observed mainly in SSP52. In our work the high P rate used (SSP52 or CP13 + SSP39) could be higher enough to promote also a large increase in the surface coverage with phosphate anion which subsequently leads to a decrease in the bonding energy of the soil for P sorption of further P additions. However, CP treatments having a steeper decrease in P sorption capacity than the SSP treatments highlighting, in our opinion, the role of the organic matter in reducing the P sorption capacity of this soil.

The b constant is the slope of the Freundlich isotherm plotted in the linear form and some authors like Barrow, 1974 [41] suggested that b values less than 1 indicated that P adsorption is the main process of P retention to soil solid phase. The b values of this work are slightly higher than 0.5 with no significant differences between the treatments indicating that the main process of P sorption did not changed significantly between the treatments.

A P concentration of 0.2 mg·L⁻¹ (standard phosphate requirement, SPR) in the soil solution is usually considered adequate for crop nutrition since it could match the critical limit for obtaining 95% of maximum yield production [33] [37] [39] [42]. The treatment CP13 + SSP39 showed the lowest level ($p < 0.001$) of SPR (4 mg·kg⁻¹, **Figure 3(a)**). In turn the control treatment showed the highest value (17 mg·kg⁻¹). Also, other works with OM addition to soil, such as poultry manure [33] or *Tithonia diversifolia* leaves [37] showed a reduction of SPR in soils non-calcareous, calcareous and acidic. The same trend was observed

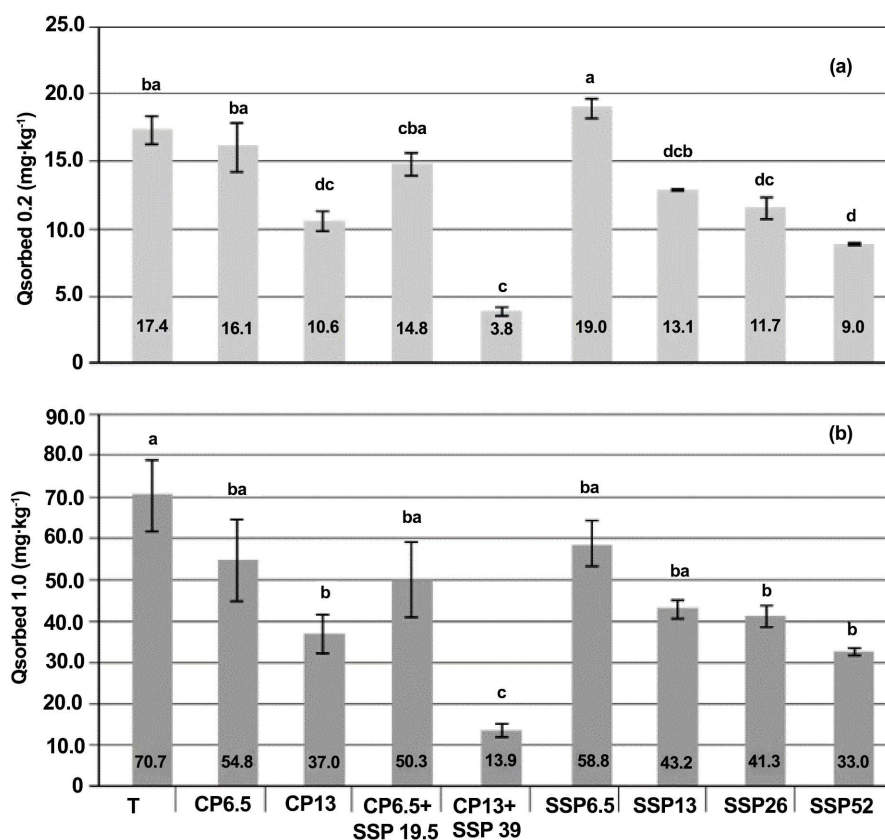


Figure 3. Amount of P sorbed ($\text{mg}\cdot\text{kg}^{-1}$) by the soil to maintain a P concentration of (a) $0.2\text{ mg}\cdot\text{L}^{-1}$ and (b) $1.0\text{ mg}\cdot\text{L}^{-1}$ in the soil solution at the end of the incubation experiment (after 140 days). Different letters over the bars indicate for each treatment significant differences at the $p < 0.05$ level.

between the treatments for the amount of P sorbed at an equilibrium P solution concentration of $1.0\text{ mg}\cdot\text{L}^{-1}$ (Q_{s1} , **Figure 3(b)**). In this case the amount of P sorbed in the CP13 + SSP39 treatment was $14\text{ mg}\cdot\text{kg}^{-1}$ while in the control treatment was $71\text{ mg}\cdot\text{kg}^{-1}$ ($p < 0.001$). A P concentration of $1.0\text{ mg}\cdot\text{L}^{-1}$ in soil solution is considered high concerning not only for crop nutrition but mainly for the risk of P losses from soil to water bodies, improving their risk of eutrophication from non-point sources such as soil P fertilisation. So, **Figure 2** and **Figure 3** showed that the addition of CP in combination with SSP causing a decrease in P sorption leads therefore to the need of the use of a lower P fertilisation rate to achieve not only an adequate level of soil P for crop nutrition (SPR) but also a lower risk for water bodies eutrophication (Q_{s1}). In addition, the results of STP through the time of the incubation experiment could help to understand the maintenance of soil P levels throughout the crop cycle. **Figure 2** showed an increase in the STP values with the time of incubation (from S15 to S140). This increase was significant for Olsen P ($p < 0.001$) but it was not significant for AL-P ($p > 0.05$). Thus, in principle the processes that occur in the soil after fertilisation with CP and SSP should maintain adequate levels of P in the soil solution during the crop cycle.

4. Conclusions

From the results obtained in this work, we can conclude that the organic matter content of the compost (CP) might prevent the soil P sorption, which further explains the higher soil P availability in all the CP treatments compared with the SSP treatments. This increase in the soil P availability after soil addition of CP could be explained not only by decrease of the sites of P sorption (decreased of Q_{max}) but also by decrease of the bonding energy for phosphate sorption (K values decreased) to the soil solid phase.

Both STP methods used (AL and Olsen methods) were able to discriminate differences in soil P availability caused by the properties of the organic (compost) and of the inorganic (SSP) P fertilisers used.

The addition of CP in combination with SSP maintained high levels of soil available P and reduced the standard phosphate requirement. From an agronomic point of view, this behaviour draws attention to the need of reducing the amount of P in fertilisation.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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