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Is Composting a Route to Solubilize Low-Grade Phosphate Rocks and Improve MAP-Based Composts?

Henrique José Guimarães Moreira Maluf[1]*, Carlos Alberto Silva[2], Everton Geraldo de Morais[1] and Leonardo Henrique Duarte de Paula[3]

[1] Universidade Federal de Lavras, Departamento de Ciência do Solo, Programa de Pós-Graduação em Ciência do Solo, Lavras, Minas Gerais, Brasil.

[2] Universidade Federal de Lavras, Departamento de Ciência do Solo, Lavras, Minas Gerais, Brasil.

[3] Instituto Federal de Educação, Ciência e Tecnologia de Minas Gerais, *Campus* Bambuí, Curso de Agronomia, Bambuí, Minas Gerais, Brasil.

ABSTRACT: In alkalinized and Ca-rich composts, solubilization of apatite from phosphate rocks (PRs) is not guaranteed; however, chelating agents and humified substances produced during composting may alter the soluble contents and P forms of monoammonium phosphate (MAP)-based composts. These effects may depend on the proportions of organic wastes and P source used in the compost piles. The aim of this study was to evaluate the effect of composting chicken manure, coffee husk, and Araxá PR, Bayóvar PR, or MAP in different proportions on the organic matter decomposition, total N, Ca contents, and soluble P fractions in the composts. The treatments consisted of a 3 × 4 × 2 factorial, through the combination of three P sources [Araxá PR, Bayóvar PR, and MAP], with four mixtures in the respective proportions: 25, 40, 50, and 75 % of P source with 37.5, 40, 25, and 12.5 % of chicken manure, and 37.5, 20, 25, and 12.5 % of coffee husk, composted or not for 150 days. The composts with PRs showed greater reductions in total C and water-soluble C and lower dry mass yields than MAP-based composts. The use of MAP in mixtures ensured lower N losses compared to composts formulated with PRs. Regardless of the mixture among chicken manure, coffee husk, and PRs, composting increased the pH and total Ca contents and did not alter the fractions of soluble P in water, in citric acid, and in neutral ammonium citrate plus water in the final PR-based composts. Composting of these mixtures was not an efficient route to solubilize P from Araxá and Bayóvar PRs. Values of pH above 8 and high Ca contents were the main factors explaining the stability and non-solubilization of the apatite of PRs in the composts. Composting with MAP, mixed in different proportions with chicken manure and coffee husk, reduced water-soluble P, maintained the pH of the mixtures in the range of 5 to 7, and enriched the composts with N and P.

Keywords: apatite, chicken manure, coffee husk, organic acids, NPK fertilizer equivalent.

INTRODUCTION

Global phosphorus (P) demand increases and reduction in phosphate rock reserves have raised the costs of P fertilizer (Cordell et al., 2009), which reinforces the importance of efficient use of P in Brazilian agriculture. Brazil imports more than 50 % of P used in crop fields (ANDA, 2011). Most of the P added to soil as a fertilizer is not efficiently used by plants, which is especially related to the intense P retention process in soil (Roy et al., 2016). This scenario leads to a search for more efficient alternative P sources (Christel et al., 2014). The process of formulating organo-mineral fertilizers (OMFs) through composting mixtures of waste products with soluble fertilizers or low-grade phosphate rocks may be an alternative for reducing P sink in Brazilian soils and for promoting nutrient release more compatible with crop demand phases, which may optimize crop capacity for P acquisition.

Application of phosphate rocks (PRs) *in natura* is not appropriate to supply the P requirements of crops, due to the low P solubility/release in soil from these rocks; this application does not meet P demand from plants in a timely manner (Novais et al., 2007). Thus, Brazilian coffee farmers have been mixing phosphate rock (PR) in composting piles with coffee husk (CH) and chicken manure (CM) as a way of producing OMFs, though they do not know the efficiency of this process for the solubilization of P from PR (P-PR). During composting, not only humic substances are produced, but also low molecular weight organic acids found in CM (Pinheiro et al., 2013). Organic acids are also synthesized by microorganisms in composting piles, and these organic substances can complex the Ca, Fe, and Al of the PR, destabilizing the apatite from PR and increasing P solubility (Welch et al., 2002; Vassilev et al., 2014).

The ratio between PR and waste in composting is another factor that influences decomposition and P solubility. Bangar et al. (1985), studying P solubilization with different proportions of PR in composting, added 25 % PR in the composting pile and found an increase in citric acid-soluble P content after 90 days of composting a low-grade P source with cattle manure and plant waste. The ratio among wastes is also important, since the combination of CM, an alkaline waste rich in Ca and N, and CH, an acid byproduct with the greatest K content among crop residues (Higashikawa et al., 2010), may provide suitable conditions for P-PR solubilization in composting. However, the composting process may increase the final pH of the compost (Fernández et al., 2016), which implies higher apatite stability (Mendes et al., 2013). Nevertheless, if there is predominance of fungi, pH may decrease and favor P solubilization during this process (Zayed and Abdel-Motaal, 2005). Therefore, there is a need for further research to define suitable conditions for P-PR solubilization during composting, mainly regarding the function of organic ligands, pH changes, and Ca content (Chien et al., 2011). Such studies have become relevant for Brazil, especially considering that the PRs used have different chemical and mineralogical composition, such as Araxá PR, which is a Brazilian rock consisting of fluorapatite of igneous origin with low reactivity (Novais et al., 2007), and Bayóvar PR, which is a francolite of sedimentary origin (Bech et al., 2010), with higher P reactivity/solubility than Araxá PR.

In addition to the use of PRs, another way to produce OMF is the application of soluble phosphate fertilizers, such as single superphosphate (SSP), triple superphosphate (TSP), and monoammonium phosphate (MAP) in the composting pile. These soluble phosphate fertilizers and their phosphate accompanying cation do not differ in P solubility, since the water-soluble P fraction constitutes 85-90 % of the total P, and the remaining fraction of P is soluble in citrate (Chien et al., 2011). The soluble P form found in MAP is mainly $NH_4H_2PO_4$, and this fertilizer has the highest P content, about 22 % (IPNI, 2017), which implies lower cost per kilogram of P in relation to SSP and TSP. For these reasons, MAP is the P source most used in OMF production in Brazil, and it enriches the compost with

N. However, little is known about the N-MAP losses during the composting process and the changes in P forms and solubility of MAP-based final composts.

Both high water-soluble P content and the acidity of soluble phosphate fertilizers promote rapid P release to the soil solution, which favors precipitation of P with Fe and Al and adsorption of phosphate to soil colloids (McLaughlin et al., 2011), contributing to reduced efficiency of P fertilizer use by crops in Brazilian soils (Prochnow et al., 2006). Composting can reduce water-soluble P content through P complexation by organic anions, forming organo-metallic complexes (Gerke, 2010; Urrutia et al., 2014) and maintaining compost pH close to neutrality. The use of SSP in composting promoted slow decomposition of organic matter, reduced the volatilization of $N-NH_3$, and maintained pH values close to 7 in the final compost (Yang et al., 2015). Therefore, the magnitude of solubilization, precipitation, and organic complexation reactions that can alter P solubility in the final compost is probably conditioned by changes in pH and Ca contents, which are controlled by the ratio among the P source, CM, and CH.

Given the several production routes for OMF and compost formulations used in Brazil, the main hypotheses of this study are: (i) increased CM proportions in PR compost piles increase Ca content and pH in the final compost, which prevents the solubilization of apatite, even in humified composts rich in organic ligands; and (ii) in composts formulated with MAP, an increased proportion of CM decreases water-soluble P without altering citrate-soluble P, and also provides an acidic character to the final compost, which reduces N losses during composting. Thus, the aims of this study were: i) to evaluate C forms, dry matter and N losses, pH, and total Ca content in mixtures of P sources, CM, and CH composted for 150 days; ii) to evaluate the effect of composting on soluble P forms in the PR mixtures; iii) to evaluate the changes in P solubility in water, in citric acid, and in neutral ammonium citrate of the mixtures composted with MAP; and iv) to determine the N, P_2O_5, and K_2O (NPK fertilizer equivalent) contents of the composts formulated.

MATERIALS AND METHODS

Organic wastes, phosphorus sources, and the composting process

Chicken manure (CM) was collected in poultry facilities located at the Department of Animal Science, and coffee husk (CH), in a postharvest facility found at the Department of Agriculture, both located at the Federal University of Lavras (UFLA), Lavras, MG, Brazil. These waste products were dried in a forced air oven for 72 h at 60 °C, then ground in a Wiley mill and passed through a 1 mm mesh sieve. Mineral P sources, Araxá phosphate rock (Araxá PR), Bayóvar phosphate rock (Bayóvar PR), and monoammonium phosphate (MAP) were purchased from commercial establishments and from fertilizer companies. Araxá and Bayóvar PRs were used in composting with particle size <0.25 mm, while MAP was used in the granulated form. The organic wastes and mineral P sources were characterized in relation to the main chemical and physicochemical properties (Table 1, Figure 1). The main chemical groups present in organic wastes and in P sources were identified by the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Figure 1), which were interpreted according to Silverstein et al. (2005) and Berzina-Cimdina and Borodajenko (2012).

Mixtures of 500 g of organic wastes and mineral P sources were stored and incubated in polyethylene bags, which constituted the experimental unit. Deionized water was added to mixtures of organic wastes and P sources to maintain moisture close to 70 % of the maximum water retention capacity of each mixture throughout the 150 days of incubation. The plastic bags containing waste-P source mixtures were composted in greenhouse conditions and inserted in hard polyethylene pots with 3 L capacity covered with aluminum foil. Bags containing mixtures were opened daily for 15 minutes to allow

Table 1. Chemical properties of phosphate rocks, monoammonium phosphate, and organic waste samples used in composting

Material	pH(CaCl$_2$)	EC	P soluble in			Total content			
			Water	Citric acid	NAC+H$_2$O	P	N	K	Ca
		dS m^{-1}			g kg^{-1}				
Araxá PR	6.9	0.1	0.1	26.6	5.7	126	nd	nd	329
Bayóvar PR	6.5	2.2	0.2	41.1	9.7	134	nd	nd	361
MAP	4.1	71.5	219	225	235	237	110	nd	nd
CM	7.1	11.6	5.4	23.9	17.9	34.2	30.2	28.4	134
CH	4.6	8.1	1.0	1.1	1.2	1.2	17.3	42.4	3.4

EC: electrical conductivity; NAC+H$_2$O: soluble P in neutral ammonium citrate plus water; Araxá PR: Araxá phosphate rock; Bayóvar PR: Bayóvar phosphate rock; MAP: monoammonium phosphate; CM: chicken manure; CH: coffee husk; nd: not determined. pH, EC, contents of P soluble in water, in citric acid, in NAC+H$_2$O, and total P content were determined according to the official methods described in Brasil (2014). Total N content by method of Tedesco (1995), and contents of K was quantified by flame emission photometer and Ca by atomic absorption spectrophotometry, after sample digestions with nitric:perchloric acids (4:1).
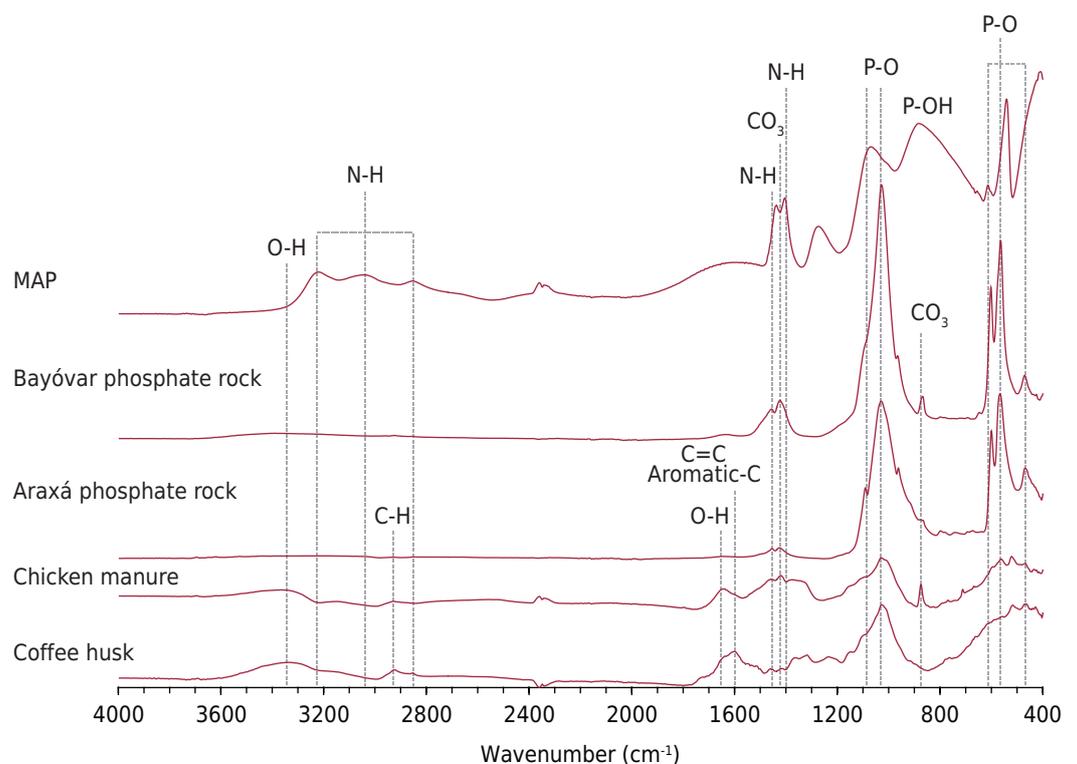
Figure 1. The ATR-FTIR spectra and the main chemical groups recorded for the coffee husk, chicken manure, Araxá phosphate rock, Bayóvar phosphate rock, and monoammonium phosphate (MAP) samples.

gas exchanges, and all plots were revolved in a sequential manner to optimize composting until the end of the incubation period.

Experimental design

A 3 × 4 × 2 factorial arrangement was chosen, in which three P sources (Araxá PR, Bayóvar PR, and MAP) were combined with four mixtures of CH and CM with P sources at different proportions (Table 2) under two incubation conditions: without composting and 150 days of composting. A completely randomized design with three replicates was used.

Chemical and physicochemical analyses

At the end of the 150 days of composting, the composted mixtures were dried in a forced air circulation oven for 72 h at 60 °C and weighed to determine dry matter. The

Table 2. Treatment description and their acronyms for each mixture among P sources (Araxá phosphate rock, Bayóvar phosphate rock, or monoammonium phosphate), chicken manure (CM), and coffee husk (CH), dry mass-based

Treatment/acronyms	P source - P	Chicken manure	Coffee husk
		%	
P25:CM37.5:CH37.5	25	37.5	37.5
P40:CM40:CH20	40	40	20
P50:CM25:CH25	50	25	25
P75:CM12.5:CH12.5	75	12.5	12.5

mixtures were then ground in a Wiley mill and sieved (<1 mm) to evaluate pH in a 0.01 mol L^{-1} $CaCl_2$ solution, and electrical conductivity (EC) in a compost:water ratio of 1:5 (w/v). Water-soluble P contents were determined in the composts after successive washings with deionized water in 1 g of compost until a final volume of 250 mL. Citric acid (CA)-soluble P was extracted stirring the mixtures with a 2 % citric acid (CA) solution for 30 min, in a compost:solution ratio of 1:100 (w/v). In addition to these fractions, neutral ammonium citrate plus water-soluble P (NAC+H_2O-soluble P) was extracted by boiling the sample with neutral ammonium citrate solution (pH 7) in a compost:solution ratio of 1:50 (w/v). Total P was determined after digestion of mixtures with concentrated nitric acid and, subsequently, with concentrated perchloric acid. These analytical procedures were performed according to the official methods described in Brasil (2014). The P fractions in composts were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Blue, Spectro Analytical Instruments, Germany). Each of the contents related to the soluble P fractions were relativized individually in relation to total P according to equation 1, on which calculation of the soluble P index was based.

$$\text{Soluble P index (\%)} = \left(\frac{\text{soluble P content}}{\text{total P content}} \right) \times 100 \qquad \text{Eq. 1}$$

The soluble P index was calculated for soluble P fractions in water, CA, and NAC+H_2O in order to equalize the content effect intensified by loss of mass at the end of composting and to determine the relative proportion of soluble P in relation to total P content, which allowed comparison of the P contents of one composted mixture with another.

Composts were also subjected to nitric-perchloric digestion in a 4:1 ratio (nitric acid:perchloric acid) for determining total K contents in a flame emission photometer and Ca by atomic absorption spectrophotometry. Total N content was determined by the Kjeldahl method after sulfuric acid digestion of the compost sample, based on the methodology proposed by Tedesco et al. (1995), which allowed estimation of N loss at the end of composting, according to equation 2:

$$\textit{N loss (\%)} = 100 - 100 \times \left(\frac{DM_2 \times N_2}{DM_1 \times N_1} \right) \qquad \text{Eq. 2}$$

in which DM_1 and DM_2 are the respective dry matters (g) of the compost at the beginning and at the end of composting, and N_1 and N_2 are the initial and final N contents (g kg^{-1}), respectively.

Contents of total P, CA-soluble P, and NAC+H_2O-soluble P of each composted mixture were also converted to P_2O_5, and the total K to K_2O, using multiplicative factors of 2.29 and 1.20 respectively, for each nutrient. These conversions were carried out to characterize the composts and to calculate their NPK fertilizer equivalent, through the sum of the contents of N, CA-soluble P_2O_5 for mixtures with PRs or NAC+H_2O-soluble P_2O_5 for mixtures with MAP, and K_2O.

Water-soluble C (WSC) in composts was extracted using the same analytical procedure chosen for water-soluble P determination, and total C and WSC were determined using a

dry combustion analyzer (Elementar, Vario Cube model, Germany). The main spectroscopic features of the compost were also identified by ATR-FTIR in a spectrometer of the Bruker Vertex 70v series. The spectra of each mixture refers to the mid-infrared region, from 400 to 4000 cm^{-1}, with a of 2 cm^{-1} resolution.

Statistical analysis

Data were subjected to analysis of variance, and means were compared by the Tukey test ($p<0.05$). Statistical analyses were performed through the computer program R 3.0.3 (R Core Team, 2014) using the ExpDes package (Ferreira et al., 2013). Principal component analysis (PCA) was also performed by grouping the infrared spectral information of each compost, specifically in the region of higher absorption frequency of phosphate and nitrogen groups (800 to 1500 cm^{-1}), to verify clustering of the composts in regard to physicochemical properties. Another PCA was performed to check for the existence of multiple and linear relationships among the factors studied (compost, incubation, and P sources) and compost properties, such as pH, EC, total N contents, Ca and C, water-soluble C, and soluble P fractions. In both PCAs, the vegan package (Oksanen et al., 2015) installed in the R 3.0.3 program was used (R Core Team, 2014). In addition, linear regression analyses were carried out to predict soluble P contents from EC values only for composts formulated with MAP.

RESULTS AND DISCUSSION

C and N changes and compost properties

Total C contents of composts reduced significantly ($p<0.05$) after 150 days of incubation (Figure 2). The total remaining C varied among the different composted mixtures, ranging from 57 to 70 % with phosphate rocks (PRs) and from 78 and 90 % in composts produced with monoammonium phosphate (MAP). The carbon losses in mixtures with PRs were similar to those verified by Dias et al. (2010), in which 54 % of total C remained in compost piles of poultry manure and coffee husk (CH), mixed at a 1:1 proportion, after 210 days of incubation. Water-soluble C (WSC) contents exhibited smaller variations in relation to total C, but with similar patterns, except in mixtures composted with MAP, in which only the compost with 25 % of MAP showed a significant reduction ($p<0.05$) in WSC. In general, composts with CH tend to maintain higher WSC contents than other organic matrices in decomposition, due to a higher amount of phenols and soluble carbohydrates in CH (Dias et al., 2010).

Reductions in total C and WSC contents of composted matrices are associated with microbial oxidation of organic substances to CO_2, indicating increased decomposition of organic matter (OM) (Gómez-Brandón et al., 2008; Wichuk and McCartney, 2010) and, consequently, loss of dry matter from composted mixtures (Table 3). Decrease in WSC contents has also been associated with the degree of compost maturation, considering that, during composting, the C processed by decomposers is converted to C-humic substances with a higher degree of condensation and, therefore, with more chemically stabilized C and less water-soluble C (Dias et al., 2010; Wichuk and McCartney, 2010). Thus, the reduction in WSC contents and the increase in C-humified contents are important properties for evaluating the progress and intensity of the composting process (Dias et al., 2010).

Losses of dry matter from the composts are related to the proportion of mineral P sources used in the mixture (Table 3). The magnitude of reductions in dry matter, and total C and WSC contents of the composts were greater with PRs than in composted materials formulated with MAP (Figure 2). This indicates that the presence of MAP, a readily available P source, decreased the OM decomposition rate and, consequently, the C-CO_2 flow to the air during composting. According to a study carried out by Yang et al. (2015), low decomposition of kitchen waste was found with the addition of 10 % single superphosphate
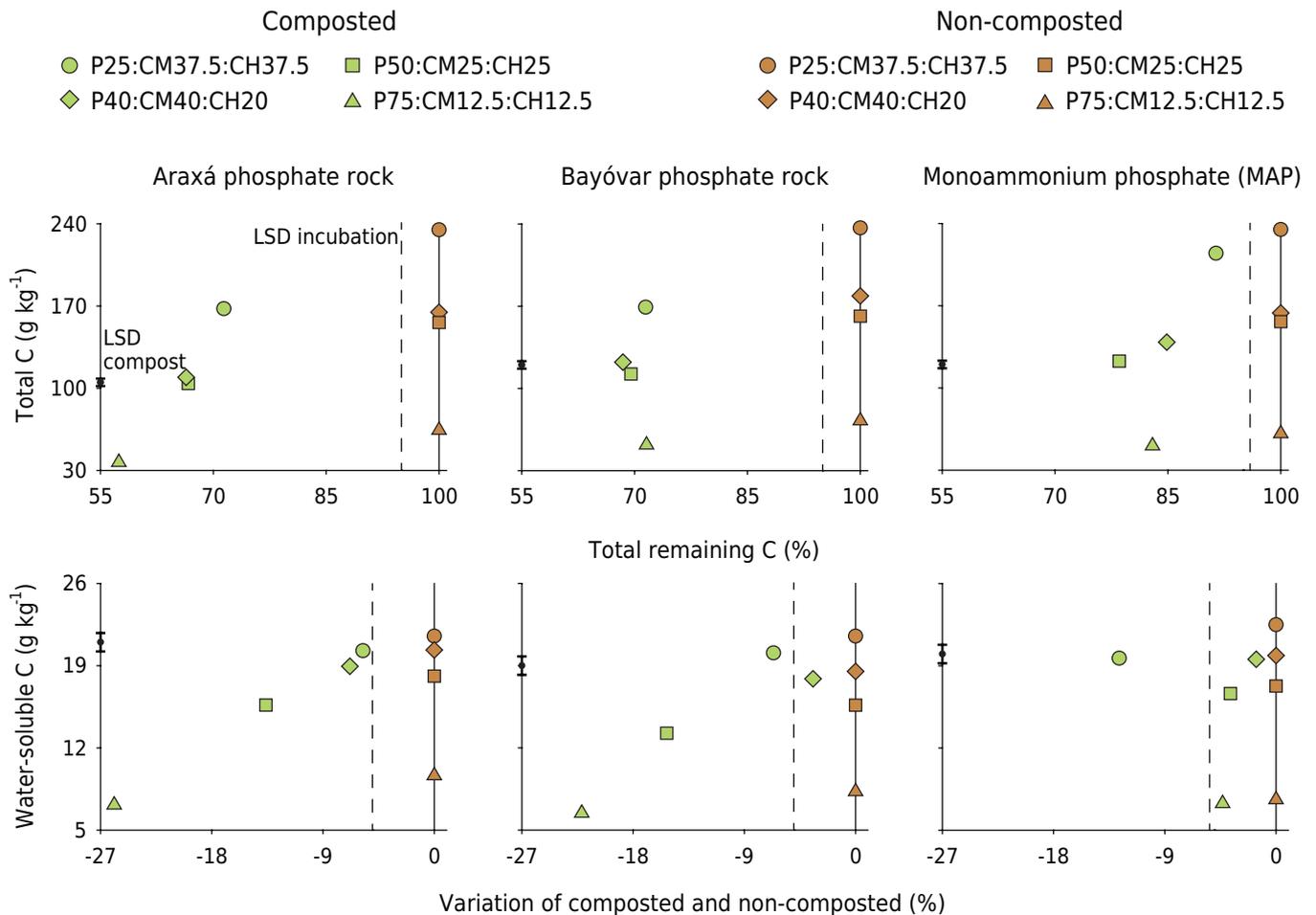
Figure 2. Total C and water-soluble C contents in composted mixtures (150 days of incubation) and non-composted mixtures (without incubation) for different proportions of chicken manure (CM), coffee husk (CH), and Araxá phosphate rock, Bayóvar phosphate rock, or MAP. LSD: Least Significant Difference by the Tukey test (p<0.05) for compost and incubation.

Table 3. Dry matter and N losses in mixtures with chicken manure, coffee husk, and Araxá phosphate rock (PR), Bayóvar PR, or monoammonium phosphate (MAP), after 150 days of composting

Compost	Dry matter loss			N loss		
	Araxá PR	Bayóvar PR	MAP	Araxá PR	Bayóvar PR	MAP
	—————— % ——————			—————— % ——————		
P25:CM37.5CH37.5	12.2 aA	12.0 aA	5.8 aB	11.0 cA	10.1 dA	0.7 aB
P40:CM40:CH20	10.5 abA	8.4 bB	4.9 aC	28.3 bA	26.3 cA	0.4 aB
P50:CM25:CH25	9.6 bA	8.6 bA	5.1 aB	32.0 bA	31.1 bA	0.1 aB
P75:CM12.5:CH12.5	5.2 cA	5.0 cA	2.1 bB	44.8 aA	42.5 aA	1.1 aB

Means followed by the same letter, lowercase for compost (column) and uppercase for P source (row), are not statistically different by the Tukey test (p<0.05).

in the composting pile, since 78 % of total C remained in the final compost. It is known that single superphosphate improves N retention in compost (Prochnow et al., 2001). Therefore, the use of soluble P sources may promote retention of C, which increases dry matter yield in the final compost in relation to PR-based composts. Lee et al. (2009) also observed slow decomposition of swine manure after mixing KH_2PO_4 in different proportions in the composting pile, which was attributed to inhibition of decomposer activity due to increased addition of soluble salts to the compost piles.

At the beginning of incubation, the pH values of mixtures containing PRs were in the range of 6.5 to 8, and when composted, the mixtures had pH close to 10 (Figure 3). In MAP-based composts, only mixtures with 25 and 40 % of P fertilizer increased the pH at the end of the
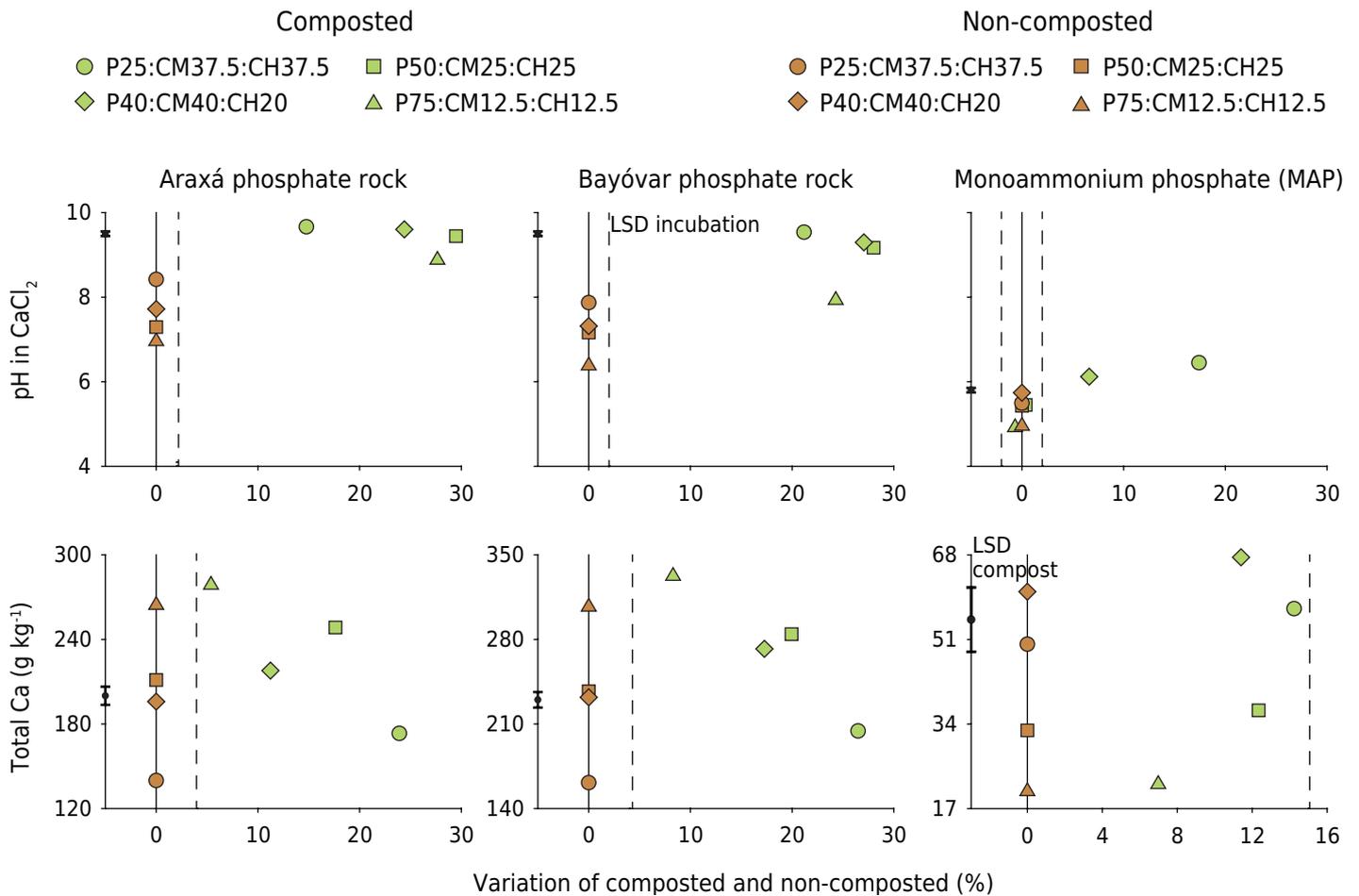
Figure 3. pH in CaCl$_2$ and total Ca content in composted mixtures (150 days of incubation) and non-composted mixtures (without incubation) for different proportions of chicken manure (CM), coffee husk (CH), and Araxá phosphate rock, Bayóvar phosphate rock, or MAP. LSD: Least Significant Difference by the Tukey test (p<0.05) for compost and incubation.

incubation, to values of 6.7 and 6.1, respectively. These values were lower than the pH values of the PR-based composts. The OM decomposition rate is regulated by pH, and pH controls microbial activity as well, since fungi act more effectively in the decomposition processes under acidic conditions and bacteria under a neutral to alkaline environment (Gómez-Brandón et al., 2008; Vassilev et al., 2014). Nitrogen loss is also regulated by pH, since ammonia (N-NH$_3$) volatilization increases when pH values reach the alkaline range (Wichuk and McCartney, 2010). This is the reason why composts with PRs lost more N than MAP-based composts (Table 3). It may be inferred that adding MAP to compost piles is a suitable strategy for retaining N-NH$_4^+$ in the final compost, probably related to lower NH$_3$ volatilization due to the lower pH of these mixtures. Trends found in this study for N losses during composting are in agreement with results obtained by Yang et al. (2015) when superphosphate was added to compost piles.

Total Ca contents increased in mixtures treated with PRs after incubation, especially in composts with higher proportions of organic wastes, which may be related to the effect of concentration caused by loss of mass in the compost produced (Figure 3). In mixtures with MAP, the total Ca contents were not affected by incubation (p>0.05), probably due to the lower loss of mass than losses found for PR-based composts (Table 3). Absence of Ca in MAP explains the lower Ca content in composts produced with MAP than the contents in composts formulated with PRs.

Compost P fractions

The indices of P soluble in water (H$_2$O-P), in citric acid (CA-P), and in neutral ammonium citrate plus water (NAC+H$_2$O-P) did not increase in mixtures with Araxá and Bayóvar

PRs after 150 days of composting (Figure 4). Thus, there was no solubilization of P-PRs at the end of composting; on the contrary, there was a reduction in CA-P when Bayóvar PR was added to mixtures at the rate of 40 and 50 %. This effect is mainly related to high pH values found for composts with PRs, which reached values close to 10, and high Ca contents (Figure 3). These chemical changes in the mixtures composted with PRs characterize an unsuitable environment for P-apatite solubilization, considering that these conditions favor the formation of stable precipitates between P and Ca, increasing the chemical stability of apatite (Mendes et al., 2013). Thus, even in an environment rich in organic matter, the effect of organic compounds in solubilizing P-apatite is overcome by other chemical factors, such as the high pH values and Ca contents in the compost pile. Although chicken manure (CM) has greater content of low molecular weight organic acids than other wastes (Pinheiro et al., 2013), the alkaline characteristic and the high Ca content, especially in the form of $CaCO_3$ of this waste (Higashikawa et al., 2010), may also explain the low P-PR solubilization after 150 days of composting.

In alkaline medium, the capacity of organic acids to complex metals and their production are reduced due to low fungal activity, reducing the potential for P-PR solubilization (Chatli et al., 2008; Wei et al., 2011). In acidic conditions, fungal activity is optimized, as well as the production of organic acids, which favors complexation of cations associated with PRs, reducing the activity of these ions and altering the saturation point of the solution, therefore increasing PR dissolution (Welch et al., 2002; Mendes et al., 2013). Thus, fungi are superior to bacteria in solubilizing P due to greater production of organic acids and, consequently, higher acidification in the surrounding medium (Chatli et al., 2008). Acidification is the main factor regulating the PR dissolution rate. In addition to complexation of cations, organic acids may contribute to reduction in effective pH. According to Kpomblekou-A and Tabatabai (1994), organic acids, such as citric and oxalic acids, are as efficient in PR solubilization as sulfuric acid.

Zayed and Abdel-Motaal (2005) inoculated *A. niger* and *T. viride* in sugarcane bagasse and PR composting and found that the action of these fungi reduced pH from 8 to 4.8, and increased water-soluble P content. However, Biswas and Narayanasamy (2006) found a reduction in water-soluble P and a small increase, less than 1 %, in citrate-soluble P in composts inoculated with *A. awamori,* which may be related to the species of fungus used in the inoculation. Vassilev et al. (1996), using a solid-state fermentation system with beet waste, PR, and *A. niger*, found pH values from 3 to 3.5 with 76 % solubilization of P-PR. In addition, the release of other chemical elements present in PRs, such as fluorine, can influence this process; fluorine inhibits microbial activity and can reduce P solubilization by 50 % (Mendes et al., 2013). Mixing elemental S with PR and inoculation with *A. thiooxidans* can also be used to acidify the medium and solubilize P (Stamford et al., 2016), which may be an alternative for increasing P-PR solubility during composting.

The biggest effects on P solubility indices were observed for MAP composts (Figure 4). Reductions in CA-P and H_2O-P were found in mixtures composted with MAP, mainly when this P source was added at rates of 40 and 50 %. Such reduction in water-soluble P may be related to the formation of more stable phosphate compounds, or even due to complexes formed between organic ligands and P. Organic-P complexes can be formed through cationic metal bridges, such as Ca^{2+}, which reduces the water solubility of the soluble P fertilizer, but it does not prevent plants from acquiring this form of P (Gerke, 2010; Urrutia et al., 2014). The NAC+H_2O-P also reduced in the composted mixture when MAP was added at the 40 % rate; however, this soluble P form did not change when the rate was at 50 %, and it increased in the mixtures when MAP was added at rates of 25 and 75 %. Reduction in H_2O-P and maintenance or increase in NAC+H_2O-P, as observed
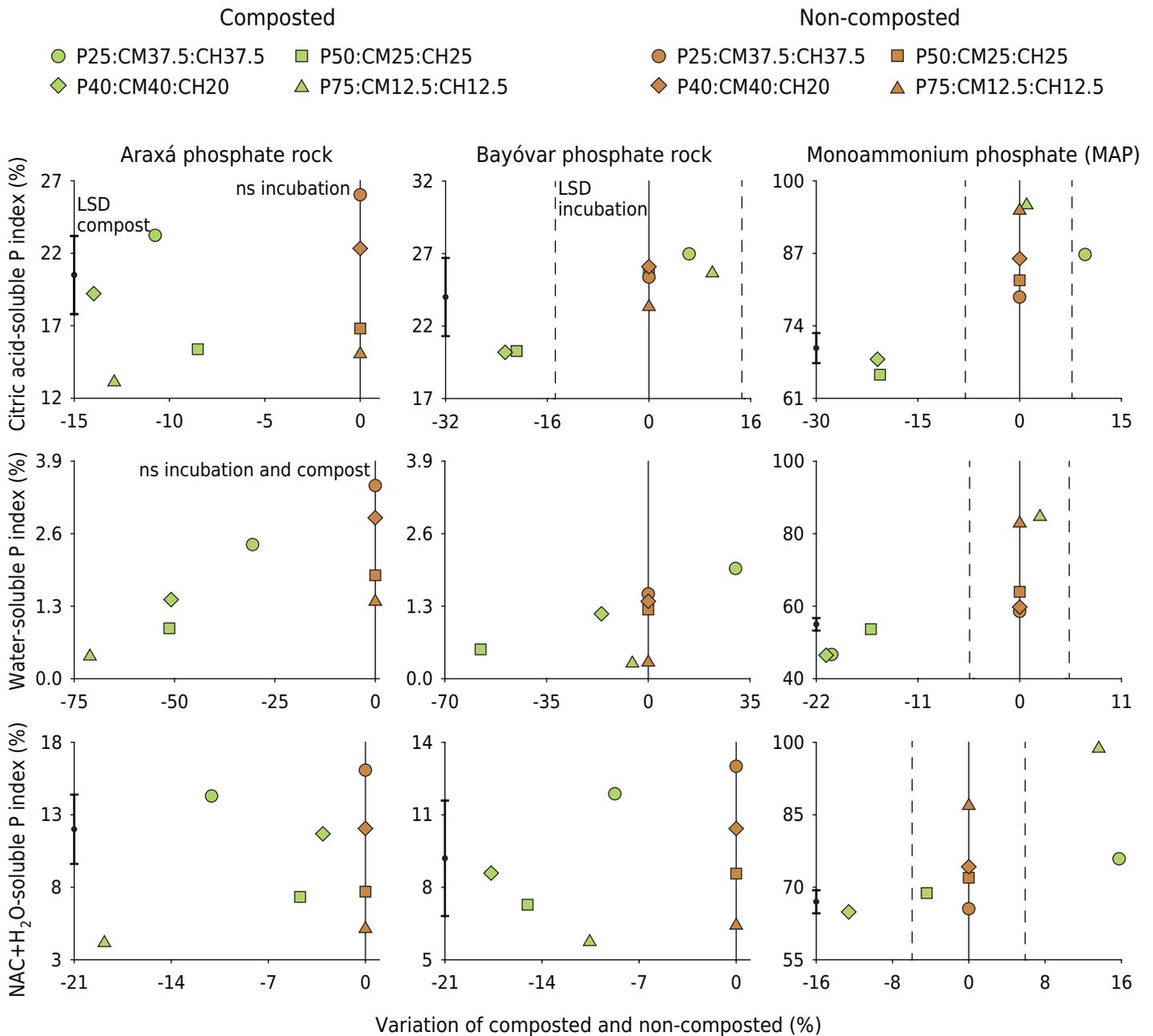
Figure 4. Indexes of soluble P in citric acid, in water, and in neutral ammonium citrate plus water (NAC+H$_2$O) of each composted mixture (150 days of incubation) and non-composted mixture (without incubation) for different proportions of chicken manure (CM), coffee husk (CH), and Araxá phosphate rock, Bayóvar phosphate rock, or MAP. LSD: Least Significant Difference by the Tukey test (p<0.05) for compost and incubation. ns: not significant.

in the mixture composted with 25 and 50 % MAP, may represent an improvement in the chemical properties of organo-mineral fertilizers (OMF).

Low solubility of P fertilizer in water and high solubility in citrate is an effective strategy in protecting P against reactions that may cause soil P retention (Urrutia et al., 2014). This effect may be particularly beneficial for Brazilian tropical soils, which have low pH and predominance of kaolinite and Fe and Al oxides in the clay fraction. In these highly weathered soils, it is not uncommon for P to be adsorbed at content of more than 2,000 mg kg^{-1}, considering a 0.00 to 0.20 m soil depth (Novais et al., 2007). Thus, fertilizers with lower water-soluble P contents can be more efficient in supplying P to plants in soils with high P adsorption capacity (Prochnow et al., 2006) due to a gradual release of P that is more synchronized with the phases of higher P requirement by crops (Urrutia et al., 2014), especially in long-cycle crops or perennials. Another improvement of MAP in

composting is the pH value in compost (Figure 2) higher than the pH of conventional MAP fertilizer (Table 1). This effect on the pH of compost also minimizes precipitation of P-Fe and P-Al and P adsorption in soil minerals, which occur in the surroundings of soluble fertilizer granules applied to the soil, as reported by McLaughlin et al. (2011). Moreover, the application of P in soil along with OM can increase P fertilizer use efficiency by plants (Roy et al., 2016), considering that organic compounds act in blocking P adsorption sites on the colloid surface (Wang et al., 2016).

Infrared spectroscopic features of compost

Principal component analysis divided the composts into two groups, distinguishing the clusters of composts with PRs from those produced with MAP, due to the contrast in ATR-FTIR spectral signatures. In each group of mixtures, little variation was identified between the composted and non-composted (Figure 5). Thus, each group was represented by the average spectrum of the mixtures related to P source, with identification of absorption bands according to the assignments found in Silverstein et al. (2005) and Berzina-Cimdina and Borodajenko (2012). Spectral bands between 3400 and 3200 cm^{-1}, and 1640 cm^{-1} represent O-H bonds. Weak peaks at 2918 and 2850 cm^{-1} were observed in mixtures composed of PRs, which are associated with aliphatic C-H groups of humic substances
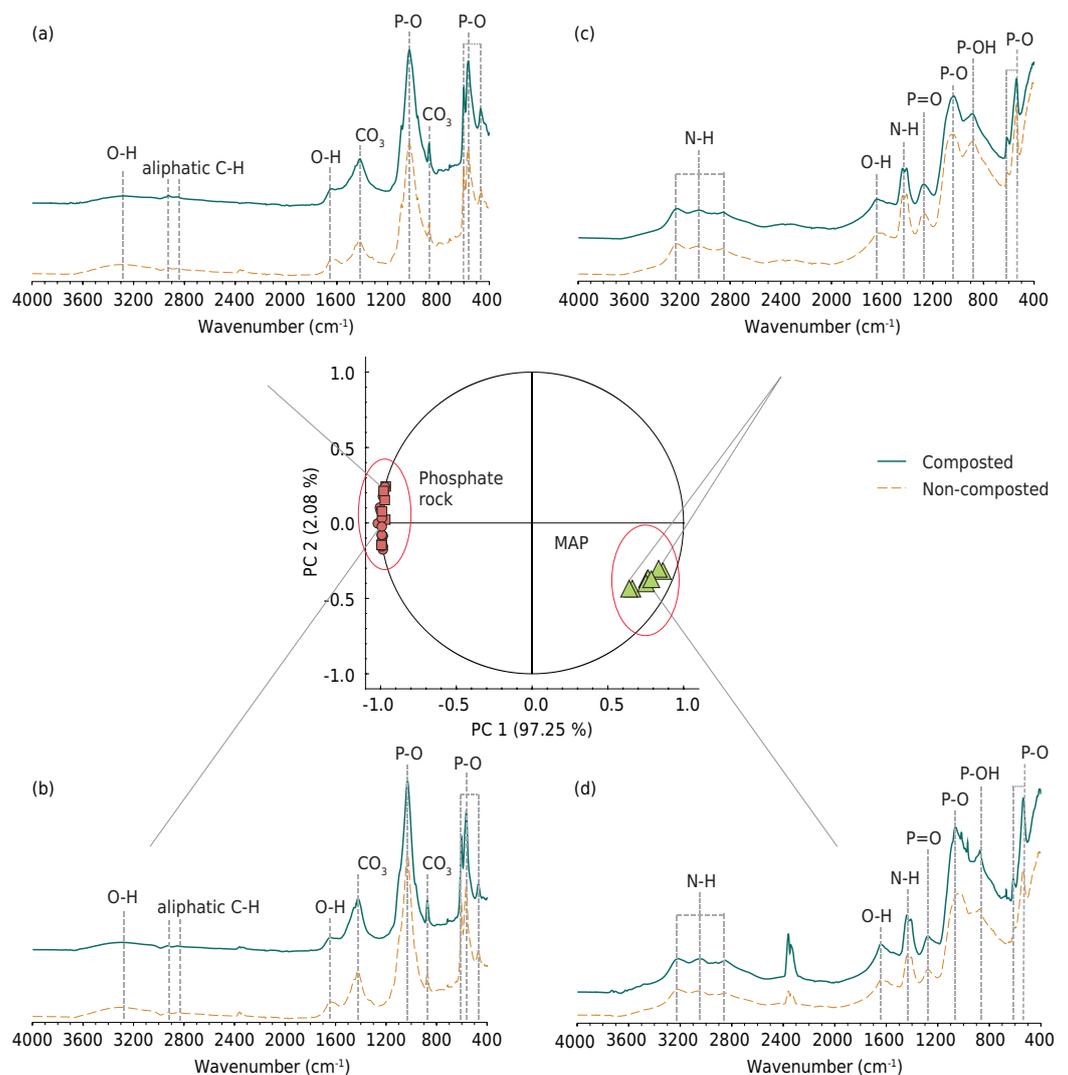
Figure 5. Principal component analysis (PCA) of absorption bands and mean spectra of ATR-FTIR and main chemical groups recorded for the mixtures with Araxá phosphate rock (a), Bayóvar phosphate rock (b), 25 and 75 % of MAP (c), and 40 and 50 % of MAP (d) composted (150 days of incubation) and non-composted (without incubation).

(Stevenson, 1994). Absorption bands at 1460 and 870 cm^{-1} found in mixtures with PRs are represented by CO_3^{2-} groups; whereas bands at 1100, 1000, 600, 560, and 470 cm^{-1} are associated with PO_4^{3-} groups through the P-O bond. Changes were not observed in the PO_4^{3-} groups between mixtures composted and non-composted with PR, which reinforces non-alteration of the soluble P fraction indices (Figure 4), demonstrating absence of P solubilization from PR at the end of composting.

In the spectra generated for MAP composts, bands of P=O and P-OH bonds were identified at 1270 and 890 cm^{-1}, respectively (Figure 5). Changes in the spectra of composted mixtures were only found in composts with 40 and 50 % of MAP, in relation to non-composted mixtures. These composts had poorly defined spectral bands at 1010 and 968 cm^{-1}, which are related to symmetrical vibrations of P-O bonds; for that reason, the average spectrum of mixtures with 40 and 50 % MAP is presented separately. These bands may be associated with the formation of phosphate compounds with greater stability or complexes among composting organic anions and PO_4^{3-} groups, since these composted mixtures were the only ones that reduced H_2O-P and CA-P, and they had the lowest NAC+H_2O-P of all the MAP composted mixtures (Figure 4). An increase in the absorption bands between 3200 and 2800 cm^{-1} and between 1440 and 1400 cm^{-1} were found in mixtures composted with 40 and 50 % of MAP, which are associated with N-H bonds.

Organo-mineral fertilizers

Composts had different chemical properties, mainly due to the P source used in the mixture (Figure 6). Contents of soluble P fractions, total N, and values of electrical conductivity
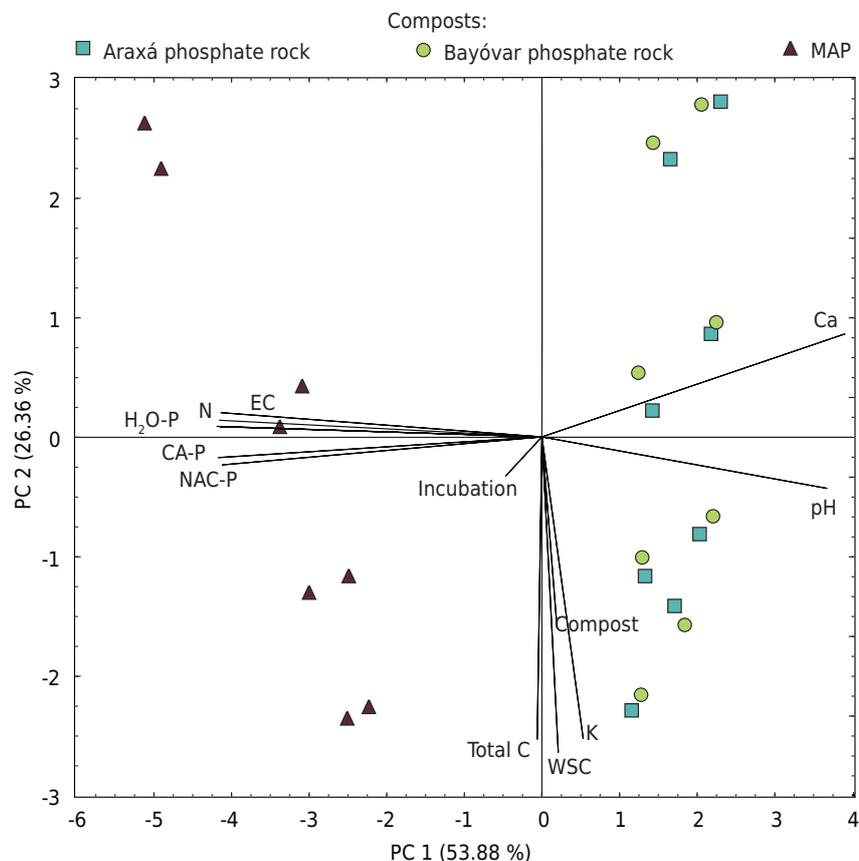
Figure 6. Principal component analysis (PCA) for P source (clustering), type of compost, incubation, and evaluated chemical variables: pH, total contents of Ca, K, N, C, and water-soluble C (WSC); indexes of P soluble in water (H_2O-P), in citric acid (CA-P), and in neutral ammonium citrate plus water (NAC-P), and electrical conductivity (EC).

(EC) were positively related to MAP-based composts (Figure 6). Composts formulated with Araxá and Bayóvar PRs had similar chemical properties and were positively related to pH values and total Ca contents. However, soluble P fraction indices were inversely related to Ca contents and pH. Therefore, using acidic agro-industrial waste with low Ca content may be a reliable strategy for improving solubilization of low-grade phosphate rocks. Along with that, the use of inputs that favor maintenance of the final compost with pH below 5 (Welch et al., 2002; Vassilev et al., 2014; Stamford et al., 2016) is a practice that may be used to increase P-apatite solubilization. It is also necessary to investigate whether composted mixtures increase the solubility of chemical elements potentially inhibitory to fungal activity, such as fluorine found in PRs (Mendes et al., 2013). The study of the liquid phase of materials under decomposition is another aspect that deserves attention to investigate changes in pH values and in Ca^{2+} and P contents during composting.

Principal component analysis indicated a high correlation between EC and indices of soluble P fractions in MAP-based composts (Figure 6). The degree of association of these variables shows that EC can be used to predict the contents of H_2O-P, CA-P, and NAC+H_2O-P of MAP composts (Figure 7). The use of EC to estimate each soluble P fraction of MAP-based composts is relevant because the analytical procedures used to measure soluble P contents are more costly and laborious than EC determination.

Among the different composts studied, mixtures with MAP produced OMFs with the highest fertilizer values. The composted mixture with 50 % MAP, 25 % CM, and 25 % CH can be highlighted. After 150 days of composting, this compost showed pH of 5.5 and 18 % reduction in H_2O-P, and it kept the same NAC+H_2O-P determined in the initial compost, without incubation. This profile of P fractions in the compost mentioned may indicate a more gradual release of P in relation to P from conventional MAP fertilizer. Moreover, this composted mixture had 18 % total P or 41 % P_2O_5 and 28 % NAC+H_2O-soluble P_2O_5. In addition to P, this and other composts have N and K (Table 4).

In order to improve capacity to act as nutrient sources to crops, there should be an increase in NPK fertilizer equivalent, since this index quantitatively indicates the available content of N, P_2O_5, and K_2O in the composted mixtures (Table 4). In composts formulated with Araxá PR, the increase in the proportion of P source in the mixture and the decrease in organic wastes reduced the NPK fertilizer equivalent of the composts, which indicates that the fertilizer value of composts is more related to CM and CH than to proportions of low-grade rocks in the compost. In MAP composted mixtures, the enrichment of NPK levels in the compost is more dependent on the P source than on the organic wastes. Increasing MAP in the composted matrices assures higher capacity of the OMFs produced in supplying N, P, and K to plants, and possibly a more gradual release of P than the use of conventional MAP fertilizer as an exclusive source of N and P.
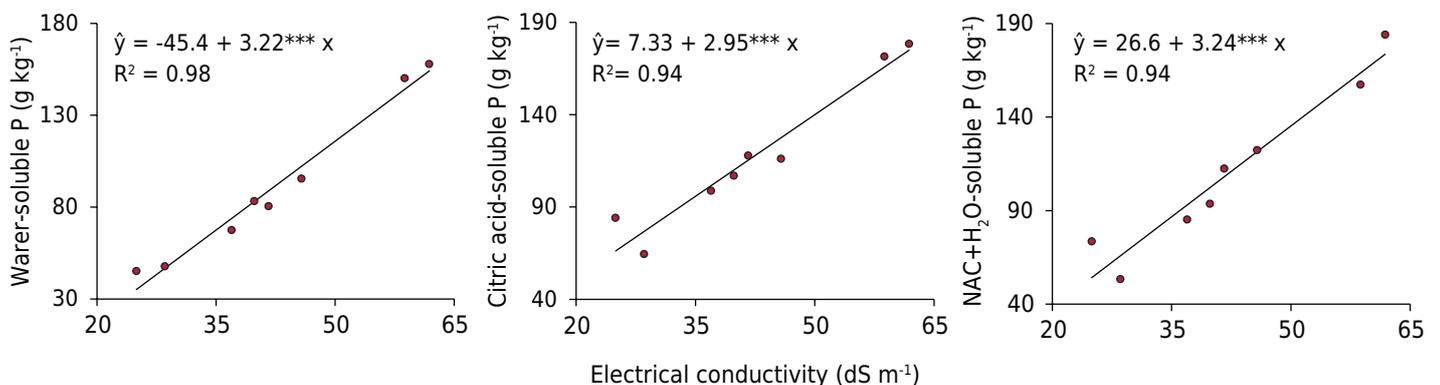
Figure 7. Contents of P soluble in water, in citric acid, and in neutral ammonium citrate plus water (NAC+H_2O) as related to electrical conductivity of different mixtures, composted or not, of chicken manure, coffee husk, and monoammonium phosphate (MAP). ***: significant at 0.01 % probability.

Table 4. Total N, P_2O_5, and K_2O contents, contents of citric acid-soluble P_2O_5 for mixtures with phosphate rocks, and neutral ammonium citrate plus water-soluble ($NAC+H_2O$) P_2O_5 for mixtures with monoammonium phosphate, and NPK fertilizer equivalent, followed by standard error, after 150 days of composting

Compost	N	Total P_2O_5	Soluble P_2O_5	K_2O	NPK fertilizer equivalent[1]
			%		
Araxá phosphate rock					
P25:CM37.5CH37.5	1.6 ±0.03	15.8 ±0.10	3.7 ±0.04	3.2 ±0.07	8.5 ±0.10
P40:CM40:CH20	1.2 ±0.01	20.6 ±0.27	3.9 ±0.04	2.9 ±0.11	8.0 ±0.12
P50:CM25:CH25	0.9 ±0.03	24.1 ±0.07	3.7 ±0.08	2.3 ±0.15	6.9 ±0.20
P75:CM12.5:CH12.5	0.5 ±0.02	30.8 ±0.38	4.0 ±0.03	1.2 ±0.03	5.7 ±0.05
Bayóvar phosphate rock					
P25:CM37.5CH37.5	1.6 ±0.01	17.3 ±0.10	4.6 ±0.23	3.5 ±0.07	9.7 ±0.17
P40:CM40:CH20	1.2 ±0.07	24.0 ±0.59	4.8 ±0.07	2.9 ±0.14	8.9 ±0.12
P50:CM25:CH25	0.9 ±0.01	26.5 ±0.63	5.4 ±0.17	2.6 ±0.05	8.9 ±0.21
P75:CM12.5:CH12.5	0.5 ±0.01	33.8 ±0.37	8.7 ±0.15	1.3 ±0.03	10.5 ±0.12
Monoammonium phosphate (MAP)					
P25:CM37.5CH37.5	5.1 ±0.02	22.2 ±0.12	16.9 ±0.36	3.9 ±0.19	25.9 ±0.58
P40:CM40:CH20	6.2 ±0.05	39.7 ±0.18	25.8 ±0.20	2.9 ±0.03	34.9 ±0.24
P50:CM25:CH25	7.2 ±0.06	40.8 ±0.41	28.1 ±0.27	2.4 ±0.09	37.7 ±0.23
P75:CM12.5:CH12.5	9.4 ±0.17	42.7 ±0.09	42.2 ±0.37	0.9 ±0.01	52.5 ±0.52

[1] NPK fertilizer equivalent (%): sum of N, citric acid-soluble P_2O_5 for composts with phosphate rocks or $NAC+H_2O$-soluble P_2O_5 for composts with MAP, and K_2O contents.

CONCLUSIONS

Regardless of the proportions of chicken manure, coffee husk, and Araxá or Bayóvar phosphate rocks, composting is not a suitable route to solubilize P-apatite. Increased Ca contents and pH values in composted mixtures favor stabilization of phosphate rock, instead of solubilizing apatite, and contribute to higher N losses during composting.

Use of MAP instead of low-grade phosphate rocks in composting increases dry matter yield, decreases N losses, maintains compost pH in the range of 5 to 7, and raises the compost NPK fertilizer equivalent.

Electrical conductivity can be used as a predictor of P contents soluble in water, in citric acid, and in neutral ammonium citrate plus water of the composted mixtures formulated with MAP.

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REFERENCES

Associação Nacional para a Difusão de Adubos - ANDA. Investimentos no Brasil; 2011 [accesso em 8 jul 2015]. Disponível em: http://www.anda.org.br/multimidia/investimentos.pdf.

Bangar KC, Yadav KS, Mishra MM. Transformation of rock phosphate during composting and the effect of humic acid. Plant Soil. 1985;85:259-66. https://doi.org/10.1007/BF02139630

Bech J, Suarez M, Reverter F, Tume P, Sánchez P, Bech J, Lansac A. Selenium and other trace elements in phosphate rock of Bayovar-Sechura (Peru). J Geochem Explor. 2010;107:136-45. https://doi.org/10.1016/j.gexplo.2009.08.004

Berzina-Cimdina L, Borodajenko N. Research of calcium phosphates using Fourier transform infrared spectroscopy. In: Theophanides T, editor. Infrared spectroscopy - materials science, engineering and technology. Rijeka: InTech; 2012. p. 123-48. https://doi.org/10.5772/36942

Biswas DR, Narayanasamy G. Rock phosphate enriched compost: an approach to improve low-grade Indian rock phosphate. Bioresource Technol. 2006;97:2243-51. https://doi.org/10.1016/j.biortech.2006.02.004

Brasil. Ministério da Agricultura, Pecuária e Abastecimento. Manual de métodos analíticos oficiais para fertilizantes e corretivos. Brasília, DF: MAPA/SDA/CGAL; 2014. Disponível em: http://www.agricultura.gov.br/assuntos/laboratorios/arquivos-publicacoes-laboratorio/manual-_in-5_-analiticos-oficiais-para-fertilizantes-e-corretivos_com_capa_final_03.pdf

Chatli AS, Beri V, Sidhu BS. Isolation and characterisation of phosphate solubilising microorganisms from the cold desert habitat of *Salix alba Linn*. in trans Himalayan region of Himachal Pradesh. Indian J Microbiol. 2008;48:267-73. https://doi.org/10.1007/s12088-008-0037-y

Chien SH, Prochnow LI, Tu S, Snyder CS. Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: an update review. Nutr Cycl Agroecosyst. 2011;89:229-55. https://doi.org/10.1007/s10705-010-9390-4

Christel W, Bruun S, Magid J, Jensen LS. Phosphorus availability from the solid fraction of pig slurry is altered by composting or thermal treatment. Bioresource Technol. 2014;169:543-51. https://doi.org/10.1016/j.biortech.2014.07.030

Cordell D, Drangert J-O, White S. The story of phosphorus: global food security and food for thought. Global Environ Chang. 2009;19:292-305. https://doi.org/10.1016/j.gloenvcha.2008.10.009

Dias BO, Silva CA, Higashikawa FS, Roig A, Sánchez-Monedero MA. Use of biochar as bulking agent for the composting of poultry manure: effect on organic matter degradation and humification. Bioresource Technol. 2010;101:1239-46. https://doi.org/10.1016/j.biortech.2009.09.024

Fernández C, Mateu C, Moral R, Sole-Mauri F. A predictor model for the composting process on an industrial scale based on Markov processes. Environ Modell Softw. 2016;79:156-66. https://doi.org/10.1016/j.envsoft.2016.02.007

Ferreira EB, Cavalcanti PP, Nogueira DA. ExpDes: experimental designs package version 1.1.2; 2013 [accessed on 15 Jul 2014]. Available at: https://cran.r-project.org/web/packages/ExpDes/index.html

Gerke J. Humic (organic matter)-Al(Fe)-phosphate complexes: an underestimated phosphate form in soils and source of plant-available phosphate. Soil Sci. 2010;175:417-25. https://doi.org/10.1097/SS.0b013e3181f1b4dd

Gómez-Brandón M, Lazcano C, Domínguez J. The evaluation of stability and maturity during the composting of cattle manure. Chemosphere. 2008;70:436-44. https://doi.org/10.1016/j.chemosphere.2007.06.065

Higashikawa FS, Silva CA, Bettiol W. Chemical and physical properties of organic residues. Rev Bras Cienc Solo. 2010;34:1743-52. https://doi.org/10.1590/S0100-06832010000500026

International Plant Nutrition Institute - IPNI. Monoammonium phosphate (MAP); 2017 (Nutrient Source Specifics, 9) [accessed on 30 May 2017]. Available at: https://www.ipni.net/publication/nss.nsf/0/2F200FA9C8C946F0852579AF00762904/$FILE/NSS-09%20Monoammonium%20Phosphate.pdf.

Kpomblekou-A K, Tabatabai MA. Effect of organic acids on release of phosphorus from phosphate rocks. Soil Sci. 1994;158:442-53. https://doi.org/10.1097/00010694-199415860-00006

Lee JE, Rahman MM, Ra CS. Dose effects of Mg and PO_4 sources on the composting of swine manure. J Hazard Mater. 2009;169:801-7. https://doi.org/10.1016/j.jhazmat.2009.04.026

McLaughlin MJ, McBeath TM, Smernik R, Stacey SP, Ajiboye B, Guppy C. The chemical nature of P accumulation in agricultural soils - implications for fertiliser management and design: an Australian perspective. Plant Soil. 2011;349:69-87. https://doi.org/10.1007/s11104-011-0907-7

Mendes GO, Vassilev NB, Bonduki VHA, Silva IR, Ribeiro Junior JI, Costa MD. Inhibition of *Aspergillus niger* phosphate solubilization by fluoride released from rock phosphate. Appl Environ Microb. 2013;79:4906-13. https://doi.org/10.1128/AEM.01487-13

Novais RF, Smyth TJ, Nunes FN. Fósforo. In: Novais RF, Alvarez V VH, Barros NF, Fontes RLF, Cantarutti RB, Neves JCL, editores. Fertilidade do solo. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 2007. p. 471-550.

Oksanen J, Blanchet FG, Kindt R, Legendre P, Minchin PR, O'Hara RB, Simpson GL, Solymos P, Stevens MHH, Wagner HH. Vegan: community ecology package. R package version 2.2-1; 2015 [accessed on 08 Mar 2016]. Available at: https://cran.r-project.org/web/packages/vegan/index.html

Pinheiro GL, Silva CA, Lima JM, Costa AL. Ácidos orgânicos de baixa massa molar em solos e materiais orgânicos. Quim Nova. 2013;36:413-8. https://doi.org/10.1590/S0100-40422013000300011

Prochnow LI, Cunha CF, Kiehl JC, Alcarde JC. Controle da volatilização de amônia em compostagem, mediante adição de gesso agrícola e superfosfatos com diferentes níveis de acidez residual. Rev Bras Cienc Solo. 2001;25:65-70. https://doi.org/10.1590/S0100-06832001000100007

Prochnow LI, Quispe JFS, Francisco EAB, Braga G. Effectiveness of phosphate fertilizers of different water solubilities in relation to soil phosphorus adsorption. Sci Agric. 2006;63:333-40. https://doi.org/10.1590/S0103-90162006000400004

R Development Core Team. R: a language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; 2014. Available at: http://www.R-project.org.

Roy ED, Richards PD, Martinelli LA, Coletta LD, Lins SRM, Vazquez FF, Willig E, Spera SA, VanWey LK, Porder S. The phosphorus cost of agricultural intensification in the tropics. Nat Plants. 2016;2:16043. https://doi.org/10.1038/nplants.2016.43

Silverstein RM, Webster FX, Kiemle DJ. Spectrometric identification of organic compounds. 7th ed. Hoboken: John Wiley & Sons, Inc.; 2005.

Stamford NP, Simões Neto DE, Freitas ADS, Oliveira ECA, Oliveira WS, Cruz L. Rock biofertilizer and earthworm compost on sugarcane performance and soil attributes in two consecutive years. Sci Agric. 2016;73:29-33. http://dx.doi.org/10.1590/0103-9016-2015-0005

Stevenson FJ. Humus chemistry: genesis, composition, reactions. 2nd ed. New York: John Wiley & Sons, Inc.; 1994.

Tedesco MJ, Gianello C, Bissani CA, Bohnen H, Volkweiss SJ. Análise de solo, plantas e outros materiais. 2. ed rev ampl. Porto Alegre: Universidade Federal do Rio Grande do Sul; 1995. (Boletim técnico, 5).

Urrutia O, Erro J, Guardado I, Francisco SS, Mandado M, Baigorri R, Yvin JC, Garcia-Mina JM. Physico-chemical characterization of humic-metal-phosphate complexes and their potential application to the manufacture of new types of phosphate-based fertilizers. J Plant Nutr Soil Sc. 2014;177:128-36. https://doi.org/10.1002/jpln.201200651

Vassilev N, Franco I, Vassileva M, Azcon R. Improved plant growth with rock phosphate solubilized by *Aspergillus niger* grown on sugar-beet waste. Bioresource Technol. 1996;55:237-41. https://doi.org/10.1016/0960-8524(96)00008-9

Vassilev N, Mendes G, Costas M, Vassileva M. Biotechnological tools for enhancing microbial solubilization of insoluble inorganic phosphates. Geomicrobiol J. 2014;31:751-63. https://doi.org/10.1080/01490451.2013.822615

Wang H, Zhu J, Fu Q, Hong C, Hu H, Violante A. Phosphate adsorption on uncoated and humic acid-coated iron oxides. J Soils Sediments. 2016;16:1911-20. https://doi.org/10.1007/s11368-016-1383-8

Wei W, Zhang X, Cui J, Wei ZG. Interaction between low molecular weight organic acids and hydroxyapatite with different degrees of crystallinity. Colloid Surface A. 2011;392:67-75. https://doi.org/10.1016/j.colsurfa.2011.09.034

Welch SA, Taunton AE, Banfield JF. Effect of microorganisms and microbial metabolites on apatite dissolution. Geomicrobiol J. 2002;19:343-67. https://doi.org/10.1080/01490450290098414

Wichuk KM, McCartney D. Compost stability and maturity evaluation - a literature review. Can J Civil Eng. 2010;37:1505-23. https://doi.org/10.1139/L10-101

Yang F, Li G, Shi H, Wang Y. Effects of phosphogypsum and superphosphate on compost maturity and gaseous emissions during kitchen waste composting. Waste Manage. 2015;36:70-6. https://doi.org/10.1016/j.wasman.2014.11.012

Zayed G, Abdel-Motaal H. Bio-production of compost with low pH and high soluble phosphorus from sugar cane bagasse enriched with rock phosphate. World J Microb Biot. 2005;21:747-52. https://doi.org/10.1007/s11274-004-5407-y