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Physico-Chemical Properties and Phosphorus Solubilization of Organomineral Fertilizers Derived from Sewage Sludge

Andre Luiz Espinoza [1,*], Henrique Raniro [2], Camille Leite [1] and Paulo Pavinato [1]

[1] Department of Soil Science, Luiz de Queiroz College of Agriculture (Esalq), University of São Paulo (USP), Av. Pádua Dias, 11, 13418-900, Piracicaba -SP, Brazil Affiliation 1; , andreluizesp@usp.br (Espinoza, A. L. F.), camille029@gmail.com (Leite, C.N.) pavinato@usp.br (Pavinato, P.S.)

[2] Department of Crop Sciences, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Strasse 24, 3430 Tulln, Austria, henrique.rasera-raniro@boku.ac.at (Raniro, H.R.)

* andreluizesp@usp.br;.

Abstract: Sewage sludge is an organic waste generated in waste-water treatment plants with certain content of nutrients, what may potentially be used as a source of slow release fertilizer, especially as phosphorus (P) source, but it demands some pre-treatment and the content of P is much lower compared to soluble mineral fertilizers. For these reasons, composted sewage sludge was used to manufacture pelletized organomineral fertilizers, mixing it with the inorganic sources monoammonium phosphate (MAP) and AshDec® (ASD) (thermochemically incinerated sewage sludge). The fertilizers were physiochemically characterized and evaluated as to the dynamics of soil P solubilization, and the forms of P remaining according to its lability. The sources evaluated were: organic compost of sewage sludge powder (SSC), pelletized SSC (SCP), pelletized organominerals SSC+MAP (S+MAP) and SSC+ASD (S+ASD), ASD alone, all compared to a soluble mineral fertilizer (MAP), and a control without P fertilizer. A test was conducted in leaching columns with 50 g of soil (Oxisol), where the fertilizers were applied at a dose of 100 mg P/column, and 30 mL of water or 2% citric acid were added daily for 30 consecutive days. The collected leachates had pH measured and P content determined. Pelletizing process resulted in denser products and promoted more gradual P release. The organomineral S+MAP was the most water-soluble recycled source, solubilizing about 70% of the total P, while the others presented much lower solubilization (<20%). In contrast, all fertilizers showed high solubility in 2% citric acid (except for S+ASD). After leaching, the greatest amount of P remaining in the soil as labile and moderately labile. Composting and the AshDec process produced materials with slow P solubilization, which would be favoured to solubilize in acidic soils and acidic rhizosphere conditions. In turn, the organomineral mixture of SSC with a highly soluble mineral fertilizer (MAP) resulted in a promising product with intermediate nutrient solubility, better synchronized with crop demand, thus increasing efficiency in P use.

Keywords: P recycling; P bioavailability; organomineral; gradual release of P

1. Introduction

Phosphate fertilizer use is mandatory in most production areas and aims to ensure a sufficient phosphorus (P) availability for crops to complete their cycles adequately [1] Most phosphate fertilizers used in modern agriculture come from the mining of phosphate rock (PR), which is acidulated to increase the water-solubility of P. However, most PR deposits are concentrated in a few regions of the planet, generating dependence on imports, increasing production costs, and making agricultural activity vulnerable to price fluctuations in the international market [2,3].

Although P fertilization is a widespread practice, the P use efficiency is very low, being on average 50% in highly weathered soils, predominant in tropical regions such as Brazil [4]. This occurs because conventional P fertilizers are highly soluble in water, presenting a rapid P release into the soil solution. If not immediately absorbed by plant roots, the soluble P can be immobilized by the soil colloidal fraction, composed of clay minerals and Fe and Al oxyhydroxides, abundant in highly

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weathered tropical soils. Over the time, the energy of these P fixing bonds increases, becoming virtually irreversible and greatly reducing P desorption to the soil solution for plant uptake [5–8].

An alternative way to increase P use efficiency in tropical soils is to utilize slow or controlled release fertilizers in the intent to allow for a gradual P solubilization, more synchronized with plant demand. Phosphate fertilizers derived from sewage sludge (SS) are among these slow/controlled release products [9–12], and besides helping to reduce the dependence on fertilizer imports, are an option to reuse and recycle nutrients from local waste that will otherwise be mostly discarded in landfills, potentially polluting the environment.

The SS is the main residue generated in wastewater treatment plants (WWTPs), material rich in organic matter, macro and micronutrients, but of P content (5.8 and 30 g kg^{-1}) considerably lower than industrialized mineral fertilizers (80 to 240 g kg^{-1}) [3,13,14], requiring the application of huge volumes to the soil to meet crops demand. Furthermore, to enable its agricultural use, the SS must undergo pre-treatments to eliminate pathogens. Among these treatments, composting can be highlighted as an economical and efficient method to SS sanitization [15], however it does not solve the low nutrient content problem, while its bulky nature makes it difficult to transport, store, handle and apply.

The use of SS as a matrix for organomineral fertilizers can increase the nutrient concentration [16], while pelletization densifies the material, reducing its volume and delaying P solubilization, avoiding losses to the environment [17,18]. Another alternative for P recovery is via thermochemical treatments of incinerated sewage sludge ash (SSA), such as the AshDec® process, that also reduces SS volume while concentrates P and sanitizes the material [12,19–21]. The AshDec® process can increase the P solubility in citric acid from 40 to 90% in the resulting product [19], with potential agricultural use, considering that the P2O5 concentration in SSA (15-25%) is comparable to commercially exploited phosphate rocks (25-36%) [22]. The whole treatment, processing and P recovery from SS aim to improve the agronomic characteristics of the final product, creating more efficient alternatives for P use as compared to conventional fertilizers.

In this research we investigated an organic sewage sludge compost (SSC) collected from a Brazilian WWTP. Besides the raw SSC, two new organomineral phosphate sources were tailored by mixing and pelletization the SSC with mineral phosphate sources, either monoammonium phosphate (MAP) or the SSA derived AshDec® product (ASD). The products were physically and chemically characterised and submitted to a leaching trial in columns to evaluate their P solubilization dynamics, influence in solution pH and in soil accumulated P forms, while being compared to conventional MAP.

2. Materials and Methods

2.1. Raw materials

The research was developed using an organic compost generated in Brazil, provided by the Bela Vista wastewater treatment plant – Piracicaba -SP, Brazil. The AshDec® fertilizer (ASD) was provided by the German Federal Institute of Materials Research and Testing (BAM), and was obtained via the thermochemical treatment of German SSA according to the method described in Stemann et al. [23], the generated the fertilizer with chemical formula $CaNaPO_4$.

To generate the SSC, the SS was mixed in windrows with tree pruning and grass clippings as a source of structuring material. The compost pile was monitored by the São Paulo Agribusiness Technology Agency (APTA), which analysed stability and maturity parameters. The SSC final product presented the following characteristics: water content = 38.1%; total, volatile and fixed solids = 59.6, 41.9 and 17.7% respectively; electrical conductivity: 3,020 µS cm^{-1}; C = 36.2%, N = 2.6%, C/N = 13.9; CTC = 1,130.50 mmolc kg^{-1}, E. coli = 3.4x102 MPN g^{-1} TS (most probable number per gram of total solids) and absence of Salmonella sp. The observed parameters fit the Brazilian national criteria for application in soils established by the National Council Environment, Resolution 498/2020 [24].

The SSC was sieved to 4 mm and ground in a mill with a vertical rotor (Biotech - BT 608). To improve physical-chemical characteristics of the product to be used as fertilizer, the pelletization and organomineral mixing of the SSC was performed.

2.2. Organomineral fertilizers (OMF) production

By using the SSC as the organic matrix, we produced two pelletized OMF. The mineral sources used in the composition of each fertilizer were ASD and MAP, both in powder form. The proportion of the OMFs were of 70% organic compound and 30% of mineral source. In addition, the pure SSC was pelletized for comparison purposes. The solids components were mixed for 15 minutes in an adapted rotary cylindrical mixer in vertical position with a slight inclination (45°), and then moistened with water until they presented adequate consistency for pellets formation. The amount of water added per kg of dry mass corresponded to 0.45 L kg^{-1} for S+ASD, 0.35 L kg^{-1} S+MAP, and 0.95 L kg^{-1} for pure SSC.

The moistened matrix was passed through the pelletizer being pressed out through 3.4 mm openings to form the pellets. The pellet strands obtained were manually shaken to break it into smaller pellets. Those were placed in a forced circulation oven at 40 °C for 2 hours. Afterwards, the pellets were air dried for 48 hours and stored.

2.3. Physical characterization

Physical properties of recycled P sources and granulated MAP like density, humidity and resistance to compression (except for the powdered fertilizers) were evaluated in triplicates according to IFDC [25]. Bulk density (g cm^{-3}) was obtained by weighing fertilizer samples in a box of known volume and dividing the weight of the sample by the volume of the container. Humidity (%) was determined by the difference between the weight of the sample before and after drying in an oven (FANEM 330) at 65°C until reaching constant weight. The compression resistance test was performed in the Texture analyzer equipment (Brookfield CT3) by applying a load force equal to 25 kg on the fertilizers. Twenty-five pellets of similar size and granules were selected, each MAP granule and pelletized organomineral was placed individually under the platform and were pressed by a metal rod with a flattened tip, until the material being broken. The force required to fracture the fertilizer was measured and recorded by the equipment in Newton force and then converted to kilograms. In addition, the length and diameter of the fertilizers were sized with a digital caliper (Digital Caliper 150 mm).

2.4. Fertilizer P solubilization dynamics

To evaluate the P solubilization dynamics of the fertilizers in soil, a leaching column experiment was conducted under lab controlled conditions for 30 days. The soil used was collected from the 0-20 cm layer of a Latossolo Vermelho-Amarelo according to Brazilian Soil Classification System, corresponding to an Oxysol according to Soil Taxonomy[26] with sandy loam texture and low P content, according to Cantarella et al. [27], located in a pasture area in Piracicaba – SP, Brazil. The soil was air dried and sieved through a 2 mm sieve and analyzed in routine laboratory, as shown in Table 1.

Table 1. Nutrient composition of the fertilizers used as treatments sources.

pH	**O.M.**	**P**	**S**	**K**	**Ca**	**Mg**	**Al**	**H+Al**	**SB**	**CEC**	**V**	**m**
$CaCl_2$	g dm^{-3}	mg dm^{-3}		------------------------ mmol$_c$ dm^{-3} ------------------------							----- % -----	
4.6	14.0	<6	9	1	4	3	2	22	8	30	27	20
					Sand	**Silt**	**Clay**					
					---------- % ----------							
					74	9	17					

[1] O.M = organic matter; SB = sum of bases; CEC = cation exchange capacity; V = base saturation; m = Aluminum saturation.

For the experimental setup, acrylic columns with 2.1 cm internal diameter and 25 cm height, had the bottom covered with nylon fabric and were fitted to a circular plastic base with an attached hose to conduct the percolated leachate to the collecting jars (80 mL capacity) positioned below. The

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columns were placed in the vertical position on a medium density fiberboard support and filled with 50 g of soil (10 cm of soil). The soil was saturated with deionized water and then the treatments were positioned on top of the soil, with the dose of 100 mg of P per column for all sources. To avoid clogging and disturbance of the soil surface by water droplets, 10 g of glass beads at the bottom and 5 g at the top were placed in the columns.

The experimental design was completely randomized, with three repetitions, composed of the following treatments/sources: 1) powdered compost (SSC); 2) pelletized compost (SCP); 3) SSC + MAP pelletized (S+MAP); 4) SSC + AshDec® pelletized (S+ASD); 5) AshDec® powdered (ASD); 6) granulated monoammonium phosphate (MAP); and 7) control nil-P (CTR). From the total of 42 soil columns, 21 were leached with deionized water and 21 with 2% citric acid.

2.5. Sampling and analyses

A solution dosing system (300 mL) was attached on the top of each column with drip adjusted not to form a water sheet on the soil surface. The columns were watered every day for 30 consecutive days with 30 mL of deionized water or 2% citric acid solution. 24 hours after every application the leachates were collected, weighed, and pH was determined with an electronic pH meter. The leachates were stored refrigerated in test tubes until the moment of the analysis. The P content was determined colorimetrically by the blue-molybdate method [28].

At the end of the experiment, soil was collected and sectioned in the depths: 0-1, 1-2, 2-6 and 6-10 cm. Soil samples were dried in an oven at 40 °C until reach constant weight and stored to undergo P fractionation as proposed by Hedley et al. [29], with modifications by Gatiboni et al. [30]. In short, 0.5 g soil samples were submitted to sequential P extractions in the following order: anion-exchange resin (Pi), $NaHCO_3$ 0.5 mol L-1 (Pi and Po), NaOH 0.1 mol L-1 (Pi and Po), HCl 0.1 mol L-1 (Pi) and NaOH 0.5 mol L-1 (Pi and Po). Every extraction was performed by shaking samples in a Wagner Shaker (Tecnal TE-160) at 33 rpm for 16 hours, being centrifuged at 3000 rpm for 15 minutes. Inorganic P was determined in each extract by blue-molybdate method [28]. Organic P was calculated by the difference between the total P (obtained by digesting the alkaline extracts) and the inorganic P of the alkaline extracts. After all the extractions, the remaining soil was dried in an oven at 40°C until constant weight, weighed 0.1 g of dry soil and submitted to H_2SO_4 + H_2O_2 digestion, to determine residual P.

The P determined in each extractor was grouped according to the lability that corresponds to the levels of P availability to plants, being the fraction labile = resin + $NaHCO_3$, moderately labile = NaOH 0.1 + HCl and non-labile = NaOH 0.5 + residual P.

The recovered P from fertilizers was calculated according to Equation I, considering the total P to be the amount of P added via fertilizers (100 mg/column) added to the total P of the control (no P application).

$$\text{I)} \qquad \text{P recovery (\%)} = (\text{Pleach} + \text{Psoil} \quad / \text{Pctr} + \text{Pfert}) \times 100$$

where Pleach corresponds to the total P leached out of the soil column for each source of P, Psoil is the soil total P determined by fractionation, Pctr is the P leached out of the soil column plus soil total P by fractionation of the control treatment, and finally Pfert corresponds to the P added via fertilizers.

2.6. Statistical analysis

The data were submitted to normality and homogeneity tests to verify if they met the model assumptions. Analysis of variance (ANOVA) was also performed and the means that presented significant difference at 5% probability were compared by the Scott-Knott test. The analyses were performed in the R statistical software through the ExpDes.pt package.

3. Results and Discussion

3.1. Physical-chemical characterization

The chemical composition of the fertilizers used to compose each treatment is presented in Table 2. Although only 16% of the total P (0.40% of 2.46%) in SSC is water-soluble, almost 90% is soluble in 2% citric acid (HCi), which has been shown to correlate well to plant-available P by mimicking the rhizospheres' environment [31,32]. By incorporating mineral sources with higher P content (MAP and ASD) in the SSC, it was possible to increase the total P content in the organomineral sources S+MAP and S+ASD in 86% and 64% respectively.

Table 2. Nutrient composition of the fertilizers used as treatments sources.

Fertilizer	N	K_2O	Ca	Mg	Na	P_2O_5 Total	P_2O_5 H_2O	P_2O_5 HCi	P_2O_5 NaC
						%			
SSC	3.73	1.10	3.08	0.63	0.09	2.46	0.4	2.20	2.30
SCP	3.73	1.10	3.08	0.63	0.09	2.46	0.4	2.20	2.30
S+MAP	5.91	0.77	2.16	0.44	0.06	17.34	13.48	-	17.21
S+ASD	2.61	0.64	4.36	0.76	3.34	6.75	0.49	6.22	-
ASD	-	0.33	9.50	1.50	11.00	16.60	0.70	15.60	-
MAP	11.00	-	-	-		52.00	44.00	-	52.00

[2] P_2O_5 soluble in: HCi = citric acid, NAC = neutral ammonium citrate; SSC = organic sewage sludge compost; SCP = peletized organic sewage sludge compost; SSC+MAP = organic sewage sludge compost + MAP; SCC+ASD = organic sewage sludge compost + AshDec®; ASD = AshDec®; MAP = monoammonium phosphate.

The total P present in recycled products is poorly soluble in water, but almost totally soluble in 2% citric acid, and the presence of other elements can also be highlighted. Due to the mixture of SS with plant material in composting, it was possible to increase the levels of K (0.19 - 1.10%) and Ca (0.82 – 3.08%) of the SSC (Table S1). In ASD composition there are considerable quantities are the basic cations Ca and Na, which come from the addition of $CaCl_2$ and Na_2SO_4 in the thermochemical treatment of SSA, whose purposes are respectively to remove heavy metals by evaporation and to form alkaline phosphate compounds with higher bioavailability of P [22]. Although Ca is an important nutrient, in high concentrations can precipitate with P and form less bioavailable compounds [21,33], while the high content of Na is worrying, as it can salinaze the rhizosphere and inhibit plant root development [34]. Therefore part of the Na can be replaced by K in the Ashdec process [22].

The physical parameters of the fertilizers are presented in Table 3. Pelletization increased the bulk density of the pure SSC by 38% (SCP), and of the organominerals S+MAP and S+ASD by 42% and 61% respectively. These results corroborate with several authors, including Nikiema et al. [35], where palletization increased the density of products from fecal sludge by 20-50% compared to the powder form, and also Hettiarachchi et al. [36], in which pelletization of organic compost increased the density by 33-45%. Because of the mechanical pressure exerted on the pelletizing process it is possible to increase the density of composted solid wastes and thus facilitate the use of SSC. Since its bulky nature the small density is one of the impediments that decrease the demand for the product because it complicates handling, generates dust, occupies more storage space and makes transportation costly [36,37].

Table 3. Physical parameters of the waste-derived fertilizers, organomineral fertilizers and granulated MAP. Means are followed by the standard deviation.

Fertilizer	Diameter (mm)	Length (mm)	Humidity (%)	Density ($g\ cm^{-3}$)	Resistance (kg)
SSC	-	-	6.40	0.44	-
SCP	3.78±0.14	15.50±2.02	5.19	0.61	10.24±2.12
S+MAP	4.16±0.23	16.63±2.22	3.98	0.67	8.08±1.38
S+ASD	3.9±0.12	19.12±2.30	4.09	0.71	6.00±1.96
ASD	-	-	0.00	1.17	-
MAP	3.80±0.48	-	1.87	1.13	6.90±1.19

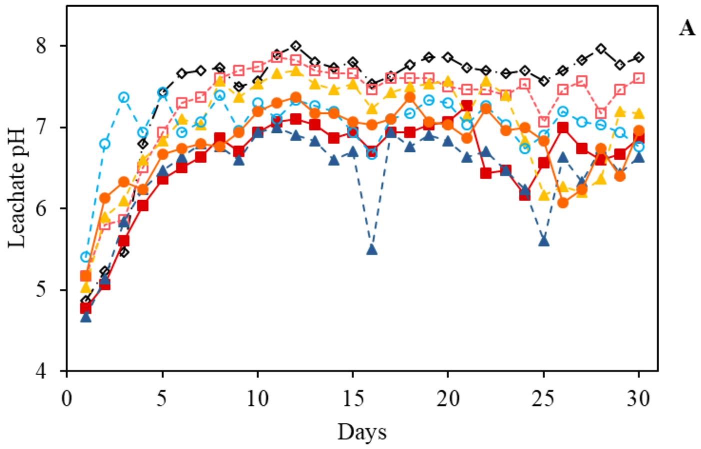
[3] SSC = organic sewage sludge compost; SCP = pelletized organic sewage sludge compost; S+MAP = organic sewage sludge compost + MAP; S+ASD= organic sewage sludge compost + AshDec®; ASD = AshDec®; MAP = monoammonium phosphate.

The importance of the pellet presenting a certain resistance to crushing is related to the maintenance of its physical integrity during transport, handling, and storage[38], therefore, the compression resistance test was performed on the pelletized fertilizers compared to granulated MAP (Table 3). The SCP pellets was the most resistant, followed by S+MAP and S+ASD wich was similar to granular MAP, signaling appropriate resistance of the pellets. These results, therefore, positively indicate that pelletize these raw materials studied using only water, could be a simple and cheapest enhancing method to be performed during the manufacturing process. Pellet formation occurs by the inter-particle bonding between solid particles in high pressure and temperature conditions [39], and substances present in SS, especially lignin and protein, act as natural bindings that favour the structuring of pellets [40,41]. Although the connection mechanisms between organic components in pellets are known, investigations into the connecting mechanisms between organic and mineral compounds are lacking, what motivated our study.

3.2. Leaching Column Experiment

3.2.1. Leachate pH values

The pH values of the leachates were monitored to relate its variations with possible reactions caused by the dissolution of fertilizers into the soil solution (Figure 1). The changes in pH values when used deionized water may have been influenced by the characteristic of factors such as soil pH, microorganisms' activity etc., rather than by the dissolution of the applied P sources. The control treatment pH was close to 5.0 at the beginning, increasing gradually until day 8 (6.8), and presented variations until the end of the incubation between 6.1 and 7.4. This same trend was also seen for all treatments, although with different amplitudes (Figure 1A).



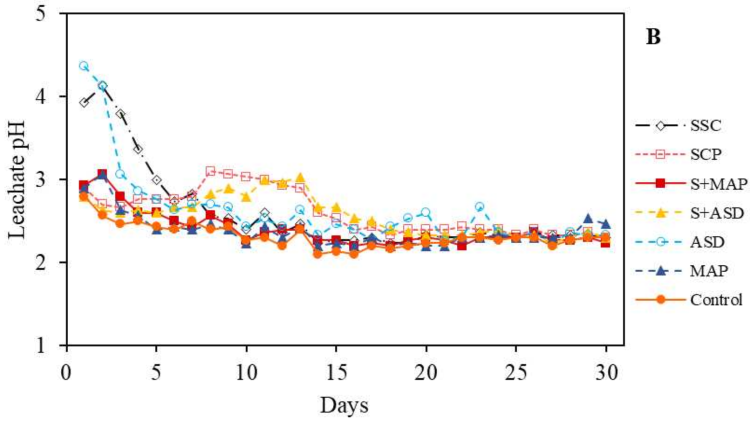


Figure 1. Daily average leachate pH under deionized water (A) and citric acid (B). SSC = organic sewage sludge compost; SCP = pelletized sludge compost; S+MAP = compost + MAP; S+ASD = compost + AshDec®; ASD = AshDec®; MAP = monoammonium phosphate; and control.

The pH variation observed initially in the treatment with S+MAP and MAP may have occurred due to the solubilization of MAP ($NH_4H_2PO_4$) and the formation of ammonium bicarbonate, a salt with high pH in solution [42]. However, it was expected that pH would decrease over time because of the dissolution of ammoniacal phosphate fertilizers, what would lead to the nitrification process of NH_4^+ that generates free acidity [43]. However, it is worth noting that the columns remained in water holding field capacity for most of the time, which may have disfavored nitrification because of the lack of oxygen. Nevertheless, the average pH value of MAP (6.4) and S+MAP (6.6) were the only ones lower than the control (6.8).

For the other treatments the average pH stabilized after 7-8 days just above the neutral value (SSC = 7.4; SCP = 7.3; S+ASD and ASD = 7.0). The SSC was the treatment with the greatest pH range (4.9 - 8.0), however a neutral/slightly alkaline pH prevailed for most of the observed time. Reports of pH increase in acidic soils due to the application of SSC are common in literature, staying in the range from neutral to slightly alkaline, due to the ammonification process that consumes H^+ and generates OH^-, however, subsequent ammonia nitrification is common, reducing it to nitrate and releasing H^+, thus acidifying the soil soon after [44]. As can be observed, the pH values of the leachate did not decrease even at the end of the trial, which may be related to the low mineralization of the organic compost in the analyzed period, on the other hand the constant leaching may have caused the removal of basic cations present in the compost, which resulted in a higher pH value of the leachate.

Under 2% citric acid leaching test there was smaller variations in pH values of the leachates over the time. This is because of the buffering capacity promoted by the percolated solution itself in the soil. The exception occurred in the first three days of leaching, where leachates from the SSC and ASD treatments were higher in the beginning, being 3.9 and 4.4 respectively, while the other treatments presented pH close to the control, 2.8 (Figure 2B). This may be due to the rapid dissolution of these sources in the citric acid solution, immediately increasing its pH. The pH ($CaCl_2$) of the SSC = 6.4 (Table S1) is a result of the composting of SS with plant material, which starts with a pH close to neutral and decreases, due to the production of organic acids and CO_2, until stabilizing due to the buffering action of humic substances formed [45,46]. The ASD, on the other hand, is a product of the mixture of phosphate with alkaline compounds ($CaNaPO_4$) with solubilization favored by the acidification of the medium [22]. However, from the sixth day and so on these two treatments stabilized the pH to values similar to other treatments (~2.5).

It is also noted that there were peaks in pH values of the SSC (3.1) and S+ASD (3.0) leachates between the 8th and the 13th day, in contrast to what occurred with the raw material of these powdered and non-pelletized sources, SSC and ASD. This observed trend reinforces the idea that the elements present in the pellet are protected and therefore solubilization is slower [16].

3.2.2. Fertilizer P solubilization dynamics

There was greater solubilization of P from recycled fertilizers when leached with 2% citric acid than with water (Figure 2), which was expected since most P in these sources is poorly water-soluble and almost totally soluble in citric acid (Table 1). When leached by deionized water treatments with MAP presented high P solubility, with similarity behavior between MAP and S+MAP, since both solubilized more than 50% of the P in 5 days (Figure 2A). The total leached P (Figure 2C) was highest in MAP (84 mg column^{-1}), followed by the organomineral S+MAP (73 mg column^{-1}), while the other sources solubilized little during the incubation period, not exceeding 20% of the applied dose (100 mg column^{-1}). This shows that the mixture of the low water-solubility SSC with a high soluble inorganic fertilizer resulted in a product that is able to release P into the soil within a short time after application.

Since MAP is an acidulated phosphate fertilizer with high water-solubility, it is rapidly available in the soil solution [3], the expected benefit of mixing such a fertilizer with a less soluble organic one is to better synchronize the availability of P with crop demand. The P from the mineral fertilizer is immediately available in the solution, supplying the demand in the early growth stages of the crop, while the P from the organic source is solubilized slowly, as the organic compounds are mineralized, meeting plants needs in later stages and potentially even being available for subsequent crops [16].

Most of the recycled sources evaluated here presented very small solubility in water (Figure 2B) but were highly soluble in citric acid (Figure 2D), where more than 85% of the applied P was leached, with the exception of the organomineral S+ASD that solubilized only 42% of the applied P. If only the water-solubility of recycled products are considered for their use as fertilizers, the agronomic potential of most would be underestimated. For example, Raniro et al. [47] observed that the poorly water-soluble ASD promoted dry biomass production of sugarcane equivalent to triple superphosphate, a high water-soluble P source. For this reason, considering the solubility of fertilizers in citric acid (organic acid synthesized and exuded by plants roots) may decrease the chance of misinterpretations related to low water-solubility of P and availability of P to crops. Furthermore, to ensure a complete picture of the agronomic potential of alternative sources, this type of study should be related to plant experiments.

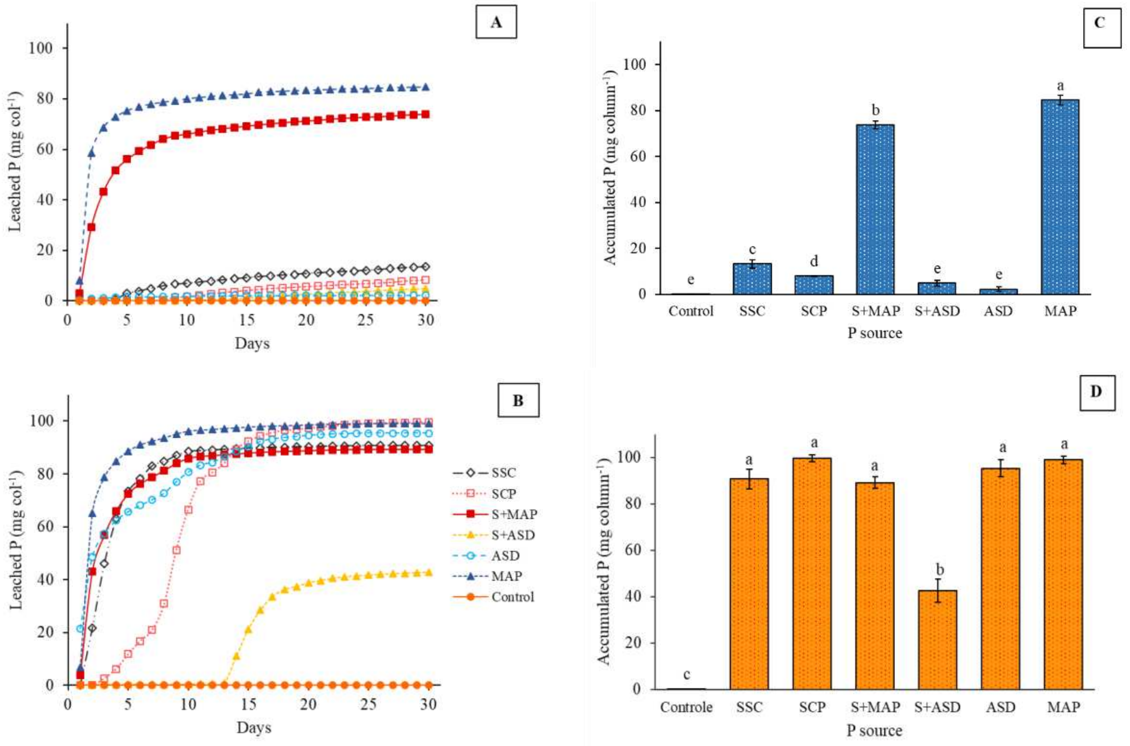


Figure 2. Accumulated daily P leached with water (A) and citric acid (B). Total P leached in water (C) and citric acid (D) in 30 days. Equal letters do not differ statistically according to the Scott-Knott test

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at 5% significance level. Error bars represent standard error of the means (n=3). SSC = organic sewage sludge compost; SCP = pelletized sludge compost; S+MAP = compost + MAP; S+ASD = compost + AshDec®; ASD = AshDec®; MAP = monoammonium phosphate; and control.

Although the total P leached in 2% citric acid was not significantly different between the recycled sources and MAP, with the exception of S+ASD, the P solubilization rate was distinct. SCP and ASD showed less pronounced curves of solubilized P, indicating slower and more gradual dissolution. SSC, S+MAP and MAP had most of their P solubilized in the first days, while S+ASD solubilized P only from the 14th day and forward.

The S+ASD treatment solubilized less P than its individual components (SCP and ASD), indicating that the pelletized mixture left the product more recalcitrant and impaired the release of P from the pellet. It was also found that the physical form modified the dissolution dynamics of the fertilizer in soil, as SSC (powder) compared to its pelletized form (SCP) solubilized more P in water and had faster initial solubilization in citric acid, which is expected due to the pellet having less specific surface area, which reduces the reactivity of the material and causes slower nutrient release [48].

Soluble phosphate fertilizers rapidly release P into the soil solution, which can be taken up by plants, shift to less labile forms through specific and nonspecific adsorption reactions with the surface of minerals or precipitate with cations ([49]. In weathered soils, where Fe and Al oxides are predominant, sorption reactions are more rapid and intense, becoming practically irreversible as P remains in the soil [7,50]. Therefore, part of the P applied via fertilizer can be immobilized in the soil, decreasing the efficiency of fertilization by reducing P bioavailability in later stages of crop development.

In order to meet the P demand of the plant during its cycle, slow release fertilizers are alternatives for supplying P in the long term, capable of making P available in a more synchronized manner with plant development, and thus avoiding environmental losses. In the initial phases, the plant does not yet have a well-developed root system, so if most of the P applied is made available immediately, little will be absorbed and most of it may be lost by surface runoff, leaching and/or erosion processes, or else reduce its lability in the soil and bioavailability at later plants stages[11,33].

3.2.3. Soil lability

Most of the remaining P in the soil from the water leached columns was found in the labile and moderately labile pools in the 0-1 cm layer (Figure 3). This is indicative that these fertilizers solubilized P very slowly or even not solubilized, making the nutrient being accumulated at the application site. The slow release of P from fertilizers is one way to avoid losses to the environment (which decreases fertilizer efficiency) either by immobilization in the soil through sorption, making P less available to plants [43], or by leaching [51].

The ASD and S+ASD were the sources that increased total soil surface P the most: 9,778 and 1,479 mg kg^{-1} respectively, with expressive amount in the labile fraction extracted with bicarbonate (Table S4). The labile P pool is the one in osmotic equilibrium with the soil solution, that is, it is more easily replaced either by mineralization of organic P or desorption of inorganic P [5,47], what demonstrates that these fertilizers are capable of increasing available soil P as they solubilize over several days after application. Despite the high soil P concentration with S+ASD, only 18.3% of the applied P was recovered, indicating that most of it remained in the pellet (Table 4).

Most of the soil P with ASD was found in the moderately labile pool (7.774,7 mg kg^{-1}) extracted by HCl (Table S2), usually associated with desorption of Ca-bound P forms [52]. The formation of P-Ca under ASD may have been favoured due to the high concentration of basic cations in this source. At high P and Ca concentrations, it may precipitate forming poorly water-soluble minerals, which can solubilize in acidic conditions such as that of the rhizosphere [53]. Furthermore, high moderately labile P values in the 0-1 cm layer under ASD could have partially come from fertilizer that was not completely dissolved, being sampled along with the soil, as supported by Nanzer et al. [54], who

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reported that the P in different thermochemically treated ashes were mostly in the forms of chloroapatite or hydroxyapatite, and 90% could be extracted by HCl.

The moderately labile pool plays an important role as a source of P to the soil, as it keeps the solution P levels in equilibrium when the supplement of available P via fertilizer is insufficient to sustain plant growth. In fact, all less labile forms of P can function as a buffer in the soil when the P exported by crops exceeds the P content in solution. Intermediate labile P fractions can switch to more labile forms in order to maintain equilibrium, however it may not solubilize as quickly as required by some crops [5,51,53].

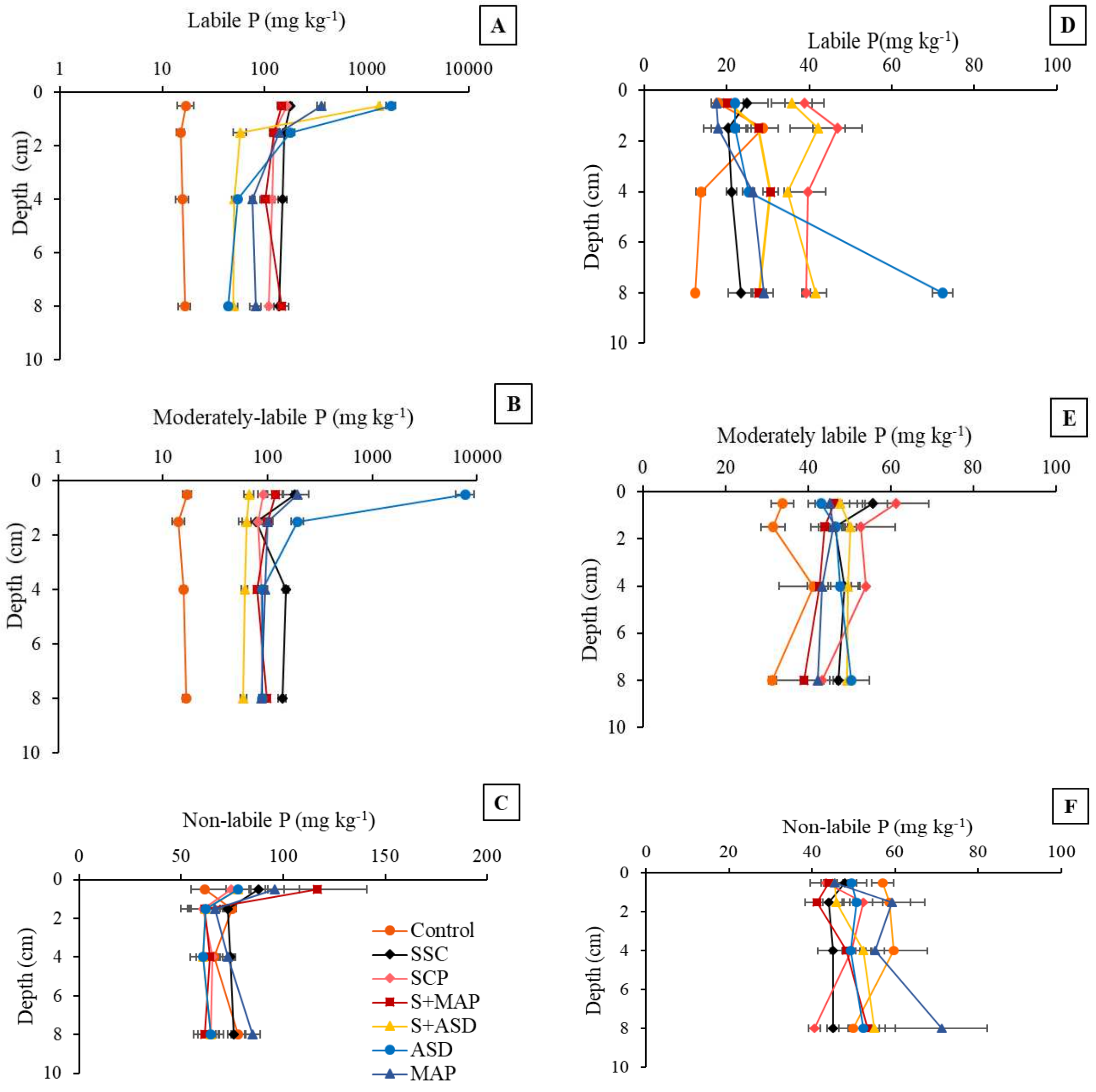

Figure 3. Soil P pools obtained by the soil fractionation method from columns leached with water (A, B, C) and citric acid (D, E, F), grouped by lability. Equal letters do not differ statistically according to the Scott-Knott test at 5% significance level. Error bars represent standard error of the means (n=3). SSC = organic sewage sludge compost; SCP = pelletized sludge compost; S+MAP = compost + MAP; S+ASD = compost + AshDec®; ASD = AshDec®; MAP = monoammonium phosphate; and control.

Under low available P conditions, plants may adopt some strategies to access more stable forms in the soil, such as increasing root system, association with microorganisms, release of phosphatase enzymes, and increasing the exudation of organic acids in rhizosphere [55]. Almeida et al. [56] found that tropical grass species such as Urochloa ruziziensis release more organic acids (citric, malic and lactic) in the rhizosphere under deficiency conditions than in P sufficiency. For this reason, plants that exude more organic acids are more likely to benefit from phosphate fertilization from slow-release sources. This was evident in the research of Talboys et al. [11], where the species that exudes more organic acids (Fagopyrum esculentum), was able to absorb more P than the species that exudes less (Triticum aestivum).

As for the recovery of P applied via fertilizers, in the treatments with S+MAP and MAP the amount of P remaining in the soil smaller than the others, because much of the solubilized P was leached out of the soil columns carried by water percolation. However, even so, the amount of P remaining in the soil was similar to SSC and SCP sources. In the latter two there was almost no dissolution of the fertilizers, as can be seen when calculated the P balance (Table 4), where only 29% (SSC) and 20% (SCP) of the applied P was recovered in the leachate or in the soil. The non-recovered part was supposedly kept in fertilizer pellets yet. Although much of the P in SSC is inorganic in nature, it does not mean that they are in readily available forms [9]. According to O'Connor et al. [57], high concentrations of Fe and Al (10-30 g kg-1) in biosolids can reduce P bioavailability, as may have occurred to SSC and SCP, and their low P solubilization is consequence of the high Fe concentration (13 g kg-1) found (Table S1).

Table 4. Percentage of P leached out and the soil accumulated labile, moderately labile, and non-labile P pools, and Recovered P relative to the total P originally in the soil + applied P dose.

Treatment	Leached P	Labile P	Moderately labile P	Non-labile P	Recovered P
		---------------------------------	(%)	-------------------------------	
			Leaching with deionized water		
Control	1.9	12.3	31.3	54.5	100.0
SSC	42.7	23.8	21.5	12.0	29.0
SCP	36.9	27.6	20.5	15.1	20.2
S+MAP	84.1	7.1	5.1	3.7	82.3
S+ASD	24.5	43.3	15.4	16.3	18.5
ASD	3.5	19.0	69.4	8.0	60.3
MAP	85.2	5.7	5.1	4.0	93.2
			Leaching with deionized citric acid		
Control	0.2	14.4	33.4	52.0	100.0
SSC	94.0	1.2	2.5	2.3	91.7
SCP	94.0	1.8	2.2	2.0	100.7
S+MAP	91.9	3.6	2.1	2.5	90.2
S+ASD	85.9	3.9	5.0	5.3	47.3
ASD	92.8	2.2	2.4	2.6	97.7
MAP	93.9	1.2	2.0	2.9	100.1

[4] SSC = organic sewage sludge compost; SCP = pelletized organic sewage sludge compost; S+MAP = organic sewage sludge compost + MAP; S+ASD= organic sewage sludge compost + AshDec®; ASD = AshDec®; MAP = monoammonium phosphate.

Regarding to the balance of P under 2% citric acid, most of the applied P leached out for all P sources (>85%), so there was minimal P remaining from fertilizer (<15%) in the soil (Table 4). Overall, the distribution of the soil P pools did not show large variations. The difference was small between the sources in the moderately labile and non-labile pools, but in the labile pool the source ASD promoted more P in the 6-10 cm layer (Figure 3), indicating that there was movement of P in the soil profile when in contact with citric acid. The presence of P far from the application site indicates that there was P displacement in the soil, but perhaps with longer duration of the experiment, this labile P would move deeply in the soil profile until it completely leaves the column system.

The fact that the sources SCC, SCP, ASD and S+ASD solubilized P in citric acid, even though they are slightly soluble in water, indicates that they are capable of supplying P to plants in such environments with low P availability. Plants use some mechanisms to mobilize and absorb the recalcitrant P, by increasing the rooting system, excrete acid phosphatases, associate with mycorrhizal fungi and exudate organic acids, including citric acid [58]. For these reasons, in addition to fertilizer solubility, plant and soil types are important factors to consider in managing soil nutrients with recycled sources. Based on the results presented, it can be inferred that sources that are poorly soluble in water, such as SCC, SCP, ASD and C+ASD, would be more suitable for the cultivation of crops with a longer cycle, with the solubilization of ASD and S+ASD being favoured in acidic environments, while SSC and SSP will depend on OM mineralization. On the contrary, OMF formed by S+MAP, which mixes sources of high and low solubility of P, has the potential to serve short-cycle crops, as it supplies P immediately and also gradually in the soil. Although these inferences can be made only after knowing the solubilization dynamics of the sources, their potential as a fertilizer must be more investigated in studies when plants are actively growing and extracting nutrients from soil solution.

4. Conclusions

Organic compost of sewage sludge proved to be in accordance with the norms for agricultural use according to brazilian normative instruction 61 [59]. By mixing the organic compost with monoammonium phosphate (MAP) it was generated a fertilizer (C+MAP) with high P content and good water solubility with good agricultural potential.

Pelletizing of the organic compost and organominerals using only water as a binding agent resulted in pellets with very suitable qualities for agricultural purpose. This indicates the feasibility of producing pellets with a relatively simple and low-cost process. Furthermore, the pelletized form of the fertilizers promoted slower release of P into the soil relative to mineral granular and organic powdered forms.

The fertilizers derived from sewage sludge presented low solubility in water, however they were highly soluble in citric acid, indicating that in acidic soil conditions, or through acidification by plant rhizosphere, this P may turn available in a feasible time for utilization by crops. Moreover, most of the P remaining in the soil from organic compost sources was found in the labile and moderately labile fractions, reinforcing the idea that these sources may have the ability to make P available in the medium to long term.

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