Agronomic Efficiency of Biochar-Based Organophosphate Fertilizers

Ronaldo Willian da Silva, Renato Ribeiro Passos,* Mateus Hastenreiter Rodrigues Silva Loquez, Felipe Vaz Andrade, Danilo Andrade Santos, Otacílio José Passos Rangel, and Eduardo de Sá Mendonça

ABSTRACT: The development of fertilizers with integrated protection has been proposed to increase the efficiency of phosphate fertilization. The aim of this work was to evaluate the efficiency of organophosphate fertilizers produced with biochars, made from coffee straw (CSB), poultry litter (PLB), and eucalyptus bark (EBB), in coating mode and homogeneous mixture, comparing them to triple superphosphate (TSP). The treatments were with three biochars that make up the fertilizers (CSB, PLB, and EBB), two methods of fertilizer preparation (homogeneous mixture and coating), and three proportions of biochar/TSP in the composition of the fertilizers (10, 20, and 30%). A dose of 30.5 kg ha^{-1} of P was applied to a Red-Yellow Latosol, and the cultivation of maize was defined as the test plant. Compared with TSP, biochar-based organophosphate fertilizers showed greater agronomic efficiency (10.8%), P recovery (2.4%), and greater P availability after harvest (11.6 mg kg^{-1}). PLB-based fertilizers stood out among the highest agronomic efficiency means and P recovery, in addition to presenting a greater amount of P available in the soil after harvest (31.94%). The fertilizers produced in the coating mode promoted the greatest P availability in the soil (5.1%). However, regarding the agronomic efficiency and P recovery, only fertilizers produced from EBB differed from each other, with fertilizers produced in coating mode showing higher means (111.4 and 29.8%, respectively). Our findings suggest that the 30% biochar/TSP ratio was most effective in enhancing soil P availability and plant uptake, while also extending the residual effect of P in the soil.

KEYWORDS: *phosphate fertilization, biochar, protected fertilizers, plant nutrition*

1. INTRODUCTION

Phosphorus is one of the most limiting nutrients for biomass productivity in tropical soils, in which less than 0.1% of P is found in solution,[1,2] particularly in highly weathered soils with high adsorption capacity on mineral surfaces of Fe and Al oxides and hydroxides.[2] The surface functional groups found on these minerals (-AlOH, -FeOH) exhibit a strong chemical affinity toward orthophosphate. This results in the formation of high-energy coordinate bonds and rapid, nonreversible reactions.[3] Consequently, when highly water-soluble phosphate fertilizers are applied under such conditions, a significant portion of phosphorus becomes inaccessible to plants. This leads to poor phosphorus uptake by plants and inefficient phosphate fertilization.[4] Therefore, heavy doses of phosphorus fertilization are required to maintain crop productivity, escalating production expenses and diminishing the efficacy of phosphate rock utilization. It is noteworthy that phosphate rock is a finite and nonrenewable resource.[5]

Given the low efficiency of phosphate fertilization in humid tropical conditions, the use of technologies has been employed to produce fertilizers that promote the best use of P.[4] These fertilizers with integrated protection, also called "smart fertilizers," reduce the interaction of P with soil constituents by promoting its release slowly or gradually.[4,5]

Phosphate fertilizers with integrated protection have been produced by coating or mixing with various materials, including polymers,[6,7] organic acids,[4] and organic waste.[5,8] Increases in agronomic efficiency were obtained with the use of protected fertilizers.[4,7,9] However, these improvements are

dependent on a set of factors, such as the type of fertilizer preparation, the soil, and the crop used, and there may also be no difference compared to mineral fertilization.[5,8,10]

Recently, the production of biochar-based organomineral phosphate fertilizers has also been proposed, which are produced from the carbonization of organic waste.[11,12] Compared to high-solubility mineral sources of P, these fertilizers have shown higher P availability in the soil[12] and higher agronomic efficiency in the cultivation of Marandu grass.[11] However, to date, the production of these fertilizers has been limited to the impregnation of these materials with mineral P sources before or after pyrolysis, and their testing has been limited to controlled environments (laboratory or greenhouse).

Biochar is indicated as a soil conditioner and may improve chemical, physical, and biological attributes, in addition to increasing carbon stock.[13] Several studies have shown that biochars may increase P availability in highly weathered soils.[14−16] However, on average, the biochar application at 15 t ha^{-1} in tropical soils is usually required to improve crop yield,[17] which is unfeasible on a large scale due to the high

cost. Studies have shown that the combination of triple superphosphate (TSP) with biochar derived from organic residues can enhance phosphorus availability through controlled release, potentially offering a cost-effective solution for tropical soils.[18] On the other hand, combining biochar with soluble phosphate fertilizers is a promising strategy for increasing the efficiency of P use, allowing the gradual application of biochar to the soil and being an environmentally friendly way of using biomass.

In this study, it is hypothesized that biochar-based phosphate fertilizers and triple superphosphate (TSP) produced by the research group, herein called organophosphate fertilizers, increase the availability of P in the soil and promote greater efficiency in P uptake by plants. This study builds on previous laboratory findings of da Silva et al.,[18] expanding into field conditions to evaluate the practical efficiency of biochar-based fertilizers in maize cultivation. The aim of this work was to evaluate the efficiency of organophosphate fertilizers produced from biochars made with coffee straw (CSB), poultry litter (PLB), and eucalyptus bark (EBB) in coating and homogeneous mixture mode in maize cultivation under field conditions.

2. MATERIALS AND METHODS

2.1. Experimental Design and Treatments. The treatments were arranged in a randomized block design, with four replications, in a $3 \times 2 \times 3$ factorial scheme, with the following factors: three biochars that compose the fertilizers produced with *conilon* coffee straw (CSB), poultry litter (PLB), and eucalyptus bark (EBB); two methods of preparing fertilizers (homogeneous mixture and coating); and three proportions of biochar in the fertilizer (10, 20, and 30% w/w). Two control treatments were also conducted: one with triple superphosphate (TSP) (positive control) and one treatment without P application (negative control).

2.2. Fertilizer Production and Characteristics. The organic bases of the organophosphate fertilizers were biochars produced with *conilon* coffee straw, poultry litter, and eucalyptus bark, which were air-dried until they had a moisture content between 11 and 12%. The biochars were produced by the slow pyrolysis process at 400 °C, with a residence time of 60 min at these temperatures. Pyrolysis was conducted in a metal reactor, model SPPT-V60, with a heating rate of 6 °C min^{-1}, in an inert gas atmosphere (N$_2$) and with a gas condenser with continuous water flow. The material produced was passed through a 0.250 mm sieve, and characterization analyses were subsequently performed (Table 1).

To produce organophosphate fertilizers, the biochars CSB, PLB, and EBB were added to a P source (triple superphosphate − TSP) of two forms (coating and homogeneous mixture) and four biochar/TSP ratios (10, 20, 30, and 40%) on a mass basis. The TSP and the biochars were ground and passed through a 250 μm (60 mesh) sieve for the formulation of fertilizers in the homogeneous mixture mode. The TSP and powdered biochar were added in an inclined rotary granulator (45°), using a rotation of about 50 rpm, with a sucrose solution (20%) as the binder, which was sprayed on the mixture during granulation. To prepare the coated fertilizers, TSP granules of 2−3 mm were selected and inserted into the working granulator, and the biochar was gradually added at the same time as the sucrose solution was sprayed. After preparation, the granules were dried in a forced air circulation oven at 45 °C until constant weight (72 h). Then, the granules were standardized by particle size separation (2.00−4.00 mm) and characterized for P content and pH (Table 2) according to the methodology proposed for organomineral fertilizers.[24]

2.3. Experimental Area. The experiment was carried out under field conditions in the experimental area of the Instituto Federal do Espírito Santo (IFES), located in the district of Rive, municipality of Alegre (20°45′40″ S and 41°29′8″ W), southern region of the State of

Table 1. Characterization of Coffee Straw (CSB), Poultry Litter (PLB), and Eucalyptus Bark (EEB) Biochars[a]

characteristics	CSB	PLB	EBB
C (%)	55.36	47.72	50.73
H (%)	3.83	1.99	3.30
N (%)	1.18	3.01	0.08
O (%)	29.31	2.69	36.65
AS (%)	10.32	44.59	9.24
pH (H$_2$O)	9.70	10.40	9.13
P (g kg^{-1})	3.82	18.57	2.12
K (g kg^{-1})	76.13	40.42	7.78
Ca (g kg^{-1})	4.37	37.07	8.34
Mg (g kg^{-1})	3.67	9.53	4.37
Na (g kg^{-1})	2.17	8.79	4.79
CEC (cmol$_c$ kg^{-1})	65.43	36.60	33.03
WDPT (s)	1137	615	884

[a]Carbon (C), hydrogen (H), and nitrogen (N) were determined by the ignition method with a PerkinElmer Series II 2400 Elemental Analyzer, and oxygen (O) was calculated by difference (O = 100 − C − H − N − ashes). Ashes (AS): by muffle incineration;[19] pH in water;[20] total levels of P, K, Ca, Mg, and Na by digestion with nitric and perchloric acids;[21] cation exchange capacity (CEC) by the sodium acetate−ammonium acetate exchange method at pH 7.0;[22] WDPT: water drop penetration time.[23]

Espírito Santo. The predominant climate of the region, according to Koppen's classification, is Cwa, characterized by the irregular distribution of rainfall throughout the year, with rainy summers and dry winters, an average annual temperature of 23.1 °C, and an average annual rainfall of 1341 mm.[25]

Data on maximum and minimum temperatures and rainfall during the experimental period were collected at a meteorological station located in the experimental area (Figure 1).

The soil of the experimental area is a medium-textured Red-Yellow Latosol, which, before planting, was characterized at a depth of 0− 0.20 m (Table 3).

2.4. Assembly and Conduction of the Experiment. Soil preparation was done by minimum tillage with light harrowing and furrowing at about a 0.10 m depth and 0.80 m width between furrows for fertilization and planting.

The procedures for soil correction and fertilization were carried out according to Prezotti et al.[28] for maize cultivation. According to the results of the soil analysis (Table 3), it was not necessary to correct the soil acidity. For planting fertilization, 15 kg ha^{-1} of N (Urea), 41.5 kg ha^{-1} of K (KCl), and 30.5 kg ha^{-1} of P were applied to the bottom of the planting furrows. The amount applied from each P source was calculated based on the total P content of the fertilizers (Table 2).

The plots consisted of four maize rows with 4 m lengths and spaced 0.80 m apart. The two central lines were taken as the useful area of the plots, with 1 m from the edges of each row.

After fertilizer distribution, the furrows were covered, and a simple hybrid maize Foreseed 2B587, genetically modified with PowerCore technology, was planted. The plant density was ten seeds per meter of furrow, with subsequent thinning 7 days after germination, leaving five plants per linear meter.

Topdressing manuring was carried out using 100 kg ha^{-1} of nitrogen (Urea), parceled out at 15, 30, and 45 days after germination, and 41.5 kg ha^{-1} of K (KCl) was applied at 30 days. Fertilizers were applied adjacent to the rows of the plants. Weed control was performed by hand weeding 15 days after planting and application of glyphosate 35 days after planting.

Complementary sprinkler irrigation was carried out with an irrigation shift every 2 days and irrigation depth according to the needs of the crop, which was established using the irrigameter technology installed next to the experimental area.

2.5. Experimental Evaluations. At the time of harvest, at 140 days after planting, the plants were cut two centimeters from the soil,

Table 2. P Content and pH of Fertilizers Based on Biochar from Coffee Straw (CSB), Poultry Litter (PLB), and Eucalyptus Bark (EBB), and on Triple Superphosphate (TSP)[a]

biochar	preparation method	BC proportion (%)	abbbreviation	pH	P (%)		
					H_2O	$NAC+H_2O$	total
CSB	coating	10	CSBC10	3.01	13.5	14.2	18.4
CSB	coating	20	CSBC20	3.13	12.5	13.0	16.5
CSB	coating	30	CSBC30	3.38	9.9	11.2	14.5
CSB	mixture	10	CSBM10	2.93	13.0	14.4	18.3
CSB	mixture	20	CSBM20	3.02	11.8	13.7	16.5
CSB	mixture	30	CSBM30	3.15	10.1	12.6	14.5
PLB	coating	10	PLBC10	2.98	10.2	14.5	19.1
PLB	coating	20	PLBC20	3.35	6.9	12.7	17.2
PLB	coating	30	PLBC30	3.59	6.9	11.8	15.6
PLB	mixture	10	PLBM10	2.95	14.3	15.1	19.1
PLB	mixture	20	PLBM20	2.99	11.0	13.8	17.3
PLB	mixture	30	PLBM30	3.15	8.4	12.6	15.4
EBB	coating	10	EBBC10	2.99	14.2	15.2	18.3
EBB	coating	20	EBBC20	3.06	11.8	13.3	16.3
EBB	coating	30	EBBC30	3.11	10.6	11.3	14.2
EBB	mixture	10	EBBM10	2.95	14.1	15.1	18.2
EBB	mixture	20	EBBM20	3.01	12.6	13.0	16.2
EBB	mixture	30	EBBM30	3.07	9.3	11.1	14.2
TSP			TSP	2.90	16.5	18.5	20.3

[a]BC: biochar; P soluble in water (H_2O); neutral ammonium citrate ($NAC+H_2O$) and total (nitro-perchloric, ratio 1:4 $HClO_4/HNO_3$), and pH in $CaCl_2$ 0.01 M.[24]
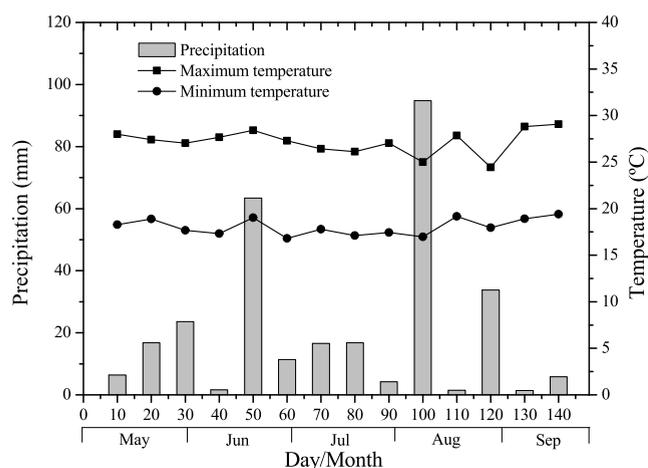

Figure 1. Mean maximum and minimum air temperature and accumulated precipitation recorded during the experiment in the district of Rive, municipality of Alegre, State of Espírito Santo, Brazil.

taking the mass of the aerial part (except grains) and, subsequently, of the grains to determine the yield. Samples of the grains were taken to determine the P concentration.[29] This analysis was also performed on samples of leaves + culm + tassel + stover and cob. Once the P contents and dry mass of the different parts of the plant were obtained, the respective P contents were calculated.

The agronomic efficiency of fertilizers for grain production was evaluated using TSP as a reference for the application of the formula (Novais and Smyth[3])

$$AE\ (\%) = \frac{fertilizer - control}{TSP - control} \times 100$$

where: AE = agronomic efficiency of the fertilizer; fertilizer = dry matter production with the fertilizer of interest (kg ha^{-1}); TSP = dry matter production with triple superphosphate (kg ha^{-1}); Control = dry matter production with the control treatment without the addition of P (kg ha^{-1}).

Table 3. Chemical and Physical Attributes of the Red-Yellow Latosol

soil attributes	values
pH (H_2O)[a]	5.96
phosphorus (mg kg^{-1})[b]	3.89
remaining phosphorus (mg L^{-1})	32.60
potassium (mg kg^{-1})[b]	51.09
sodium (mg kg^{-1})[b]	0.0
calcium (cmol$_c$ kg^{-1})[c]	2.66
magnesium (cmol$_c$ kg^{-1})[c]	0.73
aluminum (cmol$_c$ kg^{-1})[c]	0.0
hydrogen + aluminum (cmol$_c$ kg^{-1})[d,e]	2.14
CEC (cmol$_c$ kg^{-1})[d,e]	6.15
sand (%)[f]	62
silt (%)[f]	10
clay (%)[f]	28
total organic carbon (g/kg)[g]	10.7

[a]Soil-to-water ratio 1:2.5. [b]Mehlich-1 extractor. [c]Extraction with potassium chloride (KCl) 1 mol L^{-1}. [d]Extraction with calcium acetate 0.5 mol L^{-1} pH 7.0. [e]Cation exchange capacity. [f]Pipette method by slow stirring and remaining phosphorus.[26] [g]Total organic carbon.[27]

In addition, the P recovery rate was evaluated according to the following equation

$$RR\ (\%) = \frac{P\ exported - P\ control}{P\ applied} \times 100$$

where: RR = P recovery rate; P exported = P exported by harvesting the aerial part of the plants (kg ha^{-1}); P control = P obtained from the control treatment (kg ha^{-1}); and P applied = applied P content (kg ha^{-1}).

After harvest, eight soil subsamples were collected in the experiment at a depth of 0−0.10 m, adjacent to the planting row. The subsamples were thoroughly mixed to obtain a composite sample, which was oven-dried at 50 °C for 48 h and then sieved (2 mm). The

P in the soil was extracted with water and Mehlich-1 at a soil/solution ratio of $1/10$[26] and determined by colorimetry.[30]

The data set was subjected to analysis of variance using the F-test ($p \leq 0.05$). When significant effects were verified, Tukey's test was applied at 5% significance. The mean of the other treatments was compared to the control treatment (TSP) with the comparison of means by orthogonal contrast[31] tested by the F-test at a 5% probability level.

3. RESULTS

For all parameters evaluated, there were no triple interaction effects among the factors biochar used in the fertilizer, method of fertilizer preparation, and proportion of biochar in the fertilizer. Therefore, the results for the interactions among biochars and fertilizer preparation and the interactions among biochars and the proportion of biochar in fertilizer are presented.

3.1. Maize Yield and Agronomic Efficiency of Fertilizers.
Among the means of organophosphate treatments, TSP provided a lower yield of 169.9 kg of ha^{-1}. This represents an agronomic efficiency (AE) of 10.8% lower than the mean of organophosphate fertilizers (Table 4).

Table 4. Maize Yield and Agronomic Efficiency (AE) of Phosphate Fertilization Regardless of Biochar/TSP Proportions in Fertilizer[a]

source of P	productivity (kg ha^{-1})		AE (%)	
	coating	mixture	coating	mixture
CSB+TSP	10,972.4 Ba	10,941.3 Ba	110.1 Ba	108.1 Ba
PLB+TSP	11,064.3 Aa	11,062.6 Aa	115.9 Aa	115.8 Aa
EBB+TSP	10,993.4 Ba	10,872.5 Bb	111.4 ABa	103.7 Bb
TSP	10,814.5$^{(-169.9b)}$		100$^{(10.8b)}$	

[a]Means followed by the same uppercase letter for columns and lowercase for rows did not differ statistically from each other (Tukey, $p > 0.05$). (n): TSP contrast estimation vs ((CSB+TSP) + (PLB+TSP) + (EBB+TSP)) (3+, ---). [b]The mean of the control treatment differs from the mean of the factorial treatment (F-test, $p \leq 0.01$).

Regardless of the biochar/TSP ratio, fertilizers produced from PLB promoted higher grain yield and AE. These fertilizers promoted an average production of 11,064.3 kg ha^{-1}, reaching an AE 15.9% higher than the TSP (Table 4). Regarding the method of preparation, significant differences were verified for fertilizers produced from EEB, in which the preparation method in coating provided a higher yield of 120.9 kg ha^{-1} than the mixture method, which corresponds to a 7.7% higher AE.

Regardless of the method of fertilizer preparation, there was only difference between fertilizers in the proportion of 30%, where the PLB-based fertilizer produced a yield of 11,189.3 kg ha^{-1} and an AE 23.9% higher than the TSP (Table 5). In general, the fertilizers produced in the proportion of 30% biochar/TSP provided higher productivity and AE.

Fertilizers produced from PLB showed lower water solubility, and increasing the proportion of biochar/TSP reduced the solubility of the fertilizer in water (Table 2).

3.2. Absorption.
The P extraction data, corresponding to the sum of the P contents of the aerial parts, ears, and grains, showed a close relationship with the nutrient export. The grain was the destination for most (84%, on average) of the P absorbed.

Table 5. Maize Yield and Agronomic Efficiency (AE) of Phosphate Fertilization Regardless of Fertilizer Preparation Method[a]

source of P	biochar/TSP ratio (%)		
	10	20	30
	Productivity (kg/ha^{-1})		
CSB+TSP	10,909.5 Aa	10,957.1 Aa	11,004.0 Ba
PLB+TSP	10,965.6 Ab	11,035.4 Ab	11,189.3 Aa
EBB+TSP	10,868.9 Ab	10,940.0 Aab	10,990.0 Ba
	AE (%)		
CSB+TSP	106.1 Aa	109.1 Aa	112.1 Ba
PLB+TSP	109.6 Ab	114.1 Ab	123.9 Aa
EBB+TSP	103.5 Ab	108.0 Aab	111.2 Ba

[a]Means followed by the same uppercase letter for columns and lowercase for rows did not differ statistically from each other (Tukey, $p > 0.05$).

The TSP showed a P extraction and export of 0.99 and 0.63 kg ha^{-1}, respectively, lower than the mean of organophosphate fertilizers (Table 6). Consequently, the P recovery from the TSP (27.2%) was 2.39% lower than the mean of organophosphate fertilizers, presenting a lower yield.

Table 6. Concentration of P in the Vegetal Part, Export in the Grain, and Recovery Rate of P from the Fertilizer by the Maize, Regardless of the Proportions of Biochar/TSP in the Fertilizer[a]

source of P	how to prepare the fertilizer	
	coating	mixture
	P Extraction (kg ha^{-1})	
CSB+TSP	39.4 Aa	39.4 Ba
PLB+TSP	39.6 Aa	39.8 Aa
EBB+TSP	39.6 Aa	39.1 Bb
TSP	38.5$^{(-0.99b)}$	
	Export of P (kg ha^{-1})	
CSB+TSP	33.1 Aa	33.0 Ba
PLB+TSP	33.3 Aa	33.3 Aa
EBB+TSP	33.2 Aa	32.8 Bb
TSP	32.5$^{(-0.63b)}$	
	P Recovery (%)	
CSB+TSP	29.0 Ba	29.3 Ba
PLB+TSP	30.3 Aa	30.9 Aa
EBB+TSP	29.8 ABa	28.5 Bb
TSP	27.2$^{(-2.39b)}$	

[a]Means followed by the same uppercase letter for columns and lowercase for rows did not differ statistically from each other (Tukey, $p > 0.05$). (n): TSP contrast estimation vs ((CSB+TSP) + (PLB+TSP) + (EBB+TSP)) (3+, ---). [b]The mean of the control treatment differs from the mean of the factorial treatment (F-test, $p \leq 0.01$).

The treatments with organophosphate fertilizers produced in the coating mode did not show differences among them regarding the extraction and export of P (Table 6). As for the treatments with fertilizers prepared in the mixture mode, the fertilizers produced from PLB provided greater extraction and export of P. Among the preparation methods, a difference was only found for the treatments with EBB-based fertilizers, in which the mixture preparation method provided the lowest extraction, export, and recovery of P (28.5%), in accordance with the lower yield promoted by this fertilizer (Table 4).

The biochar/TSP ratios of 20 and 30% provided the highest P extractions from the soil, except for CSB-based fertilizers, in which the 10% proportion did not differ from the other proportions (Table 7). Treatments with fertilizers produced

Table 7. Extraction of P from the Soil by the Aerial Part, Export of P by the Grain, and Rate of P Recovery from the Fertilizer by the Maize, Regardless of the Fertilizer Preparation Method[a]

source of P	biochar/TSP ratio (%)		
	10	20	30
	P Extraction (kg ha^{-1})		
CSB+TSP	39.3 Aa	39.4 Ba	39.6 Ba
PLB+TSP	39.0 Ab	39.9 Aa	40.3 Aa
EBB+TSP	39.0 Ab	39.4 Bab	39.6 Aa
	Export of P (kg ha^{-1})		
CSB+TSP	33.0 Aab	32.9 Ab	33.3 Ba
PLB+TSP	33.0 Ab	33.0 Ab	34.0 Aa
EBB+TSP	32.9 Ab	32.9 Ab	33.3 Ba
	P Recovery (%)		
CSB+TSP	28.6 Aa	29.1 Ba	29.8 Ba
PLB+TSP	29.0 Ac	30.5 Ab	32.3 Aa
EBB+TSP	27.9 Ab	29.4 ABa	30.3 Ba

^{a}Means followed by the same uppercase letter for columns and lowercase for rows did not differ statistically from each other (Tukey, $p > 0.05$).

from PLB in the proportion of 20%, and PLB and EBB in the proportion of 30% showed higher P extraction. The highest P export was verified in the proportion of 30%, and in this proportion, the PLB-based fertilizer promoted higher P extraction (34 kg ha^{-1}). In general, the highest P recovery was 32.3%, corresponding to the PLB-based fertilizers in the proportion of 30%.

3.3. Phosphorus Availability in Soil Treated with Phosphate Fertilizers. After maize cultivation, the treatments with organophosphate fertilizers showed the highest P concentrations in the soil extracted with water, P fraction readily available to plants,[2,32] and higher P concentrations extracted by Mehlich-1, P fraction available or that may be available to plants.[2] The treatments with organomineral fertilizers showed, on average, concentrations of 25.4% (P−water) and 20.1% (P−Mehlich-1) higher than the respective means of the treatments with TSP (Table 8).

Table 8. Phosphorus Extracted in Water and Mehlich-1 in the Soil after Maize Cultivation Subjected to Phosphate Fertilization, Regardless of the Proportions of Biochar/TSP in the Fertilizer[a]

source of P	P−water (mg kg^{-1})		P−Mehlich-1 (mg kg^{-1})	
	coating	mixture	coating	mixture
CSB+TSP	5.7 Ba	5.9 Ab	57.6 Ba	53.5 Bb
PLB+TSP	7.5 Aa	6.0 Ab	61.8 Aa	60.0 Aa
EBB+TSP	6.0 Ca	4.8 Bb	58.2 Ba	55.4 Bb
TSP	4.6$^{(-1.55b)}$		46.1$^{(-11.61b)}$	

^{a}Means followed by the same uppercase letter for columns and lowercase for rows did not differ statistically from each other (Tukey, $p > 0.05$). (n): TSP contrast estimation vs ((CSB+TSP) + (PLB+TSP) + (EBB+TSP)) (3+, ---). ^{b}The mean of the control treatment differs from the mean of the factorial treatment (F-test, $p \leq 0.01$).

In general, PLB-based organophosphate fertilizers provided the highest P availability in the soil after cultivation (Table 8), even though maize plants recovered the highest amount of P from these fertilizers (Table 6).

Regarding the fertilizer preparation method, fertilizers coated with biochars led to the highest P availability, except for fertilizers produced from PLB, in which no difference was found between the preparation methods.

The increase in the biochar/TSP ratio provided an increase in the concentrations of P extracted with water and Mehlich-1, regardless of the biochar used. The biochar/TSP ratio of 30% promoted a higher P availability (Table 9).

Table 9. Phosphorus in the Soil Extracted in Water and Mehlich-1 after Maize Cultivation Subjected to Phosphate Fertilization, Regardless of the Preparation Method[a]

source of P	biochar/TSP ratio (%)		
	10	20	30
	P−Water (mg kg^{-1})		
CSB+TSP	4.7 Bc	6.1 Bb	7.9 Aa
PLB+TSP	5.7 Ac	6.7 Ab	8.2 Aa
EBB+TSP	4.4 Bc	5.0 Cb	6.7 Ba
	P−Mehlich-1 (mg kg^{-1})		
CSB+TSP	51.4 Ac	54.4 Bb	60.9 Ca
PLB+TSP	52.5 Ac	58.9 Ab	71.4 Aa
EBB+TSP	50.7 Ac	56.1 Bb	63.7 Ba

^{a}Means followed by the same uppercase letter for columns and lowercase for rows did not differ statistically from each other (Tukey, $p > 0.05$).

4. DISCUSSION

4.1. Maize Yield and Agronomic Efficiency of Fertilizers. The higher efficiency of fertilizers combined with biochar compared to TSP is consistent with our laboratory observations, which demonstrated a reduction in the direct interaction of phosphate fertilizers with soil minerals, thereby decreasing P sorption processes and enhancing its availability.[18] Consequently, the use of organophosphate fertilizers results in maize yields comparable to or higher than those obtained with mineral fertilizers.[9,33]

The superior efficiency of the fertilizers with integrated protection evaluated in this study can be explained by at least two main factors. The first, as expected, is the granule coating, which prevents direct contact of P with soil colloids.[4,6] The second, highlighted in our findings, is the increased proportion of P soluble in NAC. Both factors reduce the intensity of P adsorption and, consequently, increase the availability of this nutrient for maize. These characteristics provide the fertilizers with a more gradual release of P, minimizing its fixation in the soil[12,18] and ensuring greater nutrient availability during phases of intense vegetative growth and ear formation, when P demand is highest,[4] resulting in higher productivity.

The rate of P release from organomineral fertilizers is generally regulated by physical and chemical barriers.[4] Thus, increasing the biochar/TSP ratio promotes a thicker coating of the granules, creating a greater physical barrier to the contact of P with soil particles. For granular fertilizers in the mixture mode, the presence of biochar appears to influence the P solubility. The observed increase in the percentage of citrate-soluble P (P-NAC) and the corresponding decrease in water-soluble P (P−H$_2$O) suggest that chemical interactions between

biochar components (e.g., Ca and Mg) and phosphate ions may have occurred, potentially contributing to a more gradual P release. Additionally, it is important to note that the increase in P-NAC may also be a result of the less soluble phosphated content found in biochars.[34] This effect was particularly pronounced in PLB-based fertilizers, which contain higher concentrations of Ca, Mg, and P as well as higher pH.

Additionally, it is essential to consider the nutrient composition of these fertilizers, as they contain higher concentrations of other nutrients, particularly K and Mg, which are absent in TSP. This difference may have influenced the observed results, as the increased crop yield could be partially attributed to the additional K supply rather than solely to P availability. Notably, to reach the target application rate of 30 kg of P/ha, larger amounts of each biochar-based fertilizer would be required, leading to a substantial K input. This factor should be taken into account in interpreting the agronomic performance of these materials.

Evaluating maize grain yield in response to phosphate fertilization, Grohskopf et al.[9] also found an increase in productivity with the application of phosphate fertilizer with integrated protection. The authors showed that monoammonium phosphate (MAP) mixed with poultry litter provided higher maize yield in three years of cultivation, presenting an agronomic efficiency 20% higher than conventional fertilizer. Other studies have also shown positive results on the use of phosphate organomineral fertilizers in crops such as maize,[7,11,33] soybean,[35] and sugar cane.[36]

4.2. P Absorption.
The mean P recovery of organophosphate fertilizers by maize was 29.6%. This recovery was not small, considering the high P-draining character of tropical soils[3]. Evaluating phosphate fertilization in a clayey Latosol, Resende et al.[37] reported a rate of P recovery from the TSP of 49% after three maize harvests. Sousa and Lobato[38] presented data on the total recovery of 35−62% of the P applied, after 13 harvests of maize in a clayey Latosol. The source of P used in these works was a simple superphosphate.

The differences in efficiency among the P sources in our work may be related to their differences in solubility. Organomineral fertilizers have a lower solubility of P in water than TSP. Slower release of P may, therefore, have promoted greater availability of P in the soil over time for organomineral fertilizers, resulting in higher productivity and greater P recovery. In addition to the physical protection promoted by the biochar in the fertilizer, the mineral P of the organomineral fertilizers may be present in the pore cavities of the biochar[12] and precipitated with Ca and Mg.[11] All these mechanisms may prevent the sorption of P by Fe and Al oxides and hydroxides from the soil.[4] Additionally, the reactions involved in the solubilization of P from the adsorption−desorption equilibrium may increase the P availability for a long period, increasing its absorption by the plant.[12] Around the granules of organophosphate fertilizers, there may be an increase in the pH of the solution induced by the biochar present in the fertilizer,[39] which reduces the intensity of P adsorption in the soil,[2,3] keeping the P available for a long period. This hypothesis is reinforced by the higher pH values of the organophosphate fertilizers in relation to the TSP (Table 2).

The use of protected P, such as polymerized fertilizers,[6] organominerals,[8,9] and biochar-based organominerals,[11,12] have been presented as options for reducing P adsorption by soil colloids. According to Teixeira et al.,[4] a desired characteristic of these fertilizers is that they behave differently from conventional soluble sources, promoting a gradual P availability and not a total release of P in soil solution. This can be observed in our study, in which PLB-based fertilizers produced in the proportion of 30%, which have lower water solubility, promoted higher grain yield and P recovery, releasing the nutrient gradually, according to the needs of the crop.

4.3. Phosphorus Availability in Soil Treated with Phosphate Fertilizers.
When compared to soluble fertilizers such as TSP, higher concentrations of available P in the soil have been reported from biochar-based organophosphate fertilizers,[11,12,39] poultry litter-based organophosphate fertilizer,[5] and MAP coated with organic acids.[4]

Due to the high-water solubility of the TSP, when applied to the soil, in contact with water, P is released rapidly, increasing the P levels in solution.[4] However, the absorption of P at the beginning of cultivation is low due to reduced root development.[12] The P in solution that is not absorbed by plants, over time, is more likely to decrease due to its adsorption by the Fe and Al oxides and hydroxides of the clay fraction.[3,40] This lower availability of P presented by TSP at the end of the experiment explains the lower efficiency of this fertilizer.

The highest P availability in the soil after cultivation when PLB-based organophosphate fertilizers were applied (Table 8) may be attributed to the lower water solubility of these fertilizers (Table 2), which provided a slower P release in the soil solution, reducing P adsorption losses.[4] Another determining factor is the higher concentration of P in PLB (Table 1), which is less soluble than the mineral P fraction added to the fertilizer, providing a greater residual effect.

Moreover, fertilizers produced from PLB at the proportion of 30% exhibited satisfactory characteristics as integrated protection fertilizers, as the slow release of P from these fertilizers was sufficient to meet the maize crop's demand, showing higher agronomic efficiency and P recovery and maintaining a greater amount of available P after harvest. This greater residual effect could also be important to meet the nutrient demands of subsequent crops.[11]

In summary, biochar-based organophosphate fertilizers, compared to TSP, demonstrated higher agronomic efficiency, greater P recovery, and higher residual power, indicating their potential to improve crop productivity and sustain soil fertility for future harvests. Among the organophosphate fertilizers, those produced from poultry litter-based biochar stood out for their higher agronomic efficiency and P recovery, as well as the greatest amount of P available in the soil after harvest. Regarding the preparation method, fertilizers produced in the coating mode promoted the highest P availability in the soil after harvest. Additionally, the 30% biochar/TSP ratio proved to be more efficient in terms of agronomic efficiency and P recovery while also promoting a higher residual effect of P.

■ AUTHOR INFORMATION

Corresponding Author

Renato Ribeiro Passos − *Departamento de Agronomia, Universidade Federal do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil;* ⊙ orcid.org/0000-0001-7730-748X; Email: renato.passos@ufes.br

Authors

Ronaldo Willian da Silva − *Departamento de Agronomia, Universidade Federal do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil*

Mateus Hastenreiter Rodrigues Silva Loquez − *Departamento de Agronomia, Universidade Federal do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil*

Felipe Vaz Andrade − *Departamento de Agronomia, Universidade Federal do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil*

Danilo Andrade Santos − *Departamento de Agronomia, Universidade Federal do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil*

Otacílio José Passos Rangel − *Instituto Federal de Educação, Ciência e Tecnologia do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil*

Eduardo de Sá Mendonça − *Departamento de Agronomia, Universidade Federal do Espírito Santo, CEP:29500-000 Alegre, ES, Brazil;* ⊙ orcid.org/0000-0003-3284-7129

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsagscitech.5c00142

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