






## Article

# Oxalic Acid Boosts Phosphorus Release from Sewage Sludge Biochar: A Key Mechanism for Biochar-Based Fertilizers

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**Abstract:** Sewage sludge biochar (SSB) exhibits higher phosphorus (P) concentrations than the original sewage sludge (SS) and can be used as a P fertilizer. However, SSB-associated P is strongly retained in chemical compounds, which hinders its release and subsequent plant uptake. The use of organic acids facilitates P solubilization from SSB. Herein, we evaluated the effect of oxalic acid on P release from SSB applied to soil over time. Biochar was produced at 300 °C (SSB300) and 500 °C (SSB500). P release from SSB increased with an increasing concentration of oxalic acid in the SSB incubation solution and in SSB-treated soil. P speciation in SSB showed that P was predominantly inorganic (P<sub>i</sub>), which represented 81% and 92% of the total P in SSB300 and SSB500, respectively. P<sub>i</sub> in SSB consisted mainly of non-apatite P, accounting for 91% and 96% of all P<sub>i</sub> in SSB300 and SSB500, respectively. Because SSB is predominantly insoluble in water, oxalic acid is crucial for the release of P from SSB. Oxalic acid increased P release from SSB300 and SSB500 by 103- and 600-fold, respectively, compared to the control, from which P was extracted with water. Oxalic acid enhancement of P release from SSB increases the possibility of using SSB as a sustainable source of P for agriculture.

**Keywords:** pyrolysis; thermal treatment; biosolids; phosphorus



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## 1. Introduction

Sewage sludge (SS) management has become a global challenge owing to the enormous amounts of SS produced in wastewater treatment plants (WWTPs) [1]. Furthermore, this challenge is expected to intensify as the global urban population increases [2]. On the other hand, SS can be applied in agricultural areas because it is rich in organic matter and macro- and micronutrients, such that it can be used as a fertilizer and soil amendment treatment [3]. However, SS may contain pathogens, heavy metals, and a range of organic pollutants that can be harmful to plants, human health, and the environment [4]. Therefore, SS must undergo additional treatment to ensure safe management and use in agricultural fields.

Currently, the most common methods for SS treatment include biological (e.g., anaerobic digestion and aerobic composting) and thermal treatments (e.g., dry and wet pyrolysis). In particular, the pyrolysis process typically involves a high temperature (>400 °C) to promote the decomposition of organic pollutants, the unavailability of heavy metals, and the elimination of pathogens, thus allowing the use of SS from both agricultural and environmental perspectives [5–7]. The solid product of SS pyrolysis is known as sewage sludge biochar (SSB). Further, SSB shows equal or higher concentrations of carbon and plant nutrients, such as phosphorus (P), than those found in the original SS [8,9].

Phosphorus is a critical element for sustaining a wide range of human activities, including food, fiber, and biofuel production. Indeed, agriculture is the sector with the highest demand for P, accounting for up to 90% of global demand. Consequently, the global application of P fertilizer on croplands has continued to escalate, rising from approximately 5 Tg P yr<sup>-1</sup> in 1961 to 18 Tg P yr<sup>-1</sup> in 2013 [10], surpassing the estimated safe planetary boundary of 6 to 12 Tg P yr<sup>-1</sup> [11]. Moreover, projections indicate a further increase to 22–27 Tg P yr<sup>-1</sup> by 2050 [12,13]. Additionally, soil erosion will exacerbate P scarcity, with losses ranging from 4 to 19 kg ha<sup>-1</sup> yr<sup>-1</sup> [14]. As economically viable reserves of natural P for fertilizer production are finite, the need to improve the methods for P recovery and recycling has become paramount.

SSB has a higher P concentration than biochar from other raw materials (e.g., legumes, grasses, wood waste, and manure) [15], reaching up to 6% [16,17]. Thus, several studies have explored the possibility of using SSB as a phosphate fertilizer [18–21] or as a matrix for the development of new, sustainable fertilizers. For example, in a field experiment, SSB increased the total P ( $P_{\text{total}}$ ), organic P ( $P_{\text{o}}$ ), inorganic P ( $P_{\text{i}}$ ), and available P fractions, maintaining these high values in the soil for at least two years after application ceased [22]. Owing to the varied composition of sewage and the type of treatment adopted in WWTPs, SSB shows a wide range of P chemical forms [23], which can be grouped into inorganic (60–90%) and organic (10–40%) forms [24] and are highly affected by pyrolysis conditions, especially temperature and residence time [25].

Consistently, SSB mixed with soil reportedly increases the available P content and, concomitantly, corn grain yield [26,27]. Therefore, SSB allegedly increases soil available P levels despite a very low concentration of water-soluble P [23]. Another relevant process affecting available P content is the reaction time with the soil [16]. The predominant form of inorganic P in SSB is  $P_{\text{i}}$ , which is found as mineral salts with metal cations, such as Fe, Al, Mg, and Ca, whereas  $P_{\text{o}}$  is found mainly in microbial cell remains and various organic compounds [9,28]. Unfortunately, only a small fraction of  $P_{\text{total}}$  is available to plants [29]. Altogether, these variables make it difficult to recommend precise doses of SSB as P supply for soil fertilization purposes.

Consequently, it is crucial to devise new technical approaches to enhance the utilization of SSB as a phosphate fertilizer or as a matrix of biochar-based fertilizers. One promising method involves using low-molecular-mass organic acids that can improve the solubility of P in SSB, thereby increasing its release to the soil and hence its availability to plants. Soil microorganisms produce organic acids that are naturally present in the rhizosphere and are capable of solubilizing nutrients [30]. Indeed, several studies have shown the positive effects of organic acids on P solubilization from soil minerals [26,31,32]. The chelating potential is the main characteristic of organic acids responsible for increasing P solubilization. Organic acids bind to mineral ions, forming a strong bond, and then cause the release of previously insoluble minerals, in addition to affecting several biological processes that also lead to increased nutrient availability [33]. These acids can also solubilize the abundant inorganic P fractions in SSB. Among organic acids of microbial origin, oxalic acid stands out and may be more efficient than sulfuric acid for solubilizing P from phosphate rocks [32]. A case in point, Rossati [34] reported an increase in P solubilization after inoculating SSB with *Aspergillus niger*, a fungus that produces oxalic acid. This finding indicated the potential of this organic acid to increase the efficiency of mineral P sources.

However, specific studies using oxalic acid with the aim of increasing P solubilization of SSB are still rare. Vause [35] analyzes the release of elements (Al, Ca, Fe, K, Mg, Mn, Na) in SSB using a mixed solution of citric, malic, and oxalic acid. Therefore, the use of oxalic acid to increase SSB-associated P solubilization will help us to (i) elucidate the role of organic acids in P solubilization from SSB applied to the soil and (ii) understand the role of oxalic acid in the development of SSB-based fertilizers. Specifically, studies involving a sequence of oxalic acid extractions directly from SSB and SSB-amended soils are scarce. Therefore, the following hypotheses were proposed: (i) oxalic acid increases the solubilization of P in SSB both in acidic solutions and in the soil, and (ii) P solubility

in oxalic acid is different for SSB obtained at different pyrolysis temperatures. Thus, we aimed to evaluate the influence of oxalic acid on SSB-associated P solubilization from SSB obtained at two pyrolysis temperatures. This will help us to understand the dynamics of the release of P present in SSB and will also give the possibility of using this acid as an additive to sewage sludge biochar-based fertilizers with the aim of increasing the release of P and reducing the volume of SSB applied to the soil.

## 2. Materials and Methods

### 2.1. Production of SSB

The experimental biochar was produced from SS samples collected at the Melchior WWTP located in Samambaia, Distrito Federal, Brazil (15°52'21" S, 48°9'4" W). The SS samples were air-dried to approximately 10% moisture, passed through a 4 mm sieve, and then subjected to 300 °C (SSB300) or 500 °C (SSB500) in a pyrolysis furnace (Linn Elektro, Eschenfelden, Germany). The temperatures were chosen based on previous studies carried out by Figueiredo [7]. Biochar at these temperatures presents higher total and Mehlich 1 P concentrations, making it better suited for use as a fertilizer. The average rate of temperature increase was 2.5 °C min<sup>-1</sup> and the pyrolysis time was 5 h. The furnace was equipped with a mechanism to prevent oxygen flow (via a forced draft fan, helping gas and oil vapors to exit the furnace). After pyrolysis, the biochar was ground and sieved through a 1 mm mesh.

### 2.2. Chemical, Mineralogical, and Thermogravimetric Characterization of SS and SSB

#### 2.2.1. Chemical Characterization of SSB

The chemical properties of SS, SSB300, and SSB500 were quantitatively analyzed as outlined in Table 1. The pH was determined in a 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution (1:5 *w/v*) according to [36]. The moisture content was determined as a function of weight loss after heating the sample to 105 °C [37]. Total C and N contents were determined using an elemental analyzer (Euro EA3000 Elemental Analyzer, Milano, Italy). The C:N ratio was estimated from the total C and N contents. Macro- and micronutrients and heavy metals were determined after acid digestion with HNO<sub>3</sub>/HCl (3:1 *v/v*) according to [38] and quantified as follows: P was determined using the vanado-molybdo-phosphoric acid method; K was determined by flame photometry; and Ca, Mg, micronutrients, and heavy metals were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (ICPE-9000, Shimadzu, Kyoto, Japan), according to Brazil [39].

**Table 1.** Characteristics of sewage sludge (SS) and SS pyrolyzed at 300 °C (SSB300) and 500 °C (SSB500).

Properties	SS	SSB300	SSB500
pH (CaCl <sub>2</sub> )	6.4	6.0	6.4
Moisture (%)	18.5	6.6	1.5
Total C (%)	28.8	25.04	23.16
P (Total) (%)	2.2	3.9	4.6
K <sub>2</sub> O (Total) (%)	0.24	0.24	0.43
Total N (%)	3.7	4.21	3.40
Ca (%)	0.5	0.64	0.85
Mg (%)	0.21	0.25	0.29
S (%)	0.82	0.75	1.18
Cu (mg kg <sup>-1</sup> )	105	115	168
Fe (mg kg <sup>-1</sup> )	19,800	20,500	20,490
Mn (mg kg <sup>-1</sup> )	100	105	149
Zn (mg kg <sup>-1</sup> )	460	480	690
C:N Ratio	7.8	5.9	6.8
Cd (mg kg <sup>-1</sup> )	3	3.0	2.0
Ni (mg kg <sup>-1</sup> )	13	15	12
Pb (mg kg <sup>-1</sup> )	63	32.0	44.0

### 2.2.2. X-ray Diffraction (XRD)

X-ray diffraction analysis was conducted using a diffractometer (D8 Focus, Bruker, Billerica, MA, USA). Powder XRD patterns were obtained using monochromatic Cu K $\alpha$  radiation at 40 kV, 30 mA, with  $2\theta$  between 10 and 70°, with steps of  $2\theta$  0.05, and a speed of 1-degree min<sup>-1</sup>. The peak areas identified for the different minerals were compared with the XRD patterns of standard minerals compiled by the International Center for Diffraction Data (ICDD).

### 2.3. Phosphorus Sequential Extraction

During the pyrolysis process, P fractions undergo transformations that alter the level of P solubility and, consequently, its availability to plants. To understand P transformations, several analytical procedures can be adopted. Since P<sub>i</sub> is the main form of P in SSB, in the present study, the standards, measurements, and testing program (SMT) for P extraction were used [40]. This procedure made it possible to quantify P<sub>i</sub>, apatite P, and non-apatite P contents in the biochar samples. Two procedures were performed. First, a 16 h extraction in 1 mol L<sup>-1</sup> NaOH was performed to remove the extractable P. The residue was extracted with 1 mol L<sup>-1</sup> HCl for 16 h to obtain apatite P associated with carbonates. An aliquot of the initial NaOH solution was removed and treated for 16 h with a 3.5 mol L<sup>-1</sup> HCl solution to obtain non-apatite P associated with Fe, Al, and Mn oxides and hydroxides. In a second procedure, a new SSB sample was extracted in a 1 mol L<sup>-1</sup> HCl solution for 16 h to obtain P<sub>i</sub>.

In addition, the simplified procedure of Hedley [41] was used to quantify the levels of P<sub>total</sub> and then P<sub>o</sub>. P<sub>total</sub> was determined by acid digestion with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> in the presence of a saturated MgCl<sub>2</sub> solution [41]. In turn, P<sub>o</sub> was calculated by subtracting P<sub>i</sub> from P<sub>total</sub>.

### 2.4. Experiment I: Solubilization of P from Biochar by an Oxalic Acid Solution

An incubation experiment was performed to evaluate the effectiveness of an oxalic acid solution in solubilizing P from the biochar. The incubation was conducted at room temperature (~25 °C). Sterilized 50 mL conical centrifuge tubes were filled with 0.4 g of SSB300 or SSB500 and 40 mL of oxalic acid solution (Sigma-Aldrich, St. Louis, MO, USA) at concentrations of 0.33, 0.67, and 1.00 mol L<sup>-1</sup>. SSB samples were incubated in triplicate for 10 d. To determine the amount of solubilized P, aliquots of the solution were collected at 3, 12, and 24 h and at 2, 5, 7, and 10 d. The control treatment consisted of SSB in distilled water.

Samples collected at each time point were centrifuged at 3300 rpm for 5 min. This was followed by slow filtration through filter paper (80 g m<sup>-2</sup> and pore size of 8  $\mu$ m). The soluble P concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (ICP-7000, Thermo Fisher Scientific, Waltham, MA, USA).

### 2.5. Experiment II: Incubation of Biochar in Soil

In a second incubation experiment, we evaluated the influence of oxalic acid on the dynamics of P release from SSBs applied to the soil [42], for which purpose, soil samples were collected from the topsoil layer (0–20 cm) of a Typical Ustorthent (clay sand) located at the experimental farm (15°56'45" S, 47°55'43" W; 1095 m a.s.l.) of the University of Brasília. Soil samples were air-dried and passed through a 2.0 mm mesh sieve; subsequently, they were incubated after the application of a rate equivalent to 4 Mg ha<sup>-1</sup> of dolomitic limestone to increase the pH to 6.0. The soil samples were chemically characterized according to Teixeira [43] (Table 2). The soil pH was determined in CaCl<sub>2</sub> 0.01 mol L<sup>-1</sup> (1:2.5 w/v). Phosphorous and K contents were extracted by Mehlich-1 (HCl 0.05 mol L<sup>-1</sup> + H<sub>2</sub>SO<sub>4</sub> 0.0125 mol L<sup>-1</sup>) and determined by spectrophotometry and flame photometry, respectively. Ca<sup>+2</sup> and Mg<sup>+2</sup> were extracted by KCl 1 mol L<sup>-1</sup> and estimated by inductively coupled plasma optical emission spectroscopy (ICP-OES) (ICPE-9000, Shimadzu, Kyoto, Japan). The H + Al was extracted with a 0.5 mol L<sup>-1</sup> calcium acetate solution at pH 7.0. Cation

exchange capacity (CEC), aluminum saturation (m), and base saturation (V) were estimated by the indirect method [43]. Particle size analysis was carried out using the hydrometer method using sodium hydroxide (NaOH)  $4 \text{ g L}^{-1}$  + sodium hexametaphosphate  $10 \text{ g L}^{-1}$  as chemical dispersant. Soil bulk density was determined in undisturbed soil samples collected using metallic cylinders with an approximate volume of  $100 \text{ cm}^3$ . Soil particle density was determined by the pycnometer method. The specific surface area was determined by  $\text{N}_2$  adsorption isotherms at  $-196.2 \text{ }^\circ\text{C}$  using a surface area analyzer, NOVA 2200 (Quantachrome Corp., Boynton Beach, FL, USA). Soil electrical conductivity was determined at a soil/water ratio of 1:2 (v/v). This incubation test was laid in a completely randomized design with three replicates. The following treatments were evaluated: no biochar (control), SSB300, and SSB500. The treatments were duplicated; oxalic acid was applied at a concentration of  $1 \text{ mol L}^{-1}$ . The control treatments consisted of distilled water or an oxalic acid solution at the same concentration without biochar.

**Table 2.** Chemical and physical characteristics of the soil (adapted from Leão [44]).

Attribute <sup>1</sup>	Unity	Value
pH (CaCl <sub>2</sub> )	-	5.2
P (Mehlich 1)	mg dm <sup>-3</sup>	1.0
K	mg dm <sup>-3</sup>	26.0
Ca	cmol <sub>c</sub> dm <sup>-3</sup>	2.0
Mg	cmol <sub>c</sub> dm <sup>-3</sup>	0.8
H + Al	cmol <sub>c</sub> dm <sup>-3</sup>	1.6
CEC <sup>1</sup>	cmol <sub>c</sub> dm <sup>-3</sup>	4.47
M <sup>2</sup>	%	0.0
V <sup>3</sup>	%	64.0
OM <sup>4</sup>	g kg <sup>-1</sup>	20.0
Clay	g kg <sup>-1</sup>	105.3
Sand	g kg <sup>-1</sup>	846.8
Silt	g kg <sup>-1</sup>	47.9
Bulk density	g cm <sup>-3</sup>	1.1
Particle density	g cm <sup>-3</sup>	2.5
Specific surface area	m <sup>2</sup> g <sup>-1</sup>	3.0
Electrical conductivity	mS cm <sup>-1</sup>	0.157

<sup>1</sup> CEC: cation exchange capacity; <sup>2</sup> m: aluminum saturation; <sup>3</sup> V: base saturation; <sup>4</sup> OM: organic matter.

Samples (5 g) of the two biochars (SSB300 and SSB500) were packed in sachets of permeable polyester mesh (<0.500 mm) measuring 5 cm × 4 cm. The sachets containing SSB were placed in a 200 cm<sup>3</sup> plastic container containing 50 g of soil. The sachets were covered with 50 g of soil. The soil samples in the containers were moistened with distilled water to maintain a water content corresponding to a water tension of 10 kPa, which is defined as the field capacity (FC). The soil samples were subjected to different tensions using the Richards chamber method for FC determination as described by Ndoung [45]. Using a precision scale, soil humidity was monitored at 5 d intervals and maintained at FC, based on the weight of the container.

The containers prepared with the soil and the sachets filled with the SSBs remained in the incubation room at a temperature of  $\sim 25 \text{ }^\circ\text{C}$  for the following periods: 12 h and 2, 5, 15, 30, and 60 d after the start of incubation. The containers were removed from the incubator once the incubation period established for each treatment had elapsed, and the sachet was carefully separated from the soil. The entire soil mass was homogenized, and an aliquot was withdrawn to determine the extractable P content in the Mehlich 1 solution, which was estimated by the colorimetric method using a spectrophotometer (Tecnal, UV-5100) at 660 nm. The P content of the controls with and without oxalic acid solution was subtracted to determine the amount of P solubilized from the SSB materials. Both experiments (I and II) were performed in 2023.

## 2.6. Statistical Analysis

Data from the SSB solubility experiments in oxalic acid solution (experiment I) and incubation in soil (experiment II) were adjusted using the following nonlinear regression models: Hyperbola; double rectangular, four-parameter:

$$P = \frac{at}{b+t} + \frac{ct}{d+t} \quad (1)$$

Exponential single, 2-parameter:

$$P = a(1 - e^{-bt}) \quad (2)$$

Exponential decay; double, 4-parameter:

$$P = ae^{-bt} + ce^{-dt} \quad (3)$$

Exponential double, 4-parameter:

$$P = a(1 - e^{-bt}) + c(1 - e^{-dt}) \quad (4)$$

Exponential linear combination:

$$P = y_0 + ae^{-bt} + ct \quad (5)$$

Modified hyperbola:

$$P = \frac{at}{1+bt} \quad (6)$$

where  $P$  is the solubilized phosphorus content ( $\text{mg L}^{-1}$  or  $\text{mg kg}^{-1}$ );  $t$  is the incubation time (days); and  $a$ ,  $b$ ,  $c$ , and  $d$ , are constants calculated using a nonlinear regression procedure. The model that best represented the data distribution was selected based on statistical significance ( $p$ -value) and the coefficient of determination ( $R^2$ ).

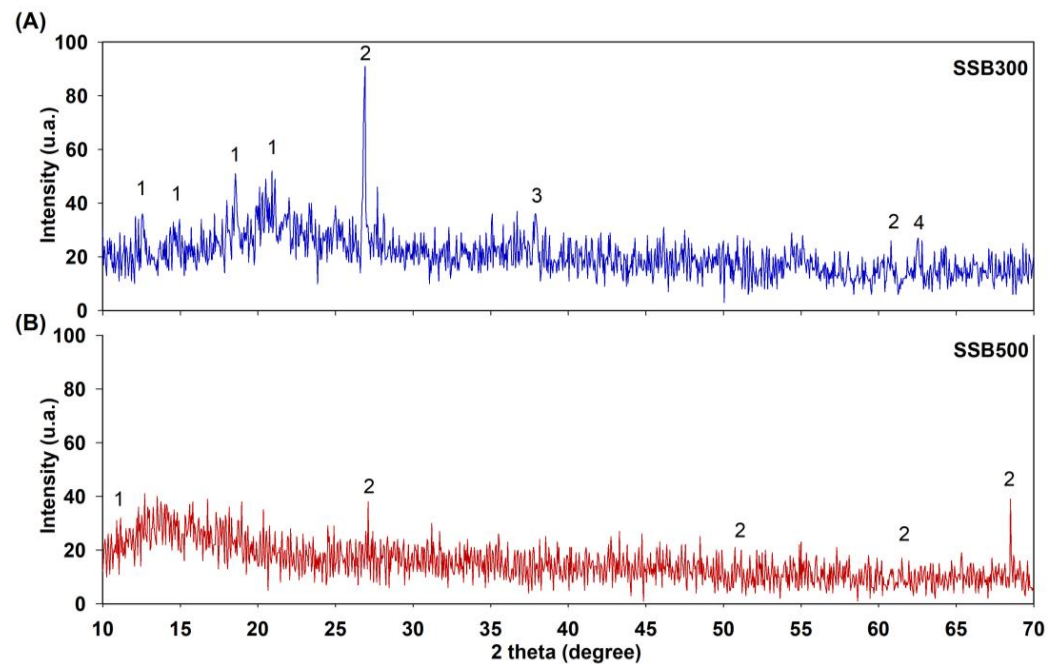
## 3. Results and Discussion

### 3.1. Mineralogical Characteristics of SSB

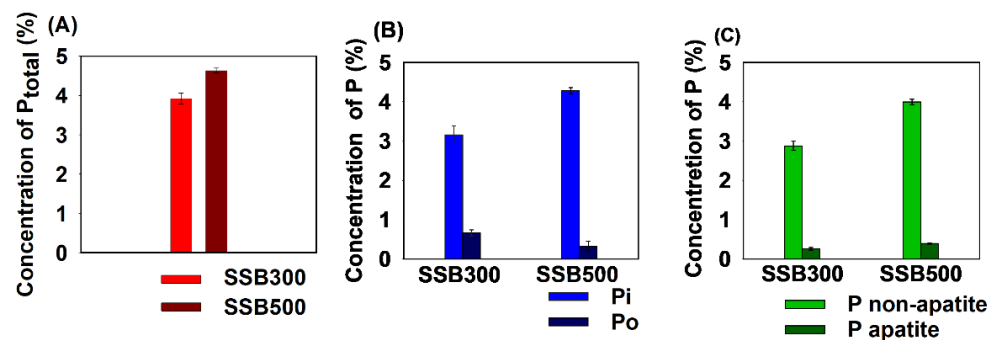
XRD was used to identify the crystal structures in SSB samples. The main phases in both SSBs tested herein were quartz ( $\text{SiO}_2$ ) and aluminum phosphate ( $\text{AlPO}_4$ ), although SSB300 also showed the presence of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) (Figure 1). The detection of  $\text{AlPO}_4$  indicated the stable presence of non-apatite P, which confirmed the effect of the  $\text{AlSO}_4$  used to precipitate P in the coagulation stage of the treatment that produced the SS used in this study. Additional characterization, thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) and energy-dispersive (XRD) analyses were carried out in order to better understand the materials analyzed, and the results are presented in Figures S1 and S2.

### 3.2. Sequential Extraction of P Present in SSB300 and SSB500

Sequential P extraction showed that SSB500 had a higher concentration of  $P_{\text{total}}$  than SSB300, at 4.64% and 3.92%, respectively (Figure 2), confirming that an increase in pyrolysis temperature favored the concentration of P in SSB500 [7]. Additionally,  $P_i$  was the predominant form of P in SSB, accounting for 80.6% and 92.2% of  $P_{\text{total}}$  in SSB300 and SSB500, respectively. In contrast, both SSBs had a low concentration of  $P_o$ , although that of SSB300 was higher than that of SSB500 (0.67% and 0.32%, respectively). These results indicate that  $P_o$  was partially converted into  $P_i$  during SS pyrolysis in a temperature-dependent manner, as previously reported [46].



**Figure 1.** X-ray diffraction (XRD) spectra of SSB300 (A) and SSB500 (B). 1: Aluminum phosphate; 2, quartz ( $\text{SiO}_2$ ); 3, aluminum oxide; 4, sodium silicate.

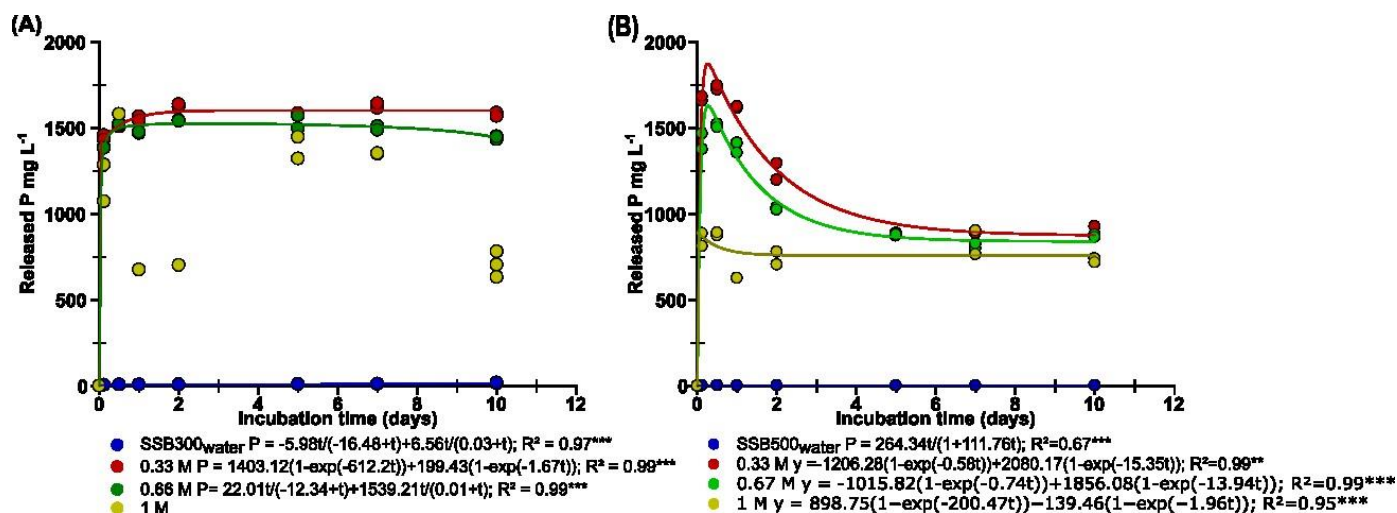


**Figure 2.** The speciation of phosphorus in SSB300 and SSB500. Pi, inorganic P; Po, organic P; P<sub>total</sub>, total P. Total P (A), organic and inorganic P (B), and apatite and non-apatite P (C).

Non-apatite P was the predominant form of P<sub>i</sub>, accounting for 91% and 96% of all P<sub>i</sub> in SSB300 and SSB500, respectively. Most P found in SSB was in the form of  $\text{AlPO}_4$  (Figure 1), formed during the precipitation of P with aluminum sulfate during the effluent treatment. This is probably the reason for the low availability of P in the soil when only water was applied to the soil amended with SSB (as shown later in Section 3.4), because non-apatite P has a lower availability for plants than apatite P [47]. In acidic media, both forms of P<sub>i</sub> (apatite P and non-apatite P) are solubilized.

### 3.3. Solubilization of P from Biochar in Oxalic Acid Solution

The oxalic acid solution promoted greater P solubilization in both SSB samples than that observed in the water-treated control, regardless of the concentration. Indeed, P solubilization was approximately 103 and 600 times higher in SSB300 and SSB500, respectively, than that in the control (Figure 3; Table S1). These results showed that the P forms present in SSB are insoluble in water but were effectively solubilized in acidic media. In fact, when the solution is acidic, both apatite and non-apatite P dissolve readily [47]. In addition, our results demonstrate that it is possible to use oxalic acid to increase the efficiency of SSB as a fertilizer.



**Figure 3.** Release of P from sewage sludge biochar (SSB) over time in solutions of oxalic acid of increasing concentration. SSB300 (A) and SSB500 (B). \*\*\* indicates  $p < 0.001$ .

The solubilizing action of oxalic acid on P in SSB depended on the acid concentration (Figure 3). However, surprisingly, pH values were the same in the three acid concentrations (Figure S3). In general, 0.67 and 0.33 M oxalic acid promoted similar P solubility. Furthermore, at the highest concentration (i.e., 1 M), there was a significant decrease in P solubilization compared to the other concentrations. Therefore, these results suggest that, under the conditions of this study, the use of oxalic acid concentrations higher than 0.33 M would not be recommended. Similar results were found by Mendes [32] when using oxalic acid to solubilize phosphate rocks. They observed that, at high concentrations of oxalic acid, calcium oxalate precipitation occurred on the phosphate rock surfaces, which slowed the solubilization of P. This phenomenon is common in the fertilizer production industry during sulfuric acid attacks on phosphate rocks owing to calcium sulfate [32,48]. All individual P and pH values are presented in Table S4 and Figure S4.

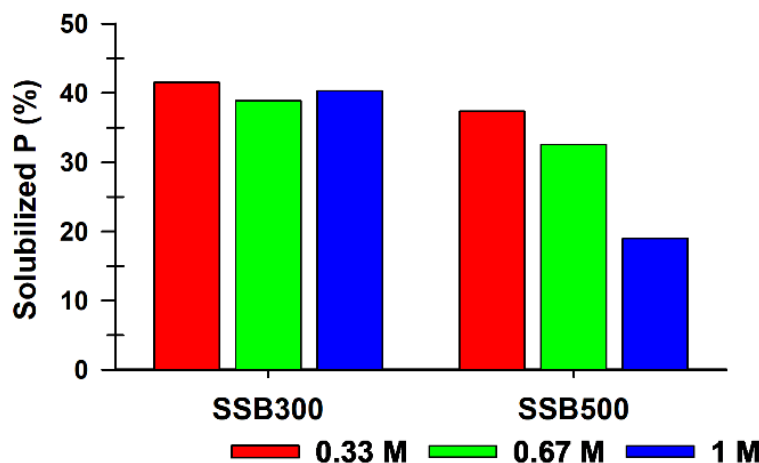
The maximum percentage of total P released from SSB300 in the presence of oxalic acid was 41.5% (at 7 d), 38.9% (at 12 h), and 40.9% (at 12 h) at concentrations of 0.33, 0.67, and 1 M, respectively (Figure 4). In contrast, SSB500 released 37.7%, 32.6%, and 19% of  $P_{total}$  at 0.33, 0.67, and 1 M, respectively. Therefore, oxalic acid solubilized a higher percentage of P in SSB300 than in SSB500, presumably owing to the higher  $P_o$  content in the former case (Figure 2B).

The higher amount of P solubilized from SSB500 in the first 12 h was explained by the higher concentration of  $P_{total}$ , apatite P, and non-apatite P (Figure 2) in that case, which was immediately solubilized in the presence of oxalic acid. The reduction in solubilized P content in SSB500 after 12 h of incubation can be partially explained by the possible re-adsorption of P by SSB500. This adsorptive capacity of biochar has been previously reported [49,50]. Because of its physicochemical properties such as high specific surface area, microporosity, high adsorption capacity, and ion exchange, biochar is a good adsorbent for phosphates and other ions such as heavy metals [6,51,52]. Increasing pyrolysis temperature increases the surface area and pore volume [53,54]. This also occurs for other types of biochar. For example, cotton stalk biochar pyrolyzed at 500 °C showed greater adsorption capacity than that obtained at lower temperatures [55]. This re-adsorption capacity of SSB500 might be interesting for tropical soils that have a high capacity to form inner-sphere complexes with P. Thus, SSB500 might function as a slow-release P fertilizer, as has been previously reported [56–58].

Acidification of the medium also favored the solubilization of other elements in SSB, including heavy metals. The increase in the concentration of oxalic acid resulted in the greater solubilization of heavy metals such as cadmium (Cd), chromium (Cr), cobalt (Co), manganese (Mn), lead (Pb), and zinc (Zn) (Table S2). However, in all evaluations,



the concentrations of heavy metals were below the maximum limits allowed for biochar, fertilizers and soils according to the regulations of Brazil [59], the European Union [60], and the International Biochar Initiative (IBI) [61]. Long-term field studies on the effect of the application of SBB of essentially domestic origin on the dynamics of heavy metals indicate the feasibility of using SBB in soil, without risks of contamination with heavy metals [62,63]. However, additional investigations are necessary to ensure the safety of the application of SSB from industrialized regions.



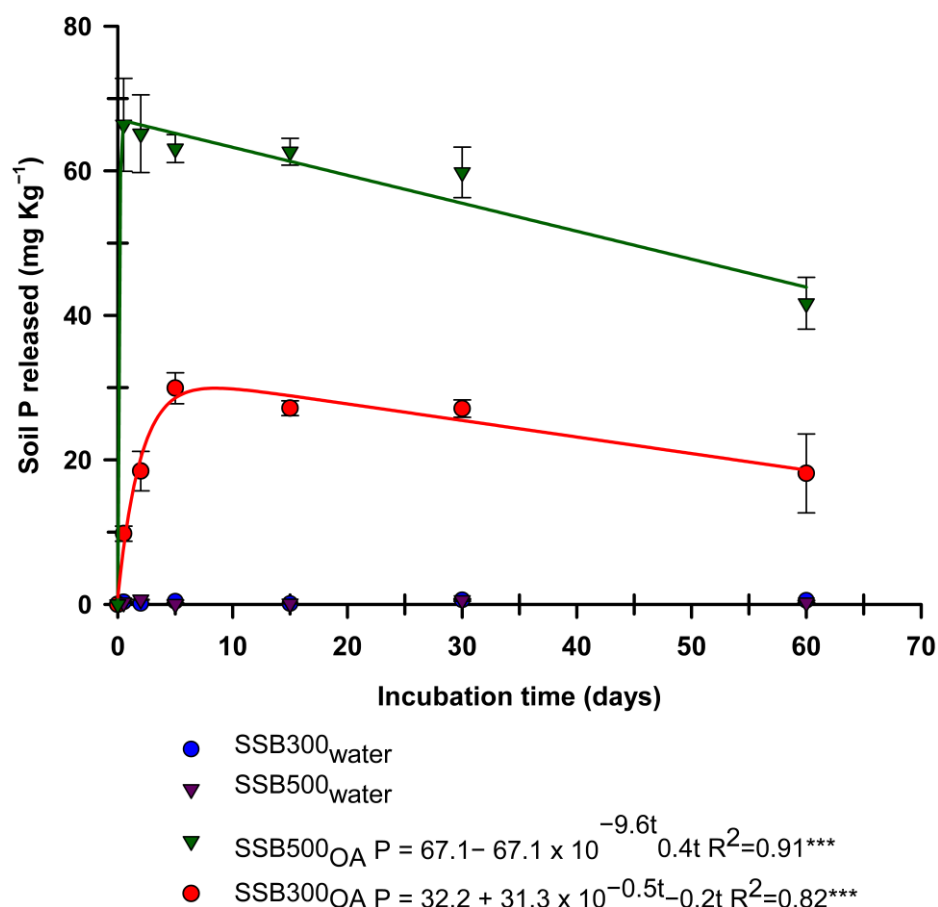
**Figure 4.** Maximum percentage of P solubilized from sewage sludge biochar (SSB) at different concentrations of oxalic acid. The values represent the percentage of  $P_{total}$  released from SSBs over time at different concentrations of oxalic acid. For SSB300: 0.33 (7 d), 0.67, and 1 M (12 h); for SSB500: 0.33, 0.67, and 1 M (12 h).

### 3.4. Solubilization of P from Biochar in the Soil

Oxalic acid (1 M) did not promote greater solubilization of P from SSB applied as a soil amendment (Figure 5). A higher acid concentration was selected based on previous tests to circumvent the dilution effect of the applied solution, which is common when applying low-molecular-weight organic acids to soil [64]. Table S3 shows the nonlinear regression models that best fit the P solubilization data from SSB-treated soil in the presence or absence of oxalic acid. Oxalic acid increased the solubilization of P from both SSB treatments compared to the water-only control (Figure 5). The ability of oxalic acid to solubilize P from phosphates present in poorly soluble rocks is well established [65], and this effect is enhanced in the presence of SSB [34]. Oxalic acid can also desorb P fixed to the soil [66]. Hence, this study presents new strategies for combining SSB with oxalic acid to make SSB an effective phosphate fertilizer.

The concentration of P extracted from SSB500-treated soil was higher than that extracted from the SSB300-treated soil over the entire experimental period. Higher concentrations of  $P_{total}$ , apatite P, and non-apatite P in SSB500 (Figure 2) allowed for a greater release of P into the soil. The greatest release of P from SSB500 into the soil occurred shortly after the application of oxalic acid, specifically, 12 h after the start of the experiment. After this peak, the P content of the soil decreased over time. Similar behavior was observed for SSB300, but with a smaller decrease in P concentration over time. These results were similar to the behavior of SSBs in solution, in which case, there was a significant reduction in the concentration of P in the SSB500 solution after 12 h of incubation. In soil, this reduction may be due to the re-adsorption of P by the SSB or the soil. Alternatively, it may be due to the neutralization of oxalic acid over time, whereby it would lose its solubilizing power. Similar to SSB500, after the application of SSB300 to the soil, there was an increase in P release followed by a reduction over time. As explained for SSB500, the reduction in the release may have occurred through a re-adsorption process or a decrease in the acid solubilization power. Regarding SSB300, P re-adsorption directly onto the biochar probably did not occur,

since SSB300 has a lower adsorption power due to its less complex carbon structure than SSB500 [67]. Thus, in SSB300, the P re-adsorption behavior probably occurred through P adsorption to the soil or acid degradation over time [68].



**Figure 5.** Release of P from SSB-treated soil over time (days) in the presence of oxalic acid (OA) or water. SSB300<sub>water</sub> and SSB300<sub>OA</sub> are sewage sludge biochars produced at 300 °C and treated with water and OA solution, respectively. SSB500<sub>water</sub> and SSB500<sub>OA</sub> are sewage sludge biochars produced at 500 °C and treated with water and OA solution, respectively. Error bars represent the standard deviation ( $n = 3$ ). \*\*\* indicates  $p < 0.0001$ .

#### 4. Conclusions

The findings summarized herein validate our hypothesis that oxalic acid enhances the solubility of P in SSB, both in solution and soil.  $P_i$  is the primary type of P in SSB, and non-apatite P compounds constitute approximately 91% and 96% of  $P_i$  in SSB300 and SSB500, respectively. These compounds represent a major portion of P present in SSB. Particularly, SSB500 demonstrated a greater capacity to release P into both the solution and soil, although it may re-adsorb some of the solubilized P over time. Our results underscore the efficacy of oxalic acid in promoting the release of P from SSB, thereby ultimately increasing P availability to plants. Oxalic acid is one of the organic acids naturally found in soil. Therefore, the use of this type of acid in fertilizer formulations has a lower impact on the soil than conventional fertilizers, in addition to promoting an efficient release of nutrients for plants. In this way, the use of biochar-based fertilizers acidified with organic acids contributes to more sustainable agricultural production. Furthermore, our study opens new avenues for exploring novel research directions focused on the development of fertilizers derived from biochar and organic acids. Future research should focus on exploring the impact of oxalic acid on the release of P from SSB in the soil–plant system. Finally, acidified SSB should be studied as a matrix for biochar-based fertilizers.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/agriculture14091607/s1>: Figure S1: Thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis conducted in an inert atmosphere for sewage sludge biochar samples produced at 300 (SSB300) and 500 °C (SSB500). Analysis carried out in an alumina crucible, under an inert atmosphere (N<sub>2</sub>) with a gas flow of 50 mL min<sup>-1</sup> from room temperature to 1000 °C at a heating rate of 20 °C min<sup>-1</sup>; Figure S2: Spectra of energy-dispersive (DRX) analysis. Obtained using an EDX 720HS spectrometer (Shimadzu, Kyoto, Japan); Figure S3: pH values in different oxalic acid solutions over a 10-day incubation; Figure S4: pH values in soil amended with sewage sludge biochar (SSB) in the presence or absence of oxalic acid (OA) over the time. H: hours; D: days; Table S1: Coefficient of determination (R<sup>2</sup>) and standard error in the solubilization of pyrolyzed biochar at 300 °C (SSB300) and 500 °C (SSB500); Table S2: Concentrations of heavy metals released into the oxalic acid solution from sewage sludge biochar (SSB) produced at 300 and 500 °C; Table S3: Coefficient of determination (R<sup>2</sup>) and standard error in the solubilization of pyrolyzed biochar at 300 °C (SSB300) and 500 °C (SSB500) in the presence or absence of oxalic acid (OA); Table S4: Concentrations of solubilized P in soil.

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