







Article

Effects of Temperature and Carrier Gas on Phosphorus Transformation in Biosolids Biochar

Shefali Aktar ^{1,2} , Md Afzal Hossain ³ , Gabriel Gasco ⁴ , Ana Mendez ⁵ , Cicero Celio de Figueiredo ⁶ , Kalpit Shah ¹ and Jorge Paz-Ferreiro ^{1,*} 

- ¹ Chemical and Environmental Engineering, School of Engineering, RMIT University, Melbourne, VIC 3000, Australia; shefali.bmb@gmail.com (S.A.); kalpit.shah@rmit.edu.au (K.S.)
- ² Department of Biochemistry and Molecular Biology, Hajee Mohammad Danesh Science and Technology University, Dinajpur 5200, Bangladesh
- ³ Department of Fisheries Management, Hajee Mohammad Danesh Science and Technology University, Dinajpur 5200, Bangladesh; afzalhstu@gmail.com
- ⁴ Department of Agricultural Production, Universidad Politécnica de Madrid, Ciudad Universitaria, 28040 Madrid, Spain; gabriel.gasco@upm.es
- ⁵ Department of Geological and Mining Engineering, Universidad Politécnica de Madrid, 28040 Madrid, Spain; anamaria.mendez@upm.es
- ⁶ Faculdade de Agronomia e Medicina Veterinária, Universidade de Brasília, Campus Universitário Darcy Ribeiro, Brasília 04508, DF, Brazil; cicerocf@unb.br
- * Correspondence: jorge.paz-ferreiro@rmit.edu.au; Tel.: +61-399250878

Abstract: Phosphorus (P) is an essential macronutrient for plants. The focus of this work is to recover P from biosolids and their derived biochar. The effect of three different pyrolysis temperatures (400 °C, 500 °C, and 600 °C) and two carrier gases (CO₂ and N₂) on P fractionation and the speciation of P on biochars produced from two biosolids were investigated. The Hedley chemical sequential extraction method and ³¹P liquid NMR were used for P characterization and quantification. Higher pyrolysis temperatures increased P fixation and decreased short-term P bioavailability. Carrier gas had also significant effects on P fractionation in the biochars. Biochar produced in a CO₂ environment had slightly higher water-soluble P, NaHCO₃-P₁, NaOH-P₁, and residual P than in biochar prepared in a N₂ environment, while HCl-P showed the opposite trend. Additionally, the predominant molecular configuration of P was present in the inorganic form identified by ³¹P liquid NMR spectra, while organic P transformed into inorganic P with increasing pyrolysis temperature.

Keywords: pyrolysis; temperature; carrier gases; CO₂; P speciation; ³¹P NMR



Citation: Aktar, S.; Hossain, M.A.; Gasco, G.; Mendez, A.; de Figueiredo, C.C.; Shah, K.; Paz-Ferreiro, J. Effects of Temperature and Carrier Gas on Phosphorus Transformation in Biosolids Biochar. *Land* **2024**, *13*, 2132. <https://doi.org/10.3390/land13122132>

Academic Editor: Claude Hammecker

Received: 19 November 2024

Revised: 5 December 2024

Accepted: 6 December 2024

Published: 9 December 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Phosphorus (P) is a major limiting macronutrient that has an important role in plant growth and development. However, P deficiency is a major constraint in global crop production, which impacts around 30–40% of the world's arable soil [1]. A large proportion of P in soil is organic, but plants can take up only orthophosphate ions (HPO₄²⁻ and H₂PO₄⁻), which are in low concentrations in soil solution. The application of organic and inorganic fertilizers can replenish the P pool, although few P minerals could be available for plant uptake. P could be quickly and strongly constrained by different interactions with other soil components, for example, co-precipitation and adsorption [1]. Moreover, the excessive use of P fertilizer and additional P in arable soils could lead to eutrophication due to surface runoff and leaching. Additionally, the source of P fertilizer is mainly mined rock and some studies claimed that the current commercial extraction rate of global commercial phosphate will be depleted in less than 100 years [2]. Recovery of P from waste materials is gaining interest to solve this problem that has drawn widespread attention [3,4].

Biosolids (dried and stabilized sewage sludge) contain a large amount of P (around 1–10%) based on the dry mass [5] and have a strong potential, by themselves or after

being thermally treated, for use as a fertilizer or soil conditioner [6,7]. The pyrolysis of biosolids has been growing interest in managing waste volume and recovering P from biosolids [3]. Pyrolysis is a thermochemical process that produces a carbon-rich solid materials under oxygen-limited conditions, called biochar. Pyrolysis is an effective option to reduce the volume of waste. It can transform endogenous P (i.e., long-chain polyphosphates) into bioavailable minerals (i.e., orthophosphate, pyrophosphate, and short-chain polyphosphates). This results in biochar being a potential P fertilizer for cultivated land. It is established that the physicochemical properties of biochar are dependent on pyrolysis temperature [8] as well as residence time [3]. There are several studies detailing the effects of pyrolysis temperature and residence time on biochar properties [9,10]. Higher temperature pyrolysis generally leads to higher total P in biochar and to the accumulation of P in semi-labile or stable pools [11]. This is due to the formation of the crystalline soluble or stable aromatic carbon structures during thermal treatment [12]. Li et al. [9] reported that the mobility and bioavailability of P are closely related to its chemical speciation, which will help us to understand the fate of P when using biochar as a soil amendment. Hedley's procedure identifies the P species mainly based on P reactivity or plant availability [13]. This method provided an easy and rapid way of measuring P in the environment and provided a model where water-soluble or organic P was transformed into a labile ($\text{NaHCO}_3\text{-P}_i$) or semi-labile pool (NaOH-P_i) and a stable pool (HCl-P and residual P) during pyrolysis. Qian et al. [14] reported that both $\text{NaHCO}_3\text{-P}$ and NaOH-P decreased with increasing pyrolysis temperature, while HCl-P significantly increased. The Hedley chemical fractionation method provides an approximate idea of relative concentrations and discrete groups of P forms in environmental samples [11]. Moreover, nuclear magnetic resonance spectroscopy (NMR) is an effective way to identify the chemical nature of P compounds in environmental samples [15]. The different forms of the molecular configuration of P, such as orthophosphate, orthophosphate monoester, and pyrophosphate, can be characterized by using solution-state ^{31}P NMR following NaOH-EDTA extraction, which dominantly remained in biochar from biosolids.

Several studies demonstrated the effects of pyrolysis temperature on P speciation [11,16]. However, the effect of carrier gas on the properties of biochar has often been ignored, with the majority of the studies focusing in biochar production under N_2 . Previous works have shown that the use of CO_2 as a carrier gas generated biochar with a higher surface area and reduced the total content of polycyclic aromatic comparing to the use of a N_2 environment [17,18]. To the best author's knowledge, there was only one published work [14] that used different carrier gases (air, N_2 , and CO_2) under fast pyrolysis or the combustion of sewage sludge to elucidate the P behavior. Therefore, the main aims are to produce biochar for agricultural uses under slow pyrolysis using three different temperatures (400 °C, 500 °C, and 600 °C) and two different atmospheric conditions (CO_2 and N_2) and to identify different P species in biosolids and their derived biochar determined by Hedley chemical fractionation. We also focused on the chemical nature of P speciation under different pyrolysis conditions determined by a solution-state ^{31}P NMR analysis. We hypothesize that using a specific carrier gas could provide a new promising way of treating biosolids and can act as a source of slow-release P fertilizer for soil application.

2. Materials and Methodology

2.1. Sample Collection and Preparation of Biochar

2.1.1. Biosolids Collection

The treated sewage sludge was sampled at Mount Martha Water recycle plant, South-east Water, Australia, in which the lagoon and aerobic digester were used for the biosolid treatment process. The collected sample was processed using a sludge blend tank, dosing polymer, and belt press, and 60% moisture was reduced by the solar dryer. The samples were collected from a solar dryer, then ground and sieved to 0.5–1.0 μm . The final sample was oven-dried before pyrolysis, and the remaining sample was stored below 4 °C in a refrigerator.

2.1.2. Biochar Preparation

For biosolids pyrolysis, a fluidized bed reactor constructed of a quartz tube was used under slow pyrolysis (reactor with an internal diameter of reactor 27 mm and a height of 680 mm long). This custom reactor was made by Monash Scientific Australia. Initially, 40 g of oven-dried biosolids was pyrolyzed. The reactor is mainly operated by atmospheric pressure and energy from three electrical zones. Three different pyrolysis temperatures (400, 500, and 600 °C) were chosen using nitrogen (N₂) and carbon dioxide (CO₂) as atmosphere. First, a high-purity gas flow, either CO₂ or N₂, was introduced to the furnace at a rate of 7.5 L min⁻¹ to eliminate the O₂-free environment. The furnace was initially heated from room temperature (25 °C) to the targeted temperature (400, 500, and 600 °C) and maintained for one hour of heating with a carrier gas (CO₂ or N₂). The biochar sample was collected and labeled based on the temperature and atmosphere used in the pyrolysis set. The collected biochar was stored in a freezer. The yield of biochar was calculated as the ratio of the total weight of biochar produced to the total dry weight of biosolids used in pyrolysis:

$$\text{Biochar yield (\%)} = \left(\frac{w_2}{w_1} \right) \times 100$$

where w_1 indicates the total dry weight of biosolids before pyrolysis and w_2 represents the total amount of solid product after pyrolysis.

The collected biochar was abbreviated as BC400, BC500, BC600, BN400, BN500, and BN600, where C and N represent the gas (CO₂ and N₂, respectively), and 400, 500, and 600 indicate the highest temperature used in pyrolysis.

2.2. Sequential Extracting Procedure for Biosolids and Its Derived Biochar

2.2.1. P Fractionation

Both biosolids and biochar were sequentially extracted using the modified sequential Hedley fractionation method [13] and described in detail by [19]. This method was used for identifying different P pools based on their solubility and bioavailability. First, 0.5 g of biosolids and biochar sample was placed in 50 mL of the centrifuge tube, sequentially extracted step by step using 30 mL deionized water, and shaken overnight (16 h) in a mechanical shaker. The P content was determined using the Murphy and Riley method. The residue from the first step was extracted with 30 mL of 0.5 M NaHCO₃ at pH 8.5 and shaken overnight (16 h). A similar procedure was followed using 0.1 M NaOH and 1 M HCl, shaken for 16 h and centrifuged at 3500 rpm for 15 min after each addition. However, the NaHCO₃ and NaOH extracts were divided into two aliquots to measure total P (P_t) and inorganic P (P_i) [20]. Finally, the residual P was measured using complete digestion using H₂SO₄ + one boiling chip H₂O₂. After preparation of each extract, P_i was determined using the molybdovanadate method (8114) Test 'N Tube (TNT), and P_t was determined using molybdovanadate with acid persulphate digestion method (10,127) TNT in a Hach DRTM 5000 spectrophotometer [3]. Organic P (P_o) was calculated by subtracting P_i from P_t [11]. The H₂O-P is considered a readily bioavailable fraction. Similarly, NaHCO₃-P also indicated the exchangeable P_i and easily mineralizable P_o, which is adsorbed to soil minerals. The NaOH-P are bound with Al and Fe mineral (P_i) and humic acid (P_o), which is considered a moderately available P. The P bound with NaHCO₃-P is considered a plant available for the short term, while NaOH-P indicates the plant available for the medium term. The non-labile HCl-P is considered non-bioavailable for plants and bound with Ca and Mg minerals and HCl-P can be slowly uptaken by the plant [14]. Residual P is a stable and recalcitrant P form that is strongly bound to P minerals [21,22].

2.2.2. Solution-State ³¹P NMR Analysis for Biosolids and Biochar

Nuclear magnetic resonance spectroscopy (NMR) is an effective method to identify the P compounds in environmental samples [15]. The chemical nature of P compounds in the biosolid sample and its derived biochar was measured by ³¹P NMR method. For the

analysis, a 0.5 g sample was added with 20 mL of extractant by mixing 0.25 M NaOH + 0.05 M EDTA solution [11,16]. The solution was shaken at room temperature for 16 h. The liquid sample was used to measure the total P concentration in NaOH-EDTA using the molybdenum blue method [11].

Then, 1 mL of 0.22 M NaHCO₃ + 0.22 M Na₂S₂O₄ solution was added and the solution was freeze-dried. Subsequently, 0.5 g of solid sample was diluted with 0.2 mL of NaOH and 0.5 mL of D₂O. Bruker 300 MHz Avance III spectrometer (Australia) was used to record the high-resolution NMR P spectra. The instrument was equipped with a 5 mm probe at 25 °C was acquired with 2000 scans with a spectral width of 400 ppm and a delay time of 2 s and 50 s. Spectra were analyzed using Topspin 3.6.3 NMR processing software. The content of individual P species was calculated using the following Equation (1) [11].

$$A_i = \langle X|Y \rangle * TP \text{ NaOH} - \text{EDTA} \quad (1)$$

where A_i = is the number of individual P species in ³¹P liquid NMR, while X and Y indicate the individual and total peak area of ³¹P NMR, respectively. TP NaOH-EDTA is the amount of P extracted by 0.25 M NaOH and 0.05 M EDTA (mg kg⁻¹) in biochar.

2.2.3. X-Ray Diffraction Analysis (XRD)

The ground biochar sample was loaded into Al-holders tubes to identify the random powder XRD patterns. The XRD spectra were measured at an angle of 5 to 65° with a scan step size of 0.02° and a time step of 1s. The peak areas identified for the different minerals were compared with XRD patterns of standard minerals compiled by comparing d-spacings in the diffraction patterns to the ICDD–PDF mineral database.

2.3. Data Analysis and Statistical Significance

Data resulting from all the analyses of biosolids and biochar were tested for normality using Kolmogorov–Smirnov and Shapiro–Wilk test. A two-way analysis of variance (ANOVA) was performed to identify the significant effects of temperature, atmosphere, and their interaction on biochar P speciation characteristics. A post hoc analysis was carried out for temperature using Tukey’s test. All data were analyzed in the SPSS 26.0 version, and the significance level was set at $p < 0.05$.

3. Results and Discussion

3.1. Effects of Pyrolysis Temperature on P Speciation of Biosolids and Biochar

The influence of pyrolysis temperature on the P availability in biosolids and their derived biochar is shown in Table 1, and the significance level is shown in Table 2. Pyrolysis temperature had a significant effect on H₂O-P_i, NaHCO₃-P_t, NaHCO₃-P_i, NaHCO₃-P_o, NaOH-P_t, NaOH-P_i, NaOH-P_o, HCl-P, and residual P. The water-soluble P (H₂O-P_i) was higher (2706 mg kg⁻¹) in biosolids, which gradually decreased from 400 °C (average 391 mg kg⁻¹) to 600 °C (137 mg kg⁻¹), respectively.

Similarly, the sum of organic and inorganic labile-P (NaHCO₃-P) was also higher at 400 °C (average 3155 mg kg⁻¹), which was diminished gradually at 600 °C (with an average value of 1647 mg kg⁻¹). The results indicate that the plant available P was decreased with increasing pyrolysis temperature [3]. The amount of inorganic P (NaOH-P_i) was around three times higher in biochar prepared at 400 °C (average value 6057 mg kg⁻¹) than in biochar produced at 600 °C (average value 2206 mg kg⁻¹). Similarly, the amount of exchangeable organic P (NaOH-P_o) in biochar prepared under 400 °C was 899 mg kg⁻¹, which was significantly increased at 500 °C (1035 mg kg⁻¹) before dropping at 600 °C (477 mg kg⁻¹). However, the amount of HCl-P in biochar was highest at 600 °C (average value 12,038 mg kg⁻¹) compared to the biochar prepared at 400 °C (average value 10,723 mg kg⁻¹). HCl-P fractions are mainly related to the P bound mostly with Ca and Mg. Therefore, the current results indicate that pyrolysis temperature significantly decreased the inorganic NaHCO₃-P and NaOH-P and increased HCl-P. A higher pyrolysis temperature (600 °C) under slow pyrolysis of biosolids biochar may result in the migration of P from

NaHCO₃-P and NaOH-P to a more stable pool (HCl-P). Qian and Jiang [14] also reported related results where biochar produced at lower temperatures may produce some labile organic matter that quickly condensed on the surface heating zone. This labile organic matter may contain carboxyl and hydroxy groups that react with Ca and Mg and prevent the formation of insoluble Ca-P and Mg-P by inhibiting the contact between Ca, Mg, and P. On the other hand, high-temperature biochar produced some recalcitrant aromatic carbons [23], having few carboxyl and hydroxyl groups that had lower impacts on the reaction between Ca, Mg, and P and significantly increased the formation of insoluble Ca, Mg-P compounds. Our previous results confirmed that biochar produced at a higher temperature contained more recalcitrant carbon, facilitating the formation of insoluble compounds of P with Ca and Mg [24]. Pyrolysis temperature significantly transformed the proportion labile and semi-labile-P into a stable fraction (HCl-P), where the P was trapped with minerals and hardly available for plant uptake.

Table 1. The amount of P in different fractions of biosolids and biochars (mg kg⁻¹) produced under three different pyrolysis temperatures, 400 °C, 500 °C, and 600 °C, where BC represents CO₂ and BN under a N₂ environment. Data represents average values and standard deviation.

P Fractions	Biosolids	BC400	BC500	BC600	BN400	BN500	BN600
H ₂ O-P _i	2706 ± 257	484 ± 38	423 ± 52	194 ± 15	298 ± 6	178 ± 13	80 ± 11
NaHCO ₃ -P _t	5946 ± 97	3081 ± 35	2459 ± 82	1743 ± 24	3230 ± 53	2138 ± 90	1550 ± 87
NaHCO ₃ -P _i	4826 ± 164	2572 ± 42	2258 ± 35	1516 ± 49	2830 ± 40	1814 ± 40	1341 ± 19
NaHCO ₃ -P _o	1119 ± 70	509 ± 35	200 ± 41	227 ± 13	399 ± 39	323 ± 29	209 ± 19
NaOH-P _t	4354 ± 28	7085 ± 16	6574 ± 12	2845 ± 10	6827 ± 13	4317 ± 08	2521 ± 22
NaOH-P _i	3245 ± 28	6267 ± 12	5405 ± 31	2278 ± 17	5847 ± 04	3414 ± 07	2134 ± 12
NaOH-P _o	2114 ± 07	818 ± 04	1168 ± 19	567 ± 27	980 ± 09	902 ± 09	387 ± 11
HCl-P	3421 ± 44	10,630 ± 18	10,951 ± 34	11,925 ± 42	10,815 ± 88	11,316 ± 94	12,150 ± 17
Res. P _t	300 ± 30	4904 ± 17	9505 ± 19	10,114 ± 21	1464 ± 25	8657 ± 14	8360 ± 17
Total P-P _t	24,802 ± 88	35,026 ± 17	37,579 ± 30	30,618 ± 81	31,313 ± 94	31,738 ± 88	28,099 ± 69

Table 2. The two-way ANOVA study of the amount of P fractions in biochar produced at different temperatures (400 °C, 500 °C, and 600 °C) under two (CO₂ and N₂) atmospheres. Significance was set at $p < 0.05$.

Tests of Between-Subjects Effects						
Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Temperature	H ₂ O-P _i	300,385.256	2	150,192.628	46.519	<0.001
	NaHCO ₃ -P _t	9,163,254.583	2	4,581,627.291	250.454	<0.001
	NaHCO ₃ -P _i	6,484,043.721	2	3,242,021.861	140.633	<0.001
	NaHCO ₃ -P _o	252,454.661	2	126,227.331	3.441	0.054
	NaOH-P _t	75,116,270.954	2	37,558,135.477	593.817	<0.001
	NaOH-P _i	59,734,061.367	2	29,867,030.683	286.233	<0.001
	NaOH-P _o	1,355,725.909	2	677,862.955	6.216	0.009
	HCl-P	347,498.284	2	173,749.142	0.114	0.893
	Residual P _t	409,908,059.994	2	204,954,029.997	383.615	<0.001

Table 2. Cont.

Tests of Between-Subjects Effects						
Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Environment	H ₂ O-P _i	312,500.245	1	312,500.245	96.791	<0.001
	NaHCO ₃ -P _t	88,985.394	1	88,985.394	4.864	0.041
	NaHCO ₃ -P _i	86,828.252	1	86,828.252	3.766	0.068
	NaHCO ₃ -P _o	13.234	1	13.234	0.000	0.985
	NaOH-P _t	5,375,567.101	1	5,375,567.101	84.991	<0.001
	NaOH-P _i	4,355,221.547	1	4,355,221.547	41.739	<0.001
	NaOH-P _o	53,643.270	1	53,643.270	0.492	0.492
	HCl-P	30,669,771.101	1	30,669,771.101	20.172	<0.001
	Residual P _t	49,108,186.942	1	49,108,186.942	91.916	<0.001
	Temperature x Environment	H ₂ O-P _i	41,575.336	2	20,787.668	6.439
NaHCO ₃ -P _t		235,494.559	2	117,747.280	6.437	0.008
NaHCO ₃ -P _i		502,530.144	2	251,265.072	10.899	0.001
NaHCO ₃ -P _o		55,168.121	2	27,584.060	0.752	0.486
NaOH-P _t		5,159,576.512	2	2,579,788.256	40.788	<0.001
NaOH-P _i		3,972,398.784	2	1,986,199.392	19.035	<0.001
NaOH-P _o		204,697.579	2	102,348.789	0.938	0.410
HCl-P		2,569,374.571	2	1,284,687.286	0.845	0.446
Residual P _t		25,876,886.580	2	12,938,443.290	24.217	<0.001

Residual P was significantly higher at 600 °C (average value of 9237 mg kg⁻¹) compared to 400 °C (3184 mg kg⁻¹). Moreover, pyrolysis temperature significantly converted organic P (NaHCO₃-P_o and NaOH-P_o) into inorganic P or other forms of stable organic. The total P content in biochar was slightly increased from 400 °C (average value 33,170 mg kg⁻¹) to 500 °C (average value 34,658 mg kg⁻¹), while the concentration was found to decrease slightly (29,358 mg kg⁻¹) at 600 °C. The reason could be that the high volatilization of the organic compound could reduce the amount of P at higher pyrolysis temperatures. Liu et al. [25] reported that the decompositions of stable organic compounds in sewage sludge biochar will release more intracellular P for microbes, further react with inherent heavy metals (for example, Fe, Al, and Mg) at higher temperatures, and form more inorganic P.

3.2. Influence of Pyrolysis Atmosphere on P Speciation of Biosolids and Biochar

The pyrolysis environment had a significant effect on H₂O-, NaHCO₃-P_t, NaOH-P_i, NaOH-P_t, HCl-P, and residual P. The current results indicated that biochar produced under the CO₂ environment contained more H₂O-P_i (average 367 mg kg⁻¹) than under the N₂ environment (average 185 mg kg⁻¹). Similarly, biochar produced under the CO₂ environment contained more total P (34,408 mg kg⁻¹), NaHCO₃-P_t (2428 mg kg⁻¹), NaOH-P_t (5501 mg kg⁻¹), and residual P (8175 mg kg⁻¹) than that prepared in the N₂ environment, the value representing total P (30,383 mg kg⁻¹), NaHCO₃-P_t (2306 mg kg⁻¹), NaOH (4555 mg kg⁻¹), and residual P (9127 mg kg⁻¹). However, the stable fraction of P (HCl-P) was slightly higher under N₂ (11,427 mg kg⁻¹) than under CO₂ (11,169 mg kg⁻¹). Zhang et al. [26] also reported similar results, where the total P recovery rates were higher under CO₂ than higher than N₂. Tan and Yuan [27] also reported similar results, where the relative content of inorganic P was higher in the atmosphere of CO₂ than in the N₂ atmosphere. The reason could be that the adsorption mechanism of phosphate ions in sewage sludge

biochar includes the hydrolysis of minerals at their first stage, such as calcite or dolomite, which subsequently increases the interaction between Ca^{2+} and $\text{PO}_4^{3-}/\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ ions, leading to the formation of crystal or precipitates. For instance, X-ray diffraction (XRD) results in Figure 1 revealed that the percentage of calcite decreased more under CO_2 than under N_2 with increasing pyrolysis temperature [28].

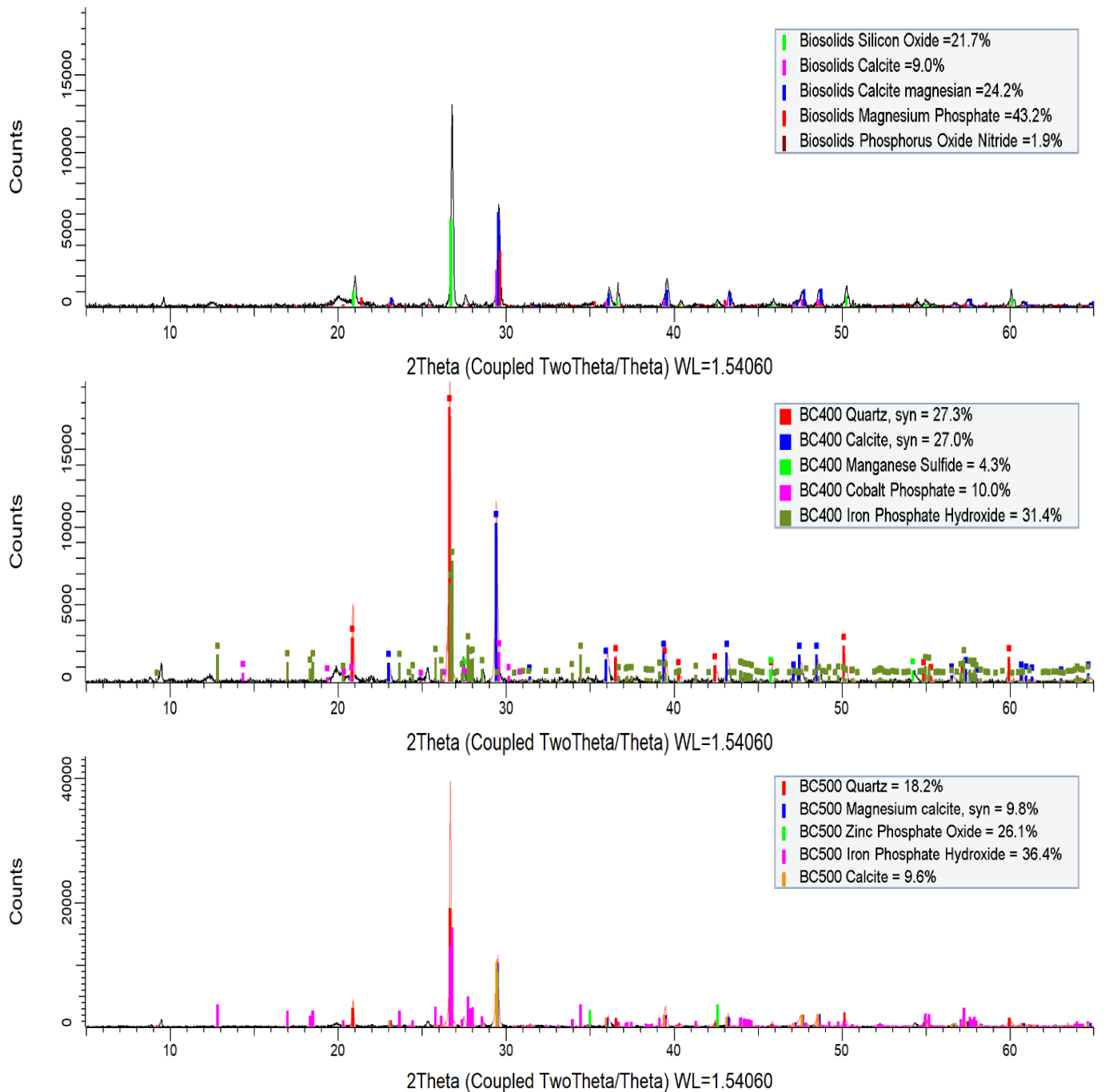


Figure 1. Cont.

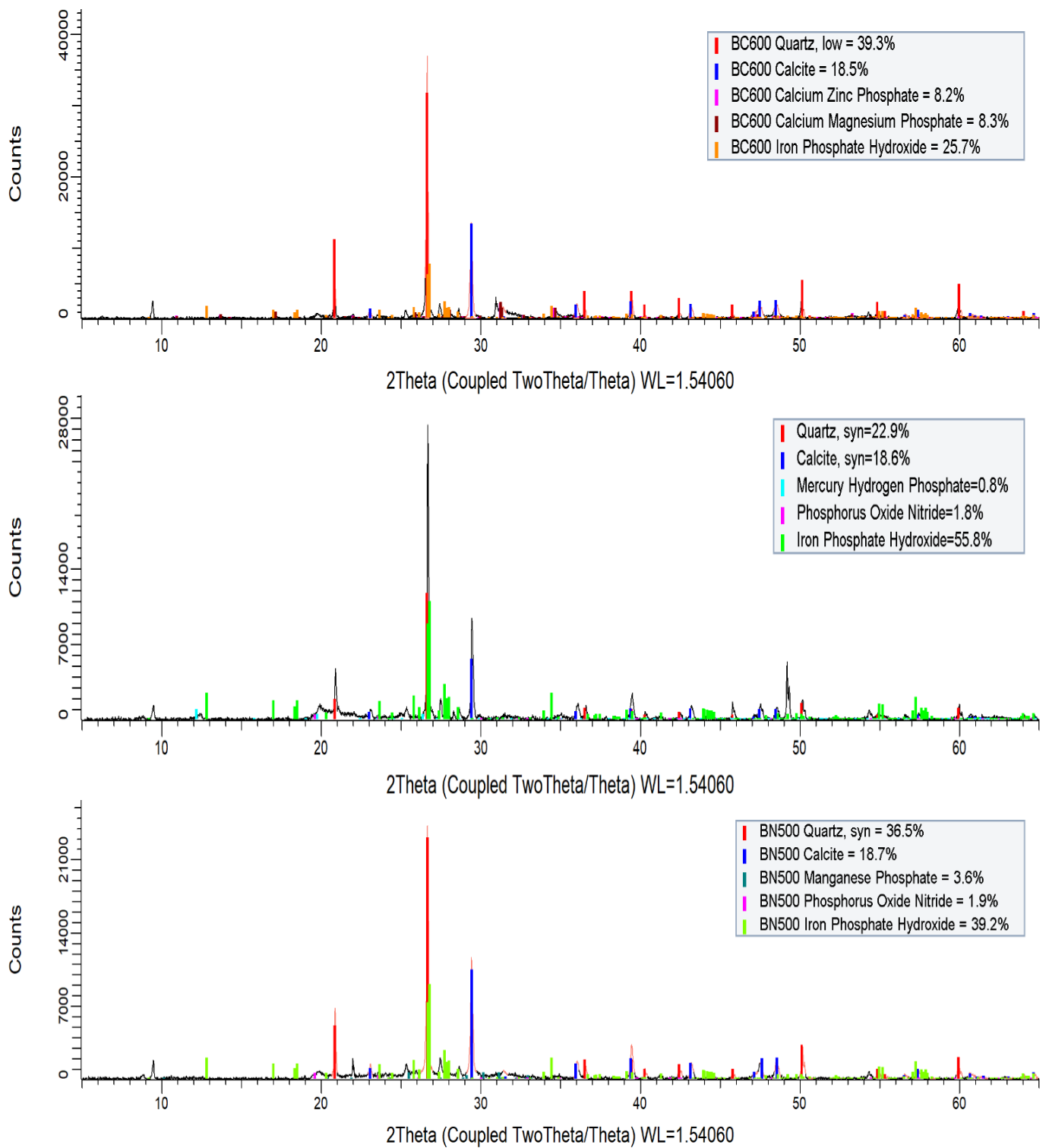


Figure 1. Cont.

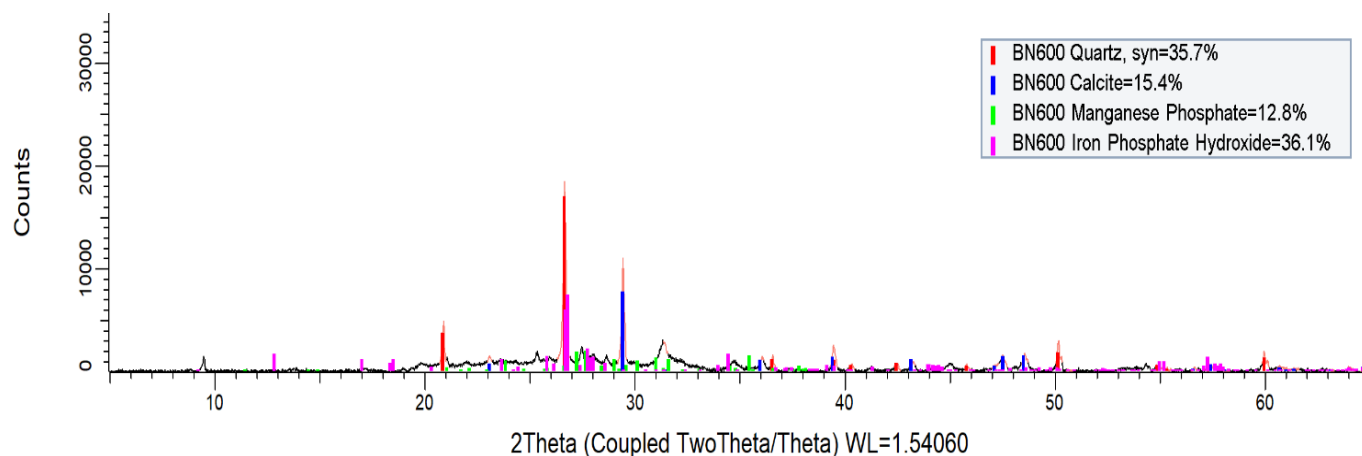


Figure 1. XRD pattern in biosolids and their biochars. From top to bottom, biosolids, BC400, BC500, BC600, BN400, BN500 and BN600.

The interaction between temperature \times environment also had a significant effect on H_2O-P_i , $NaHCO_3-P_t$, $NaHCO_3-P_i$, $NaOH-P_i$, $NaOH-P_t$, and residual P. The total content of labile and exchangeable P was nearly 2 times higher in biochar produced at BC400 and BC500 under CO_2 compared to all other treatments. Similar results were also reported in a previous study [14]. Therefore, the results indicate that biochar produced at lower pyrolysis temperatures (BC400 and BC500) under the CO_2 environment contain more labile-P, exchangeable P, and residual P than a N_2 environment, while biochar exhibits more stable P.

3.3. ^{31}P Liquid NMR

The NaOH/EDTA method was used to understand the extractable individual P species in both biosolids and their derived biochar using ^{31}P liquid NMR. Biosolids contained the highest concentration of NaOH/EDTA- P_t (14,352 $mg\ kg^{-1}$, Table 3), and the value gradually decreased from 400 $^{\circ}C$ (10,059 $mg\ kg^{-1}$) to 600 $^{\circ}C$ (4681 $mg\ kg^{-1}$) after pyrolysis in a CO_2 environment. Similarly, the value gradually decreased from pyrolysis at 400 $^{\circ}C$, 500 $^{\circ}C$, and 600 $^{\circ}C$ under N_2 , from 6849 $mg\ kg^{-1}$, 5643 $mg\ kg^{-1}$, and 3873 $mg\ kg^{-1}$, respectively. Therefore, our current results indicate that P condensation was higher at lower pyrolysis temperatures (400 $^{\circ}C$), which was similar to previous studies [3]. Similarly, Uchimiya and Hiradate [16] reported that NaOH-EDTA solution was more effective for P extractant in biochar prepared under 500 $^{\circ}C$ due to the stabilization of the organic phase to an inorganic fraction by the formation of different organo-mineral interactions during pyrolysis. These studies also reported that the organic phosphate gradually transformed into inorganic P, mainly orthophosphate and pyrophosphate, with increasing pyrolysis temperature. At even higher temperatures, pyrophosphate is also converted into orthophosphate.

Table 3. Amount and percentage of phosphorus speciation of NaOH-EDTA extract determined by solution ^{31}P NMR ($mg\ kg^{-1}$).

	Ortho-P	Ortho-Monoester	Pyro-P
Biosolids	12,737.47 (88%)	1439.46 (10%)	175.54 (1%)
BC400	6980.00 (70%)	-	3079.41 (30%)
BC500	6149.055 (86%)	-	999.46 (14%)
BC600	4518.02 (96%)	-	163.16 (4%)
BN400	5098.11 (74%)	-	1751.39 (25%)
BN500	5019.12 (88%)	-	624.44 (12%)
BN600	3772.66 (97%)	-	100.60 (3%)

The total P recovery under the NaOH-EDTA solution was slightly higher under CO₂ than under N₂. Moreover, biochars produced under N₂ had pH values ranging from 7.47 to 11.26 at temperatures from 400 °C to 600 °C, respectively. When produced under CO₂, the pH ranged from 6.53 to 8.08, as it could be seen in our previous work [24]. Xu et al. [11] reported that the pH of biochar significantly affected the P extractability, as P is tightly bound under alkaline conditions. Therefore, the extraction recovery rates were lower than in the acidic conditions. Three signals can be identified for the P compound, which was mainly orthophosphate, pyrophosphate, and orthophosphate monoesters in liquid NMR spectra in Figure 2. Orthophosphate (5–7 ppm) and pyrophosphate (−4 to −5 ppm) are the two most dominant species of P species identified in biochars [15] and major constituents of P pools. However, there was an additional signal identified for biosolids, which are represented by organic P (i.e., orthophosphate monoesters) [15], which disappeared in biochar produced under different temperatures and carrier gases, which is similar to previous studies [3]. The peak corresponding to organic P disappeared, while inorganic P (Ortho and Pyro-P) remained with increasing pyrolysis temperatures (Figure 2), indicating that the organic P migrated into ortho-P and pyro-P during pyrolysis [11].

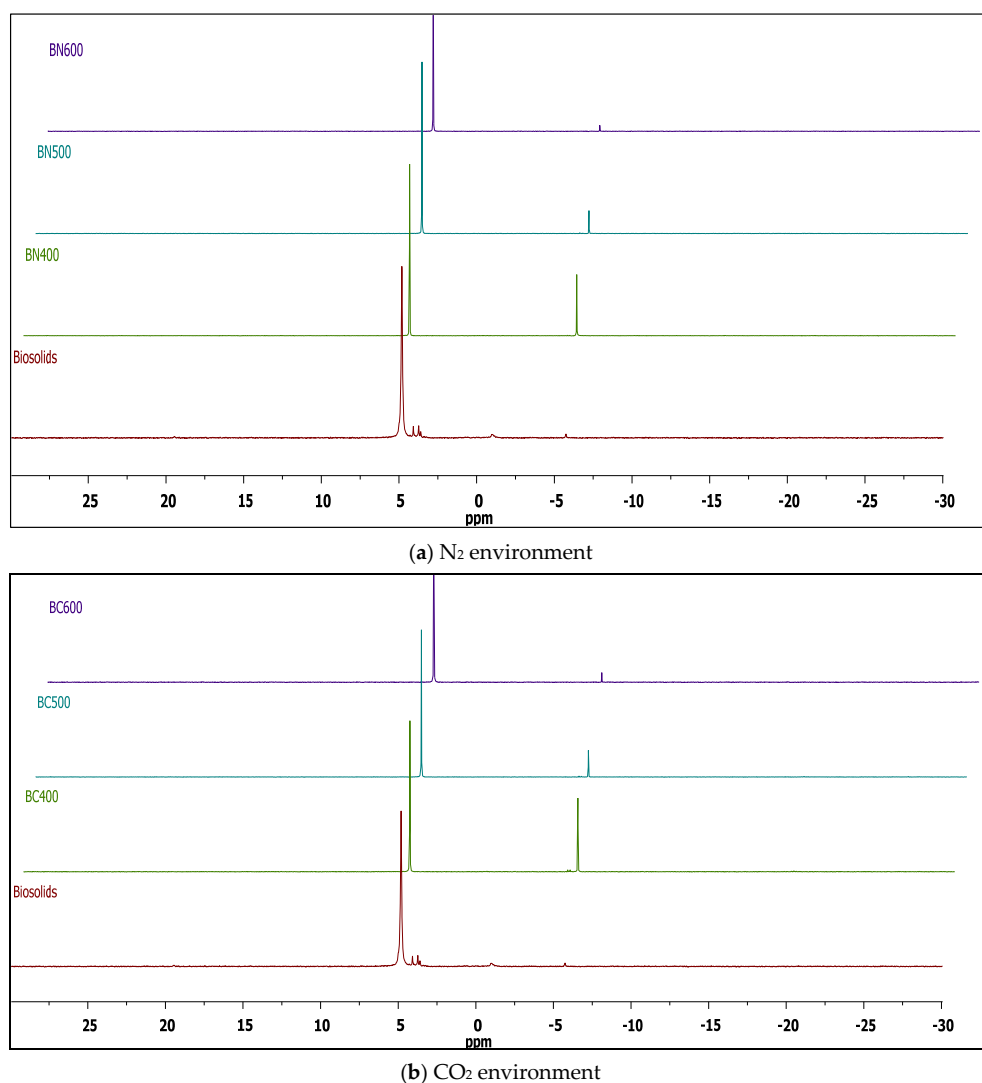


Figure 2. Liquid ³¹P NMR spectra for biosolids and their derived biochar under different pyrolysis conditions ((a) N₂ environment and (b) CO₂ environment).

Pyrolysis temperature significantly decreased the amount of organic P and ortho-P in the resulting biochar and increased the production of pyro-P at 400 °C after pyrolysis. This reason for the higher formation of pyro-P is related to the transformation of organic P and dehydration of ortho-P in sewage sludge [14]. However, the amount of both ortho-P and pyro-P gradually decreased at 600 °C, which might be related to the decomposition of inorganic matter, such as calcite and quartz [29]. The peak position was slightly varied under different pyrolysis temperatures, and atmospheric conditions could represent the phase transformation of inorganic P species that includes metal complexation, mineral adsorbed species, and phosphate minerals [10].

3.4. XRD Analysis

The XRD spectra showed the crystalline mineral phases present in both biosolids and their derived biochar samples (Figure 2). From the XRD pattern, the main crystalline phase was quartz after pyrolysis [26]. The presence of calcite, magnesium calcite, and iron phosphate hydroxide indicated that the Ca, Mg, Fe, and P were the main inorganic components in biochar [9]. Initially, the signal intensity for different biochar samples was varied; for example, the intensity for quartz was initially low (21.7%, Figure 2) in biosolids, which was gradually increased at 600 °C, and the value was 39.9% under a CO₂ environment and 35.7% under a N₂ environment. With increasing pyrolysis temperature, the peak intensity for calcite was reduced due to the decomposition of calcite into CaO [30]. The change in the XRD pattern for P was different under different pyrolysis temperatures, which also proved the migration of P under different pools (i.e., NaOH-P to HCl-P) [14].

4. Conclusions

A better understanding of phosphorus speciation and fractionation is needed for its use as a smart fertilizer. Pyrolysis can eliminate pathogens in the biosolids. Moreover, biochar produced at lower pyrolysis temperatures could be beneficial for immediate P availability for plants, while higher-pyrolysis-temperature-produced biochar with more stable P has the potential to be used as a slow-release fertilizer, leading to the development of smart fertilizers. The atmosphere used can be also utilized to fine-tune biochar synthesis. In particular, biochars prepared under N₂ showed a higher potential as a slow-release fertilizer. Further studies should be performed to assess the release of P from biochars produced under different gases in the soil–plant system.

Author Contributions: S.A.: Conceptualization, Data collection, interpretation and analysis of data, Writing—original draft, Data curation, Investigation. M.A.H.: Conceptualization, Writing—Data analysis, review and editing. G.G.: Conceptualization, Writing—review and editing. A.M.: Conceptualization, Writing—review and editing. C.C.d.F.: Conceptualization, Writing—review and editing. K.S.: Conceptualization, Supervision, Writing—review and editing. J.P.-F.: Conceptualization, Supervision, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: The first author would like to acknowledge the School of Engineering, RMIT University, for providing a Ph.D. scholarship and associated research funds. We appreciate the support from the School of Science, RMIT, in the NMR analyses for this work.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Li, H.; Li, Y.; Xu, Y.; Lu, X. Biochar phosphorus fertilizer effects on soil phosphorus availability. *Chemosphere* **2020**, *244*, 125471. [[CrossRef](#)] [[PubMed](#)]
2. Zhu, J.; Li, M.; Whelan, M. Phosphorus activators contribute to legacy phosphorus availability in agricultural soils: A review. *Sci. Total Environ.* **2018**, *612*, 522–537. [[CrossRef](#)]
3. Adhikari, S.; Gascó, G.; Méndez, A.; Surapaneni, A.; Jegatheesan, V.; Shah, K.; Paz-Ferreiro, J. Influence of pyrolysis parameters on phosphorus fractions of biosolids derived biochar. *Sci. Total Environ.* **2019**, *695*, 133846. [[CrossRef](#)] [[PubMed](#)]
4. Zhu, Y.; Zhai, Y.; Li, S.; Liu, X.; Wang, B.; Liu, X.; Fan, Y.; Shi, H.; Li, C.; Zhu, Y. Thermal treatment of sewage sludge: A comparative review of the conversion principle, recovery methods and bioavailability-predicting of phosphorus. *Chemosphere* **2022**, *291*, 133053. [[CrossRef](#)] [[PubMed](#)]
5. Mayer, B.K.; Baker, L.A.; Boyer, T.H.; Drechsel, P.; Gifford, M.; Hanjra, M.A.; Parameswaran, P.; Stoltzfus, J.; Westerhoff, P.; Rittmann, B.E. Total value of phosphorus recovery. *Environ. Sci. Technol.* **2016**, *13*, 6606–6620. [[CrossRef](#)]
6. Hossain, M.K.; Strezov, V.; Chan, K.Y.; Ziolkowski, A.; Nelson, P.F. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J. Environ. Manag.* **2011**, *92*, 223–228. [[CrossRef](#)]
7. Huang, R.; Tang, Y. Speciation dynamics of phosphorus during (hydro) thermal treatments of sewage sludge. *Environ. Sci. Technol.* **2015**, *49*, 14466–14474. [[CrossRef](#)]
8. Xu, H.; Wang, Z.; Li, Y.; He, J.; Wu, X. Physicochemical properties of biochars produced from biosolids in Victoria, Australia. *Int. J. Environ. Res. Public Health* **2018**, *15*, 1459. [[CrossRef](#)]
9. Li, M.; Tang, Y.; Lu, X.-Y.; Zhang, Z.; Cao, Y. Phosphorus speciation in sewage sludge and the sludge-derived biochar by a combination of experimental methods and theoretical simulation. *Water Res.* **2018**, *140*, 90–99. [[CrossRef](#)]
10. Xiong, Q.; Wu, X.; Lv, H.; Liu, S.; Hou, H.; Wu, X. Influence of rice husk addition on phosphorus fractions and heavy metals risk of biochar derived from sewage sludge. *Chemosphere* **2021**, *280*, 130566. [[CrossRef](#)]
11. Xu, G.; Zhang, Y.; Shao, H.; Sun, J. Pyrolysis temperature affects phosphorus transformation in biochar: Chemical fractionation and ³¹P NMR analysis. *Environ. Sci. Technol.* **2016**, *569*, 65–72. [[CrossRef](#)] [[PubMed](#)]
12. Thygesen, A.; Wernberg, O.; Skou, E.; Sommer, S.G. Effect of incineration temperature on phosphorus availability in bio-ash from manure. *Environ. Technol.* **2011**, *32*, 633–638. [[CrossRef](#)]
13. Hedley, M.J.; Stewart, J.; Chauhan, B. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* **1982**, *465*, 970–976. [[CrossRef](#)]
14. Qian, T.-T.; Jiang, H. Migration of phosphorus in sewage sludge during different thermal treatment processes. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1411–1419. [[CrossRef](#)]
15. Cade-Menun, B.J. Characterizing phosphorus in environmental and agricultural samples by ³¹P nuclear magnetic resonance spectroscopy. *Talanta* **2005**, *66*, 359–371. [[CrossRef](#)]
16. Uchimiya, M.; Hiradate, S. Pyrolysis temperature-dependent changes in dissolved phosphorus speciation of plant and manure biochars. *J. Agric. Food Chem.* **2014**, *62*, 1802–1809. [[CrossRef](#)] [[PubMed](#)]
17. Guo, S.; Xiong, X.; Che, D.; Liu, H.; Sun, B. Effects of sludge pyrolysis temperature and atmosphere on characteristics of biochar and gaseous products. *Korean J. Chem. Eng.* **2021**, *38*, 55–63. [[CrossRef](#)]
18. Kończak, M.; Oleszczuk, P. Co-pyrolysis of sewage sludge and biomass in carbon dioxide as a carrier gas affects the total and leachable metals in biochars. *J. Hazard. Mater.* **2020**, *400*, 123144. [[CrossRef](#)]
19. Tiessen, H.; Moir, J. Characterization of available P by sequential extraction. In *Soil Sampling and Methods of Analysis*, 2nd ed.; Carter, M.R., Gregorich, E.G., Eds.; CRC Press: Boca Raton, FL, USA, 2007; pp. 293–306. ISBN 9780429126222.
20. Murphy, J.; Riley, J.P. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **1952**, *27*, 31–36. [[CrossRef](#)]
21. Alotaibi, K.D.; Arcand, M.; Ziadi, N. Effect of biochar addition on legacy phosphorus availability in long-term cultivated arid soil. *Chem. Biol. Technol. Agric.* **2021**, *8*, 47. [[CrossRef](#)]
22. Lajtha, K.; Driscoll, C.T.; Jarrell, J.M.; Elliott, E.T. Soil phosphorus: Characterization and total element analysis. In *Standard Soil Methods for Long-Term Ecological Research*; Robertson, G.P., Coleman, D.C., Bledsoe, C.S., Eds.; Oxford University Press: Oxford, UK, 1999; pp. 115–142. ISBN 9780195120837.
23. Lehmann, J.; Joseph, S. *Biochar for Environmental Management: Science, Technology and Implementation*; Routledge: Oxford, UK, 2024; ISBN 9781032286150.
24. Aktar, S.; Hossain, A.; Rathnayake, N.; Patel, S.; Gasco, G.; Mendez, A.; de Figueiredo, C.; Surapaneni, A.; Shah, K.; Paz-Ferreiro, J. Effects of temperature and carrier gas on physico-chemical properties of biochar derived from biosolids. *J. Anal. Appl. Pyrolysis* **2022**, *164*, 105542. [[CrossRef](#)]
25. Braun, T.; Reuter, J.; Rudolph, J. Phosphorus speciation and bioavailability of sewage sludge derived biochar amended with CaO. *Waste Manag.* **2019**, *87*, 71–77. [[CrossRef](#)]
26. Zhang, Z.; Ju, R.; Zhou, H.; Chen, H. Migration characteristics of heavy metals during sludge pyrolysis. *Waste Manag.* **2021**, *120*, 25–32. [[CrossRef](#)] [[PubMed](#)]
27. Tan, Z.; Yuan, S. The effect of preparing temperature and atmosphere on biochar's quality for soil improving. *Waste Biomass Valorization* **2019**, *10*, 1395–1405. [[CrossRef](#)]

28. Zhang, L.; Liu, J.; Guo, X. Investigation on mechanism of phosphate removal on carbonized sludge adsorbent. *J. Environ. Sci.* **2018**, *64*, 335–344. [[CrossRef](#)]
29. Zhao, B.; Xu, X.; Li, H.; Chen, X.; Zeng, F. Kinetics evaluation and thermal decomposition characteristics of co-pyrolysis of municipal sewage sludge and hazelnut shell. *Bioresour. Technol.* **2018**, *247*, 21–29. [[CrossRef](#)]
30. Zhang, J.; Lü, F.; Zhang, H.; Shao, L.; Chen, D.; He, P. Multiscale visualization of the structural and characteristic changes of sewage sludge biochar oriented towards potential agronomic and environmental implication. *Sci. Rep.* **2015**, *5*, 9406. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.