Carbon Dioxide and Release of Primary Nutrients in Contrasting Soils Incubated with Feedstocks and Biochar from Cull Potato and Pine Bark

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Abstract: Disposal of potato waste at landfills results in nutrient losses and pollution of air and groundwater. Biochar from the waste could minimise carbon dioxide (CO_2) emission, increase storage of carbon (OC) and recycle nutrients in soil. This study determined effects of biochar from cull potato (CP) and pine bark (PB) on CO_2 emission and available nitrogen (N), phosphorus (P), and potassium (K) in contrasting soils. Biochar pyrolysed at 350 °C (CP350; PB350) and 650 °C (CP650; PB650), and feedstocks were applied to Luvisol and Ferralsol soils at rates equivalent to 10 Mg C ha^{-1} and incubated at 25 °C. The carbon dioxide (CO_2-C) was captured in 1 M NaOH and the solution was back-titrated with 0.5 M HCl after 3, 7, 14, 21, 28, 42, 56, and 84 days. A similar experiment was conducted, with destructive sampling, including after 112 and 140 days, for analysis of ammonium-N, nitrate-N, and available P and K. Biochar increased CO_2 in the Luvisol but decreased it in the Ferralsol when compared with the feedstocks and the control. Higher CO_2 was emitted from PB biochar than from CP in the Luvisol. Ammonium-N increased in the Luvisol, reaching a peak after 14 days, and decreased after 42 days, while, in the Ferralsol, it decreased to below detection after 21 days. Nitrate-N increased with decline in ammonium-N, except in CP, in both soils. Available P increased within 14 days and declined after 28 days, with generally higher levels in the Ferralsol. Available K increased with addition of CP and its biochar, with greater availability at higher pyrolysis temperatures for both soils throughout the incubation. The findings showed that application of CP biochar causes emission of CO_2 to increase in Luvisol and decrease in Ferralsol, while available K increase, with no effects on N availability, relative to control soils.

Keywords: carbon storage; cull potato; mineral nitrogen; phosphorus; potassium; pyrolysis

1. Introduction

The large amount of organic carbon [1] and nutrients [2] in organic waste materials suggests their potential value in soil fertility improvement. Potato waste, such as cull potato and potato peels, is among the most abundant organic waste and often presents disposal challenges and contains up to 2.14% N [3], 2.47% K, and 0.35% P [4]. The carbon and nutrient compositions suggest that the application of potato waste to soil could have significant organic fertiliser value. Its benefits as an organic fertiliser may, however, be short-lived due to rapid decomposition in soil [5], which consequently increases emission of carbon in the form of carbon dioxide (CO_2-C) [6]. Pyrolysis of the potato waste to biochar may reduce these negative effects and enhance the potential benefits.

Recently, biochar has been advocated for as a stable, organic soil amendment with the ability to carbon sequestration and soil fertility, coupled with the ability to reduce nutrient leaching [7]. Biochar is recalcitrant to decomposition relative to the feedstock and has high capacity for nutrient retention and may slowly release the nutrients [8]. Different forms of carbon-based functional groups that characterise biochar are dominated by aromatic C groups [9], which explains the recalcitrant nature of biochar, making it resistant to microbial

attack, decreasing CO_2-C emission, and contributing to climate change mitigation [10]. However, the recalcitrance does not indicate complete biological inertness because of the presence of labile aliphatic C, which promotes decomposition [11]. Some authors suggest that the application of biochar to soil can decrease or increase overall organic matter decomposition through its interaction with resident soil organic matter and through the priming effect [12]. The priming effect is a short-term increase or decrease in the decomposition of soil organic matter as influenced by soil treatment [13], which usually affects the mineralisation of nutrients and carbon dioxide (CO_2) release. According to Igalavithana et al. [6], high-temperature biochar has a negative priming effect, whilst low-temperature biochar has a positive effect. As such, high-temperature biochar can be used for C sequestration due to high stable C, whereas low-temperature biochar can be used for improving nutrient availability due to presence of high labile carbon [14]. Smith et al. [15] reported that young (newly produced) biochar provides labile C, which is available for microbes for a short period of time. Consequently, this could mean that the application of biochar, irrespective of pyrolysis temperature, could lead to carbon dioxide emission. Conversely, the recalcitrant nature could limit the overall decomposition of the biochar.

Evidence in the literature shows that the application of biochar to soil improves soil quality characteristics [16–19] as it contains organic matter and nutrients [20]. Biochar addition is associated with increases in soil pH, electrical conductivity (EC), organic carbon (SOC), and available phosphorus (P), nitrogen (N), and cation exchange capacity (CEC) [21]. For example, Shafie et al. [22] observed that increasing the pyrolysis temperature increased available K and decreased available P in a sandy soil after 15 days of incubation with biochar from empty fruit bunch. The persistence of the beneficial effects of biochar could depend on the stability of the biochar, which is determined by feedstock and pyrolysis conditions.

Many studies have been conducted on the behaviour of biochar from other wastes, including pine bark, which is locally abundant in South Africa, on carbon dioxide emission and nutrient release when applied to the soil. Unfortunately, no published research could be accessed in the literature on the carbon sequestration potential, nutrient release pattern, and liming potential of potato waste biochar produced at different pyrolysis temperatures. Our preliminary experiments showed that potato waste biochar has lower fixed carbon, C/N ratio, and aromaticity (O/C) and higher contents of ash and nutrients (N, P, and K), pH, and liming potential, especially at higher pyrolysis temperatures, when compared to the pine bark biochar tested by Vilakazi [23]. Based on the preliminary results, we hypothesised that the application of the highly alkaline potato waste biochar (up to pH 12) could lime the soil and result in higher CO_2 emission and availability of primary nutrients (NPK) than pine bark biochar, especially in acidic soils.

Angst and Sohi [24] reported that the decomposition of biochar depends on soil condition, with faster rates in alkaline than acidic soils. Addition of alkaline potato waste biochar was expected to lime acidic soil, thus increasing organic matter decomposition, mineral N, available P, and exchangeable bases, especially available K. There was, thus, a need to assess the ability of potato waste biochar to store carbon and release nutrients relative to pine bark biochar when applied to contrasting soils. This information will be valuable for using potato waste and potato-waste-derived biochar for managing soil fertility as a beneficial waste management strategy. The objective of this study was to determine the effects of feedstock and pyrolysis temperature on CO_2 emission, mineral N and P, and available K during incubation of contrasting soils amended with biochar from potato waste and pine bark.

2. Method and Materials

The incubation study was conducted under laboratory conditions at the Pietermaritzburg campus of the University of Kwa-Zulu Natal (29°37′33.9″ S; 30°24′14″ E) in the KwaZulu-Natal Province of South Africa.

2.1. Soils

The two soils (Figure 1) used in this study were collected from the University of KwaZulu-Natal Research Farm, Ukulinga (29°39′33.9″ S; 30°24′14″ E), and Bulwer (29°48′27″ S; 29°45′35″ E). Ukulinga receives a mean annual precipitation of 750 mm, while Bulwer receives 877 mm. The soil from Ukulinga was under natural vegetation and was classified as Bonheim form [25], which was translated to Luvisol according to the IUSS Working Group WRB [26]. The soil from Bulwer was used for maize production and was classified as a Clovelly form [25] and translated to Ferralsol according to the IUSS working group WRB [26]. Bulk soil samples were collected from 0–20 cm depth, mixed, homogenised, air-dried and sieved (<2 mm), before analysis. The soils were analysed for pH in 1 M KCl, as described by the Non-Affiliated Soil Analysis Work Committee [27]. Phosphorus was extracted with the AMBIC-2 method [28] and analysed with a UV/VIS spectrophotometer following the molybdenum blue method [29]. Total carbon (C) and nitrogen (N) were measured using the LECO Trumac CNS Autoanalyser [30]. Exchangeable bases (calcium, Ca^{2+}; magnesium, Mg^{2+}; potassium, K^+; and sodium, Na^+) were extracted using the ammonium acetate (pH 7) method followed by analysis with atomic adsorption spectrophotometry (Varian 2600). Exchangeable acidity was extracted with 1 M KCl, followed by titration with 0.1 M NaOH with phenolphthalein indicator, as described by Lourenzi [31]. The characteristics of the soils are shown in Table 1. Both soils were acidic, with the Luvisol having lower exchangeable acidity, extractable P, and extractable K and higher clay content and exchangeable Ca and Mg than the Ferralsol.
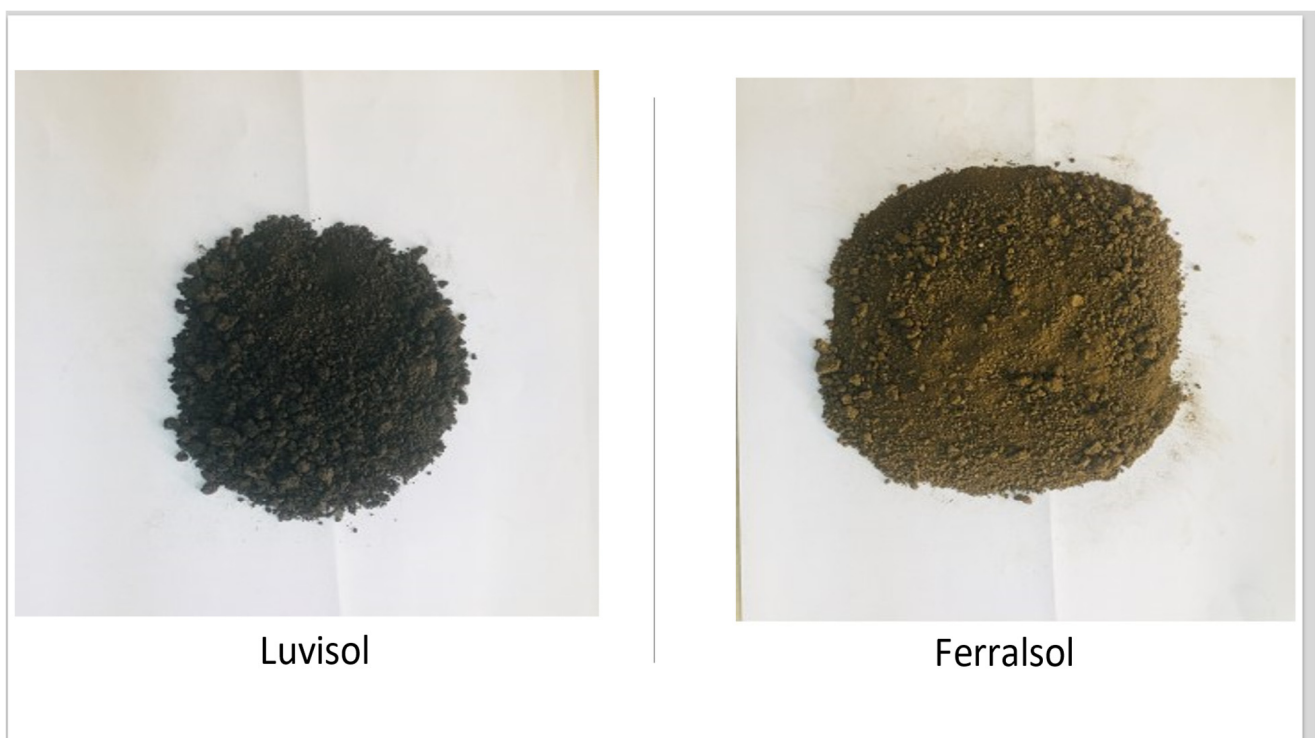

Figure 1. Comparison of the two soils used for the incubation study.

Table 1. Selected physico-chemical properties of the soils used in the study.

Property	Luvisol	Ferralsol
pH (KCl)	4.67	3.97
Carbon (%)	4.45	5.40
Nitrogen (%)	0.268	0.403
C/N	16	13
Clay (%)	39.0	23.0
Bulk density (g cm^{-3})	1.29	1.12
Extractable P (mg kg^{-1})	2.73	18.6
Extractable K (cmol$_c$ kg^{-1})	0.063	0.338
Exchangeable Ca (cmol$_c$ kg^{-1})	2.24	1.02
Exchangeable Mg (cmol$_c$ kg^{-1})	2.24	0.577
Exchangeable acidity (cmol$_c$ kg^{-1})	1.60	8.00

2.2. Biochar Production and Characterisation

Cull potato (CP), rotten potato waste that could not be marketed, was collected from the Pietermaritzburg Fresh Produce Market located in Mkondeni, Pietermaritzburg. Pine bark (PB) was collected from a private forestry by-product factory located at Cramond, Pietermaritzburg. The CP and PB samples were ground to <2 mm particle size using a grinding mill machine, Retsch KG 5657 HAAN, West Germany model, and stored in plastic bags. The samples were then oven-dried at 80 °C for 24 h and pyrolysed at 350 °C and 650 °C for 2 h in a muffle furnace [32]. The biochars were characterised as detailed in Koetlisi and Muchaonyerwa [32]. The biochar liming potential (calcium carbonate equivalent; CCE) was evaluated following the method by Singh et al. [33]. The results were used to calculate the calcium carbonates equivalents using Equation (1).

$$\text{CaCO}_3 \text{ equivalent (\%)} = \frac{M \times (b - a) \times 10^{(-3)} \times 100.09 \times 100}{2 \times W} \quad (1)$$

where "*M*" is molarity of NaOH (mol L^{-1}), "*b*" is the NaOH volume (mL) used by the blank, "*a*" is volume (ml) of NaOH used by the biochar sample, and "*W*" is the mass (g) of biochar used.

Selected characteristics of the feedstocks and biochar types are presented on Table 2. The yield and total C were higher, while ash, pH, available P and K, and CCE were lower for PB than CP biochar. Increasing the pyrolysis temperature increased ash and pH and reduced yield for both feedstocks, while available P and CCE were increased for CP biochar.

Table 2. Selected characteristics and calcium carbonate equivalents of feedstocks and biochar.

Treatment	Yield	Ash	Total C	Total N	pH	Extrac. P	Exch.K	CCE
	(%)	(%)	(%)	(%)		mg kg^{-1}	cmolc kg^{-1}	(%)
CP	100 [e]	4.40 [d]	39 [a]	1.1 [b]	8.12 [c]	81.9 [b]	22.7 [c]	6.97 [a]
PB	100 [e]	0.436 [a]	50.9 [b]	0.249 [a]	4 [a]	14.1 [a]	1.14 [a]	7.47 [a]
CP350	30.1 [b]	10.7 [e]	66.1 [c]	2.19 [d]	11.1 [e]	718 [c]	15.9 [b]	11.5 [b]
PB350	52.2 [d]	0.92 [b]	70.3 [d]	0.346 [a]	6.65 [b]	0 [a]	0.92 [a]	8.01 [a]
CP650	21.8 [a]	15.5 [f]	71.5 [d]	1.45 [c]	12.1 [g]	1077 [d]	13.7 [b]	17.5 [c]
PB650	33 [c]	2.15 [c]	90.1 [e]	0.367 [a]	9.1 [d]	0 [a]	2.55 [a]	9.43 [ab]

CP = cull potato waste; PB = pine bark; CP350, CP650, PB350, and PB650 represent biochar from cull potato and pine bark pyrolysed at 350 °C and 650 °C. The feedstocks were considered as having a yield of 100%. Values in the same column with similar letters indicate a non-significant difference (*p* < 0.05), and those with different letters indicate a significant difference (*p* < 0.05). Extrac. P = extractable phosphorus; Extr. K = extractable potassium; CCE = calcium carbonate equivalent.

Figure 2 shows the morphological structure of the biochars and feedstocks. The external morphology of the biochars was heterogeneous with more pores at a pyrolysis temperature of 350 °C.
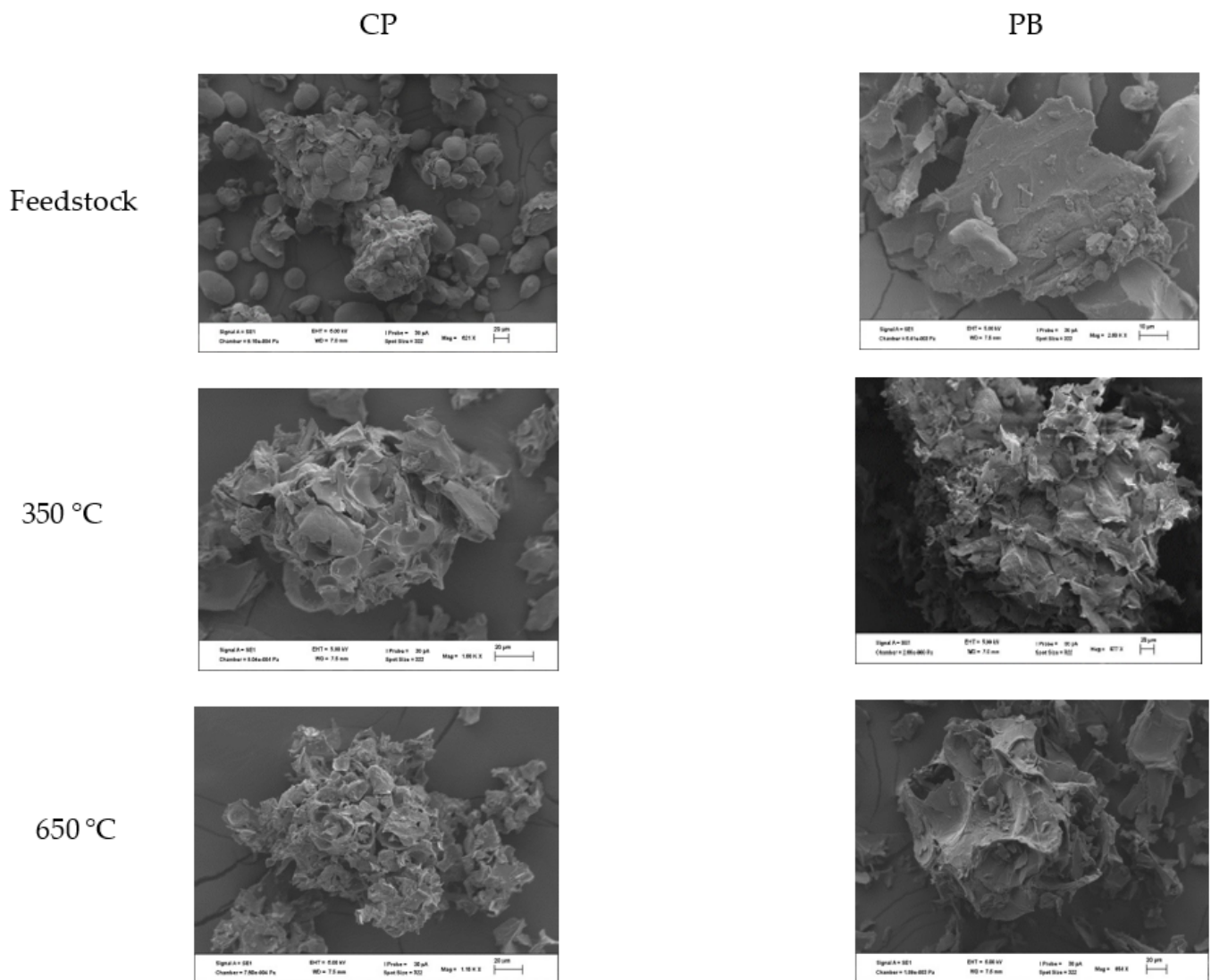
CP PB

Figure 2. Morphological comparison of 4 studied biochars and their feedstocks at different pyrolysis temperatures using scanning electron microscopy. CP = cull potato waste; PB = pine bark.

2.3. Evolution of CO_2-C from Soils Amended with Feedstocks and Biochar Types

The experiment was a 2×6 factorial in a completely randomised design with two soil types and six organic materials (cull potato (CP) and pine bark (PB) and their biochars pyrolysed at 350 °C and 650 °C. The treatments were mixed with 100 g of soil at rates equivalent to 10 Mg C ha^{-1} in both soils and were replicated three times. Treatments where no amendment was added (0 Mg C ha^{-1}) were included for both soils as the control. Carbon dioxide (CO_2) emission was measured by a standard method [34]. The study was conducted for 84 days in a constant-temperature room at 25 °C with sampling at days 0, 7, 14, 21, 28, 42, 56, and 84. The soil samples were maintained at 100% field-capacity moisture content throughout the incubation period by frequent correction based on weight loss. In each 500 mL jar, two vials (one with 100 g moist soil and another with 50 mL of 1 M NaOH) were placed, sealed using cling film, and incubated in the dark (to avoid growth of algae). The CO_2 trapped in the NaOH was analysed. The initial CO_2 at the time of setting up the experiment was assumed to be zero (0). The NaOH was then treated with 2 mL of 1 M $BaCl_2$ and 3 drops of phenolphthalein indicator before titrating the mixture with 0.5 M HCl from pink to a colourless end point. The volume of 0.5 M HCl used was recorded for calculations. The CO_2-C emission was calculated as the mass of C in mg kg^{-1} soil

following the equation depicted below. The cumulative CO_2-C was calculated by adding CO_2-C emitted per sampling day until day 84.

$$\text{Moles (NaOH reacted with } CO_2\text{) (x)} = \text{total moles of NaOH - Moles of HCl added} \quad (2)$$

$$\text{Mass of } CO_2 = \frac{x}{2} \times 44 \quad (3)$$

$$\text{Mass of } CO_2 \text{ in mg kg}^{-1} \text{soil} = \frac{\text{mass of } CO_2}{10000} \quad (4)$$

$$\text{Mass of C in mg kg}^{-1} \text{ soil} = \frac{\text{Mass of } CO_2 \text{inmg/kgsoil} \times 12}{44} \quad (5)$$

The "x" signifies the moles of NaOH that reacted with CO_2. The 12 and 44 indicate the molar mass of carbon and that of carbon dioxide, respectively.

2.4. Changes in Mineral Nitrogen, Phosphorus, and Potassium in Soils Amended with the Biochars

The incubation experiment set-up was the same as described for CO_2 emission in terms of treatments and management, except that there were enough replicates to allow for destructive sampling at each period and that the jars used were not sealable in order to allow for continuous replenishment of oxygen. The soil–biochar mixtures were placed in 500 mL plastic containers which were tightly closed with lids and had four holes drilled below the rim to allow for gas exchange. The soils were maintained at 100% water-holding capacity, and the moisture was corrected weekly throughout the incubation based on weight loss. The soils were incubated for 140 days in a constant-temperature room at 25 °C with destructive sampling at days 0, 7, 14, 21, 28, 42, 56, 84, 112, and 140. The samples were analysed for mineral-N (NH_4^+-N and NO_3-N), pH, extractable P, and extractable K per sampling day.

2.5. Analysis

Ammonium- and nitrate-N were determined using the Gallery Discrete Analyzer [35] with a detection limit of 0.0198 after extraction with 2 M KCl solution. For this, soil (2 g), suspended in 20 mL of 2 M KCl solution, was shaken using a reciprocal shaker (Model E5850 Thomas Scientific, Swedesboro, NJ, USA) at 180 cycles per minutes for 30 min, followed by filtration using Whatman No. 1 filter paper into storage bottles before analysis. Extractable P was determined calorimetrically following AMBIC-2 extraction, as described by Mansons et al. [28] and analysed by the molybdenum blue method [29]. Extractable K was analysed from the supernatant of AMBIC-2 following the process of Manson et al. [28], followed by addition of 5 mL of cesium chloride (1200 mg L^{-1}) solution as an ionisation suppressant. The solution was analysed for K using the atomic absorption spectrophotometer Varian AA 280 Fast Sequential Atomic Absorption (FS-AA), with a detection limit of 1.131.

2.6. Statistical Analysis

The results of CO_2-C evolution and nutrient release for each incubation (sampling) time for each soil were subjected to analysis of variance (ANOVA) using GenStat, 18th edition. Mean separation was performed using least significant difference (LSD) at $p < 0.05$, which was used on the graphs. The Tukey–Kramer test was also used to separate treatment means at $p < 0.05$ and was used in the description of the results.

3. Results

3.1. Carbon Dioxide Emissions (CO$_2$-C)

There were significant differences in CO_2-C emission among treatments on the different sampling days for the two soils (Figure 3A,B). The CO_2-C emission had two peaks for the Luvisol (Figure 3A) and three peaks for the Ferralsol (Figure 3B), with the cull potato (CP) treatment following the same trend as the unamended control. The CO_2-C emission increased from day 0 to 3 for all treatments for both soils (Figure 3A,B). After 7 and 14 days, higher CO_2-C emission was observed for pine bark (PB) and PB-derived biochar than all other treatments, with PB increasing up to day 21 for the Luvisol. After 14 days, the CP treatment had lower CO_2-C than all other treatments (including its biochar), except the control, which had lower. The CO_2-C emission sharply decreased between 14 and 28 days in the CP, CP 350, and control treatments and between 21 and 28 days for CP 650, PB, and PB-based biochars (Figure 3A). Thereafter, there was a sharp increase in CO_2-C emission from day 28, reaching a maxima of 1079 mg CO_2-C kg^{-1} for Luvisol amended with PB 350 at day 42, followed by a sharp decrease for all treatments up to day 84.
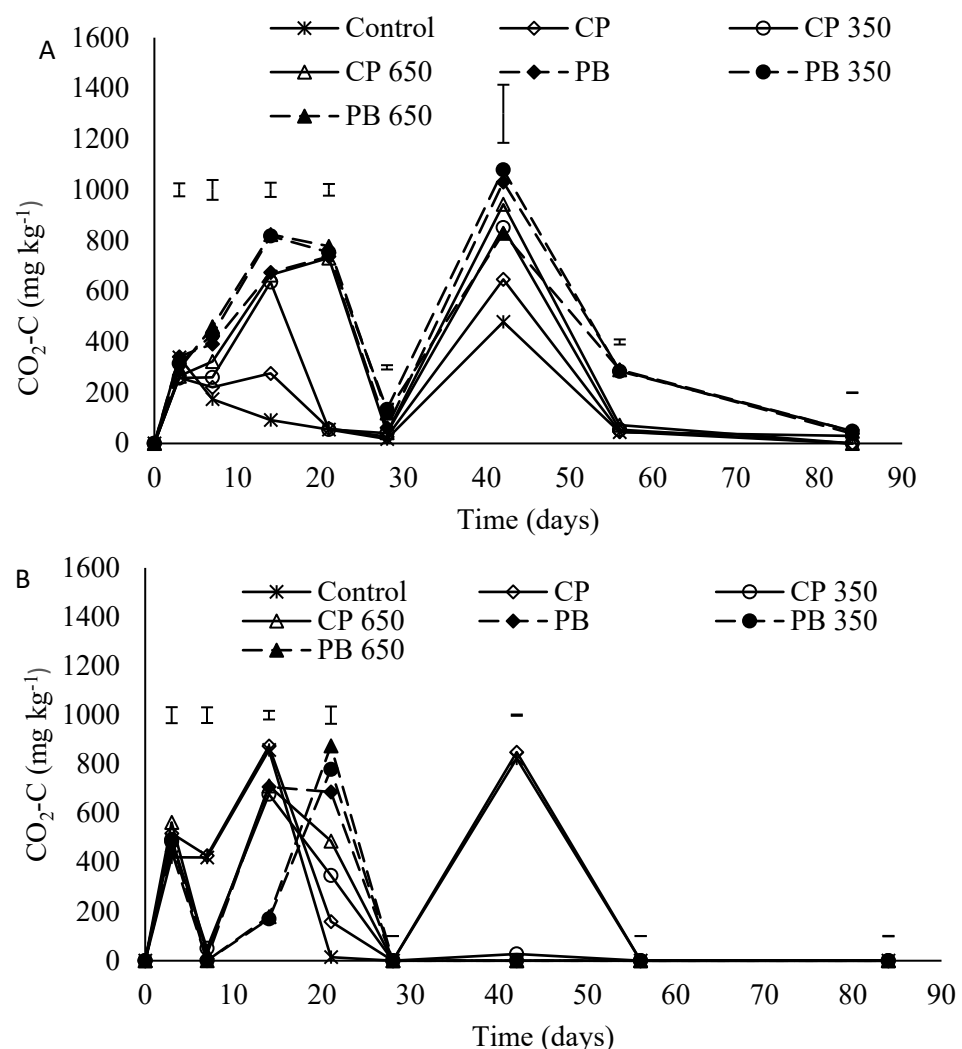

Figure 3. Carbon dioxide (CO_2−C) emission during incubation of Luvisol (**A**) and Ferralsol (**B**) amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP 650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD ($p < 0.05$).

In the Ferralsol, the CO_2-C emission in the control and CP treatments was higher after 7, 14, and 42 days and lower after 21 days than in all other treatments (Figure 3B). The CO_2-C from treatments with biochar from PB (PB350 and PB650) was lower after 14 days and higher after 21 days compared to other treatments. After 21 days, addition of PB and its biochar to the Ferralsol resulted in higher CO_2-C than CP and its biochar (CP350, CP650), and, in both cases, the emissions were increased by higher pyrolysis temperature (Figure 3B). The CO_2-C rapidly declined between 14 and 28 for CP and its biochar and between 21 and 28 days for PB and its biochar. Beyond 28 days, the emissions remained low, except for those of the control and CP, which reached another peak after 42 days, after which there was a sharp decrease to day 56 and 84, where CO_2-C was below detection for all treatments.

3.2. Cumulative Carbon Dioxide Emissions (CO_2-C)

Cumulative CO_2-C emission was significantly different among treatments (Figure 4A,B), and was generally higher in the Luvisol than in the Ferralsol. The PB 350 treatment showed the highest CO_2-C relative to the control throughout the incubation period, reaching a maximum value of 3811 mg CO_2-C kg^{-1} in the Luvisol (Figure 4A). The biochars resulted in higher cumulative CO_2-C emission than the feedstocks. The cumulative emission was, in order, PB 350 (3811 mg CO_2-C kg^{-1}) > PB 650 (3600 mg CO_2-C kg^{-1}) > PB (3482 mg CO_2-C kg^{-1}) > CP 650 (3044 mg CO_2-C kg^{-1}) > CP 350 (2137 mg CO_2-C kg^{-1}) > CP (1422 mg CO_2-C kg^{-1}) > control (1933 mg CO_2-C kg^{-1}) at the end of incubation in the Luvisol. All treatments emitted >100% more CO_2-C than the control, except for the CP, which emitted 35.9% more than the control (Figure 4A). In the Ferralsol, CP followed a similar trend to the control, and they were both higher than PB feedstock and PB biochars (Figure 4B). Addition of biochar decreased cumulative CO_2-C emission, as shown by higher CO_2-C in the control than in all treatments, except the CP, which had higher (Figure 4B). The cumulative CO_2-C emission decreased in the following order at the end of incubation in the Ferralsol: CP (2828 mg CO_2-C kg^{-1}) > control (2533 mg CO_2-C kg^{-1}) > PB (1895 mg CO_2-C kg^{-1}) > CP 650 (1778 mg CO_2-C kg^{-1}) > CP 350 (1585 mg CO_2-C kg^{-1}) > PB 350 (1434 mg CO_2-C kg^{-1}) > PB 650 (1414 mg CO_2-C kg^{-1}). The treatments with the biochar types, which were not significantly different, had 30–44% lower CO_2-C than the control in the Ferralsol.
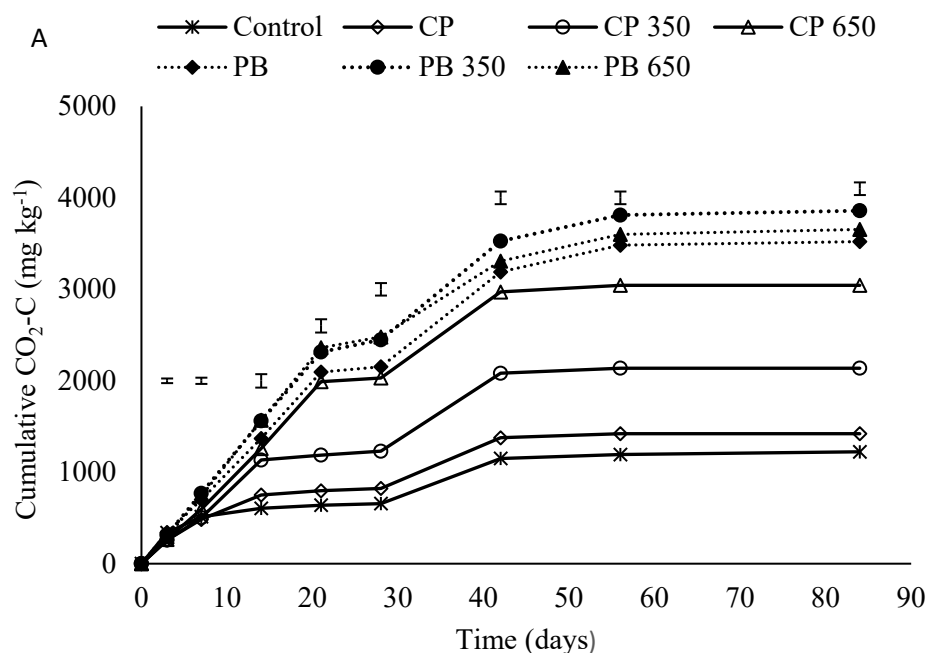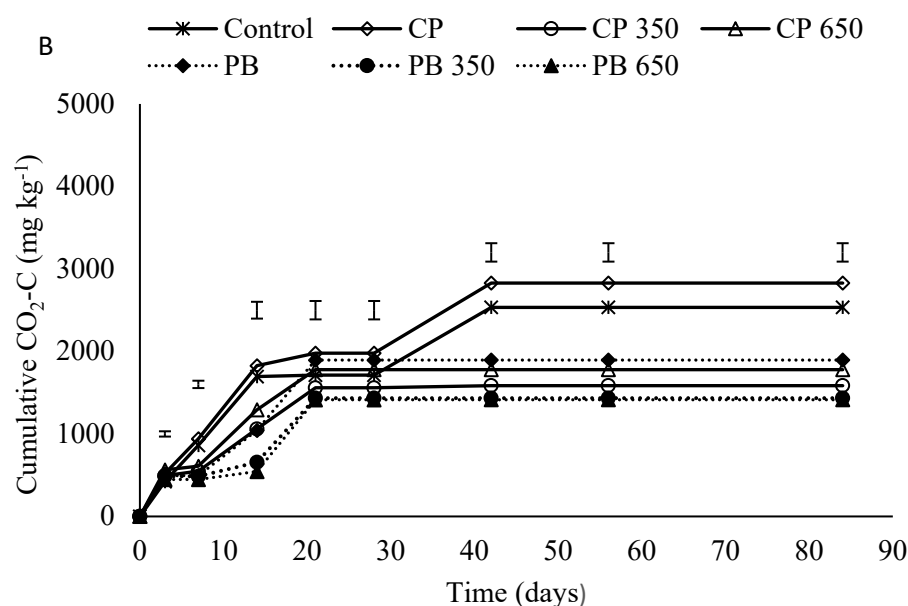

Figure 4. *Cont.*

Figure 4. Cumulative CO_2-C during incubation of Luvisol (**A**) and Ferralsol (**B**) amended with biochar from cull potato (CP) and pine bark produced at varying pyrolysis temperatures. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP 650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD ($p < 0.05$).

3.3. Ammonium-N Concentration

Ammonium-N concentration was significantly reduced by the application of raw CP relative to the control, while there were no significant differences between biochar types and controls (Figure 5A,B). A rapid increase was observed within the first 14 days of incubation in the Luvisol (Figure 5A), reaching a peak that lasted from day 14 to 42, followed by a subsequent decrease between day 42 and 84 for all treatments, except for CP. After day 84, ammonium-N was below detection for all treatments up to day 112, followed by a slight increase, with the highest at 2.619 mg kg^{-1} after 140 days. In the Ferralsol, ammonium-N concentration decreased in all treatments, approaching levels below detection after 21 days, and remained low up to 112 days of incubation, after which there was a slight increase in all treatments, with the highest having 2.513 mg kg^{-1} (Figure 5B). Only the PB and CP had lower ammonium-N than the control after 14 days of incubation, with no differences among treatments for all other sampling periods.

3.4. Nitrate-N Concentration

Application of raw CP significantly reduced nitrate-N concentration compared to the control and all other treatments (Figure 6A,B). The concentration of nitrate-N was generally higher in the Ferralsol than the Luvisol throughout the incubation. The initial concentrations were around 3 mg kg^{-1} for Luvisol and 42 mg kg^{-1} for Ferralsol. There were no significant differences among all other treatments for nitrate-N concentration in both soils throughout the incubation, except the PB after 112 days of incubation in the Luvisol (Figure 6A,B). The nitrate-N rapidly increased between 56 and 84 days of incubation in the Luvisol (Figure 6A), while, in the Ferralsol, the rapid increase in concentration occurred within the first 14 to 21 days (Figure 6B).
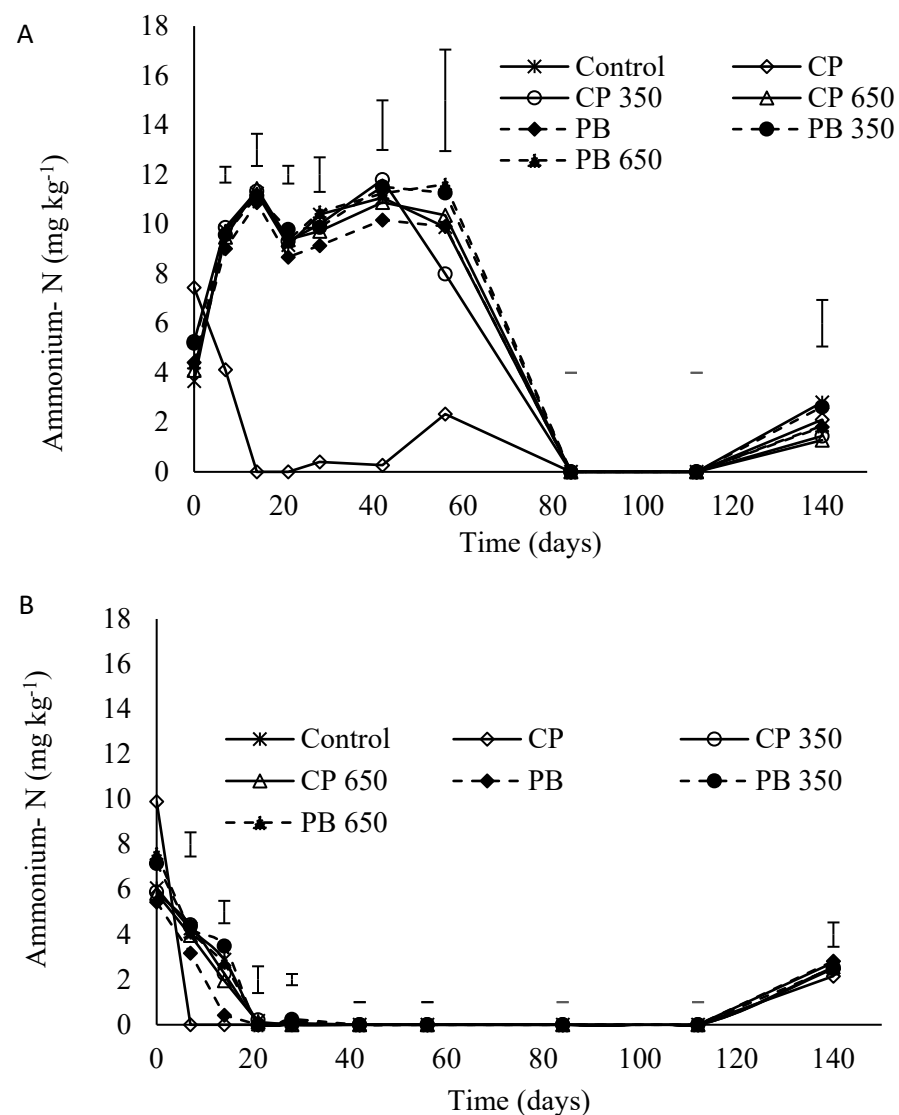
Figure 5. Concentrations of ammonium-N during incubation of Luvisol (**A**) and Ferralsol (**B**) amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP 650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD ($p < 0.05$).

3.5. Extractable P

The Luvisol generally had lower extractable P than the Ferralsol. In the Luvisol soil, there were no significant treatment effects on extractable P, except after 14 and 112 days of incubation (Figure 7A). After 14 days of incubation, the extractable P was higher in the CP350, CP650, and the PB treatments than the PB350, PB650, CP, and the control treatments. The PB-based biochars had higher extractable P than the other treatments after 112 days of incubation. There were three peaks of extractable P in the Ferralsol (Figure 7B). After seven days of incubation, extractable P was higher in the biochars CP350 and CP650 followed by the PB feedstock treatment and the control, with the PB350, PB650, and the CP feedstock treatments having the lowest. After 14 days, the extractable P was in the order PB650 > PB > PB350 = CP650 = CP350 = control > CP (Figure 7B). No biochar treatments were significantly different in extractable P after 42 and 56 days of incubation, with the CP and control treatments having lower. After 112 days, the CP350 had higher extractable P than PB and PB650 treatments, with all other treatments being similar.
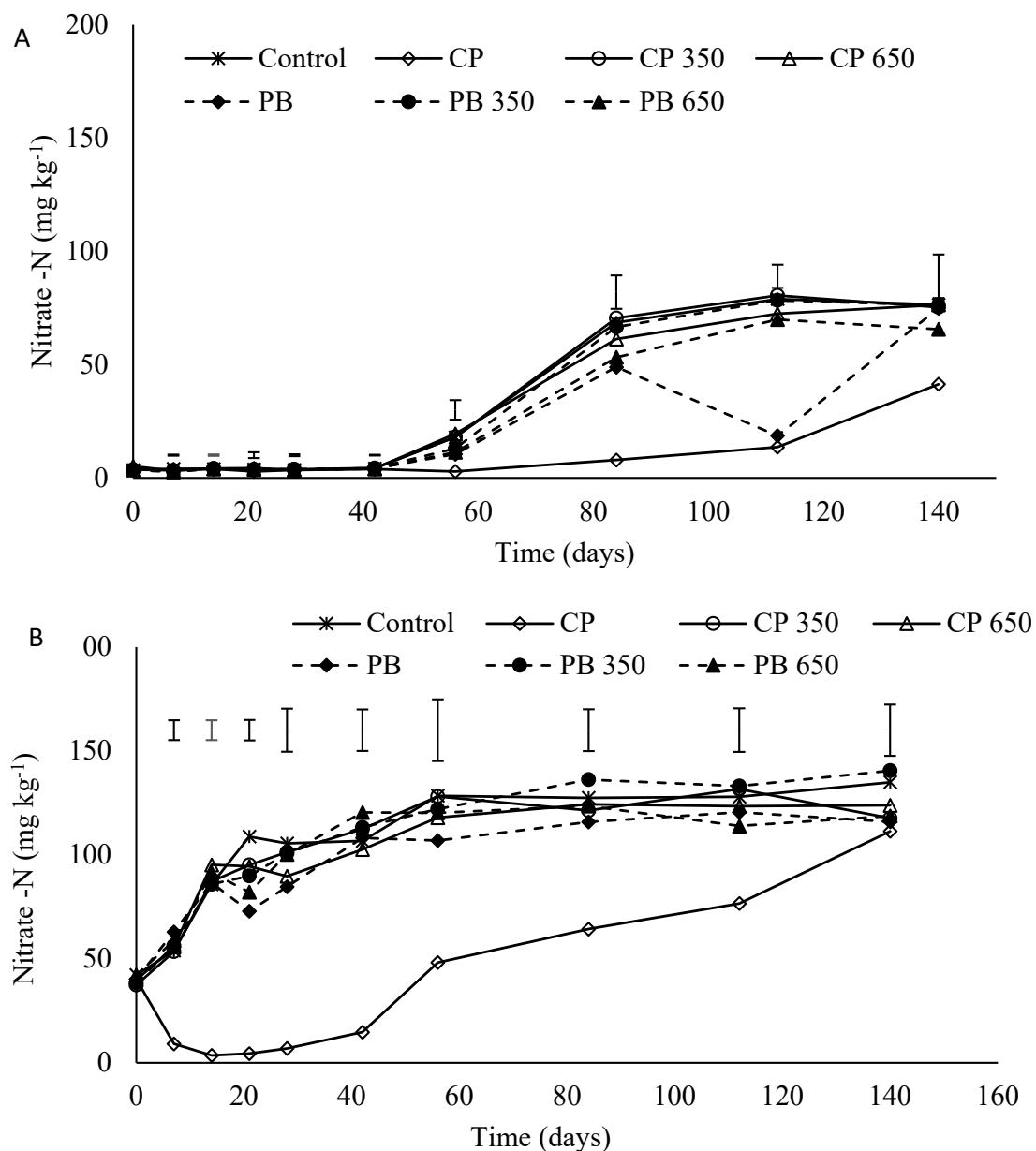
Figure 6. Concentrations of nitrate−N during incubation of Luvisol (**A**) and Ferralsol (**B**) amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP 650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD (*p* < 0.05).

3.6. Extractable K

Addition of CP feedstock and its biochars (CP350 and CP650) to soil significantly increased extractable K concentration when compared to PB feedstock, its biochars (PB350 and PB650), and the control treatments for both soils and at all sampling periods (Figure 8A,B). The increase in extractable K was greater for higher temperatures (CP 650 °C > CP 350 °C > CP) for both soils. Pyrolysis temperature did not affect extractable K in treatments with PB biochars. Although the results appeared to fluctuate between sampling periods, there was no major change throughout the incubation. Generally, the Ferralsol had higher extractable K than the Luvisol throughout the experiment
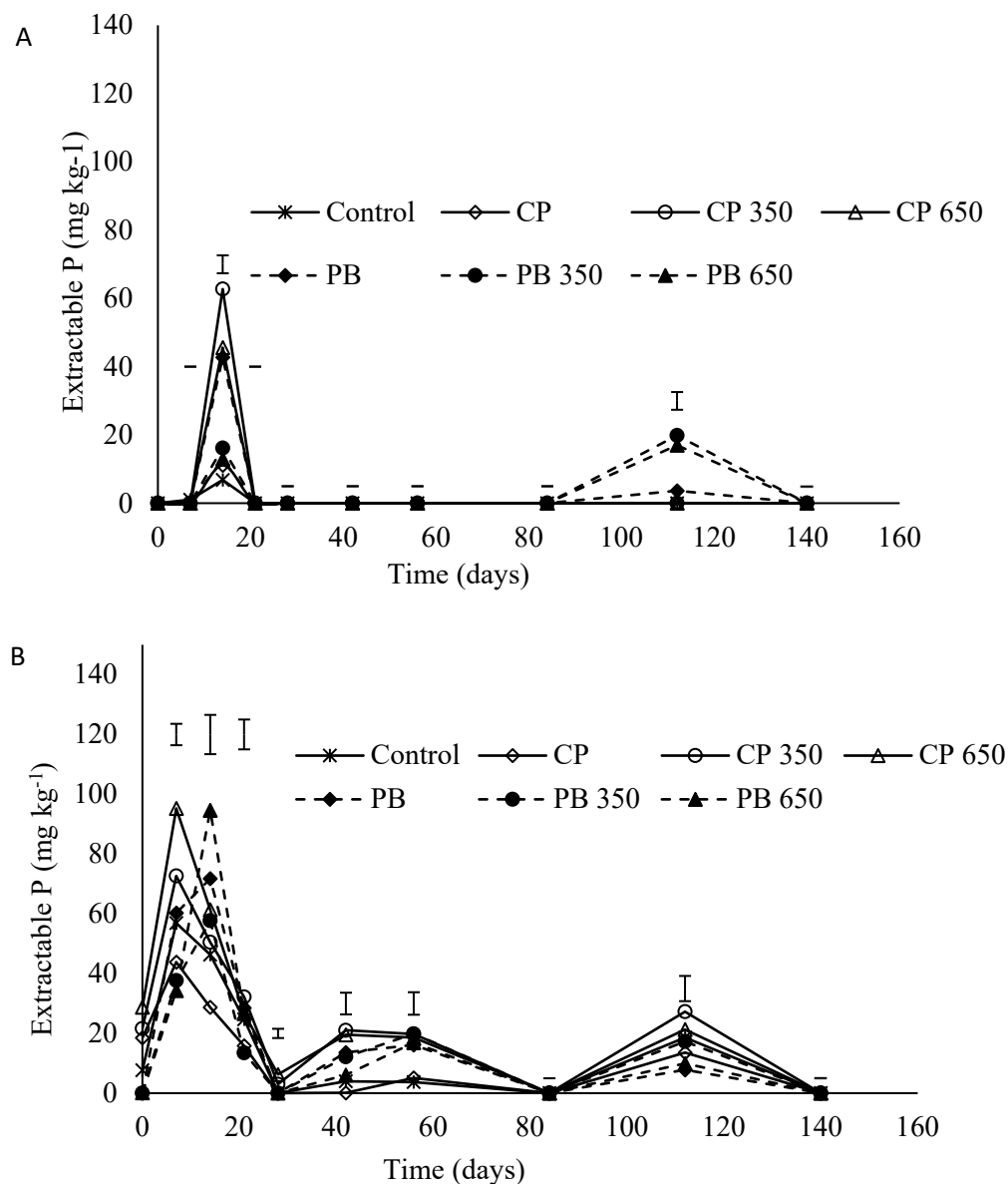
Figure 7. Concentrations of extractable P during incubation of Luvisol (**A**) and Ferralsol (**B**) amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP 650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD ($p < 0.05$).

3.7. Soil pH

For the Luvisol, there were significant differences throughout the incubation, except for on day 7 and 84 (Figure 9A). The soil pH was higher for CP-based biochars than the PB treatment, PB-based biochars, CP treatment, and the control. In Ferralsol, there were three peaks (Figure 9B). Throughout the incubation period, soil pH was higher in the CP-based biochars, with CP at 650 °C having a higher soil pH relative to the PB treatments and the control. All treatments were not significantly different in soil pH after 28 and 56 days of incubation, with the CP at 350 °C being higher after day 28 and PB being higher after day 56.
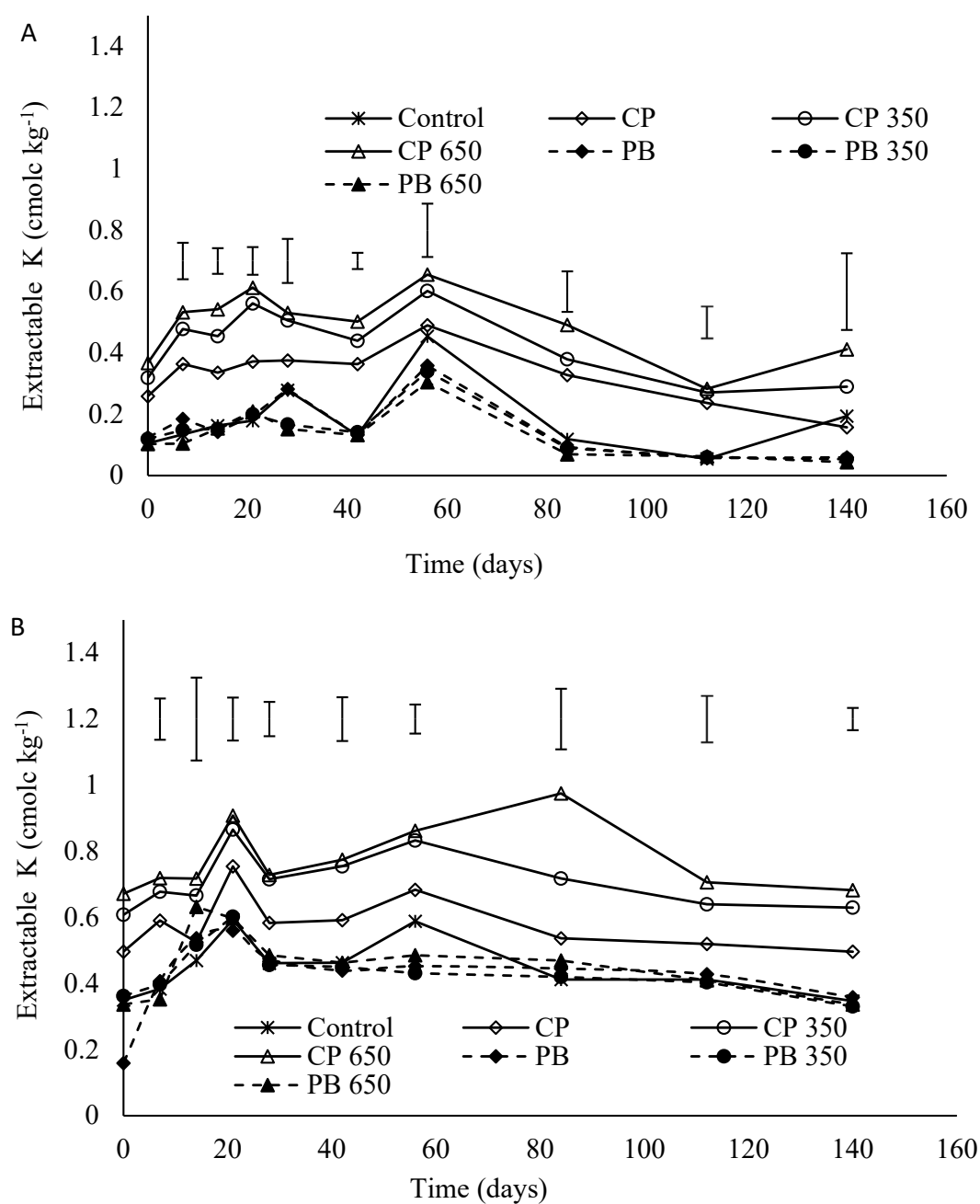
Figure 8. Concentrations of extractable K during incubation of Luvisol (**A**) and Ferralsol (**B**) amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperatures. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD ($p < 0.05$).
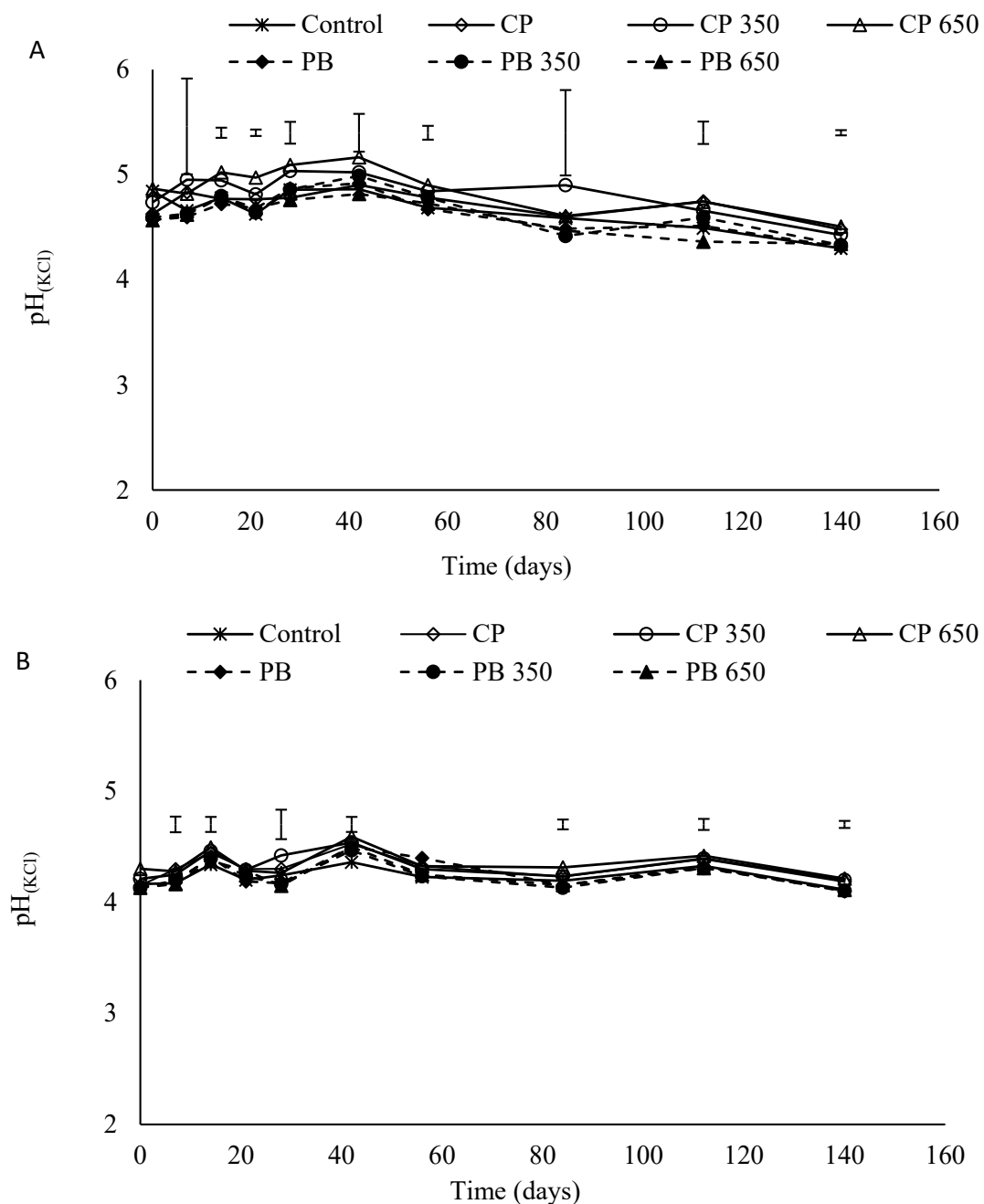
Figure 9. The pH (KCl) during incubation of (**A**) Luvisol and (**B**) Ferralsol amended with biochar from cull potato (CP) and pine bark (PB) produced at varying pyrolysis temperature. CP = cull potato; PB = pine bark; CP 350 = cull potato biochar at 350 °C; CP650 = cull potato biochar at 650 °C; PB 350 = pine bark biochar at 350 °C; PB 650 = pine bark biochar at 650 °C. The vertical error indicates LSD ($p < 0.05$).

4. Discussion

The increase in carbon dioxide (CO_2-C) emission in the first three days, with no significant differences among all treatments, (Figure 3A,B), could have been due to the rapid increase in activities of microorganisms due to addition of moisture [36]. The results corroborated the observation of Miller et al. [37], who observed an increase in microbial activity following rewetting a dry soil. The increase in CO_2-C, particularly in the biochar treatments compared to the control in the Luvisol, coincided with the increase in extractable P and ammonium-N, suggesting that the biochars limed the soil and increased availability of P and enhanced activity of microorganisms, resulting in soil organic matter (SOM) de-

composition and mineralisation of C (CO_2-C) and N. The liming could be due to hydroxide and bicarbonate ions that are produced when carbonates react with soil water (dissociation of carbonates) [38]. Bruun et al. [38] reported a sharp CO_2-C emission in an acidic soil due to carbonates dissociation. The negatively charged carboxyl groups could be another possible explanation for the increased soil pH in CP-biochar-treated soils. Chintala et al. [39] elucidated that the negatively charged functional groups on the biochar surfaces bind with the H^+ ions from the soil solution, hence, reducing H^+ ions in the soil solution and consequently increasing soil pH. The increase in pH due to addition of CP biochars reduces P fixation and increases microbial activity and decomposition of organic matter, resulting in mineralisation of C and N.

The delayed peak in treatments with pine bark (PB) biochar in both soils could have been because of lower acid-neutralising power (CCE). The explanation for low CO_2-C after 28 days of incubation for all treatments in both soils is the result of moisture, as watering was skipped during this day due to COVID-19 restrictions imposed on accessing the laboratory. However, the stabilisation in cumulative CO_2-C emission beyond 42 days of incubation (Figure 4A,B) could have been due to depletion of the labile C for microorganisms with the increase in incubation period.

The higher cumulative CO_2-C in amended soil compared to the control in the Luvisol was due to higher C added through the amendments. Since the amendments were added at the same C rate, the explanation for the higher CO_2-C in the PB and PB biochar treatments than CP and CP biochars in the Luvisol (Figure 4A) is not clear. However, the lower CO_2-C for cull potato (CP) could have been due to the low water-soluble carbohydrates in the raw feedstock. It is expected that the higher CCE and lower C:N of CP biochars can have increased microbial activity and CO_2-C than PB biochars. The higher cumulative CO_2-C in the PB350 than PB650 and PB treatments supports the view that low-temperature biochar releases more CO_2-C compared to high-temperature biochars [40]. However, for CP biochars CO_2-C increased with increased pyrolysis temperature, possibly because of the liming of the soil, which increased microbial activity. The CO_2-C may also have been derived from the calcium carbonates ($CaCO_3$) of the biochar, especially in high pyrolysis.

The generally lower CO_2-C (and cumulative CO_2-C) in Ferralsol than the Luvisol was a result of differences in soil characteristics, including lower pH and exchangeable Ca and Mg in the Ferralsol (Table 1). Although the SOC was slightly higher in the Ferralsol, this soil had lower labile C due degradation caused by tillage operations for the production of maize compared to that in the Luvisol, which was under natural vegetation. The pH (KCl) in the Luvisol ranged from 4.6 to 5.1 (5.6 to 6.1 in water), while it ranged from 4.1 to 4.6 (5.1 to 5.6 in water) in Ferralsol, with only the CP 650 being higher than pH 4.5 (pH 5.5 in water). The lower soil pH in the Ferralsol limited microbial activity, irrespective of treatment. The effects of biochar addition on CO_2-C emission, therefore, appears to depend on the characteristics of the soils, especially the level of acidity and possibly organic matter quality. Similar findings were reported by Keith et al. [12] and Fang et al. [41], who reported that more C was mineralised in high pH soils relative to low pH soils due to high microbial activity. Fang et al. [41] reported that biochar-C mineralisation varies in soils of contrasting properties, and that biochar–clay interactions contribute significantly to the stabilisation in the variable charge soils than in soils dominated by permanent charge. In addition, Brodowski et al. [42] showed that there is a chemical interaction between the oxidised biochar surfaces and the functional groups of clay minerals and native SOC. The Luvisol (moderately weathered with high clay content) is dominated by permanent charge clay minerals, limiting ligand exchange reaction, hence, making the biochar susceptible to microbial breakdown. The acidic pH of Ferralsol may contribute to enhanced organo-mineral association through ligand exchange reactions [43]. This could occur between Al oxides and carboxyl and phenolic groups through electrostatic process [44] and possibly due to stabilisation through micro-aggregates. Ferralsol soils are dominated by micro-aggregates [45], protecting C from microbial oxidation [46].

The addition of the biochars to the Ferralsol resulted in suppressed CO_2-C emission (and cumulative CO_2-C) compared to the control, possibly due to adsorption of recalcitrant biochar-C by Al and Fe oxides, particularly in a highly acidic soil with limited microbial activity. This view was supported by the CO_2-C results of the CP treatment, which were higher than the control, while the lower levels for the PB were a result of the C:N ratio of the pine bark (204:1), which was much higher than that of CP (35:1). Yu et al. [47] reported that acidic soils retard soil organic matter (SOM) decomposition by limiting activities of microorganisms and enzyme activities. Although the soil pH was increased by CP350 and CP650 more than other treatments and the control for both soils, the soil pH in the first 42 days (where most microbial activity occurred) ranged from 4.5 to 5.2 (about 5.5 to 6.2 in water) in the Luvisol and 4.2 to 4.6 (about 5.2 to 5.6) in the Ferralsol. The soil pH after biochar application might not have been conducive for microbial activity, particularly as the bacteria community favour neutral-to-alkaline pH, whereas fungal communities favour slightly acid pH [48]. The higher CO_2-C in the feedstock treatments (CP and PB) could be due to greater labile C as a substrate for microorganisms, which were rapidly decomposed. The pyrolysis of the feedstocks and subsequent application sequestered C relative to direct application of feedstocks in the Ferralsol.

The increase in ammonium-N for Luvisol for the first 14 days could be the result of SOM decomposition and N mineralisation releasing ammonium-N. This coincides with the high CO_2-C emission. A similar observation was reported by Cao et al. [49] using rice hull biochars. The peak, which lasted from day 14 to 42 (Figure 5A), was attributed to slower rate of nitrification, as supported by the lower nitrate-N results in the Luvisol. The rapid decline in ammonium-N between days 42 and 84 (Figure 5A) in the Luvisol coincided with the decline in CO_2-C and and was attributed to nitrification, which was supported by the increase in nitrate-N from day 42 (Figure 6A). The decline in ammonium-N from the beginning of incubation in the Ferralsol was also associated with an increase in nitrate-N, suggesting that N mineralisation occurred rapidly and that the conditions in this soil were more conducive for nitrification. The lack of differences between the different biochar treatments and the controls for both soils suggest that, considering all the liming effects and additions as components of the materials, the contribution of the biochar to mineral N is minimal. The lack of accumulation of ammonium-N could be explained by higher aeration in the Ferralsol, with its lower clay content (23%), than in the Luvisol (39%). The abundance of oxygen in the moist soil favours nitrification [50], which resulted in a slight decline in soil pH during incubation. These findings are coherent with Zhao et al. [51], who reported a decline in soil pH after applying crop residue biochar due to nitrification. The CP reduced ammonium-N availability compared to the control possibly due to immobilisation of the N by microorganisms. The CP treatment showed N immobilisation in both soils, possibly due to high labile C without sufficient nitrogen (C:N = 35:1). As a result, the microbes scavenged nitrogen from the soil environment, resulting in N immobilisation [52]. The nitrogen immobilisation, including the readily available N associated with raw CP, suggested that more N fertiliser is required compared to the control, while pyrolysis of the material does not affect the fertiliser requirements when compared to the control. However, the Luvisol was dominated by ammonium-N and lower nitrate-N than the Ferralsol soil for the first 56 days. The higher nitrate-N in the Ferralsol (Figure 6B) could partly be explained by higher N contents in the original soil than Luvisol (Figure 6A). The same trend was observed for extractable P in the original soils, possibly due to remnants of fertilisers added to the cultivated soil, compared to the uncultivated soil from Luvisol.

The increase in extractable P concentration for biochars and its relative feedstocks from day 7 to 14 for Luvisol (Figure 7A) and day 0 to 14 for Ferralsol (Figure 7B) could be attributed to increase in soil pH [53]. The increase in soil pH increases the negative surface charges which cause less adsorption of P, increasing its availability. Similar observations have been reported where P availability increased following biochar application [54,55]. Naeem et al. [56] reported a decrease in P adsorption to Fe with biochar application and the desorbability of adsorbed P increased. Additionally, the increase in soil pH promotes

activities of microorganism and abundance, favouring organic matter decomposition and mineralisation of organic P. The high extractable P in CP biochars could be explained by the higher P concentration (Table 2), as well as their liming effects. This suggests that CP needs to be pyrolysed to ensure that P is available, while NO_3^- and NH_4^+ are not affected when compared with the control. The sharp decrease after day 14 for Luvisol was possibly due to microbial immobilisation, considering the high CO_2-C in a soil low in available P. At day 84, the increase in P could be explained by the release of previously immobilised P by microorganisms, thus causing an increase at day 112.

Application of CP biochars significantly increased available K and maintained it up to 140 days in both the soils (Figure 8A,B). The high extractable soil K throughout the incubation, where CP biochars were added, was because the K is not organically bound in the plant tissue and is immediately released [57], as such, its availability is minimally affected by incubation time. The higher extractable K in soils treated with CP biochars at increasing pyrolysis temperature could be explained by the high K in the CP feedstock and the associated biochars (15–23 mg kg^{-1}). Although the K in the biochars decreased with pyrolysis, this might be because some of the K formed stable compounds such as potassium carbonate (K_2CO_3) [57]. Similarly, other authors reported an increase in soil K after amendment with crop residue biochar [22,58]. The lack of a significant effect when PB biochars were added to the soil could be linked to the levels of K in PB being low enough that even the biochars cause no significant change. The generally higher soil K in the Ferralsol than Luvisol for all treatments can be explained by the composition of the original soils (Table 1). In the context of applying CP as source of K, it is ideal to use pyrolysed CP to ensure that NO_3^- and NH_4^+ are not limited.

5. Conclusions

The study showed that, at the same rate of carbon, cull potato (CP) biochar results in lower carbon dioxide (CO_2-C) emission in the Luvisol and higher soil pH and available P and K in both soils when compared with PB biochar. The CO_2-C emission due to amendment with biochar is increased in the Luvisol and is suppressed in the more acidic Ferralsol relative to the unamended control and soils amended with the feedstocks. Higher CO_2-C is emitted from soils amended with CP biochar at higher pyrolysis temperatures in both soils, and PB biochar at lower pyrolysis temperatures in the less acidic Luvisol. The application of the biochar types may not affect ammonium and nitrate-N relative to the control, although ammonium-N and nitrate-N accumulated in the Luvisol and Ferralsol, respectively, in the first 56 days. It is essential to note that the CP feedstock resulted in N immobilisation compared to the control and biochar-amended soils. Cull potato waste should thus be applied as biochar to increase SOC storage, soil pH, available P, and extractable K, with greater benefits in the more acidic Ferralsol. Further research on the applications of the CP biochar and its cost–benefit analysis is of paramount importance to provide strong scientific knowledge on optimally utilising the products of this organic waste, especially for crops grown in contrasting soils.

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